Research on In-depth Treatment Efficacy of Reclaimed Water with Heterogeneous Catalytic Ozonation

Li Subo, Liu Yongze, Zhang Liqiu, Feng L

Beijing Forestry University, No.35 Tsinghua East Road Haidian District, Beijing, 100083, China
15534006532@163.com

Abstract. The secondary biological effluent of a sewage treatment plant in Beijing City is treated deeply with heterogeneous catalytic ozonation and the efficacy is evaluated. The results indicate that the organic degradation efficacy in the effluent after heterogeneous catalytic ozonation increases along with the ozone dosage, but the ozone utilization ratio decreases along with the ozone dosage. Through the research of residual ozone concentration in the reactor friction, the catalyzer is added in the section between 30cm and 80cm far from the aeration device, and it can effectively promote ozone utilization ratio while further strengthening organic degradation efficacy. The results indicate that when the ozone dosage is 15mg/L, SCOD, UV254 and DOC in the effluent may be decreased to 6.74 mg/L, 0.0361 cm$^{-1}$ and 5.85 mg/L respectively through catalytic ozonation of heterogeneous catalyzer A (aluminum silicon alloy). Meanwhile, the ozone utilization ratio is increased from 84.76% (when only ozone is oxidized) to 94.2%. Three-dimensional fluorescence analysis results indicate that macromolecules such as protein and humus in the effluent may be well removed. The reclaimed water after in-depth treatment reaches higher water quality standard, the applicable scenarios are greatly increased, and the water quality problem of reclaimed water can be effectively solved during reuse.

1. Introduction

The reclaimed water refers to the water which reaches the water quality standard, meets some using requirements for beneficial application after the sewage is properly treated$^{[1]}$. The water quality is between the sewage and the tap water, and the reclaimed water is the non-potable water which reaches national relevant standards and it can be applied in a scope after the urban sewage and wastewater is treated. The reclaimed water is widely applied in each country in the world, mainly including river and lake landscaping environment, municipal miscellaneous uses, underground water supply, agricultural irrigation, industrial and domestic water for residents, etc. The requirements for reclaimed water in different reusing scenarios differ. The further in-depth treatment of reclaimed water can greatly increase the applicable reusing scenarios.

The heterogeneous catalytic ozonation adopts solid catalyzer to decrease activation energy or change the reaction progress so as to achieve in-depth oxidation$^{[2]}$. It has good application prospects due to its easy separation, easy absorption and circulation for many times, etc. However, among various catalyzers, the systematic and transverse comparison of all catalyzers’ catalysis efficacy is not made. This test aims to select practical and commercial catalyzers and optimize the technique of in-depth treatment of reclaimed water$^{[3]}$. 
2. Material and approach

2.1. Test material
The test water is the secondary biological effluent from a sewage treatment plant in Beijing City. The basic procedures of treatment technique in the sewage plant include raw water of domestic sewage, grill, grit chamber, primary sedimentation tank, A2/O pond, secondary sedimentation tank, effluent. The following is the basic index of the secondary effluent. SCOD=13.5 mg/L; UV254=0.127cm-1; DOC=9.73 mg/L; total nitrogen=18.06mg/L, total phosphorus=0.001 mg/L. The reagent in this test is indigo carmine, phosphate buffer, amylum solution, deionized water and other common reagent. 0.45μm filtration membrane, Hach COD reagent, and selected commercial heterogeneous catalyzer A (aluminum silicon alloy), B(SiO2) and C(Fe2O3-Al2O3).

2.2. Test approach
Three catalyzer materials including A (aluminum silicon alloy), B (SiO2) and C (Fe2O3-Al2O3) are primarily selected. When the ozone dosage is 5mg/L and 20mg/L, the reaction duration of three reagents in the reactor is controlled for 60min respectively. SCOD, UV254 and DOC in the effluent are sampled and measured every 10 minutes. Three commercial catalyzers and blank degradation effect are evaluated and compared, and the best catalyst is selected.

It is assumed that the incoming gas flow of the incoming ozone test is 500ml/min, the incoming water flow is 127L/min, water contact time is 30min, the ozone dosage of the ozone generator is controlled at 5mg/L, 10mg/L, 15mg/L and 20mg/L respectively. The ozone concentration changes of the reactor friction are measured under 4 different concentration gradient when single ozone is treated.

2.3. Analysis approach
(1) Indigo method\textsuperscript{[4]} is adopted to measure the concentration of residual ozone in the reaction solution:

\[ C_{solution} = 2.40(A_0 - A_i) \times \frac{100}{V_s} \]

Where \( C_{solution} \) is the concentration of residual ozone in the reaction solution, mg/L;
\( A_0 \) is blank absorbance (take the average value);
\( A_i \) is sample absorbance
\( V_s \) is the sample volume, mL

(2) Determination of ozone consumption
Due to dissolution and effusion of ozone in the liquid, the ozone may not fully react with the solution, so the actual consumption of ozone concentration is calculated as follows:

\[ C = C_{gas} - C_{solution} - C_{effluent} \]

Where \( C \) is the ozone consumption, mg/L
\( C_{gas} \) is the ozone concentration in the gas phase, mg/L;
\( C_{solution} \) is the residual ozone concentration in the reaction solution, mg/L;
\( C_{effluent} \) is the ozone concentration in the effluent absorption solution, mg/L.

(3) Determination of ozone cumulative utilization ratio
Ozone cumulative utilization ratio is the ratio between cumulative ozone consumption and cumulative yield, i.e.

\[ \text{cumulative utilization ratio} = \frac{\text{consumption}}{\text{yield}} \]

3. Result and discussion

3.1. SCOD removal efficacy of ozonation and catalytic ozonation
Excessive potassium dichromate and sulfuric acid were added into the water sample. It was heated, and silver sulfate was used as the catalyzer to facilitate oxidization. Ferroin is used as the indicator for excessive potassium dichromate. Ferrous sulfate standard solution is used for back titration. The heavily polluted industrial wastewater is used to explain the pollution due to organism. COD (chemical oxygen demand) is one of the important indicators of organic wastewater pollution degree, and it means the amount of reduction materials which can be oxidized by strong oxidant in the water sample. This test takes soluble chemical oxygen demand as the water quality indicator, investigates soluble chemical oxygen demand removal efficacy of different catalyzers in the static condition.

Figure 2-1 Removal efficacy photo of static and selected SCOD

Figure 2-1 indicates that the initial concentration of SCOD in the incoming water is 14.02mg/L~15.42mg/L. Along with the reaction time of ozone, when the reaction time is 10 min, 20 min, 30 min, 40 min, 50 min and 60 min, the removal ratio of SCOD which is added with catalyzer A is 23.05%, 36.81%, 43.72%, 42.03%, 44.20% and 43.88% respectively. The final SCOD removal ratio of catalyzer A group in 60 minutes is 43.90%. The final SCOD removal ratio of blank group in 60 minutes is 20.38%. The final SCOD removal ratio of catalyzer B group in 60 minutes is 23.57%. The final SCOD removal ratio of catalyzer C group in 60 minutes is 33.35%. Compared with other three groups, the soluble chemical oxygen demand degradation ratio in catalyzer A group is more efficient. In the first 30 minutes of reaction, the removal speed of catalyzer A catalytic ozonization for SCOD in the reclaimed water is high. It basically does not increase after 30 minutes. The ozone oxidizes and degrades the easily degradable SCOD at first. The removal efficiency of SCOD is high. Along with the reaction, some recalcitrant macromolecular organisms are oxidized into metabolic intermediate by the ozone, and they are constantly accumulated in the reaction system, so COD removal efficiency in this stage is low. In the late period of reaction, the residual inert SCOD components in the reclaimed water are difficult to be oxidized and degraded by the ozone, so the removal efficiency of SCOD no longer rises.

3.2. UV\textsubscript{254} removal efficacy of ozonation and catalytic ozonation

UV absorbance (UV\textsubscript{254}) is the absorbance value of the water sample at the wave length of 254 nm. It is an important parameter of evaluating specific organic content such as unsaturated organisms (such as organisms containing C=C dual bonds and C=O dual bonds\cite{5}). It is often used to evaluate the reclaimed water quality and water treatment effects. Figure 2-2 indicates that the initial concentration of UV\textsubscript{254} in the incoming water is 0.105cm\textsuperscript{-1}~0.123cm\textsuperscript{-1}. Along with the reaction time of ozone, when the reaction time is 10 min, 20 min, 30 min, 40 min, 50 min and 60 min, the removal ratio of UV\textsubscript{254} which is added with catalyzer A is 25.20%, 39.03%, 58.54%, 60.16%, 60.79% and 63.41% respectively. Along with ozonation, the value of UV\textsubscript{254} significantly decreases. The final UV\textsubscript{254} removal ratio in catalyzer A group for 60min is 63.41%. The final UV\textsubscript{254} removal ratio in blank group for 60min is 53.09%. The final UV\textsubscript{254} removal ratio in catalyzer B group for 60min is 56.19%. The final UV\textsubscript{254} removal ratio in catalyzer C group for 60min is 59.04%. For catalyzer A group, when the reaction time is 30min, the removal
ratio of UV$_{254}$ is stable, indicating that the unsaturated dual-bond materials characterized by UV$_{254}$ are well removed during single ozonation.

![Figure 2-2 Removal efficacy photo of static and selected UV$_{254}$](image)

It is analyzed that the reaction speed of ozone with the materials containing C=C dual bond is $10^{3}$–$10^{7}$ L/(mol·s). The ozone directly reacts with materials containing conjugated double bonds, so the value of UV$_{254}$ significantly decreases.

3.3. **DOC removal efficacy of ozonation and catalytic ozonation**

Dissolved organic carbon (DOC) often refers to dissolved organic materials which can pass 0.45μ filtration membrane and may not be lost due to evaporation during the measurement and analysis in the future. The components of DOC are extremely complicated, and its mass concentration in the water is low. Its components include carbohydrate (monosaccharide and polysaccharide), amino acid, hydrocarbon and halohydrocarbon, vitamin and humus.$^{[6]}$

Dissolved organic matters characterized by DOC are indicators which shall be prudently considered during reuse of reclaimed water. During sewage treatment, most dissolved organic matters can be degraded and used by microorganisms, and further removed. However, a small quantity of recalcitrant dissolved organic matters are left in the effluent. These remnant dissolved organic matters may have adverse influence on the subsequent in-depth treatment process such as THM$_3$ and other disinfectant byproducts during use of chlorination disinfection, and they may be used by microorganisms during subsequent reuse of reclaimed water so that microorganisms may be bred and the biological stability of reclaimed water may be damaged. As the incoming water quality and treatment process of each sewage treatment plant differ, the structure and components of DOM in the reclaimed water produced by different sewage treatment plants differ.
Figure 2-3 Removal efficacy photo of static and selected DOC

Figure 2-3 indicates that the initial concentration of DOC in the incoming water is 10.45mg/L~13.42mg/L. Along with the reaction time of ozone, when the reaction time is 10 min, 20 min, 30 min, 40 min, 50 min and 60 min, the removal ratio of DOC which is added with catalyzer A is 13.39%, 22.90%, 29.85%, 36.79%, 37.93% and 38.74%. Along with ozonation, the value of DOC decreases. The final DOC removal ratio in catalyzer A group for 60min is 38.74%. The final DOC removal ratio in blank group for 60min is 19.83%. The final UV$_{254}$ removal ratio in catalyzer B group for 60min is 56.19%. The final DOC removal ratio in catalyzer C group for 60min is 22.35%. The degradation efficacy of catalyzer A for DOC is relatively high, and it is sable at 40min. The removal ratio of DOC in the blank ozone is relatively low. It is analyzed that during single ozone oxidization, the first oxidized materials are alkene and aromatic materials. When the alkene functional group is located in the terminal of organic molecular formula, the terminal carbon atom may be oxidized into carbon dioxide, so DOC decreases. However, ozonation may oxidize other macromolecular organism into micromolecular organism, and mineralization is relatively weak, so the level of mineralization is low in whole. The addition of catalyzer can activate the hydroxyl radical in the reaction system, promote macromolecular degradation, and improve DOC degradation efficiency.

3.4. Change rule of ozone concentration friction

Figure 2-4 indicates that as regards cross-flow ozone reactor, when the concentration of dosage is low (5 mg/L, 10 mg/L), the residual ozone in the water is low. The ozone utilization ratio is 97.54% when the ozone dosage is 5 mg/L. The utilization ratio is 94.32% when the dosage is 10 mg/L. Therefore, the ozone utilization ratio is high in case of low-concentration dosage. The dosed ozone can be effectively used without catalytic oxidization. When the concentration of dosage is high at 15 mg/L, the maximum residual ozone concentration is 3.108mg/L, the ozone utilization ratio is 84.76%. When the ozone dosage is 20 mg/L, the maximum residual ozone concentration is 5.112mg/L, and the ozone utilization ratio is further decreased to 80.31%. In the catalysis and oxidization of the ozone, when there exists residual ozone concentration in the water, the catalyzer can catalyze ozone degradation, generate hydroxyl radical, and strengthen oxidization of organisms. Figure 2-4 also indicates that the high position of residual ozone concentration is mainly 30cm-80cm far from the aeration device. Therefore, the selected catalyzer A (aluminum silicon alloy) is added in the section 30cm-80cm far from the aeration device. Other test conditions are controlled to be consistent with the blank group. Four positions of reactor friction and the effluent residual ozone concentration are measured.
Figure 2-4 Friction residual concentration when the ozone reaction column is blank

Figure 2-5 Residual ozone concentration change of reaction column friction in the catalyzer group

Figure 2-5 and Table 1 indicate that the dosage of catalyzer significantly decreases the residual ozone concentration in the water. When the ozone dosage is 5-10 mg/L, the ozone utilization ratio is further increased to 97.72~98.66%. When the ozone dosage is 15-20 mg/L, the maximum residual ozone concentration is decreased to 1.554mg/L and 2.52mg/L respectively. The ozone utilization ratio increases significantly to 94.20% and 90.89%. In case of high-concentration ozone dosage, the catalyzer can effectively catalyze ozone reaction to produce hydroxyl radical, and strengthen oxidation of organisms.

Table 1 Comprehensive ozone utilization ratio of reactors when ozone dosage is different

| Ozone injection | Blank     | Catalyzer A (aluminum silicon alloy) |
|-----------------|-----------|--------------------------------------|
| 5mg/L           | 97.54%    | 97.72%                               |
| 10mg/L          | 94.32%    | 98.66%                               |
| 15mg/L          | 84.76%    | 94.20%                               |
4. Conclusion

(1) The research results on the removal efficacy of three catalysts indicate that the degradation of three catalysts increases compared with the blank group, but the removal efficacy of catalyst A (aluminum silicon alloy) is the best. The removal efficacy of TOC, COD and UV$_{254}$ is 54.51%, 58.57% and 75.51%. The effluent after in-depth treatment has more applicable reusing scenarios.

(2) Among three catalysts, the effect of catalyst A (aluminum silicon alloy) for catalysis and oxidation of the reclaimed water is better. When the dosage is 15mg/L, TOC in the effluent can be decreased to 4.28mg/L-5.03 mg/L on average. COD can be decreased to 4.25 mg/L-4.77 mg/L on average. UV$_{254}$ can be decreased to 0.0361cm$^{-1}$-0.0375cm$^{-1}$. Through three-dimensional fluorescence analysis, heterogeneous catalytic ozonation can effectively degrade aromatic protein and humus.

(3) Through friction measurement of continuous flow reactor in the pilot site, it is found that the overall ozone utilization ratio of the reactor is high when the concentration of ozone dosage is low (5mg/L, 10mg/L) while the overall ozone utilization ratio of the reactor is low when the concentration of ozone dosage is high (15mg/L, 20mg/L). However, for cross-flow reactor, the high position of friction residual ozone concentration is 30cm-80cm far from the aeration device, the addition of catalyst can significantly promote the ozone utilization ratio and removal efficiency when the ozone dosage is identical.

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