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Degradation of antibiotic wastewater based on high-pressure submerged cavitation jet and synergetic methods

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ABSTRACT

In the present work, degradation of antibiotic wastewater is carried out using high-pressure submerged cavitation jet technique in combination with multiple synergetic methods, that is, UV/Fenton, analogous Fenton, and photocatalytic oxidation. Three kinds of common antibiotics, such as amoxicillin, doxycycline, and sulfadiazine sodium, are selected as model pollutants. Individual operation of hydrodynamic cavitation under different nozzle inlet pressure conditions is first carried out. It is observed that higher jet inlet pressure is more favorable for chemical oxygen demand (COD) reduction and the maximum COD reduction is 13.52%. Then, the degradation process is intensified by introducing UV/Fenton method. Effects of important parameters are investigated and the optimum operating conditions are obtained, that is, pH of 2.7, H_2O_2/COD molar ratio of 1.99 and $FeSO_4$ concentration of 8.33 mg/L. The maximum COD reduction of 51.10% is achieved under these optimum conditions and the synergetic index is 2.121. Subsequently, the analogous Fenton and photocatalytic oxidation are successively introduced for further enhancing the COD reduction, and the synergetic indices of various combinations are evaluated. The comparison of the different approaches indicates that the most effective and economical approach for antibiotic wastewater treatment is the combination of hydrodynamic cavitation, UV/Fenton, analogous Fenton, and photocatalytic oxidation, with the maximum COD reduction of 66.63% and the synergetic index of 2.581.

Keywords: Submerged cavitation jet; Antibiotic wastewater; UV/Fenton; Analogous Fenton; Photocatalytic oxidation

1. Introduction

With the development of the pharmaceutical industry, the pharmaceutical wastewater has become one of the important pollution sources, and the treatment of pharmaceutical wastewater is a severe challenge for environmental protection [1]. Among all the pharmaceutical compounds that cause the environmental contamination, antibiotics occupy an important place due to their high consumption rate in both veterinary and human medicine [2–4]. Antibiotics usually have high toxicity, weak biodegradability, and long-time stability [5]. Hence, the traditional biochemical processing methods may not be efficient to treat antibiotic wastewater, and it is imperative to develop new treatment techniques.

In recent years, the advanced oxidation processes (AOPs), which are characterized by the generation of hydroxyl radicals (OH), have aroused extensive attention worldwide [6–8]. Hydroxyl radicals have strong oxidation ability, high reaction activity, and non-selectivity, and thus can completely decompose or mineralize various organics. Therefore, the AOPs have prominent advantages and good application prospect in dealing with refractory organic wastewater. Hydrodynamic cavitation is one of the AOPs and has such advantages as simple reactor design, easy operation, no secondary pollution, and capacity to easily operate in large scale [9–11]. Due to the collapse of cavitation bubble, local extreme

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environment with temperature of 1,000–10,000 K, pressure of 100–5,000 bar, and high-speed micro-jet (10^2 m s^{-1} magnitude) can be formed [12]. Water vapor inside the bubble will be dissociated in the local extreme environment, generating reactive hydrogen atoms and hydroxyl radicals [13]. These radicals can participate in oxidation reactions of organic pollutant.

Many researchers have reported degradation of organic wastewater using different types of hydrodynamic cavitation devices. Patil and Gogate [14] carried out degradation of methyl parathion using hydrodynamic cavitation induced by orifice plates. Effects of operating parameters were investigated and the maximum degradation extent was 23.1% for the individual application of hydrodynamic cavitation. Presence of different process-intensifying additives such as H_2O_2, CCl_4, and Fenton reagent was also studied. More than 90% degradation rate and a maximum 76% total organic carbon (TOC) reduction were obtained. Using slit venturi device, Bagal and Gogate [15] performed the treatment of diclofenac with the novel combination of hydrodynamic cavitation and photocatalysis. The individual utilization of hydrodynamic cavitation generated 26.85% degradation extent under the optimized operating conditions. A degradation rate of 95% together with 76% reduction in TOC was achieved by using hydrodynamic cavitation in conjunction with UV/TiO_2/H_2O_2. Patil et al. [16] worked on the hydrodynamic degradation of imidacloprid using orifice plate and slit venturi as hydrodynamic cavitation device. Only by means of hydrodynamic cavitation, a 23.85% degradation of imidacloprid was obtained under the optimized operating parameters for the orifice plate, while a 27.93% degradation of imidacloprid was achieved in the case of slit venturi under the same operating parameters. Chakinala et al. [17] used hydrodynamic cavitation induced by a liquid whistle reactor in conjunction with the advanced Fenton process to treat the real industrial wastewater. Wang et al. [18] carried out degradation experiments of rhodamine B and brilliant red K2-BP [19] by using the swirling jet hydrodynamic cavitation reactor. Considering that the opposite movements of two shear layers can generate shear cavitation, Petkovšek et al. [20] used a novel rotation cavitation generator to remove pharmaceuticals in water. The generator included two facing rotors with special radial grooves spinning in the opposite direction. Using a rotor and a stator, Badve et al. [21] proposed a novel cavitation reactor that was presented in the form of a solid cylinder with indentations on its surface. The cavitation was formed on the surface of the cylinder as well as within the indentations due to high-speed rotation. Treatment of wastewater from wood finishing industry was carried out.

Although many investigations on the application of hydrodynamic cavitation into wastewater treatment have been reported in the previous literatures, to the best of our knowledge, few studies use hydrodynamic cavitation technique to treat antibiotic wastewater. A possible reason is that the weak cavitation intensity generating in the hydrodynamic cavitation reactors leads to the poor degradation rate because antibiotics have very stable molecular structure and quite refractory nature. The cavitation intensity can be enhanced by increasing the pressure drop in the cavitation reactor. By using high-pressure submerged cavitation jet technique, a device that can generate hydrodynamic cavitation with higher intensity and provide strong turbulence, efficient heat and mass transfer, and intensive chemical reactions has been innovatively used for degradation of antibiotic wastewater in the present work. Three kinds of antibiotics, namely amoxicillin, doxycycline, and sulfadiazine sodium, are selected as model pollutants. The synergetic methods of UV/Fenton, analogous Fenton, and photocatalytic oxidation are also introduced to intensify the degradation process. The individual utilization of hydrodynamic cavitation can obtain 13.52% chemical oxygen demand (COD) reduction under the optimized operating conditions. While the maximum COD reduction of 66.63% is achieved by using hydrodynamic cavitation in conjunction with Fenton, analogous Fenton, and photocatalytic oxidation. A comparison of all the approaches used in the present study indicates that the most effective and economical method is the combination of hydrodynamic cavitation, UV/Fenton, analogous Fenton, and photocatalytic oxidation.

2. Materials and methods

2.1. Materials

The commercial grade amoxicillin, doxycycline, and sulfadiazine sodium were purchased from Hua Xu Veterinary Medicine Co., Ltd., China. All other chemicals used in the present work were purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing, and they were used as received from the supplier: hydrogen peroxide (30%, AR), ferrous sulfate (AR), sulfuric acid (AR), sodium hydroxide (AR, flake), copper powder (2.7N purity, 15 μm), and anatase titanium dioxide (4N purity, 5 nm particle diameter). Purified water was used throughout all the experiments.

2.2. Experimental setup and methodology

The experimental system is shown in Fig. 1. It is a closed circulation loop, which essentially consists of three pipelines, that is, the main line, the pressure regulating bypass line, and the cooling line. The main line contains a water container of 50 L, a high pressure plunger pump of 5.5 kW,

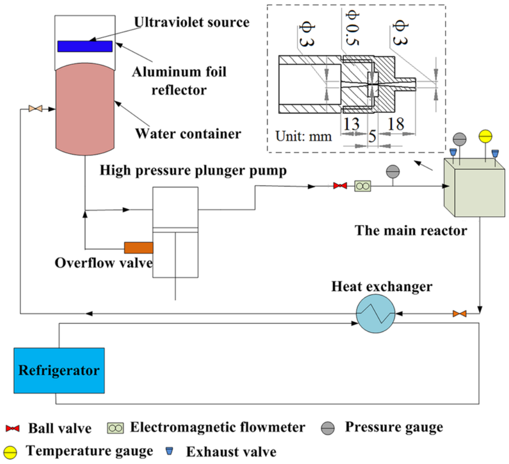

Fig. 1. The schematic of the experimental system.

a main reactor chamber, and a heat exchanger. Aqueous solution is drawn from the container by the plunger pump and flows into the main line after being pressurized to the desired values by adjusting the pressure-regulating valve in the bypass line. After flowing through the high-pressure ball valve, the electromagnetic flow meter and the pressure gauge in sequence, it enters into the cavitation nozzle, which has a converging–diverging flow channel (the dimensions are shown in the enlarge figure at the upper-right corner of Fig. 1). Hydrodynamic cavitation takes place inside the nozzle and the high-speed cavitating jet enters into the main reactor chamber, where the bubble collapse and the resultant antibiotics degradation mainly take place. After that, aqueous solution flows out of the main reactor from the outlet at the bottom of the chamber. Subsequently, the liquid is cooled in the heat exchanger and then flows back into the liquid container. An ultraviolet source of 30 W is installed above the water container, the ultraviolet which is used to accelerate Fenton reaction and also induce photocatalytic oxidation. The ultraviolet source is wrapped up by an aluminum foil reflector to reduce the ultraviolet loss.

The container is filled with 30 L aqueous solution of amoxicillin, doxycycline, and sulfadiazine sodium. The initial COD value of the solution is 236 ± 2 mg/L, with 8 g of each antibiotic added into 30 L water (concentration proportion 1:1:1). The nozzle inlet pressure is adjusted by the overflow valve which controls the flow rate in the by-pass line. The effect of inlet pressure on the COD reduction is investigated over the range of 6–10 MPa. The initial pH of solution is kept over the range of 2–8.5 by varying the amount of sulfuric acid and sodium hydroxide addition. The individual operation of hydrodynamic cavitation is first carried out under different nozzle inlet pressure conditions, and the optimum nozzle inlet pressure is selected for the remaining experiments. Then the UV/Fenton, analogous Fenton, and photocatalytic oxidation processes are introduced to enhance the COD reduction. In the intensifying processes, the loadings of chemicals are set as: H_2O_2 (200–600 mg/L), $FeSO_4$ (6.67–10 mg/L), Cu powder (0–3 mg/L), and TiO_2 (0–3.33 mg/L). The total duration of each run is set to be 60 min and the samples are taken out from the tank at an interval of 10 min for an analysis of instantaneous COD value. All the experiments are repeated four times and the reported values are an average of the different experimental runs. The errors are within ±3% for the reported average values.

2.3. Analysis

The COD value, which is a comprehensive index to evaluate the amount of organics in water, is tested using 5B3C (V7) COD fast detector bought from Lian Hua Technology Development Co., Ltd., Beijing. The pH value of the solution is measured by Mettler SevenExcellence multi-functional water tester, and the Mettler ML204T electronic balance is used to accurately weigh the dissolved antibiotic drugs.

3. Results and discussion

3.1. Individual application of hydrodynamic cavitation

Degradation of antibiotic wastewater is first carried out by individual application of hydrodynamic cavitation. By adjusting the pressure-regulating overflow valve, the effect of nozzle inlet pressure on the degradation process is investigated over the range of 6–10 MPa. The hydrodynamic characteristic of the experimental system is shown in Table 1, in which the cavitation number is defined as [22,23]:

$$C_v = \frac{P_2 - P_v}{\frac{1}{2}\rho v_0^2} \tag{1}$$

where P_2 is the pressure in the main reaction chamber and approximately equals to 0.1 MPa. P_v is saturated vapor pressure, ρ is the water density, and v_0 is the flow velocity at the nozzle hole.

Fig. 2 depicts the obtained results. It is observed that the extent of COD reduction increases obviously with increase of the pressure from 6 to 8 MPa, but varying the jet inlet pressure from 8 to 10 MPa shows less obvious increase of COD

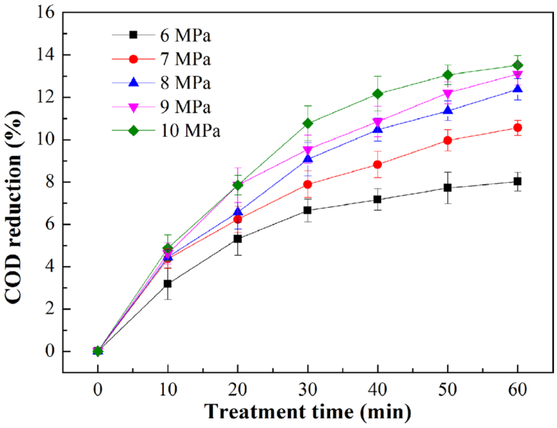

Fig. 2. Effect of nozzle inlet pressure on the COD reduction (conditions: liquid temperature, 22°C; pH, 2.7; initial COD, 236 mg/L).

Table 1
Hydrodynamic characteristics of the experimental system

Nozzle inlet pressure (MPa)	Flow rate at the nozzle upstream (L/h)	Flow velocity at the nozzle hole (m/s)	Cavitation number
6	53.7	75.97	0.0342
7	57.7	81.63	0.0296
8	61.9	87.57	0.0257
9	64.5	91.25	0.0237
10	68.7	97.19	0.0209

reduction. The maximum extent of COD reduction is 13.52% at the nozzle inlet pressure of 10 MPa. The initial obvious increase in the degradation extent should be attributed to a decrease of the cavitation number, which increases the number of cavities and also the cavitation intensity, as proved in bubble dynamics studies [24]. However, as the bubble number density further increases, some bubbles will coalesce and form larger bubbles. The incomplete or cushioned collapse of the larger bubbles will reduce the cavitation intensity [25], and thus the COD reduction increases less obviously. Using salicylic acid dosimetry, Amin et al. [26] proved that higher upstream pressure resulted in an increase in hydroxyl radical production in an orifice plate reactor. Similar result was reported by Chakinala et al. [27,28] for oxidation of I^- and phenolic compounds using hydrodynamic cavitation generated by liquid whistle reactor.

It is no doubt that higher inlet pressure leads to higher degradation rate. Of course, the energy input into the main reactor also increases with increasing the inlet pressure. In the practical application, an optimal balance between the degradation rate and the energy consumption should be considered according to the practical wastewater discharge standard. Therefore, the operating pressure of the nozzle inlet should be finally specified based on different situations.

3.2. Combination with UV/Fenton chemistry

3.2.1. Effect of solution pH

Fenton process is one of the AOPs, in which the highly reactive hydroxyl radicals are produced by decomposition of hydrogen peroxide with ferrous ion (Fe^{2+}) as catalyst in an acidic condition. The exact reaction mechanism leading to hydroxyl radical generation is given as follows [29]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \tag{2}$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \tag{3}$$

$$Fe^{3+} + H_2O_2 \rightarrow \left[FeOOH\right]^{2+} + H^+ \tag{4}$$

$$\left[FeOOH\right]^{2+} \rightarrow Fe^{2+} + HOO\cdot \tag{5}$$

$$Fe^{3+} + HOO\cdot \rightarrow Fe^{2+} + O_2 + H^+ \tag{6}$$

Using hydrodynamic cavitation in combination with UV/Fenton method, the effect of solution pH on the degradation of antibiotics has been investigated by varying initial pH over the range of 1.8–8.5. The results are shown in Fig. 3. The COD reduction increases as the pH of the solution decreases until the maximum COD reduction is obtained at pH value of 2.7. The observed result can be attributed to the fact that the generation of hydroxyl radicals is more favored and also the oxidation capacity of hydroxyl radicals is higher under acidic conditions [14]. The further decreasing of the solution pH from 2.7 to 2 results in a decrease of COD reduction. When the pH is lower than 2.7, the concentration of hydrogen ions is too high, and it will slow down the formation of $[FeOOH]^{2+}$, which consecutively causes the production rates of ferrous ions and hydroxyl radicals to decrease as well [30]. The effect of solution pH on the degradation of diclofenac sodium was investigated by Bagal and Gogate [15] with variation of the initial pH in the range of 4–7.5. The degradation rate rose from 14.7% to 26.8% when changing the pH from 7.5 to 4. Similarly, the experiment of imidacloprid degradation by Patil et al. [16] also demonstrated that the maximum degradation rate was obtained at an optimum pH of 3.

3.2.2. Effect of H_2O_2/COD molar ratio

Effect of H_2O_2/COD molar ratio is investigated by adjusting the amount of H_2O_2 addition and the initial COD value. It can be seen from Fig. 4 that the extent of COD reduction first increases with increasing the H_2O_2/COD molar ratio and then reaches the maximum of 48.98% when the H_2O_2/COD molar ratio is about 1.99. After that, it begins to drop with further increasing the H_2O_2/COD molar ratio. As the H_2O_2/COD molar ratio increases, the formation of free radicals due to continuous dissociation of hydrogen peroxide under the cavitation condition increases, and thus the degradation reaction rate of

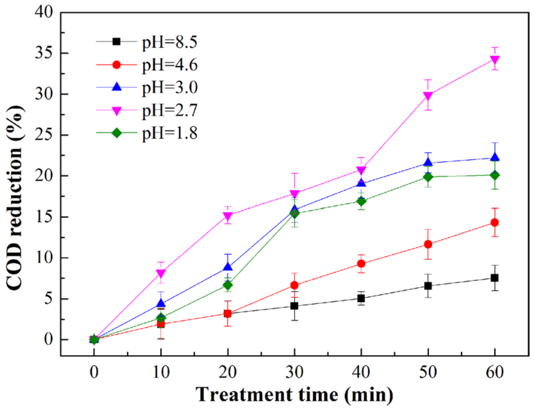

Fig. 3. Effect of solution pH on the COD reduction (conditions: nozzle inlet pressure, 10 MPa; liquid temperature, 22°C; initial COD, 236 mg/L; H_2O_2, 200 mg/L; $FeSO_4$, 10 mg/L).

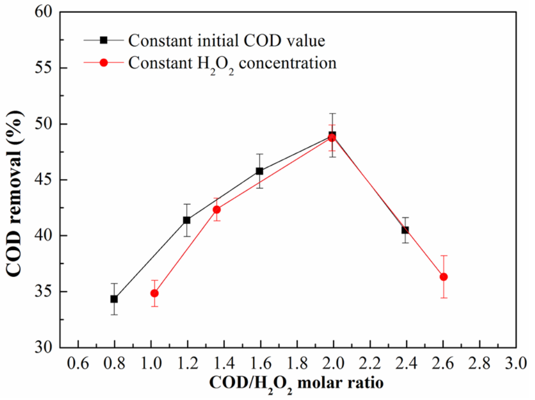

Fig. 4. Effect of H_2O_2/COD molar ratio on the COD reduction (conditions: nozzle inlet pressure, 10 MPa; liquid temperature, 22°C; pH, 2.7; $FeSO_4$, 10 mg/L).

antibiotics is enhanced. However, when the H_2O_2/COD molar ratio is too high, detrimental effect is observed since the recombination reaction of hydroxyl radicals is more predominant and also hydrogen peroxide acts as a scavenger for hydroxyl radicals [17]. Besides, the excessive high concentration of hydrogen peroxide can also lead to the generation of vaporous cavities, resulting in a low cavitation intensity [31]. From the perspective of electron exchange, the stoichiometrical requirement for 1 mole COD reduction is 2 moles H_2O_2, which is consistent with the present experimental result that the optimum H_2O_2/COD molar ratio is 1.99. Elmolla and Chaudhuri [3] carried out photo-Fenton–sequencing batch reactor treatment of antibiotic wastewater containing amoxicillin and cloxacillin with H_2O_2/COD molar ratio in the range of 1–3. The maximum COD reduction of 59% was obtained at optimum H_2O_2/COD molar ratio of 2.5. Guo et al. [32] have also reported the existence of an optimum concentration of H_2O_2 for the degradation of 2,4-dinitrophenol with its concentration changing from 100 to 800 mg/L. Therefore, it can be inferred that the use of hydrogen peroxide is favored only in optimum concentration. The specific optimum value is affected by the concentration and type of the pollutant and the structure of cavitation reactor due to the resultant different dissociation of hydrogen peroxide [25].

3.2.3. Effect of $FeSO_4$ concentration

The loading of ferrous ion is also an important parameter affecting the efficacy of the treatment process. The concentration of $FeSO_4$ was varied from 6.67 to 10 mg/L to study its effect on the degradation reactions. The results are shown in Fig. 5. The maximum COD reduction of 51.10% is achieved when $FeSO_4$ concentration is 8.33 mg/L. Both higher and lower $FeSO_4$ concentrations led to the drop of the COD reduction. As a kind of catalyst, Fe^{2+} can accelerate the decomposition of H_2O_2, resulting in the enhanced production of hydroxyl radicals and thus promoting antibiotics degradation. However, due to the consumption of hydroxyl radicals by Fe^{2+}, an excess loading of $FeSO_4$ can bring a negative effect on the COD reduction [29]. Similar result was also obtained by Wang et al. [33] in the experiments of reactive brilliant red degradation using a combination of swirling-jet induced cavitation with Fenton process.

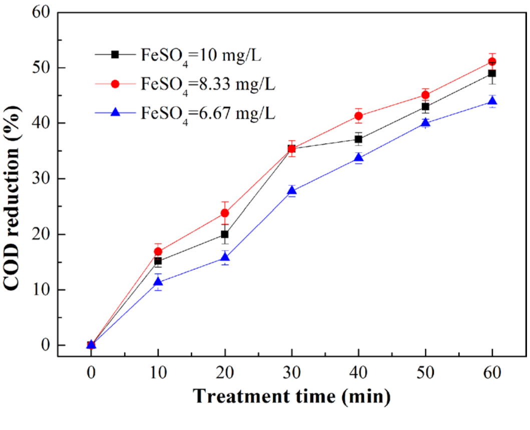

Fig. 5. Effect of ferrous sulfate concentration on the COD reduction (conditions: nozzle inlet pressure, 10 MPa; liquid temperature, 22°C; pH, 2.7; H_2O_2, 500 mg/L; initial COD, 236 mg/L).

3.2.4. The synergetic effects

A serial of experiments using hydrodynamic cavitation, UV/Fenton process and their combination are conducted to study the synergetic effects. The results are shown in Fig. 6. Compared with 13.52% COD reduction in the case of only hydrodynamic cavitation, 51.10% COD reduction is achieved when initially adding 500 mg/L H_2O_2 and 8.33 mg/L $FeSO_4$ to the solution. The COD reduction is only 13.73% using the same amount of H_2O_2 and $FeSO_4$ when the solution is kept standing still. The COD reduction process approximately fits the first-order kinetics for all the approaches with different kinetic constants k (min^{-1}). The synergistic index f, as suggested in the literature [34], for the combined process is calculated as:

$$f = \frac{k_{\text{Hydrodynamic cavitation+UV/Fenton}}}{k_{\text{Hydrodynamic cavitation}} + k_{\text{UV/Fenton}}} = \frac{0.1014}{0.0236 + 0.0242} = 2.121 \quad (7)$$

Thus, the synergistic effect is observed for the combined process of hydrodynamic cavitation and UV/Fenton. On one hand, both the hydrodynamic cavitation and the addition of Fenton reagent provide oxidizing agents. On the other hand, hydrodynamic cavitation can enhance the decomposing of H_2O_2 and also the micro-mixing of reactants [35]. Thus, the combined process has a better effect as compared with the individual application of these processes.

3.3. Combination with analogous Fenton chemistry

3.3.1. Effect of Cu loading

As shown in Eqs. (8)–(10), copper powder can react with H^+, generating Cu^{2+}/Cu^+ reaction system and leading to analogous Fenton reaction [36]:

$$Cu + 2H^+ \rightarrow Cu^{2+} + H_2 \quad (8)$$

$$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + H^+ + O_2 \quad (9)$$

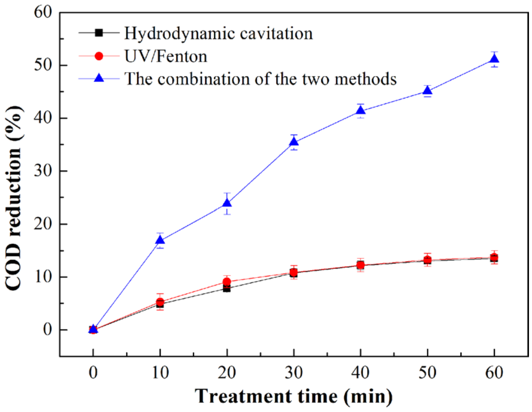

Fig. 6. Variation of COD reduction with treatment time using different treatment methods (conditions: nozzle inlet pressure, 10 MPa; liquid temperature, 22°C; pH, 2.7; initial COD, 236 mg/L; H_2O_2, 500 mg/L; $FeSO_4$, 8.33 mg/L).

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + \cdot OH + OH^{-} \quad (10)$$

Different loadings of copper powder are added to the solution to investigate the effect on the degradation of antibiotic. As shown in Fig. 7, compared with 51.10% COD reduction in the absence of copper powder, adding a small amount of copper powder improves the COD reduction. The maximum COD reduction of 59.13% is achieved when the initial concentration of Cu is 2 mg/L. But the effect has not been augmented along with further increasing the concentration of copper powder. This is due to the consumption of hydrogen peroxide by excessive Cu^{2+}, as shown in Eqs. (11)–(14). The same trend was observed by Sunaric et al. [37] in the degradation of doxycycline by analogous Fenton reaction:

$$Cu^{2+} + H_2O_2 \rightarrow CuO_2 + 2H^{+} \quad (11)$$

$$CuO_2 + 2H_2O \rightarrow CuO_2 \cdot 2H_2O \quad (12)$$

$$CuO_2 \cdot 2H_2O \rightarrow Cu(OH)_2 + O_2 \quad (13)$$

$$Cu(OH)_2 + 2H^{+} \rightarrow Cu^{2+} + H_2O \quad (14)$$

3.3.2. The synergetic effect

The variations of COD reduction using hydrodynamic cavitation, UV/Fenton, analogous Fenton, and combination of the three methods are shown in Fig. 8. Individual operation of analogous Fenton only obtains a COD reduction of 1.86%, while the combination of the three methods realizes 59.13% COD reduction. The synergetic index f is 2.576 (according to Eq. (15)). Hydrodynamic cavitation, Cu^{+}, and Fe^{2+} can accelerate the reaction of H_2O_2 dissociation and more hydroxyl radicals are generated. Under the effect of hydrodynamic cavitation, hydroxyl radicals are in full contact with the antibiotics. Hence, the combination of the three methods shows a significant synergetic effect.

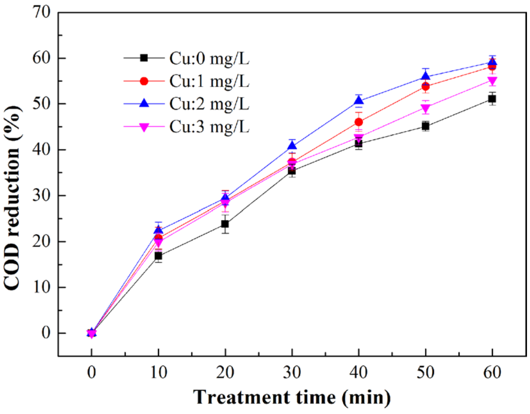

Fig. 7. Effect of Cu loading on the COD reduction (conditions: nozzle inlet pressure, 10 MPa; pH, 2.7; temperature, 22°C; H_2O_2, 500 mg/L; $FeSO_4$, 8.33 mg/L; initial COD, 236 mg/L).

$$f = \frac{k_{\text{Hydrodynamic cavitation+UV/Fenton+Analogous Fenton}}}{k_{\text{Hydrodynamic cavitation}} + k_{\text{UV/Fenton}} + k_{\text{Analogous Fenton}}} = \frac{0.1311}{0.0236 + 0.0242 + 0.0031} = 2.576 \quad (15)$$

3.4. Combination with photocatalytic oxidation

3.4.1. Effect of TiO_2 loading

Photocatalytic oxidation is another promising AOP for wastewater treatment. The photocatalytic oxidation process is characterized by the production of hydroxyl radicals (·OH) and superoxide anions (O_2^-), which are generated when a semiconductor catalyst absorbs radiation as it is in contact with water and oxygen [38]. TiO_2 is the most commonly used photocatalyst due to its non-toxicity, low cost, and long-term stability [39]. With addition of different loadings of TiO_2, degradation of antibiotic wastewater has been carried out and Fig. 9 depicts the results. The maximum COD reduction of 66.63% is achieved at the TiO_2 loading of 1.67 mg/L. When the TiO_2 concentration increases from 0 to 1.67 mg/L, an enhancement in COD reduction is observed. This is because the number of active surface sites increases with increasing the amount of TiO_2. Besides, TiO_2 can also provide additional nuclei for cavitation, leading to the enhanced degradation. However, it should be noted that the COD reduction decreases with the progressive increase of TiO_2 concentration when the concentration is above 1.67 mg/L. This should be attributed to the unfavorable light scattering and the reduction of light penetration at a relatively high TiO_2 loading. Giraldo et al. [40] investigated degradation of the antibiotic oxolinic acid by photocatalytic oxidation with TiO_2 in suspension and reported that the degradation rate first increased with increasing TiO_2 loading till an optimum TiO_2 loading was achieved and then reduced after that. Similar results have been reported in the literature for the degradation of antibiotics using UV/TiO_2 and $UV/H_2O_2/TiO_2$ photolysis [4].

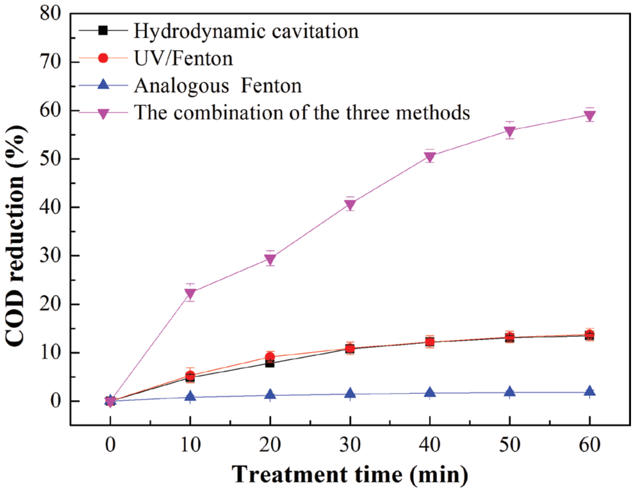

Fig. 8. Variation of COD reduction with treatment time using different treatment methods (conditions: nozzle inlet pressure, 10 MPa; liquid temperature, 22°C; pH, 2.7; H_2O_2, 500 mg/L; $FeSO_4$, 8.33 mg/L; Cu, 2 mg/L).

3.4.2. The synergetic effect

The COD reduction using hydrodynamic cavitation, UV/Fenton, analogous Fenton, photocatalytic oxidation, and their combination are depicted in Fig. 10. The extent of COD reduction using photocatalytic oxidation is only 5.01%, whereas the combination of the four methods achieves a COD reduction of 55.71%. The synergetic index is 2.581 (according to Eq. (16)). TiO_2 can provide additional nuclei for cavitation. Meanwhile, the micro-jets, shear stress, and turbulence formed during bubble collapse can refresh and disperse the TiO_2 particles and enable the full contact with the reactants. Besides, the existence of TiO_2, Cu^+, and Fe^{2+} plus hydrodynamic cavitation can promote the decomposition of hydrogen peroxide. Therefore, the combination of the four methods shows the significant synergetic effect.

$$f = \frac{k_{\text{Hydrodynamic cavitation+UV/Fenton+Analogous Fenton+Photocatalytic oxidation}}}{k_{\text{Hydrodynamic cavitation}} + k_{\text{UV/Fenton}} + k_{\text{Analogous Fenton}} + k_{\text{Photocatalytic oxidation}}} = \frac{0.1520}{0.0236 + 0.0242 + 0.0031 + 0.0073} = 2.581 \quad (16)$$

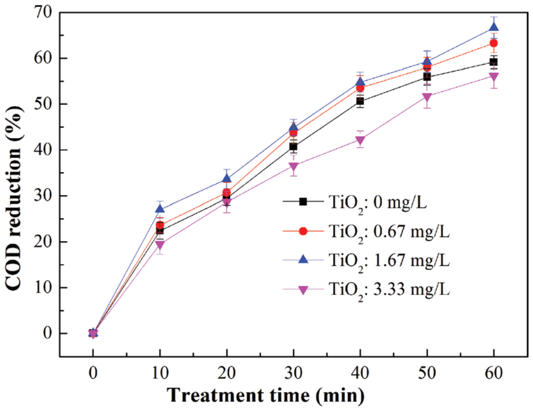

Fig. 9. Effect of TiO_2 loading on the COD reduction (conditions: nozzle inlet pressure, 10 MPa; pH, 2.7; temperature, 22°C; H_2O_2, 500 mg/L; $FeSO_4$, 8.33 mg/L; initial COD, 236 mg/L; Cu loading, 2 mg/L).

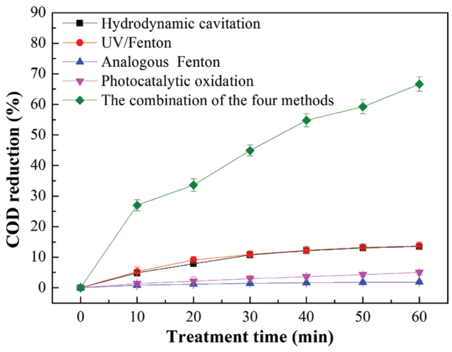

Fig. 10. Variation of COD reduction with treatment time using different treatment methods (conditions: nozzle inlet pressure, 10 MPa; liquid temperature, 22°C; pH, 2.7; H_2O_2, 500 mg/L; $FeSO_4$, 8.33 mg/L; Cu, 2 mg/L; TiO_2, 1.67 mg/L).

3.5. Comparison of the catalytic activity of TiO_2 and Cu

Experiments with the same addition concentration of TiO_2 and Cu are also carried out for the comparison of the catalytic activity. As shown in Fig. 11, compared with 51.10% COD reduction using the combined process of hydrodynamic cavitation and UV/Fenton, adding 2 mg/L TiO_2 enhances the COD reduction to 61.13%, while the COD reduction is 59.13% in the case of 2 mg/L Cu addition. On one hand, TiO_2 may have higher activity for promoting H_2O_2 dissociation. On the other hand, TiO_2 particles can also induce surface cavitation, enlarging the cavitation effect. Therefore, TiO_2 addition is more effective for enhancing the extent of COD reduction as compared with the same addition concentration of Cu.

3.6. Assessment of the treatment methods

To obtain the best treatment condition, a comparison of the approaches used in the present work has been conducted. The comparison is based on the COD reduction at the expense of per unit cost. To reduce the complexity, only the maximum cavitation yields achieved under the optimum conditions are considered. The detailed calculation process is illustrated in Appendix A and the results are shown in Table 2. As can be seen from Table 2, the most effective and economical method is the combination of hydrodynamic cavitation, UV/Fenton, analogous Fenton, and photocatalytic oxidation, with the maximum synergetic index of 2.581 and COD reduction of 66.63%. The cost of per dollar can bring 187.88 mg/L COD reduction.

4. Conclusions

By making use of high-pressure submerged cavitation jet, a device that can provide high cavitation intensity, strong turbulence, efficient heat and mass transfer, and intensive chemical reactions has been innovatively used for the degradation of antibiotic wastewater. A serial of experimental study on the combination of high-pressure submerged cavitation jet and the synergetic methods, that is, UV/Fenton, analogous Fenton and photocatalytic oxidation, has been carried out. Following conclusions can be drawn based on the experimental results:

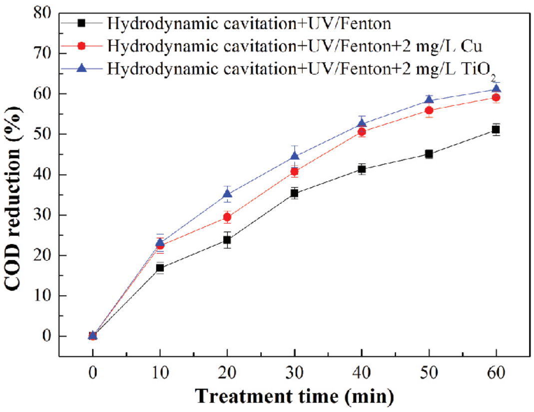

Fig. 11. Comparison of Cu and TiO_2 activity for enhancing COD reduction (conditions: nozzle inlet pressure, 10 MPa; pH, 2.7; temperature, 22°C; H_2O_2, 500 mg/L; $FeSO_4$, 8.33 mg/L; initial COD, 236 mg/L).

Table 2
Comparison of the different treatment methods

Method	Maximum extent of COD reduction (%)	Synergetic index	Total COD reduction (mg/L)	Total cost ($)	COD reduction per unit cost (11 mg/L/$)
M1	13.52	–	31.9	0.65	48.73
M2	51.10	2.121	146.7	0.81	147.86
M3	59.13	2.576	155.9	0.82	170.67
M4	66.63	2.581	165.6	0.84	187.88

M1: hydrodynamic cavitation; M2: hydrodynamic cavitation and UV/Fenton; M3: hydrodynamic cavitation, UV/Fenton, and analogous Fenton; M4: hydrodynamic cavitation, UV/Fenton, analogous Fenton, and photocatalytic oxidation.

- High-pressure submerged cavitation jet can be effectively used for the degradation of antibiotics at relatively large operating capacity (30 L as used in the present work).
- In the case of only hydrodynamic cavitation, the maximum COD reduction within 60 min is 13.52% under an optimal nozzle inlet pressure of 10 MPa.
- For the combination of hydrodynamic cavitation, the synergetic index is 2.121, and the maximum COD reduction of 51.10% is achieved. The optimum operating conditions are as follows:

  pH: 2.7; H_2O_2/COD molar ratio: 1.99; and $FeSO_4$ concentration: 8.33 mg/L.
- The combination of hydrodynamic cavitation, UV/Fenton, analogous Fenton has a synergetic index of 2.576 and the maximum COD reduction under the optimum conditions is 59.13%.
- The combination of hydrodynamic cavitation, UV/Fenton, analogous Fenton, and photocatalytic oxidation brings a COD reduction of 66.63% under the optimum condition and the synergetic index rises to 2.581.
- TiO_2 addition is more effective to enhance the extent of COD reduction as compared with the same addition concentration of Cu.
- The most effective and economical method for antibiotic wastewater degradation is the combination of hydrodynamic cavitation, UV/Fenton, analogous Fenton, and photocatalytic oxidation.

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Appendix A

The price and specifications of the chemicals used in the present work are as follows:

1. $FeSO_4$: 500 g, \$1.9228;
2. H_2O_2: 500 mL, 30%, \$1.7749;
3. Cu: 500 g, \$16.8614; and
4. TiO_2: 25 g, \$9.6288.

Taken the treatment process using hydrodynamic cavitation, UV/Fenton, analogous Fenton, and photocatalytic oxidation (M4 in Table 2) as an example, the maximum COD reduction of 70.16% is achieved under such conditions: H_2O_2, 500 mg/L; $FeSO_4$, 8.33 mg/L; Cu loading, 2 mg/L; TiO_2 loading, 1.67 mg/L; initial COD, 236 mg/L. The total cost consists of two parts: electricity cost and chemicals cost.

The electricity cost means the power consumption of pump and UV light within 1 h, and can be calculated as:

\$0.1184/(kW h)*(5.5 kW + 30 W/1,000)*1 h = \$0.654752.

The chemicals cost includes:

1. $FeSO_4$: 8.33 mg/L*30 L*\$1.9228/500 g/1,000 = \$0.000961;
2. H_2O_2: (500 mg/L*30 L)/(1,110 mg/mL)/0.3*\$1.7749/500 mL = \$0.159901;
3. Cu: (2 mg/L*30 L)*(\$16.8614/500 g/1,000) = \$0.002023; and
4. TiO_2: (1.67 mg/L*30 L)* (\$9.6288/25 g/1,000) = \$0.019296.

The total cost is the summation of the above terms, that is, \$0.836933.

Therefore, the COD reduction per unit volume per unit cost is:

(66.63%*236 mg/L)/0.182178 = 187.88 mg/L/\$.