Photocatalytic oxidation of gold processing wastewater from a gold mine in Southwest Guizhou Autonomous Prefecture

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ABSTRACT

Wastewater of gold dressing and smelting has dual nature of toxicity and difficult to be treated. Thiocyanate needs to be pretreated before treatment of ammonia nitrogen in the wastewater. So the new treatment method to realize the coupling of thiocyanate treatment and downstream wastewater treatment is important. In this study, wastewater from the tailing-water treatment station of Jinfeng Mining Company is chosen as the research object. Photocatalytic reaction is carried out with phosphorus modified platinum supported titanium dioxide as the catalyst under combined action of chlorine dioxide. Residual amount of ammonia nitrogen, thiocyanate, chemical oxygen demand (COD) and other pollutants after reaction are analyzed to find out their remains. Fourier-transform infrared spectroscopy, transmission electron microscope, scanning electron microscope and electrochemical are used to analyze the effect of the catalysts. The results show that platinum-supported titanium dioxide which is modified by phosphorus has a good response to light environment. When the reaction time is 560.22 min, the light intensity is 5,297.97 lx, the amount of catalyst is 0.33 g, and the amount of chlorine dioxide is 8.88 g, the conversion of thiocyanate can reach 34.71% with a good treatment effect on ammonia nitrogen and COD.

Keywords: Wastewater from gold dressing and smelting; Photocatalysis; Thiocyanate, Ammonia nitrogen; Chemical oxygen demand

1. Introduction

The wastewater from gold ore dressing and metallurgy contains cyanide, which is generated in the process of gold ore processing and smelting, using cyanide solution to dissolve the gold element in the ore and extract gold from it through a series of adsorption and replacement operations. In this process, wastewater containing cyanide is often generated [1], containing complex compositions, high salt content and high-concentration pollutants, which make it difficult to be treated [2]. There is a large amount of thiocyanate, Cu, Zn, Pb, Cd heavy metal elements and sulfate ion in the wastewater, which shows strong acidity and high toxicity and is difficult to be degraded and treated [3].

The sampling place of this study is Guizhou Jinfeng Mining Co., Ltd., China, (hereinafter referred to as Jinfeng Company, China), a company located in Southwest Guizhou Autonomous Prefecture, Qianxinan Prefecture Guizhou Province, with a geographical location of 105°50′34″ E to 105°54′08″ E and 25°06′48″ N to 25°10″36′ N. It is a huge

gold mine with a capacity of 100 tons. The ore is a primary gold deposit of fine-grained disseminated type. The designed annual production of the mine is 1.2 million tons. The core technology of beneficiation and metallurgy is biological oxidation pretreatment process. The daily treatment capacity of gold concentrate is 790 tons, ranking the third in the world, with an annual output of about 4 tons of fine gold. At present, the mine has more than 60 tons of reserves.

According to the field survey, the current treatment capacity of tailing water treatment station of Jinfeng Mining is 1,500 m³/d. Contact oxidation was used in the original design. However, due to a large number of scaling in the operation process, the original design did not work. Therefore, the original packing was removed and the operation mode was changed to activated sludge process. Table 1 is for the recent operation data, Table 2 for hardness test data of wastewater, and Table 3 for the nitrogen test data of wastewater. The effluent should meet Class I Standard of Integrated Wastewater Discharge Standard (GB8978-1996), which is a part of the National Standard of the People's Republic of China.

Through the field survey and the analysis of the above data, it can be seen that the existing wastewater treatment operation mode of Jinfeng Company has a sound thiocyanate-removal effect, the thiocyanate and TCN in the effluent meet the discharge standard. However, due to the large amount of ammonia nitrogen generated in the process of biological treatment of thiocyanate, the concentration of ammonia nitrogen in the effluent is high, which does not meet the requirements of the discharge standard. In addition, there are a lot of calcium ions, magnesium ions, carbonate and bicarbonate, etc. in the effluent, so the total hardness and the conductivity is a bit high, which leads to serious scaling phenomenon when it reacts with CO_2 produced by biological action. Moreover, in the existing water treatment system, thiocyanate is mainly

removed by microorganisms, and nitrifying bacteria and denitrifying bacteria are not cultivated.

Usually, SO_2/air, chlorination, acidification recovery and precipitation were applied worldwide for the treatment of cyanide wastewater and have been widely used in industrial production [3], but according to the analysis of Table 4 [4], there are still many problems in the previous methods, such as incomplete treatment, easy secondary pollution, high treatment cost, inadequate treatment process, poor adaptability of treatment methods, unable to recover metal or cyanide from the treatment process and so on. Therefore, these methods still need further improvement.

According to the relevant requirements of the technical policy of pollution control in gold industry in China, the prevention and control of gold industrial pollution should follow the principle of "source reduction, process control, end treatment and resource utilization", focus on the prevention and control of cyanide tailings, cyanide-containing wastewater and heavy metal pollution, actively popularize advanced and mature pollution-prevention-and-control technology, and improve the level

Table 2
Hardness test data of wastewater

Test items	Test result
Calcium (mg/L)	486
Sodium (mg/L)	3.4×10^3
Magnesium (mg/L)	64.9
Sulfate (mg/L)	4.88×10^3
Carbonate (mg/L)	16.4
Bicarbonate (mg/L)	166
Total alkalinity (based on $CaCO_3$) (mg/L)	164
Total hardness (based on $CaCO_3$) (mg/L)	1.59×10^3

Table 1
Recent monitoring data of the project

Date	Time	Sample	SCN	CN	As	TCN	Hg
2019/7/26	10:00	Equalization basin	1,542	0.364	0.247	4.27	0.1540
	22:00	Drainage tank	0.061	0.036	0.095	0.206	0.0403
	10:00	Equalization basin	1,529	0.393	0.209	2.5	0.1336
	22:00	Drainage tank	0.113	0.049	0.098	0.212	0.0512
2019/7/27	10:00	Equalization basin	1,539	0.386	0.398	3.617	0.1293
	22:00	Drainage tank	0.031	0.049	0.118	0.166	0.449
	10:00	Equalization basin	1,507	0.790	0.315	2.32	0.1472
	22:00	Drainage tank	0.042	0.047	0.096	0.231	0.0532
2019/7/28	10:00	Equalization basin	1,635	0.529	0.133	3.486	0.2038
	22:00	Drainage tank	0.081	0.054	0.065	0.146	0.0569
	10:00	Equalization basin	1,576	0.424	0.164	1.98	0.1472
	22:00	Drainage tank	0.126	0.056	0.130	0.274	0.0532
2019/7/29	10:00	Equalization basin	1,627	0.502	0.658	4.01	0.0923
	22:00	Drainage tank	0.087	0.053	0.080	0.101	0.0358
	10:00	Equalization basin	1,378	0.329	0.449	1.98	0.2436
	22:00	Drainage tank	0.179	0.053	0.134	0.202	0.0478

Table 3
Nitrogen detection data of wastewater

	Ammonia nitrogen (mg/L)	Nitrous oxide (mg/L)	pH	Conductivity (µs/cm)
Equalization basin	99.997	4.3	8.97	3,840
Primary drainage	320.51375	0.275	7.13	3,628
Secondary drainage	315.80725	0.0174	6.66	3,348
Drainage	293.6355	0.4	7.12	2,969

of preventing and controlling gold industrial pollution. At the same time, it is also clear in the document that acid wastewater from gold concentrate pretreatment process should be encouraged to be used for the treatment of cyanide tailings; thiocyanate from circulating water in cyanide process should be encouraged to be converted into cyanide for reuse; methods with less secondary pollution such as ozone and hydrogen peroxide are encouraged to be used for harmless treatment of cyanide-containing wastewater; and new technologies, processes and equipment for the treatment and disposal of gold-smelting wastewater, which are suitable for the national and regional characteristics of China, are encouraged to be developed.

For the treated gold metallurgical wastewater, according to the Integrated Wastewater Discharge Standard (GB8978-1996), the wastewater that meets the standard is allowed to be discharged.

After secondary treatment, sewage is sometimes difficult to meet the discharge requirements. Therefore, three-stage treatment is needed to further purify the sewage. Common technologies include ozone or ultraviolet disinfection, filtration and the rest. However, these methods have shortcomings, such as the possibility of secondary pollution, or the relatively high cost, which leads to the limited application of these methods. Therefore, searching for treatment methods of sewage which are efficient, advanced and low-cost has become a hot spot [5].

In 1972, two Japanese scientists, Fujishima and Honda found that TiO_2 Electrode could decompose water into H_2 and O_2 under ultraviolet irradiation [6]. In 1976, the research by Carey et al. found that photocatalytic technology of TiO_2 had a good effect on the degradation of highly toxic polychlorinated biphenyl [7]. The method of photocatalysis technology to remove pollutants, especially highly toxic substances, which are difficult to remove or expensive by conventional technology, has since entered the eyes of scholars all over the world.

Semiconductor photo-catalysis is a process that converts light energy into chemical energy and promotes the synthesis or decomposition of compounds. As a new wastewater treatment technology, photo-catalysis has two remarkable characteristics compared with the traditional purification technology: first, photo-catalysis technology takes sunlight as the light source and is of low cost; second, photo-catalysis can completely oxidize organic pollutants in air, water and so on to CO_2, water and other products without secondary pollution.

The current photo-catalysts are mainly divided into metal oxide photo-catalysts, modified metal oxide photo-catalysts and supported photo-catalysts. TiO_2, ZnO, and SnO_2 are some popular and practical metal oxide photo-catalysts [8]; Cost of ZnO is lower than TiO_2. However, it has some disadvantages such as low visible light catalytic efficiency, faster electron-hole pair recombination and light corrosion [9], which need to be combined with other photo-catalysts to improve their photo-catalytic performance [10]. TiO_2 is a good photo-catalyst with advantages of high stability, high photo-catalytic efficiency and no secondary pollution, so it is widely used in air purification, water purification, antibacterial and so on [11], and has already had a mature theory system as its support. Like ZnO, the photo-catalytic property of pure SnO_2 is not high, so other composite materials are needed to meet the needs of photo-catalysis [12]. Single metal oxide photo-catalyst is deficient in photo-catalytic response, so it needs to be modified to improve its photo-catalytic performance. Common modification methods include metal ion doping, precious metal deposition, semiconductor recombination and surface photo-sensitization [13]. The most widely used modification method is metal ion doping, such as Pt doping TiO_2 to produce Pt/TiO_2 and Fe doping TiO_2 to produce Fe/TiO_2 [14]. Since both the metal oxide photo-catalysts and the modified metal oxide photo-catalysts are basically suspended under stirring, the floating supported photo-catalyst is more suitable for the treatment of floating pollutants than the first two catalysts [15].

TiO_2 can be used as an activator of the redox reaction process of photoreduction due to its full valence band and the electronic structure of the empty conduction band. TiO_2 band gap is 3.2 eV. When it is irradiated by light with a wavelength less than or equal to 387.5 nm, the electrons of the valence band becomes excited and cross the band into the conduction band, and the corresponding holes are generated on the valence band. Electron and hole separation and migration to different positions on the particle surface, thereby accelerating redox reaction, reduction and oxidation of adsorbed substances on the surface [16].

According to the research of Elsie et al. [17], the application of TiO_2 photo-catalytic technology in the removal of industrial circulating sewage chemical oxygen demand (COD) has good effect and advantages, its treatment effect is stable and sustainable, no secondary pollution is caused, and the catalyst raw materials are cheap, so it is feasible. The results of Haidong et al. [18] showed that when the reaction time was 3 h, pH was 10, dosage of photo-catalyst was 7 g/L, the aeration rate was 0.2 m³/h and temperature was 32°C, TiO_2 photo-catalytic technology had the best ammonia nitrogen removal effect and the maximum removal rate could reach 58.32%. Zhang Dongwang's research suggested that when TiO_2 at 20%, photolysis rate

Table 4
Comparison of existing processes for treatment of cyanide wastewater from gold extraction

No.	Method	Principle	Advantages	Shortcomings	Application scope
1	Precipitation method	Adding specific chemicals to convert pollutants into sediment	Heavy metal ions and CN^- can be removed simultaneously	It is difficult to separate solid phase from liquid phase completely, resulting in lots of residue formation, and easy to block pipeline, which is difficult to deal with	Low-concentration cyanide wastewater
2	Acidification	Metal cyanide complex is decomposed into HCN in strong acid environment and absorbed by alkali solution	Cyanide could be recovered	High equipment investment and operation costs, produce HCN toxic gases, heavy metal ions cannot be removed	High-concentration cyanide wastewater
3	Chlorine oxidation	Oxidation of cyanide into CO_2 and N_2 with chlorine in alkaline	Can oxidize most pollutants, process is mature, simple equipment, less investment and easy management	Limited removal capacity, easy to produce secondary pollution, cyanide cannot be recovered, large dosage of medicament, high pH may corrode equipment	High-concentration cyanide wastewater
4	H_2O_2 Oxidation	Oxidation of cyanide with H_2O_2 as oxidant	Can be discharged up to standard without secondary treatment. Good treatment effect and simple operation	Complex equipment operation, high investment and operation cost, no recovery of cyanide	Low-concentration cyanide wastewater
5	O_3 Oxidation	Oxidation of cyanide with O_3 as an oxidant	Complete oxidation and avoid secondary pollution	Limited removal capacity, high investment and operating costs, no recovery of cyanide	Low-concentration cyanide contained in wastewater or secondary treatment
6	SO_2/Air	Convert CN^- to low toxicity CNO^- with SO_2 and air as oxidant, with copper ions as catalyst in alkaline	Oxidant is easy to obtain, low cost, good treatment effect	High corrosive, not completely oxidized CN^-, no cyanide recovery	Low-concentration cyanide wastewater
7	Electrolytic oxidation	Cyanide oxidizes to CO N_2 on anode and reduction of metal ions on cathode	Can effectively decompose cyanide complex to be recycled back to the process, and metals recovery	High investment operation cost, effluent is not up to standard	High-concentration cyanide wastewater

(Continued)

Table 4 *Continued*

No.	Method	Principle	Advantages	Shortcomings	Application scope
8	Microbiological method	Cyanide and thiocyanate as carbon and nitrogen source were decomposed through microbial metabolization and heavy metals were adsorbed by bio-film	Can remove SCN^- completely, process simple, low cost, strong applicability, high removal efficiency, no secondary pollution	Long processing period, small load, poor adaptability, large area	Wastewater with low-concentration cyanide, low concentration fluctuation and low load,
9	Ion exchange resin	Ions in the solution are separated with ionic exchange agents	Can recover gold, valuable metals and cyanide, effluent quality is good	Long processing cycle single resin is difficult to treat the wastewater effectively, high investment cost, difficult popularize	Cyanide containing wastewater with small amount, high toxicity and recycling value
10	Active carbon adsorption	Cyanide removed by adsorption, oxidation, hydrolysis and blowing of cyanide with activated carbon	Simple process equipment, easy to operate, metal recyclable	Need pretreat, high investment and operation cost, only clarified water can be treated, not suitable for treatment of high-concentration wastewater, and the regeneration capacity is poor	Small amount of clear water
11	Membrane Separation	Utilize membrane material of allowing only micromolecular CN^- to separate CN^- in solution, and use NaOH solution to absorb in the other side of the membrane	Low energy consumption, simple process, small area, no pollution	Poor fouling resistance and regeneration of membranes	Cyanide-containing wastewater with free state of cyanide
12	Solvent Extraction	Extraction of metals in wastewater by amine extractant and free CN^- remain in the solution was extracted with NaOH solution	Good separation effect, simple process, small area, no pollution	Adaptive poor	High-concentration cyanide wastewater

of CN$^-$ was the highest, the photo-catalytic effect was the best, and it could reach more than 80%, which showed a good application prospect [19]. Water samples of cyanide-containing wastewater produced by gold industry were collected, and the contents of ammonia nitrogen, COD and thiocyanate in water samples were detected. The conversion of ammonia nitrogen, COD and thiocyanate in wastewater was studied by photo-catalytic experiments under different light intensity and catalyst.

Gold smelting wastewater is of high toxicity and difficult to be treated. The photocatalytic technology can effectively remove thiocyanate from gold smelting wastewater, and also remove COD and ammonia nitrogen from sewage, which realizes not only the non-toxicity of gold smelting wastewater but also the purification of gold smelting wastewater.

Because the wastewater contains highly-toxic thiocyanate and the concentration of pollutants is high, this paper analyzes the photo-catalytic decomposition products of gold smelting wastewater and explores the photo-catalytic performance of gold smelting wastewater. The relationship between thiocyanate and catalytic performance of gold smelting wastewater can provide experimental basis and theoretical support for photocatalytic decomposition of thiocyanate and downstream wastewater treatment technology.

2. Materials and methods

Contents of this research includes four aspects:

(1) Screening, preparation and characterization of wastewater photo-catalyst for gold smelting;
(2) Exploring the degree of photo-catalytic decomposition of thiocyanate in gold smelting wastewater, and selecting the best photo-catalytic conditions by comparing them under different conditions;
(3) Exploring the degree of photo-catalytic decomposition of ammonia nitrogen in gold smelting wastewater, and selecting the best photo-catalytic conditions by comparing them under different conditions;
(4) Exploring the degree of photo-catalytic decomposition of COD in gold smelting wastewater, and selecting the best photo-catalytic conditions by comparing them under different conditions.

2.1. Research methodology

(1) Phosphorus is loaded on TiO$_2$;
(2) Metal (Platinum Pt etc.) is then loaded on the TiO$_2$ of phosphating;
(3) With the participation of chlorine dioxide, titanium dioxide catalyst catalyzes the photolysis of wastewater in the reactor.

2.2. Technical route

(1) 5 wt.% of phosphate TiO$_2$ (5 PTiO$_2$) technical route:
  • Phosphate precursor (0.085 g) was dissolved in water. Dry hydrated TiO$_2$ (2 g) was added and then stirred at room temperature for 4 h.

  • The obtained fluid was dried at 80°C for 12 h to evaporate excess water.
  • Pure and phosphated TiO$_2$ NPs were obtained after calcination at 600°C for 4 h.

(2) Technical route of Platinum Pt loaded on the TiO$_2$ of phosphating:

  • 0.062 g acetylacetone platinum and 0.5 g phosphorus hydrated titanium hydroxide were impregnated and stirred at 500 rpm under 70°C for 12 h overnight. And the resulting solution was black liquid.
  • The black liquid was evaporated to remove excess liquid.
  • The obtained material was sintered at 600°C in the atmosphere furnace for 4 h, and air was passed into it.
  • When the procedure is finished and the temperature dropped to room temperature, the sample was taken out, grinded and preserved.
  • The hydrogen reduction experiment was carried out at 400°C for 3 h, during which hydrogen was added at a flow rate of 0.1 L/h. When the procedure was finished and the temperature dropped to room temperature, the sample was taken out and saved.

(3) Technical route of wastewater photo-catalysis

TiO$_2$ and ClO$_2$ were weighed according to pre-designed dosage, and then TiO$_2$ was well mixed with sewage by ultrasonic waves. After that the mixed fluid was poured into the reactor and the rotor agitator was turned on. The dark reaction lasted for 30 min and the product of it was extracted. After extraction, the xenon lamp was turned on to modulate the designed light intensity, and the light reactions were carried out for a certain time according to the experimental design.

2.3. Sampling instructions

2.3.1. Brief introduction of the Sources of Gold Selection and Metallurgical Wastewater

The sampling point of this study is Guizhou Jinfeng Mining Co., Ltd., China (hereinafter referred to as Jinfeng Company). Jinfeng Company is mainly engaged in geological exploration, mining, metallurgy and gold sales of Jinfeng Gold Mine (also known as Lannigou Gold Mine) project. Jinfeng Company is located in Qianxinan Prefecture, Guizhou Province, which is a jurisdiction area of Shaping Town, Zhenfeng County, and 68 km away from Zhenfeng location of Mingu Town southeast. The geographical location is: E 105°50"34' to 105°54'08", N 25°06'48" to 25°10"36'. It is 304 km away from Guiyang, the capital city.

The design and treatment capacity of the water treatment project containing thiocyanate tailings in this plant is 2,500 ton/d. The original design adopts contact oxidation method. Because of a large number of scaling phenomena in the operation process, the original design cannot run normally, so the original packing is removed and the operation mode was modified to activated sludge process for processing.

2.4. Sample collection

2.4.1. Tools used are: sampler and sewage bucket

Water sample collection: sampler was used to collect the influent water sample in the sewage treatment plant; the sundries in the water sample were screened out with the sieve; the water sample was loaded into the sewage bucket; the sampling bottle was sealed; and the sampling tool was cleaned and set aside.

2.5. Sample processing

All samples were stored at room temperature in 105 Laboratory of the Institute of Resource and Environmental Engineering of Guizhou University.

2.6. Catalyst screening and preparation

The reagents used in this study and their sources are shown in Table 5. The main instruments and equipment used in the study are shown in Table 6.

2.7. Catalyst preparation

(1) Phosphorus impregnation with hydrated titanium hydroxide:

- Phosphate precursor (0.085 g) was added to a 100 mL beaker and then dissolved by stirring with appropriate amount of water.
- Dry hydrated titanium hydroxide (2 g) was added to the beaker and stirred at room temperature for 4 h.
- The resulting mixture was dried under 80°C in an oven for 12 h to evaporate the excessive water.
- Pure and phosphated TiO_2 NPs were obtained after calcination at 600°C for 4 h.

(2) Pt/TiO_2 preparation:

- 0.062 g acetylacetone platinum and 0.5 g phosphorus hydrated titanium hydroxide were impregnated and stirred at 500 rpm under 70°C for 12 h overnight.
- The obtained black samples were evaporated in oven.

- The obtained material was sintered under 600°C in atmosphere furnace for 4 h and then it was aired.
- After the procedure was finished, it was reduced to room temperature, and the sample was taken out, grinded and saved.
- Hydrogen reduction experiment was carried out on the material at 400°C for 3 h, during which the hydrogen was joined with the flow control at 0.1 L/h. When the program was finished and the temperature dropped to room temperature, the sample was taken out and saved.

2.8. Operation parameters optimization

2.8.1. Design-Expert parameter optimization design

The software, Design-Expert 8.0 which was specially developed by State-Ease Company for experiment design, is used in this experiment design. By using the response surface method (RSM) of the software to optimize the design function, we can identify the key factors that affect the experimental design and the experimental process, and then improve it pertinently. The process is shown as follows:

(1) Click on the new design tab to create a new experiment;
(2) Factor design: shield independent factors, and point out important factors;
(3) Click on the Box-Behnken tab to enter information on the factors to be examined, including names, units, etc;
(4) Click on the "continue" to continue, the actual value of the test design will be obtained.

2.8.2. Experimental design of optimization parameters for COD, ammonia nitrogen (total nitrogen) and thiocyanate

A systematic study is carried out according to the central composite design involving four experiments to evaluate the effects of relevant process variables on thiocyanate conversion, ammonia nitrogen conversion and COD conversion. The range of process variables is shown in Table 7, and all experimental design results are shown in Table 8.

Table 5
Main reagents used in the experiment and their sources

Name	Molecular expression	Manufacturer
Platinum acetylacetonate(II)	$Pt(C_5H_7O_2)_2$	Shanghai Aladdin Biochemical Technology Co., Ltd., (China)
Chlorine dioxide solution reference material	ClO_2	Beijing Tianwei TEDA Technology Co., Ltd., (China)

Table 6
Main instruments used in the experiment

Name	Product model	Manufacturer
Atmosphere furnace	GF12Q 500*400*400	Nanjing Huike Electric Furnace Co., Ltd., (China)
Photocatalytic reactor	CEL-APR100H	Beijing Zhongjiao Jinyuan Technology Co., Ltd., (China)

Table 7
Experimental design process conditions

Variables	Acronym	Standard (item 2)	Systematic study
Catalyst intake (g)	Cat_{in}	0.25	0–0.5
Chlorine dioxide (g)	ClO_{2in}	5	0–10
Time (h)	t	305	10–600
Light intensity (lx)	Str	15,000	0–15,000

Table 8
Experiment parameters designed in IPA

|		Factor 1	Factor 2	Factor 3	Factor 4
Std.	Run	A: Time	B: Strength	C: Catalyst intake	D: ClO_2 concentration
		min	lx	g	%
25	1	305	15,000	0.25	5
16	2	305	30,000	0.5	5
19	3	10	15,000	0.5	5
15	4	305	0	0.5	5
17	5	10	15,000	0	5
12	6	600	15,000	0.25	10
2	7	600	0	0.25	5
27	8	305	15,000	0.25	5
1	9	10	0	0.25	5
7	10	305	15,000	0	10
20	11	600	15,000	0.5	5
4	12	600	30,000	0.25	5
21	13	305	0	0.25	0
5	14	305	15,000	0	0
29	15	305	15,000	0.25	5
9	16	10	15000	0.25	0
3	17	10	30,000	0.25	5
18	18	600	15,000	0	5
28	19	305	15,000	0.25	5
24	20	305	30,000	0.25	10
23	21	305	0	0.25	10
14	22	305	30,000	0	5
22	23	305	30,000	0.25	0
6	24	305	15,000	0.5	0
26	25	305	15,000	0.25	5
13	26	305	0	0	5
11	27	10	15,000	0.25	10
8	28	305	15,000	0.5	10
10	29	600	15,000	0.25	0
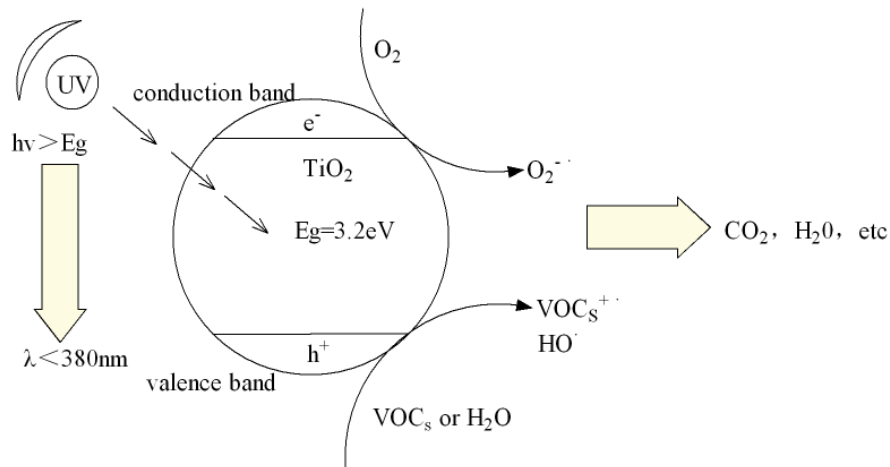
Fig. 1. Mechanism of TiO$_2$ degradation of pollutant (Source Google Public Images).
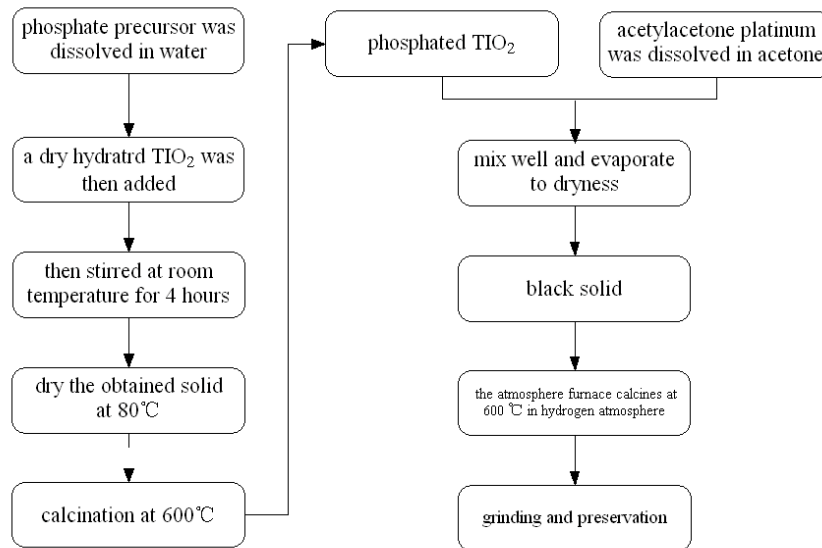

Fig. 2. Flowchart of catalyst preparation.

2.9. Analysis and detection method

2.9.1. Thiocyanate

According to GB/T1397-92, isonicotinic acid-pivarin-done spectrophotometry was used to detect thiocyanate.

2.9.1.1. Sample prepared

Two 5 ml wastewater was poured into 400 mL beakers.10 mL sodium thiosulfate solution was added to the beaker containing sample, followed with 2 mL sulfuric acid solution and more than 10 glass beads, then the beaker was covered with surface dishes. When the solution was heated carefully on the electric furnace until the micro-boiling of the solution gradually evaporated to its volume of 100 mL, 100 mL water was then added and the evaporation of the solution was conducted again until the solution reduced to 100 mL. At last, the solution was removed and cooled to room temperature.

After that, 2 drops of phenolic acid indicator solution and 5 mL sodium phosphate solution were added to the solution. With the adjustion of sodium hydroxide solution, the solution appeared red and then was transferred into a 150 mL bottle. Then the beaker was washed with water, and the lotion was incorporated into the Rong Tan bottle, diluted to the mark line with water, and mixed evenly. At last, it was filtered with dry slow filter paper in dry plug container as test material.

2.9.1.2. Standard working solutions preparation

0, 1.00, 2.00, 4.00, 6.00, 8.00, 10.00 mL sodium thiocyanate standard solution were poured into 400 mL beakers respectively and treated with the same process applied to sample.
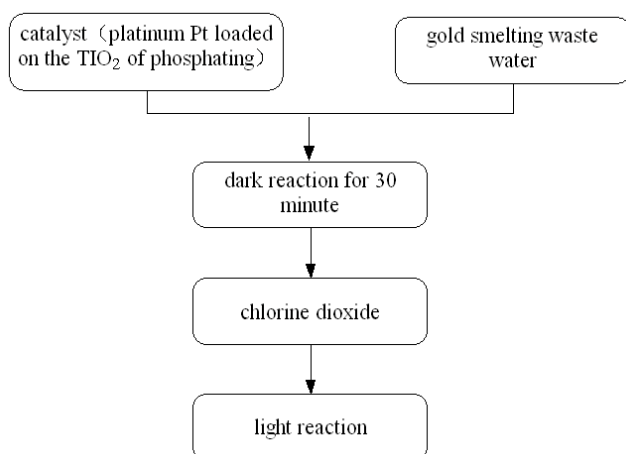
Fig. 3. Flowchart of sewage photocatalysis.

2.9.1.3. Color rendering

First, 10.00 mL test material was poured into a 25 mL capacity bottle, and acetic acid solution was dropped into the bottle until the test solution appeared red. Then 5 mL phosphate buffer solution and 0.4 mL Chloramine T solution were added into it, after which the bottle was plugged with a wetted cork immediately. Right after that the bottle was mixed in 50°C water bath for 5 min, and then removed. When it was cooled, 5 mL isonicotinic acid-pavarindone color solution was added, and then water was added to dilute the solution to the mark line. When the solution was mixed well, it was placed in a constant temperature water bath at 40°C ± 2°C for 30 min and then removed from the water bath to cool down quickly.

2.9.1.4. Measurement

With blank test solution as a reference, the absorbance of each concentration standard working solution and the sample to be tested was determined at 638 nm wavelength with 10 mm colorimetric dishes. The amount of thiocyanate in the test material was found from the calibration curve.

2.10. Chemical oxygen demand

According to the research of Ji Fangying, for the study of laboratory self-matching HACH-COD [24], this method is used to detect COD.

2.10.1. Drawing of standard curves

0.03 g $HgSO_4$ and 0.50 mL potassium dichromate were added in 12 heating colorimetric tubes, and 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 mL high-concentration H_2SO_4-Ag_2SO_4 were then added respectively (Two colorimetric tubes in a group, one as blank, one as sample) to form an alternative reagent. After that, the working curve of the alternative reagent was entered into the COD measuring instrument (2010 photometer system), so that the sample could be measured by direct reading through the adaptation program.

2.10.2. Determination of specimens

0.03 g $HgSO_4$ and 0.50 mL high-concentration potassium dichromate standard solution were added in 6

Fig. 4. Atmosphere furnace (left) and photocatalysis reaction unit (right).

heating colorimetric tubes, followed by adding 2.5 mL high-concentration H_2SO_4-Ag_2SO_4 solution. Then 3 tubes with 2 mL test water samples and 3 tubes with 2 mL distilled water were taken as blank samples in imported original reagent bottles, mixed well and were heated to 150°C in heater. According to the national standard of HJ535-2009, Nessler reagent colorimetric method was used to detect.

2.10.2.1. Water sample pretreatment: distillation

Water was added to 2.5 mL water sample until it reached 250 mL, and the mixed solution was removed into Kjeldahl flask. Then several drops of bromocresol blue indicator solution was added, followed by adding sodium hydroxide solution and hydrochloric acid solution until the pH value was about 7. After that, 0.25 g light magnesium oxide and several glass beads were added to connect the nitrogen ball and the condensate tube immediately, and then the lower end of the tube was placed below the liquid level of the absorbent (50 mL boric acid solution). Then it was distilled by heating until the distillate reaches 200 mL, after which the volume was set to 250 mL.

2.10.2.2. Drawing of standard curves

In 8 50 mL colorimetric tubes, the standard working solutions of 0, 0.50, 1.00, 2.00, 4.00, 6.00, 8.00 and 10.0 mL ammonium were added respectively, and the corresponding ammonia nitrogen contents were 0, 5, 10, 20, 40, 60, 80 and 100 µg respectively. Then water was added to the mark line, after that, 1.0 mL potassium sodium tartrate solution was added, and when the solution was mixed well, 1 mL of Nessler's reagent was add. After 10 min, the absorbance was determined at wavelength 420 nm, A colorimetric dish mm 10 degrees of light, With water as references. At last, with blank-corrected absorbance as abscissa and the corresponding ammonia nitrogen content (µg) as the ordinate, the standard curve was drawn.

2.10.2.3. Water sample determination

First, appropriate amount of water sample (ammonia nitrogen content does not exceed 100 µg) was added to 50 mL colorimetric tube to dilute to mark line, and then 1.0 mL potassium sodium tartrate solution (this reagent was not added to distilled pretreated water sample, water sample and standard tube) was added. After it was mixed well, 1 mL Nessler reagent was added and mixed well. Then it was placed for 10 min. At last, the absorbance was measured according to the same steps as the calibration curve.

2.10.2.4. Blank test

This test was done by replacing water sample with no ammonia water and it was pretreated and determined according to the same steps as the sample.

2.10.2.5. Experimental data processing

After subtracting the absorbance of blank test from the absorbance measured by water sample, the ammonia nitrogen content (mg) was obtained from the standard curve, $NH_3 - N(mg/L) = \dfrac{m}{v} \times 1,000$. m is the ammonia nitrogen obtained from the standard curve (mg); V is the water sample volume (mL).

2.11. Characterization of catalysts

2.11.1. Fourier-transform infrared spectroscopy characterization

Fourier-transform infrared spectroscopy is used to characterize the catalyst in order to reflect the reaction speed and selectivity of the catalyst. By analyzing and identifying the absorption peaks of the catalyst functional groups shown in the infrared spectrum of the catalyst obtained by infrared spectroscopy, the types of functional groups in the catalyst can be displayed, and the surface structure and catalytic process of the catalyst can be further understood [25].

2.11.2. Transmission electron microscope characterization

Transmission electron microscope projects accelerate and aggregate electron beams onto very thin samples and analyzes the images formed by scattering due to collision with samples by imaging devices, thus reflecting the properties of the characterized materials. The ultrastructure of the catalyst surface can be clearly observed by using transmission electron microscope to confirm the existence of platinum supported on titanium dioxide and its binding state with titanium dioxide.

2.11.3. Scanning electron microscope characterization

Scanning electron microscope (SEM) is an electronic system that controls the deflection of electron beam. It reflects the structural properties of the image through the interaction between the beam and matter, and is formed in chronological and spatial order and imaged on an out-of-mirror imaging tube. SEM imaging is featured by high resolution, high level sense and high stereoscopic sense, so the surface of the material can be clearly observed by SEM to characterize the catalysts.

2.11.4. Electrochemical characterization

With electrochemical workstation, catalyst to be tested is loaded on the carbon cloth as the research electrode, and a three-electrode system is formed together with the reference electrode and the auxiliary electrode. Through the relationship between the current and time of the system, the response ability of the catalyst to light can be reflected.

3. Results and discussion

3.1. Preparation and characterization of catalysts

3.1.1. Catalyst preparation

Catalysts are prepared according to the above methods. First, the preparation of phosphorus impregnated hydrated titanium hydroxide was carried out:

(1) Phosphate precursor (0.085 g) was added to a 100 mL beaker and then dissolved by stirring with appropriate amount of water.
(2) Dry hydrated titanium hydroxide (2 g) was added and stirred at room temperature for 4 h.
(3) The resulting mixture was dried under 80°C in oven for 12 h to evaporate the excessive water.
(4) Pure and phosphated TiO_2 NPs were obtained after calcination at 600°C for 4 h

The heating program of atmosphere furnace was set as follows:

C001: 15°C	T001: 60 min	C002: 600°C
C003: 600°C	T002: 240 min	C004: 600°C
C005: 600°C	T003: 60 min	C006: 15°C

Then, on the basis of the phosphorus-impregnated hydrated titanium hydroxide, Platinum was loaded to prepare Pt/TiO_2:

(1) 0.062 acetylacetone platinum and 0.5 g phosphorus were impregnated with hydrated titanium hydroxide and stirred at 500 rpm under 70°C for 12 h overnight.
(2) The black sample obtained were evaporated in the oven.
(3) The obtained material was sintered under 600°C in the atmosphere furnace, heat preserved for 4 h and then aired.
(4) After the procedure of setting atmosphere furnace was finished, it was reduced to room temperature, and then taken out, grinded and saved.

The heating program of atmosphere furnace was set as follows:

C001: 15°C	T001: 60 min	C002: 600°C
C003: 600°C	T002: 240 min	C004: 600°C
C005: 600°C	T003: 60 min	C006: 15°C
C007: 15°C	T004: –121 (Termination proceedings)	

(5) Hydrogen reduction experiment was carried out under 400°C for 3 h, during which the hydrogen was joined with flow control at 0.1 L/h. After that, when it was cooled to room temperature, the sample was taken out and saved.

The heating procedure of atmosphere furnace was set as follows:

C001: 15°C	T001: 60 min	C002: 400°C
C003: 400°C	T002: 180 min	C004: 400°C
C005: 400°C	T003: 60 min	C006: 15°C
C007: 15°C	T004: –121 (Termination proceedings)	

3.1.2. Electrochemical characterization

For the purpose of examining the Pt/TiO_2 prepared to the illumination response, considering TiO_2 is also an excellent semiconductor, timing current analysis was used in this experiment. With electrochemical workstation, the catalyst is loaded on carbon cloth as research electrode. Together with the reference electrode and auxiliary electrode, a three-electrode system could be formed. The response ability of the catalyst to light can be reflected by recording the relationship between the current and time of the system when the light source is turned on and off per 20 s. Fig. 5 is the result of time-current diagram.

As seen in Fig. 5, after 200 s, the system becomes stable, and the measured photocurrent increases rapidly under the illumination of the light source when the switch is turned on, and when the power supply of the closed light source is in dark condition, the measured photocurrent decreases exponentially and almost disappears after a period of time, indicating that the catalyst is very sensitive to light source. However, it also can be observed that the generated photocurrent has not completely returned to zero when the illumination power is turned off, indicating that there is still a certain continuous photoconductivity phenomenon.

3.1.3. Operation parameters optimization

After testing and analyzing the thiocyanate, COD and ammonia nitrogen in the products of each group of experiments, the corresponding position in the experimental design of the optimization parameters was filled in, as shown in Table 9.

3.1.3.1. Modeling

After the data was obtained, simulated, modeled and compared in the Analysis, the best mathematical model was finally selected. The default value was taken in the Model tab, and then the variance analysis (ANOVA) was clicked to test the significance of the equation, which was realized by constantly adjusting the factors. Finally the Model Graphs tab was clicked to select 3D Surface to view the response diagram.

3.1.3.2. RSM prediction of optimal conditions and treatment effects

The optimization target was in the Criteria tab in the Optimization, and then the Solution tab was clicked to
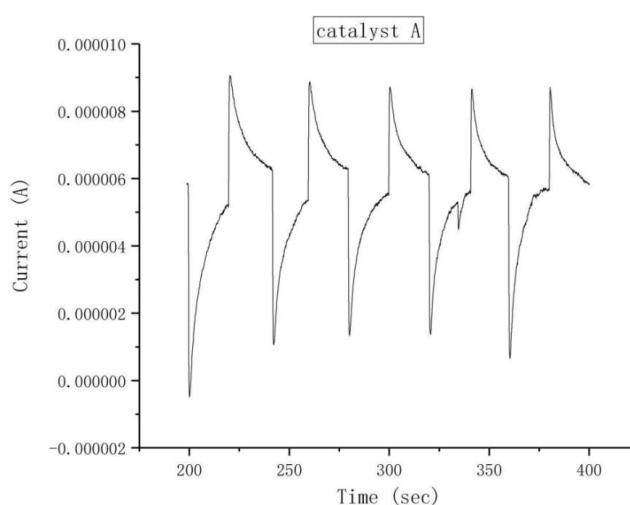

Fig. 5. Time-current diagram.

get the best optimization conditions and forecast processing effect calculated by the system.

3.1.4. Optimal results and analysis of operation parameters of thiocyanate

With the experimental data of thiocyanate given in Table 9 input into the software, a multivariable nonlinear regression model as a function of process conditions is established. The model relationship between process conditions and thiocyanate conversion is given in Eq. (1):

$$
\begin{aligned}
\text{SCN \%} = {} & 9.9600 + 0.00410296 \times \text{Time} + 0.00073742 \times \text{Strength} \\
& - 19.58352000 \times \text{Catalyst Intake} + 0.85397000 \\
& \times \text{ClO}_2 \text{ Concentration} - 0.00000144 \times \text{Time} \\
& \times \text{Strength} + 0.04864900 \times \text{Time} \times \text{Catalyst Intake} \\
& + 0.00182680 \times \text{Time} \times \text{ClO}_2 \text{ Concentration} \\
& - 0.00073391 \times \text{Strength} \times \text{Catalyst Intake} \\
& - 0.00004323 \times \text{Strength} \times \text{ClO}_2 \text{ Concentration} \\
& + 2.37464000 \times \text{Catalyst Intake} \times \text{ClO}_2 \text{ Concentration}
\end{aligned} \tag{1}
$$

The p-value of the model is very low (<0.05), which indicates that the model is statistically significant. The residual normal probability distribution map (Fig. 6) shows that the model agrees well with the experimental data.

Effect of related process variables on thiocyanate conversion is shown in Fig. 7. Both the amount of chlorine dioxide and the amount of catalyst have great influence on the conversion of thiocyanate. Within the experimental range of experimental design, the maximum conversion rate reaches 27% at moderate reaction time and light intensity when maximum chlorine dioxide dosage (10 g) and catalyst dosage (0.5 g) are used. As expected, a positive effect on thiocyanate conversion can be observed at higher catalyst and chlorine dioxide dosage. However, at low chlorine dioxide dosage, the effect of catalyst dosage on the conversion of thiocyanate is very limited.

When the maximum or minimum reaction time and light intensity are used at the same time, as shown in Fig. 7, the conversion of thiocyanate is very low. When the maximum reaction time and light intensity are used at the

Table 9
Summary of experimental data

| Std.	Run	Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2	Response 3
		A: Time	B: Strength	C: Catalyst intake	D: ClO$_2$ concentration	SCN concentration	COD	NH$_4$–N
		min	lx	g	%	mg/L	mg/L	mg/L
25	1	305	15,000	0.25	5	1,474	1,658.4	159.6
16	2	305	30,000	0.5	5	1,337	1,474	172.3
19	3	10	15,000	0.5	5	1,662	1,542.7	164.5
15	4	305	0	0.5	5	1,276	1,539.1	159.3
17	5	10	15,000	0	5	1,273	1,662.3	160.8
12	6	600	15,000	0.25	10	1,208	1,285.8	165.5
2	7	600	0	0.25	5	1,246	1,650.3	154.6
27	8	305	15,000	0.25	5	1,501	1,470.5	172.7
1	9	10	0	0.25	5	1,584	1,463.5	153.5
7	10	305	15,000	0	10	1,378	1,372	161.5
20	11	600	15,000	0.5	5	1,572	1,670.4	164.1
4	12	600	30,000	0.25	5	1,556	1,727.8	147.4
21	13	305	0	0.25	0	1,531	1,830	151.9
5	14	305	15,000	0	0	1,486	1,905.6	149.6
29	15	305	15,000	0.25	5	1,316	1,640.5	151.7
9	16	10	15,000	0.25	0	1,509	1,534.3	148
3	17	10	30,000	0.25	5	1,452	1,709.6	141.3
18	18	600	15,000	0	5	1,432	1,705.5	150.8
28	19	305	15,000	0.25	5	1,228	1,881	143.2
24	20	305	30,000	0.25	10	1,406	1,977.1	146.1
23	21	305	0	0.25	10	1,190	1,697.3	138.5
14	22	305	30,000	0	5	1,348	1,462.6	149.2
22	23	305	30,000	0.25	0	1,522	1,556.4	156.3
6	24	305	15,000	0.5	0	1,532	1,738.9	155.8
26	25	305	15,000	0.25	5	1,372	1,777.5	133.2
13	26	305	0	0	5	1,478	1,747.5	146.1
11	27	10	15,000	0.25	10	1,336	1,909.2	137.5
8	28	305	15,000	0.5	10	1,218	1,445.2	154.1
10	29	600	15,000	0.25	0	1,568	1,857.8	166.2
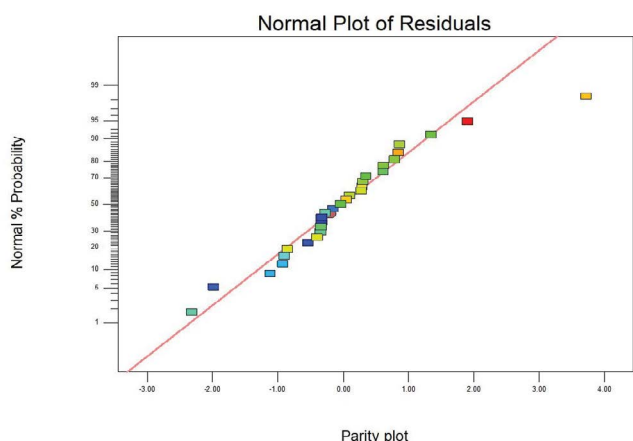
Fig. 6. Thiocyana conversion residual normal probability distribution map.
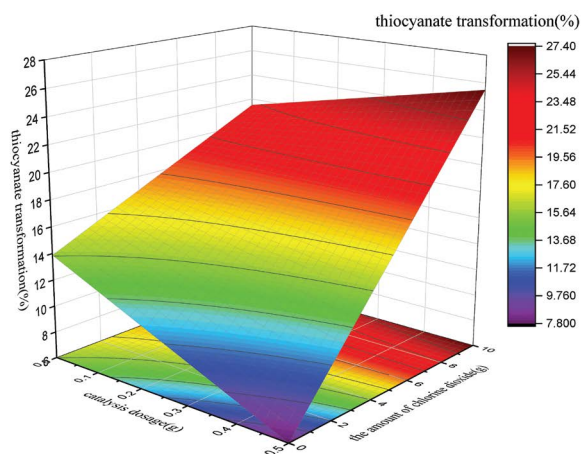

Fig. 7. 3D curved surface response diagram of thiocyanate transformation-catalysis dosage and the amount of chlorine dioxide.

same time, chlorine dioxide will decompose under super strong light, which makes it difficult for the catalyst to act on thiocyanate. When the minimum reaction time and light intensity are reached at the same time, the conversion of thiocyanate reduces because the photocatalytic reaction becomes difficult to carry out.

Next, the optimization goal was selected in the Criteria tab in the Optimization. The optimum conditions of thiocyanate and the effect of prediction were calculated with a click on the Solution tab. Based on DE calculations, when the reaction time is 560.22 min, the light intensity is 5297.97 lx, the amount of catalyst is 0.33 g, and the amount of chlorine dioxide is 8.88 g, the conversion rate of thiocyanate can reach 34.71%, which is the highest value.

3.1.5. COD operation parameter optimization results and analysis

With the COD experimental data given in Table 9 entered into the software and a multivariate nonlinear regression

model as a function of process conditions is established. A model relationship between process conditions and COD conversion is given in Eq. (3).

$$
\begin{aligned}
COD\ \% =\ & 36.25886000 + 8.23935000 \times \text{Catalyst intake} \\
& + 0.64423000 \times ClO_2 \text{ Concentration} - 0.00000020 \\
& \times \text{Time} \times \text{Strength} + 0.00175997 \times \text{Time} \\
& \times ClO_2 \text{ Concentration} + 0.00037523 \times \text{Strength} \\
& \times \text{Catalyst intake} - 0.00002095 \times \text{Strength} \\
& \times ClO_2 \text{ Concentration} - 1.71357000 \\
& \times \text{Catalyst Intake} \times ClO_2 \text{ Concentration}
\end{aligned}
\tag{2}
$$

The *p*-value of the model is very low (<0.05), which indicates that the model is statistically significant. The residual normal probability distribution map (Fig. 8) shows that the model agrees well with the experimental data.

Effects of related process variables on COD transformation are shown in Figs. 9–11. As seen from Fig. 9, light intensity inhibits COD transformation. Combined with Fig. 10, it can be concluded that the conversion rate of COD increases with the addition of chlorine dioxide over time. Within the experimental range of experimental design, the highest conversion can be obtained when the maximum amount of chlorine dioxide (10 g) and the reaction time (600 min) are used under moderate catalyst dosage and light intensity, which can reach 47%.

According to Fig. 11, the conversion rate of COD can reach 42% when chlorine dioxide is not added, but only with the photocatalytic action of oxygen as oxidant. As a result, the amount of chlorine dioxide and the amount of catalyst have a great effect on the COD transformation.

Next, the optimization goal was selected in the Criteria tab in the Optimization. Then with a click on the Solution tab, the optimal conditions of COD and the effect of prediction were calculated by system. Based on DE calculations, when the reaction time is 600 min, the light intensity is 1,107.04 lx, the catalyst dosage is 0 g, and the chlorine dioxide dosage is 10 g, the COD conversion is the highest. The NH_4–N experimental data given in Table 9 were input into the software to establish a multivariate nonlinear regression model as a function of process conditions. The model relationship between process conditions and NH_4–N conversion is given in Eq. (3):

$$
\begin{aligned}
NH_4\text{–N}\ \% =\ & 53.13138000 - 0.00184023 \times \text{Time} + 0.29089000 \\
& \times ClO_2 \text{ Concentration} - 16.38107000 \\
& \times \text{Catalyst Intake}^2 + 0.00312208 \times \text{Time} \\
& \times \text{Catalyst intake}^2 - 0.00006629 \times \text{Time} \\
& \times ClO_2 \text{ Concentration}^2 - 0.000000001097460 \\
& \times \text{Strength}^2 \times \text{Catalyst Intake} + 0.47067000 \\
& \times \text{Catalyst intake}^2 \times ClO_2 \text{ Concentration}
\end{aligned}
\tag{3}
$$

The *p*-value of the model is very low (<0.005), which indicates that the model is statistically significant. The residual normal probability distribution map (Fig. 12) shows that the model agrees well with the experimental data.

Effects of related process variables on COD transformation are shown in Figs. 13 and 14. Both the amount of chlorine dioxide and the amount of catalyst have great influence on the conversion of ammonia nitrogen. Within
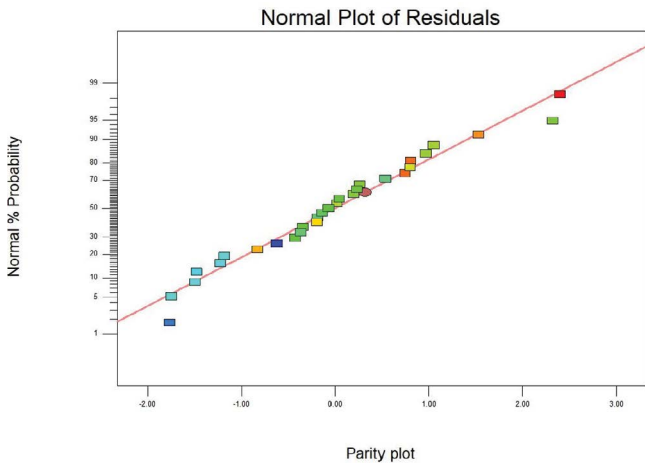
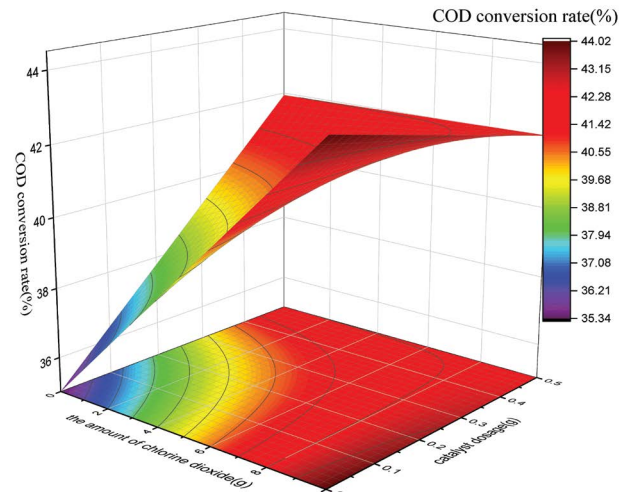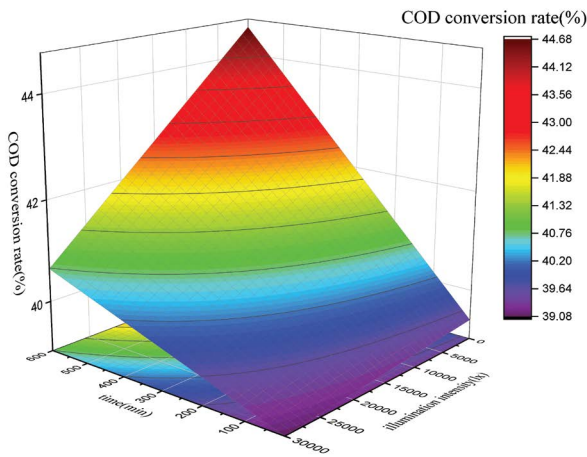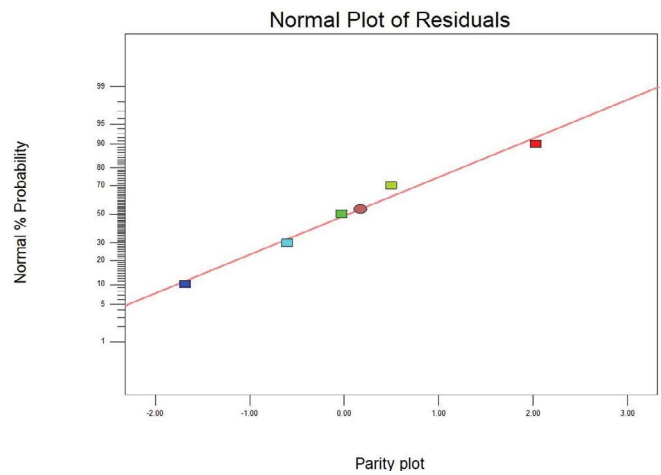Fig. 8. COD conversion residual normal probability distribution map.

Fig. 9. 3D curved surface response diagram of COD transformation-time and illumination intensity.

Fig. 10. 3D curved surface response diagram of COD transformation-time and the amount of chlorine dioxide.

Fig. 11. 3D curved surface response diagram of COD transformation-catalyst dosage and the amount of chlorine dioxide.

Fig. 12. Ammonia nitrogen conversion residual normal probability distribution map.
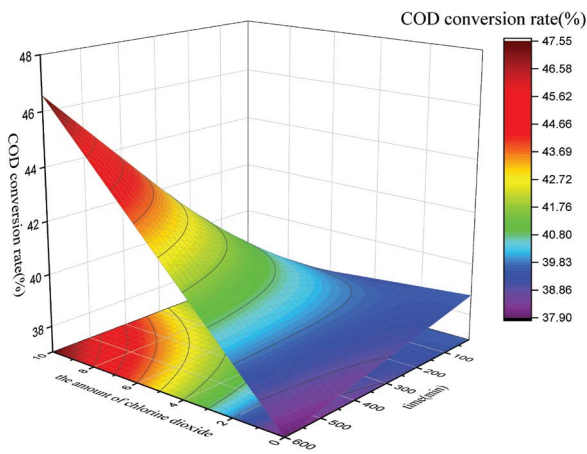
the experimental range of experimental design and under moderate reaction time and light intensity, the highest conversion of ammonia nitrogen can be obtained under moderate chlorine dioxide dosage and catalyst dosage, while the conversion rate of ammonia nitrogen reduces when too high or too low amount of catalyst or too low amount of chlorine dioxide are used.

From Fig. 13, it can be found that under the conditions of moderate catalyst dosage (0.25 g), minimum time (10 min) and maximum chlorine dioxide dosage (10 g), the conversion rate of ammonia nitrogen reaches the maximum value of 55.18%, and the treatment effect is the best at this time. When reaction time is prolonged, the effect of oxidation is reduced by the continuous evaporation consumption of chlorine dioxide, but under the condition without others oxidant, the effect of photocatalytic action on ammonia nitrogen treatment is small, which leads to the decrease of conversion rate.
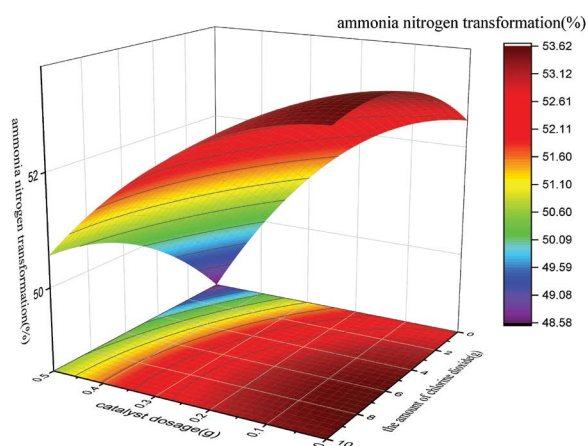
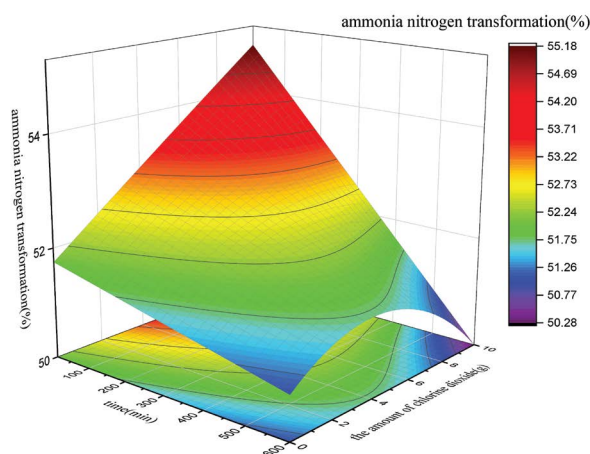Fig. 13. 3D curved surface response diagram.

Fig. 14. 3D curved surface response diagram of ammonia nitrogen transformation-time and the amount of chlorine dioxide.

Next, the optimization goal was selected in the Criteria tab in the Optimization, and then with a click on the Solution tab, the optimum conditions of ammonia nitrogen optimization and the effect of prediction were calculated by system. Based on DE calculations, when the reaction time is 10.01 min, the light intensity is 4.32 lx, the amount of catalyst is 0.2 g, and the amount of chlorine dioxide is 10 g, the conversion rate of ammonia nitrogen reaches 58.18%, which is the highest value.

3.1.6. Optimization results of operating parameters for COD, ammonia nitrogen and thiocyanate

The optimum conditions of ammonia nitrogen optimization and the effect of prediction are obtained. Based on DE calculations, when the reaction time is 10 min, the light intensity is 29,999.89 lx, the catalyst dosage is 0.01 g, and the chlorine dioxide dosage is 0.01 g, thiocyanate, COD and ammonia nitrogen achieve the best treatment effect: the conversion rate of thiocyanate reaches 31.41%, COD conversion

reaches 49.22%, and conversion rate of ammonia nitrogen reaches 56.74%.

4. Conclusion

4.1. Catalyst selection

The catalyst in this experiment is supported by platinum on the basis of preparing phosphorus impregnated hydrated titanium dioxide. Results shows that the conversion of thiocyanate in the sample reaches 34.71% with the participation of photocatalysis. It shows that the catalyst has a certain catalytic effect on thiocyanate conversion.

4.2. COD treatment effects

Optimized results of COD treatment obtained from this experiment shows that COD conversion can reach 53.85% when the reaction time is 600 min, the light intensity is 1,107.04 lx, the catalyst dosage is 0 g, and the chlorine dioxide dosage is 10 g. To conclude, the added chlorine dioxide has an ideal effect on the COD treatment of the sample, but the effect of photocatalytic reaction is not as significant as that of chlorine dioxide.

4.3. Treatment of ammonia nitrogen

The results shows that when the reaction time is 10.01 min, the light intensity is 4.32 lx, the amount of catalyst is 0.2 g, and the amount of chlorine dioxide is 10 g, the conversion rate of ammonia nitrogen can reach 58.18%. It shows that the photocatalytic reaction and chlorine dioxide act together on the water sample, which has a better treatment effect on ammonia nitrogen.

4.4. Treatment of thiocyanate

The optimized results shows that when the reaction time is 560.22 min, the light intensity is 5,297.97 lx, the amount of catalyst is 0.33 g, and the amount of chlorine dioxide is 8.88 g, the conversion rate of thiocyanate can reach 34.71%. It shows that photocatalytic reaction can treat thiocyanate in gold smelting wastewater to a certain extent, can be used as a pretreatment of secondary treatment of sewage, and also has good treatment effect on ammonia nitrogen and COD. The treatment results of gold smelting wastewater can be further optimized.

4.5. Outlook

In this research, the photocatalytic treatment of gold smelting wastewater from Guizhou Jinfeng Mining Co., Ltd., (China) is carried out. The effect of photocatalytic technology on the treatment of this high concentration cyanide wastewater is studied, and a meaningful conclusion is obtained.

However, further in-depth studies can be carried out in the following areas:
(1) Influence of different kinds of catalysts on the treatment effect of gold smelting wastewater.
(2) Exploration on adding chlorine dioxide in addition to other additives to optimize the treatment.

(3) Treatment effect of this research can be further optimized by changing other conditions, such as pressure, pH and temperature.

(4) Further optimization experiment for smelting wastewater is needed. It is difficult to determine whether there is an improved method on the basis of the optimal parameters, and it is still necessary to investigate the further optimization conditions in the later stage.

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