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Sewage Odor Elimination Based on Photocatalytic Oxidation

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The odorous gas discharged during the treatment of municipal sewage can not only reduce the wastewater reproducibility but also cause harm to the human health. It is mainly composed of ammonia nitrogen and sulfides. This paper focuses on odor elimination for sewage treatment plant based on photocatalytic oxidation. Study results reveal that when using WO_3 or TiO_2 alone, a higher degradation will be active for sulfides. Under visible light conditions, the catalytic performance of WO_3 is higher than that of TiO_2. The addition of WO_3 to the TiO_2/WO_3 can improve the photocatalytic activity that gets more intense for ammonia nitrogen and sulfides as the content of TiO_2 increases. While the degradation of organic pollutants is on the decline when TiO_2 increases to a certain extent. Three types of catalysts are prepared by different ratios of TiO_2 and WO_3 for the sewage odor removal. It is found that, among them, the catalyst 2 (WO_3: TiO_2, 3.2:1) has a significantly better effect against inorganic pollutants than others.

1. Introduction

In recent years, China has witnessed the rapid development in the economy and the urbanization in China also moves forward constantly. The discharge of municipal sewage has increased year by year, beyond doubt, which will possibly have a major impact on the way the people live and on the balance and sustainable development of the ecological environment (He et al., 2009). Currently, many cities attach great importance to the sewage treatment, but they ignore the harm of toxic gases emitted during the sewage treatment process. Lots of odorous gas emitted during the sewage treatment process not only reduces the wastewater renewability but also causes harm to the human body (Chen et al., 2010; Sed et al., 2018). Photocatalytic oxidation technology, as one of the most advanced processing technologies, has been widely applied in the fields of medicine, printing and dyeing, etc. Applied in the sewage treatment plants, it, on the one hand, can eliminate odor emitted during sewage treatment, and on the other hand, it can effectively reduce the pollution produced after sewage treatment, thus avoiding secondary pollution. As above, it is supposed that this technology would be bound to have a strong practical application prospect in many fields (Besov and Vorontsov, 2008).

Currently, many scholars and experts at home and abroad have made extensive studies on the elimination of odor emitted after sewage treatment, and their efforts have borne fruits. Some scholars have studied the physicochemical treatment technology in odor elimination process (Quiroz et al., 2013; Lestinsky et al., 2014); some have explored the sources and types of odor in sewage treatment process (Li et al., 2007; Bernardi et al., 2016); and some have also lucubrated the odor treatment (Kastner et al., 2002; Peng et al., 2015). This paper focuses on the odor elimination for sewage treatment plant based on photocatalytic oxidation. It indeed has a strong practical significance.

2. Description of relevant theories

Contaminants from odorous gases produced by the sewage treatment plants mainly include ammonia nitrogen and hydrogen sulfides, which can irritate human body and endanger human health (Ju et al. 2013; Mazzelli et al., 2018). Ammonia nitrogen mainly exists in the forms of organic nitrogen, nitrite nitrogen and nitrate nitrogen, etc., while sulfur does in the forms of sulfides, hydrogen sulfide, and the like.

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The photocatalytic oxidation technology mainly includes the catalyst-active and catalyst-free types. Catalyst-free type depends more on oxygen molecules in the air as oxidants to oxidize and decompose organic matter under ultraviolet light (Denenberg et al., 1969). Catalytic oxidation technology involving oxidant mainly uses H_2O_2, O_3, etc., to produce HO by photo-Fenton reaction in order to degrade various organic pollutants.
Photocatalytic oxidation technology degrades organic pollutants and convert them into H_2O, CO_2 and corresponding inorganic ions such as Cl^-, NO_3^-. Compared to other more advanced oxidation technologies, photocatalytic oxidation technology is less expensive and can degrade most of organic contaminants (Warren et al., 1926). The photocatalytic reaction of the light includes both the oxidation and reduction reactions, and can be widely applied to the odor treatment for water quality. Organic pollutants and even most inorganic pollutants can be converted under photocatalytic reactions and degraded into some micromolecular non-toxic substances (Baylis, 1936).
The main reaction mechanism is expressed as:

$$TiO_2 + hv \rightarrow h^+ + e^- \quad (1)$$

$$h^+ + OH^- \rightarrow OH + H^+ \quad (2)$$

$$h^+ + NH_3 \rightarrow NH_3^+ \quad (3)$$

$$O^2 + e^- \rightarrow O^{2-} \quad (4)$$

$$2\mathrm{OH} + 2NH_3^+ + O^{2-} \rightarrow N_2 + H_2O \quad (5)$$

The total reaction formula is as follows:

$$4\mathrm{NH}_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad (6)$$

$$2H_2S + 2O_2 \rightarrow 2S + 2H_2O \quad (7)$$

However, photocatalytic oxidation technology is also subject to some factors during the degradation process of organic matter, where some intermediate substances adsorbed on the surface of the catalyst sometimes generate, thus weakening the action of the catalyst and suppressing the oxidation and degradation of the pollutants (Schellinck & Brown. 2000). The reaction kinetics are given as follows:

$$\mathrm{rA} = \mathrm{kCAn} \quad (8)$$

Where, CA represents the concentration of the reactants; k represents the rate constant. In general, there is a close relationship between the photocatalytic degradation rate of odor and many impact factors (Gong et al., 2017).

3. Catalyst photolysis experiment

3.1 Standard curve for determination of ammonia nitrogen and sulfides

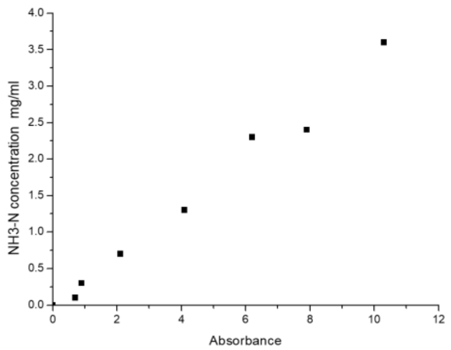

Figure 1: Standard curve for absorbance of NH3-N

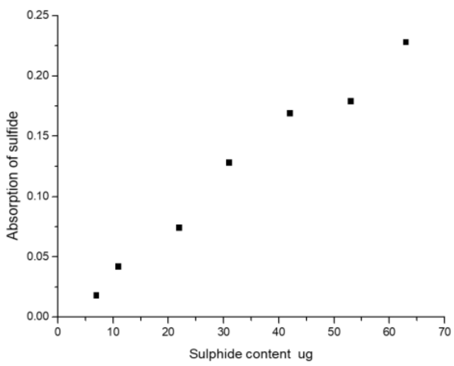

Figure 2: Standard curves for absorbance of sulfide

The ammonia nitrogen standard curve is determined by Nessler's reagent colorimetry. Weigh 0, 0.50, 2.00, 4.00, 6.00, 8.00, and 10.0 mL ammonium and infuse them into the colorimetric tube, and add 1.0 mL sodium potassium tartrate solution to them for stirring. After 10 minutes, the absorbance is measured, and the standard curve of the ammonia nitrogen absorbance is plotted, as shown in Fig. 1.

The standard curve of sulfide is determined using methylene blue spectrophotometry. 0, 0.50, 1.00, 2.00, 4.00, 6.00 and 7.00 mL sodium sulfide are added to the colorimetric tube, respectively, and then 20 mL zinc acetate and sodium acetate solution for stirring. After 10 minutes, the absorbance is measured and a blank test is conducted. The standard curve of sulfide absorbance is shown in Fig. 2.

3.2 Determination of photocatalytic activity of monomer catalyst

In this paper, the photocatalytic activity of two monomer catalysts, TiO_2 and WO_3, is determined. The test method is such that TiO_2 and WO_3 are placed into a muffle furnace and then heated up to 600 degrees, and continue to calcine for 4 h and then cool it.
In the test, the sewage discharged from a sewage treatment plant is taken as a study sample. 0.6 g TiO_2 is added to a 300 ml reactor, allowing it react for 2 h. The solid and liquid are separated by a centrifuge. After the catalyst is separated, the supernatant should be taken to measure the ammonia nitrogen or sulfides.
The test results for TiO_2 are shown in Tables 1 and 2.

Table 1: Comparison of the catalytic effect of TiO_2 on NH_3-N under different light sources

	Original sample	Visible light reaction	Blank test	Ultraviolet light reaction
Add the amount of TiO_2(mg)	/	0.6	0	0.6
UV	/	/	Yes	Yes
The amount of NH_3-N after degradation(mg/ml)	6.74	4.385753	3.583721	2.583948
Removal rate of NH_3-N (%)	/	40.24%	53.98%	58.42%

Table 2: Comparison of catalytic effects of TiO_2 on sulfide under different light sources

	Original sample	Visible light reaction	Blank test	Ultraviolet light reaction
Add the amount of TiO_2(mg)	/	0.6	0	0.6
UV	/	/	Yes	Yes
The amount of NH_3-N after degradation (mg/ml)	1.58	0.41	0.39	0.27
Removal rate of NH_3-N (%)	/	82.47%	74.92%	91.27%

As shown in Tables 1 and 2, it is found that the catalyst TiO_2 is effective in the degradation of inorganic substances.
The test results for WO_3 are shown in Tables 3 and 4.
It is found from Tables 3 and 4 that the catalytic performance of WO_3 is higher than that of TiO_2 under visible light conditions. WO_3 has more advantage in the degradation of inorganic substances. In addition, when WO_3 or TiO_2 is used alone, they all have a high degradation activity for sulfides.

Table 3: Comparison of the catalytic effect of WO_3 on NH_3-N under different light sources

	Original sample	Visible light reaction	Blank test	Ultraviolet light reaction
Add the amount of TiO_2(mg)	/	0.6	0	0.6
UV	/	/	Yes	Yes
The amount of NH_3-N after degradation(mg/ml)	7.02	3.584574	3.395865	2.583472
Removal rate of NH_3-N (%)	/	44.38%	52.96%	64.63%

Table 4: Comparison of the catalytic effect of WO_3 on sulfide under different light sources

	Original sample	Visible light reaction	Blank test	Ultraviolet light reaction
Add the amount of TiO2 (mg)	/	0.6	0	0.6
UV	/	/	Yes	Yes
The amount of NH3-N after degradation(mg/ml)	1.61	0.193	0.237	0.152
Removal rate of NH3-N (%)	/	88.73%	86.94%	92.15%

3.3 Determination of photocatalytic activity of composite catalyst

If WO_3 is constant, different doses of TiO_2 are added, respectively, repeat the test. There is 0.5 g WO_3 as given value. The test results are shown in Tables 5 and 6.

Table 5: Comparison of the catalytic effect of WO_3 on NH_3-N under different light sources

	Original sample	1#	2#	3#	4#	5#	6#
Add the amount of TiO_2 (mg)	/	0	50	100	200	250	300
The amount of NH_3-N after degradation (mg/ml)	6.84	3.483475	3.248755	3.048575	2.498576	3.957674	3.403845
Removal rate of NH_3-N (%)	/	42%	54%	58%	65%	47%	53%

Table 6: Comparison of catalytic effects of WO_3 on sulfide under different light sources

	Original sample	1#	2#	3#	4#	5#	6#
Add the amount of TiO_2 (mg)	/	0	50	100	200	250	300
The amount of NH_3-N after degradation (mg/ml)	1.72	0.16	0.138	0.097	0.085	0.085	0.121
Removal rate of NH_3-N (%)	/	92%	92%	95%	95%	96%	94%

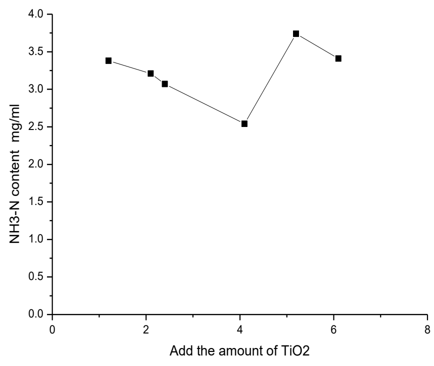

Figure 3: The catalytic effect of WO_3/ TiO_2 composite system on NH_3-N

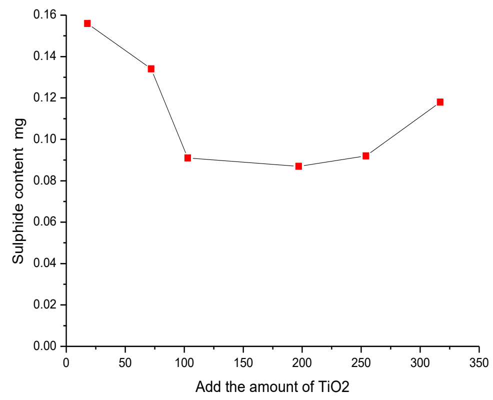

Figure 4: The catalytic effect of WO_3/ TiO_2 composite system on sulphide

It can be seen from Tables 5 and 6 and Fig. 3 and 4, the addition of WO_3 to the TiO_2/WO_3 can improve the photocatalytic activity. As the content of TiO_2 increases, the photocatalytic activities of ammonia nitrogen and sulfides can be strengthened. However, when TiO_2 increases to a certain extent, the degradation of organic pollutants decreases, mainly because some of the substances contained in the reaction solution will produce light scattering effect, resulting in loss of light energy.

3.4 Determination of odors in wastewater treatment plant by composite catalyst

Select a sewage treatment plant in Beijing to conduct the test on odor elimination. Three types of catalysts, i.e. catalyst 1(WO_3: TiO_2, 4:1); 2(WO_3: TiO_2, 3.2:1); 3(WO_3: TiO_2, 3:2), are prepared by different ratios of TiO_2 and WO_3. They are then placed in different reactors, filled with oxygen. Let them react under ultraviolet light for 2 h, and the ammonia nitrogen or sulfides are measured. The test results are shown in Fig. 5.

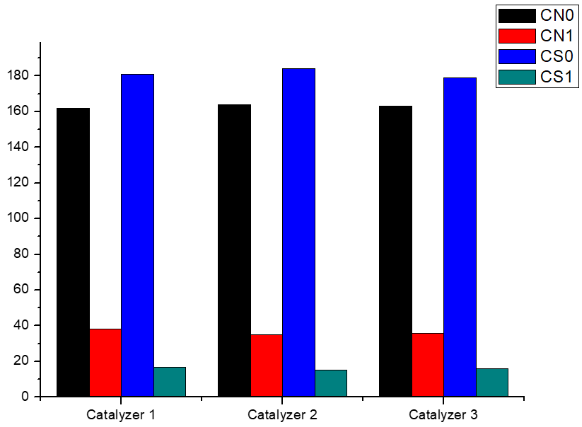

Figure 5: Photocatalytic activity of composite catalyst

As shown in the figure, the three types of catalysts all have a good degradation effect on sewage odor pollutants, but the catalyst 2 (WO_3: TiO_2, 3.6:1) presents a significantly higher elimination effect of inorganic pollutant than other types. The removal rate of sulfide by photocatalyst can reach more than 90%, which can effectively suppress the pollution of S^2 in sewage.

4. Conclusion

4.1 In the process of odor elimination in sewage treatment plant, TiO_2 is more active in the degradation of inorganic materials as photocatalytic activity of monomer catalyst; under visible light conditions, the catalytic performance of WO_3 is higher than that of TiO_2; when using WO_3 or TiO_2 alone, a higher degradation activity can all be enabled for sulfides.
4.2 The addition of WO_3 to TiO_2/WO_3 system can improve the photocatalytic activity. The photocatalytic activity of ammonia nitrogen and sulfides can be strengthened as the content of TiO_2 increases. when TiO_2 increases to a certain extent, the degradation of organic pollutants decreases.
4.3 Take a sewage treatment plant in Beijing as example. In the test, three types catalysts are prepared by different ratios of TiO_2 and WO_3. It is found that the three types of catalysts have good degradation effect on sewage odor, but the catalyst 2(WO_3: TiO_2, 3.2:1) more outperforms others for removing inorganic pollutants.

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