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Successive advanced oxidation of pyridine by ultrasonic irradiation: effect of additives and kinetic study

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ABSTRACT

Pyridine has received considerable attention from environmental scientists and engineers, due to its undesirable effect in the water environment. Pyridine contaminated wastewater presents a great threat on water resources safety. In this research, the degradation and advanced oxidation of pyridine in aqueous solution by ultrasonic waves were studied under various process variables including different initial concentration, H_2O_2, NaCl, and Fenton reagent. The results show that the degradation efficiency of pyridine decreases with the increasing of the initial concentration of pyridine. The removal rates of pyridine decreased from 52 to 15% with increasing the initial concentration from 10 to 100 mg/L. In the concentration range studied, the amount of H_2O_2 and NaCl added has positive contribution on the degradation of pyridine. The removal effect of ultrasound and Fenton is better than ultrasound or H_2O_2 alone acting on pyridine. A possible degradation pathway for pyridine was also proposed. In the end, it could be proposed that ultrasonic irradiation was an effective method for the removal of pyridine from wastewater.

Keywords: Pyridine; Ultrasonic irradiation; Wastewater treatment; Fenton reagent

1. Introduction

Over the last two decades, advanced oxidation processes (AOP) have been developed to remove low to trace amounts of organic compounds from both aqueous and gaseous waste streams. Free radicals involved in AOP can be generated using several radiation methods, including UV, γ-radiation, electron–beam, and ultrasonic waves. Among the above, ultrasonication is probably one of the less studied methods despite its very unique and extreme conditions generated without using complicated and expensive apparatus. Ultrasonication not only promotes oxidative degradation of the target compound by hydroxyl radicals, but also provides a possible route for thermal decomposition in the gas phase [1].

Nowadays, ultrasonic irradiation has received considerable interest as an advanced oxidation process because it leads to rapid degradation of chemical contaminants in water. Ultrasound can enhance or promote chemical reactions and mass transfer and offer the potential for shorter reaction cycles, cheaper reagents, and less extreme physical conditions. So far, ultrasound has been applied in studies of cleaning, organic synthesis, catalysis, extraction, emulsification, material processing, food processing, and wastewater treatment [2,3].

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The chemical effect of ultrasound is produced through the phenomenon of cavitation, which is caused by the expansion and contraction of cavitation nuclei due to the compression and rarefaction cycles of ultrasonic waves. Cavitation causes the formation, rapid growth, and finally implosive collapse of the bubbles, resulting in unusual reaction environment in the vicinity of the bubbles [4].

In the unusual chemical environment, water undergoes thermal decomposition to release atomic and radical species (˙OH, OH) [5]. These species can recombine to form hydrogen and hydrogen peroxide, or attack organic substrates. Mostly, volatile organic compounds in the imploding cavities or nearby participate in the primary sonochemical reaction and are pyrolyzed during sonication [6].

Since pyridine is a common refractory pollutant in wastewater effluents, the conventional volatile organic compound control technologies, including condensation, adsorption [7], extraction, membrane separation, and so on, have been commonly utilized to control its escaping. However, these technologies require high operating costs or secondary disposal treatments [8].

In recent years, studies suggest that volatile contaminants could be quickly destroyed by ultrasonic irradiation [9–11]. However, there is a lack of research related to the use of high-frequency ultrasound for pyridine degradation in pyridine aqueous solutions.

In this study, an investigation was focused on the ultrasonic degradation of pyridine in aqueous media. A variety of different operating conditions were examined. The effects of different initial concentration, H_2O_2, NaCl, and, Fenton reagent on kinetic rate constants were also examined in order to gain insight into the kinetics of the degradation of pyridine.

2. Materials and methods

2.1. Materials

Pyridine standard solution was supplied by Fluka with purity better than 98.0%. It was used to prepare a synthetic wastewater. Aqueous solutions were made using deionized water, which was prepared by an Elga B114 Deionizer using C114 cartridges, (EC = 5 μS. cm at 25˚C and TDS = 3.5 ppm). All other reagents were reagent grad obtained from Fluka and used as received.

2.2. Ultrasonic setup reactor

The degradation experiments were carried out in ultrasonic cleaner bath (capacity 15 L) as shown in Fig. 1. The bath operates at 360 W and 40 KHZ. Erlenmeyer flask was used as reaction vessel. The volume of the solution was 100 ml. The bath temperatures were maintained by proper recirculation of water. Solution temperature was also monitored regularly. The efficiency of a reaction vessel placed in an ultrasonic bath depends strongly on the distance of the bottom of the reaction vessel to the bottom of water bath. The distance was carefully measured through preliminary experiments, so that ultrasonic intensity reached maximum at the bottom of the flask. For ultrasonic frequency 40 kHZ, this distance value was 2 cm. In the present study, ultrasonic device provides indirect sonication, which will inevitably cause energy loss. A limited quantity of energy is transmitted into the reaction vessel. So, it should be kept in mind that the power used is not the real power of ultrasonic energy transmitting into the reaction mixture. All sonochemical experiments were conducted twice in parallel. The averages of the parallel experimental data were calculated and taken into account in analyses of sonochemical kinetics. The error of all parallel experiments was under 5%.

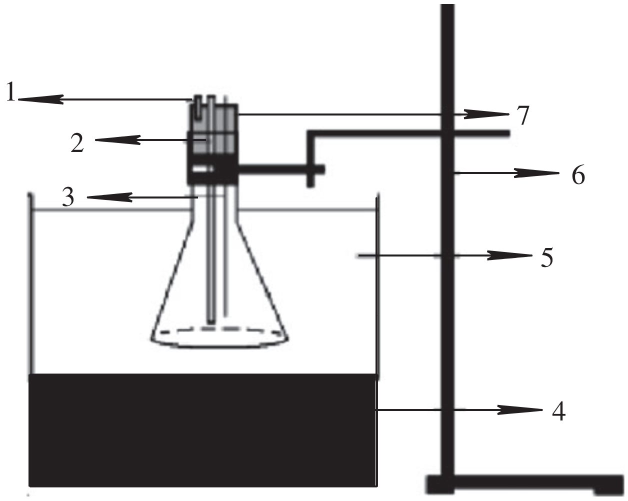

Fig. 1. Setup for the ultrasonic bath reactor. 1. Septum for sampling, 2. gas diffuser, 3. thermometer, 4. cleaning bath, 5. water bath, 6. steel stand, and 7. silicone stopper.

2.3. Quantitative analysis experiments

Quantitative analysis of pyridine concentration was determined by measuring its absorbance using Shimadzu UV–visible spectrophotometer. Initially, tests were carried out by UV scans from a wavelength of 200 to 500 nm to determine the absorption maxima of the pyridine molecule. Fig. 2 shows the UV spectrum of pyridine in which we observe; an absorption

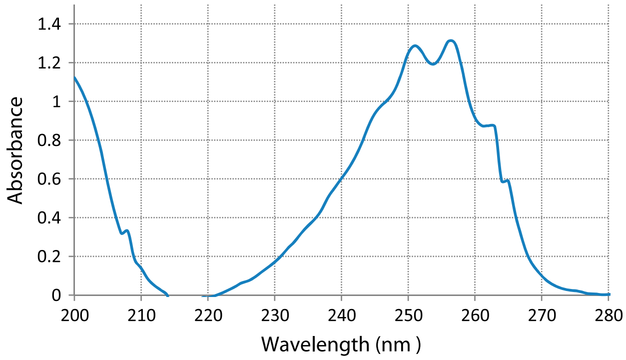

Fig. 2. UV-spectrum of pyridine.

maximum at 254 nm to this wavelength is able to detect that component by UV–visible analysis, two peaks at 250 and 262. Pyridine is a heterocyclic compound, so these peaks show the electronic transitions resulting from the combination of π–π^* and n–π^* transition. We also note that there is a maximum absorbance at a wavelength of 200 nm which may be due to the presence of nitrogen in the pyridine molecule. In this study, pyridine was detected at 254 nm.

2.4. Qualitative analysis of the degradation products by GC–MS techniques

GC–MS analyses were performed on a Shimadzu QP 2000 instrument, equipped with an Equity-5 column (Supelco) (30 m × 0.25 mm × 0.25 μm), coated with 5% phenyl 95% methyl poly-siloxane. Separation of the by-products was conducted under the following chromatographic conditions: injector temperature 240 ℃, oven temperature program 50 ℃ ramped at 5 ℃ min^{-1}–250 ℃ followed by another ramp of 10 ℃ min^{-1}–290 ℃ held for 2 min. Helium was used as carrier gas at a flow of 1 ml min^{-1}. The temperatures of the ion source and the interface were set at 240 and 290 ℃, respectively. The MS operated in electron ionization mode with a potential of 70 eV and the spectra were obtained at a scan range from m/z 50–450 (full scan mode). The scan time was 46 min and 1.0 μl injections were made using a split ratio varying from 2 to 20.

3. Results and discussion

3.1. Study and optimization of the operating conditions

3.1.1. Effect of initial pyridine concentration

Since the industrial wastewater contains pollutants in varying concentration, the effect of initial concentrations on the sonochemical reaction rate was tested for pyridine. The effect of solute concentration on the degradation of pyridine was investigated at 40 kHz, 20 ± 1 ℃, 360 W, and initial concentration 10, 20, 60, 80, and 100 mg/L. As shown in Fig. 3 with increase in sonication time, the concentration of pyridine in the solution decreases and thus the removal increases. It follows from the data obtained that degradation of pyridine depends upon sonication time. The removal rates of pyridine decreased from 52 to 15% with increasing the initial concentration from 10 to 100 mg/L. This suggests that increasing the initial concentration of the solution would decrease the removal rates of pyridine. This is because the increment of initial concentration of the volatiles results in the weakening effect of cavitation reactions [12]. However, the total amount of pyridine degraded after 60 min at 100 mg/L was as much as three times larger than that degraded at 10 mg/L.

The degradation rates can be expressed by the following equation:

$$\ln C_t/C_0 = -kt \tag{1}$$

where C_0 and C_t are the initial and remaining concentrations of pyridine, respectively, k is the degradation rate constant, and t is the sonication time.

A typical ln C_t/C_0 vs. t Fig. 4 shows that, the reaction kinetics for the degradation followed first-order rate laws ($R^2 > 96$) at all initial concentrations. In addition to, as is seen from the Fig. 5, the apparent first-order rate constants decreased with an increasing initial concentration of the pyridine, indicating non-elementary nature of the sonochemical reactions. This dependence of reaction rate constants on initial concentration compared well with existing literature [12–15].

The reaction conditions vary as the concentration of the pyridine compound changes. The products

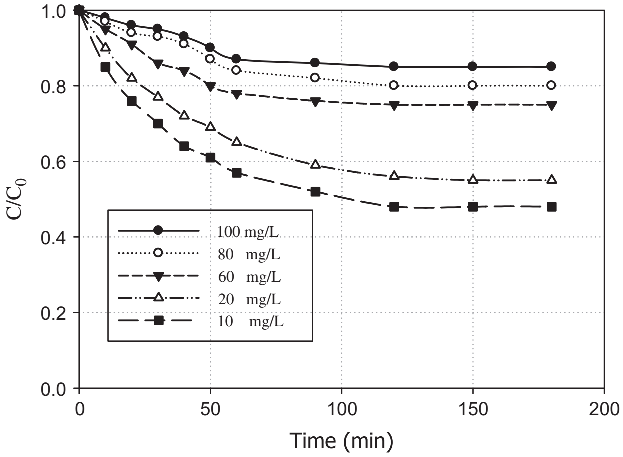

Fig. 3. Effect of initial concentration on the degradation of pyridine (40 kHz, 20 ± 1 ℃ and 360 W).

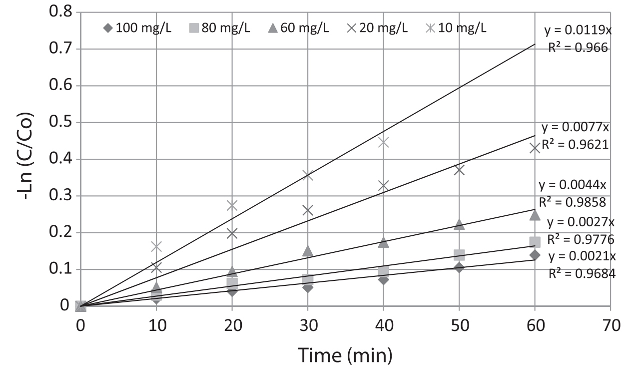

Fig. 4. The first-order kinetic of pyridine degradation (40 kHz, 20 ± 1˚C and 360 W).

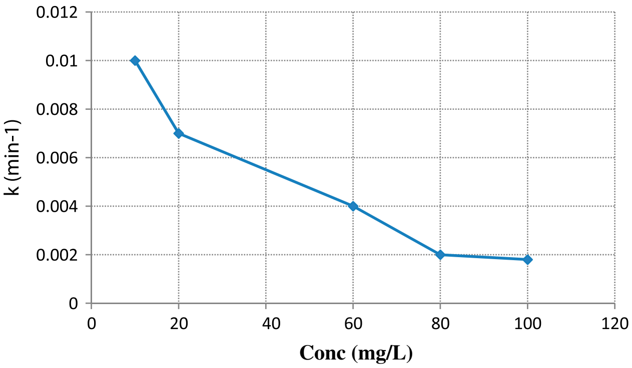

Fig. 5. Apparent first-order rate constants vs. initial concentration of pyridine (40 kHz, 20 ± 1˚C and 360 W).

formed by the degradation of pyridine should affect the reaction rate due to their influence on the cavitation temperature; however, it is difficult to evaluate and establish. According to De Visscher et al. (1996), [12], for relatively small mole fractions of the volatile compounds in the cavitation bubble (x_1), γ, the specific heat ratio varies with the initial concentration as:

$$\gamma = \gamma_0 + x_1 \frac{(\gamma_0 - 1)(\gamma_1 - \gamma_0)}{\gamma_1 - 1} \quad (2)$$

where γ_0 and γ_1 are the specific heat ratios for pure gas water mixture and organic compound, respectively, in the cavitation bubbles. Since the term $(\gamma_1 - \gamma_0)$ will be negative, the specific heat ratio decreases with the increase in initial concentration. The decrease in γ will cause a decrease in cavitation temperature, consequently reducing the reaction rates.

It seems that the major route for degradation of pyridine during ultrasonic irradiation alone without any additives is by pyrolytic reactions in the gas phase, and thus it shows a greater dependence on initial concentration. Ultrasonication not only promotes oxidative degradation of pyridine by hydroxyl radicals, but also provides a possible route for thermal decomposition in the gas phase.

3.1.2. Effect of hydrogen peroxide

Hydroxyl radicals generated in water by ultrasonication can produce hydrogen peroxide in the system. Whether additional hydrogen peroxide has a synergistic effect on the overall degradation of pollutants, some experiments were conducted at various concentrations of added H_2O_2.

In this part of study, sonication experiments were repeated with pyridine solutions including H_2O_2 to study the effect of H_2O_2 addition for degradation of pyridine at 40 kHz, 20 ± 1˚C and 360 W. H_2O_2 was added to 100 ml pyridine solution with initial concentration of 100 ppm in such amount that its concentration was 100, 300, or 500 ppm in solution.

Fig. 6 displays the effect of H_2O_2 amount added to pyridine solution. As seen from Fig. 6 and in the concentration range studied, the amount of H_2O_2 added has positive contribution on the degradation of pyridine when compared with the absence of H_2O_2. Increasing the amount of H_2O_2 increases the degradation of pyridine.

According to the theory of hot spot, the temperature and pressure of localized hot spots formed can excessively reach 5,000 K and 1,000 atm, respectively, in the ultrasonic cavitation. Under these conditions, hydrogen peroxide readily decomposes into hydroxyl radicals, according to the following equations, causing high degradation rate.

$$H_2O_2 + us \rightarrow 2{}^{\cdot}OH \quad (3)$$

$$^{\cdot}H + H_2O_2 \rightarrow {}^{\cdot}OH + H_2O \quad (4)$$

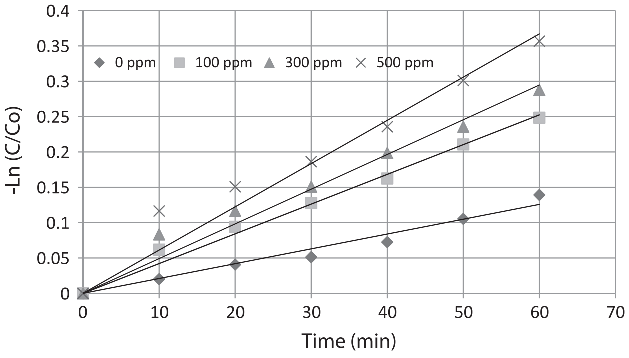

Fig. 6. Effect of H_2O_2 on the degradation of pyridine (40 kHz, 20 ± 1˚C, 360 W and initial concentration of pyridine $C_0 = 100$ ppm).

The amount of H_2O_2 that can be produced by ultrasound itself is too small to dissociate into large amount of $^{\cdot}OH$. Thus, additional amount of H_2O_2 is generally needed to significantly accelerate the degradation process. H_2O_2 will increase the formation of $^{\cdot}OH$ in two ways. It could either through the self-decomposition as a result of ultrasound irritation or as the reduction of H_2O_2 at the conduction band as shown in reactions (3) and (4), respectively [16,17].

In conclusion, in order to accelerate ultrasonic degradation of organic compounds, many researchers investigated the addition of external oxidants such as H_2O_2 to increase the efficiency of the degradation process. Under the hot spot conditions (localized generation of extreme conditions, high temperature, and pressure) in ultrasonic cavitation, H_2O_2 readily undergoes sonolysis and decomposes into $^{\cdot}OH$ as the dissociation energy for the O–O bond in H_2O_2 is only 213 kJ/mol which is significantly less than that of the O–H bond in H_2O which is 418 kJ/mol [15,16]. This dissociation is also facilitated by the low H_2O_2 concentration inside the cavitation bubbles due to its low volatility and the high solubility in water [18]. However, after analyzing different works reporting the use of H_2O_2 to enhance the degradation rate of organic compounds, it is clearly noted that the optimum value of H_2O_2 is strongly dependent on the types of organic compound, operating conditions, and the equipment configuration. All these factors are known to directly affect the production rate of $^{\cdot}OH$. Finally, it should be noted that the concentration of H_2O_2 should not be higher than a certain optimum value as it could recombine with the $^{\cdot}OH$. This will lead to a decrease in the overall rate of degradation [19–21].

3.1.3. *Effect of electrolyte*

In this part of study, sonication experiments were repeated with pyridine solutions including NaCl to study the effect of NaCl addition for degradation of pyridine at 40 kHz, 20 ± 1˚C, and 360 W. NaCl was added to 100 ml pyridine solution with initial concentration of 100 ppm in such amount that its concentration was 0.5 M, 0.75, or 1.0 M in solution.

Table 1
Effect of NaCl concentration on the degradation of pyridine (40 kHz, 20 ± 1˚C, 360 W and initial concentration of pyridine $C_0 = 100$ ppm)

NaCl concentration (M)	Rate constant (min^{-1})
0.0	0.002
0.5	0.004
0.75	0.008
1.0	0.001

Table 1 presents the effect of NaCl salt added on sonolytic degradation degree of pyridine in aqueous solution. As it can be seen from Table 1, addition of 0.5 M and 0.75 M NaCl can achieve to enhance the degradation slightly when compared with the absence of NaCl salt. However, 1 M NaCl has negative contribution on the decomposition of pyridine. So, there may be an optimum amount of NaCl to increase degradation rate. Excessive amount of NaCl may interfere with the introduction of ultrasound into the liquid.

The addition of salt increases ionic strength of the aqueous phase which drives the organic compounds to the bulk-bubble interface. However, ionic strength is not the only effect brought about by the dissolved electrolytes. Other properties of solution such as viscosity, vapor pressure, and heat capacity will also change accordingly. The combined effect of these parameters is difficult to estimate. Similar results for sonolytic degradation of phenol, chlorobenzene, and p-ethylphenol [22,23] were reported in literature; that the enhancement can be attributed to an increase in the destruction in the presence of NaCl leading to accumulation of the pollutant species at the cavitation sites. In addition to the destruction enhancement, presence of salt decreases the vapor pressure and increase the surface tension which will help in promoting a more violent collapse of cavitation bubble.

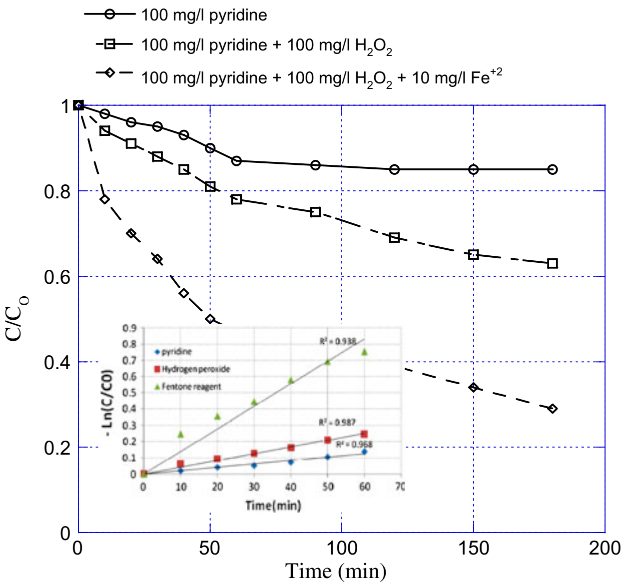

Fig. 7. Effect of Fe^{2+} with and without H_2O_2 on the degradation of pyridine (40 kHz, 20 ± 1˚C, 360 W and initial concentration of pyridine $C_0 = 100$ ppm).

3.1.4. *Effect of US/Fenton reagent/H_2O_2 system*

In this part of study, sonication experiments were repeated with pyridine solutions including Fentone/H_2O_2 system, to study the effect of Fe^{2+} addition for degradation of pyridine at 40 kHz, 20 ± 1 °C, and 360 W. Fig. 7 displays the effect of Fentone/H_2O_2 amount added to pyridine solution, while the embedded Figure shows the reaction kinetics for the degradation, in which all reactions kinetic followed first-order rate laws ($R^2 > 93$). The result shows that by the addition of Fenton reagent the degradation of pyridine increased significantly. At 10 mg/l of Fe^{2+} and 100 mg/l of H_2O_2, 71% of pyridine was removed in 180 min. while 100 mg/l H_2O_2 without Fe^{2+}, result in only 37% removal. Combination of methods between ultrasonic irradiation and Fenton reagent utilize the advantages of these two methods to generate more $^{\cdot}OH$ and improve the degradation rate of pyridine.

It is well known that the ferrous hydrogen peroxide constitutes the Fenton process. Hydrogen peroxide reacts with water and generates hydroxyl radicals. The Fenton reaction involves the following sequence of major steps [24].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\cdot} \quad (5)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^- \quad (6)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^- \quad (7)$$

$$HO^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (8)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^+ + O_2 \quad (9)$$

$$Fe^{3+} + O_2^{\cdot} \rightarrow Fe^{3+} + O_2 \quad (10)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO_2^{\cdot} \quad (11)$$

Lin and Ma (2000) found that the high concentration of hydroxyl radicals produced by Fenton method can enhance the ultrasonic degradation of 2-chlorophenol [24]. At 10 mg/l of Fe^{2+} and 500 mg/l of H_2O_2, 99% of 2-chlorophenol was removed, while 0.5 mg/l Fe^{2+} without H_2O_2 results in only 31% removal. Neppolian et al. (2002) also noted that the coupled US/Fenton method results in complete degradation of MTBE, whereas only 48% removal has taken place in ultrasonication alone [25]. In recent works, an optimum concentration of Fe^{2+} when used in conjunction with ultrasonic irradiation was identified. When the Fe^{2+} salt concentration was higher than the optimum concentration, the solution became saturated with Fe^{2+} ions and would undergo self-quenching of $^{\cdot}OH$ reaction (7) [26,27].

Generally, during the collapse of cavitations bubbles high temperatures and pressures are obtained, leading to the formation of chemical species such as $H^{\cdot}$, $OH^{\cdot}$, $O^{\cdot}$, and H_2O_2. Those high-energy phenomena cause degradation of pyridine in aqueous solutions. The degradation proceeds mainly by two reaction mechanisms: direct pyrolysis in and around the collapsing bubbles and oxidation by $OH^{\cdot}$ radicals [28,29]. However, it seems that the total mineralization of pyridine in aqueous solution is difficult with the application of ultrasound alone, because the time scale and the dissipated power necessary to mineralize chemically. However, sonochemical treatment can be combined with other techniques to increase the efficiency of destruction. Some chemicals may be utilized as an effective sonolytic catalyst for reactions involving the $OH^{\cdot}$ radical [30,31].

4. GC–MS analysis of the degradation product

Pyridine is largely soluble in water so that the main reaction site for their destruction during

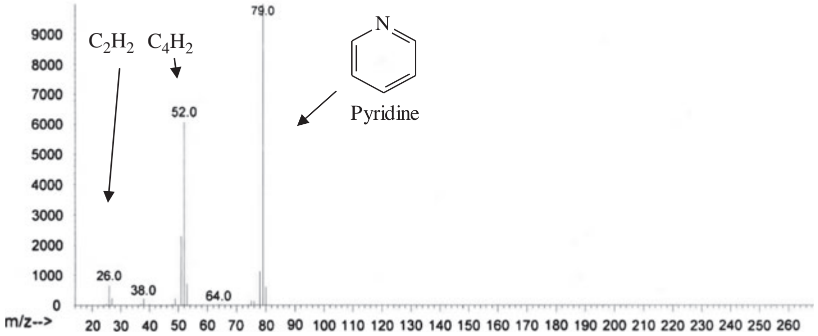

Fig. 8. GC-MS analysis (10 min irradiation time, 40 kHz, 20 ± 1 °C, 360 W and initial concentration of pyridine $C_0 = 20$ ppm).

ultrasonic irradiation is the bulk liquid, where the attack of hydroxyl radicals on the ring carbons results in various intermediates. After sufficiently long contact times mineralization occurs. The sonochemical degradation of pyridine and the major degradation product as detected by GC–MS analysis is as shown in Fig. 8.

Fig. 8 shows the GC–MS response of pyridine sample (20 mg/l) injection which was subjected to ultrasonic irradiation 10 min. The pyridine retention time is at 4.435 min. The chromatogram shows two other peaks which could be attributed to the pyridine degradation products. The result show that the ultrasonic cleavage of the ring to produce acetylene and diacetylene at 26 and 52 *m*/*z*, respectively, as a degradation products are only barely detectable. In addition to, the abundance of pyridine (concentration) decreased by increasing the sonication time.

The degradation of pyridine compounds by ultrasonic cavitation is shown to involve two distinct pathways: (1) oxidation by hydroxyl radicals (Fig. 9) and (2) pyrolytic decomposition (Fig. 10). During cavitational bubble collapse, which occurs within 100 ns, H_20 undergoes thermal dissociation within the vapor phase to give hydroxy radical and hydrogen. The concentration of $OH^{\cdot}$ at a bubble interface in water has been estimated to be 4×10^3 M [29]. Many of the chemical effects of ultrasonically induced cavitation have been attributed to the secondary effects of $OH^{\cdot}$ and H production.

However, earlier studies clearly demonstrated the radical chain nature of the thermal decomposition. Some studies in fact proposed that the pyrolysis is initiated primarily via C–H fission, most likely from the carbon atom adjacent to the nitrogen atom [32,33]. The o-pyridyl radical is believed to be the most stable of the three possible pyridyls and the only major pyridyl radical whose fission leads to the primary decomposition products, HCN, C_2H_2, and C_4H_2. Based on the mechanism of the pyrolysis of pyridine, the sonolytic mechanism of pyridine is postulated to be as follows:

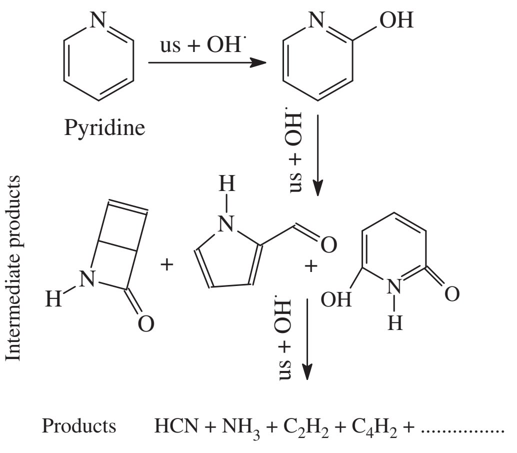

Fig. 9. Tentative degradation pathway proposed for ultrasonic degradation of pyridine by hydroxyl radicals.

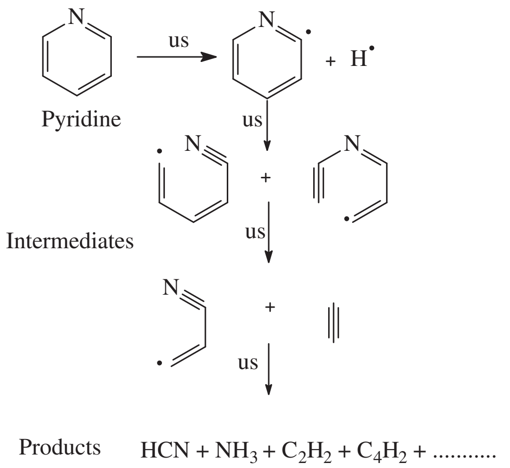

Fig. 10. Tentative degradation pathway proposed for ultrasonic degradation of pyridine by pyrolytic decomposition.

In previous work, Zechmeister et al. reported the ultrasonic cleavage of the pyridine ring in aqueous silver nitrate [34]. Roughly, 5% of the ring atoms are precipitated as a mixture of silver acetylide, silver diacetylide, and silver cyanide. It has been shown that similar cleavage reactions can also be realized in the absence of silver, with pyridine and pyrrole. Under these conditions, free acetylene and hydrogen cyanide evolved [35]. Very volatile products are directly formed through pyrolysis of substrates during the collapse of the cavitation bubbles. It has been previously proven that acetylene, diacetylene, and hydrogen cyanide can be formed during aquasonolyses of pyrrole, N-methylpyrrole, and pyridine [34–36]. In the future, products from sonolyses of pyridine should be further investigated.

The results obtained from this study revealed the ability of ultrasonic irradiation in transforming the aromatic inhibitory compounds pyridine to less toxic intermediates, which can be further decomposed by addition of oxidizer such as H_2O_2 or Fenton reagent.

5. Conclusion

The sonochemical effect of ultrasound is a highly exciting and versatile field. The simplicity and convenience of the operation are one of the high points of this method. Ultrasonic irradiation has the potential for use in environmental decontamination due to the production of high concentrations of oxidizing species such as ·OH and H_2O_2 in the solution and localized transient high temperatures and pressures. It does not require the addition of chemical additives to achieve viable degradation rates. However, some chemicals may be utilized as an effective sonolytic catalyst for reactions involving the OH· radical.

In this study, sonochemical degradation of pyridine under different process parameters was conducted. Effects of different process variables such as initial concentration, addition of electrolyte, H_2O_2, and Fenton reagent on the degradation kinetics were tested. The reaction rate was observed to be a function of the initial concentration of the pyridine. It decreases with the increase in initial concentration. The addition of an external oxidant like hydrogen peroxide and an electrolyte like sodium chloride has a significant effect on the decomposition rate. The enhancement in sonochemical decomposition of pyridine was achieved by employing the hybrid system US/Fenton. The research has shown that it is technically feasible to decompose pyridine compound by sonolysis. The advantage of ultrasonic degradation lies in the amount of energy stored in the microbubbles. If properly utilized, it can be a truly useful technology for large scale water treatment. The process is easier to operate and there are practically no hazards associated with it.

References

[1] N.H. Ince, I.G. Tezcanl, R.K. Belen, I.G. Apikyan, Ultrasound as a catalyzer of aqueous reaction systems: The state of the art and environmental applications, Appl. Catal. B 29 (2000) 167–176.

[2] K.S. Suslick, Ultrasound: Its Chemical, Physical, and Biological Effects, VCH, New York, NY, 1988, pp. 97–122.

[3] T.J. Mason, J.P. Lorimer, Ultrasonics in Sonochemistry: Theory Applications and Uses of Ultrasound in Chemistry, Ellis Horwood, Chichester. 1988, pp. 1–16.

[4] J.M. Joseph, H. Destaillats, H.M. Hung, M.R. Hoffmann, The sonochemical degradation of azobenzene and related azo dyes: Rate enhancement via Fenton's reaction, J. Phys. Chem. A 104 (2000) 301–307.

[5] E.J. Hart, A. Henglein, Free-radical and free atom reactions in the sonolysis of aqueous iodide and formate solutions, J. Phys. Chem. 89 (1985) 4342–4347.

[6] I. Hua, M.R. Hoffmann, Optimization of ultrasonic irradiation as an advanced oxidation technology, Environ. Sci. Technol. 31 (1997) 2237–2243.

[7] S. Zhu, P.R.F. Bell, P.F. Greenfield, Adsorption of pyridine onto spent rundle oil shale in dilute aqueous solution, Water Res. 22(10) (1988) 1331–1337.

[8] P. Hunter, S.T. Oyama, Control of Volatile Organic Compound Emissions: Conventional and Emerging Technologies, Wiley-Interscience, New York, NY, 2000.

[9] Y. Jiang, C. Petrier, T.D. Waite, Sonolysis of 4-chlorophenol in aqueous solution: Effects of substrate concentration, aqueous temperature and ultrasonic frequency, Ultrason. Sonochem. 13 (2006) 415–422.

[10] G. Thoma, M. Gleason, Sonochemical treatment of benzene/toluene contaminated wastewater, Environ. Prog. 17(3) (1998) 154–159.

[11] A.D. Visscher, H.V. Langenhove, P.V. Eenoo, Sonochemical degradation of ethylbenzene in aqueous solution: A product study, Ultrason. Sonochem. 4 (1997) 145–151.

[12] A.D. Visscher, P.V. Eenoo, D. Drijvers, H.V. Langenhove, Kinetic model for the sonochemical degradation of monocyclic aromatic compounds in aqueous solution, J. Phys. Chem. 100 (1996) 11636–11642.

[13] Y. Jiang, C. Petrier, T.D. Waite, Kinetics and mechanisms of ultrasonic degradation of volatile chlorinated aromatics in aqueous solutions, Ultrason. Sonochem. 9 (2002) 317–323.

[14] M.R. Hoffmann, I. Hua, R. Hochemer, Applications of ultrasonic degradation of chemical contaminants in water, Ultrason. Sonochem. 3 (1996) S163–S172.

[15] G. Zhang, I. Hua, Cavitation chemistry of polychlorinated biphenyls: decomposition mechanisms and rates, Environ. Sci. Technol. 34 (2000) 1529–1534.

[16] M. Abbasi, N.R. Asl, Sonochemical degradation of Basic Blue 41 dye assisted by nanoTiO_2 and H_2O_2, J. Hazard. Mater. 153 (3) (2008) 942–947.

[17] M. Goel, H. Hongqiang, A.S. Mujumdar, M.B. Ray, Sonochemical decomposition of volatile and non-volatile organic compounds—A comparative study, Water Res. 38(19) (2004) 4247–4261.

[18] X. Wang, J. Wang, P. Guo, W. Guo, C. Wang, Degradation of rhodamine B in aqueous solution by using swirling jet-induced cavitation combined with H_2O_2, J. Hazard. Mater. 169 (2009) 486–491.

[19] A. De Visscher, H. Van Langenhove, P. Van Eenoo, Sonochemical degradation of ethylbenzene in aqueous solution: A product study, Ultrason. Sonochem. 4(2) (1997) 145–151.

[20] S. Merouani, O. Hamdaoui, F. Saoudi, M. Chiha, Sonochemical degradation of Rhodamine B in aqueous phase: Effects of additives, Chem. Eng. J. 158(3) (2010) 550–557.

[21] N. Shimizu, C. Ogino, M.F. Dadjour, T. Murata, Sonocatalytic degradation of methylene blue with TiO_2 pellets in water, Ultrason. Sonochem. 14(2) (2007) 184–190.

[22] P.R. Gogate, S. Mujumdar, J. Thampi, A.M. Wilhelm, A.B. Pandit, Sep. Purif. Technol. 34 (2004) 1–11.

[23] J.D. Seymour, R.B. Gupta, Ind. Eng. Chem. Res. 36 (1997) 3453–3457.

[24] J. Lin, Y.S. Ma, Oxidation of 2-Chlorophenol in water by ultrasound/Fenton method, J. Environ. Eng. 126(2) (2000) 130–137.

[25] B. Neppolian, H. Jung, H. Choi, J.H. Lee, J.W. Kang, Sonolytic degradation of methyl tert-butyl ether: The role of coupled fenton process and persulfate ion, Water Res. 36 (2002) 4699–4708.

[26] M. Inoue, Y. Masuda, F. Okada, A. Sakurai, I. Takahashi, M. Sakakibara, Degradation of bisphenol A using sonochemical reactions, Water Res. 42(6–7) (2008) 1379–1386.

[27] H. Ghodbane, O. Hamdaoui, Degradation of Acid Blue 25 in aqueous media using 1700 kHz ultrasonic irradiation: Ultrasound/Fe(II) and ultrasound/H_2O_2 combinations, Ultrason. Sonochem. 16(5) (2009) 593–598.

[28] D. Drijvers, H.V. Langenhove, M. Beckers, Decomposition of phenol and trichloroethylene by the ultrasound/H_2O_2/CuO process, Water Res. 5 (1999) 1187–1194.

[29] Y. Jiang, C. Petrier, T.D. Waite, Effect of pH on the ultrasonic degradation of ionic aromatic compounds in aqueous solution, Ultrason. Sonochem. 9 (2002) 163–168.

[30] C. Wu, X. Lu, D. Wei, J. Fan, L. Wang, Photo sonochemical degradation of phenol in water, Water Res. 35(16) (2001) 3927–3933.

[31] B. David, M. Lhote, V. Faure, P. Boule, Ultrasonic and photochemical degradation of chlorpropham and 3-chloroaniline in aqueous solution, Water Res. 32 (1997) 2451–2461.

[32] J.C. Mackie, M.B. Colket, P.F. Nelson, Shock-Tube Pyrolysis of Pyridine, J. Phys. Chem. 94 (1990) 4099–4106.

[33] J.H. Kiefer, Q. Zhang, R.D. Kern, J. Yao, B. Jursic, Pyrolyses of aromatic azines: Pyrazine, pyrimidine, and pyridine, J. Phys. Chem. A 101 (1997) 7061–7073.

[34] L. Zechmeister, E.F. Magoon, On the ultrasonic cleavage of the pyridine ring, J. Am. Chem. Soc. 78 (1956) 2149–2150.

[35] D.L. Currell, L. Zechmeister, On the ultrasonic cleavage of some aromatic and heterocyclic rings, J. Am. Chem. Soc. 80 (1958) 205–208.

[36] D.L. Currell, S. Nagy, G. Wilheim, Effect of certain variables on ultrasonic cleavage of phenol and of pyridine, J. Am. Chem. Soc. 85 (1963) 127–130.