Research of wastewater treatment from non-destructive detection by “wet oxidation-biochemical process-intelligence oxidation”

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Abstract: Non-destructive detection with colored-liquid was an effective detection method, which was widely used in non-destructive detection industry. High-concentration of wastewater with COD, color and surfactants would be produced in detection process. Through the biochemical treatment combined with wet oxidation, the COD dose would be reduced from 49200 mg/L to less than 100 mg/L. The color will be degraded from 5000 times to less than 40 times, which will match the requirements for reuse and discharge. Through the molecular distribution and bacteria toxicity test, wet oxidation reduced the inhibition rate of toxicity from 99.99% to 90.88%, which promoted the biochemical treatment performance. The average molecular weight of non-destructive wastewater was reduced obviously from 1486118 to 20376. In the end, the residual chlorine indicator was used to control dose of chlorine less than 3 mg/L to ensure that the color was less than 40 times and residual chlorine was not harmful to environment. The oxidation process was intelligence oxidation. The lab-scale experiment provided potential and available treatment process for non-destructive detection-wastewater.

1 Introduction
Penetration test was an effective non-destructive detection method to inspect defects of non-pore solid materials with blood capillary principals. The principal was to coat colored dye liquid over material surfaces, which could inspect the penetration points for non-destructive detection [1-3]. In non-destructive detection process, high concentration of waste liquid would be produced. Many pollution control methods were used to degrade the high concentration of liquid. Ozone oxidation process could produce uncontrollable bubbles [4], which did not degrade the non-destructive detection wastewater with high-dosed surfactants. Traditional advanced oxidation method, such as Fenton oxidation [5], should add a lot of acid and ferrous ions, which would produce a lot of sludge. Adsorption method, such as activated carbon adsorption, could absorb non-polar pollutants effectively and also produce huge sludge as hazardous waste [6]. Due to the high concentration of oil and surfactants, biochemical treatment could suffer from oxidation transfer and bubble issues. Wet Oxidation (WO) is one of the numerous technologies [7] that have been studied for sludge minimization and treatment, which were conducted under the temperature 150-320 °C and pressure 20-150 bar. In WO process, organic pollutants are partially converted to carbon dioxide, water and inorganic salts, avoiding the generation of harmful emissions [8]. The WO process could reduce the high concentration of COD and surfactants, which could provide available situation for sequent biochemical treatment.
The treatment of non-destructive was rarely reported. The lab-scale treatment with “wet oxidation-biochemical process-intelligence oxidation” was discussed to systematically treat non-destructive detection wastewater, which could enhance the environmental competition ability for enterprises.

2 Materials and methods

2.1 wastewater source
The non-destructive detection wastewater was sampled from Suzhou HongDa Detection Instruments Co. Ltd. The color of wastewater was dark red. The concentrations of pH, COD and color were 7.25, 49200 mg/L and 5000 times respectively.

2.2 Wet oxidation
All experiments in this study were performed in a 100 mL SUS316 autoclave reactor equipped with a mechanically driven stirrer, as shown in Figure 1. The reactor was purchased from Anhui Kemi Machinery Technology Co. Ltd., Hefei, China. Temperature was modified in the range of 180-260℃ using an electric jacket, and the initial oxygen partial pressure was varied in the range of 0.2~1.0 MPa. Stirring speed was 350 rpm/min. Once the desired temperature was reached, this moment is taken an experimental procedure is as follows: 50 mL of pharmaceutical sludge solution and a certain amount catalyst were put into the reactor, then the reactor was heated to expected temperature. After the desired reaction time, the reactor was removed from the oven and allowed to cool to room temperature. The reaction pressure corresponded to the self-pressurization with saturated.

![Figure 1. Diagram of wet oxidation reactor.](image)

**Figure 1.** Diagram of wet oxidation reactor.1: Oxygen supply; 2: Heating jacket; 3: Oxidation reactor; 4: Thermocouple; 5: Discharge of gas; 6: Bleeder valve; 7: Pressure meter; 8: Stirrer;

2.3 Biochemical treatment process
The biochemical treatment process was using batch tank of 1 L with magnetic stirrer on the bottom. The stirring speed was 60 rpm. The anaerobic and aerobic tanks were 1 L respectively. The activated sludge was fetched from Shanghai Fakai Chemical Co.Ltd, which produced APG surfactants. The biochemical treatment sustained the sludge dose with 4 g/L at 25 ℃. The dissolved oxygen was over 2 mg/L. The hydraulic retention time of anaerobic and aerobic tanks was 144 hours. The sedimentation time of mixed sludge in aerobic tank was 3 hours.

2.4 Intelligence oxidation
Sodium hypochlorite was added to supernatant from aeration tank. The residual chlorine indicator was connected to measure total chlorine in the solution. The stirring speed in the intelligence oxidation tank was 150 rpm. The intelligence oxidation tank was 1L.
2.5 Analysis
COD concentration was measured by HACH DR5000 spectrophotometer. The pH was measured by HACH Qd40. The color was measured by diluted testing method. The residual chlorine was measured by HACH residual chlorine test, based DPD method. Molecular distribution test was sampled by LC-10ATVP gel chromatography (Shimazduo, Japan). The bacteria toxicity test was using Vibrio-qinghaiiensis sp.-Q67 as indicators, which could use luminous intensity to demonstrate the inhibition intensity of wastewater. All the data were measured 3 times for mean values and analyzed by Origin 2018.

3 Results and discussion

3.1 Removal efficiency of COD and color in wet oxidation tank
With the initial oxygen pressure of 1.0 MPa, the removal efficiency of COD and color in different temperatures were demonstrated in figure.2, in which the reaction time was 30 min. When the reaction time was promoted from 160℃ to 260℃ gradually, the effluent of COD reduced from 13200 mg/L to 9120 mg/L. When the temperature reached 200℃, the removal efficiency of COD increased slowly. In addition, the high temperature would accelerate the disruption of wet oxidation materials. The temperature of 200℃ was chosen for this study, which was verified by previous studies [9-10]. According to the color reduction, when the temperature was 200℃, the color of influent was reduced from 5000 times to 100 times. While the temperature increased, the color did not change. The reaction temperature was set as 200℃, which guaranteed the removal efficiencies of COD and color were over 80% and 98% respectively.

![Figure.2 Removal efficiency of COD and color in different temperatures](image)

3.2 Removal efficiency of aeration tank
The supernatant from wet oxidation equipment was filled into “anaerobic and aerobic tank”. Through the cultivation of activated sludge and 400%-rate inner circulating back flow, the effluent of anaerobic tank was about 1200 mg/L. According to aeration tank, hydraulic time is critical. Through the 6-days retention time, the influent of COD was reduced from 1200 mg/L to 95 mg/L, which was less than 100 mg/L. The residual organic substances were non-degradable microorganism metabolism substances. Figure.3 demonstrated the effluent aeration tank was reduced with the time. When the retention time was 120 hours, the effluent of COD would not decrease. According to sludge production and stable operation, the hydraulic of aeration tank was designed as 144 hours.
3.3 Removal efficiency of color with intelligence oxidation

According to figure.4, the effluent of aeration tank was added NaClO solution. With dosage increasing, the removal efficiency of color was promoted. The color was reduced from 100 times to 40 times with the removal efficiency of 60%. The color would not change even the NaClO solution was added. The residual chlorine was 0.2 mg/L when the concentration of NaClO was 10 mg/L. When the NaClO solution was 40 mg/L, the residual chlorine was over 2 mg/L, when the color would not decrease. With the NaClO solution was 60 mg/L, the residual chlorine was over 8 mg/L. According to the removal efficiency of color and operation stability, the residual chlorine could be maintained over 3 mg/L to ensure de-coloring efficiency, which satisfied intelligence control[11].

3.4 Molecular weight distribution before and after wet oxidation

Through the wet oxidation process, the average molecular weight of non-destructive wastewater was reduced obviously from 1486118 to 20376, which guaranteed stable operation of biochemical process. According to figure.5 and figure.6, the new two peaks were showed lately, which demonstrated that the molecular was obviously decreased.

Figure.3 Removal efficiency of COD in aeration tank with time

Figure.4 Removal efficiency and residual chlorine with NaClO adding

Figure.5 Molecular weight distribution of non-destructive detection wastewater before WO
3.5 Bacteria toxicity before and after wet oxidation

Through the wet oxidation treatment, the inhibition rate of bacteria toxicity was reduced obviously from 99.99% to 90.88%, which could guarantee the effluent with biochemical adaption was available. The bacteria toxicity of municipal sewage wastewater was 70.68% as comparison sample. The inhibition rate after WO also demonstrated the importance of high-rate backflow in biochemical process was necessary.

![Figure 6](image_url)

**Figure.6** Molecular weight distribution of non-destructive detection wastewater after WO

4 conclusions

According to high concentrations of COD, color and surfactants in non-destructive detection wastewater, the potential treatment process was investigated in this study. Based on the characteristics of non-destructive detection wastewater, the combination of “wet oxidation-biochemical process-intelligence oxidation” could degrade the pollutants of wastewater effectively. The concentrations of COD and color were from 49200 mg/L and 5000 times to less than 100 mg/L and 40 times respectively, which was potential treatment process. The main pollutants including COD, color and surfactants were effectively degrade by the lab-scale study equipment. The wet oxidation was a key point treatment process for molecular weight reduction and bacteria toxicity decreasing. The molecular weight was degraded from 1486118 to 20376. Besides, the inhibition rate of bacteria toxicity was reduced obviously from 99.99% to 90.88%. In the final treatment, intelligence oxidation with NaClO was using residual chlorine indicator to control the adding dose of chemicals which could guarantee the de-coloring efficiency and be friendly to environment. The results implied that “wet oxidation-biochemical process-intelligence oxidation” was an effective and potential technical process to systematically solve issues of non-destructive detection wastewater.

References:

[1] Solodov I, Dillenz A, Kreutzbruck M, 2017. *J. App. Phy*, 121(24):26-31

[2] Nigrelli V, 2008. *J.Adh*, 84(10):811-829

[3] Ma Baoquan, Zhou Zhenggan, Zhao Hanxue and Zhang Dongmei, 2015. *INSIGHT*, 57(9):499-507

[4] Margot J, Kienle C, Magnet A, et al., 2013. *Sci of the Total Environ*, 461-462(7):480-498
[5] Wang Wenxuan, Sha Jun et al., 2018. Sci of the Tot Environ, 634(9):243-250
[6] Moniri E, Panahi HA, Aghdam K and Sharif AA, 2015. J AOAC Int, 98(1):206-212
[7] Zeng XU, Liu Jun and Zhao Jiangfu, 2018. Catal, 67(8):1-8
[8] Liu Weimin, Hu Yiqiang and Tu Shan-Tung, 2010. J. Hazard. Mater. 179:545-551
[9] Basim Abussaud, Ihsan Khan, Dimitrios Berk and George J. Kubes, 2019. Indus & Eng Che Res, 58(23):1
[10] Meredith M K, Baldwin Sidney, Andresen A A, 2020. ASS Offic Anal Chem J, 1(1)
[11] Ding Shunke, Chu Wenhai, Tom Bond et al., 2018. J of Hazard Mat, 341(1):112-119