

Ozone Oxidation of Photographic Processing Wastewater in a Batch Reactor

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Abstract—The photographic processing wastewater comes from the photographic film fixing, developing and bleaching processes. This kind of wastewater is bio-recalcitrant for conventional bio-treatment processes and has a great impact on neighborhood environment because it contains high concentration noxious contaminants, such as cyanide, aniline and phenol compounds. Ozone oxidation is an effective approach to treat the wastewater. The wastewater was taken from a studio discharge in Zhenjiang and the ozone oxidation was carried out in a batch reactor. The results showed that cyanide, aniline compounds and COD_{Cr} were removed 92% above, 89% above and 80% around, respectively. And more importantly, the biodegradation of the wastewater was enhanced significantly ($\text{BOD}_5/\text{COD}_{\text{Cr}}$ from 0.12 to 0.54). Over the followed treatment of Sequencing Batch Reactor (SBR), aniline and COD_{Cr} concentrations decreased to 0.45mg/L and 50mg/L, respectively. Based on the results, the wastewater could meet the demands of Integrated Wastewater First-degree Discharge Standard of China ($\text{COD}_{\text{Cr}} \leq 100\text{mg/L}$, aniline $\leq 1.0\text{mg/L}$, etc.).

Keyword: Ozone oxidation, Photographic processing wastewater, Batch reactor, Biodegradation, Contaminant

I. INTRODUCTION

The photographic processing wastewater comes from the photographic film fixing, developing and bleaching processes. There is plenty of silver ion in the fixation wastewater from the used fixative, containing various bio-reluctant organics, such as aniline and phenol compounds, and cyanide, etc. The photographic developing and bleaching wastewater has the same contaminants except silver ion. The aniline compounds and cyanides are highly toxic organics, which could cause cancerization, aberration and mutation and stay at long retention time in the environment, and are very difficult to biodegrade by conventional biochemical processes.

Most of the research and development for the photographic waste treatment had been generally focused on how to effectively separate and recover the precious silver from the photographic processing waste. For example, the use of TiO_2 photocatalysis for removal of silver [1, 2]; silver recovery from the medical X-ray and photographic process effluents using activated carbon under acidic conditions [3]; separation and preconcentration of silver by di (n-propyl) thiuram disulfide bonded on silica gel [4]; Sonoelectrochemical recovery of silver [5]; silver adsorption with chitin [6]; separation of silver from liquid photographic waste by an emulsion liquid membrane [7]. The treatment of the wastewater containing many high-strength toxic organics had rarely been discussed in literature. There are only several papers related to this serious issue. Wet air oxidation (WAO) and Supercritical wet air oxidation (SWAO) were used for the treatment of the photographic wastewater [8, 9]. Obviously it is a costly approach to

deal with the photographic wastewater by WAO or SWAO. Yang et al. and Hirata et al. applied the advanced oxidation by fibrous catalyst with hydrogen peroxide and the anaerobic-aerobic biofilm processes for the wastewater treatment, respectively [10, 11]. The COD_{Cr} removal efficiency only reached 52% within 24 h by hydrogen peroxide oxidation. It would take years to acclimatize the sludge and to get the effective microorganisms for the treatment of photographic processing wastewater by the anaerobic-aerobic biofilm process. Furthermore, the application of the biochemical process were restricted with many factors, such as sludge, pH value, temperature, wastewater quality, and so on.

For decades, ozone has been and is becoming more used in water and wastewater treatment. Ozonation is based on the direct or indirect reactions (mainly, free hydroxyl radical) with many pollutants. Ozone oxidation process has been applied to the degradation of miscellaneous contaminants and treatment of various wastewaters, such as bromacil [12], wine distillery wastewater [13], sodium dodecylbenzenesulfonate [14], Orange II [15], textile wastewater [16], etc. Moreover, ozonation also has been used as pre- or post- treatment combined with biochemical process, and assisted with other approaches [17-22].

This study demonstrates a reliable approach to degrade high-strength photographic processing wastewater and to meet the strict demands from wastewater discharge standards in P.R.China.

II. MATERIALS AND METHODS

The photographic processing wastewater was fetched from a studio in Zhenjiang city. They were sequenced A1-A5 according to sampling time. Each sample had been analyzed separately within 24 h.

According to Discharge Standard of the Film

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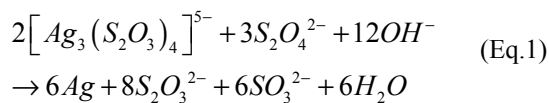
Developing Wastewater Pollutants (GB3553-83) of China and the correlative studies mentioned above, the analyzed indexes in the experiment were COD_{Cr} , BOD_5 , pH, Ag^+ , aniline, and cyanide. The analytical methods followed the reference [23]. Table I shows the results of the photographic processing wastewater indexes.

TABLE I.
INDEXES OF THE PHOTOGRAPHIC PROCESSING WASTEWATER

Sample	A1	A2	A3	A4	A5	Average
COD_{Cr} (mg/L)	4812	4576	4145	3246	2588	3874
BOD_5 (mg/L)	577.5	549.2	497.4	389.5	310.5	464.8
Cyanide (mg/L)	2.4	2.6	1.8	1.7	1.4	2.0
Aniline (mg/L)	120.5	114.5	104.2	81.3	66.5	97.4
Ag^+ (g/L)	2.54	2.43	2.36	2.61	2.45	2.50

A. Pretreatment of wastewater

Recycling silver from the fixative wastewater included electrolysis, ion exchange, silver sulfide precipitation, sodium hydrosulfite reduction and substitution techniques. Sodium hydrosulfite reduction was adopted to draw silver ion from the fixation wastewater in the experiment. Sodium hydrosulfite ($Na_2S_2O_4$), as a strong reductant, deoxidized the silver ion of silver sulfate complex ion to metallic silver in alkaline medium. The mechanism followed Eq.1.



Considered silver ion concentration as 2.50 g/L around, the amount of $Na_2S_2O_4$ should be 6.60 g/L to be added into the fixative wastewater. The pretreatment results are listed in Table II. The pretreated fixative wastewater was mixed with the developing & bleaching wastewater at the rate of 2:1. Furthermore the pre-treated wastewaters, named B1-B5 (corresponding to those pre-treated A1-A5), respectively, would be treated by ozone oxidation.

B. Ozone treatment process

The layout of the experimental facilities used in ozone oxidation of the wastewater is illustrated by Fig.1. The pre-treated photographic processing wastewater 5 L was put into the batch reactor. The rotating speed was set at 600 rpm. The oxygen cylinder was opened and the oxygen flux was adjusted to 2.0 L/min. Then the ozone generator had been powered and the mixing gas was flowed into the reactor until the ozone concentration was stable. At the same time, "zero time" ($t = 0$) was beginning to be reckoned. During the reaction, samples (30-40 ml at a time) were withdrawn periodically. Samples had been measured in 2 hours. During the reaction process, the stability of ozone concentration was

TABLE II.
THE RESULTS OF THE SODIUM HYDROSULFITE REDUCTION FROM THE FIXATIVE WASTEWATER

Serial number	B1	B2	B3	B4	B5
Original amount of silver (g/L)	2.54	2.43	2.36	2.61	2.45
Amount of sodium hydrosulfite (g/L)	6.60	6.32	6.14	6.79	6.37
Amount of silver after reaction (mg/L)	0.81	0.76	0.89	0.78	0.92

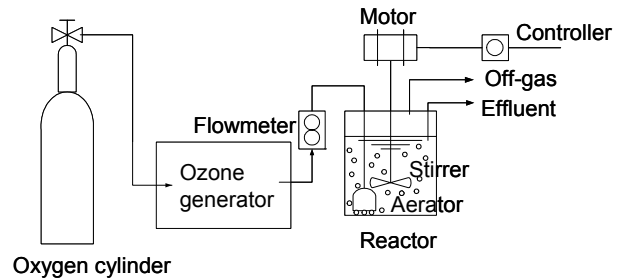


Fig. 1. Schematic diagram of the ozone oxidation setup

very important because it had a great effect on the reaction.

III. RESULTS AND DISCUSSION

A. Conversion of COD_{Cr} during the reaction

The ozone concentration into the reactor fluctuated from 45 mg/L to 46 mg/L and the flux of mixing gas leveled off as 2.0 L/min. COD_{Cr} conversion during reaction time is presented in Fig.2. At the initial stage of the reaction, the amount of COD_{Cr} increased obviously while the biochemical index, BOD_5/COD_{Cr} , also increased and CO_2 was monitored in the exhaust. It could be presumed that benzene ring of organics ruptured during the reaction and the recalcitrant organics were degraded to the degradable one. As seen in the reference (23), some kinds of arene could not be mineralized in the course of COD_{Cr} analysis.

B. Effect of gas influx on contaminant removal

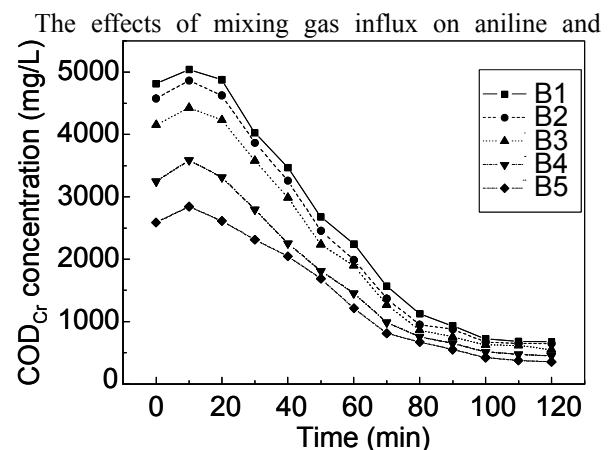


Fig. 2. COD_{Cr} conversion during the reaction

COD_{Cr} removals are illustrated with Fig.3 and Fig.4. The removal efficiencies of aniline and COD_{Cr} enhanced along with the increase of the mixing gas (oxygen and ozone) flux. The profile in Fig.3 shows that the increase of amount of ozone promoted the aniline removal significantly at the range of 0-1400 mgO₃. Beyond the range, the removal almost kept invariably. Fig.4 illustrates just the same trend of the effect of reaction time on COD_{Cr} removal.

C. Effect of pH value on COD_{Cr} removal

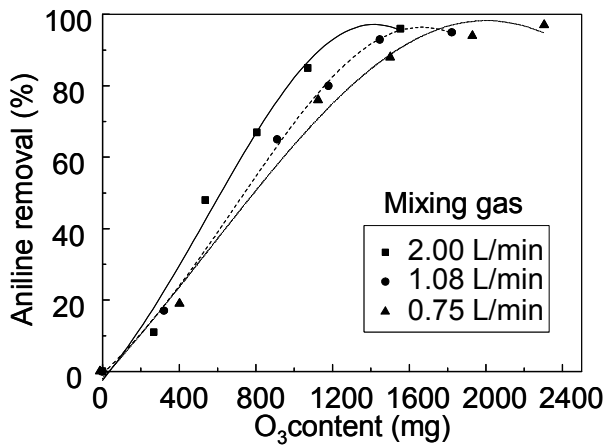


Fig. 3. The effect of gas influx on aniline removal

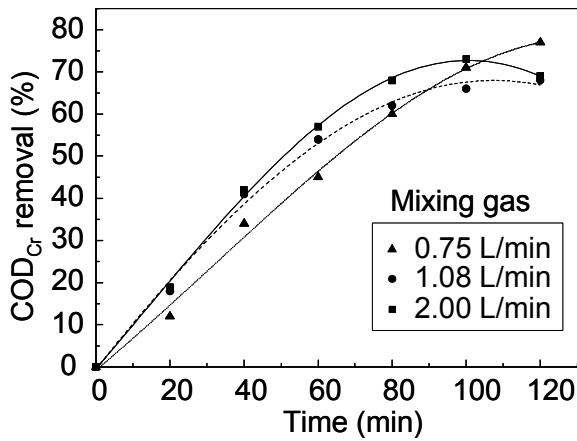


Fig. 4. The effect of gas influx on COD_{Cr} removal

The pH value has a certain effect on the ozone oxidation as shown in Fig.5. COD_{Cr} removal was approximately linear with reaction time (0-100 min) at different pH value. Generally compared to acid condition, alkaline condition advanced the ozone reaction to a degree. Whereas pH value of the original photographic processing wastewater just ranged from 11.0 to 13.0, it was not necessary to adjust pH value for the wastewater treatment process.

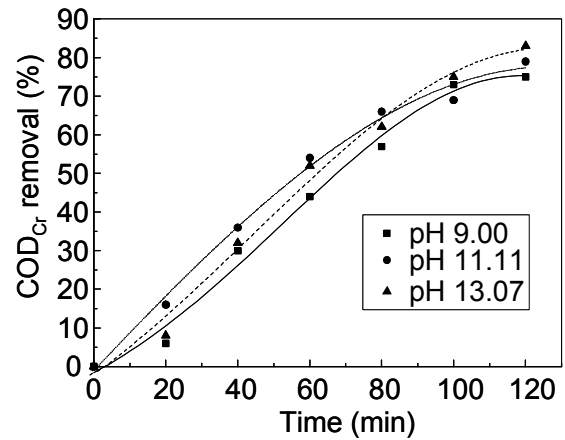
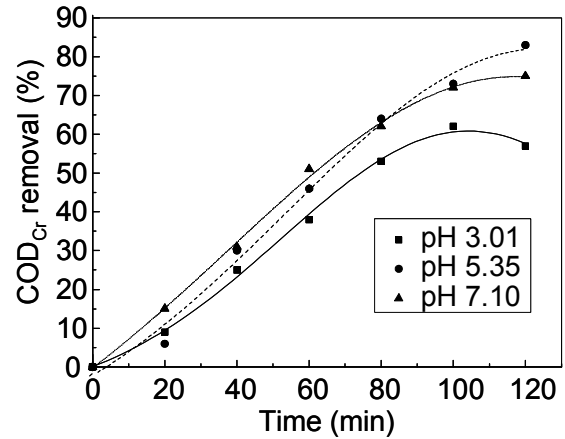


Fig. 5. The effect of pH value on COD_{Cr} removal

D. Change of ozone concentration in exhaust

Three different pre-treated wastewater samples named C1, C2 and C3 were pre-treated by the same process of B1-B5 wastewater. COD_{Cr} removal and ozone concentration in the exhaust at a time are presented in Fig.6 and Fig.7, respectively. The consumption of ozone decreased with the underway oxidation reaction when the utilization efficiency of ozone was reducing.

Based on the following experimental results: COD_{Cr} average concentration of the wastewater, 3874 mg/L; ozone initial concentration, 45.5 mg/L; mixing gas flux, 2 L/min; ozone average concentration by the quadric polynomial regression equation, (C1) 13.4 mg/L, (C2) 15.1 mg/L, (C3) 7.2 mg/L; ozone consumption, (C1) 12.8 mg(O₃)/L·min, (C2) 12.2 mg(O₃)/L·min, (C3) 11.3 mg(O₃)/L·min. Therefore the COD_{Cr} removals per gram ozone were calculated, (C1) 2.9 mg(COD_{Cr})/mg(O₃), (C2) 2.2mg(COD_{Cr})/mg(O₃), (C3)1.7mg(COD_{Cr})/mg(O₃). On the basis of the average consumption of 2.3 mg(COD_{Cr})/mg(O₃), the demand of ozone was 1467 mg(O₃)/L while COD_{Cr} of the wastewater was removed from the initial 3874 mg/L to 500 mg/L.

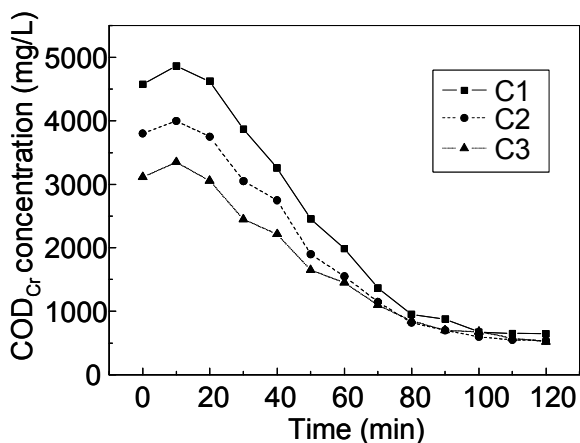
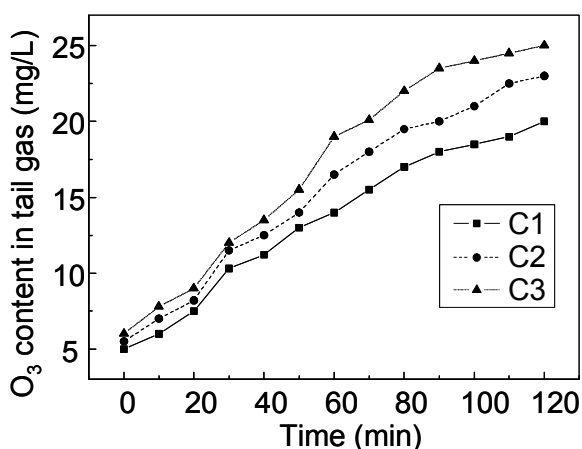
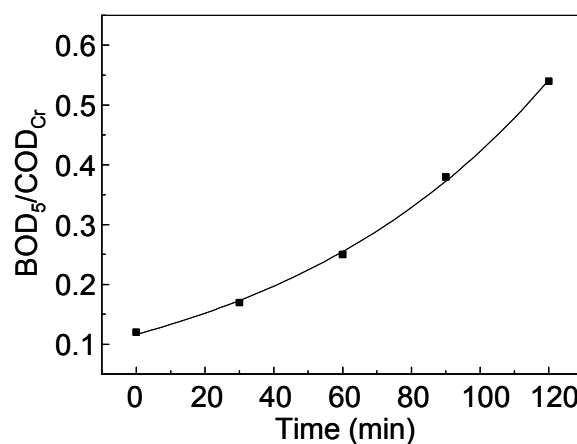
Fig. 6. COD_{Cr} concentration during the reaction

Fig. 7. Ozone concentration in off-gas during the reaction

reaction, especially for aniline.

F. Analysis of biodegradable character

Because of the inhibition for micro-organism, the photographic processing wastewater was hardly biodegraded by conventional biochemical processes. The biochemical index BOD₅/COD_{Cr}, also known as B/C index, was commonly introduced to measuring the biodegradable characteristics of the wastewater. The profile of B/C index of the wastewater B1 by ozone oxidation is presented in Fig.8. Ozone oxidation could evidently improve the biodegradable character of the wastewater according to B/C index from 0.12 to 0.54. It was highly advantageous to the followed biological treatment.

Fig. 8. BOD₅/COD_{Cr} conversion during the reaction

E. Effect of ozone concentration on cyanide and aniline

The removal efficiencies of cyanide and aniline in several wastewaters are summarized in Table III. Both the initial concentration and the ozone concentration had some effects on the removal efficiency. Generally, high concentration ozone was advantageous for the oxidation

G. Biochemical treatment

Sequencing batch reactor (SBR) was adopted for the followed treatment of the wastewater (COD_{Cr} 512 mg/L, aniline 12.8 mg/L). The activated sludge from the phenol wastewater treatment process was cultivated before the SBR experiment. The experimental parameters were aeration 120 min, precipitation 60 min, and air flux 150

TABLE III.
INDEXES OF THE PHOTOGRAPHIC PROCESSING WASTEWATER REMOVAL OF CYANIDE AND ANILINE (OZONE CONCENTRATION 45-46 MG/L AND 25-26 MG/L, MIXING GAS FLUX 2 L/MIN) RESULTS IN PARENTHESES FOR OZONE CONCENTRATION 25-26 MG/L

Sample	B1	B2	B3	B4	B5
Cyanide initial concentration (mg/L)	2.4	2.6	1.8	1.7	1.4
Cyanide concentration after reaction (mg/L)	0.12(0.18)	0.14(0.20)	0.11(0.17)	0.13(0.18)	0.10(0.16)
Cyanide removal (%)	95.0(92.5)	94.6(92.3)	93.9(90.6)	92.4(89.4)	92.9(88.6)
Aniline initial concentration (mg/L)	120.5	114.5	104.2	81.3	66.5
Aniline concentration after reaction (mg/L)	6.1(10.2)	7.2(10.8)	6.4(10.6)	6.8(11.7)	5.3(9.2)
Aniline removal (%)	93.8(89.2)	92.1(88.2)	92.3(87.5)	89.5(82.1)	90.2(82.6)

L/h. COD_{Cr} and aniline concentration of the effluent from SBR were reached to 50 mg/L and 0.45 mg/L, respectively. The effluent could meet the demands of Integrated Wastewater First-degree Discharge Standard of China (GB8973-1996).

H. Analysis on reaction mechanism

During ozone oxidation, the aromatic ring of aromatics was split, and then organics degraded to small molecule products, such as carboxylic acids, the alcohols, the aldehydes, and so on. Some small molecule organics were mineralized to CO₂ and H₂O, and the others interacted and produced the aliphatic compounds. For example, some reactions on the branch chain in benzene ring caused aromatic ester compounds. At the same time, the intermediate products could continue to progress a series of complex reactions by ozone.

The possible approaches of electrophilic addition reaction between hydroxyl free radical (or other free radicals) and phenol are that: (1) the reaction on the hydroxyl of phenol forms quinonoid compounds. (2) the reaction on ortho-position or *p*-position of the hydroxyl creates hydroquinone, which is oxidized to *o*-benzoquinone and *p*-benzoquinone. Over a series of complex reactions, the benzene ring is broken, and then alcohols, aldehydes and carboxylic acids, the degradable organics, are formed. Finally, they are mineralized to CO₂ and H₂O.

By Gas Chromatography-Mass Spectrometry (GC-MS) analysis, in the wastewater from ozone oxidation, there were esters, ethers, and anhydrides, which contained hydroxyl and acyl structures. Only carboxylic and aldehydic organics could form the above molecular structures over reactions. It was concluded that the benzene ring was broken and alcohols, aldehydes and carboxylic acids were produced in the oxidation reaction process.

IV. CONCLUSION

The pretreatment could recover silver from the fixative wastewater. In the ozone oxidation process, most pollutants in the wastewater were oxidized to biodegradable small molecule organics, and part of them mineralized to H₂O, CO₂, N₂, and so on. Aniline and cyanide are eliminated effectively (removal efficiency 82-95%). The experimental conditions significantly affected the COD_{Cr} removal. Alkaline condition, increase of mixing gas flux and ozone concentration might enhance the oxidative reaction. Moreover, the biodegradability of the wastewater was distinctly improved by ozone oxidation (B/C from 0.12 to 0.54). After the SBR treatment, the effluent could meet the demands of Integrated Wastewater First-degree Discharge Standard of China. The integrated process consisting of ozone oxidation and SBR offered a

promising approach to treat the photographic processing wastewater effectively and would fulfill the strict demands from wastewater discharge standards.

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