Effect of H₂O₂ dosing strategy on sludge pretreatment by microwave-H₂O₂ advanced oxidation process

Yawei Wang, Yuansong Wei *, Junxin Liu

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, PR China

1. Introduction

As the most widely used biological wastewater treatment for both domestic and industrial plants in the world, one of the drawbacks of activated sludge processes is high sludge production. Treatment and disposal of sewage sludge from wastewater treatment plants (WWTPs) accounts for about half, even up to 60%, of the total cost of wastewater treatment [1]. To manage the excess sludge volume [5,6], to recover nutrients (nitrogen and phosphorus) from sludge [7,8], to reduce sludge production [1,9]. Nowadays, among these sludge pretreatment technologies based on physical, chemical and biological methods [1], microwave (MW) heating (CH) in chemical reactions is becoming popular, mainly due to dramatic reductions in reaction time [10], i.e., most of previous researches with regard to microwave irradiation have used the thermal effects of galvanic heating. Recently the application of microwave heating in combination with hydrogen peroxide (H₂O₂) for sludge pretreatment has shown to be an efficient advanced oxidation process (AOP) technology [8,10–14]. H₂O₂ is a strong chemical oxidant that destroys the cell walls of micro-organisms, which leads to the release of cytoplasm, as well as oxidation of many recalcitrant organic compounds. AOPs related to the formation of OH radicals are a new approach to treat waste sludge, which will accelerate an oxidative degradation of numerous organic compounds dissolved in supernatant.

Catalase (H₂O₂:H₂O₂-oxidoreductase, EC 1.1.1.6), a terminal respiratory enzyme, is present in all aerobic living cells, can break down H₂O₂ into water and molecular oxygen by catalase in waste activated sludge (WAS). The effect of H₂O₂ dosing strategy on sludge pretreatment by the advanced oxidation process (AOP) of microwave-H₂O₂ was investigated by batch experiments for optimizing H₂O₂ dosage. Results showed that the catalase in sludge was active at the low temperature range between 15 °C and 45 °C, and gradually lost activity from 60 °C to 80 °C. Therefore, the H₂O₂ was dosed at 80 °C, to which the waste activated sludge was first heated by the microwave (MW), and then the sludge dosed with H₂O₂ was continuously heated till 100 °C by the microwave. Results at different H₂O₂ dosages showed that the higher the H₂O₂ dosing ratio was, the more the SCOD and total organic carbon (TOC) were released into the supernatant, and the optimum range of H₂O₂/TCOD ratio should be between 0.1 and 1.0. The percentages of consumed H₂O₂ in the AOP of microwave and H₂O₂ treating the WAS were 25.38%, 22.53%, 14.82%, 13.61% and 19.63% at different H₂O₂/TCOD dosing ratios of 0.1, 0.5, 1, 2, 4, respectively. Along with the increasing H₂O₂/TCOD ratio, the contents of TCOD on particles, soluble substances and mineralization increased and the TCOD distribution on solids decreased.

© 2009 Published by Elsevier B.V.
is concerned, it should consider the impact of catalase on sludge disintegration, i.e. which temperature is suitable to begin dosing H$_2$O$_2$ during the AOP of microwave and H$_2$O$_2$ treating waste activated sludge. However, the information is yet unknown about the impact of catalase on sludge pretreatment by the AOP of microwave and H$_2$O$_2$. In addition, high operational pressure in the closed test system using the AOP of microwave and H$_2$O$_2$ in these researches [8,10–12] may limit its full-scale application of sludge pretreatment. Therefore a H$_2$O$_2$ dosing strategy was proposed in this study, in which H$_2$O$_2$ should be dosed at a suitable temperature which the catalase loses its activity during sludge pretreatment by the AOP of microwave and H$_2$O$_2$. Through investigating the impact of H$_2$O$_2$ dosing strategy on sludge disintegration, the aims of this study were to optimize H$_2$O$_2$ dosage in the AOP of microwave and H$_2$O$_2$ treating the waste activated sludge, and to elucidate the fate and distribution of organic matters in the waste activated sludge.

2. Materials and methods

2.1. Sludge and apparatus

The waste activated sludge was obtained from Gaobeidian municipal wastewater treatment plant (WWTP) with conventional activated sludge process in Beijing, which is the largest full-scale municipal wastewater treatment plant in China. The design capacity of this WWTP is 600,000 t/d, and its sludge age is operated at 20 d. In this study, total suspended solids (TSS) concentration of the waste activated sludge was adjusted to about 15 g/L for batch tests, and characteristics of the WAS are listed in Table 1.

An industrial microwave oven set at 2450 MHz is made by Julong Corp (BaoDing, China) on the basis of our design, which is equipped with a rotating blade homogenizer, and a thermocouple temperature sensor to monitor the real-time temperature. The power of the microwave oven is in the range from 0 W to 1000 W, but the microwave oven was operated at 600 W in this study. Hydrogen peroxide (A.R., 30%, w/w) at density of 1.12 g/ml was used in this study. The concentration of residual H$_2$O$_2$ in sludge samples was determined by the colorimetric method with Ti [16]. Samples’ filtrate of 0.45 μm membrane was used to measure concentrations of soluble total organic carbon (TOC) and soluble chemical oxygen demand (COD). The soluble TOC was determined by a TOC-VCPH analyzer (Shimadzu, Japan). The total TOC of the waste activated sludge was measured by a solid TOC analyzer SSM-5000A (Shimadzu, Japan).

Because the residual H$_2$O$_2$ in the WAS has strong interference on COD measurement [17], COD were thus determined after the removal of residual H$_2$O$_2$ by adding catalase (Sigma C9322). The COD, TSS, VSS (volatile suspended solids) are measured according to the APHA [18], SEM pictures of the WAS before and after the treatment by the AOP of H$_2$O$_2$ and microwave were taken by a HITACHI S-3000N (Hitachi, Japan).

2.3. Analysis

The concentration of residual H$_2$O$_2$ in sludge samples was determined by the colorimetric method with Ti [16]. Samples’ filtrate of 0.45 μm membrane was used to measure concentrations of soluble total organic carbon (TOC) and soluble chemical oxygen demand (COD). The soluble TOC was determined by a TOC-VCPH analyzer (Shimadzu, Japan). The total TOC of the waste activated sludge was measured by a solid TOC analyzer SSM-5000A (Shimadzu, Japan). Because the residual H$_2$O$_2$ in the WAS has strong interference on COD measurement [17], COD were thus determined after the removal of residual H$_2$O$_2$ by adding catalase (Sigma C9322). The COD, TSS, VSS (volatile suspended solids) are measured according to the APHA [18], SEM pictures of the WAS before and after the treatment by the AOP of H$_2$O$_2$ and microwave were taken by a HITACHI S-3000N (Hitachi, Japan).

2. Results and discussion

3.1. Catalase activity

As shown in Fig. 1, the concentrations of residual H$_2$O$_2$ in the WAS decreased more drastically at the low temperatures of between 15 °C and 45 °C than those at the high temperatures (60 °C and 80 °C) in the first minute. These results clearly revealed that the catalase remained active until 45 °C, and gradually lost its activity beyond 45 °C, confirming their research results [15].

According to the enzyme activity definition, one unit of catalase activity corresponds to the breakdown of 1 μmol of H$_2$O$_2$ per

![Fig. 1. Changes of H$_2$O$_2$ decomposition by catalase activity in waste activated sludge at different temperatures (initial TCOD of the WAS = 5000 mg/L; initial H$_2$O$_2$ dosage = 11,000 mg).](image-url)
minute under specified conditions [14]. In this study, the specific catalase activity in the waste activated sludge was 32.1 units/mgVSS at 25°C, and decreased to 3.7 units/mgVSS at 80°C. Evaluation of catalase activity in waste activated sludge is helpful to optimize H2O2 dosage in order to save H2O2 cost in sludge pretreatment by the AOP using H2O2.

On the basis of this study and other study [8] about sludge pretreatment by the AOP of microwave and H2O2, the ramp time was set at the rate of 20°C/min, which means that it takes about 1 min to reach the temperature (40°C or 45°C) of the denature point of catalase in activated sludge. In this short time, the H2O2 dosed at temperature lower than 45°C will be decomposed by over 60%. Therefore the preheating sludge before H2O2 dosing could save the usage of H2O2 and make the sludge pretreatment by the AOP of microwave and H2O2 more cost effective.

3.2. Temperature of H2O2 dosing

Compared to minor soluble COD (SCOD) release into the supernatant in the control experiment of sludge pretreated only by the microwave in the absence of H2O2, a considerable increase in sludge solubilization occurred in batch experiments with the AOP of microwave and H2O2 (Fig. 2). The higher temperature H2O2 dosed at, the quicker SCOD released. For example, the rate of SCOD release in the batch experiment of H2O2 dosing at 80°C was much higher than that at 60°C, though their behaviors of SCOD release were similar from 90°C to 100°C. These results indicated that the sludge disintegration by the AOP of microwave and H2O2 was rapid and temperature sensitive since 60°C. As mentioned above, catalase is active in the range of the low temperature (15–45°C) and gradually inactive beyond 45°C. In the test of H2O2 dosing at 15°C, the residual H2O2 concentration sharply decreased from 11,000 mg/L to 3190 mg/L in the temperature range of 15°C to 40°C due to catalase actively decomposing H2O2, and then maintained stable at the range of 3190–2631 mg/L between 40°C and 80°C. Different from the behavior of H2O2 at 15°C, the residual H2O2 concentrations in both tests of H2O2 dosing at 60°C and 80°C, respectively, decreased slowly along with temperature increasing, but were higher than that at 15°C in the end of batch experiments. Due to lost activity of catalase at high temperatures (60°C and 80°C), such decrease of H2O2 concentration nearly resulted from the AOP of microwave and H2O2 treating the WAS rather than catalase degradation. These results showed that the amount of H2O2 dosage should be optimized in order to reduce H2O2 by catalase degradation and then save H2O2 consumption in sludge pretreatment by the AOP of microwave and H2O2.

3.3. Optimization of H2O2 dosage

On the basis of the above mentioned results of H2O2 dosing at different temperatures, the waste activated sludge was firstly heated to the temperature of 80°C, at which H2O2 was thus dosed in the sludge in order to avoid its degradation by the catalase, and the WAS with the addition of H2O2 was then continuously heated till 100°C by the microwave oven. For optimizing the H2O2 dosage, batch experiments were carried out to investigate the impact of H2O2 dosages on sludge pretreatment by the AOP of microwave and H2O2. As shown in Fig. 3, the degree of sludge solubilization was strongly affected by the dosage of H2O2. The higher the H2O2 dosing ratio was, the more the SCOD and TOC released into the supernatant. Compared to the SCOD and TOC released in the test of sludge only pretreated by the microwave without H2O2, the SCOD release rates at 0.1, 0.5, 1, 2, 4 of dosing ratios of H2O2/TCOD, respectively, in the WAS pretreated by the AOP of microwave and H2O2 were 63.67%, 91.87%, 140.59%, 181.61% and 246.36%, respectively, and the TOC release rates at these different dosing ratios of H2O2/TCOD were 42.20%, 115.50%, 167.15%, 211.98% and 282.52%, respectively. Although the AOP of microwave and H2O2 was effective for sludge pretreatment in this study, there were still high concentrations of residual H2O2 in the WAS, ranging 436–18773 mgH2O2/L. The higher the H2O2/TCOD dosing ratio was, the less the consumed H2O2 was. The percentages of consumed H2O2 in the AOP of microwave and H2O2 treating the WAS were 25.38%, 22.53%, 14.82%, 13.61% and 19.63% at different H2O2/TCOD ratios of 0.1, 0.5, 1, 2, 4, respectively, neglecting the degradation of H2O2 by catalase in the WAS because of H2O2 dosing at 80°C. Therefore, the optimum range of H2O2/TCOD ratio should be between 0.1 and 1.0 based on the results of SCOD and TOC releases and the residual H2O2 concentration in the batch tests.

In a study of comparing mechanical, thermal and oxidative disinfection techniques, thermal treatment with or without the H2O2 addition was considered the least interesting sludge pretreatment technology among the four based on results of specific energy and COD release [19]. Sludge thermal pretreatment [20] and sludge ozonation [21] have been successfully applied in practice. However, compared with the threshold value of released COD at 150°C in sludge thermal treatment processes [19], the sludge disintegration in the AOP of microwave and H2O2 mainly occurred in the range of 80°C and 100°C (Fig. 2), which implied that it would save energy consumption if the recovered heat were used to preheat the excess sludge before the AOP of microwave and H2O2. The sludge pretreatment by the AOP of microwave and H2O2 is less cost effective than that by ozonation, because the prices of ozone and H2O2 were $1.0–1.5/kgO3 [21] and $1.0/kgH2O2 [22], and the recommend ozone dosage (0.2 kgO3/kgTSS) [23] in sludge pretreatment.
by ozonation was less than that (1 kg H$_2$O$_2$/kg TSS) in the AOP of microwave and H$_2$O$_2$ of this study. Notably, it is found in this study that the residual H$_2$O$_2$ in the sludge bulk solution was as high as over 75%, which means that there is great potential to reduce the dosage of H$_2$O$_2$. Therefore the H$_2$O$_2$ dosage in the AOP of microwave and H$_2$O$_2$ for sludge pretreatment still needs further optimization to increase the amounts of H$_2$O$_2$ consumption in order to make it cost effective technology through reducing both H$_2$O$_2$ costs and residual H$_2$O$_2$ in sludge.

3.4. Fate of organic matters in the WAS

Due to disintegration, solubilization and mineralization in the WAS pretreatment by the AOP of microwave and H$_2$O$_2$, the waste activated sludge was transferred into four parts as residual solids, particles in suspension (after 30 min settling), soluble substances, and CO$_2$. In this study, the changes of these four parts were investigated using their distribution in TCOD. Fig. 4 shows changes of the TCOD distribution in the WAS pretreated by the AOP of microwave and H$_2$O$_2$. It is clear that nearly all TCOD contents in the raw sludge are distributed on solids, which are similar to the sludge pretreatment by the ozonation [23]. Along with the increasing H$_2$O$_2$/TCOD ratio in the WAS pretreated by the AOP of microwave and H$_2$O$_2$, the contents of TCOD on particles, soluble substances and mineralization increased, and the TCOD distribution on solids decreased, i.e., contents of TCOD on particles, soluble organic matters and mineralization were increased from 1.04%, 10.16% and 0% in the WAS pretreated only by microwave without H$_2$O$_2$, respectively, to 8.69%, 35.59% and 14.48% at 4 of H$_2$O$_2$/TCOD ratio in the sludge pretreated by the AOP of microwave and H$_2$O$_2$; the content of TCOD on residual solids were correspondingly decreased from 88.79% to 41.23%. The fractions of soluble organic matters and particles significantly

Fig. 4. The fate of organic matters in the WAS pretreated by the AOP of microwave and H$_2$O$_2$ at different ratios of H$_2$O$_2$/TCOD (TCOD = 5850 mg/L) (concentration unit in the table, mg/L).

Fig. 5. Changes of TSS, ash and VSS/TSS in the sludge pretreatment by MV–H$_2$O$_2$ process at different H$_2$O$_2$ dosages (TSS = 5784 mg/L, TCOD = 5850 mg/L).

Fig. 6. Morphological changes of sludge. (A) Sludge suspension after pretreatment (1, raw sludge; 2, sludge treated by microwave; 3, sludge treated by microwave–H$_2$O$_2$ at 4 g H$_2$O$_2$ g TCOD$^{-1}$; (B)–(D) are SEM photos of these three samples (×10 K)).
increased with the H$_2$O$_2$ dosage increasing at the low range of H$_2$O$_2$/TCOD ratio between 0.1 and 1.0, meanwhile the fraction of mineralization was relatively small, less than 5%. However, the rate of mineralization increased faster than those of solubilization at high H$_2$O$_2$ dosages (ratios of 2 H$_2$O$_2$/TCOD and 4 H$_2$O$_2$/TCOD), e.g., the concentration of soluble substances at 4.0 of H$_2$O$_2$/TCOD ratio was 2.12 times of that at 0.1 of H$_2$O$_2$/TCOD ratio, but the mineralization at 4.0 of H$_2$O$_2$/TCOD ratio was as high as 5.65 times of that at 0.1 of H$_2$O$_2$/TCOD ratio. For sludge pretreatment, disintegration and solubilization are preferred to mineralization because it is advantageous to recycle the released organic matters in the biological wastewater treatment processes, i.e., cryptic growth for reducing sludge production and providing carbon source for denitrification, as well as mineralization would result in more CO$_2$ emission and more H$_2$O$_2$ consumption.

The effects of sludge disintegration, solubilization and mineralization by the AOP of microwave and H$_2$O$_2$ were also determined in terms of VSS/TSS ratio, TSS and ash contents in the WAS. As shown in Fig. 5, the ratio of VSS/TSS in the range of 0.1–1.0 of H$_2$O$_2$/TCOD ratios decreased more sharply than that in the range of 2.0 to 4.0 of H$_2$O$_2$/TCOD ratios, but it is interestingly found that the contents of ash in the WAS pretreated by the AOP of microwave and H$_2$O$_2$ at different H$_2$O$_2$ dosages maintained stable and varied in the range of 1617–1406 mg/L. These results, as well as the above mentioned fate of organic matters, clearly showed that both the solubilized and the mineralized fractions increased along with the WAS reacted more H$_2$O$_2$.

3.5. Morphological changes of sludge

From direct observation as shown in Fig. 6(A), the color of sludge was changed from the original dark-brown to the pale after treatment by the AOP of microwave and H$_2$O$_2$. And the bulk solution was changed to green after 5 min treatment gradually with the increasing H$_2$O$_2$/TCOD ratio of 4.0, in which H$_2$O$_2$/TCOD ratios increased along with the WAS reacted more H$_2$O$_2$.

Along with the increasing H$_2$O$_2$/TCOD ratio in the WAS pretreated by the AOP of microwave and H$_2$O$_2$, the contents of TCOD on particles, soluble substances and mineralization increased, and the TCOD distribution on solids decreased.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (50408021) and the National Hi-Tech Development Program (863 Program) of China (2007AA062347).

References