



## Study on Oxidation Effect of Ozone on Petroleum-Based Pollutants in Water

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### Abstract

The removal of petroleum-based pollutants from water by ozone is studied. The results indicate that the oxidation effect of ozone on the petroleum-based pollutants is associated with water temperature, pH, dosage of ozone and reaction time. The removal efficiency of petroleum-based pollutants increases with the rise of temperature, pH, amount of ozone and reaction time, and reaches 83% under the conditions that the ratio of ozone to petroleum-based pollutants is 1:1 and the reaction time is 10 min. GC/MS analysis reveals that the amount of petroleum-based pollutants in water is reduced 39% from the previous 61 organics to 37 organics, the total peak area is reduced 36% after ozone oxidation treatment. Therefore, ozone has an excellent effect on the removal of petroleum-based pollutants and can be applied in the treatment of petroleum wastewaters.

**Keywords:** Ozone, Petroleum-based pollutants, Oxidation, Water treatment

### Preface

Petroleum has become a major pollutant in sea, river and lake in China because of the excessive discharge of petroleum wastewaters, frequently occurred leakage accidents of petroleum, settlement of oil and hydrocarbon emitted in atmosphere, as well as oil spill from sea bottom (Chen, Guohua, 2002, p. 5-27), it resulted in severe harm to environment and human health. Ozone has so powerful oxidation that it is able to change the composition and structure of petroleum, and oxidize the high molecular organics into low molecular organics, or decompose some organics directly into CO<sub>2</sub> and H<sub>2</sub>O. As a result, the nonbiodegradable organics in the raw water are converted into biodegradable organics (Lin C K et al, 2001, p. 699-704; Jiangning Wu et al, 2007, p. 1-5; Jin Anotai et al, 2007, p. 345-349). For finding an effective method to remove the petroleum-based pollutants from water, this paper investigates the oxidation effect of ozone on petroleum-based pollutants through GC/MS analysis and determination of petroleum content in water before and after ozone oxidation.

### 1. Experiment

#### 1.1 Reagents and equipments

##### (1) Reagents

Designated grade of carbon tetrachloride and anhydrous sodium sulfate, from Tianjin Changmao Chemical Reagent Company; Analytically pure potassium permanganate, from Tianjin No. 1 Chemical Reagent Factory; Sodium oxalate (standard reagent), from Beijing Chemical Company.

##### (2) Equipments

JDS-105U infrared spectrophotometric oil analyzer, from Jilin Beiguang Analytical Instrument Company; 5890-5971 gas chromatography-mass spectrometry (GC/MS) analyzer, from Agilent Technologies of US.

#### 1.2 Process flow

Figure 1 is a process flow diagram of the experiment. Ozone is prepared by passing oxygen or an oxygen-containing gas through an ozone generator. Output and concentration of ozone are controlled by regulating the electric current of ozone generator and the oxygen input. Ozone, flowing into the reactor from the bottom, reacts with the petroleum-based pollutants that flow from the top of the reactor. The ozone generator ( $\Phi 1600$  mm $\times$ 85 mm) is made from quartz glass.

## 2. Result and discussion

### 2.1 Effects of ozone oxidation on the removal of petroleum-based pollutants from water

Ozone oxidation includes direct reaction and indirect reaction. Its reaction rate is associated with the concentrations of pollutants, ozone and  $\cdot\text{OH}$ , as well as the direct reaction constant of ozone and indirect reaction constant of  $\cdot\text{OH}$ . Therefore, there are many factors that have effects on the ozone oxidation. This paper mainly discusses the effects of ozone dosage, reaction time, reaction temperature and pH on the oxidation of petroleum-based pollutants.

#### 2.1.1 Ozone dosage

Ozone dosage refers to the amount of ozone that flows from the ozone generator into the oxidation reactor, which includes the consumed ozone, residual ozone in water and residual ozone in tail gas. Ozone dosage is an important parameter in the ozone treatment of water, and directly affects the processing efficiency and operation cost. Overflow dosage results in a poor oxidation efficiency; whereas overhigh dosage results in the formation of intermediate products which have adverse effects on the following treatment, and lead to the increase of investment and operation cost.

Table 1 indicates that the residual ozone in either water or tail gas is associated with the ozone dosage. When the ozone dosage is lower than the petroleum content, the residual ozone is low and utilization rate of ozone is high; however, when the ozone dosage is higher than the petroleum content, the residual ozone is high and utilization rate of ozone is low.

Figure 2 exhibits the effect of ozone dosage on the oxidation of petroleum when the reaction is 10min. The results indicate that the petroleum removal and oxidation efficiency increase with the rise of ozone dosage. The petroleum removal efficiency is higher than 80% when the ozone dosage is equal to the petroleum content, and declines in its growth rate with the further rise of ozone dosage. It is because the increase of ozone dosage results in the rise of ozone concentration in water and oxidation ability, in turn leads to an increased petroleum removal efficiency. However, the reaction between ozone and petroleum reaches an equilibrium when the ratio of ozone dosage to petroleum content is 1:1, and the petroleum removal efficiency cannot be increased significantly any more with the further increase of ozone dosage.

#### 2.1.2 Reaction time

Figure 3 exhibits the effect of reaction time on the oxidation of petroleum under the condition that the ratio of ozone dose to petroleum content is 1:1. It indicates that the petroleum removal rate increases with the reaction going on, and levels off after 10 minutes.

#### 2.1.3 Reaction temperature

Reaction rate constant of ozone with organics in water increases with the rise of temperature. Figure 4 exhibits the effect of reaction temperature on the oxidation of petroleum under the conditions that the ratio of ozone dose to petroleum content is 1:1 and the reaction time is 10 min. With the rise of water temperature, the oxidation ability of ozone increases, the petroleum removal rate in turn increases. However, the solubility of ozone in water decreases with the rise of reaction temperature, which leads to the decline of utilization ratio (Rischbieter E et al, 2000, p. 338-340).

#### 2.1.4 pH

Reaction rate of ozone with organics in water is associated with the form of organics. That is to say, the reaction rate of ozone with dissociated organics is faster than that with associated organics under the same conditions. Figure 5 exhibits the effect of pH on the oxidation. It indicates that the oxidation effect of ozone on petroleum increases with the rise of pH. It is because the proportion of dissociated organics increases, in turn the reaction rate increases with the rise of pH. However, the turbidity and chroma of the studied petroleum-polluted water increase remarkably when pH is higher than 7, which has an adverse effect on the investigation of experimental results.

In fact, ozone directly reacts with petroleum at low pH; whereas,  $\cdot\text{OH}$ , a strong oxidant resulted from the reaction of  $\text{OH}^-$  with ozone at high pH, initiates the chain reaction of ozone oxidation which is nonselective and very rapid (Nemes A et al, 2000, p. 287-304).

### 2.2 Removal effect of petroleum-based pollutants by ozone

Ozone has an excellent effect on the removal of petroleum-based pollutants from water under the conditions of 23 °C, pH of 7.2, 4.0 mg/L ozone dosage and 10 min reaction. Figure 6 reveals that the petroleum content decreases from 4.0 mg/L to 0.7 mg/L and the average removal rate is 82.50% after ozone treatment. Petroleum mainly consists of alkane, aromatic hydrocarbons, cycloalkane and etc. High molecular organics can be turned into low molecular organics by oxidation of ozone, and parts of them are directly decomposed into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

### 2.3 GC/MS analysis

#### 2.3.1 Raw water

By combining GC boiling point separation with MS fragment pattern identification, organics in water can be identified on the basis of their boiling point differences resulting from the differences in inter-molecular force, namely, Van der Waals force, which is associated with polarity of molecular. Figure 7 shows GC/MS chromatograms of raw water containing 4.0 mg/L petroleum. There are in total 72 peaks arranged from low to high in order of boiling point, and each peak is correspond to a certain organic compound. The total peak area is  $1.14 \times 10^8$ .

The results of GC/MS analysis indicate that 61 organics have been detected from raw water, including 24 alkanes, 10 esters, 6 olefins, 5 acids, 3 alcohols, 2 ethers, 2 amines and 9 other compounds. Most of them have molecular weights of 100~300. Alkanes constitute 39.34% of the total organics, and their peak areas constitute 64.76% of the total peak area, which indicates petroleum is a mixture of alkanes.

#### 2.3.2 Ozone-oxidized water

Figure 8 shows GC/MS chromatograms of ozone-oxidized water under the conditions of 23 °C, pH of 7.2, 4.0 mg/L ozone and 10 min reaction. There are in all 53 peaks with the total area of  $7.30 \times 10^7$  which declines 35.96% comparing with the raw water. From the ozone-oxidized water, we have detected 37 organics including 6 alkanes, 5 esters, 2 olefins, 7 acids, 3 alcohols, 2 aldehydes, 1 ethers, 5 amines and 6 other compounds which decline by 39.34% comparing with the raw water. 48 organics are removed from the raw water by ozone oxidation. As a result, there are 13 organics that can not be removed, together with 25 newly increased organics in the ozone-oxidized water. The removed organics mainly include alkanes, olefins, esters, ethers and etc. The newly increased organics mainly include acids, amines and aldehydes. It indicates that most organics in petroleum can be oxidized into low molecular intermediate products, and about 35% organics are directly decomposed into CO<sub>2</sub> and H<sub>2</sub>O.

The column temperature in GC/MS analysis is commonly between 45~300 °C, which makes the organics of high boiling point difficult to be separated, and the volatile organics easy to be evaporated. In addition, some polar organics of low molecular weight need deriving before they can be effectively separated. Therefore, there is a certain range for the organics detectable by GC/MS analysis: organics of either too high molecular weight or too low molecular weight can not be effectively detected.

### 3. Conclusion

Ozone has so powerful oxidation that it is able to change the composition and structure of petroleum, and oxidize the high molecular organics into low molecular organics, or decompose some organics directly into CO<sub>2</sub> and H<sub>2</sub>O. As a result, the nonbiodegradable organics in the raw water are converted into biodegradable organics. In short, the petroleum-based pollutants can be effectively removed from water by ozone. Ozonation can be used separately or combined with biodegradation, membrane separation technique and etc. to process petroleum-contained water.

### References

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Table 1. The correlation between ozone dosage and residual ozone

Ozone dosage (mg/L)	Residual ozone in water (mg/L)	Residual ozone in tail gas (mg/L)
1.21	0.01	0.50
2.80	0.01	0.62
4.09	0.02	0.87
9.46	1.22	2.56
12.40	2.50	3.10

\* Petroleum content is 4.5 mg/L; Flow rate of water is 1 L/min; Flow rate of tail gas is 2 L/min.

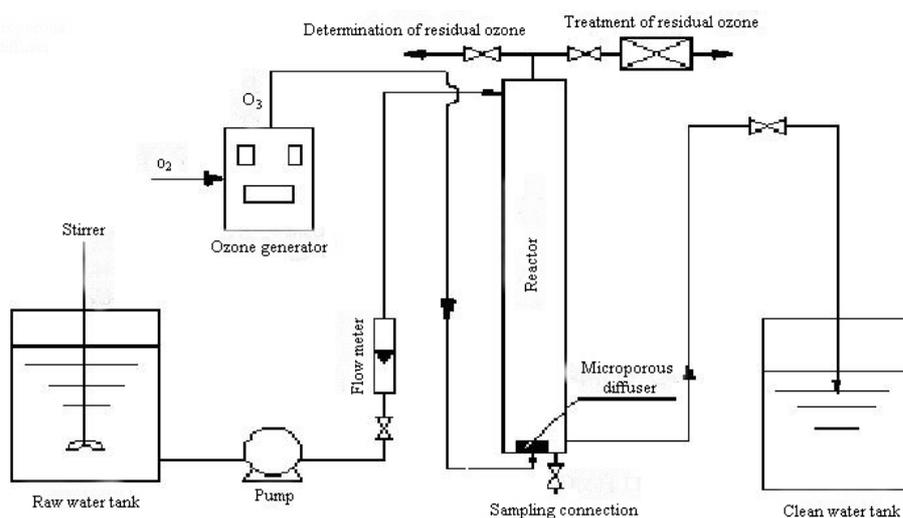


Figure 1. Process flow diagram of the experiment

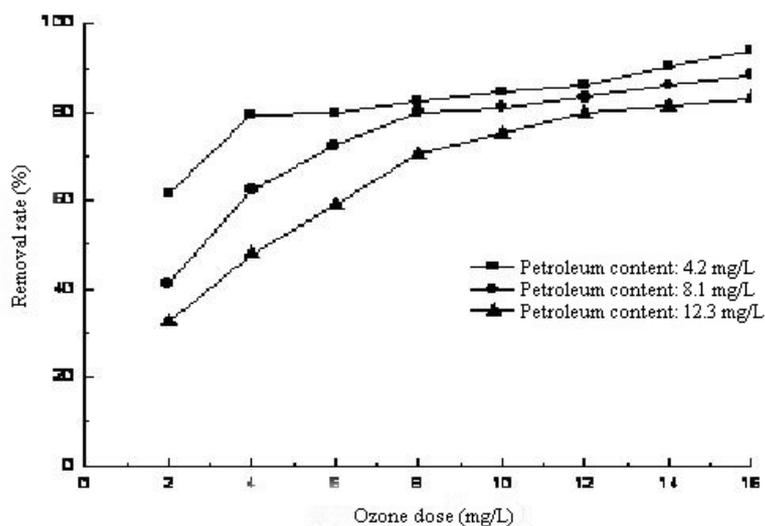


Figure 2. The effect of ozone dosage on the oxidation of petroleum

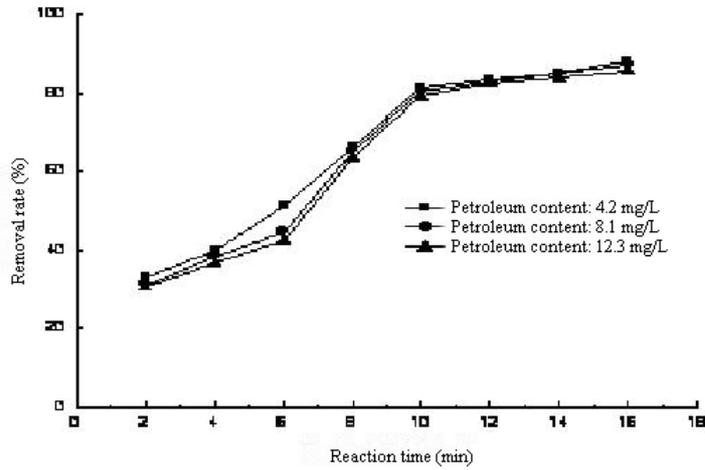


Figure 3. The effect of reaction time on the oxidation of petroleum

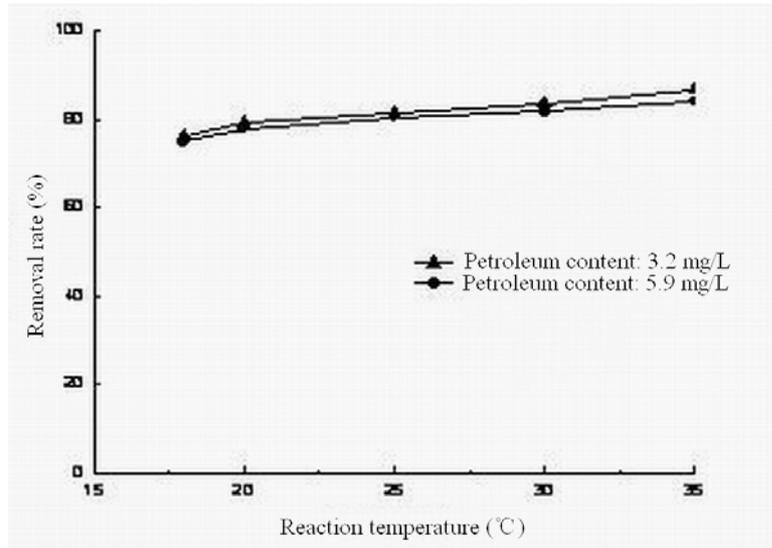


Figure 4. The effect of reaction temperature on the oxidation of petroleum

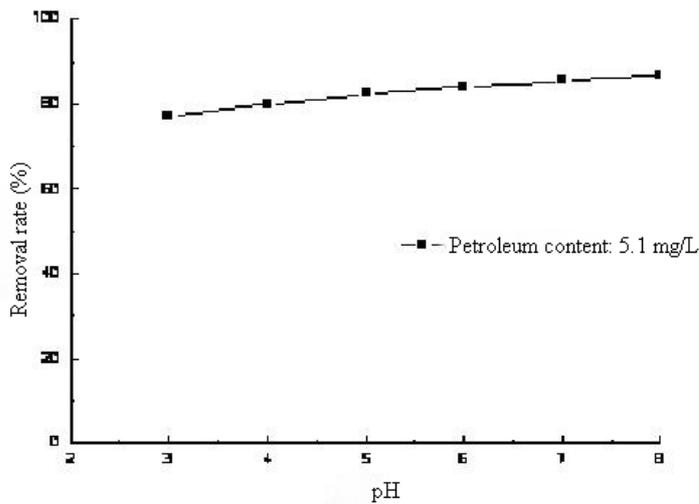


Figure 5. The effect of pH on the oxidation of petroleum

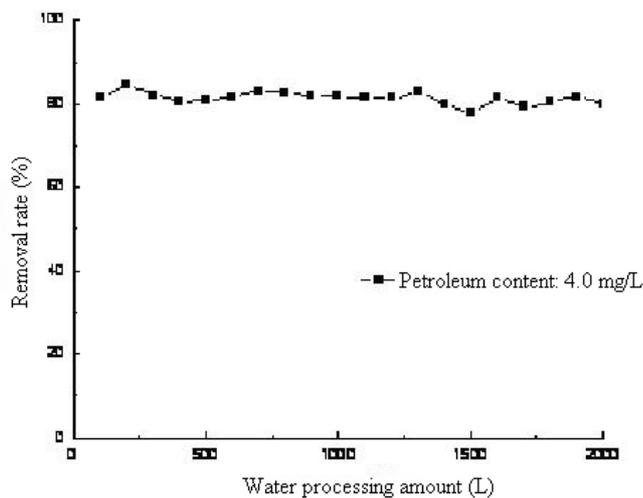


Figure 6. The removal effect of petroleum-based pollutants by ozone

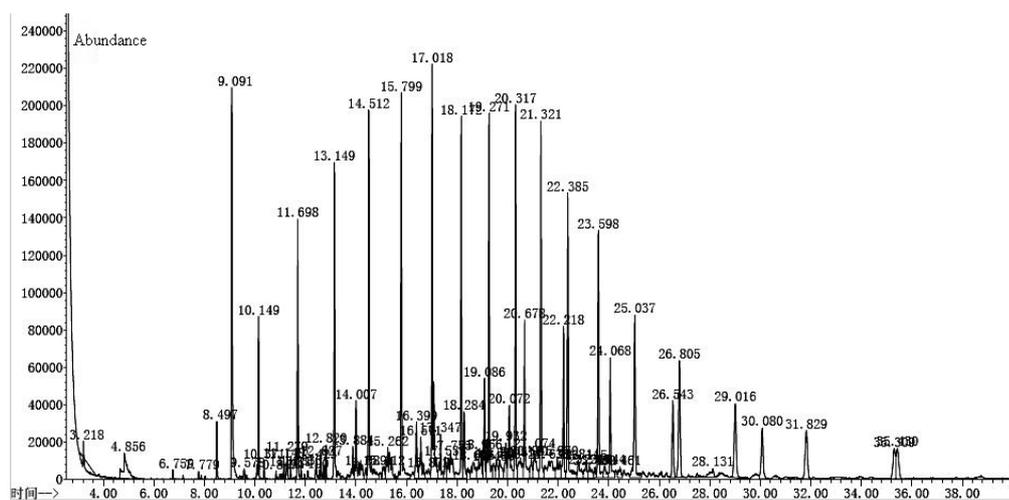


Figure 7. GC/MS chromatograms of raw water

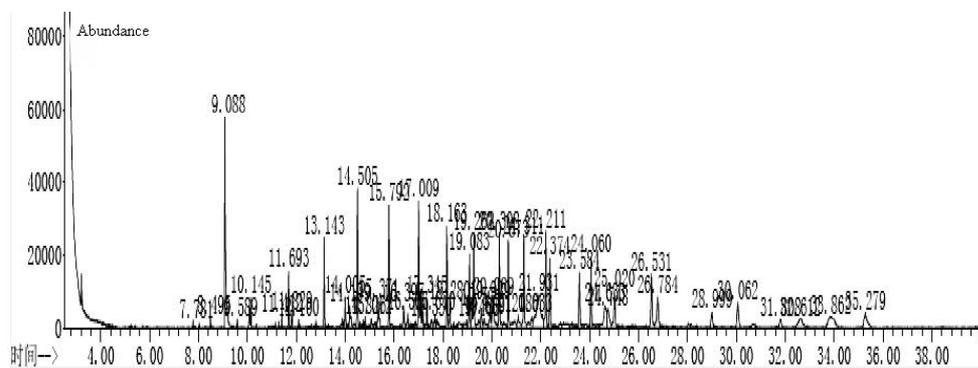


Figure 8. GC/MS chromatograms of ozone-oxidized water