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Odor Removal in Sewage Treatment Plant Based on Photocatalytic Oxidation

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Odor gas ejected during urban sewage treatment can not only weaken the renewability of wastewater, but also endanger the human health. It is mainly composed of ammonia nitrogen and sulfide. This paper aims to shed new light on the odor elimination for the sewage treatment plant based on photocatalytic oxidation method. The findings show that WO_3 or TiO_2, if used alone, has a higher degradation activity for sulfides. Under the condition of visible light shines, the catalytic performance of WO_3 is higher than that of TiO_2; TiO_2/WO_3 system doped with WO_3 can improve the photocatalytic activity. As the dose of TiO_2 continues to rise, the photocatalytic activity of ammonia nitrogen and sulfide can be enhanced; but when it increases to a certain extent, the degradation of organic pollutants is on the decline. According to different contents of TiO_2 and WO_3, the sewage odor is treated by three sets of catalysts. After the test, It is found that the catalyst 2 (WO_3: TiO_2, 3.2:1) removes inorganic pollutants significantly better than other two sets.

1. Introduction

In recent years, China has witnessed the rapid development in the economy, bringing with it a flood of the urban sewage discharged year by year, and worse, which has ruined the living environment of the general public by breaking the ecosystem equilibrium and hindering sustainable development of the ecological environment (He et al., 2009). For now, many cities have attached a great importance to the sewage treatment, but a key fact they always ignore is that There are toxic gases exhausted during the sewage treatment process, which will not only reduce the renewability of the wastewater (Diallo et al., 2018) but also produce hazards to human health and environment (Chen et al., 2010). Photocatalytic oxidation, as one of the most advanced treatment technologies, has been widely applied in the fields of pharmaceuticals, printing and dyeing, etc. Now, the application of the odor elimination in sewage treatment plants can effectively reduce the pollution occurred after sewage treatment, and more importantly, it will also curb the occurrence of secondary pollution. For these reasons, it indeed has a strong application value in practices (Besov and Vorontsov, 2008).

By far, many scholars and experts at home and abroad have made extensive studies on the elimination of odor produced after sewage treatment. These efforts have borne fruits. Some scholars have explored the physicochemical treatment technology for odor treatment (Quiroz et al., 2013; Lestinsky et al., 2014); some have investigated the sources and the types of odors produced in sewage treatment process (Li et al., 2007; Bernardi et al., 2016); some also have studied how to effectively treat the odors (Kastner et al., 2002; Peng et al., 2015). This paper allows the study of the odor elimination in sewage treatment plant based on photocatalytic oxidation technology, providing the clues to the odor removal in future paractices.

2. Relevant theories

Contaminants from odorous gases produced by sewage treatment plants mainly include ammonia nitrogen and hydrogen sulfide, which will irritate human body and endanger human health (Ju et al., 2013). Ammonia nitrogen mainly exists in the form of organic nitrogen, nitrite nitrogen and nitrate nitrogen. Sulfur is mainly

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sulfide, hydrogen sulfide, and the like.

The photocatalytic oxidation technology mainly includes the two types, that is, catalyst and catalyst-free types. Catalyst-free mainly uses the oxygen molecules in the air as oxidants to perform oxygenolysis on organic matter under ultraviolet light irradiation (Denenberg et al., 1969). Catalytic oxidation technology involving oxidant mainly utilizes H_2O_2, O_3, etc., to generate HO by photo-Fenton reaction so that various organic pollutants are degraded.

Photocatalytic oxidation technology degrades the organic pollutants to end up with converting them into H_2O, CO_2 and the inorganic ions such as Cl^-, NO_3^-. Compaed with other more advanced oxidation technologies, photocatalytic oxidation technology is less expensive and can degrade the most part of organic contaminants (Warren et al., 1926). It also includes both oxidation and reduction reactions, so has been widely applied to the odor treatment of water. Organic pollutants and even most of inorganic pollutants can be transformed under the photocatalytic reactions and degraded into non-toxic substances with small molecules.

The prime 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 general reaction equation is

$$4\mathrm{NH_3} + 3O_2 \rightarrow 2N_2 + 6H_2O \quad (6)$$

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

However, photocatalytic oxidation technology is also susceptible to some factors in the degradation process of organic matters. During the degradation process, there are intermediate substances sometimes produced, which are adsorbed on the surface of the catalyst, restricting the action of the catalysts, inhibiting the oxidation and degradation of the pollutants (Schellinck and Brown, 2000). The reaction dynamics equation is:

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

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 test

3.1 Standard curve for the determination of ammonia nitrogen and sulfide

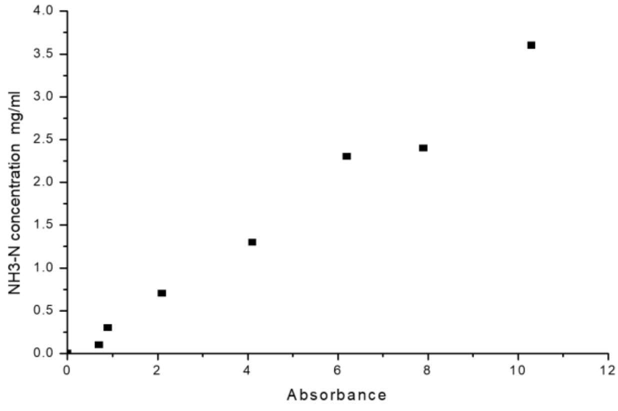

Figure 1: Standard curve for absorbance of NH_3-N

The ammonia nitrogen standard curve is determined by Nessler reagent colorimetry. In the colorimetric tube, inject 0, 0.50, 2.00, 4.00, 6.00, 8.00, and 10.0 mL ammonium, and add 1.0 mL sodium potassium tartrate solution, stir them. After 10 minutes, the absorbance is measured, and the standard curve of the absorbance of ammonia nitrogen is plotted out, as shown in Fig. 1.

The standard curve of sulfide is determined by 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, in conjunction with 20 mL zinc acetate sodium acetate solution, and then stirred. After 10 minutes, the absorbance is measured, and a blank test is conducted to plot out the standard curve of sulfide absorbance, as shown in Fig. 2.

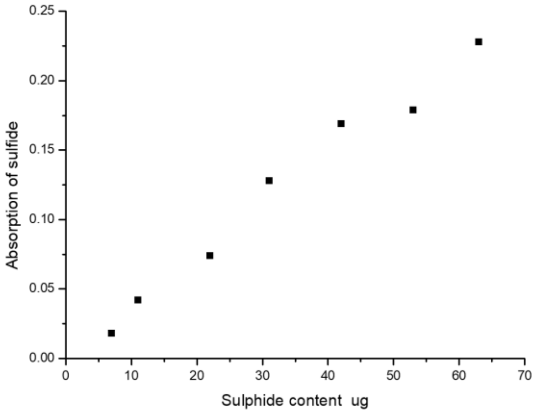

Figure 2: Standard curves for absorbance of sulfide

3.2 Determination of photocatalytic activity of monomer catalyst

Here, the photocatalytic activities of two monomer catalysts, TiO_2 and WO_3, are determined. The test method is to add TiO_2 and WO_3 to a muffle furnace and then ramp up to 600 degrees, continuously calcine it for 4 hours and then cool it.

We take a sewage treatment plant as a study sample, the sewage discharge from there is simulated in the test. 0.6 g TiO2 is added to a 300 ml reactor, let them react with each other for 2 h. Separate solid and liquid by a centrifuge, remove the supernatant from the separated catalyst, and measure the content of ammonia nitrogen or sulfide.

The test results for TiO2 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%

From data 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 property of WO_3 is higher than that of TiO_2 under the condition of visible light shines. WO_3 is more superior for the degradation of inorganic substances. In addition,

WO_3 or TiO_2, if used alone, has 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 TiO_2(mg)	/	0.6	0	0.6
UV	/	/	Yes	Yes
The amount of NH_3-N after degradation(mg/ml)	1.61	0.193	0.237	0.152
Removal rate of NH_3-N(%)	/	88.73%	86.94%	92.15%

3.3 Determination of photocatalytic activity of composite catalyst

WO_3 is 0.5g as a constant, and different doses of TiO_2 are added, repeat the test. 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%

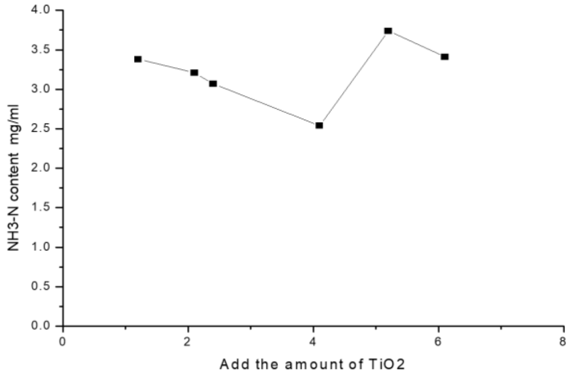

Figure 3: The catalytic effect of WO_3/ TiO_2 composite system on NH_3-N

As shown in Tables 5 and 6 and Figures 3 and 4, it is found that the addition of WO_3 to the TiO_2/WO_3 system can enhance the photocatalytic activity. As the content of TiO_2 increases, the photocatalytic activity of ammonia nitrogen and sulfide can be enhanced. However, when the dose of TiO_2 increases to a certain value, the degradation of organic pollutants starts to decline due to the fact that some substances contained in the reaction solution will produce a scattering effect on light beam, resulting in the loss of light energy.

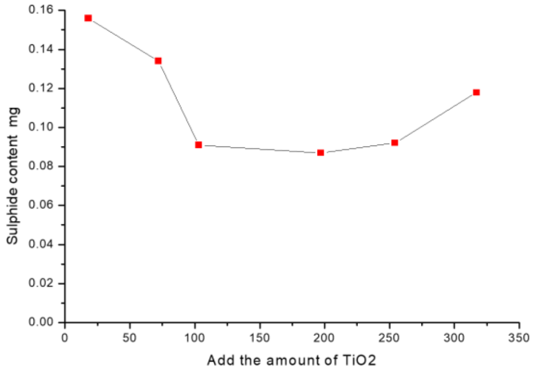

Figure 4: The catalytic effect of WO_3/ TiO_2 composite system on sulfide

3.4 Determination of odors in sewage treatment plant in the case of composite catalyst

A sewage treatment plant in Beijing, for example, is sampled to conduct the test in an attempt to study the odor elimination. Subject to the different contents of TiO_2 and WO_3, there are three sets of catalysts, i.e. catalyst 1 (WO_3: TiO_2, 4:1); catalyst 2(WO_3: TiO_2, 3.2:1); catalyst 3(WO_3: TiO_2, 3:2). Different sets of catalysts are placed in different reactors, respectively, fill it with oxygen, and let them react with each other under ultraviolet light for 2 hours; the contents of ammonia nitrogen or sulfide are measured. The test results are shown in Fig. 5.

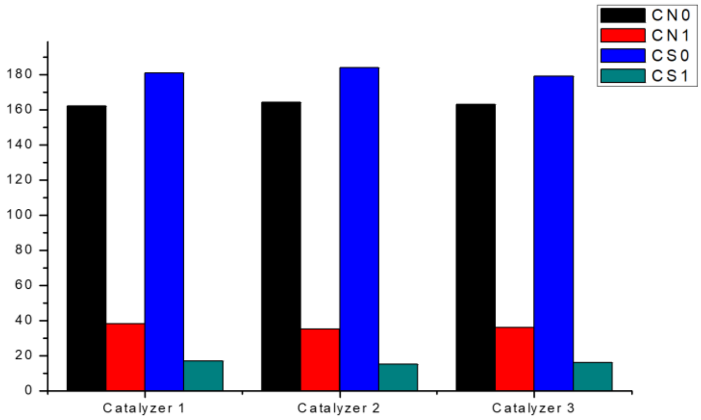

Figure 5: Photocatalytic activity of composite catalyst

From the results shown in the figure, the three sets of catalysts have a good degradation effect on sewage odor pollutants, and the catalyst 2 (WO_3: TiO_2, 3.6: 1) has a higher capacity to remove inorganic pollutants than other two sets. The photocatalyst can realize a more than 90% removal rate of sulfide, so that it can effectively mitigate the pollution of S^{2-} in sewage.

4. Conclusion

(1) In the process of odor treatment in sewage treatment plant, TiO_2 is effective to degrade inorganic substance in terms of photocatalytic activity of monomer catalyst, so that it has more advantages; under the condition of visible light shines, the catalytic performance of WO_3 is higher than that of TiO_2; when using WO_3 or TiO_2 alone, they all present a higher degradation activity for sulfides.

(2) The addition of WO_3 to the TiO_2/WO_3 system can enhance the photocatalytic activity. As TiO_2 increases, the photocatalytic activity of ammonia nitrogen and sulfide can be raised. However, when the dose of TiO_2 increases to a certain extent, the degradation of organic pollutants starts to decline.
(3) A sewage treatment plant in Beijing, for example, is sampled to conduct the test. According to the different contents of TiO_2 and WO_3, there are three sets of catalysts. After test, it is found that these catalysts all have a good degradation effect on sewage odor, but the catalyst 2 (WO_3: TiO_2, 3.2:1) is highest for eliminating the inorganic contaminants than other sets of catalysts.

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