Treatment of dinitrodiazophenol industrial wastewater by an ozone/persulfate process

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ABSTRACT

An ozone-persulfate (O$_3$-PS) process was used to treat dinitrodiazophenol (DDNP) industrial wastewater. Under optimized operational parameters, such as O$_3$ flow rate of 0.250 L/min, reaction temperature of 70°C, PS dose of 2 g/L, and initial pH of 4.5, the treatment efficiencies of O$_3$-PS and other processes (O$_3$, PS, and thermal/PS) were compared. The results revealed that the chemical oxygen demand and color number removal efficiencies of O$_3$-PS process were 90.66% and 96.99%, respectively. The treatment efficiency of O$_3$-PS process was obviously higher than that of other processes examined. Ultraviolet-visible spectra analysis showed that the O$_3$-PS process had a significant effect on the degradation of benzene-ring compounds in wastewater, and that the chromophores and auxochrome groups were completely degraded. In conclusion, this study provides a theoretically feasible method for the treatment of DDNP industrial wastewater.

Keywords: Ozone; Persulfate; Dinitrodiazophenol; Ultraviolet-visible spectra; Hydroxyl radical; Sulfate radical

1. Introduction

Dinitrodiazophenol (DDNP) is frequently used as a primary explosive in industries as well as military defense owing to its complex production process, relatively low cost, and good detonation performance [1–4]. Its characteristics are shown in Table 1 and the majority production reactions include the neutralization process (Fig. 1a), reduction process (Fig. 1b), and diazo process (Fig. 1c).

During its production, 200–300 kg DDNP industrial wastewater will be produce when 1 kg DDNP was produced. Hence, DDNP industrial wastewater contains partial DDNP and a great amount of DDNP intermediates. Due to the complexity in the organics constitution, DDNP industrial wastewater is characterized by high color number (CN), high toxicity, and high structural complexity, and can cause serious damage to the ecosystem if inadequately treated before discharge [5,6]. Therefore, an effective method for the treatment of DDNP industrial wastewater is necessary.

Currently, the commonly used methods for DDNP wastewater treatment include the condensation–incineration method, electrochemical oxidation, and Fenton method [2,7]. However, as the condensation–incineration method has many disadvantages, such as the requirement of a large amount of coal for incineration and production of SO$_2$ and NO$_x$, it can only be applied as a temporary solution. Traditional Fenton method, an environmental friendly procedure, is widely used for wastewater treatment because it can efficiently oxidize organic pollutants and improve biodegradability; however, narrow optimal pH range and iron-based sludge production are the main drawbacks of this method [8,9]. Recently, persulfate (PS) oxidation method has received widespread attention for degrading toxic organics including atrazine, bisphenol A, sulfamethoxazole, tetrabromobisphenol A, etc. [10–15]. Activation PS possesses exhibited higher oxidation capacity than ozone (O$_3$), it can produce sulfate radical (SO$_4$$^{\cdot-}$, $E_0 = 2.6$ V, $t_{\text{half-life}} = 4$ s), which has a longer half-life than
hydroxyl radical (OH, \( E_0 = 2.8 \) V, \( t_{\text{half-life}} < 1 \) s), to effectively degrade many recalcitrant organics [16–21]. The common PS activation methods include thermal activation, ultrasound, transition metals, etc., among which thermal activation can produce ideal treatment outcomes, but require long reaction time [14,22–24].

Ozonation is an effective process for organic pollutants degradation and water decontamination [25–28]. Under acidic condition, O\(_3\) can directly degrade organic pollutants, whereas under neutral and basic conditions, O\(_3\) produces •OH [29], which, together with O\(_3\), can degrade recalcitrant organics. Numerous studies have reported that electron-rich moiety can be preferentially attacked by O\(_3\), whereas certain small organic acids are resistant to O\(_3\) [29–31]. For a long time, O\(_3\)-combined processes have been applied for wastewater treatment [32–34]. Cao et al. [3] applied Fe/Cu/O\(_3\) process to the treatment of DDNP manufacturing wastewater and found that O\(_3\)-combined process can achieve efficient treatment efficiency for DDNP manufacturing wastewater. Furthermore, it was reported that O\(_3\)/PS process had a strong synergetic effect for wastewater treatment [35,36]. Thus, theoretically, satisfactory outcome can be achieved by employing O\(_3\)-combined PS activation process to treat DDNP wastewater (containing electron-rich moiety and unsaturated bond) [37].

Accordingly, in the present study, O\(_3\)/PS process was applied for the treatment of DDNP wastewater, and the operational parameters were optimized. In addition, the characteristics of effluent obtained under various parameters were investigated using ultraviolet-visible (UV-Vis) spectra, and control experiments were performed to compare the treatment efficiency of the O\(_3\)/PS process. The findings of this study provide guidance and reference for developing a useful method for DDNP industrial wastewater treatment.

2. Materials and methods

2.1. DDNP industrial wastewater

DDNP industrial wastewater was collected from a DDNP production factory in Southwest China. The basic characteristics of the wastewater were as follows: dark-brown color, no odor, chemical oxygen demand (COD) of 3,260 mg/L, CN of 4.2, and pH of 9.04.

2.2. Experimental materials

Potassium persulfate (K\(_2\)S\(_2\)O\(_8\), analytical grade) was purchased from Kelong Chemical Factory (Chengdu, China), and O\(_3\) was produced from an ozone generator (3S-T3, Beijing Tonglin Technology Ltd., Beijing, China) via an oxygen bottle supplying pure oxygen. A flow meter (ZB-3WB, Shuanghuan, Changzhou, China) was used to control the O\(_3\) flow rate. The O\(_3\) flow rate of 0.1, 0.15, 0.175,
2.4. Analytical method

The COD was determined by the rapid microwave digestion method (HJ 828-2017) in accordance with previous studies [18,25]. CN was used to characterize the color of the wastewater according to Eq. (1) [13], where $A_{436}$, $A_{525}$, and $A_{620}$ represent the absorbance of wastewater at 436, 525, and 620 nm, respectively.

$$CN = \frac{A_{436}^2 + A_{525}^2 + A_{620}^2}{A_{436} + A_{525} + A_{620}}$$  (1)

UV-Vis spectra showed the absorbance of wastewater at each wavelength and characterized the organic and certain functional groups contents in wastewater. After filtering through a 0.45 μm glass fiber membrane and then diluting for certain times, each sample was examined by UV-Vis spectrophotometer (Perkin-Elmer Lambda 950, USA) at a wavelength of 220–600 nm and scan interval of 1 nm.

3. Results and discussion

3.1. Optimization of O₃/PS process parameters

The effects of factors such as O₃ dosage, reaction temperature, PS dosage, and initial pH on DDNP wastewater treatment by O₃/PS process were investigated. DDNP wastewater mainly contains DDNP, which has two nitro groups and one diazo group, and some effluents from other production processes [14]. As a result, DDNP wastewater is characterized by high COD concentration and high CN value. Accordingly, the COD and CN removal rates were used as evaluation indices in this study to determine the treatment efficiency of the O₃/PS process, and the effluent pH of each sample was monitored to further confirm the result. Furthermore, the UV-Vis spectra were analyzed to evaluate the characteristics of organic pollutants degradation.

3.1.1. Reaction temperature

In thermal-activated PS process, the reaction temperature considerably influences PS activation. As the key reaction of SO₄²⁻ production is fission of O–O bond via absorbing energy [38,39], the effect of reaction temperature on COD and CN removals was investigated.

As illustrated in Fig. 2a, when the reaction temperature was increased from 30°C to 70°C, the COD and CN removal efficiencies significantly increased from 78.10% and 90.51% to 90.60% and 96.99%, respectively. However, a further increase in the reaction temperature to 90°C resulted in a decrease in the COD and CN removal rates to 85.49% and 95.72%, respectively. As shown in Fig. 2b, the overall absorbance of each sample decreased with increasing reaction temperature (in a certain range), suggesting that a higher reaction temperature favors organics removal. However, a further rise in the reaction temperature to 90°C caused a considerable increase in the absorbance. Moreover, a modified temperature range promoted degradation of benzene-ring compounds and functional groups, whereas the content of organic macromolecules significantly decreased after the reaction. These results indicated that an appropriate increase in reaction temperature favored the removal of organics, whereas very high temperature decreased organic pollutants removal [10].

The effluent pH dropped with the increasing reaction temperature, demonstrating that many small organic acids were produced during organics degradation at higher reaction temperature. It must be noted that a suitable reaction temperature can effectively activate PS to produce SO₄²⁻ [14]. In DDNP wastewater, organics containing diazo and nitro groups (chromophores and auxochrome groups) occur, which exhibit a faster reaction rate with O₃ [1,14]; as a result, significant CN removal efficiency could be achieved by the O₃/PS process. In addition, the higher reaction temperature can enhance the irregular molecular motion, causing an increase in the possible exposure of oxidants and organics and subsequent improvement in the O₃/PS treatment efficiency. However, very high temperatures may not be constantly favorable for high organics removal efficiency. It has been reported that excess SO₄²⁻ content can initiate radical quenching reactions, which can decrease treatment efficiency [1].

3.1.2. O₃ dosage

In addition to its direct reaction with organic pollutants, O₃ can also indirectly react with these pollutants by producing OH [25,26]. As the reaction between O₃ and electron-rich moieties is faster, a significant decrease in CN could be achieved by O₃/PS process for DDNP wastewater treatment.
As depicted in Fig. 3a, both COD and CN removal rates decreased with increasing O₃ dosage. An increase in O₃ dosage from 9.8 to 25.92 mg/min resulted in an increase in both COD and CN removal efficiencies from 62.25% and 68.20% to 90.60% and 96.99%, respectively. In addition, a further increase in O₃ dosage to 52.65 mg/min caused a slight increase in COD (3.74%) and CN (2.82%) removal efficiencies, respectively. Moreover, the effluent pH continuously declined with the increasing O₃ dosage. Thus, although high O₃ content in the system favored organics removal, excess O₃ did not significantly improve organics removal. A higher O₃ concentration in the system could result in the accumulation of small organic acids as well as an increase in OH concentration. As SO₄²⁻ produced in thermally activated PS process and OH enrich the ROS content, many organics, especially small organic acids, could be significantly degraded during the O₃/PS process.

As shown in Fig. 3b, the absorbance of wastewater gradually decreased with increasing O₃ dosage, indicating that the benzene-ring compounds and other functional groups containing unsaturated bond and/or electron-rich moiety could be significantly degraded by the O₃/PS process. It must be noted that considerable absorbance below 250 nm was observed, and that the absorbance increased at higher O₃ concentration. This finding can be attributed to the accumulation of small organic acids generated from organics degradation, which have low reaction rate with O₃. Previous studies have also reported that O₃ can effectively degrade aromatic compounds with unsaturated bond and electron-rich moieties, but has a lower reaction rate with small organic acids [40,41].

![Fig. 2](image-url)  
Fig. 2. (a) Effect of reaction temperature on COD and CN removals and effluent pH variation and (b) UV-Vis spectra of each sample by reaction temperature varying. Reaction conditions: O₃ dosage = 25.92 mg/min, PS dosage = 2 g/L, initial pH = 4.5, and reaction time = 20 min.

![Fig. 3](image-url)  
Fig. 3. (a) Effect of O₃ dosage on COD and CN removals and effluent pH variation and (b) UV-Vis spectra of each sample by reaction temperature varying. Reaction conditions: reaction temperature = 70°C, PS dosage = 2 g/L, initial pH = 4.5, and reaction time = 20 min.
3.1.3. PS dosage

In the thermal-activation process, the concentration of PS, which acts as an SO$_4^{–}$$_2$ producer, determines the SO$_4^{–}$$_2$ content in the process [26,11,42]. Hence, the effect of PS dosage on the O$_3$/PS treatment efficiency was examined.

As shown in Fig. 4a, the COD removal efficiency decreased by 2.01% and 1.80% when the PS dosage was increased from 2 to 4 and 6 g/L, respectively, which could be attributed to measurement error. With a further increase in PS dosage to 14 g/L, the COD and CN removal efficiencies reached 94.56% and 99.93%, respectively, while the effluent pH progressively decreased. As shown in Fig. 4b, absorbance above 250 nm gradually decreased with increasing PS dosage, indicating that the organics and functional groups in wastewater were considerably degraded. However, absorbance below 250 nm first decreased and then increased with increasing PS dosage. These results revealed that a certain increase in the PS dosage can improve the degradation of organic pollutants by the O$_3$/PS process, whereas very high PS dosage can lead to organic acids accumulation and increased salt concentration in the treated wastewater. It has been reported that PS can quench SO$_4^{–}$$_2$ under acidic condition and decrease the ROS concentration in the process, resulting in significant decrease in treatment efficiency [1]. However, in the present study, an increase in PS dosage from 2 to 14 g/L did not result in PS quenching reaction, suggesting that the highest PS dosage (14 g/L) did not reach the specific inhibition concentration.

3.1.4. Initial pH

O$_3$ is known to produce more OH under basic condition, and the formation and concentration of radicals can be considerably affected by ambient pH. For instance, it has been reported that SO$_4^{–}$ plays a dominant role under acidic condition, OH is the primary ROS under basic condition, and the two radicals equally contribute to organics degradation under neutral condition [1,23,43]. Therefore, the effect of initial pH on O$_3$/PS treatment efficiency was investigated.

As shown in Fig. 5a, with the increase in initial pH, COD removal first increased and then gradually decreased. The highest COD removal was achieved at an initial pH of 4.5. With regard to CN removal, the initial pH range of 2.5–9.5 resulted in more than 95% CN removal, indicating that O$_3$/PS process could be applied at a wide pH range to treat DDNP wastewater. These results in terms of CN reduction suggested that O$_3$/PS process could efficiently degrade organic pollutants containing chromophores and auxochrome groups in wastewater. Moreover, as the predominant ROS varied with the pH, it could be concluded that the major contributor to CN reduction is O$_3$. As shown in Fig. 5b, the variation trend of overall absorbance was consistent with that of COD removal. Thus, regardless of the predominant ROS in the process, which could only significantly influence the degradation of small organic acids, benzene-ring compounds, and unsaturated moieties could be considerably degraded in the presence of O$_3$. Besides, the presence of ROS in the process could predominantly enhance the treatment efficiency of O$_3$-resistant organics.

3.2. Control experiments (including O$_3$ and/or PS)

The results obtained revealed that the optimum O$_3$/PS process parameters were O$_3$ dosage of 25.92 mg/min, reaction temperature of 70°C, PS dosage of 2 g/L, and initial pH of 4.5. Under these conditions, control experiments were conducted to compare the treatment efficiency of O$_3$/PS and other processes that included O$_3$ and/or PS.

Fig. 6a shows the treatment efficiencies of controlled processes (O$_3$/PS, O$_3$, thermal/PS, and PS processes). It can be seen from the figure that the best treatment efficiency was exhibited by O$_3$/PS process. In the PS process, the COD and CN removal efficiencies were only 56.82% and 26.40%, respectively. However, following thermal activation, the
COD and CN removal efficiencies significantly increased to 61.36% and 64.43%, respectively. Notably, the increase in CN reduction was significant, indicating activation of PS and production of SO$_4$\(^{-}\). In contrast, O$_3$ process achieved COD and CN removal efficiencies of 68.18% and 70.82%, which were 11.36% and 44.42% (COD) and 6.82% and 6.39% (CN) higher than those achieved by PS process and thermal-activated PS process, respectively, suggesting that O$_3$ could degrade organic pollutants in wastewater to a certain extent. Nevertheless, the treatment efficiency of these processes followed order of “O$_3$/PS > O$_3$ > Thermal/PS > PS” which is consistency with observations from Fig. 6b, and the best COD and CN removal efficiencies (90.60% and 96.99%, respectively) were presented by the O$_3$/PS process (at 70°C). This can be attributed to two aspects: (1) an increase in reaction temperature enriched the species and content of radicals which can effectively degrade organic pollutants and (2) solubility of O$_3$ increased under this condition, and as a result, oxidants could completely react with target organics. Besides, processes involving O$_3$ showed superior treatment efficiency than the others examined because DDNP wastewater mainly contains benzene-ring compounds and functional groups with an unsaturated bond as well as electron-rich moieties, both of which preferentially react with O$_3$. Moreover, in the thermal-activated PS process, the concentration and content of ROS significantly increased, resulting in further degradation of small organic acids that are relatively resistant to O$_3$ degradation.

4. Conclusions

For achieving high COD and CN removal efficiencies in DDNP wastewater treatment by O$_3$/PS process, the optimal operational parameters were determined as follows: O$_3$ dosage = 25.92 mg/min, reaction temperature = 70°C, PS dosage = 2 g/L, and initial pH = 4.5. After 20 min of reaction, the COD and CN removal efficiencies were 90.60% and 96.99%, respectively. UV-Vis spectra analysis showed that O$_3$/
PS process can effectively degrade benzene-ring compounds and functional groups containing unsaturated bond as well as electron-rich moieties. The thermal-activated PS process increased the ROS content, thus considerably enhancing the treatment efficiency. Taken together, these findings confirmed that O$_3$/PS process was an effective method for DDNP wastewater treatment, and that O$_3$-based technology could accomplish superior treatment efficiency for DDNP wastewater treatment.

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