

Article

A study on the removal of ammonia nitrogen and sulfides in tannery wastewater using photocatalytic oxidant

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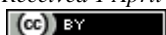
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Abstract

Odoriferous substances such as sulfides and ammonia nitrogen in tannery wastewater pose serious threats to the environment and public health, yet effective treatment methods remain limited. This study investigates the removal of these inorganic pollutants using photocatalytic oxidation with TiO₂ and WO₃ as catalysts. Simulated and real tannery wastewaters were treated under UV light (253.7 nm) in a batch reactor. The photocatalytic activity of single catalysts (TiO₂, WO₃) and their composites with different mass ratios was evaluated. Results showed that WO₃ exhibited superior degradation of inorganic pollutants compared to TiO₂, achieving over 91% sulfide removal under UV. The composite catalyst WO₃/TiO₂ significantly enhanced performance, with the optimal mass ratio determined as approximately 3.6:1 via mathematical modeling. Under this ratio, sulfide removal exceeded 90%, and ammonia nitrogen removal was also improved. X-ray diffraction analysis revealed that the enhanced activity is attributed to the heterostructure formation, which facilitates charge carrier separation and extends light absorption range. Notably, this work focuses on photocatalytic degradation of inorganic odoriferous compounds (sulfides and ammonia nitrogen) in the liquid phase, a rarely reported area rather than conventional organic pollutants. The composite catalyst shows promising potential for industrial application in tannery wastewater odor control.

Keywords tannery wastewater; photocatalytic oxidation; WO₃/TiO₂ composite; sulfide removal; ammonia nitrogen removal.

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1 Introduction

1.1 Research Review

The leather industry is a significant contributor to water pollution, generating complex wastewater streams laden with organic compounds, dyes, heavy metals, and high levels of volatile organic compounds (VOCs,

including ammonia nitrogen and sulfides) (Natarajan et al., 2013; Zhao et al., 2017). These VOCs, including aromatic hydrocarbons like BTEX (benzene, toluene, ethylbenzene, xylene) and other harmful compounds such as 2-phenylethanol, present severe environmental and public health risks (Emmanuel et al., 2023; Natarajan et al., 2013). While conventional treatment methods often fail to degrade these recalcitrant pollutants efficiently, advanced oxidation processes, particularly heterogeneous photocatalysis, have emerged as a promising and cost-effective solution (Zhao et al., 2017; Kamalesh et al., 2025).

Photocatalytic oxidation technology is an efficient treatment method for wastewater containing organic pollutants (Hunaiti et al., 2024). The process relies on a semiconductor catalyst, typically titanium dioxide (TiO_2), which when illuminated with light of sufficient energy generates electron-hole pairs (Natarajan et al., 2013). These species react with water and oxygen to form highly reactive radicals, primarily hydroxyl radicals ($\cdot\text{OH}$) and superoxide radicals ($\cdot\text{O}_2^-$), which can non-selectively oxidize and mineralize organic pollutants, including VOCs, into carbon dioxide and water (Emmanuel et al., 2023; Zhang et al., 2020).

The composition of VOCs in leather wastewater is complex. Research has identified specific organic compounds within leather industry wastewater, including nonadec-1-ene, 2-phenylethanol, and 2,4-di-tert-butylphenol (Natarajan et al., 2013). In a key study, these compounds were separated, purified, and characterized using advanced techniques like GC-MS and NMR spectroscopy (Natarajan et al., 2013). The same study demonstrated that 2-phenylethanol, a prevalent VOC, could be completely degraded (100%) using a standard Degussa P-25 TiO_2 photocatalyst under UV light irradiation after prolonged treatment (30 hours) (Natarajan et al., 2013). This confirmed the efficacy of photocatalysis for mineralizing specific target compounds (Natarajan et al., 2013).

Efforts to enhance the performance of TiO_2 have focused on increasing its surface area and porosity. Mesoporous TiO_2 materials, synthesized via a sol-gel route, possess a high surface area ($40.03 \text{ m}^2/\text{g}$) and exhibit excellent photocatalytic activity towards the degradation of organic pollutants in tannery wastewater under both UV-light and natural sunlight irradiation (Zhao et al., 2017). The performance of these materials is influenced by key parameters including catalyst dosage, solution pH, and H_2O_2 concentration (Zhao et al., 2017). A novel continuous photocatalytic system using a TiO_2 -coated plate, activated by UV light, has also proven highly effective (Shahbazi and Pedram, 2021). This setup, when combined with a FeCl_3 coagulation pre-treatment, significantly reduced chemical oxygen demand (COD) from 370 to $50 \text{ mg}\cdot\text{L}^{-1}$ and substantially lowered sulfate and chromium ion concentrations, demonstrating its potential for real-world industrial applications (Shahbazi and Pedram, 2021).

While TiO_2 is the most widely studied photocatalyst, its wide band gap (approx. 3.2 eV) limits its activity to the UV spectrum. To extend activity into the visible light range and improve charge separation, composite photocatalysts have been developed. A visible-light-driven ternary catalyst, $\text{TiO}_2\text{-NiFe}_2\text{O}_4\text{-Chitosan}$, was shown to remove up to 95% of xylene, 99% of toluene, and 90% of 1-methyl naphthalene from water within 120 minutes, with hydroxyl radicals identified as the key active species (Hunaiti et al., 2024). Furthermore, heterogeneous structures like WO_3/TiO_2 have shown great promise. Adding WO_3 to TiO_2 can improve the overall photocatalytic activity for pollutants, and a catalyst with a $\text{WO}_3:\text{TiO}_2$ ratio of 3.6:1 (catalyst 2) was found to have a superior elimination effect for inorganic pollutants in a real sewage treatment plant in Beijing, achieving a sulfide removal rate of over 90% (Yang et al., 2018). Similarly, spray-deposited stratified WO_3/TiO_2 photoelectrodes have achieved up to 98% degradation of organic dyes within 30 minutes under sunlight, due to an extended absorption spectrum and high stability (Hunge et al., 2018).

Research is also expanding beyond traditional metal oxides. Zeolite-based composites have been explored for their dual function in adsorption and photocatalysis, showing significant potential for the removal of VOCs from wastewater (Liaquat et al., 2024). Other highly efficient materials are also emerging. For example, a

CQDs/Bi₂WO₆ hybrid material, synthesized via an in situ hydrothermal method, achieved 96.9% degradation of gaseous toluene and 97.1% for formaldehyde within just 120 minutes under visible light, and exhibited high stability for reuse (Liu et al., 2020). Additionally, the integration of photocatalysis with adsorption, such as using a TiO₂/diatomite composite, has been shown to be a highly effective strategy, where factors like relative humidity and reaction atmosphere play a crucial role in the overall VOC removal efficiency (Zhang et al., 2025).

In general, photocatalytic oxidation stands as a highly effective technology for the removal of hazardous VOCs from tannery and other industrial wastewaters. Key advancements include the targeted identification of specific pollutants (Natarajan et al., 2013), the development of high-surface-area mesoporous TiO₂ (Zhao et al., 2017), and the design of novel composite systems like TiO₂-NiFe₂O₄-Chitosan and WO₃/TiO₂ heterojunctions that offer improved efficiency under visible light (Hunaiti et al., 2024; Yang et al., 2018). The transition from batch to continuous reactor systems (Shahbazi and Pedram, 2021) and the exploration of materials like zeolite-based composites and CQDs/Bi₂WO₆ (Liaquat et al., 2024; Liu et al., 2020) are significant strides towards practical application. Future research should focus on optimizing these advanced materials for real-world, mixed-wastewater conditions and developing scalable, cost-effective photocatalytic reactors to fully realize the potential of this green technology for industrial pollution control.

1.2 Purpose and Framework of This Study

China is a major producer and consumer of leather products, with leather production enterprises mainly concentrated in most areas south of the Yangtze River, especially the Pearl River Delta region. On one hand, the leather industry brings significant economic benefits to local areas; on the other hand, it is also a severely polluting industry, causing substantial pollution and ecological damage to surrounding areas. With China's economic transformation, extensive industries are gradually transitioning towards intensive and concentrated models. The previous pattern of reckless economic growth is no longer suitable for current societal needs. Past treatments of tannery wastewater mainly focused on the removal of organic matter, heavy metals, and dyes. However, insufficient attention has been paid to odorous pollutants generated during leather manufacturing, which are often left untreated or rarely treated. The gaseous pollution caused by the leather industry, especially VOCs, threatens both the atmosphere and public health. Studies indicate that when H₂S content in water exceeds 0.5 mg/L, it becomes toxic to fish and other aquatic organisms (Liu and Zhang, 1998). When released into the air, its olfactory threshold is mostly in the order of 10⁻⁴ ppm, producing an extremely unpleasant odor even at very low concentrations, and it has toxic effects on the human central nervous system, causing nausea and headaches at low concentrations, and potentially spasms or even suffocation at higher concentrations (Zhang and Han, 1995).

In recent years, TiO₂ photocatalytic technology has gained increasing favor among researchers due to its high catalytic activity against chemical pollutants and strong antimicrobial properties. Numerous studies have demonstrated the effectiveness of photocatalytic oxidation technology against EEDs (Environmental Endocrine Disruptors). Chemicals and organic compounds present in air and water pose serious threats to human health and are the root cause of various diseases. As people become more health-conscious, photocatalytic technology is being widely applied in water treatment and the degradation of harmful substances due to its universal degradation advantages. In fact, photocatalytic oxidation technology has already been commercialized for indoor air purification. However, its application in wastewater treatment remains largely at the laboratory stage. Solving the industrialization of photocatalytic oxidation technology for wastewater treatment holds significant practical implications and economic benefits.

Previous research on photocatalytic oxidation has mostly focused on the semiconductor material TiO₂, primarily targeting the degradation of organic compounds. Although there is some research on inorganic

compounds, reports are scarce. Given that most pollutants generated during the leather-making process are inorganic chemical additives, this study builds upon previous research by using nanocatalysts to degrade volatile gases produced during leather processing. Research has shown that different catalysts possess varying oxidative and reductive capabilities for different pollutants, consistent with the characteristic that the reaction substrate influences the catalytic activity of photocatalysts.

Based on a summary of existing work, this study utilizes techniques such as heterogeneous polymer photocatalytic oxidation, targeting VOCs generated during leather processing, to study the effects and mechanisms of photocatalytic oxidation for harmful substance removal, thereby conducting further exploration for the practical industrial application of this technology.

1.3 Research Approach of This Study

Starting from the perspective of application and practical technology research, this study characterizes the wastewater from the industrial production process. Using this as the research object, we investigate the photolysis of ammonia nitrogen and sulfides present in the wastewater and studies their mechanisms.

Specific contents include:

- (1) Water quality analysis of a specific tannery wastewater;
- (2) Photocatalytic oxidation effects of catalysts TiO_2 and WO_3 on tannery wastewater;
- (3) Application of X-ray diffraction to analyze the crystal forms of TiO_2 and WO_3 to explore the influence of catalyst crystal phase structure on catalytic performance;
- (4) Composition of TiO_2/WO_3 composite catalysts in a certain ratio and testing of their catalytic performance;
- (5) Treatment to enhance the catalytic activity of TiO_2 and determination of the catalytic ability of mixed-crystal TiO_2 ;
- (6) Exploration of external conditions for the photocatalytic oxidation reaction to determine the optimal reaction conditions.

On this basis, due to limited conditions, the study of photocatalytic oxidation degradation of VOCs only progressed to the effectiveness study. Future research could focus on the immobilization and modification of semiconductor materials and further investigation of the mechanisms, providing more direct and effective references for the industrial application of this technology in wastewater treatment.

2 Materials and Methods

2.1 Collection, Storage, and Analysis of Waste Liquid

The waste liquid was collected from a tannery in Jiangmen City, Guangdong, China. Water samples were taken from various stages of the leather-making process. Due to the complexity of the tanning process, different chemical raw materials are added at different stages. For example, soaking and dehairing wastewater has a high pollutant load, accounting for over 20% of the total production wastewater, containing large amounts of lime, sulfides, pigments, soluble proteins, fats, hair, and organic matter. The sulfide concentration ranges from 1 to 2 g/L, COD_{Cr} concentration ranges from 20 to 40 g/L, and the wastewater is strongly alkaline with a pH of 13-14. Tanning wastewater comes from the tanning stage, with major pollutants being heavy metals and a weakly acidic pH. Additionally, there are dyeing wastewater, washing wastewater, etc. Due to the particularity of the tanning process, the pollutants in the discharged wastewater vary significantly, and the discharge is intermittent, causing large fluctuations in the quality of the comprehensive wastewater at different times of the day. Current tannery wastewater treatment often adopts centralized treatment methods, resulting in poor treatment efficiency and difficulty meeting standards. Given the wastewater characteristics, we performed segmented sampling during the collection process based on the different pollutants in the waste liquid

discharged from different processes, to understand the variation patterns of sulfides and ammonia nitrogen in the wastewater over time.

Table 2-1 Water sample collection.

Section	Process Name	pH	Color and Odor
Preparation Workshop	Liming	12.4	Translucent milky white, putrid odor
	Soaking		Milky white, putrid odor
Production Workshop	Pickling	6.5	Turbid, foul odor
	Deliming/Softening	8.9	Turbid, foul odor
	Neutralization		Brown, pungent odor

Table 2-2 Analysis results of tannery wastewater quality.

Sample Name	Analysis Item	Result	Unit	Detection Method
Liming	Sulfide (as S ²⁻)	1640	mg/L	"Water and Wastewater Monitoring Methods"
	Ammonia Nitrogen (as N)	896	mg/L	Spectrophotometry (HJ 535-2009)
Soaking	Total Nitrogen	896	mg/L	UV Spectrophotometry
	Ammonia Nitrogen (as N)	353	mg/L	Spectrophotometry (HJ 535-2009)
Pickling	Total Nitrogen	366	mg/L	UV Spectrophotometry
	Sulfide (as S ²⁻)	7.35	mg/L	"Water and Wastewater Monitoring Methods"
	Ammonia Nitrogen (as N)	/	mg/L	Spectrophotometry (HJ 535-2009)
Softening	Total Nitrogen	/	mg/L	UV Spectrophotometry
	Sulfide (as S ²⁻)	185	mg/L	"Water and Wastewater Monitoring Methods"
Neutralization	Ammonia Nitrogen (as N)	6990	mg/L	Spectrophotometry (HJ 535-2009)
	Total Nitrogen	7050	mg/L	UV Spectrophotometry
	Sulfide (as S ²⁻)	2.21	mg/L	"Water and Wastewater Monitoring Methods"
	Ammonia Nitrogen (as N)	24.2	mg/L	Spectrophotometry (HJ 535-2009)
Comprehensive Wastewater	Total Nitrogen	27.1	mg/L	UV Spectrophotometry
	Sulfide (as S ²⁻)	1.78	mg/L	"Water and Wastewater Monitoring Methods"
	Ammonia Nitrogen (as N)	27	mg/L	Spectrophotometry (HJ 535-2009)
	Total Nitrogen	34.1	mg/L	UV Spectrophotometry

The appearance of the tannery wastewater sample was dark brown-black, opaque, with a small amount of suspended solids and a strong pungent odor. The collected waste liquid was from the wastewater discharged by the factory on the previous day, collected at different times and stored refrigerated at low temperatures for experimental analysis. The collected water samples are shown in Table 2-1.

The results of the water sample analysis are shown in Table 2-2.

According to the national "Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant" (GB18918-2002), the primary standard for sulfides in discharged industrial wastewater is 0.5 mg/L; secondary standard: 0.5 mg/L; tertiary standard: 1.0 mg/L. For ammonia nitrogen, the primary standard is 1.0 mg/L; secondary standard: 1.0 mg/L; tertiary standard: 2.0 mg/L. The analysis results show that sulfides and ammonia nitrogen can be up to over 1600 times and 7000 times these standards, respectively. The highest sulfide content in the liming stage is due to the large amount of sodium sulfide added. As the pH of the wastewater changes, the sulfide content in the comprehensive wastewater drops to 1.78 mg/L, because during the pickling stage of the tanning process, the pH changes, causing a large amount of sulfide to convert to hydrogen sulfide and escape into the air. Similarly, the ammonia nitrogen content peaks during the deliming/softening stage, attributed to the large amount of ammonium salts added. In subsequent stages, ammonia nitrogen escapes into the air as NH_3 , causing air pollution.

For treating VOCs (mainly sulfides and ammonia nitrogen) in tannery wastewater, segmented pre-treatment technology should be adopted. The pH of the wastewater varies at different stages, which is the main reason for the conversion of large amounts of toxic substances from the liquid phase to the gas phase. Once converted to the gas phase, treatment becomes more difficult.

2.2 Experimental Setup and Reagents

2.2.1 Experimental Setup

A 500 ml beaker was used as the reactor for the photocatalytic oxidation test. Two 40W ultraviolet lamps were used as the photolysis light source. Each lamp tube is approximately 1.2 meters long with a wavelength spectrum of 253.7 nm. They have independent switches. An aluminum reflector lined with aluminum foil was installed above each mercury lamp. The vertical distance from the UV light source to the reaction liquid surface was 25 cm. The experimental setup is shown in Fig. 2-1.

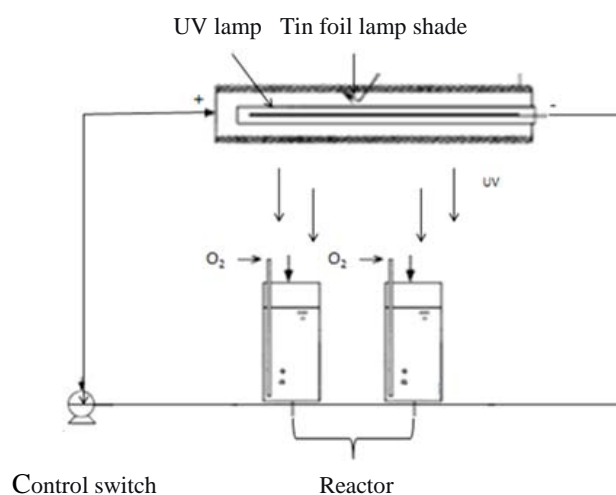


Fig. 2-1 Diagram illustration of test device.

2.2.2 Materials and Instruments

Test Materials:

The various catalysts used in the experiment are solid powders, all nanomaterials. German degussa nano titanium dioxide P25 (anatase to rutile ratio approx. 70:30);

WO₃ analytical grade, Fe₂O₃ analytical grade, tungsten powder;
Sodium sulfide: AR, Zinc acetate; Sodium acetate;
Antioxidant; Ferric ammonium sulfate; N,N-dimethyl-p-phenylenediamine (p-amino dimethylaniline);
K₂Cr₂O₇; NaOH; Concentrated sulfuric acid; 95% ethanol: AR; Anhydrous ethanol: AR; Guangzhou Reagent
Factory; Distilled water: homemade; Deionized water: homemade.

Test Instruments:

Electronic balance JH502 (sensitivity 0.1g) Shanghai Precision Scientific Instrument Co., Ltd.;
Low-pressure mercury lamp ZSZ type 253.7nm Guangzhou Fuhua Experimental Equipment Co., Ltd.;
Constant temperature magnetic stirrer HT-3 Guangzhou Fuhua Experimental Equipment Co., Ltd.;
Electric drying oven CS 202-B Chongqing Galaxy Test Instruments Co., Ltd.;
Centrifuge 800 Jiangsu Yancheng Scientific Instrument Factory;
Air pump CTB-608;
Box-type resistance furnace (Muffle furnace) 5-12;
721 Spectrophotometer;
X-ray photoelectron spectrometer Thermo-VG Scientific;
Beakers, weighing paper, graduated cylinders, glass rods, pipettes, etc.

2.2.3 Preparation of Solutions

The method for determining ammonia nitrogen in this experiment is the Nessler's reagent colorimetric method.
The method for determining sulfides is the methylene blue spectrophotometric method.

Preparation of chromogenic reagents:

Nessler's reagent, HgCl₂-KI-KOH (Mercuric chloride-Potassium iodide-Potassium hydroxide): Dissolve 15g of potassium hydroxide (KOH) in 50 mL of water, cool to room temperature. Dissolve 5g of potassium iodide (KI) in 10 mL of water. While stirring, add 2.5g of mercuric chloride (HgCl₂) powder in small portions to the potassium iodide solution until the solution turns deep yellow or a slight micro-red precipitate appears and dissolves slowly. Stir well, then switch to adding saturated mercuric chloride solution dropwise. Stop adding when a small amount of vermilion precipitate no longer dissolves. While stirring, slowly add the cold potassium hydroxide solution to the above mixture of mercuric chloride and potassium iodide, and dilute to 100 mL. Let stand in the dark for 24 hours, decant the supernatant, store in a brown bottle with a rubber stopper in a dark place.

N,N-dimethyl-p-phenylenediamine solution: Dissolve 2g of N,N-dimethyl-p-phenylenediamine hydrochloride [NH₂C₆H₄N(CH₃)₂·2HCl] in water. Slowly add 200 ml of concentrated sulfuric acid, cool, then dilute with water to 1000 ml and shake well. Store tightly sealed in a brown bottle at room temperature.

Ferric ammonium sulfate solution: Dissolve 25g of ferric ammonium sulfate [Fe(NH₄)(SO₄)₂·12H₂O] in water containing 5 ml of concentrated sulfuric acid, dilute to 250 ml with water, and shake well. If the solution is turbid or contains insoluble matter, filter before use.

Simulated ammonia nitrogen wastewater: Pipette 8.35 ml of 25% ammonia water, dissolve in 300 ml of deionized water to prepare a simulated wastewater containing 6.99×10^3 mg/L.

Simulated sulfide wastewater: Weigh 0.5g of Na₂S, dissolve in 300 ml of deionized water to prepare a simulated wastewater containing 1.65×10^3 mg/L.

2.3 Experimental Methods

The experimental method adopted was the suspended photocatalytic oxidation method:

(1) The reactor is a 500 mL beaker;

(2) The light source consists of two 40W low-pressure UV lamps (253.7 nm) with independent switches. A reflector lined with aluminum foil is installed above the UV lamps. The vertical distance from the light source to the bottom of the beaker is 30 cm;

(3) Use an electronic balance to weigh an appropriate amount of photocatalyst and place it into the reactor containing simulated wastewater. Stir with a constant temperature magnetic stirrer while simultaneously bubbling oxygen using an oxygen pump, allowing the photocatalyst to be uniformly suspended in the semi-closed reactor for adsorption and reaction experiments.

(4) After UV or visible light treatment for a certain period, take out the reaction solution and centrifuge at 4500 r/min for 15 minutes to separate solid and liquid. Separate the catalyst, then draw the supernatant for analysis and determination of ammonia nitrogen or sulfide values.

Adjust the pH of the reaction system using appropriately concentrated HNO_3 and NaOH solutions. Visible light adsorption/oxidation experiments were carried out under sunlight, while UV adsorption/oxidation experiments were carried out under low-pressure mercury lamps.

2.4 Evaluation of Experimental Effects

This experiment evaluated the photocatalytic oxidation effect using two parameters: the measured value of each indicator after the test with different light sources for catalytic excitation, and its removal rate. The experimental effect calculation method for the removal rate η can be obtained by the following equation:

$$\eta = (C_0 - C) / C_0 \times 100\%$$

Where C_0 is the initial concentration of the untreated waste liquid (mg/L), and C is the remaining amount of the indicator to be measured (mg/L) after the photocatalytic oxidation reaction or dark reaction of the waste liquid.

3 Catalytic Activity of Photocatalysts

3.1 Standard Curves for Ammonia Nitrogen and Sulfide Determination

3.1.1 Preparation of Standard Curve for Ammonia Nitrogen Determination

Nessler's reagent colorimetric method was used.

Preparation of standard curve (Fig. 3-1): Pipette 0, 0.50, 1.00, 3.00, 5.00, 7.00, and 10.0 mL of ammonium standard solution into 50 mL colorimetric tubes, add water to the mark. Add 1.0 mL of potassium sodium tartrate solution and mix. Add 1.5 mL of Nessler's reagent and mix. Let stand for 10 minutes, then measure the absorbance at a wavelength of 420 nm using a 20 mm cuvette with water as reference.

Subtract the absorbance of the zero-concentration blank tube from the measured absorbance to obtain the corrected absorbance. Plot the standard curve with ammonia nitrogen content (mg) on the x-axis against corrected absorbance on the y-axis.

Obtain the ammonia nitrogen content (N; mg) from the standard curve based on the measured absorbance of the water sample minus the absorbance of the blank test.

$$N \text{ (mg/L)} = m / V * 1000$$

Where: m = ammonia nitrogen amount found from the calibration curve (mg); V = water sample volume (mL).

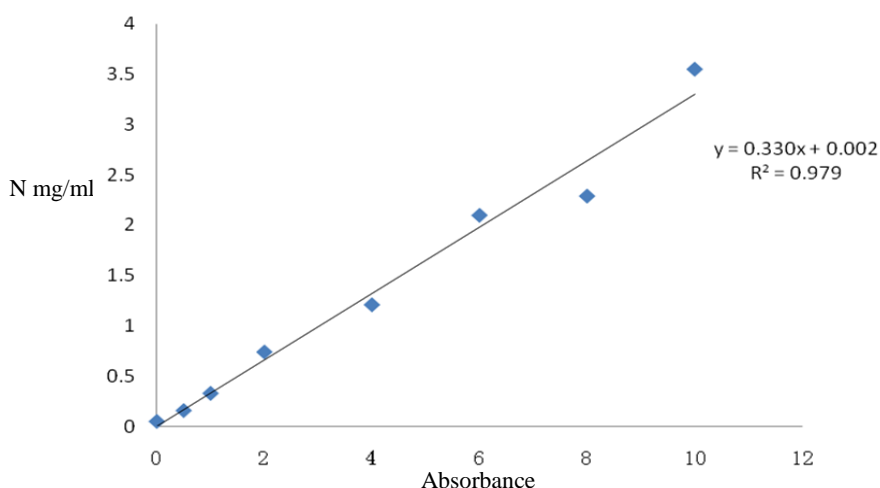


Fig. 3-1 Standard curve for NH₃ absorbance.

3.1.2 Preparation of Standard Curve for Sulfide Determination

Methylene blue spectrophotometry method HZ-HJ-SZ-0098 was used.

Preparation of standard curve (Fig. 3-2): Take nine 100 mL stoppered colorimetric tubes, add 20 mL of zinc acetate-sodium acetate solution to each. Pipette 0, 0.50, 1.00, 2.00, 3.00, 4.00, 5.00, 6.00, and 7.00 mL of sodium sulfide standard solution into the tubes, add water to about 60 mL. Slowly add 10 mL of N,N-dimethyl-p-phenylenediamine solution along the tube wall, immediately stopper and gently invert once. Add 1 mL of ferric ammonium sulfate solution, immediately stopper and shake thoroughly. Let stand for 10 minutes, then dilute to the mark with water and shake well. Using a 1 cm cuvette with water as reference, measure the absorbance at a wavelength of 665 nm. Perform a blank test simultaneously. Plot the calibration curve with the absorbance of each standard solution minus the blank test absorbance on the y-axis and the corresponding sulfide ion content (µg) in the standard solution on the x-axis.

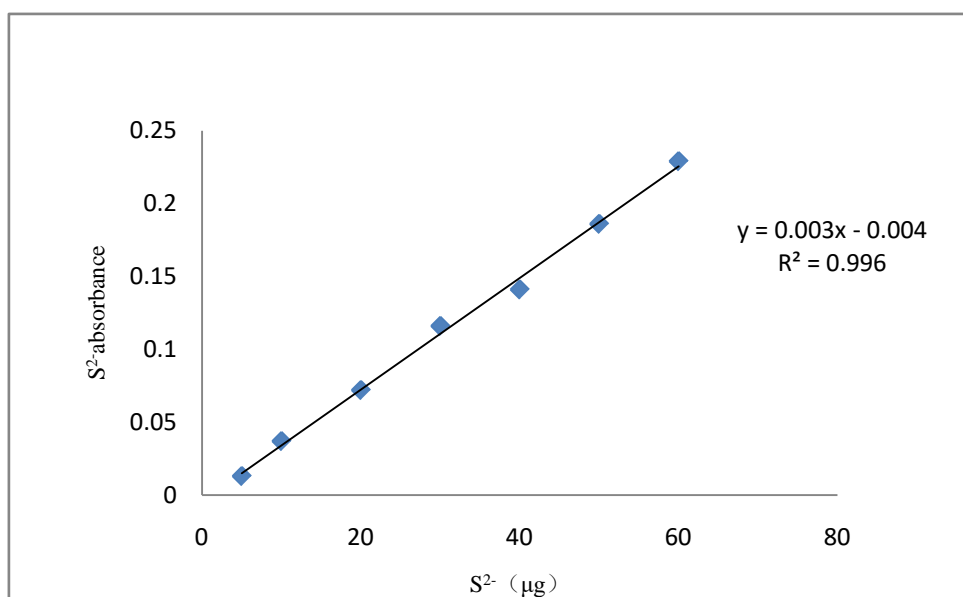


Fig. 3-2 Standard curve for S²⁻ absorbance.

Sulfide content c (S^{2-} ; mg/L) is calculated as follows:

$$c = m / V * 1000$$

Where: m = amount of sulfide found from the calibration curve (mg); V = water sample volume (mL).

3.2 Determination of Photocatalytic Activity of Single Catalysts

3.2.1 TiO₂ Photocatalytic Activity

3.2.1.1 Activation of Catalyst TiO₂

Current research confirms that TiO₂ is the photocatalyst with the highest activity and no photocorrosion. Studies indicate that the photocatalytic activity of TiO₂ is related to its crystal type and particle size (Wei et al., 1989). TiO₂ mainly has four crystal types: anatase, rutile, brookite, and a metastable TiO₂ (B) phase. However, anatase and rutile are the two most common crystalline forms in photocatalysis research. Anatase is a low-temperature phase, while rutile is a relatively stable high-temperature phase; at 500-600°C, anatase irreversibly converts to rutile at high temperatures. From an energy level perspective, rutile has a narrower bandgap than anatase, indicating it can absorb a wider range of wavelengths. Commercially available German Degussa nano titanium dioxide P25 (anatase to rutile ratio about 70:30), produced by gas-phase method, was used. To enhance catalyst activity, following the method of Lyu Hong, it was calcined at a high temperature of 600°C to change its crystal structure for catalyst modification. This is because as the calcination temperature increases, the bandgap energy of the crystal structure gradually decreases, and the specific surface area also gradually decreases, exhibiting quantum size effects.

Test method: Place TiO₂ in a muffle furnace and slowly heat to 600°C. The starting temperature is 30°C, increase by 5°C every 5 minutes. Calcine at 600°C for 4 hours, then cool to room temperature in air. The catalyst activation used in the following experiments all refers to this calcination method.

3.2.1.2 Catalytic Performance of Catalyst TiO₂

The catalyst selected for the experiment was German Degussa nano titanium dioxide P25 powder. The simulated wastewater used for the photocatalytic oxidation reaction on tannery wastewater was prepared using deionized water based on the amounts of ammonia nitrogen (7.05×10^3 mg/L) and sulfides (1.64×10^3 mg/L) present in the raw tannery wastewater discharged during the leather-making process. The following tests all used 300 ml of the reaction solution in the reactor. The TiO₂ dosage was 0.8 g, the solution pH was 12, the reaction temperature was room temperature, air was bubbled in, the UV lamp power was 80 W, and the reaction time was 120 minutes. After the reaction, the solution was centrifuged at 4500 r/min for 15 minutes to separate solid and liquid. The catalyst was separated, and the supernatant was drawn for analysis and determination of ammonia nitrogen or sulfide values. The test results are shown in Table 3-1.

Table 3-1 Comparison of catalytic effects of TiO₂ on ammonia nitrogen under different light sources.

	Original Sample	Visible Light Reaction	Blank Test	UV Light Reaction
Amount of TiO ₂ added (g)	/	0.8	0	0.8
UV	/	/	Yes	Yes
Ammonia nitrogen amount after degradation (mg/ml)	6.99	4.226719	3.232516	2.852671
Ammonia nitrogen removal rate (%)	/	39.50%	54%	59%

*Table shows dark reaction & blank reaction of TiO₂ photocatalysis.

It can be found from Tables 3-1 and 3-2 that when using semiconductor photocatalytic treatment agents for VOCs in wastewater, the semiconductor catalyst can partially decompose or adsorb harmful substances even in the absence of light, causing a decrease in VOCs concentration in the solution. Moreover, under UV lamp irradiation, VOCs also undergo decomposition, reducing pollutant concentration, which is consistent with previous research on UV lamp deodorization. To verify the role of semiconductor photocatalysis in the degradation of inorganic harmful substances, this experiment performed orthogonal tests with and without catalysts and under different light sources. The results showed that TiO₂ photocatalysts are effective in the degradation of inorganic substances.

Table 3-2 Comparison of catalytic effects of TiO₂ on sulfides under different light sources.

	Original Sample	Visible Light Test	Blank Sample	UV Light Test
Amount of TiO ₂ added (g)	/	0.8	0	0.8
UV	/	/	Yes	Yes
Sulfide amount after degradation (mg/ml)	1.64	0.3	0.42	0.16
Sulfide removal rate (%)	/	81.80%	75%	90%

*Table shows dark reaction & blank reaction of TiO₂ photocatalysis).

3.2.2 WO₃ Photocatalytic Activity

The catalyst selected for the experiment was nano tungsten trioxide powder. The simulated wastewater used for the photocatalytic oxidation reaction on tannery wastewater was prepared using deionized water based on the amounts of ammonia nitrogen (7.05×10^3 mg/L) and sulfides (1.64×10^3 mg/L) present in the raw tannery wastewater. The following tests all used 300 ml of the reaction solution in the reactor. The WO₃ dosage was 0.8 g, the solution pH was 12, the reaction temperature was room temperature, air was bubbled in, the UV lamp power was 80 W, and the reaction time was 120 minutes. After the reaction, the solution was centrifuged at 4500 r/min for 15 minutes to separate solid and liquid. The catalyst was separated, and the supernatant was drawn for analysis and determination of ammonia nitrogen or sulfide values. The test results are shown in Table 3-3.

Table 3-3 Comparison of catalytic effects of WO₃ on ammonia nitrogen under different light sources.

	Original Sample	Visible Light Test	Blank Sample	UV Light Test
Amount of WO ₃ added (g)	/	0.8	0	0.8
Illumination	/	/	Yes	Yes
Ammonia nitrogen amount after degradation (mg/ml)	6.99	3.869995	3.2909791	2.569714
Ammonia nitrogen removal rate (%)	/	45%	53%	63%

*Table shows dark reaction & blank reaction of WO₃ photocatalysis.

Table 3-4 Comparison of catalytic effects of WO_3 on sulfides under different light sources.

	Original Sample	Visible Light Sample	Blank Sample	Test Sample
Amount of WO_3 added (g)	/	0.8	0	0.8
UV	/	/	Yes	Yes
Sulfide amount after degradation (mg/ml)	1.64	0.185	0.225	0.143
Sulfide removal rate (%)	/	88.70%	86%	91%

*Table shows dark reaction & blank reaction of WO_3 photocatalysis.

As seen from Tables 3-3 and 3-4, the photocatalytic oxidant WO_3 exhibits stronger oxidation activity for degrading VOCs in wastewater than TiO_2 . This may be because WO_3 is a semiconductor with a narrower bandgap (bandgap of WO_3 is 2.7 eV, smaller than TiO_2 's bandgap of 3.2 eV). The photocatalytic oxidation reaction occurs when the semiconductor absorbs photons with energy greater than its bandgap width, causing electron transitions that generate electron-hole pairs. Thus, semiconductors with narrower bandgaps can absorb longer wavelength light. Consequently, the catalytic performance of WO_3 under visible light is higher than that of TiO_2 . Previous research suggested that TiO_2 has a better oxidation effect on organic matter. However, this experiment shows that WO_3 has an advantage in the degradation of inorganic substances.

Furthermore, when WO_3 or TiO_2 is used alone, both show high degradation activity for sulfides. This is because the presence of anions in the water can compete for reactive oxygen species (e.g., hydroxyl radicals), thereby reducing the rate of pollutant oxidation (Wakits et al., 2005). Carp et al. confirmed this regarding the effect of anions on the photolysis of organic compounds. Carp suggested that anions like sulfate and phosphate form specific radicals during the catalytic reaction, which in turn initiate and promote the degradation reaction of organic compounds.

3.3 Determination of Photocatalytic Activity of Composite Catalysts

3.3.1 Catalytic Performance of Composite Catalysts

Single TiO_2 or WO_3 have their own advantages and disadvantages when treating pollutants. Current research on catalysts increasingly focuses on the modification of catalytic materials and the synthesis of novel composite materials, including doping and the development of composite materials for bandgap engineering. This experiment mixed two effective catalysts to investigate the photocatalytic oxidation effect of the composite material on inorganic pollutants.

Tada proposed that ternary composite nanocatalysts possess strong photocatalytic reduction activity. By using narrow bandgap semiconductors and metal doping, novel catalyst materials were constructed (Irie et al., 2008).

Based on the different catalytic efficiencies, this experiment fixed the amount of WO_3 and doped it with different amounts of TiO_2 to form WO_3/TiO_2 novel composite semiconductor materials with different ratios. Their ability to photocatalytically treat inorganic pollutants was tested to study the performance and catalytic mechanism of the novel catalyst. The reaction conditions were the same as the single catalyst tests: the initial fixed amount of WO_3 was 0.5 g. After the reaction, the solution was centrifuged at 4500 r/min for 15 minutes to separate solid and liquid. The catalyst was separated, and the supernatant was drawn for analysis and determination of ammonia nitrogen or sulfide values.

Table 3-5 Effect of WO₃ on ammonia nitrogen under different light sources (TiO₂ doping effect on WO₃ photocatalysis).

	Original Sample	1#	2#	3#	4#	5#	6#
Amount of TiO ₂ added (mg)	/	0	50	100	200	250	300
Ammonia nitrogen amount after degradation (mg/ml)	6.99	3.322	3.269	3.065	2.489	3.728	3.393
Ammonia nitrogen removal rate (%)	/	43%	53%	56%	64%	46%	51%

Table 3-6 Effect of WO₃ on sulfides under different light sources (TiO₂ doping effect on WO₃ photocatalysis).

	Original Sample	1#	2#	3#	4#	5#	6#
Amount of TiO ₂ added (mg)	/	0	50	100	200	250	300
Sulfide amount after degradation (mg/ml)	1.64	0.15	0.125	0.098	0.084	0.084	0.119
Sulfide removal rate (%)	/	91%	92%	94%	94%	94%	93%

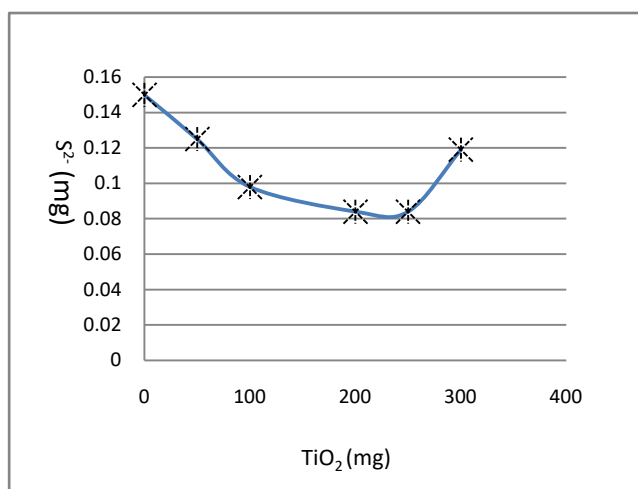
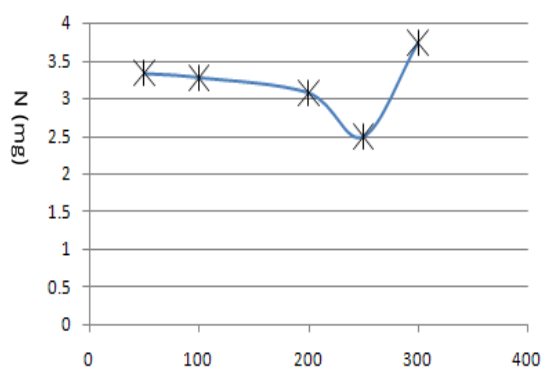


Fig. 3-3 Comparison of catalytic effects of WO₃/TiO₂ composite system.

As shown in Tables 3-5, 3-6, and Fig. 3-3, adding a certain amount of WO_3 to the WO_3/TiO_2 system can enhance the photocatalytic activity of the reaction system. As the amount of TiO_2 gradually increases, the photocatalytic activity for both ammonia nitrogen and sulfides increases to varying degrees (Sajjad et al., 2010). This is consistent with Irie et al.'s findings that WO_3 can increase photocatalytic activity by extending the light absorption wavelength of TiO_2 materials. When alone, TiO_2 can absorb light only up to 410 nm, whereas doping with WO_3 extends this to 460 nm for visible-light-excited photolysis. However, we also noticed that when the TiO_2 amount increased to a certain point, the degradation of organic pollutants decreased. This is because the semiconductor materials in the reaction solution scatter light, causing light energy loss.

3.3.2 Quantitative Analysis of Composite Catalyst

Based on the removal rates of ammonia nitrogen and sulfides for different component ratios in the composite catalyst (Tables 3-5 and 3-6), fitting was performed using SPSS software. The fitting is shown in Fig. 3-4.

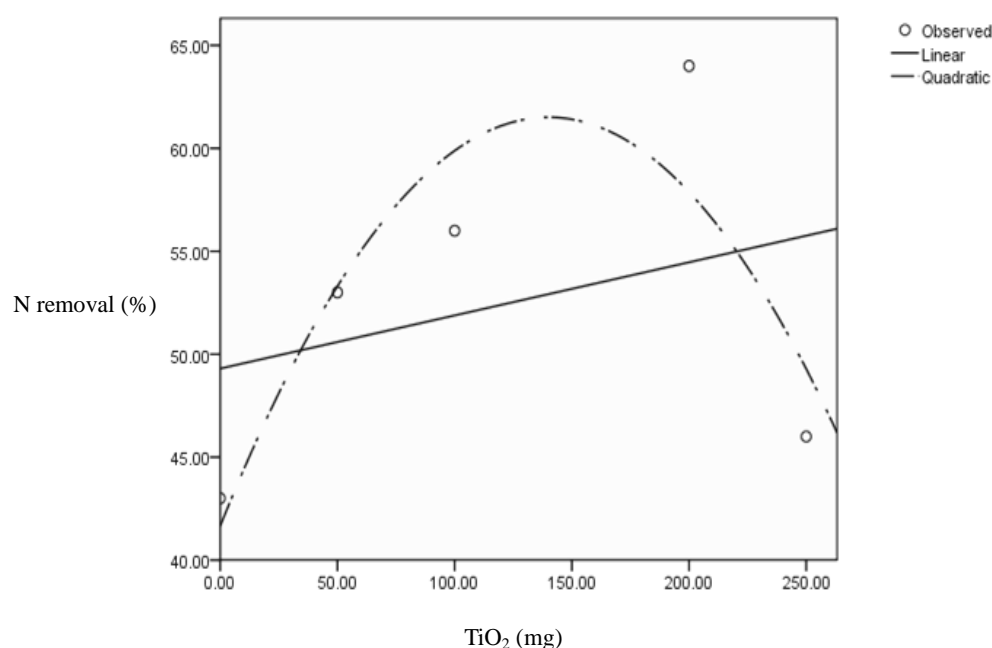


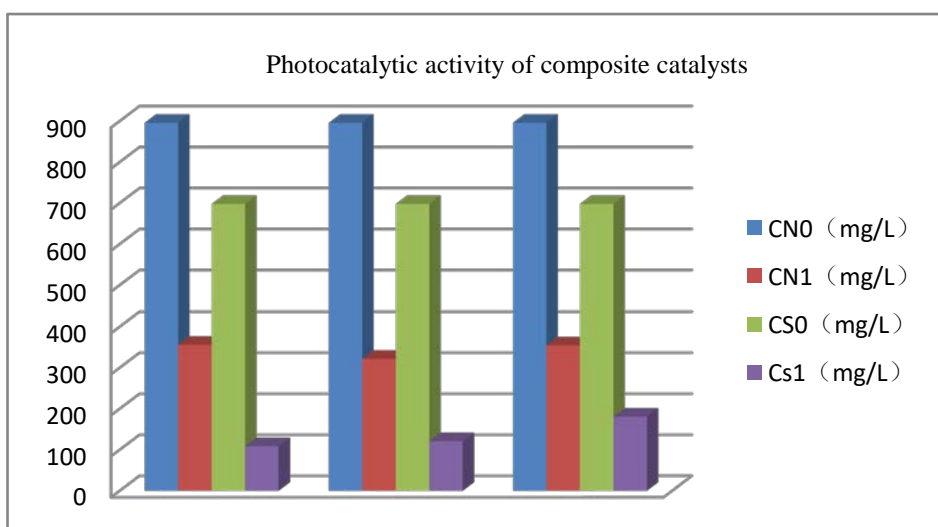
Fig. 3-4 Mathematical model fitting for optimal WO_3/TiO_2 ratio.

Obtained fitted mathematical model: $y = 41.66 + 0.28x - 0.00101x^2$ (Correlation coefficient $R=0.765$; $F=3.247$). Deriving the equation gives: $y' = 0.28 - 0.00202x$. Setting $y' = 0$, we find $x_1 = 138$. The calculation results show that with a fixed amount of WO_3 , the optimal degradation effect for ammonia nitrogen is achieved when the TiO_2 dosage is 138 mg. Therefore, the optimal mass fraction ratio for the effective components in the composite material is approximately $\text{WO}_3:\text{TiO}_2 \approx 3.6:1$.

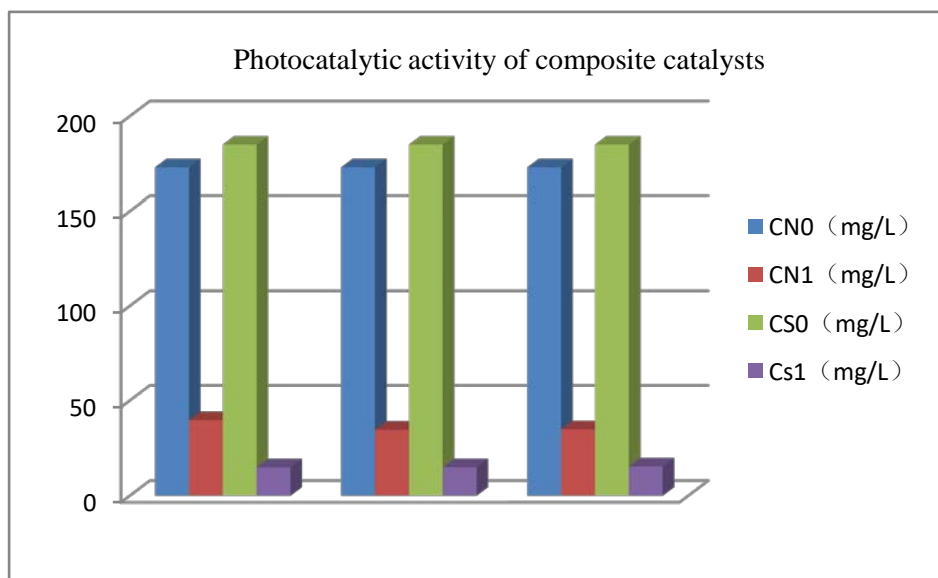
3.4 Determination of Composite Catalyst on Real Tannery Wastewater Odor Cases

To overcome the challenges of complex tannery wastewater composition and significant water quality variations, and to ensure that the photocatalyst can still effectively remove ammonia nitrogen and sulfides in complex water matrices, this experiment used the materials obtained from the above research under the same conditions on real wastewater generated during the leather production process. This tested its feasibility for industrial application. It also examined whether the component mass fraction ratio derived from the mathematical model for optimal catalyst performance indeed yields high removal rates for both ammonia nitrogen and sulfides.

This experiment used wastewater from a tannery in Jiangmen, specifically from the liming and softening stages. The suspended photocatalytic oxidation method was still used. Catalysts with different ratios of WO_3 to TiO_2 were prepared: Catalyst I ($WO_3:TiO_2$, 5:1); Catalyst II ($WO_3:TiO_2$, 3.6:1); Catalyst III ($WO_3:TiO_2$, 5:2). An appropriate amount of photocatalyst was weighed using an electronic balance and placed into reactors containing wastewater from different stages. A constant temperature magnetic stirrer was used for stirring, while an oxygen pump bubbled oxygen to keep the photocatalyst uniformly suspended in the semi-closed reactor for adsorption and reaction. After reacting under UV light for 2 hours, the reaction solution was taken out and centrifuged at 4500 r/min for 15 minutes to separate solid and liquid. The catalyst was separated, and the supernatant was drawn for analysis and determination of ammonia nitrogen or sulfide values. All reactions were carried out at room temperature. The tests were repeated three times.



Case 1: Wastewater taken from the liming stage.



Case 2: Wastewater taken from the softening stage.

Fig. 3-5 Photocatalytic oxidation degradation of tannery wastewater. Concentrations: CN0 initial ammonia, CN1 after photolysis, CS0 initial sulfide, and CS1 after photolysis; From left to right: Catalyst I, Catalyst II, Catalyst III.

The most important condition for the photocatalytic redox reaction is the acquisition of light energy. The photocatalytic reaction occurs when the semiconductor material absorbs sufficient light energy to excite electrons and holes, leading to the migration of photogenerated charge carriers at the semiconductor surface energy level structure, producing reactive species. However, tannery wastewater not only contains high concentrations of pollutants like ammonia nitrogen and sulfides but also has a significant problem of deep color, which limits the penetration of the light source, preventing the semiconductor from obtaining enough energy for excitation. In this experiment, to mitigate this effect, two UV lamps were positioned at different angles to irradiate the solution, ensuring it received sufficient energy as much as possible. The test results are shown in Fig. 3-5.

The results show that this composite catalyst material has good degradation effects on both ammonia nitrogen and sulfides present in high concentrations in tannery wastewater, indicating good application potential. Furthermore, Catalyst II was more effective at removing inorganic pollutants from tannery wastewater than the other test groups, suggesting that the ratio derived from the model has some scientific basis. From the figure, we can also see that all three catalyst groups degraded odorous pollutants in tannery wastewater to varying extents. The experimental results show that the photocatalyst can achieve a sulfide removal rate exceeding 90%. The figure also indicates that the photocatalyst performs better in lower concentration wastewater than in higher concentration wastewater. This is related to the possibility of catalyst poisoning at high pollutant concentrations. This can effectively solve the problem of S^{2-} pollution in wastewater. However, regarding the removal rate of ammonia nitrogen, although the light absorption threshold was expanded, it still could not be effectively removed. This may be due to the varying effects of different reaction substrates on the activity of the photolysis catalyst. To completely solve the problem of ammonia nitrogen pollution in tannery wastewater, further research on catalyst modification is needed to find novel catalysts with stronger activity, wider applicability, and broader light absorption bands.

Wakits et al. (2005) found that when metal catalysts and transition metal oxide catalysts are used to treat industrial organic waste gases, the presence of high concentrations of sulfur, chlorine compounds, especially SO_2 , H_2S , etc., in VOCs can easily poison the catalyst. The wastewater discharged from the liming stage contains a higher concentration of S^{2-} than that from the softening stage, which is also the reason for the poorer degradation effect of sulfides and ammonia nitrogen in this stage.

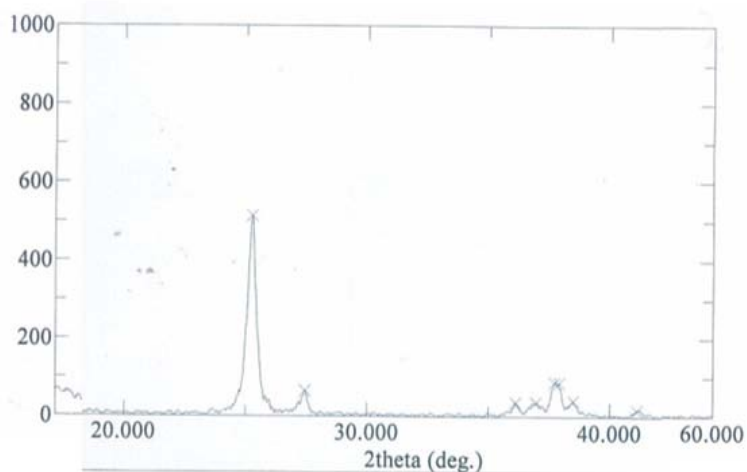
This experiment aimed to solve practical problems, focusing more on the effectiveness of the composite catalyst. It did not extensively discuss the mechanism of inorganic photolysis, the influence of different substrates on photolysis activity, or the poisoning reaction during the photocatalytic process. The poisoning mechanism is also one of the future research directions for photocatalysts. Understanding the underlying mechanisms will help develop efficient and regenerable catalysts.

In summary, this experiment used WO_3 , which has high catalytic activity for inorganic substances, as the primary catalyst, and TiO_2 , with lower catalytic activity, as the co-catalyst, to degrade odorous components in tannery wastewater. All three different ratios showed strong removal capabilities. Catalyst II ($WO_3:TiO_2$, 3.6:1) exhibited the best removal effect for both ammonia nitrogen and sulfides, validating the conclusion from the optimal ratio model. It also proved that WO_3 is superior to TiO_2 in the oxidation ability for inorganic pollutants. The use of narrow bandgap semiconductor material WO_3 and wide bandgap material TiO_2 exhibits a good co-catalytic effect when treating inorganic pollutants.

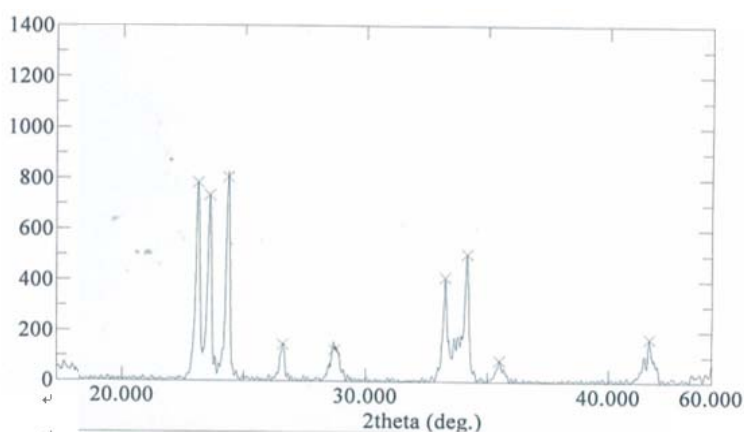
4 Crystal Structure Analysis of Catalysts

4.1 X-ray Diffraction (XRD)

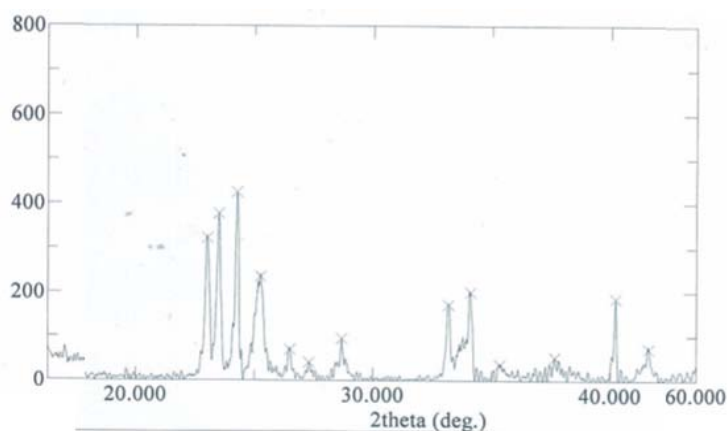
X-ray Diffraction (XRD) phase analysis technology is based on the X-ray diffraction effect of the polycrystalline form of a sample. The measurement principle is that when a monochromatic X-ray irradiates atoms in a crystal, due to the arrangement of atoms, elastic scattering waves interfere with each other, causing a diffraction phenomenon. This allows for the determination of different existing forms and phase structures of sample components. The content determined by XRD includes the crystal condition and phase structure of each component, as well as the valence state and bonding state of various elements in the crystal.



TiO₂ X-ray diffraction pattern



WO₃ X-ray diffraction pattern



WO₃/TiO₂ X-ray diffraction pattern

Fig. 4-1 X-ray diffraction patterns of different materials: TiO₂, WO₃, WO₃/TiO₂.

Many factors influence the photocatalytic activity of catalysts, such as specific surface area, crystal size, synthesis process, and surface morphology. Limited by experimental conditions and time, we only consider the influence of catalyst crystal form on the degradation of tannery pollutants. The incident angle range is $0^\circ < 2\theta < 60^\circ$. The sample diffractograms are shown in Fig. 4-1.

From the diffraction data in Fig. 4-1, it can be seen that TiO_2 shows obvious diffraction peaks at d-spacings of 3.52, 1.89, and 1.66, while only a few weak diffraction peaks appear at d-spacings of 2.48, 2.43, and 1.65. This indicates that most of the crystal structure has converted to the anatase type, while the rutile type crystal has essentially disappeared. Co-activation of the composite material changed the crystal structure, increasing the number of X-ray diffraction peaks. Peaks appear at d-spacings of 3.86, 3.78, 3.66, 3.52, 2.69, 2.62, 2.24, and 1.82. It can be seen that the intensity of the diffraction peaks for the composite material is much greater than that for the single catalyst samples, indicating that the crystal form of the new material has changed. From the earlier single catalyst experiments, it is known that in terms of inorganic catalytic performance, the catalytic activity of WO_3 is stronger than that of TiO_2 , which has good catalytic activity for organic matter. The mechanism can be understood through quantitative phase analysis of the XRD patterns. WO_3 has more diffraction peaks. According to the principle of quantitative phase analysis (Zhao, 2011), each phase has its own characteristic diffraction lines, and the intensity of these characteristic lines is proportional to the number of crystal cells of the sample phase participating in diffraction, indicating that WO_3 possesses more crystal forms.

Literature shows that the photocatalytic degradation effect of semiconductor catalysts on harmful substances is closely related to the crystal structure, and the crystal phase often changes to varying degrees after high-temperature calcination activation. Analyzing the phases of single and composite catalysts is important for understanding the mechanism of photocatalysts.

4.2 Energy Level Structure Model of the Composite Catalyst

For the composite catalyst, experiments have shown that even adding a small amount of composite material significantly improves the removal effect of sulfides. This is related to the increase in co-catalyst crystal forms. Establishing a catalyst coordination model can better explain its effect. Exploring the photocatalytic mechanism of semiconductor catalysts also aids in developing new, efficient catalyst materials.

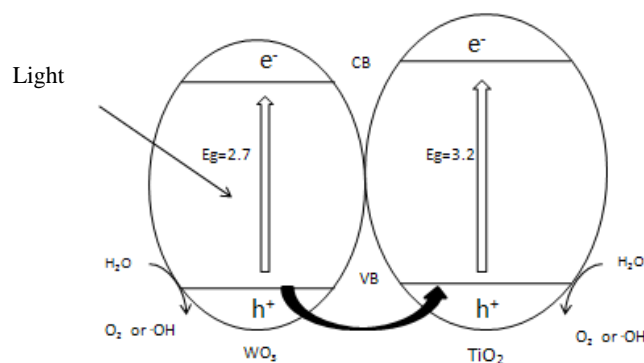


Fig. 4-2 Suggested mechanism of degradation by WO_3/TiO_2 composite - energy level diagram.

The enhancement mechanism of WO_3 on TiO_2 in the WO_3/TiO_2 composite catalyst system is as follows: According to the energy level model in Fig. 4-2 (Abdullah et al., 1990), when the composite semiconductor is irradiated with high-energy light, electrons from the VB (Valence Band) of WO_3 can not only transition to its

CB (Conduction Band) but can also be excited to the VB and CB levels of TiO_2 , because the VB and CB energy levels of TiO_2 are both higher than those of WO_3 . Electrons in the conduction band can migrate to the conduction band of WO_3 , generating photogenerated holes. Electrons migrating to the valence band of TiO_2 can also excite hole sites. Thus, electrons and holes in the valence band of the composite material are effectively separated, enhancing the photocatalytic effect of the composite material. The separated electrons or hole sites can effectively undergo oxidation reactions with pollutants adsorbed on the semiconductor surface. The series of active species formed on the particle surface, such as H_2O_2 , $\cdot\text{OH}$ radicals, O^{2-} singlet oxygen, etc., will also have higher oxidation capabilities than unmodified catalysts.

X-ray diffraction analysis of the crystal structures of single and composite catalysts, combined with previous experimental results, indicates that the increased activity for photocatalytic oxidation of pollutants is closely related to the crystal phase structure. This validates literature conclusions regarding the influence of crystal form on the photocatalytic oxidation effect of pollutants. The novel catalyst synthesized by modifying the single catalyst in this study shows improvement in both crystal phase structure and catalytic performance. It is an efficient, novel composite catalyst material with a high removal efficiency for sulfides and ammonia nitrogen present in tannery wastewater.

5 Summary and Perspective

Odors generated during the leather-making process constitute one of the significant air pollutants currently endangering the atmospheric environment. China is a major leather producer, and the Pearl River Delta region hosts numerous leather industry bases. Due to its unique characteristics, leather-generated pollution is severe and difficult to treat using conventional methods.

Conventional treatment methods are often high-cost and low-efficiency, unsuitable for eliminating and controlling such pollutants. Therefore, there is an urgent need to develop new clean technologies. Photocatalytic technology has garnered much attention due to its high efficiency and lack of secondary pollution. Current research on photocatalysts has shifted from focusing on visible light response performance to achieving high photocatalytic activity. Research approaches have also moved from designing single-phase catalysts to constructing various semiconductor composite structures, with significant progress already made.

Summarizing previous research results and considering the unique characteristics of tannery wastewater, this study proposed using photocatalytic oxidation technology to solve odor problems in tannery wastewater. Experimental results show that applying this technology to treat wastewater odor is feasible, and it has a good purifying effect on water bodies. This study focuses on ammonia nitrogen and sulfides, the main sources of odor in tannery wastewater, studying the efficiency and mechanism of their photolysis using photocatalytic oxidation water purification technology (Fig. 5-1).

5.1 Summary

The work accomplished is summarized as follows:

First, building on the preliminary laboratory work involving on-site investigation of wastewater conditions during leather processing, the main components and sources of wastewater odor were identified, and the pollutants and their biochemical characteristics were studied.

Results show that the odor in tannery wastewater mainly originates from the liming and softening stages. Ammonia nitrogen is primarily due to the addition of large amounts of ammonium salts during production, while sulfides result from the addition of large amounts of sodium sulfide. As the pH of the wastewater changes, ammonia nitrogen and sulfides volatilize into the air, causing air pollution. In subsequent experiments, these two substances were used as research objects to compare the degradation efficiency of different catalysts.

Second, utilizing the properties of nanomaterials, research was conducted on catalyst modification to explore novel composite catalysts and investigate their catalytic activity mechanisms.

Results indicate that under UV lamps (wavelength 253.7 nm), the catalysts have a strong degradation effect on inorganic substances. It was further demonstrated that the narrow bandgap semiconductor catalyst WO_3 has a good enhancement effect on the wide bandgap semiconductor TiO_2 , and the catalytic oxidation ability of the composite catalyst is stronger than that of single catalysts.

Third, using X-ray diffraction technology, the photocatalytic oxidation mechanism of the composite catalyst was explored through crystal structure analysis.

Experiments further confirmed the mechanism by which the composite material enhances photocatalytic effect by separating electrons and holes in the valence band and facilitating charge carrier migration.

Fourth, based on previous work, different ratios of WO_3 and TiO_2 in the composite material were prepared. The removal efficiency of each composite formulation for ammonia nitrogen and sulfides in tannery wastewater was determined. Using mathematical model fitting, the model equation $y = 41.66 + 0.28x - 0.00101x^2$ was obtained, leading to an optimal ratio of approximately 3.6:1.

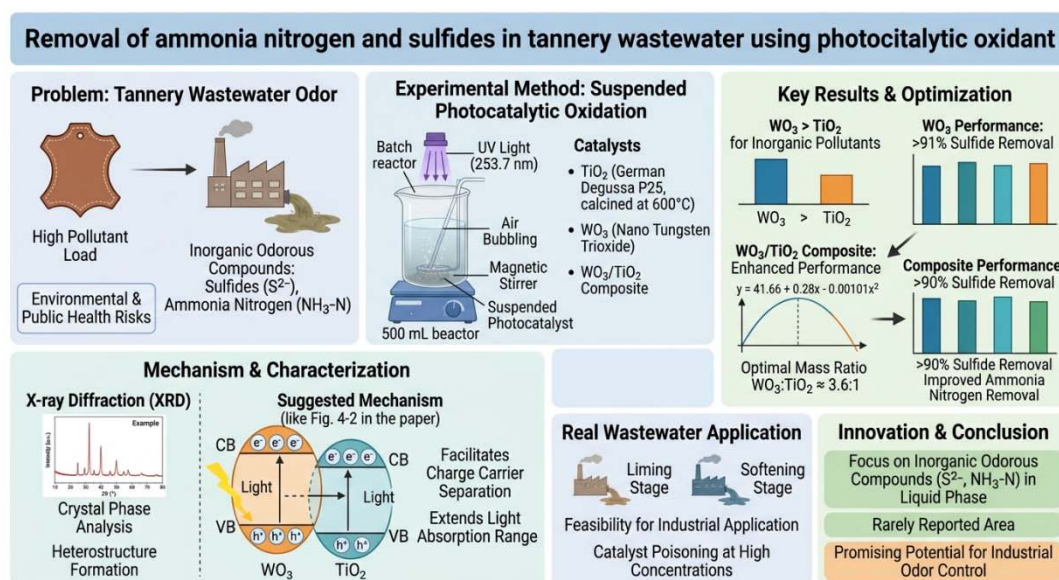


Fig. 5-1 Systematic diagram of removal of ammonia nitrogen and sulfides in tannery wastewater using photocatalytic oxidant.

Although certain achievements have been made in this study, due to time and energy constraints, several aspects still require improvement and refinement:

- (1) Further in-depth research on photocatalysis is needed to achieve new breakthroughs in key scientific issues. A deeper understanding of the fundamental principles of photocatalysis will not only guide the design of new materials but also help develop new functions.
- (2) Further research is needed on the composition, crystal structure, preparation methods, and catalyst modification of novel photocatalytic materials to obtain more efficient and suitable photocatalytic materials for industrial application.
- (3) Regarding application, this study confirms the photolysis effect of the novel catalyst on inorganic pollutants. However, further development is required for system engineering, such as solving technical problems like catalyst immobilization, to make photocatalysis more mature in the field of water purification.

5.2 Innovations

There are many reports in the literature on the degradation of organic pollutants by semiconductor catalysts. However, there are few reports on the degradation and removal of inorganic pollutants, especially sulfides and ammonia nitrogen. Some studies exist on the photocatalytic oxidation of gaseous VOCs, but studies in the liquid phase are rare.

This study selects the narrow bandgap semiconductor WO_3 as a light absorber to sensitize the wide bandgap semiconductor TiO_2 . A composite heterostructure material was formed to broaden the spectral absorption range and promote charge carrier migration through the heterostructure, thereby enhancing photocatalytic activity. A novel catalytic material was constructed, and its reaction mechanism was preliminarily explored through crystal structure studies, laying a theoretical foundation for industrial application (Fig. 5-1).

A novel water purification photocatalyst was obtained through experiments. It has an ideal removal effect on both sulfides and ammonia nitrogen and can be further developed into a commercial product.

Additionally, X-ray diffraction (XRD) was used to further reveal the relationship between the crystal phase composition of different catalysts and their catalytic properties.

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