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Removal of isopropyl ethylthionocarbamate from aqueous solution by oxidation

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ABSTRACT

To efficiently treat wastewater containing Isopropyl ethylthionocarbamate (also known as Z-200) which proved difficult to be degraded, a novel process of oxidation degradation of Z-200 was studied by sodium hypochlorite oxidation (NaClO). Then, the mechanism of oxidation degradation was further examined by Ultraviolet (UV) spectrometer, Fourier transform-infrared (FT-IR) spectroscopy, and Gas Chromatography coupled with Mass spectrometry (GC-MS). Results showed that the degradation efficiency of Z-200 reached 76% under the optimized conditions with initial pH value of 6.5, NaClO dosage of 1,000 mg/L, and reaction time of 6 min. The degradation efficiency can be significantly improved by adding H_2O_2 to this oxidation system. When the NaClO/H_2O_2 molar ratio was 1:1, the degradation rate could increase to 87%. The measurements of UV, FT-IR, GC-MS confirmed that Z-200 was effectively degraded and small molecules of carbonyl compound with very low concentrations were generated during oxidation. The main degradation pathway that possibly occurred during the whole process was also deduced in this study.

Keywords: Hypochloriteoxidation; Hydrogen peroxide; Isopropyl ethylthionocarbamate; Degradation; Infrared spectrum analysis; GC-MS

1. Introduction

O-Isopropyl-N-ethylthionocarbamate (IPETC) was first introduced by the Dow Chemical Company in 1954 with the trade mark of Z-200.It has been widely used in ore dressing plant for decades [1,2]. This collector is recommended for the flotation of copper minerals and has the advantageous properties of providing excellent selectivity against pyrite in alkaline media,which is always effective in acid circuits [3]. In present days, more and more new ester collectors which have similar properties as Z-200 have been produced to apply in concentrators [4,5]. However, there are several serious environmental problems associated with these flotation reagents in mineral processing plant [6]. It is known that even small concentration of these reagents in water streams is toxic to water life, besides their deleterious influence during recycling [7–9]. Seldom studies have been reported on the treatment of these flotation reagents from processing wastewater. Therefore, it is imperative to treat flotation wastewater with respect to the removal of Z-200.

Compared with xanthate, aerofloat or diethyldithiocarbamate, Z-200 is very difficult to be biodegraded and it can hardly be degraded by chelating or coagulation settlement. The treatment of Z-200 has been reported to be biodegraded by Chen et al. [10] through anaerobic digested sludge. However, the high degradation rate need longer processing period meanwhile moderate medium must be added to obtain excellent development of bacteria. Except for this treatment, no other reports concerning the removal of Z-200 were studied. Consequently, it is necessary to investigate

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the treatment of Z-200 with high degradation rate and efficiency. NaClO, a type of disinfectants in drinking water, can also be applied in wastewater treatment. NaClO oxidation possess lots of merits of simple operation, strong oxidation capacity, quick reaction rate, low operation cost, etc. which can effectively remove organic matter in wastewater. More importantly, compared with traditional chlorine-based oxidants like chlorine, NaClO is not only safe used without hazardous leakage, but also can reduce the generation of degradation by-products [11]. Under a certain condition, sodium hypochlorite exits in the solution in the form of NaClO and HClO, and oxygen can be generated by the decomposition of HClO. The hydrolysis reaction equation of sodium hypochlorite in the water is as follows:

$$NaClO + H_2O \rightarrow HClO + NaOH \quad (1)$$

$$HClO \rightarrow HCl + O_2 \quad (2)$$

In recent years, as a cheap and highly efficient oxidant reagent, sodium hypochlorite is widely used in the removing process of some organic compounds, especially ammonia compound and cyanide. NaClO oxidation method has been broadly used in many fields of wastewater treatment, including landfill leachate and industrial wastewater [12–14].

In this study, the natural degradation characteristics of Z-200 were first investigated. Then, the optimal reaction conditions, including optimal pH, chemical dosages and reaction time were studied. In addition, a combination of $NaClO/H_2O_2$ was used to enhance the degradation effect. Finally, the related reaction mechanism was revealed by UV spectroscopic, FT-IR and GC-MS analysis. This study is aimed to provide a theoretical basis and technical guidance for actual wastewater plant.

2. Materials and methods

2.1. Materials

Z-200 was purchased from Zhuzhou Flotation Reagents Factory, China. Z-200 was of technical grade and used without purification. NaClO (16%) and H_2O_2 (30%) were used as received. All other chemicals were of analytical grade. The solutions were prepared with distilled water. The initial concentration of Z-200 was 0.5 g/L, and then the solution was diluted into other levels. The wastewater was adjusted to the desired pH by H_2SO_4 or NaOH.

2.2. Methods

2.2.1. Determination of the concentration of Z-200

Ultraviolet (UV) spectrophotometry was determined with a UV–vis spectrophotometer UV-2100 (Shimadzu Corporation, Japan). The standard curve of Z-200 solution was prepared in advance by using UV spectrophotometry at the wavelength of 241 nm, where Z-200 solution has a strong absorbance. Through linear fitting by Origin 8.0 software, the standard curve of Z-200 solution was shown in Fig. 1. It shows that the relationship between the absorbance and the concentration of Z-200 solution can be expressed as Eq. (3). When an absorbance value is known, the concentration of Z-200 can be calculated based on the equation.

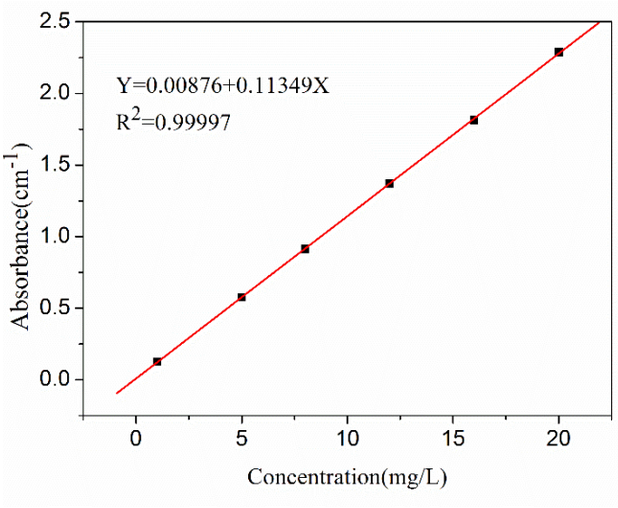

Fig. 1. The standard curve of Z-200 solution.

$$Y = 0.00876 + 0.11349X \quad (3)$$

where X is the mass concentration of Z-200, mg/L; Y is the corresponding absorbance, cm^{-1}.

2.2.2. Fourier transform infrared measurement

In order to examine the mechanism of oxidation process, Fourier transform infrared (FT-IR) measurement was conducted with a FT-IR spectrometer Nicolet 6700 (Nicolet Corporation, America). The products before and after oxidation degradation were mixed with hexane separately and were shaken for a few minutes, then the organic phase was extracted to measure after centrifuging for 10 min.

2.2.3. GC-MS analysis

The qualitative analysis was made with the use of GCMS-QP2010 gas chromatograph (GC) coupled with mass spectrometer (MS) with electron ionization (EI) by Shimadzu Corporation, Japan. Chromatograph was equipped with 30 m × 0.25 mm i.d. DB-5 ms capillary column of 0.25 μm film thickness. Helium 5.0 was used as the carrier gas. All the experiments were carried out at 160°C and by an increase of 20°C/min up to 300°C temperature. Temperature of both GC oven and injector was 280°C. All the injections were made in split mode. The standard NIST 11 mass spectral library database was used to identify the organic compounds that were detected and to allow them to be analyzed qualitatively.

2.2.4. Degradation experiments

Z-200 water samples used in the oxidation experiment were diluted from 0.5 g/L to 20 mg/L. Control pH value

of wastewater and a certain amount of oxidant was added into 200 mL Z-200 water samples under a stirring speed of 400 r/min for minutes. All of the above processes were carried out in 300 mL beakers with several single-paddle gang stirrers at room temperature. After deposited for 1 h, the sample solution was taken from beakers and further analysis was conducted.

Through the previous experiments, the optimal NaClO dosage has been found by a detailed analysis. Under the optimal NaClO dosage, the moderate pH could be worked out. Under the optimum pH level and NaClO dosage, the reaction time was investigated. Based on the above experiment condition, the combination of NaClO and H_2O_2 was studied. While the total dosage of oxidants was maintained at 1,000 mg/L, the NaClO/H_2O_2 molar ratios were changed with values of 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1 and 10:0. Then the optimum molar ratio could be worked out. By this way, an optimal degradation effect could be achieved.

Determination of the concentration of Z-200 was achieved by UV spectrophotometry using a UV–vis spectrophotometer UV-2100 (Shimadzu Corporation, Japan) and pH was analyzed by a portable pH meter PHS-3C (Shanghai Leici Corporation, China).

3. Results and discussion

3.1. The natural degradation characteristics of Z-200

To investigate the natural degradation of Z-200, factors of the deposited time, concentration of Z-200, and pH of the solution were studied. Results can be seen in Fig.2.

According to the results presented in Fig. 2, the natural degradation rate of Z-200 is relatively low. When Z-200 was deposited for more than 4 days, the removal efficiency remains small changes. In addition, pH value of solution and the concentration of Z-200 have little effect on degradation rate. Therefore, Z-200 is relatively stable and hard to be degraded naturally. Chemical precipitation and coagulation settlement also makes no effect. (Experiment results not listed in this paper) So, other methods should be studied.

3.2. Degradation process of Z-200 by oxidation

3.2.1. Effect of NaClO dosage on Z-200 removal ratios

The effect of NaClO addition on Z-200 removal ratio was investigated under conditions of pH 8 and stirring time of 5 min with 400 rpm, and the results are shown in Fig. 3. When dose level is between 100 and 1,000 mg/L, the removal ratio of Z-200 in the wastewater sample sharply increases with the NaClO addition. While the NaClO addition further increases, it presents a little slower change with Z-200 removal ratio. From the overall point of view, the degradation rate can reach 95% or more with NaClO continuously increased, which indicates that Z-200 can be effectively degraded by NaClO oxidation. However, the solution pH also increases sharply with the NaClO addition. Because of the excessive alkalinity, the wastewater after treatment cannot be emitted directly. All factors considered, the optimal dose of NaClO is 1,000 mg/L, which was selected for further optimization in the oxidation process.

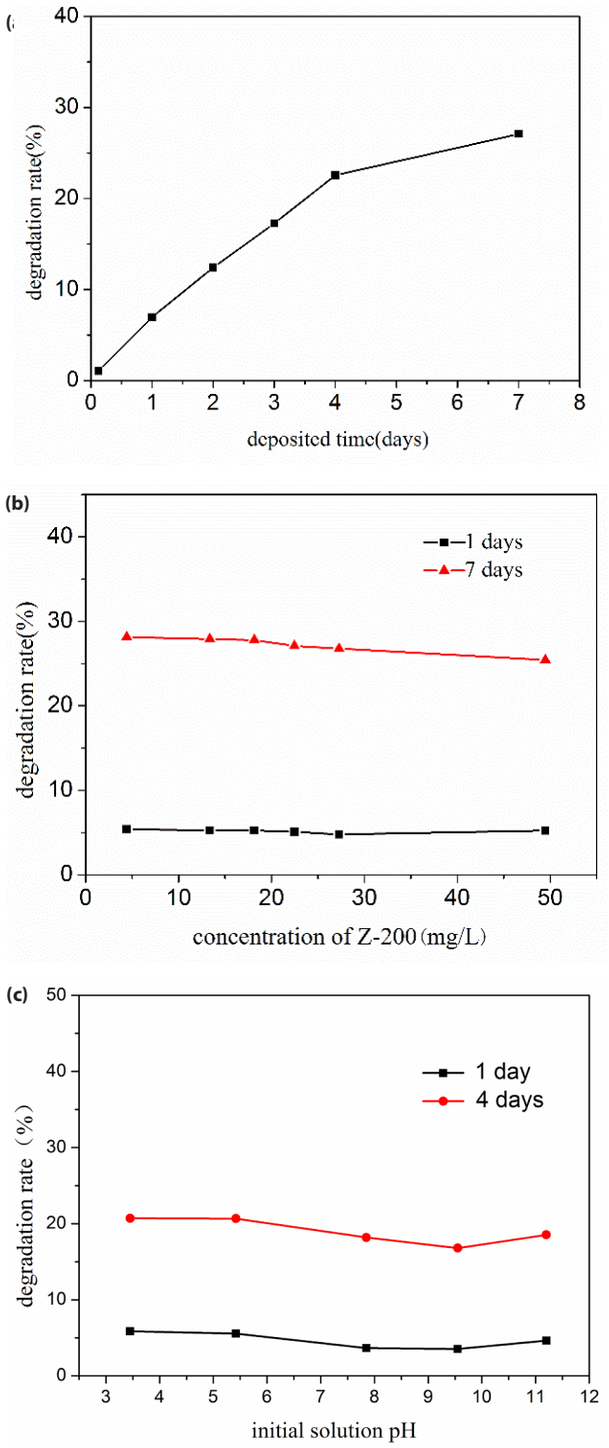

Fig. 2. The natural degradation of Z-200: (a) aging time, (b) concentration, and (c) pH.

3.2.2. Effect of initial pH on Z-200 removal ratios

Several groups of Z-200 samples were prepared with the pH values from 3.0 to 10.0. After an oxidation treatment by NaClO, the detection result of each sample is shown in

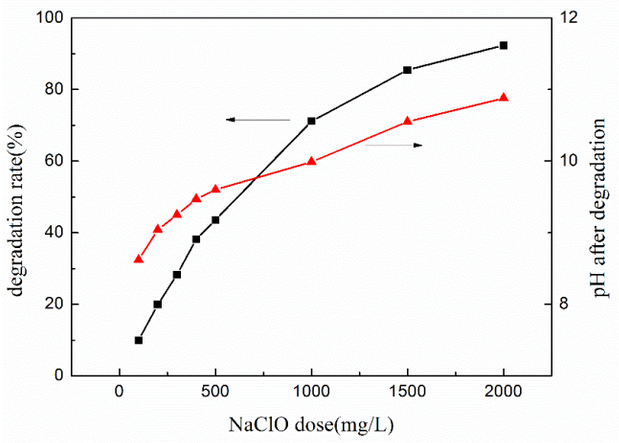

Fig. 3. Influence of NaClO dosage on the degradation rate of Z-200 Conditions: initial solution pH 8.0, stirring time 5 min.

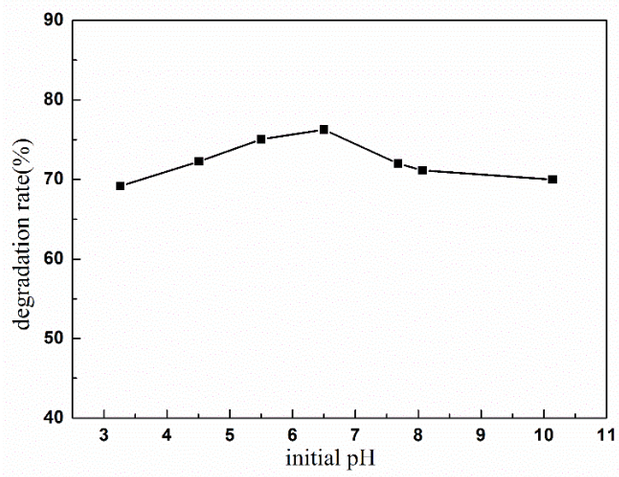

Fig. 4. Influence of initial pH on the degradation rate of Z-200 conditions: NaClO dosage 1,000 mg/L, stirring time 5 min.

Fig. 4. The Z-200 removal ratio increases with the increase in pH when the pH value is between 3 and 6.5, whereas the pH value is higher than 6.5, opposite results are worked out, in other words, Z-200 removal ratio decreases with the continuous increase in pH. The pH value of solution has an effect on hydrolysate of NaClO. As the pH of the solution is decreased, NaClO is easier to be decomposed. NaClO mainly acts as a bleaching role under alkaline conditions. When it comes to the range of pH ≥ 9, the solution exists mainly in the form of NaClO. When it comes to the range of neutral to slightly acidic solution, two components of HClO and NaClO mainly exist. While the pH is under strongly acidic conditions, the solution is primarily Cl_2 contained. When the solution is in two forms of HClO and NaClO, oxidation works the best [15]. Experiment results show that pH of the solution has some effect on Z-200 removal, but the changeable is not significant. While NaClO is added, the pH of the solution has sharply changed, which covers the influence of initial pH on Z-200 removal to some extent. Accord-

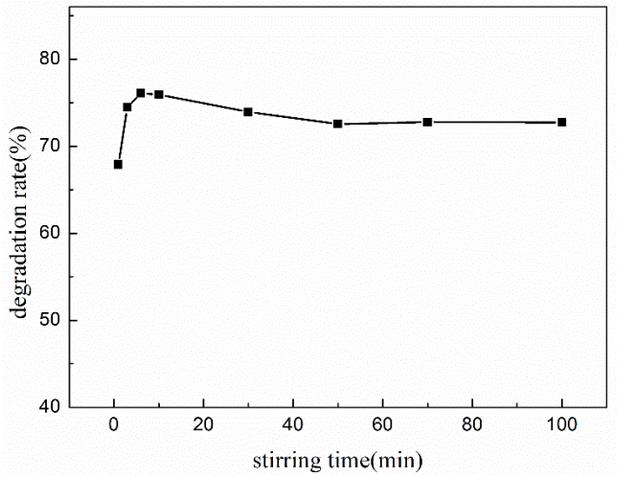

Fig. 5. Influence of reaction time on the degradation rate of Z-200 Conditions: NaClO dosage 1,000 mg/L, initial solution pH 6.5.

ing to the results in Fig. 4, pH value of 6.5 was selected for further optimization in the oxidation process.

3.2.3. Effect of stirring time on Z-200 removal ratios

Under the condition of initial pH value 6.5, NaClO dosage 1,000 mg/L, the stirring time of oxidation was investigated. Results are presented in Fig. 5. A significant improvement can be observed in Z-200 removal to the stirring time of 6 min with no further improvement at longer time, which indicates that Z-200 can be degraded in a short time and stirring time has slight influence on the degradation of Z-200. Equilibrium of oxidation process can be achieved in a short time.

3.2.4. Degradation process of Z-200 by NaClO/H_2O_2 system

When NaClO is combined with H_2O_2, singlet oxygen ([O]) of relatively high oxidation is generated by the synergistic effect of NaClO and H_2O_2. Moreover, the best oxidation effect can be achieved when the molar ratio of NaClO/H_2O_2 is 1:1. Under the condition of pH 6.5, stirring time 6 min and total oxidation 1,000 mg/L, different molar ratios of NaClO/H_2O_2 was investigated. According to Fig. 6, the best oxidation effect is under the condition of NaClO/H_2O_2 molar ratio 1:1. The closer to this optimum ratio, the more singlet oxygen is generated and the better degradation rate can be achieved. When the total amount of the oxidant is certain, synergistic effect of NaClO/H_2O_2 is superior to the effect of adding NaClO alone, which can maximize the effect of degradation under the condition of minimum oxidant cost.

3.3. The oxidation mechanism of Z-200

3.3.1. UV–Vis spectroscopy

UV-vis spectrophotometry is an analysis method to investigate the spectrum of molecular absorption in the UV-visible region. Based on the characteristic of absorption

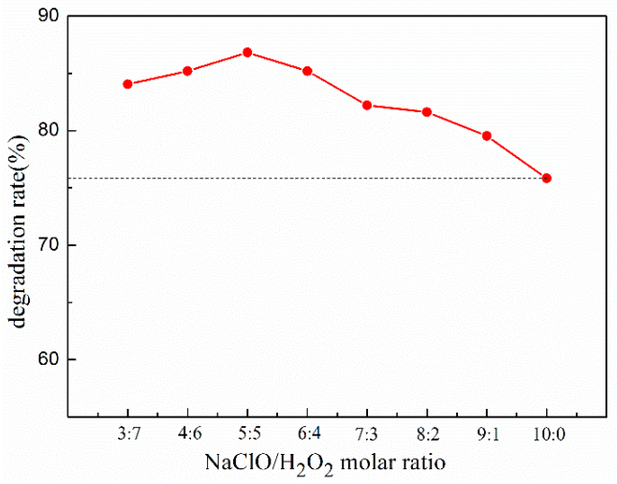

Fig. 6. Variation of the degradation rate of Z-200 by $NaClO/H_2O_2$ system Conditions: $NaClO/H_2O_2$ total dosage 1,000 mg/L, initial solution pH 6.5, stirring time 6 min.

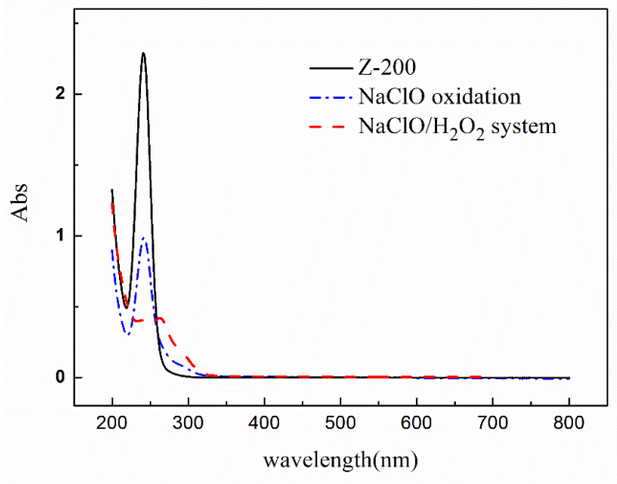

Fig. 7. Ultraviolet spectrum scan of Z-200 before and after oxidation degradation.

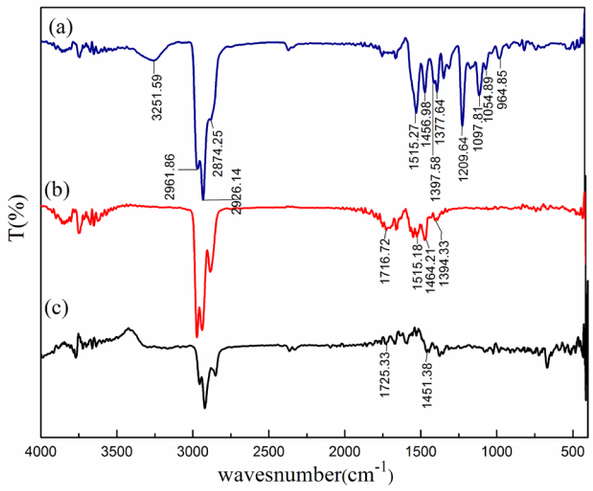

Fig. 8. Infrared spectrum scan of Z-200 before and after oxidation degradation: (a) sample of Z-200 before oxidation, (b) sample of Z-200 after NaClO oxidation, (c) sample of Z-200 after $NaClO/H_2O_2$ oxidation.

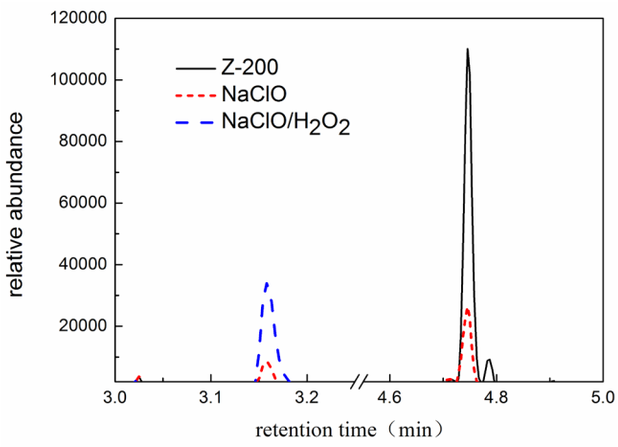

Fig. 9. GC-MS TIC spectrum of Z-200 before and after oxidation.

spectra, it can be combined with other analytical methods to deduce the molecular structure of organic compounds. UV spectrum of Z-200 before and after degradation are shown in Fig. 7. As presented in Fig. 7, the absorption peak in the characteristic wavelength of 241 nm is obviously reduced after oxidation treatment, which indicates that Z-200 is effectively degraded. After oxidative degradation by NaClO, the characteristics of molecular absorption spectrum is similar to that before oxidation, indicating that part of the molecular structural features of Z-200 is retained without destroyed. By contrast, after $NaClO/H_2O_2$ synergistic oxidation, the molecular structure of the original Z-200 is completely destructed, with some series of smaller molecules generated. Moreover, there exists weak UV absorption band in the wavelength region from 250 to 300 nm of both the two kinds of oxidation system, indicating that small molecules with carbonyl group are generated [16]. For further research of the oxidative degradation process of Z-200, FT-IR and GC-MS measurements were conducted and results are shown in Figs. 8 and 9.

3.3.2. FT–IR analysis

The FT-IR spectra is recorded as a qualitative analysis to determine the main functional groups and Fig. 8 shows the FT-IR spectra of Z-200 sample and oxidation product. As presented in Fig. 8(a), absorption peaks of 2,961.86 cm^{-1}, 2,874.25 cm^{-1} contribute to the $–CH_3$ asymmetry and symmetry stretching vibration. Peaks at 1,456.98 cm^{-1}, and 1,377.64 cm^{-1} are derived from asymmetry and symmetry bend vibration of $–CH_3$, and peaks at 2,926.14 cm^{-1} and 1,456.98 cm^{-1} are caused by $–CH_2–$ asymmetry stretching vibration and bend vibration. Peaks at 3,251.59 cm^{-1}, 1,209.64 cm^{-1} and

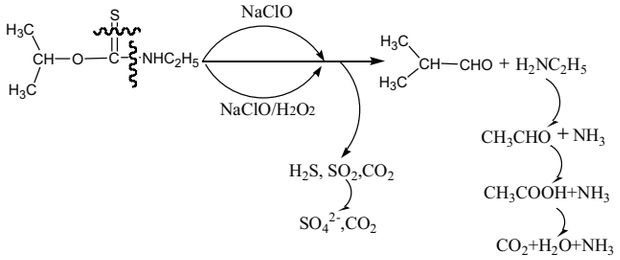

Fig. 10. Oxidation pathway of Z-200.

1,054.89 cm^{-1} are vibrations of –NH–, C–N from secondary amine, and C–O from formic acid ester separately. Peaks at 1,515.27 cm^{-1}, 1,397.58 cm^{-1}, 1,097.81 cm^{-1} and 964.85 cm^{-1} are characterized by a coupled vibration between C=S and C–N. IR characteristic peaks described above show an exact agreement with the chemical group of the structure of Z-200 ($CH(CH_3)_2OSCNHC_2H_5$) [17,18].

It can be seen that there are characteristic absorption peaks of $–CH_3$ and $–CH_2–$ remained after oxidation (peaks at 2,961.86 cm^{-1}, 2,874.25 cm^{-1}, 2,926.14 cm^{-1}, 1,464.21 cm^{-1}, 1,451.38 cm^{-1}), mainly due to the hydrocarbon impacts of extraction agent of n-hexane. It is obvious that the characteristic absorption peaks of Z-200 become weaker or even disappear after oxidation, which indicates that Z-200 is effectively degraded. It also can be seen from Fig. 8(b) that there are part of the characteristic peaks remained (such as peaks at 1,515.18 cm^{-1}, 1,394.33 cm^{-1}), indicating that Z-200 is not completely degraded, which shows a good agreement of UV measurement results. Furthermore, there appears a new absorption peak of aldehyde at 1,716.72 cm^{-1}.

Compared with Fig. 8(b), Fig. 8(c) shows that the characteristic peaks before oxidation completely disappear, indicating that Z-200 is completely degraded by $NaClO/H_2O_2$ oxidation. Results are in correspondence with UV measurement and above experiment results. There also appears to be a new absorption peak of aldehyde at 1,725.33 cm^{-1} [18].

3.3.3. GC–MS analysis

The wastewater and the products after oxidation treatment were analyzed by GC–MS to further evaluate their compositions [19]. According to the NIST 11 mass spectral library database, it is O-Isopropyl-N-ethylthionocarbamate where the retention time is 4.747. After oxidation treatment, the relative abundance of Z-200 is significantly weaker and even disappears, and there exists a new kind of compound where the retention time is 3.158. According to the NIST 11 mass spectral library database and the structure of Z-200, the compound was probably isobutyl aldehyde. The peak intensity of the sample after $NaClO/H_2O_2$ oxidation is a little stronger than that after NaClO oxidation, which shows a good agreement with UV-vis. results. And the concentration of it was relatively low, indicating that the oxidation by-products can be further oxidized, until eventually oxidized to CO_2, H_2O, NH_3, etc.

By analyzing the combination of UV, FT-IR and GC-MS results, it is obvious that Z-200 can be effectively degraded by NaClO oxidation and the degradation effect can be enhanced by adding H_2O_2. By $NaClO/H_2O_2$ synergistic oxidation, Z-200 is more completely degraded. Original molecular structure of Z-200 is disrupted, and gradually oxidized into smaller molecules. The bonds of C=S, and C–N are relatively weaker where the disruption always occurs. Therefore, chemical reaction that possibly occur during oxidation degradation can be deduced, which is shown in Fig. 10 [20].

4. Conclusions

1. Z-200 can be effectively degraded by NaClO oxidation. Degradation rate of Z-200 increases significantly with the increase of NaClO dosage. Adjusting to the desired pH can improve degradation effect. Oxidative process can reach equilibrium in a short time. Under the optimized conditions of initial pH 6.5, NaClO dosage 1,000 mg/L, and reaction time 6 min, degradation rate can reach 76%. Regardless of the excessive alkalinity, the degradation rate can reach 95% or more with NaClO continuously increased. The concentration of Z-200 can be reduced by NaClO to a level which has no damage to environment.
2. The degradation effect can be obviously enhanced by the synergistic effect of $NaClO/H_2O_2$ with the degradation rate of 87%. As a result, the best degradation effect can be reached under the condition of minimum oxidant cost.
3. UV, IR spectroscopy and GC-MS analysis shows that aldehyde can be generated during oxidation process and the concentration of that is relatively low. Small molecules can be further oxidized to CO_2, H_2O, NH_3 etc. eventually. This method can be efficiently and eco-friendly used in the wastewater treatment.

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