Remediation of organics contaminated groundwater by ozone micro-nano bubble

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ABSTRACT

Nowadays groundwater contamination widely spreads in China. Organic pollutants are of the public concern since they are toxic and with long life cycle, causing considerable remediation cost. The innovative remediation technologies are urgently needed. In this paper, the micro-nano bubbles (MNBs) technology with the ozone oxidation method was proposed, and laboratory tests were conducted for both surface water and groundwater remediation to degrade methyl orange, which was selected as the representative pollutant. In the test, deionized water was used to configure methyl orange solution of certain concentration, then the concentrations of methyl orange were monitored during the treatment process of ozone macro bubbles, oxygen MNBs, and ozone MNBs. Glass beads with the diameter of 4.0-4.5 mm were selected to simulate highly permeable soils, and the concentrations of both methyl orange and the dissolved ozone were measured during groundwater remediation process by ozone MNBs. The results indicated that oxygen MNBs did not degrade methyl orange, while the degradation effect of ozone bubbles was obvious. The degradation effect of ozone MNBs can even be 41 times greater than ozone macro bubbles for polluted surface water. The groundwater remediation tests further verified that ozone MNBs have significant capability in the remediation of organic contaminated subsurface.

Keywords: micro-nano bubbles; organic contaminant; groundwater remediation; ozone oxidation

1 INTRODUCTION

Groundwater is an important water supply for most cities in China. The groundwater quality inspection reported that organic pollution is getting increasingly serious. There are several major pollution sources such as the excessive application of fertilizer and pesticide, by-product wastes of petrochemical industry. The contaminated groundwater in city area is seriously threatening the safety of drinking water.

The Micro-nano Bubbles (MNBs) is an attractive technology, and great breakthrough has been made in recent years. Many researches aiming at the physical properties of MNBs have been taken. High pressure around MNBs may lead to hydrate formation (Takahashi 2003). The applicability of Young-Laplace equation is confirmed by molecular dynamics simulation (Matsumoto 2008). MNBs improve the mass transfer effect and oxidation ability of ozone significantly (Chu 2008). MNBs in water increase the concentration of dissolved oxygen (Shu 2009). The interfacial charge of MNBs inhibits the bubbles from coalescence for longer existence (Ushikubo 2010). Interfacial charge properties is the main reason for the stability of MNBs (Bunkin 2012). The MNBs can not only last longer in water and increase the contact area of gas and water, but also enhance the mass transfer efficiency (Li 2013). MNBs technology has also been applied in water treatment. Studies on the degradation of phenol by MNBs prove that oxygen MNBs have strong effect on the degradation of phenol under acid condition (Li 2009). MNBs are proved to have accelerated the degradation of methyl orange (Tasaki 2009).

MNBs technology has great potential in organic pollutants removal. In this study, ozone MNBs technology was employed for the chemical oxidation of organic pollutants in laboratory conditions. Methyl orange was selected as representative pollutant. The remediation efficiencies were tested under different conditions. The degradation rates were measured through the concentration of residual methyl orange. This study is aimed to figure out the effect of MNBs on the degradation of methyl orange, to lay the foundation for further research on the feasibility of MNBs application in groundwater remediation.
2 MATERIALS AND METHODS

2.1 Experimental Setup

2.1.1 MNBs Generation method

The generation method affects the properties of MNBs. Four major methods, including hydrodynamic, acoustic, optic, and particle cavitation, are commonly used in the MNBs generation (Agarwal 2011).

The generation method used in this research combined spiral liquid flow type with pressurized dissolution type. Both of them are based on hydrodynamic method (Terasaka 2011). The mixtures of gas and liquid are injected into cylinder to be sheared by the revolving flywheel. At the same time the negative pressure in cylinder will continually suck gas and liquid up to be mixed and sheared (Ohnari 1999).

The properties of MNBs are affected by the inlet flow rate of gas and liquid. The liquid flow rate stays at 10.0 L/min. The most suitable gas flow rate is 1.0 L/min for gas hold-up.

2.1.2 Ozone oxidation method

The Ozone Oxidation Method (OOMs) is one of the most widely used Advanced Oxidation Processes (AOPs) types (Snyder 2006), which contains direct oxidation and indirect oxidation (Binbin 2005). The ozone can directly oxidize the organics, such as some kinds of unsaturated aliphatic hydrocarbon and aromatic hydrocarbon compounds. In the indirect way, ozone decomposes into hydroxyl radicals, and then the organic pollutants can be oxidized. Ozone can rapidly reduce organic contaminants such as benzene, toluene, ethyl benzene & xylene (BTEX) and volatile organic compounds (VOCs). However, the oxidizing ability is limited by dissolved ozone concentration. MNBs will not burst out like macro bubbles but remain stable in aqueous solution for a long period of time, supplying ozone to water continuously. Therefore ozone MNBs will lead to a high concentration of dissolved ozone and increase the chemical treatment efficiency.

2.1.3 Ultraviolet spectrophotometer

Ultraviolet spectrophotometer (DR5000, Hach, USA) was used to measure the concentration of methyl orange. Lambert-William’s law shows the linear relationship between absorbance and concentration of absorbing species. The characteristic wavelength of the azo bond in methyl orange is 464 nm.

2.1.4 Dissolved ozone sensor

The concentration of dissolved ozone was measured by dissolved ozone sensor (OZS30, Clean, USA), ranging from 0 to 10 ppm, with the accuracy of ±1%.

2.2 Materials

All the water used in the experiment was deionized water produced by water purification system (Direct Q3, Merck Millipore Ltd, USA). The ozone was produced by ozone generator (RQ-30G, Ruiqing, CHINA). The capacity of ozone was 30 g/h with the concentration of 100 mg/L. The methyl orange solution was diluted into certain concentration by deionized water. The glass beads were used to simulate highly permeable soil. The diameter was 4.0-4.5 mm and the specific gravity was 2.65.

2.3 Experimental procedure

The degradation experiments were conducted in a designed tank (80 cm*20 cm*20 cm), which was made of plexiglass plate. The model tank is shown in Figure 1. The volume of deionized water was 20 L and the initial concentration of methyl orange solution was 10.0 mg/L.

Fig. 1. Designed model tank.

For the MNBs experiments, the MNBs generation was operated directly in the tank for 30 min. The solution was extracted in certain times for concentration measurement. For the macro bubble experiments, the gas was injected into water directly by a 4 mm diameter tube for 30 min. An additional research on the macro bubble experiment was to decrease the water volume from 20 L to 2 L, and the initial concentration of methyl orange remains 10.0 mg/L. The experimental conditions were shown in Table 1.

Table 1. Test conditions.

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Bubble type</th>
<th>Gas-liquid ratio</th>
<th>Gas injection rate</th>
<th>Water circulation velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oxygen MNBs</td>
<td>3:2</td>
<td>1.0L/min</td>
<td>10 L/min</td>
</tr>
<tr>
<td>2</td>
<td>Ozone MNBs</td>
<td>3:2</td>
<td>1.0L/min</td>
<td>10 L/min</td>
</tr>
<tr>
<td>3</td>
<td>Ozone macro bubbles</td>
<td>3:2</td>
<td>1.0L/min</td>
<td>No circulation</td>
</tr>
<tr>
<td>4</td>
<td>Ozone macro bubbles</td>
<td>30:1</td>
<td>1.0L/min</td>
<td>No circulation</td>
</tr>
</tbody>
</table>

The experiment in model soils for groundwater remediation was conducted using MNBs technology. The tank was separated into three chambers (20 cm/40 cm/20 cm) by porous stone. The simulated soil was 15 cm thick and well distributed in the medial part. The water was pumped out from one side of the tank for MNBs generation, and then the MNBs water was injected into the other side. The MNBs permeated with the water flow. The methyl orange concentration and the dissolved ozone concentration in different parts of the simulated soil were measured at certain times.

All the tests mentioned above were carried out at a temperature of 20°C.
3 RESULTS AND DISCUSSION

3.1 Surface water treatment

3.1.1 Results

Ozone macro bubbles, oxygen MNBs and ozone MNBs were used for surface water treatment. Changes of concentration within 30 minutes were shown in Figure 2.

In the oxygen MNBs test, concentration of methyl orange remained unchanged, which obviously showed that oxygen MNBs do not react with methyl orange and no oxidation degradation occur.

In the ozone MNBs test, concentration of methyl orange showed a rapid decline in the first 5 minutes. The concentration fell from 10 ppm to less than 3 ppm. Over 71% of the methyl orange was degraded. From the fifth minute to tenth minute, the degradation started to slow down, and the concentration declined to 0.9 ppm. The degradation rate reached 91% at the tenth minute. After the tenth minute, the degradation slowed down, and the contaminant remained at a low concentration of 0.2 mg/L. The ozone MNBs showed great oxidation ability on methyl orange.

In the ozone macro bubbles test with a gas-liquid ratio of 3:2 (gas volume 30 L; liquid volume 20 L), the macro ozone bubbles showed slight oxidation ability. The degradation rate was near 10% at the thirtieth minute. The macro bubbles also showed oxidation ability on methyl orange. However, the degradation efficiency is limited by low concentration of dissolved ozone in water.

As a supplement of the above ozone macro bubbles test, another test with a gas-liquid ratio of 30:1 (gas volume 30 L; liquid volume 1L) was performed. In the test, the decreasing rate of concentration was much faster. After 30 minute, the concentration fell to 0.8 ppm and the degradation rate was 92%.

3.1.2 Discussion

In the surface water treatment tests, oxygen showed no oxidation ability on methyl orange. The concentration of methyl orange remained unchanged during the injection of oxygen MNBs. On the other hand, ozone bubbles showed great oxidation ability in the degradation. The ozone macro bubbles test with the gas-water ratio of 3:2 showed that slight reaction occurred during the injection, however the degradation rate was limited by the gas-water ratio. When the liquid volume was decreased to 1 L, the degradation was more optimum and the degradation rate reached 92% in 30 minutes. In the ozone MNBs test, although the gas-liquid ratio was 3:2, same as in the ozone macro bubbles test, the degradation rate of methyl orange reached 91% in 10 minute. The degradation effect of ozone MNBs was 41 times greater than the macro bubbles. The MNBs technology can enhance the degradation process more efficiency.

3.2 Groundwater treatment

3.2.1 Results

Ozone MNBs were used in groundwater treatment. The tank and the sampling points were shown in Figure 3. The concentrations of methyl orange in different position were measured and shown in Figure 4. The concentration of dissolved ozone at different positions is shown in Figure 5.

In the ozone MNBs test, the concentration of methyl orange showed a rapid decline in first 5 minutes, which was similar with the surface water test. The average degradation ratio during the first 30 minutes reached 87%. The concentrations of methyl orange in different position showed slight differences. The closer to the water inlet, the lower the concentration was. The concentration of dissolved ozone increased along with the time, and decreased from water inlet to the water outlet.

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Fig. 3. Model tank and sample point positions.

Fig. 4. Methyl orange concentration in different position.
3.2.2 Discussion

Fig. 5 shows that MNBs gradually diffuse with water from the inlet to the outlet. MNBs reacted with methyl orange during the diffusion process. The concentration of methyl orange was influenced by the concentration of dissolved ozone. Therefore the concentration increased from water inlet to the water outlet. The average degradation rate in tenth minute reached 95% of that in surface water treatment. Ozone MNBs showed great oxidation ability in water treatment and groundwater remediation.

The groundwater treatment test can be improved in several aspects in future research. The permeability coefficient of simulated soil is 1 cm/s, which is quite big compared with practical engineering. The volume of simulated soil is not large enough compared with the volume of water. Therefore the degradation results may be affected. More model tests are needed to simulate practical engineering conditions.

4 CONCLUSION

In this paper, laboratory tests were conducted for surface water and groundwater remediation by means of MNBs technology. The following conclusions can be drawn:
1. Oxygen MNBs have no oxidation ability upon methyl orange.
2. Ozone macro bubbles produce slight oxidation effect on methyl orange, but the efficiency is limited by the quantity of ozone supply.
3. Ozone MNBs have great oxidation ability upon methyl orange, and show great potential in groundwater treatment.
4. MNBs technology can be a potential in-situ groundwater remediation technology.

5 ACKNOWLEDGMENTS

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