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Removal of tetrabromobisphenol-A from wastewater by ozonation

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Abstract

The tetrabromobisphenol-A (TBBPA)-bearing wastewater contains high concentration of salt and TBBPA, which is difficult to be treated by conventional biological methods because of its high toxicity and refractory to microorganisms. Therefore, the Ozonation technology has been selected to remove TBBPA from this wastewater. In this paper, the effect factors of pH, ozone dosage, reaction time, and salt concentration were investigated. The results indicate that under the conditions of TBBPA= 50mg l\(^{-1}\), pH= 9.0, ozone dosage=52.3 mg h\(^{-1}\), and reaction time=25 min, TBBPA can be efficiently decomposed by ozone oxidation, and the TBBPA removal has come to 99.3%. The content of salt in wastewater has low effect on the performance of ozone oxidation. However, suitable addition of salt concentration was benefit to the development of reaction.

Keywords: tetrabromobisphenol-A; ozonation; high salinity

1. Introduction

Tetrabromobisphenol-A {TBBPA; 4, 4'-isopropylidenebis (2, 6-dibromophenol)} is a flame retardant extensively used in the epoxy resin, polyester resin, phenolic resin and many other consumer goods. It can easily contaminate the environment during the production, usage, and disposal of TBBPA –containing products, and imperil ecological environment and human health frequently [1]. China has been becoming a very large TBBPA manufacturer and amount of wastewaters containing high concentration TBBPA will be produced, which poses high risks to the ecosystems. Therefore, how to efficiently treat the wastewaters containing TBBPA is an important issue in the protection of ecosystems.

TBBPA is difficult to be degraded under natural conditions. It can be decomposed through anaerobic-aerobic biological process when microorganisms are domesticated for a long period [2]. However, for production wastewater containing high-concentration TBBPA which discontinuously discharge, it is difficult to keep a stable biological wastewater treatment. TBBPA in wastewater can be efficiently mineralized through photo-catalysis oxidation technology, but this method is impractical because of the difficulty in operation [3]. By contrast, ozonation technology has been widely applied for the treatment or pretreatment of refractory wastewater because of its reasonable cost performance and facility of operation [4].

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In this study, ozonation technology has been adopted to the treatment TBBPA–bearing wastewater. The effects of pH, ozone dosage and reaction time on the removal of TBBPA have already been investigated. Moreover, because TBBPA is one of the leading products in marine chemical industry of our country and its wastewater contains high concentration salt, the effect of salt concentration on ozonation efficiency was also investigated.

2. Experimental

2.1. Materials

The wastewater containing TBBPA was simulated and concentration of TBBPA is 50mg l$^{-1}$. Methanol (chromatographic grade), TBBPA (High purity grade) and NaOH (analytical grade) were purchased from the Sigma Chemical Company (USA).

2.2. Experimental procedure

![Schematic diagram of ozonation system](image)

Fig. 1. Schematic diagram of ozonation system

The schematic diagram of ozonation process was shown in Fig. 1. The oxygen was passed to the ozone generator, which produced the ozone. All experiments were carried out at an oxygen gas flow rate of 400 ml min$^{-1}$ and different dosage of Ozone was achieved by adjusting the voltage of ozone generator. Ozone produced feed into the reactor, which contains TBBPA-bearing wastewater, and after reaction for a given time, the samples was collected and then analyzed. The ozone outlet of the reactor was absorbed in KI trap.

2.3. Analytical methods and procedures

The concentration of ozone was determined by iodometric method $^{[5]}$. Concentration of TBBPA in the water can be measured by liquid chromatograph (HPLC) equipped with a JASCO UV-2070 UV/vis diode array multi-wavelength detector and a WATERS C-18S column; the eluent was a mixed solution of methanol/water (85:15 v/v ratio).

UV$_{254}$ was measured to instead of the measuring of TOC $^{[6]}$, and UV$_{254}$, was analyzed by U-2800 spectrophotometer.

3. Results and discussion

3.1. The effect of pH on Ozone oxidation
To establish a suitable pH for the treatment of the TBBPA-bearing wastewater by Ozone oxidation, the pH is changed under the conditions of initial TBBPA concentration =50mg l\(^{-1}\) and reaction time=20 min.

![Removal of TBBPA and UV\(_{254}\) at different pH](image)

Fig. 2. The TBBPA and UV\(_{254}\) removal at different pH

Fig.2 shows the removal efficiency of TBBPA concentration and UV\(_{254}\) under the different pH. The removal efficiency of TBBPA has gradually increased with the increase of pH, reaching the maximal value of 91.3% at pH of 9.0. Then, the removal efficiency of TBBPA has gradually decreased with the further increase of pH. Ozone has higher oxidation capacity in alkaline conditions, because ozone produces more active hydroxyl radicals under the catalytic of hydroxyl \(^7\). Moreover, under higher pH conditions, TBBPA has bigger solubility in water, which can reduce the mass transfer resistance of reaction process which benefited ozone oxidation of TBBPA. However, with the increase of pH, the decomposition rate of ozone itself gradually increased \(^8\). When pH is above 9.0, the decomposition rate of ozone itself is super to its reaction rate and the removal efficiency of TBBPA decreased gradually. In the case of UV\(_{254}\) removal, it has a same trend. Therefore, the optimal pH is determined as 9.0 based on the above results.

3.2. The effect of ozone dosage on the ozone oxidation

The effects of ozone dose on TBBPA removal was investigated at the initial pH of 9.0. Fig. 3 shows the variations of TBBPA removal and use efficiency with the Ozone dosage of 26.2, 43.0, 52.3, 69.4, and 86.5 mg h\(^{-1}\).  

![Removal of TBBPA and ozone use efficiency at different ozone dosage](image)

Fig. 3. The removal of TBBPA and ozone use efficiency at different ozone dosage

From Fig. 3, it can be seen that the TBBPA removal increased with the increase the ozone dosage. This is because the more ozone dosage added and the more concentration of hydroxyl radicals produced, which speeded up
the TBBPA to be oxidized. When the ozone dosage increased to 86.5 mg h\(^{-1}\), TBBPA was almost completely removed. Beside, along with the increase of ozone dosage, the use efficiency of ozone gradually decreased, which indicates that some ozone can not react with organic and directly discharged from the system at higher dosage added. Therefore, from the economic aspect and TBBPA removal, the ozone dosage was determined as 52.3 mg h\(^{-1}\).

3.3. The effect of reaction time on ozone oxidation

The effects of reaction time on the performance of ozone oxidation were investigated under the ozone dosage of 17.3 mg h\(^{-1}\). Variations of TBBPA and UV\(_{254}\) removal were shown in Fig.4.

![Fig. 4. The effect of reaction time on removal of TBBPA and UV\(_{254}\)](image)

It can be seen that the removal of TBBPA and UV\(_{254}\) increased with the extension of reaction time. When the reaction time was 25min, the TBBPA and UV\(_{254}\) removal has come to 99.3% and 66.7% respectively. After that, further increase of reaction time, the removal of TBBPA and UV\(_{254}\) showed no significant improvement. Therefore, the 25 min was selected for ozonation to remove TBBPA. Compared the removal of TBBPA with that of UV\(_{254}\) at 25 min, it is easily found that the UV\(_{254}\) removal is lower than that of TBBPA, which indicates that some intermediate organic matters difficult to be oxidized by ozone were formed, and if these had been removed, it would be added a biological technology after ozonation.

3.4. The effects of salt concentration on ozone oxidation

![Fig. 5. The effect of concentration of NaCl on removal of TBBPA and UV\(_{254}\)](image)

Under the conditions of TBBPA= 50mg h\(^{-1}\), pH= 9.0, ozone dosage=52.3 mg h\(^{-1}\), and reaction time=20 min, the
effects of salt concentration on the performance of ozone oxidation was studied. The result was shown in Fig.5.

With the increase of NaCl concentration, the removal of TBBPA and UV$_{254}$ has increased too. However, when the NaCl concentration is above 7%, further addition of NaCl concentration, the removal of TBBPA and UV$_{254}$ decreased. TBBPA is a weak electrolyte and its solution has low activity coefficient. When adding a certain amount of salt in its solution, the activity coefficient was increased $^{[9,10]}$ and thereby enhanced the reaction rate. Moreover, with the increase of salt concentration, the solution salinity also increased, which reduced the mass transfer rate. $^{[10]}$ Therefore, with the increase of salt concentration, the removal of TBBPA and UV$_{254}$ increased firstly and then decreased. In general, the experimental range, the effect of salt concentration on the performance of ozone oxidation was low.

4. Conclusion

- Under the conditions of TBBPA= 50mg l$^{-1}$, pH= 9, ozone dosage=52.3 mg h$^{-1}$, and reaction time=25min, TBBPA can be efficiently decomposed by ozone oxidation, the TBBPA removal has come to 99.3%.
- The effect of salt concentration on the performance of ozone oxidation was low. However, suitable addition of salt concentration was benefit to development of reaction.

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References