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Research Article

Study on the Degradation of Sodium Diethyldithiocarbamate (DDTC) in Artificially Prepared Beneficiation Wastewater with Sodium Hypochlorite

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The degradation of DDTC in beneficiation wastewater has become an increasingly concerned issue due to the serious effects on the environment. In this study, the degradation characteristics of DDTC in artificially prepared beneficiation wastewater were investigated by adding sodium hypochlorite as an oxidant, and the influences of different degradation conditions on removal efficiency of DDTC were analyzed systematically. The results indicated that the degradation rate of DDTC without sodium hypochlorite added can reach 88.4% in a stewing time of 6 h. When the dosage of sodium hypochlorite was 400 $mg \cdot L^{-1}$, the degradation rate of DDTC can reach 91.28% for 1 min reaction time under the natural condition of pH value 5.98 and reaction temperature 25°C. The DDTC in the wastewater was firstly degraded into carbon disulfide and diethylamine, and then carbon disulfide was further degraded into CO_2, S, or SO_4^{2-}, while diethylamine was degraded into N_2 and CO_2. The research results can provide a technical basis for the treatment of beneficiation wastewater containing DDTC.

1. Introduction

Flotation is one of the most important methods of mineral processing. With the difficulties of infertility and fineness of ore resources, the flotation processing has become extremely complex. And thus, the variety and dosage of flotation reagents used are increasing dramatically [1–4]. DDTC ($(C_2H_5)_2NCSSNa$), as a typical collector reagent of flotation for sulfide ore, has superior ability of collection, good selectivity, and other advantaged performances, and it has been widely used in the flotation process of galena, chalcopyrite, jamesonite, and other minerals [5, 6]. Generally, the DDTC presents the instability in acidic condition as the aqueous solution of DDTC is alkaline. Therefore, the applications of DDTC centralized more extensively in alkaline conditions [7]. In addition, it is able to obtain a better flotation technical index contributed by the good adaptability of DDTC to the various characteristics of ore, even with the lower dosage [8–10]. In the condition of high alkalinity, the DDTC can obviously improve the separation performance of lead-zinc sulfide ore, by using less or no toxic sodium cyanide [11, 12].

In recent years, the treatment of beneficiation wastewater, especially the wastewater containing organic chemicals, is getting notable attention as a contribution to protecting the environment [13–15]. The technical index of separation in the whole process will decline when the beneficiation wastewater containing DDTC is reused directly without special treatment [16, 17]. Direct discharge of beneficiation wastewater containing DDTC also brings serious damage to the environment [12, 17]. At present, the methods of wastewater treatment containing DDTC mainly include natural degradation, coagulation sedimentation, acid-base neutralization, chemical oxidation, and biodegradation [12, 16–25]. The natural degradation is one of the most primitive methods of treating beneficiation wastewater. The advantages of this method are simple operation and low cost, and the disadvantages are long time-consuming, unstable effluent quality, and large floor space [12, 16, 17]. The method of acid-base neutralization not only has the same advantages of natural degradation but it is necessary to provide the available waste in acidic or alkaline nearby, which can achieve the strategy of treating waste by waste [17–19]. The method of coagulation sedimentation utilizes coagulants to degrade organic and inorganic contaminants within beneficiation wastewater in the form of suspension or colloid, even some soluble pollutants and heavy metal ions can also be degraded. This method has the advantages of simplification of process, various selectivity for coagulants, and high rate of sedimentation but also has the disadvantages of large dosage of coagulants, exceeding amount of slags, and limitation of treating residual chemicals of low concentration, and secondary pollution of the slags is the biggest obstacle to its development [12, 20, 21]. Biodegradation, as a focused direction studied method currently, makes use of microorganisms to degrade organic pollutants while adsorbing and degrading heavy metals in wastewater. This method is characterized by low cost and no secondary pollution, while with the disadvantages of large equipment investments, high operation requirements, and poor adaptability. It is only suitable for wastewater treatment with low concentrations of organic pollutants [12, 15, 19–21]. Chemical oxidation is an effective method to remove organic pollutants from wastewater, with the advantages of variety of oxidants, rapidity of reaction, and good quality of effluent which make it be one of the most widely used methods for treating residual chemical reagents in beneficiation wastewater, meanwhile with the disadvantages of large dosage of oxidants and relatively high cost [12, 21–25]. In conclusion, chemical oxidation is the most appropriate method for the treatment of the beneficiation wastewater which is of large capacity and complicated composition, with the requirements of stability and rapidity of reusing. Research shows that common oxidants such as ozone, hydrogen peroxide, potassium ferrate, and hypochlorite all can be used in the processing of chemical oxidative degradation of DDTC; a simple comparison of these oxidants is shown in Table 1 [22–25].

Meanwhile, it can be seen that researches of chemical oxidative degradation of DDTC mostly focus on the theoretical field, and there are only a few studies on the degradation of DDTC in true beneficiation wastewater or in wastewater similar to the beneficiation wastewater. In this paper, degradation behavior and products of DDTC in artificially prepared beneficiation wastewater were investigated, with sodium hypochlorite selected as an oxidant due to the advantages listed and the low impact of residual chlorine on the flotation process [26]. Correspondingly, the investigation is to further reveal the mechanism of oxidative degradation of DDTC and provide a technical basis for the treatment of beneficiation wastewater containing DDTC.

2. Experimental

2.1. Reagents and Materials. DDTC ($(C_2H_5)_2NCSSNa{\cdot}3H_2O$) was obtained from Guoan Chemical Reagent Co., Ltd. (China), and it was prepared for the artificial beneficiation wastewater. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were selected as the pH regulators, sodium hypochlorite (NaClO) was selected as the oxidant for enhancing the degradation property of DDTC, and these three kinds of reagents were all manufactured by Tianjin Kermel Chemical Reagent Co., Ltd. (China). Sodium sulfate (Na_2SO_4) was from Sinopharm Chemical Chemical Reagent Co., Ltd. (China). All the above reagents were analytically pure.

Sodium *n*-butylxanthate ($C_4H_9OCSSNa$) and terpenic oil ($C_{10}H_{17}OH$) were of technical grade and manufactured by Tieling Flotation Regent Co., Ltd. (China); they were auxiliary reagents for the artificially prepared beneficiation wastewater.

2.2. Experimental Methods

2.2.1. Reagents Concentration Test. The concentration of DDTC in artificial prepared beneficiation wastewater was tested by using a UV spectrophotometer (SP-2000, Shanghai Spectrum Instrument Co., Ltd., China). The DDTC solution of $20\,mg{\cdot}L^{-1}$ was spectrally scanned to search the strongest absorption peak. Then, DDTC solutions of different concentrations were prepared for separately measuring the absorbance in matching the strongest absorption peak. And thus, the standard curve of working of DDTC could be obtained between the concentration and the absorbance.

The contents of COD (chemical oxygen demand), TOC (total organic carbon), and sulfide in the beneficiation wastewater were analyzed by the Analysis and Testing Agency of Northeastern University, China. Further, microwave digestion method, Vario TOC cube (Elementar Analysensysteme GmbH, Germany), and methylene blue spectrophotometry method were applied, respectively. These methods of tests were not described in detail in this study, and works of literature had made them quite clear [25, 26].

2.2.2. Degradation Process Investigation. The artificially prepared beneficiation wastewater, with several copies of each 50 mL in the laboratory, was stirred continuously in a heating magnetic stirrer for 30 min (SH-3A, Beijing Jinbeide Industrial Co., Ltd., China). Then, the absorbance in matching the strongest absorption peak was measured by using a UV spectrophotometer in the condition that the wastewater was diluted 5 times after stirring. Also, the degradation rate of DDTC was calculated to explore the influences of the pH value, reaction temperature, dosage of sodium hypochlorite, and the reaction time on degradation efficiency. With the degradation cost being taken into account, the degradation investigation of DDTC in artificially prepared beneficiation wastewater would be conducted as much as possible in the normal temperature and natural pH value conditions.

2.2.3. Degradation Products Analysis. The wastewater was also diluted 5 times after reaction and then scanned by using a UV spectrophotometer including the solution before reaction. The degradation pathway and products of DDTC were analyzed by comparing UV spectra before and after the reaction. During the analysis of the degradation products,

Table 1: Simple comparison of common oxidants.

Oxidants	Advantages	Disadvantages	Applicable
Ozone	Strong oxidizing ability, no other reaction by-products.	High equipment cost, toxic when high concentration.	Mainly used as supplement for other water treatment methods
Hydrogen peroxide	Strong oxidizing ability, wide range of application.	Preparation and storage process of the reagent is complicated, high treatment cost.	Suitable for the treatment of low concentration and small capacity of wastewater, used as a pretreatment or advanced treatment method for refractory organic wastewater.
Potassium ferrate	Extremely strong oxidizing ability, minor secondary pollution, quick reaction.	Relatively high cost of reagent, high requirement of storage environment.	A novel method of wastewater treatment, the flocculation performance of reduction product of Fe^{3+} or $Fe(OH)_3$ can affect the beneficiation process.
Hypochlorite	Easy to use, low cost, wide range of application.	High requirement of storage environment.	The most commonly used method of wastewater treatment.

the UV spectrophotometer worked on the condition of a scanning wavelength from 190 nm to 400 nm and an interval of 1 nm at a medium speed.

2.2.4. Degradation Rate Calculation. The degradation rate of DDTC was calculated as follows:

$$\text{degradation rate} = \frac{C_0 - C}{C_0} \times 100\%, \quad (1)$$

where C_0 (mg·L^{-1}) is the initial concentration of DDTC and C (mg·L^{-1}) is the residual concentration of DDTC after treatment in wastewater.

2.3. Standard Curve of Working of DDTC Solution. The standard solution of DDTC with concentration of 100 mg·L^{-1} was scanned by using a UV spectrophotometer, and the results are shown in Figure 1.

It is presented in Figure 1 that there were three UV absorption peaks at 202 nm, 256 nm, and 282 nm in the solution of DDTC. The maximum absorption peak was at 256 nm, which was selected as the characteristic absorption wavelength of DDTC solution.

Separately, we had taken 2 mL, 5 mL, 10 mL, 20 mL, and 25 mL of standard solution of DDTC with concentration of 100 mg·L^{-1}, put into five volumetric flasks of 100 mL, and diluted with water to the scale line. The tests of absorbance at 256 nm wavelength of each solution were conducted, and the standard curve of working corresponding to the DDTC concentration is shown in Figure 2. Furthermore, the linear equation between absorbance (Y) and solution concentration (X) is as follows:

$$Y = 0.04577X + 0.026, \quad R^2 = 0.9993. \quad (2)$$

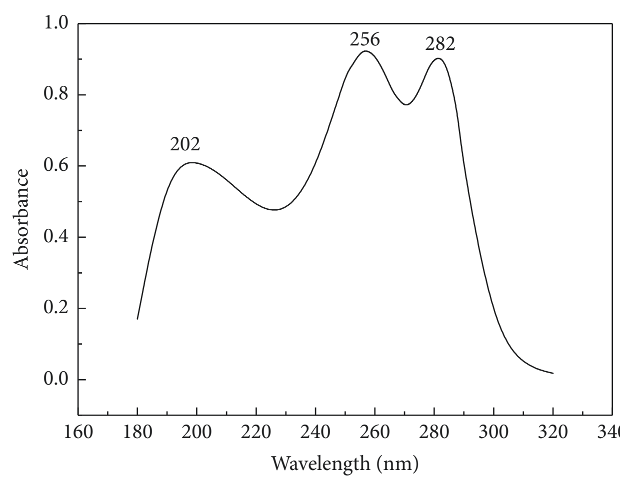

Figure 1: UV absorption spectrum of DDTC.

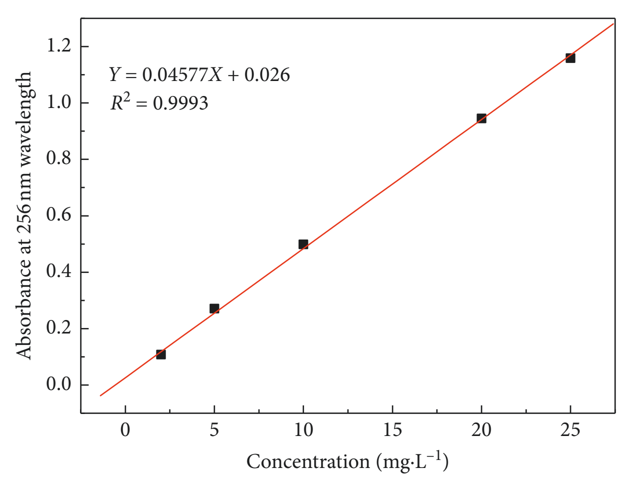

Figure 2: Standard curve of working of DDTC solution.

3. Results and Discussion

3.1. Preparation of Artificial Beneficiation Wastewater. In a concentration plant of lead-zinc, the process of lead-zinc separation after bulk flotation was adopted. Calcium oxide was selected as the pH regulator, DDTC and sodium *n*-butylxanthate were used as collectors, terpenic oil was employed as frother, and zinc sulfate and copper sulfate were employed as inhibitors and activators of sphalerite, respectively. The test results of wastewater discharged from the overflow of the thickener treating final tailings are shown in Table 2. It is noteworthy that the natural pH value of the

Table 2: Analysis results of the true beneficiation wastewater.

pH value	Content ($mg{\cdot}L^{-1}$)				
	COD	TOC	DDTC	SO_4^{2-}	Sulphide
5.98	267	139.55	93.75	87.43	0.49

beneficiation wastewater was 5.98 rather than alkaline. From the analysis of TOC and content of DDTC, it was clear that the beneficiation wastewater was a mixture of DDTC and other organic pollutants. Furthermore, it could be inferred that a certain amount of sodium *n*-butylxanthate and terpenic oil were mixed from the reagent system of flotation.

In order to study the degradation process and products of DDTC more accurately in the laboratory and to avoid the influences of some uncertain factors, the artificial flotation wastewater was prepared according to the analysis results of beneficiation wastewater, with the concentration of DDTC $100\,mg{\cdot}L^{-1}$, sodium sulfate $133\,mg{\cdot}L^{-1}$, sodium n-butylxanthate $20\,mg{\cdot}L^{-1}$, terpenic oil $10\,mg{\cdot}L^{-1}$, and sodium sulfide $0.5\,mg{\cdot}L^{-1}$, respectively.

3.2. Degradation Characteristics of DDTC without Sodium Hypochlorite. In order to explore the ability of natural degradation of DDTC without oxidant to achieve the rapid recycling of wastewater or not, the degradation of DDTC in artificially prepared beneficiation wastewater was investigated systematically by changing the pH value, stewing time, and reaction temperature.

3.2.1. Influence of the pH Value on the Degradation of DDTC. The pH value of artificially prepared beneficiation wastewater was adjusted by NaOH or HCl under the condition of stewing time 1 h and reaction temperature 25°C. The results of degradation characteristics of DDTC in artificially prepared wastewater of flotation under different pH values are shown in Figure 3.

From Figure 3, the degradation of DDTC was almost constant at the beginning, with the increase of the pH value of the wastewater; the degradation property of DDTC firstly decreased linearly and then tended to be stable. When the pH value was 2.5, the degradation rate of DDTC reached up to 99.95%, and when the pH value increased to 4, the degradation rate was 99.91%. With the further increase of the pH value of the wastewater, the degradation rate of DDTC decreased sharply. When the pH value was 7, the degradation rate of DDTC was just 15.88%. And then, with the pH value continuing to increase, the concentration of DDTC almost remained stable. When the pH value of wastewater was 11, the degradation rate of DDTC was just 12.38%. Thus, the DDTC was extremely unstable in the acidic environment, but it was relatively stable in the neutral or alkaline environment.

3.2.2. Influence of Stewing Time on the Degradation of DDTC. Under the condition of pH value 5.98 and reaction temperature 25°C, the effect of stewing time on the degradation of DDTC in artificially prepared beneficiation wastewater was

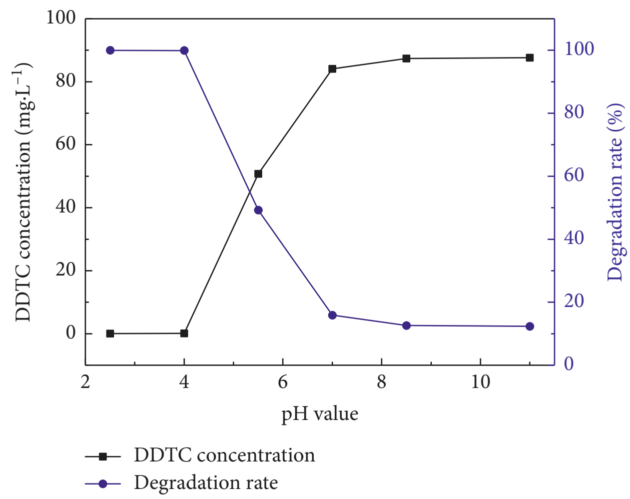

Figure 3: Influence of the pH value on the degradation of DDTC.

investigated, correspondingly the results are shown in Figure 4.

Figure 4 presents that, with the extension of stewing time, the concentration of DDTC in wastewater decreased gradually. The concentration of DDTC decreased rapidly when the stewing time changed from 1 h to 3 h, then decreased slowly. When the stewing time was 6 h, the concentration of DDTC in wastewater could reach to $11.60\,mg{\cdot}L^{-1}$, with the degradation rate of 88.4%. However, hours of stewing time were unable to achieve the timely reuse of the beneficiation wastewater.

3.2.3. Influence of Reaction Temperature on the Degradation of DDTC. Under the condition of pH value 5.98 and stewing time 1 h, the effect of reaction temperature on the degradation of DDTC in artificially prepared beneficiation wastewater was investigated, and the results are shown in Figure 5.

It can be seen from Figure 5 that the degradation of DDTC basically followed the Arrhenius equation when the reaction temperature ranged from 25°C to 65°C, correspondingly the degradation rate of DDTC increased from 30.00% to 66.68%. Then, when the temperature increased from 65°C to 75°C, the degradation rate of DDTC rocketed by 31.79% and up to 98.47%, but such high temperature was meaningless for the natural degradation of DDTC.

3.3. Characteristics of Degradation of DDTC with Sodium Hypochlorite. The ability of natural degradation of DDTC without oxidant cannot generally satisfy the timely reuse of the beneficiation wastewater. Due to the advantages of sodium hypochlorite and low impact of residual chlorine on the flotation process, sodium hypochlorite was added to accelerate the degradation of DDTC. The influences of the dosage of sodium hypochlorite, reaction time, and reaction temperature on the degradation of DDTC were investigated systematically, where the initial pH value of 5.98 was maintained according to the true beneficiation wastewater before sodium hypochlorite added.

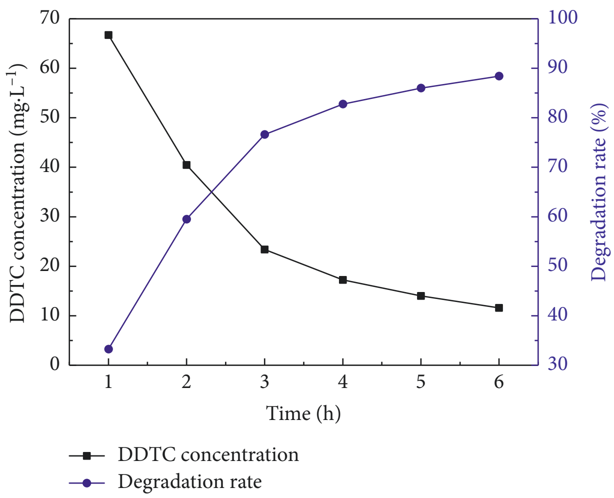

Figure 4: Influence of the stewing time on the degradation of DDTC.

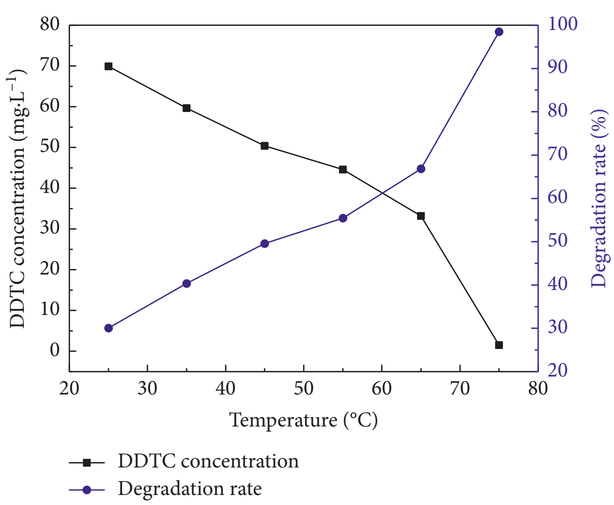

Figure 5: Influence of the temperature on the degradation of DDTC.

3.3.1. Influence of the Dosage of Sodium Hypochlorite on the Degradation of DDTC. Under the condition of pH value 5.98, reaction time 1 min, and temperature 25°C, the effect of the dosage of sodium hypochlorite on the degradation of DDTC in artificially prepared beneficiation wastewater was investigated, and the results are shown in Figure 6.

It can be seen from Figure 6 that the degradation rate of DDTC increased obviously, with the increase of the dosage of sodium hypochlorite in the scope of experiments. When the dosage of sodium hypochlorite increased from 10 $mg{\cdot}L^{-1}$ to 100 $mg{\cdot}L^{-1}$, the degradation rate increased from 37.95% to 68.32% with an approximate linear upward trend. When the dosage ranged from 100 $mg{\cdot}L^{-1}$ to 400 $mg{\cdot}L^{-1}$, the degradation rate increased from 68.32% to 91.38%, showing a similar linear relationship presented before, but the upward slope of the curve became smaller than the previous stage. Then, the dosage of sodium hypochlorite had a less effect on the degradation of DDTC even when the dosage continuously increased.

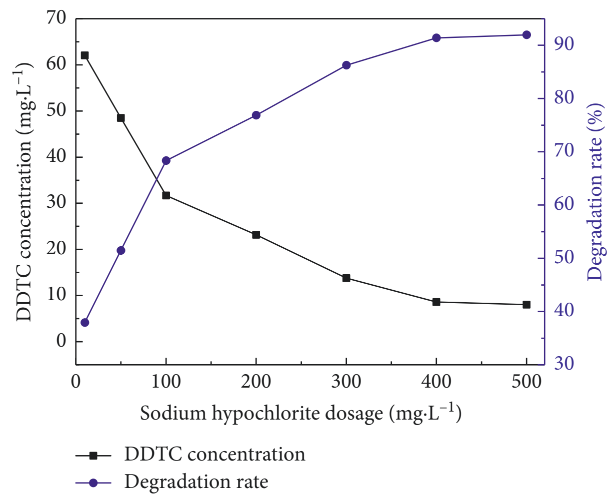

Figure 6: Influence of the dosage of sodium hypochlorite on the degradation of DDTC.

3.3.2. Influence of Reaction Time on the Degradation of DDTC with Sodium Hypochlorite. Under the condition of pH value 5.98, the dosage of sodium hypochlorite of 400 $mg{\cdot}L^{-1}$, and reaction temperature 25°C, the influence of the reaction time on the degradation of DDTC in artificially prepared beneficiation wastewater was investigated, as shown in Figure 7.

As is presented in Figure 7, the curve of degradation rate of DDTC was divided into 3 stages with the extension of the reaction time. The first stage was from 1 min to 5 min, and the concentration of DDTC decreased rapidly, while the degradation rate increased rapidly from 91.28% to 99.29%. The second stage was from 5 min to 7 min, and the concentration of DDTC in wastewater remained about the same as that of the first stage. The third stage was from 7 min to 11 min, and the concentration of DDTC increased slightly. The reason for the phenomenon above may be that, with the increase of oxidation time, further degradation of DDTC or its products occurred and that some substances with absorbance at the wavelength of 256 nm were generated. Further research is needed to validate the hypothesis.

3.3.3. Influence of Reaction Temperature on the Degradation of DDTC with Sodium Hypochlorite. Under the condition of pH value 5.98, dosage of sodium hypochlorite 400 $mg{\cdot}L^{-1}$, and reaction time 1 min, the influence of reaction temperature on the degradation of DDTC in artificially prepared beneficiation wastewater was investigated, as shown in Figure 8.

From Figure 8, the degradation rate of DDTC increased with the increase of temperature. Further, when the temperature ranged from 25°C to 55°C, the degradation rate of DDTC was approximately linearly dependent on the

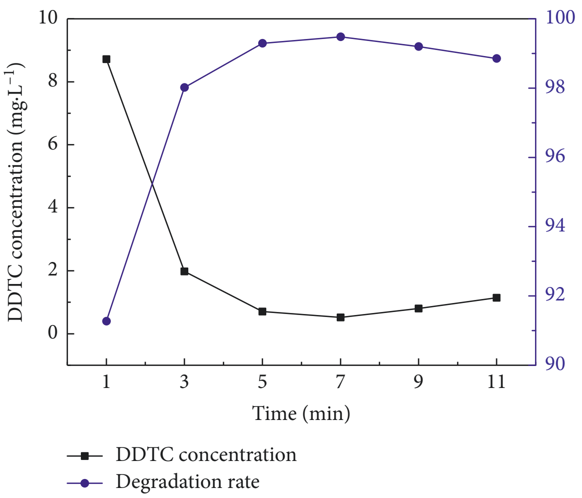

FIGURE 7: Influence of reaction time on the degradation of DDTC.

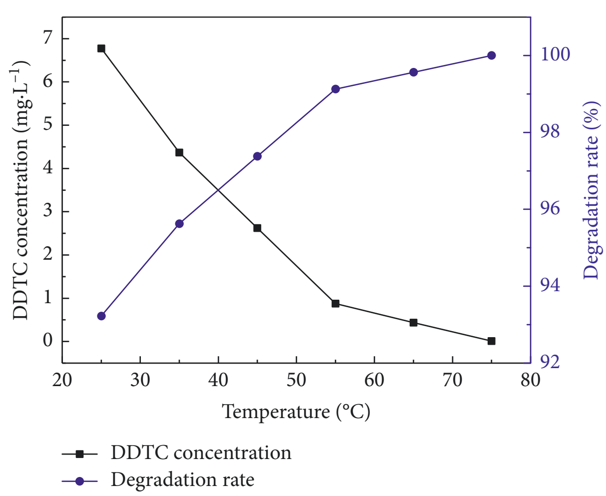

FIGURE 8: Influence of reaction temperature on the degradation of DDTC.

temperature. The degradation rate of DDTC at 55°C reached as high as 99.13%, and DDTC almost completely degraded.

3.4. Degradation Products of DDTC

3.4.1. Degradation Products of DDTC without Sodium Hypochlorite. Under the natural conditions of pH value 5.98 and reaction temperature 25°C, the degradation products of DDTC were investigated without sodium hypochlorite. The scanning results of UV spectrophotometry of each reaction solution at different stewing time periods are shown in Figure 9.

From Figure 9, with the increase of stewing time, the absorption peak of artificially prepared beneficiation wastewater gradually decreased at the wavelength of 256 nm and 282 nm, which meant that the degradation of DDTC gradually occurred. And, a new strong absorption peak appeared at the wavelength of 206 nm. DDTC was made by addition reaction of diethylamine, carbon disulfide, and sodium hydroxide as follows [27]:

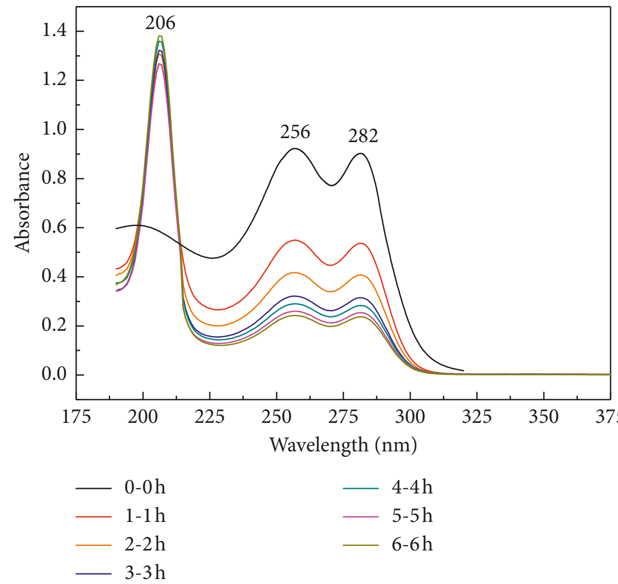

FIGURE 9: Influence of stewing time on the UV absorption spectrum of reaction solution.

$$\begin{aligned}&(CH_3CH_2)_2NH + CS_2 + NaOH + 2H_2O \\ &\quad\longrightarrow (CH_3CH_2)_2NCSSNa \cdot 3H_2O\end{aligned} \tag{3}$$

The wavelength of 206 nm was exactly the characteristic absorption peak of carbon disulfide [28, 29], indicating that the main product of DDTC degradation in wastewater was carbon disulfide as follows:

$$\begin{aligned}(C_2H_5)_2NCSSNa + H_2O &\longrightarrow (C_2H_5)_2NCSSH + NaOH \\ (C_2H_5)_2NCSSH &\longrightarrow (C_2H_5)_2NH + CS_2\end{aligned} \tag{4}$$

Figure 9 shows that with the extension of stewing time, the concentration of carbon disulfide increased slightly, indicating the degradation rate of DDTC increased gradually.

3.4.2. Degradation Products of DDTC with Sodium Hypochlorite. The scanning results of UV spectrophotometry of each reaction solution for reaction time 1 min at different dosages of sodium hypochlorite are shown in Figure 10, on the natural pH value and temperature as before.

From Figure 10, the peaks at the wavelength of 256 nm and 282 nm almost disappeared under the dosage of sodium hypochlorite of 100 mg·L^{-1} and more, indicating that most DDTC had been degraded in wastewater. At the wavelength of 206 nm, absorption peaks appeared obviously, suggesting that carbon sulfide existed in the degradation products. The characteristic absorption peak of carbon disulfide decreased with the increasing dosage of sodium hypochlorite. When the dosage of sodium hypochlorite was 400 mg·L^{-1}, the absorption peak at 206 nm disappeared and the characteristic absorption peak of sulfate at 191 nm presented clearly [29], indicating that carbon disulfide was further degraded

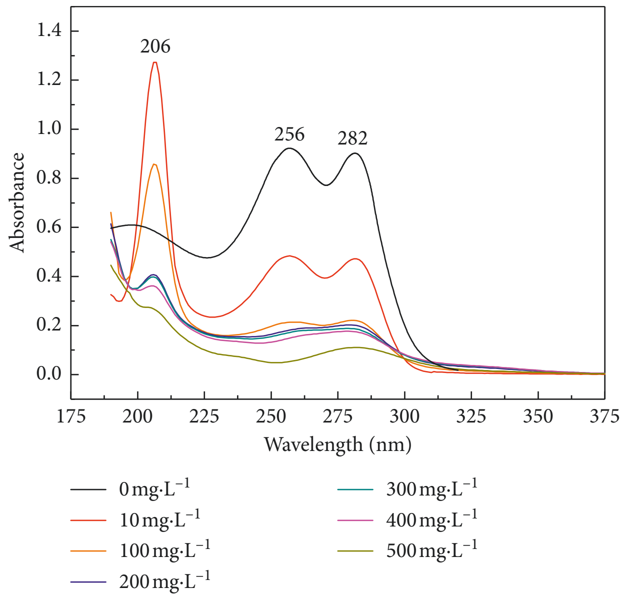

FIGURE 10: Influence of the dosage of sodium hypochlorite on the UV absorption spectrum of reaction solution.

and the products of decomposition should be CO_2, S, or SO_4^{2-}. Further, with the increase of the dosage of sodium hypochlorite, the characteristic absorption peak of diethylamine became weaker, indicating that the diethylamine was further degraded, with possible products of CO_2 and N_2 as follows [30]:

$$\begin{aligned} CS_2 + 2H_2O &\longrightarrow CO_2 + 2H_2S \\ H_2S + NaClO &\longrightarrow S + H_2O + NaCl \\ H_2S + 4NaClO &\longrightarrow H_2SO_4 + 4NaCl \\ 2(C_2H_5)_2NH + 26ClO^- &\longrightarrow 8CO_2 + 10H_2O + N_2 + 26Cl^- \end{aligned} \tag{5}$$

4. Conclusion

The characteristics and products of degradation of DDTC in artificially prepared beneficiation wastewater were investigated with or without sodium hypochlorite as an oxidant. The conclusions were as follows:

(1) Without adding sodium hypochlorite, the property of degradation of DDTC itself was weak and unable to achieve the timely reuse of the beneficiation wastewater. Under the natural conditions of pH value 5.98 and reaction temperature 25°C, the degradation rate of DDTC was only 88.4% with the stewing time of 6 h. In the acidic environment, DDTC was easily degraded, while relatively stable in the neutral or alkaline environments.

(2) The DDTC in artificially prepared beneficiation wastewater could be degraded by sodium hypochlorite effectively. Under the natural condition, the degradation rate of DDTC can reach 91.38% in 1 min with the dosage of sodium hypochlorite of 400 mg·L^{-1}. The degradation rate of DDTC was affected observably by the dosage of sodium hypochlorite, reaction time, and reaction temperature. Sodium hypochlorite should be an effective oxidant for the degradation of DDTC in true beneficiation wastewater due to its advantages and weak impact of low residual chlorine on the flotation process.

(3) Without adding sodium hypochlorite, the degradation of DDTC gradually occurred with the increase of stewing time. The characteristic absorption peak of carbon disulfide at 206 nm could be observed clearly, where carbon disulfide was one of the main degradation products of DDTC in wastewater.

(4) Under the natural condition, DDTC had been almost completely degraded when the dosage of sodium hypochlorite was 100 mg·L^{-1}, while carbon disulfide and diethylamine could be acquired from the UV absorption spectrum. And, with the increase of the dosage of sodium hypochlorite, carbon disulfide was further decomposed into CO_2, S, or SO_4^{2-}, while the diethylamine was decomposed into N_2 and CO_2. The research results can provide a reference for the treatment of beneficiation wastewater containing DDTC.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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