Review on the treatment of organic pollutants in water by ultrasonic technology

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ABSTRACT

The application of ultrasonic technology in the treatment of organic pollutants in water has attracted more and more attention in recent years. Compared with conventional treatment, ultrasonic treatment is more efficient and time saving. Ultrasonic technology is effective for the degradation of many refractory organic pollutants. In this paper, the principle, influencing factors and various methods of ultrasonic degradation of organic pollutants are studied in view of ultrasonic treatment alone, ultrasound treatment methods combined with biocatalysts, chemical oxidation and adsorption techniques, respectively. In addition, the problems existing in the treatment of organic pollutants in water by ultrasonic technology are analyzed and the development direction is put forward.

1. Introduction

With the rapid development of the economy, the continuous advancement of industrialization has brought tremendous pressure on water resources, therefore, how to treat industrial wastewater has become a problem that must be solved.

At present, the main methods of polymer degradation are physical degradation, chemical degradation and biodegradation. However, each degradation method has its limitations. For example, the physical degradation method treatment is unreliable, and often fails to achieve effective degradation; chemical degradation typically provides adequate treatment, but is likely to cause secondary pollution; biodegradable methods can necessitate stringent requirements for successful applications [1–3].

Ultrasound technology is a clean and efficient new treatment method for the degradation of toxic organic pollutants. Especially for organic pollutants that are difficult to degrade with conventional methods. It has the advantages of high removal efficiency, short reaction time, simple facilities and small footprint. It has attracted extensive attention of researchers and has become a research hotspot in recent years. In particular, great achievements have been made in the treatment of micro-polluted water, difficult-to-degrade high concentration organic wastewater, sludge, disinfection of drinking water, scale inhibition and scale removal of industrial wastewater. It combines the characteristics of advanced water treatment technologies such as enhanced oxidation technology, incineration, and supercritical oxidation. It has mild degradation conditions, fast degradation speed and a wide application range. It can be used alone or in combination with other water treatment technologies [4–7]. Therefore, it is a technology with great development potential and application prospects.

In this paper, the principle, influencing factors and various methods of ultrasonic degradation of organic pollutants are studied in view of ultrasonic treatment alone, ultrasound treatment methods combined with biocatalysts, chemical oxidation and adsorption techniques, respectively. In addition, the problems existing in the treatment of organic pollutants in water by ultrasonic technology are analyzed and the development direction is put forward.

2. Research on the principle of ultrasonic degradation

The efficacy of ultrasound chemical reactions is mainly due to the cavitation of ultrasound. When a certain frequency and intensity of ultrasonic waves are applied to a liquid, a large number of tiny bubbles are generated. These tiny bubbles cause a series of physical and chemical changes during their formation, oscillation, growth, and contraction to collapse. This effect is called cavitation [8].

In a sparse half cycle, negative pressure is formed inside the liquid. When the ultrasonic intensity is large enough, the average distance betwe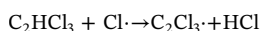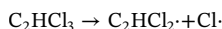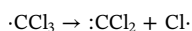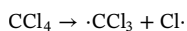en molecules changes and exceeds the critical value of the liquid molecular distance, and the gravity between liquid molecules is destroyed and cavitation bubbles are formed. Cavitation bubbles undergo a process of formation, growth, and collapse [9]. When the cavitation bubble collapses, a large amount of energy is released inside and around the cavitation bubble [9].

The "hot spot" theory holds that when the cavitation bubble collapses, the "instantaneous hot spot" of up to 5000 K high temperature and 1000 atm high pressure can be generated in the very small space inside and around the cavitation bubble in a very short period of time. The change rate of temperature is as high as 10^9 K/s, such a high temperature can promote the degradation of organic matter. A series of ultrasonic (355 kHz) experiments on argon saturated aqueous solutions containing C_1-C_5 aliphatic alcohols have been carried out, based on the yield of recombination of hydrocarbon radicals CH_3· from the ultrasonic degradation products of alcohols in aqueous solution, the average temperature range for cavitation bubbles generated by ultrasonic cavitation is measured to be 4600 ± 200 K to 2300 ± 200 K, which is consistent with the hot spot theory [10].

Currently, there are three reaction pathways for degradation of organic compounds by ultrasonic cavitation.

2.1. Pyrolysis reaction at high temperature

According to the hot spot theory, the inside of the bubble is a high temperature and high-pressure gas phase, so the non-polar and volatile hydrophobic solute vapor is easy to enter the cavity, where high temperature pyrolysis occurs. For example, CCl_4 and C_2HCl_3 can undergo the following sonochemical degradation process, after high-temperature pyrolysis, organic pollutants are degraded into small molecular compounds that are environmentally friendly [10].

$CCl_4 \rightarrow \cdot CCl_3 + Cl\cdot$

$\cdot CCl_3 \rightarrow :CCl_2 + Cl\cdot$

$C_2HCl_3 \rightarrow C_2HCl_2\cdot + Cl\cdot$

$C_2HCl_3 + Cl\cdot \rightarrow C_2Cl_3\cdot + HCl$

$C_2HCl_3 \rightarrow C_2Cl_2 + HCl$
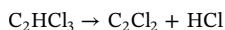
2.2. Free radical oxidation

In the high temperature and high-pressure region of bubbles, water molecules are prone to react as follows, producing strong oxidizing substances H_2O_2 and ·H, ·OH radicals [10].

$H_2O +))) \rightarrow \cdot H + \cdot OH$))) represents ultrasound

$2\cdot OH \rightarrow H_2O_2$
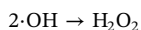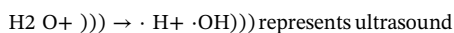
Free radicals contain unpaired electrons, which are very active and have strong oxidation ability. In solution, the shock wave generated by bubble collapse can cause free radicals and hydrogen peroxide in the bubble to enter the solution. These oxidants can oxidize and degrade non-volatile polar organic compounds in solution. For example, the degradation process of 4-p-bromophenylazo-3,6-dihydroxy-naphthalene-2,7-disulfonic acid molecule (Fig. 1) is such a free radical oxidation process. The molecule is first oxidized by ·OH to a radical with a single electron. Then, OH undergoes a nucleophilic substitution reaction, and then the azo bond of the molecule is broken and degraded into small molecules [10–13].

2.3. Supercritical water oxidation reaction

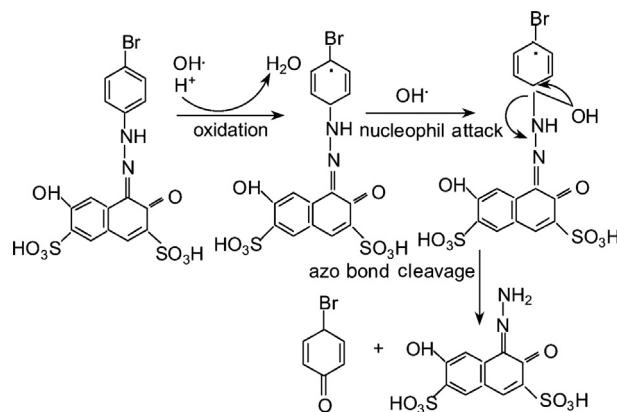In the transition zone between bubbles and solution, water is in a
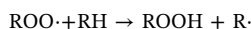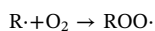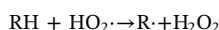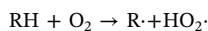

Fig. 1. The degradation process of 4-p-bromophenylazo-3,6-dihydroxy-naphthalene-2,7-disulfonic acid molecule.

high temperature and high-pressure state, i.e. supercritical state, above the critical point (22.1 MPa, 374 °C). This kind of water is called supercritical water [10]. It has the same diffusion coefficient as gas (10–100 times higher than ordinary liquid) and lower viscosity. It also has the same density as liquid and good solubility to substances. Therefore, non-volatile organic compounds can also be soluble in supercritical water and react with oxidants such as air and oxygen [10]. For example, organic matter undergoes the following reaction processes and is oxidized to peroxide ROOH:

$RH + O_2 \rightarrow R\cdot + HO_2\cdot$

$RH + HO_2\cdot \rightarrow R\cdot + H_2O_2$

$R\cdot + O_2 \rightarrow ROO\cdot$

$ROO\cdot + RH \rightarrow ROOH + R\cdot$

The resulting peroxide ROOH is unstable and usually decomposes into smaller compounds, such as formaldehyde and acetic acid, which are eventually oxidized to water and CO_2, leading to complete degradation [10].

3. Study on the main factors affecting the process of ultrasonic degradation

3.1. Ultrasonic frequency

Studies have shown that the effect of ultrasonic degradation of organic pollutants is not getting better with the increase of ultrasonic frequency. Ultrasonic frequency is related to the degradation mechanism of organic pollutants. There is an optimum frequency for the degradation of free radicals. For pyrolysis-based degradation reactions, the degradation efficiency increases with the increase of frequency when the ultrasonic intensity is greater than the cavitation threshold.

3.2. Ultrasonic intensity

Within a certain range, the degradation degree of organic pollutants in aqueous solution increases with the increase of sound intensity. When the area of the acoustic emission end is constant, the sound intensity is proportional to the ultrasonic amplitude [11–14]. The temperature and pressure generated by collapse of the cavitation bubble are related to the amplitude of the ultrasonic wave. As the amplitude of the ultrasonic wave increases, the cavitation bubble collapses more violently, resulting in higher temperature and pressure [18]. At the same time, the concentration of free radicals, the mass transfer and the solution rate of organic matter in the solution are all increased. Different ultrasound reactors have been used to degrade rhodamine B. in order to study the optimization of power parameters [18]. results

indicate that various ultrasonic reactors have their best sound intensity, and the degradation rate decreases with increasing sound intensity when the sound is stronger than the optimal value. This could be caused by two aspects: (a) higher sound intensity can increases the cavitation bubbles in the solution, which results in the scattering of ultrasonic waves and the loss of some energy; (b) the increase in the sound intensity also makes the cavitation bubble in the negative sound pressure phase grow too large to form an acoustic shield, which reduces the energy of the sound field available to the system.

3.3. Dissolved gas

Studies have shown that the cavitation bubble nuclei produced by injecting dissolved gas into the solution during the ultrasonic degradation process were helpful to the formation of cavitation bubbles so as to improve the degradation rate [15–18]. The nature of the gas has a great influence on the cavitation effect. These properties include:

(1) Specific heat ratio. The specific heat of monatomic gas is higher than that of polyatomic gas and air, therefore, the cavitation efficiency is improved by saturated aqueous solution of monatomic gas, which is helpful to the degradation of organic matter [18].
(2) Thermal conductivity. As the thermal conductivity of the dissolved gas increases, the heat generated by the collapse of the cavitation bubbles can be more easily transmitted to the surrounding, weakening the cavitation effect and adversely affecting the degradation of organic matter [18].
(3) Solubility. Highly soluble gases are more likely to diffuse into the cavitation bubble and lower the cavitation strength, affecting the degradation of organic matter.
(4) The order of solubility of commonly used dissolved gases in aqueous solution is: $CO_2 > Ar > O_2 > H_2 > He$; if the carbon disulfide is decomposed ultrasonically with different gases as dissolved gases, the order of decomposition rate is: $He > H_2 > air > Ar > O_2 > CO_2$. It can be seen that the gas with high solubility reduces the decomposition rate of carbon disulfide by affecting the cavitation efficiency [18].
(5) Although the solubility of O_2 is relatively large, the degradation rate of some organic substances increases due to the free radicals participating in the degradation reaction under ultrasonic radiation. For example. when the 4-chlorine-2-methyl Phenoxy Acetic Acid (MCPA) is degraded by ultrasound, the mixture of Ar and O_2 is used as a dissolved gas. This approach not only uses the large specific heat ratio of Ar, but also utilizes the characteristic that O_2 can be decomposed into O· and OH radicals by ultrasound. This method makes MCPA degradation easier than using Ar or O_2 as dissolved gas alone [18].

3.4. pH value

The effect of pH value of solution on the ultrasonic degradation of organic acids and alkaline substances are mainly as follows:

(1) When the PH value of the solution is small, the organic matter mainly exists in the form of molecule in the aqueous solution, which is easy to approach the gas-liquid interface of the cavitation bubble, and can evaporate into the cavitation bubble and pyrolyze directly in the cavitation bubble. In addition, the free radicals produced by cavitation can be oxidized at the gas-liquid interface of the cavitation bubble and in the bulk solution, and the degradation efficiency is high.
(2) When the PH value of the solution is high, the ionization of organic substances occurs in the solution as ions, which can not evaporate into the cavitation bubble, but can only oxidize with free radicals at the gas-liquid interface of the cavitation bubble and in the bulk solution. The degradation efficiency is low. Ultrasound degradation

occurs in the cavitation core or at the gas-liquid interface of the cavitation bubble. Ions are difficult to approach the gas-liquid interface and enter the cavitation bubble. Therefore, the adjustment of pH value of the solution should be beneficial to the existence of organic compounds in the form of neutral molecules and easy to volatilize into the bubble nucleus [19–23].

3.5. Temperature

Temperature has a very important influence on the intensity and kinetics of ultrasonic cavitation, which leads to the change of ultrasonic degradation rate and degree. Experiments show that higher temperature is beneficial to accelerate the reaction rate, but ultrasound-induced degradation is mainly caused by cavitation effect. When the temperature is too high, the water will boil and the high pressure generated by cavitation will be reduced in the half period of negative pressure of acoustic wave. Meanwhile, the cavitation bubble will immediately fill with water vapor and reduce the high temperature generated by cavitation, thus reducing the degradation efficiency. General chemical efficiency increases exponentially with temperature drop, therefore, low temperature (20 °C) is less than the more conducive to the ultrasonic degradation experiments, so the degradation is usually conducted at room temperature [19–25].

4. Study on the removal of organic pollutants in water by ultrasound combined with other techniques

Ultrasound is usually combined with other techniques to increase degradation efficiency. Usually ultrasound is combined with other technologies to improve degradation efficiency. These technologies include ultrasound-catalyst method, ultrasound-ozone method (US-O_3), ultrasonic-biological method, ultrasound-ultraviolet-titanium dioxide method (US-UV-TiO_2), ultrasonic-electrochemical method [24].

4.1. Ultrasound-catalyst method

When sewage is treated by ultrasound, the addition of catalyst will accelerate the degradation of hydrophobic and non-volatile pollutants, such as phenols, chlorobenzene, nitrobenzene, methyl blue, etc. The commonly used catalysts are SnO2, TiO_2, SiO_2, MnO_2, H_2O_2, $NiSO_4$, $CuSO_4$, NaCl and Fen-ton reagents [24–28].

The effects of various factors on the ultrasonic degradation of methyl orange were studied using SiO_2 doped titanium dioxide synthesized in the laboratory as the catalyst The results show that the degradation of methyl orange by ultrasound with SiO2 doped titanium dioxide catalyst is better than that with un-doped anatase-type titanium dioxide [24].

In addition, experimental treatment of coking wastewater with ultrasound, electrolysis with and without Fenton reagent showed minimal effect without reagent on decolorization, with or without H_2O_2, with a CODc removal rate of only about 2%. However, for the same treatment duration, the combined treatment of ultrasound and Fenton reagent showed that the chroma can be reduced by 16 times, and the CODc can be reduced to 37.7 mg/L.

4.2. Ultrasound-ozone method (US-O_3)

The combined effect of ozone and ultrasound on MTBE was studied. It was found that the primary degradation rate constant of MTBE removal increases from $4.1 \times 10^{-4} s^{-1}$ to $8.5 \times 10^{-4} s^{-1}$ with the decrease of MTBE from 1.0 M to 0.01 mM at the frequency of 205 kHz and the power density of 200 W·L^{-1}. The yields of the main intermediates, *tert*-butyl methyl ester, *tert*-butyl alcohol, methyl ethyl ester and acetone were 8%, 5%, 3% and 12%, respectively [24,29–31].

In addition, the degradation of phenol by US-O_3 was found to be greatly increased compared to US alone.

4.3. Ultrasonic-biological method

Using 2–5 h of ultrasonic oscillation (2 h of oscillation and 1.6 GJ·m³ of dispersed energy) significantly decreased the toxicity of pentachlorophenol in sludge, while causing no harm to the bacteria [24].

In addition, with treatment of refractory dye wastewater by ultrasound followed by activated Sludge Batch Reaction (SBR) the BODS/COD value of wastewater increased from 0.21–0.23 to 0.44–0.51, and the concentration of aniline decreased to less than $20\,mg\cdot L^{-1}$, which created good conditions for subsequent biological treatment.

4.4. Ultrasound-ultraviolet-titanium dioxide method (US-UV-TiO₂)

Tests of ultrasound degradation of aniline wastewater showed a small synergistic effect with TiO_2 for ultrasound plus ultraviolet radiation. The degradation rate of aniline after treatment by ultrasound/TiO_2 was 30%and for UV-TiO_2 was 35%, while the combination of all three had a degradation rate of 72% (7% synergistic effect).

In addition, when the aniline dye wastewater was treated by ultrasound/ultraviolet synergistic oxidation process, it was found that the combined action of ultrasound and ultraviolet light followed a Quasi-First-Order kinetic equation, which facilitates achieving high degradation rates [24].

4.5. Ultrasonic-electrochemical method

Study of the Electrolytic oxidation treatment for reactive violet dye in wastewater showed that the degradation of dye in wastewater is enhanced, but not dramatically, by combination with ultrasound treatment.

However, the decolorization rate with the combined action of ultrasonic/micro-electric field is much higher than that under the action of micro-electric field alone. The decolorization rate can reach 96.6% when the initial mass concentration is $370\,mg\,L^{-1}$, the pH = 2 and the cell voltage is 5 V for 60 min [24,33].

In addition, the degradation of phenol in water by ultrasonic-electrochemical method also achieved good results. The ultrasonic treatment functions in two ways one is mechanical action by cavitation that can renew the surface of electrodes continuously; the other is the chemical action of cavitation that can degrade organic pollutants in water. For example, a study showed that the combined action of ultrasound and electrochemistry required only about 30 min to remove aniline completely, whether the concentration of aniline was low or high, while the electrochemical action alone took about 120 min [24].

5. Application of ultrasonic technology in the treatment of organic pollutants in water

5.1. Ultrasonic treatment for organic dyes

The pretreatment of indigo dye wastewater by sonochemical oxidation was studied. The results show that BOD/COD of biorefractory indigo dye wastewater can be increased from 0.21–0.23 to 0.44–0.51. After treatment by activated Sludge Batch Reaction (SBR), the effluent indexes all meet the discharge standards. The treatment of reactive violet dye wastewater by ultrasonic-electrolysis method is studied. The experimental results show that the decolorization rate of wastewater can be greatly improved by the synergistic action of ultrasound and micro-electric field. Under the optimum technological conditions, the color removal rate of wastewater can reach 99.6% after 60 min of ultrasonic-electrolysis treatment [32–36].

It is found that the decolorization rate and the removal rate of organic carbon are all related to the dye structure from the study on the ultrasonic photodegradation of reactive red 141, reactive black 5, alkaline brown 4 and alkaline blue. Azo dyes are more easily degraded than azo dyes with low molecular weight [35–37].

From the study of ultrasonic degradation of acid orange 7 and active orange 16, it is found that for the aryl-azo-naphthol type mono-azo dyes, the acid orange 7 with simple structure and small molecular weight is more easily discolored than the active orange 16 having a complex structure and a large molecular weight. This indicates that the size of the dye molecule and the type and position of the substituent have some influence on the ultrasonic degradation.

Ultrasonic degradation of the azo dye reactive red 22 is in accordance with Langmuir-Hinshelwood or Eley-Rideal multiphase kinetic model. It is found that acid orange 7 was degraded by ultrasonic degradation and photocatalytic degradation respectively. By GC–MS analysis, the intermediate product of acid orange 7 was mainly composed of low aliphatic compounds. The intermediate products of photocatalytic degradation of acid orange 7 can be classified into three categories: naphthalene ring compounds such as 2-naphthol, aromatic compounds such as phenylethanol 2-methylphenol and ring-opening compounds such as 2-ethyl-hexanol. From the formation of intermediate products, ultrasonic degradation is better than photocatalytic degradation of TiO_2.

5.2. Ultrasonic degradation for pesticides

The effects of ultrasonic power, frequency, sound intensity, horn diameter, pH value and types of dissolved gases on the degradation of Metamorphose in pesticide wastewater were studied. The degradation of Methamidophos is little affected by changing the frequency of ultrasound in the low frequency range. The degradation rate of Methamidophos was significantly increased with the increase of ultrasonic power, sound intensity and the diameter of horn. When the diameter of horn equals 25 mm, the degradation rate can reach 61.7%. The acidic condition is favorable for the degradation of methamidophos, and the filling of dissolved gas is favorable for the degradation of methamidophos. The order of influence is air > Ar > O_2 > N_2 [38–41].

The degradation rate of 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine) can be increased by ultrasonic ozone or titanium dioxide combined with ultrasonic light.

The photocatalytic removal of atrazine by TiO_2 takes 4 h, and the same effect can be achieved by using TiO_2 combined with ultrasonic light for only 1 h. The ultrasonic photodegradation effect of TiO_2 combined with ultrasonic light is slightly worse than that of ultrasonic ozone.

Ultrasound combined with ozone or ultrasound combined with TiO_2 photocatalysis can improved the degradation rate, but did not change the degradation mechanism (compared with ozonation alone or TiO_2 photocatalysis). The combination of ultrasound and titanium dioxide photocatalysis can accelerate the process of ATRAZINE dealkylation and dechlorination, while the combination of ultrasound and ozone can accelerate the process of ATRAZINE dechlorination. When nano-sized titanium dioxide (rutile type) is used as catalyst for ultrasonic degradation of parathion, the degradation rate can exceed 90% under the optimal conditions (parathion concentration is 50 mg L, titanium dioxide dosage is 1 000 mg L, pH = 10, 30 ~ 50 kHz, 50 W, 20 C, 120 min). Ion chromatography can be used to detect the degradation products NO^{3-}, NO^{2-}, PO_4^{3-}. This method is undoubtedly an effective means for the degradation of parathion, both in terms of degradation rate and final product [42–44].

5.3. Ultrasonic degradation for aromatic hydrocarbons

The degradation of aromatic hydrocarbons mainly includes the degradation of monocyclic aromatic hydrocarbons (benzene, toluene, ethylbenzene, hexyl benzene, styrene, o-chlorotoluene) and polycyclic aromatic hydrocarbons (biphenyl, anthracene, phenanthrene, pyrene) [45].

Benzene, ethylbenzene, styrene and o-Chlorotoluene solutions were irradiated by ultrasound with a frequency of 520 kHz, respectively. The

results show that the ultrasonic degradation of the four substances follows the first-order reaction kinetics. Benzene solution with initial concentration of 0.45 m mol/L is treated for 100 min, and its first-order degradation kinetic rate constant is 0.023 min^{-1}. The first-order degradation kinetics constant of ethylbenzene solution with initial concentration of 0.50 m mol/L is 0.036 min^{-1} after 100 min treatment, and the first-order degradation kinetics constant of o-Chlorotoluene solution with initial concentration of 0.34 m mol/L is 0.029 min^{-1} after 75 min treatment. The first-order degradation kinetics constant of styrene solution with initial concentration of 0.49 m mol/L is 0.024 min^{-1} after 80 min treatment [46–50].

5.4. Ultrasonic degradation for alcohols

Degradation of alcohols mainly includes degradation of methanol and ethanol. It has been found that when ultrasonically decomposing organic substances having a small molecular weight such as ethanol, the degradation products are formic acid and acetic acid [51–53].

The results show that when methanol solution is injected into argon under 1 MHz ultrasound radiation, H_2, HCHO, CO, CH_4 and a small amount of C_2H_4 and C_2H_6 are produced; When oxygen is introduced, CO_2, CO, HCOOH, HCHO, H_2 and a small amount of H_2 are produced; the amount of product varies with the proportion of methanol to water. When the volume fraction of methanol solution is 10%, the amount of degradation products is much higher than that of pure water, while in 80% methanol solution, almost no chemical reaction occurs [54–58].

6. Conclusion

Ultrasound degradation of chemical pollutants in water, especially refractory organic pollutants, is a new water treatment technology developed in recent years. It combines the characteristics of advanced oxidation technology, incineration, supercritical oxidation and other water treatment technologies. It has the advantages of mild degradation conditions, fast degradation speed and wide application range. It can be used alone or in combination with other water treatment technologies, and is a technology with great development potential and application prospects. It will provide a new way for the treatment of human water pollution and have a broad prospect of development and application.

At present, the new ultrasonic cavitation technology is still at the stage of basic research, mainly in small-scale experiments in the laboratory, and it must be developed into a mature water treatment technology that can be widely used. There are still many problems that need further study about: (1) the effect of ultrasound technology on the degradation of mixed organic substances or industrial wastewater, and the promotion and inhibition of various organic substances when they are degraded, so as to broaden the scope of application of sonochemistry; (2) the reaction mechanism and kinetics of ultrasonic participation in the degradation of organic matter, and theoretical parameters for the optimal design of the reactor to further improve the degradation efficiency; (3) the combination of ultrasonic technology and other technologies. Extend ultrasonic technology to the industrial level, and study the optimal working parameters to solve the actual problems after the upgrade, making it more technically and economically feasible; (4) the detection of intermediate or final degradation products and their impact on the environment. Although great progress has been made in the study of ultrasonic degradation of various organic compounds, there are few reports on this aspect, especially for organic compounds with complex structures.

Acknowledgement

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2019.01.017.

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