Influence of ultrasound on the heterogeneous Fenton-like oxidation of acetic acid

Aydın Cihanoglu, Gönül Gündüz and Meral Dükkanc

ABSTRACT

The main objective of this study is to investigate the effect of ultrasound on the heterogeneous Fenton-like oxidation of acetic acid, which is one of the most resistant carboxylic acids to oxidation. For this purpose, firstly, the degradation of acetic acid was examined by using ultrasound alone and the effects of different parameters such as: type of sonication system, ultrasonic power, and addition of $\text{H}_2\text{O}_2$ were investigated on the degradation of acetic acid. There was no chemical oxygen demand (COD) reduction in the presence of sonication alone. In the presence of the heterogeneous Fenton-like oxidation process alone, at 303 K, COD reduction reached only 7.1% after 2 h of reaction. However, the combination of the heterogeneous Fenton-like oxidation process with ultrasound increased the COD reduction from 7.1% to 25.5% after 2 h of reaction in an ultrasonic bath operated at 40 kHz, while the COD reduction only increased from 7.1% to 8.9% in the ultrasonic reactor operated at 850 kHz. This result indicates that the hybrid process of ultrasound and heterogeneous Fenton-like oxidation is a promising process to degrade acetic acid.

Key words | acetic acid, heterogeneous sonoFenton-like oxidation, hybrid system, sonolytic degradation, ultrasound

INTRODUCTION

Over the past few decades, growing world population and developing industrial processes have caused a variety of environmental related issues such as protection of air, soil and water from the point of contaminants and removal of them. Especially, increasing concern about the removal of pollutants from wastewater, which includes organic refractory compounds that are difficult to remove, has been a driving force for the development of treatment technologies.

In accordance with these requirements, advanced oxidation processes (AOPs) such as sonolysis, Fenton, photo-Fenton, ozonation, and wet air oxidation in chemical treatment approaches have attracted considerable attention for the destruction of various recalcitrant organic pollutants (Tang & Chen 1996; Bandala et al. 2002; Kavitha & Palanivelu 2005; Primo et al. 2008; Yalfani et al. 2009; Zhou et al. 2009; Daud & Hameed 2010) when compared with other conventional treatment processes, including incineration, biological and physical approaches. AOPs are based on the generation of highly reactive hydroxyl radicals. Among these AOPs, the Fenton process is one of the most promising processes for decomposition of non-biodegradable and recalcitrant organic pollutants (Deng et al. 2008) due to the simplicity of equipment, ambient conditions (atmospheric pressure and low temperature), rapid oxidation rate, low investment cost and easy to operate and maintain (Tang & Chen 1996; Feng et al. 2004; Zazo et al. 2005; Masomboon et al. 2009; Zhou et al. 2009).

Ultrasonic irradiation, which is called sonolysis, has received considerable interest as an AOP because it leads to rapid degradation of chemical contaminants in water. Also, ultrasonic processes can be used as a pre-oxidation step before biological treatment. Thus, complex compounds in the wastewater are converted into lower molecular weight compounds before discharging them into a classical wastewater treatment plant (Dükkancı & Gündüz 2006; Demir et al. 2015).

The chemical effect of sonication is caused by acoustic cavitation. When applied to a liquid, the ultrasound waves consist of a cyclic succession of expansion (rarefaction) and compression phases imparted by mechanical vibration. The compression cycles exert a positive pressure and push the liquid molecules together, while expansion cycles exert...
a negative pressure and pull the molecules apart. When pressure amplitude exceeds the tensile strength of the liquid in the rarefaction regions, small vapor-filled voids called cavitation bubbles are formed (Mason & Peters 2002). Acoustic cavitation consists of three different and consecutive stages: (1) nucleation (cavitation bubble), (2) bubble growth (expansion and contraction), and (3) implosive collapse (Ince et al. 2001). The bubble collapse produces intense local heating and high pressures (extreme temperatures in the order of 5,000 K and pressures in the order of 1,000 atm) for a short lifetime of a few nanoseconds and act as micro-reactors. The heat from the cavity implosion decomposes water into extremely reactive hydrogen atoms (H) and hydroxyl radicals (HO). During the quick-cooling phase, hydroxyl radicals and hydrogen atoms recombine to form hydrogen peroxide (H2O2) and molecular hydrogen (H2), respectively. Thus, in such a molecular environment, organic compounds and inorganic compounds are oxidized or reduced depending on their reactivity (Jiang et al. 2002; Sivakumar et al. 2002; Nam et al. 2005).

However, the total mineralization of pollutants in a mixture is difficult with the application of ultrasound alone. Therefore, sonochemical treatment can be combined with other techniques to increase the efficiency of destruction. Such hybrid techniques can be cited as sonication followed by Fenton, photo-Fenton, O3/H2O2, UV/H2O2, O5, sono-photochemical destruction and sonoelectrochemical methods (Dükkanci & Gündüz 2006; Nikfar et al. 2016).

The classical Fenton reaction (homogeneous Fenton process) is the combination of H2O2 and ferrous (Fe2+) ions which can be outlined as follows:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^* + \text{OH}^- \quad (1)
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2^* \quad (2)
\]

\[
\text{Fe}^{3+} + \text{HO}_2^* \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad (3)
\]

However, in addition to the formation of very reactive HO* radicals, many competitive reactions can occur and they affect the oxidation process negatively:

\[
\text{H}_2\text{O}_2 + \text{HO}^* \rightarrow \text{HO}_2^* + \text{H}_2\text{O} \quad (4)
\]

\[
\text{Fe}^{2+} + \text{HO}^* \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (5)
\]

\[
\text{HO}^* + \text{HO}^* \rightarrow \text{H}_2\text{O}_2 \quad (6)
\]

\[
\text{HO}^* + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^* + \text{H}_2\text{O} \quad (7)
\]

The perhydroxyl radicals (HO2) are less reactive than hydroxyl radicals. The generated hydroxyl and perhydroxyl radicals degrade the organic compounds to CO2 and H2O:

\[
\text{HO}^*(\text{and HO}_2^*) + \text{organics} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (8)
\]

In this study, a hybrid technique, heterogeneous sono-Fenton-like oxidation, was used for degradation of acetic acid which was chosen as a model substance. If the heterogeneous Fenton oxidation technique is used in combination with ultrasonic irradiation, not only will the rate of the generation of hydroxyl radicals be increased, but mass transfer limitations affecting the Fenton technique will be avoided due to the turbulence created by ultrasonic irradiation, as well. Additionally, the turbulence created by ultrasonic irradiation provides a good opportunity for the cleaning of the catalyst surface which increases its efficiency (Demir et al. 2015).

Acetic acid is formed during the destruction of substances with longer chains of aliphatic acids or phenolic compounds. It is resistant to oxidation because the methyl group in a position of the carboxylic group cannot be easily destroyed even under severe conditions such as a temperature of 260°C and a pressure of 20 bar (Centi et al. 2000). According to the Occupational Safety and Health Administration (OSHA), the legal permissible exposure limit of acetic acid is 10 mg/dm3, therefore, the removal of acetic acid from wastewater is very important (Debellefontaine et al. 1996).

In literature, there are only two studies on sonolysis of acetic acid (Fındık et al. 2006; Fındık & Gündüz 2007), and there are few studies on the destruction of acetic acid by heterogeneous Fenton reaction. In these studies, transition metal (Fe2+, Fe3+, Cu2+, Mn2+)-exchanged NaY zeolites (Larachi et al. 1998), iron containing ZSM-5 zeolite catalyst (Cenci et al. 2000), Pt/SiO2 catalyst (Karacan 2008), LaFeO3, LaMnO3 and LnFeO3 perovskite catalysts (Sannino et al. 2010, 2011) were used.

Our research group studied the degradation of acetic acid by heterogeneous Fenton-like oxidation in the presence of several iron-containing ZSM-5 zeolites (Cihanoglu et al. 2015). The catalyst with iron content of 8.5% (in wt) was found to be the most active catalyst and the optimum conditions were determined to be 0.2 g of catalyst, 333 K of temperature, solution pH of 4 and H2O2 amount of 8.35 mmol for an acetic acid concentration of 0.1 g/dm3 with a chemical oxygen demand (COD) removal of 50.5%.

However, so far, no study has been reported on the effect of sonication on the heterogeneous Fenton-like oxidation of...
acetic acid. The aim of this study is to investigate the effect of direct and indirect sonication on the degradation of acetic acid with heterogeneous Fenton-like oxidation. Firstly, the individual effects of several parameters such as ultrasonic power, and the addition of H2O2, were studied on the oxidation of acetic acid by ultrasound alone and then, the heterogeneous Fenton-like oxidation of acetic acid was investigated in the presence of ultrasound. Iron containing ZSM-5 zeolite was used as catalyst in the heterogeneous Fenton-like oxidation of acetic acid.

EXPERIMENTAL

Materials

A commercial ZSM-5 type zeolite, H-MFI (90), was used for the preparation of the heterogeneous catalyst and was purchased from Clariant-Süd-Chemie (Germany). Acetic acid (glacial, 100%) and hydrogen peroxide solution (in mass % of 35) of analytical grade were provided by Merck (Germany). They were used without further purification process. All aqueous solutions containing 0.025 g/dm³ acetic acid were prepared with distilled water obtained from a Millipore Direct Q purification unit (France).

Ultrasonic degradation experiments

Sonolytic degradation of acetic acid was studied using an ultrasonic reactor with a frequency of 850 kHz and an ultrasonic bath with a frequency of 40 kHz. After reaching the desired experimental conditions, the experiment was started and 2 mL sample was taken at the end of the reaction duration for COD analysis. COD removal was measured using COD equipment (Lovibond Checkit Direct COD Vario device, UK). The percentage COD removal was determined by Equation (9). Ultrasonic degradation runs were repeated at least 3 times, and the obtained results were averaged. The standard deviation of the average of independent runs changed in the range of ±0.45 to ±2.01 and the error bars were added in the related figures for each independent run. Each run was 2 h in duration.

\[
\text{COD removal, } % = \frac{\text{COD}_{\text{initial}} - \text{COD}_{\text{t}}}{\text{COD}_{\text{initial}}} \times 100 \quad (9)
\]

The ultrasonic reactor system includes an ultrasonic signal (power) generator (Meinhardt, Model K8, Germany), ultrasonic transducer (Meinhardt, Model E/805/T, Germany), and an ultrasonic reactor with a jacket (Meinhardt, Model 5/1575, Germany). The high frequency generator can be used in two different modes, continuous or pulse. The ultrasonic power can be adjusted in four steps with 25 W intervals from minimum value of 25 W to maximum value of 100 W. Temperature is kept constant by circulating water in the jacket. The transducer operates at the frequency of 850 kHz. The schematic diagram of the ultrasonic reactor is shown in Figure 1 (Dükkançı 2010).

In this system, the direct sonication of acetic acid was studied. For a typical run, 0.25 dm³ of an aqueous solution of acetic acid with known concentration was charged to the reactor for the sonolytic degradation of acetic acid in the continuous mode for 2 h. The temperature of the reaction mixture was kept at a constant temperature of 303 ± 3 K by circulating water in the jacket around the reactor. The power was adjusted to a desired value. The effects of the ultrasonic power, and H2O2 concentration were determined on the sonolytic degradation of acetic acid and then, the contribution of ultrasound to the heterogeneous Fenton-like oxidation of acetic acid was investigated.

The ultrasonic bath (C.E.I.A model CP 102 digit, Italy) has a fixed frequency of 40 kHz and ultrasound power can be changed from 70 W to 140 W. The operational temperature of the ultrasonic bath can be set between 20 °C and 80 °C. The sonication time of the bath can be adjusted to a desired time of 1–60 min. In the ultrasonic bath, indirect sonication was applied to the solution.

For a typical run, the ultrasonic bath was filled with 1.5 dm³ of deionized water. Then, 0.15 dm³ of acetic acid solution with specified concentration was put into an 0.4 dm³ beaker reactor covered with aluminium foil and then placed into the water bath. The reactor was located in the bath 2 cm from the bottom of the bath in all experiments. In the ultrasonic bath system, the effects of ultrasonic power, and H2O2 concentration were investigated on the sonolytic degradation of acetic acid and then, the contribution of ultrasound to the heterogeneous Fenton-like oxidation of acetic acid was studied. The schematic diagram of the ultrasonic reactor is shown in Figure 2 (Dükkançı 2010).

Experimental set-up for the heterogeneous Fenton-like oxidation of acetic acid

The heterogeneous Fenton-like oxidation of acetic acid was carried out under isothermal condition (303 K) in a
shaded temperature-controlled glass batch reactor. Details of experimental set-up and experimental procedure are given elsewhere (Cihanoglu et al. 2015). In the presented study, firstly, the degradation of acetic acid was studied by ultrasound and then its contribution to the heterogeneous Fenton-like oxidation of acetic acid was investigated.

Catalyst

The ion exchange method by Schwidder et al. (2005) was applied to prepare FeZSM-5 sample which was labelled as IE-FeZSM-5 (90) catalyst. The prepared catalyst was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), inductively coupled plasma atomic emission spectroscopy (ICP-AES), nitrogen adsorption, and Brönsted-Lewis acid sites measurements. The precise procedures for preparation and characterization of the catalyst are described in detail in our previous study (Cihanoglu et al. 2015). The Si/Al ratio and the Fe content (in weight percentage, wt%) of IE-FeZSM-5 (90) catalyst were 42 and 8.5%, respectively. The Brunauer–Emmett–Teller (BET) surface area, total pore volume, and average pore diameter of the IE-FeZSM-5 (90) were 358.2 m²/g, 0.1259 cm³/g, and 0.55 nm, respectively.

RESULTS AND DISCUSSION

Sonication in the ultrasonic reactor

The effects of the ultrasonic power, and the addition of H₂O₂ on sonolytic degradation of acetic acid (AA) were investigated in ultrasonic reactor as a direct sonication application using 0.25 dm³ of 0.025 g/dm³ (COD_initial = 32 ppm) acetic acid aqueous solution. The sonication temperature was kept at a constant 303 ± 3 K.

The effect of the ultrasonic power in the ultrasonic reactor was investigated at three different power settings, 25 W, 50 W, and 75 W, at a high frequency of 850 kHz. At the end of 1 h of sonication, no COD reduction was observed at all the power settings applied. At a very high frequency, the rarefaction cycle is extremely short. The production of a cavity in the liquid requires a finite time to permit the molecules to be pulled apart so that when the rarefaction cycle shorter than this finite time, formation of cavitation becomes difficult or small bubbles may form which collapse less violently. At high frequency of ultrasound, it is necessary to increase the amplitude (power) of sonication to achieve...
cavitation (Mason & Peters 2002). In this study, it is clear that the studied power of 25, 50 and 75 W are not high enough to succeed the formation of cavitation bubble and sonication effect.

However, in sonication literature, in general, it is known that the higher the ultrasonic power at the proper frequency, the more the HO\(^{\cdot}\) radicals are formed (Sivakumar et al. 2002). For this reason, in the following investigations, an ultrasonic power of 75 W was applied to the system.

The effect of the contribution of H\(_2\)O\(_2\) to the sonication of acetic acid was studied in an ultrasonic reactor. An ultrasonic power of 75 W was applied to 0.25 dm\(^3\) of 0.025 g/dm\(^3\) (COD\(_{\text{initial}}\) = 32 ppm) acetic acid solution with 2 mmol, 3 mmol, 4 mmol, 8.35 mmol, and 10 mmol H\(_2\)O\(_2\) at 303 ± 3 K. In the runs, in the presence of H\(_2\)O\(_2\), initial COD value of acetic acid was measured just after the addition of each amount of H\(_2\)O\(_2\), and the COD values of acetic acid were 57 ppm, 63 ppm, 72 ppm, 111 ppm, and 135 ppm, respectively. These values were taken as the initial COD values in the related runs. The obtained results are given in Figure 3.

It is known that H\(_2\)O\(_2\) is one of the most significant oxidants and increases the number of HO\(^{\cdot}\) radicals by decomposing during the collapse of the bubbles as shown in Equation (10):

\[
\text{H}_2\text{O}_2 \rightarrow 2 \text{HO}^{\cdot}
\]  

(10)

where \(\rightarrow\) refers to ultrasound (sonication).

H\(_2\)O\(_2\) contributes positively to degradation by sonication. As seen in Figure 3, at the end of 2 h of sonication, COD reduction increased from zero (without H\(_2\)O\(_2\)) to 9.5\% when 4 mmol H\(_2\)O\(_2\) was added to the acetic acid solution. For H\(_2\)O\(_2\) amounts higher than 4 mmol, a decrease in COD removal was observed. This result indicates the scavenging effect of H\(_2\)O\(_2\) when it is used in excess amount (Torrades et al. 2004). In this case, according to Equation (11):

\[
\text{H}_2\text{O}_2 + \text{HO}^{\cdot} \rightarrow \text{HO}_2^{\cdot} + \text{H}_2\text{O}
\]  

(11)

H\(_2\)O\(_2\) reacts with HO\(^{\cdot}\) radicals to produce less reactive perhydroxyl radicals, HO\(_2^{\cdot}\), which causes a reduction in COD removal.

In addition to this, as the OH\(^{\cdot}\) radicals have a very short lifetime, they tend to combine with each other to produce H\(_2\)O\(_2\) again (Equation (12)):

\[
\text{HO}^{\cdot} + \text{HO}^{\cdot} \rightarrow \text{H}_2\text{O}_2
\]  

(12)

These two effects decreased the COD reduction in sonication of acetic acid due to the decline in the amount of OH\(^{\cdot}\) radicals available to oxidize acetic acid.

**Effect of sonication on the heterogeneous Fenton-like oxidation of acetic acid**

Heterogeneous Fenton-like oxidation and sonication were applied together in an effort to observe the potential benefit of a combined use of heterogeneous Fenton-like oxidation and sonication on the degradation of acetic acid. For this purpose, 0.25 dm\(^3\) of 0.025 g/dm\(^3\) (COD\(_{\text{initial}}\) = 32 ppm) acetic acid aqueous solution in the presence of 0.34 g...
(1.3 g/dm³) IE-FeZSM-5 (90) catalyst and 8.35 mmol H₂O₂/0.25 dm³ solution was sonicated using an ultrasonic reactor at an ultrasound power of 75 W at 303 ± 3 K at an initial pH around 4.0. After the addition of H₂O₂ into the solution, the initial COD value of acetic acid increased from 32 to 111 ppm and this value was taken as initial COD value. The results after 2 h of oxidation are given in Figure 4. As seen, under the same conditions, in the absence of sonication, a COD removal of 7.1% could be obtained at 303 K. In the presence of sonication, COD reduction could be increased from 7.1% to 8.9%. The rate of heterogeneous Fenton-like oxidation reaction begins to be important at temperatures around 333 K (Cihanoglu et al. 2015). For this reason, at a temperature of 303 K, the reaction rate is very low.

As seen in Figure 4, sonication alone (without H₂O₂) was not effective on COD reduction in acetic acid degradation, the application of the heterogeneous Fenton-like oxidation alone to the degradation of acetic acid was also not as effective as the combined use of the heterogeneous Fenton-like oxidation and sonication under the conditions studied. In the combined use of the heterogeneous Fenton-like oxidation and sonication, more HO⁻ radicals form via Equations (1)–(3) and (10). In addition to this, the formed H₂O₂ (Equation (12)) in sonication can react with Fe²⁺ in the catalyst to form OH⁻ radicals. Besides, in the presence of solid particle (here IE-FeZSM-5 (90) catalyst) the effect of sonication might be increased by providing additional nuclei for the formation of the cavitation bubble. Thus, the COD reduction of acetic acid increased.

**Sonication in the ultrasonic bath**

The effects of ultrasonic power, and the addition of H₂O₂ on sonolytic degradation of acetic acid (AA) was investigated in ultrasonic bath as an indirect sonication application using 0.15 dm³ of 0.025 g/dm³ (COD<sub>initial</sub> = 32 ppm) acetic acid aqueous solution. The sonication temperature was kept constant at 303 ± 5 K.

The effect of ultrasonic power in ultrasonic bath was examined at three different power settings, 70 W, 84 W and 98 W. At the end of 1 h of sonication, no COD reduction was observed at the powers settings applied. As mentioned above, sonication was applied indirectly in the ultrasonic bath. This means that the ultrasonic energy has to be transferred through coupling fluid (water) and then the glass walls of the vessel and finally into the reaction itself (Figure 2). So, the amount of power dissipated into the reaction from the bath may not be high. Due to this insufficient energy transfer into the reaction vessel COD reduction could not be achieved.

The effect of the contribution of H₂O₂ to sonication was studied in ultrasonic bath. An ultrasonic power of 98 W was applied to 0.15 dm³ of 0.025 g/dm³ (COD<sub>initial</sub> = 32 ppm) acetic acid solution with 2.4 mmol, 5 mmol, 6 mmol, and 8.35 mmol H₂O₂ at 303 ± 5 K. At the corresponding H₂O₂ concentrations, the initial COD values of acetic acid were taken as 69 ppm, 109 ppm, 123 ppm, and 144 ppm, respectively. At the end of 2 h of sonication, no COD reduction was achieved. This result indicated that the mentioned insufficient energy transferred into the liquid could not degrade H₂O₂ into HO⁻ radicals (Equation (10)) which would

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**Figure 4** | Effect of sonication on the heterogeneous Fenton-like oxidation of acetic acid over IE-FeZSM-5 (90) catalyst in ultrasonic reactor (ultrasonic power = 75 W, H₂O₂ concentration = 8.35 mmol, solution amount = 0.25 dm³, temperature = 303 ± 3 K, and acetic acid concentration = 0.025 g/dm³).
oxidize acetic acid in aqueous solution, so it was not possible to degrade acetic acid under the conditions studied.

**Effect of sonication on the heterogeneous Fenton-like oxidation of acetic acid**

Heterogeneous Fenton-like oxidation and sonication were applied together in order to observe the potential benefit of combined use of heterogeneous Fenton-like oxidation and sonication in acetic acid degradation. For this purpose, 0.15 dm$^3$ of 0.025 g/dm$^3$ (COD$_{\text{initial}} = 32$ ppm) acetic acid aqueous solution in the presence of 0.20 g (1.3 g/dm$^3$) IE-FeZSM-5 (90) catalyst and 8.35 mmol H$_2$O$_2$/0.15 dm$^3$ of solution was sonicated using an ultrasonic bath at an ultrasound power of 98 W at 303 $\pm$ 5 K and at initial pH around 4.0. Just after adding H$_2$O$_2$, the measured initial COD value of acetic acid was 144 ppm.

The results are given in Figure 5 after 2 h of oxidation. As seen in Figure 5, sonication alone (without H$_2$O$_2$) was not effective in COD reduction in acetic acid degradation; the application of heterogeneous Fenton-like oxidation to acetic acid degradation was also not as effective as the combined use of heterogeneous Fenton-like oxidation and sonication at 303 $\pm$ 5 K. However, in the presence of sonication, COD reduction increased significantly from 7.1% to 25.5%. This significant increment in COD reduction of acetic acid arises from the presence of catalyst and H$_2$O$_2$ together in the sonication system. As explained before, sonication leads to degrading H$_2$O$_2$ into hydroxyl radicals. But as mentioned before it was hard to achieve this degradation into hydroxyl radicals in indirect sonication using ultrasonic bath. However, the presence of catalyst increased the cavitation activity by providing additional nuclei, thus the number of cavitation bubble increased. In addition, the formed H$_2$O$_2$ (Equation (12)) in sonication can react with Fe$^{2+}$ in the catalyst to form more OH$^-$ radicals which react with acetic acid.

The comparison of Figures 4 and 5 indicates that contribution of sonication in ultrasonic bath to the heterogeneous Fenton-like oxidation of acetic acid is more significant than that in the ultrasonic reactor. One of the reason of this positive effect may arise from that; at low frequency (in this study 40 kHz) where a long acoustic cycle exits, large bubbles are created and large bubbles collapse violently. In addition, this comparison reflects the combined effects of the power applied, the solution volume used, and type of sonication (direct or indirect) on acetic acid degradation, as well.

In literature, there are several studies about the positive effect of sonication on Fenton-like oxidation at low frequencies. For example, in the study done by Ioan et al. (2007) Fenton and sonoFenton oxidation of Bisphenol-A (BPA) was compared using low frequency of ultrasound (43–47 kHz). Sonication increased the degradation of BPA by Fenton reaction from 80% to 88% after 2 h of reaction.

In another study from Ji et al. (2013), 98% of degradation of carbazole was achieved in sonoFenton oxidation using low frequency ultrasound of 40 kHz after 3 h of oxidation.

A similar result was also obtained in sonoFenton oxidation of 2,4-dichlorophenol at a frequency of 35 kHz. Almost 95% of degradation was achieved after 2 h of reaction (Dorathi et al. 2008).

![Figure 5](https://iwaponline.com/wst/article-pdf/76/10/2793/241747/wst076102793.pdf)

**Figure 5** Effect of sonication on the heterogeneous Fenton-like oxidation of acetic acid over IE-FeZSM-5 (90) catalyst in ultrasonic bath (ultrasonic power = 98 W, H$_2$O$_2$ concentration = 8.35 mmol, solution amount = 0.15 dm$^3$, temperature = 303 $\pm$ 5 K, and acetic acid concentration = 0.025 g/dm$^3$).
CONCLUSIONS

In this study, the degradation of acetic acid dissolved in water was investigated by direct and indirect ultrasonic irradiation alone. No significant COD removal was obtained by the individual application of ultrasound to the degradation of acetic acid. The highest COD removal was achieved as 9.5% by direct sonication in an ultrasonic reactor at 850 kHz in the presence of 4 mmol of H₂O₂. However, when the heterogeneous Fenton-like process is combined with ultrasound, the degradation of acetic acid is improved and COD removal increases to 25.5% in the ultrasonic bath with indirect sonication. The synergy observed in the combined system of ultrasound and heterogeneous Fenton-like oxidation is mainly due to the effect of ultrasound to yield additional hydroxyl radicals.

These preliminary results show that looking at the degradation of acetic acid through the window of the hybrid process of sonication and Fenton-like oxidation may be a significant contribution to degrade such a resistant carboxylic acid.

However, for this purpose, further detailed studies are required to increase the efficiency and to explain the mechanism of the hybrid system of ultrasound and heterogeneous Fenton-like oxidation in the degradation of acetic acid.

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