Study on the degradation of rhodamine B by the cavitation impinging stream-fenton

Qin LI1, Yingda HUO1, Hao WU1, Fubao LI1, Liang ZHANG2
1Shenyang University of Technology, Liaoyang 111003, Liaoning, China
2Jinzhou City Health School, Jinzhou 121007, Liaoning, China
prf_qinli@126.com

Abstract: Experiments of rhodamine B wastewater treatment by cavitation impinging stream (CIS) technology and CIS-fenton reaction coupling technology are carried out. Results showed that the removal rate of COD and colority reached 19.6% and 34.1% by using cavitation impinging stream technology only and 98.1% and 97.2% by CIS and fenton reagent combination, and 24.3% and 18.4% higher than that by using fenton method only, and higher than that by using the both mentioned above. These experiments showed that the two have synergy, also proved that the CIS and fenton reagent combination can be more efficient in organic wastewater treatment.

1. Introduction
With the continuous development of industry, the compositions of more and more organic wastewater discharged from petroleum chemical industry, food processing, paper making and other industries are more and more complex, not only contains a large number of recalcitrant organics, but also the chroma is high and with a peculiar smell, extremely easy to cause the deterioration of water quality, causing adverse effects on human health and the ecological environment around the water body. However, because of the cost and efficiency problems of wastewater treatment, the pollution of water environment can not be solved at all. Therefore, the research of new and efficient organic wastewater treatment processes and equipment has become one of the focus of scientific research.

Combining cavitation technology with impinging stream technique\textsuperscript{[1]}, the concept of CIS\textsuperscript{[2]} is proposed. The research team has carried out relevant correlation theory and experimental research, 4 generation of CIS reactor has been designed at present. The core component of CIS reactor is two special structure nozzle placed in opposite direction along the same axis, the basic working principle is ejecting two fluid by using external power and special structure of internal nozzle and impinging in high speed on the impinging surface, which causes the cavitation effect and forms cavitation impinging area. An instant local high temperature and high pressure causes of cavitation effect provides good physical and chemical environment\textsuperscript{[3]} for the progress of a chemical reaction. The cavitation effect mainly occurs at two positions of the cavitation nozzle and the center of the impinging zone. CIS technology integrates impinging effect and the flow field of impinging stream characteristics, and the unique mechanical property characteristics of the impinging area will make the cavitation effect more comprehensive, and in turn cavitation effect of cavitation will strengthen the turbulence of impinging area, so the cavitation coupling impinging stream concept in the theory of technology is reasonable and feasible, and development great potential.
Preliminary study shows that the technology characteristics of the CIS has a certain influence on the kinetics: macro mixing effect of CIS can promote the macro mixing of the reactants of impinging zone, and improve the concentration of the area of the reactant molecule; CIS micro mixing effect can improve the concentration of the reactant molecules encounter, so as to improve the collision probability of the reactant molecule; pressure fluctuation characteristics of CIS can change the energy distribution of molecular, so that more molecules become activated molecules, thereby increasing the effective collision frequency. Therefore, the use of CIS technology can effectively increase the rate of chemical reaction. Our research group has done a lot of experimental research on various methods for different industrial wastewater\cite{4}, but considering the industrial wastewater is large quantity, variety, complex composition, and there are many problems of the CIS technology applied to solve the industrial wastewater treatment. In order to further explore the feasibility of CIS technology applied to industrial wastewater treatment, degradation experiments of rhodamine B was conducted by using CIS technology and fenton reagent. The investigation of comparison results of the removal rate of COD and colority with the use of a single technology proved that the two method have a synergistic effect, which lays the foundation for further research.

2. Experimental part

2.1. Main experimental instruments and reagents

The reaction equipment is vertical liquid continuous phase CIS reactor, its structure diagram is shown in figure 1, which is based on the liquid as the continuous phase in multiphase reaction system, and the effective area of transfer process locates in two parallel opposed nozzle, the flow field distribution is symmetrical and can reduce the flow resistance, and two fluid move quickly relative to one another coaxiality, which impinges on the impinging surface that produces the highly turbulent region, and reached a relatively high speed at the moment of impinging, at the same time retention time of fluid particles in the impinging increases relatively, and the reactor is close to full mixing, which can enhance the mass and heat transfer process in the impinging region and micromixing in the reactor, so as to reduce the amount of short circuit materials. Therefore, the impinging stream couples with other conventional organic wastewater degradation way means adding a high efficiency impeller, which greatly increased the number of impinging between molecules, so as to improve the rate of chemical reaction.

![Figure 1. Structure diagram of CIS reactor](image)

The other main experimental apparatus are plastic self-priming pump (Jingjiang Quanye Pump Co.Ltd No. 103); visible spectrophotometer (Shanghai Yoke Instrument Co.Ltd); type 572 COD-Analyzer (Shanghai Leici) etc.

The main experimental reagents are 10mg/L rhodamine B wastewater (analytically pure rhodamine B dissolved in deionized water); 30% H$_2$O$_2$ solution; ferrous sulfate (FeSO$_4$·7H$_2$O, analytical grade) etc.
2.2. Determination of the optimum oxidation condition of fenton
CIS coupling on the fenton reaction role is mainly reflected in the micro environment of high temperature and high speed jet, and has no effect on the physical and chemical environment of the macro, such as the change of macro temperature, pH value, concentration of H$_2$O$_2$ of the reaction system, so using the single fenton method for determination of optimum oxidation conditions, and its optimized conditions similarly apply to the combination using of CIS and fenton reagent.

Taking three pieces of each one liter of rhodamine B wastewater (concentration 10mg/L) in the experimental operation, and the initial pH value of wastewater was adjusted by adding 3mol/L H$_2$SO$_4$ solution to pH equals to 2, 3 and 6 respectively. Weighing FeSO$_4$·7H$_2$O solid by using the analytical balance, and the dosage of Fe$^{2+}$ is controlled at 5mg/L, and the ratio of Fe$^{2+}$ to H$_2$O$_2$ is controlled. In the reaction process, stir constantly to keep the complete reaction, when pH value of wastewater is about 7, remove the remaining H$_2$O$_2$ and iron ions by adding 3mol/L NaOH solution, take the supernatant liquor to proceed the determination of COD and absorbance value after stirring sedimentation.

2.3. Determination of CIS-fenton coupling effect
Take 50L rhodamine B wastewater with a concentration of 10mg/L into a clean plastic bucket, and convey the wastewater into the CIS reactor system by vacuum pump. After the reactor is filled with the wastewater and the circular reaction in it is formed, the reaction officially starts. Manual operation is no need during the reaction process but to ensure the safety operation. Redo the above experimental procedure with adding fenton reagent into the CIS reactor system as a contrast. The absorptivity of COD and absorbance value are measured every half hour, and the removal rate of COD and chromaticity are calculated.

3. Results and discussion

3.1. Optimum oxidation condition of fenton reagent
The removal rate of COD and colority at different pH values is shown in figure 2. When the initial pH value is 3, the removal rate reached the maximum value of 78.4%. The combination of COD and colority data can be analyzed reasonably. It is proved that the fenton reagent reacts under acidic conditions, but if pH is too small, the concentration of hydrog en ions in the solution is too high and hydrogen peroxide will be stable in the form of H$_3$O$_2^+$, and most organic compounds are stable and resistant to decomposition in highly acidic environments, which is difficult to lead to the oxidation reaction of fenton. Results show that the maximum removal rate of COD and colority reached 73.8% and 78.4% when the reaction time is 60min, the dosage ratio of Fe$^{2+}$ to H$_2$O$_2$ is 1:4, and the initial pH value is 3.

![Figure 2. The removal rate of COD and colority at different pH values](image)

The initial pH of the correction system is 3, and the different ratios of Fe$^{2+}$ to H$_2$O$_2$ are changed. Other conditions remain unchanged, and the contrast of the removal rate of COD and colority is shown in figure. 3. With the increasing proportion of H$_2$O$_2$, the removal rate of colority increased slowly, while the maximum removal rate of COD appears in the ratio is 1:4. Results show that the removal rate of COD reached the highest of 73.8% and the removal rate of colority reached 78.8%
when the ratio of Fe$^{2+}$ to H$_2$O$_2$ is 1:4. Taking the amount of reactants and the subsequent costs, ratio of 1:4 is regarded as the optimum oxidation condition of fenton reagent.

![Figure 3. The contrast of the removal rate of COD and colority](image)

### 3.2. CIS-fenton coupling effect

Under the optimum oxidation conditions, the removal rate of COD and colority for the experiment of rhodamine B wastewater degradation treatment by CIS-fenton reaction coupling, CIS-only and fenton-only are shown in table 1 and tablet 2.

CIS-only can make COD and absorbance of the wastewater decreased, which proved that CIS can break some of the molecular bond in wastewater, or decompose the O-H bond in water molecules to get a small amount of hydroxyl radical. At the same time, the removal rate of COD and colority growth ratio is higher at the beginning of the reaction in the 60 minutes and becomes stable after 60 minutes, which indicated that the energy provided by the CIS is not sufficient.

Results show that the removal rate of COD is low by CIS-only and increase with time is small, the total removal rate is not high; the early removal rate is rapid growth by fenton-only, but it tend to stabilized later, which is consistent with the general trend of fenton reaction. The removal rate of COD is 8.6%, 65.2% and 87.8% at 30 minutes, and 13.6%, 73.8% and 96.2% at 60 minutes by CIS only, fenton-only, and CIS-fenton. The removal rate of COD by CIS-fenton is always higher than that by the other two, which proved that CIS and fenton have a synergistic effect and it is obvious at the initial stage of reaction.

| Degradation method | t (min) |
|-------------------|--------|
|                   | 10     | 30     | 60     | 120    | 180    |
| CIS-only          | -      | 8.6    | 13.6   | 17.9   | 19.6   |
| Fenton-only       | 20.8   | 65.2   | 73.8   | 74.2   | 74.9   |
| CIS-fenton        | 56.4   | 87.8   | 96.2   | 97.4   | 98.1   |

| Degradation method | t (min) |
|-------------------|--------|
|                   | 10     | 30     | 60     | 120    | 180    |
| CIS-only          | -      | 18.5   | 29.7   | 30.7   | 32.1   |
| Fenton-only       | 30.2   | 70.2   | 78.4   | 78.6   | 79.2   |
| CIS-fenton        | 52.5   | 95.2   | 95.4   | 96.5   | 97.2   |

CIS-fenton method also has obvious advantages on wastewater colority removal, and the removal rate of reaction has reached 52.5% at the beginning of ten minutes and after an hour the reaction almost completely, and the removal rate increased obviously slowly, and the sum of wastewater colority removal rate of using CIS only and fenton method only is less than the coupling of the two at 30 minutes. It is reasonable to think the CIS-fenton reaction can strengthen the organic wastewater treatment process, and the two have a synergistic effect which is very obvious in the initial stage of the reaction.
3.3. Mechanism analysis of CIS enhanced fenton process for organic wastewater treatment

Advanced oxidation technology of organic pollutants remove organic pollutants mostly through producing hydroxyl radicals by oxidation, but the production efficiency of free radical is not stable and has human factors and be more effected by the fluctuation of water quality. Fenton reagent itself is a mixture of H$_2$O$_2$ acting as an oxidizing agent and Fe$^{2+}$ making homogeneous catalyst, and the catalytic decomposition of H$_2$O$_2$ generates hydroxyl radicals (·OH) by Fe$^{2+}$ with strong oxidation, and causes more other free radicals. It can oxidize many kinds of organic compounds in organic waste water, and has certain effect on organic wastewater which is difficult to be degraded by biological degradation and physical chemical treatment [5]. The extreme conditions of the instantaneous high temperature and high pressure produced by cavitation effect can pyrolyse the gas which is easily dissolved and volatilized inside the cavity, sometimes some nonpolar substances can also be direct pyrolysis and at the same time cavitation caused by cavitation will produce instantaneous high temperature and water jet in the collapse, according to the existing research theory that instantaneous high temperature can open some chemical bonds (about 377-418KJ/mol), this energy can even break hydrogen bond of water molecules and produce free radicals. However, the CIS technique can provide limited energy and lower yield rate of hydroxyl radicals. Therefore, the fundamental reason of the CIS strengthened the Fenton method of organic wastewater treatment effect is that the O-O bond energy in the hydrogen peroxide is much lower than the O-H bond energy of water molecules, and easy to fracture in the promoting of CIS, and greatly improve the yield rate of hydroxyl radicals in unit time. While the promotion of CIS and the promoting effect of Fe$^{2+}$ catalysis bond together can effectively improve the concentration of strong oxidant in wastewater not only can improve the removal rate of pollutants and shorten processing time but also improve processing efficiency. Therefore, the use of CIS technique coupled with Fenton method allows for more efficient oxidation removal of organic pollutants.

4. Conclusion

The optimum oxidation conditions of fenton reagent were determined by contrast experiments of treatment of rhodamine B wastewater by methods of CIS-only and CIS-fenton, and an conclusion is drawn as follows: The initial pH value is 3 and the dosage ratio of Fe$^{2+}$ and H$_2$O$_2$ is 1:4 and the reaction time of more than 60 minutes are the best oxidation conditions for fenton treatment, and this condition is suitable for CIS-fenton method. The maximum removal rate of COD and colority reached 19.6% and 34.1% by CIS-only, which proved that CIS can provide higher energy to break part chemical bond of organic molecular in wastewater. The maximum removal rate of COD and colority reached 98.1% and 97.2% by CIS-fenton, which is higher than the sum removal rate of COD and colority when the two were used alone. Results showed that the degradation effect was greatly improved, which proved that the CIS and fenton reagent combination of rhodamine B wastewater treatment has a synergistic effect, and the CIS can strengthen the using effect of fenton reagent to reduce the cost of wastewater treatment.

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