

Influence factors of photocatalytic activity of the filter media modified by TiO₂

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Abstract

The gangle filter media was modified by the titanium dioxide (TiO₂) through the liquid phase deposition method. Some influence factors of photocatalytic activity were investigated, including the mole ratio of initial solution, the water bath temperature, the deposition time, the calcination temperature and the heat preservation time of calcination. The morphology of the film was examined by SEM, EDS and crystallite structure by X-Ray Diffraction (XRD). The SEM, EDS and XRD data showed that new TiO₂ crystal was found in the modified filter media. And the specific surface area of the modified filter media greatly increased. By the orthogonal experiment, the optimum parameters of modification were (NH₄)₂TiF₆:H₃BO₃ = 1:2, water bath temperature of 80 °C, deposition time of 5 h, calcination temperature of 500 °C, and 1 h heat preservation time of calcination. Under above conditions, the heavy nitrogen wastewater of 1589.94 mg/L COD and 18750 times chroma was treated by the modified filter media. After 1 h catalytic reaction, the decolorization rate and COD removal rate reached 65.89 and 47.87%, respectively.

Keywords: TiO₂, liquid phase deposition, heavy nitrogen, decolorization rate, COD.

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2-Diazo-4,6-dinitrophenol (DDNP) has been widely used in commercial and military detonators as an important and effective primary explosive. It is an energetic compound without lead [1,2], and its good energy capability is comparable with that of high explosives. Among existing primary explosives, DDNP is a very promising initiator [3,4]. But in the process of DDNP producing, large amount of heavy nitrogen wastewater was produced, which had the characteristics of higher chroma, higher COD, higher toxicity, complicated composition, etc. [5]. If the heavy nitrogen wastewater without being treated was discharged into river, it would severely pollute the environment and threaten the health of people living in the downstream [6]. This problem has attracted the researchers' attention and puzzled the local industry and environmental protection institution.

Nowadays, the main treatment methods of heavy nitrogen wastewater are adsorption method, micro-electrolysis/H₂O₂ method, and biochemistry method, etc. But the initial cost of these methods was high. Some enterprises could not afford it. And some methods are in the period of exploration, and it is difficult for them to be applied and promoted.

Photocatalytic oxidation is a newly developed technology for wastewater treatment [7,8]. Sunlight was used as a potential radiation source in this method. It

could stimulate the generation of hole and electron pair for the catalyst, so strong redox occurred in this method. Many pollutants such as refractory organics could be treated by this method. It was difficult for the heavy nitrogen wastewater of higher chroma to be treated. So, it is particularly important for the heavy nitrogen wastewater to find an economic and efficient treatment technology.

Titanium dioxide (TiO₂) is widely used as a photocatalyst in the photocatalytic oxidation method because it is relatively highly efficient, cheap, non-toxic, chemically and biologically inert and photo stable [9–13]. TiO₂ in the anatase phase has been used as an excellent photocatalyst and it is well applied for purification [9,10]. As a promising material, TiO₂ has been used in the photocatalytic degradation of polluted water and air [9–11]. TiO₂ was also widely applied in pollutants processing, sensors, photovoltaics and dye-sensitized solar cells due to its nontoxicity, high stability and photoelectric properties [14–19].

Photocatalytic oxidation was an effective method for the chroma reduction of wastewater [11–18], and it was easy to be operated. In this study, the feasibility of photocatalytic oxidation for heavy nitrogen wastewater was explored. The core was to investigate the influence factors of modification and the photocatalytic activity of the filter media modified by TiO₂. And the optimum technological conditions of modification were determined by the orthogonal experiment.

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EXPERIMENTAL

Preparation of the filter media

The main materials for the preparation of the filter media were coal gangue, waste glass, little CaCO₃ as the additive, and the volatile organic matter as the forming agent. Gangue was selected from the deserted gangue in the coal mine, and the waste glass was the ordinary flat glass. Coal gangue and waste glass were fine ground in the ball mill and uniformly mixed according to certain ratio. Forming agent along with the little blended powder were put into the ball mill as the mother bulb. The blended materials were continuously added onto the scrolling ball particles and sprayed by a small sprayer. Then the mother bulb grew bigger and denser. After certain time, the bigger mother bulb was filtered by the 5 mm sieve and the smaller mother bulb was returned into the rotary. The average remaining time of the ball in ball mill was 1h and the particle sizes were between 3 mm and 6 mm. Then the raw ball was roasted in the muffle furnace under the certain technological conditions.

Preparation of the filter media modified by TiO₂

The filter media modified by TiO₂ was prepared by the liquid phase deposition method using the gangue filter media as the carrier, and (NH₄)₂TiF₆ and H₃BO₃ as precursors. Firstly, the solutions of (NH₄)₂TiF₆ and H₃BO₃ were prepared with the distilled water. And 250 mL reaction solution in different ratios was acquired in the coating container by taking certain volume of two solutions. Secondly, the coating container was put into the constant temperature water bath, and 100 g filter media was put into the coating container under the condition of stir. The filter media was taken out from the coating container after it had deposited for certain time at constant temperature. Thirdly, the filter media was washed with the distilled water and then was dried in the dryer at 120 °C. Fourthly, the dried filter media was put into the muffle furnace whose temperature rose from the room temperature to the set tempera-

ture at the speed of 15 °C/min. After certain time the gangue filter media modified by TiO₂ was obtained. The preparation device is shown in Figure 1.

Photocatalytic reaction device

Photocatalytic reactor was the laminated glass container. The interlayer was photocatalytic reaction unit filled with the filter media modified by TiO₂ (Figure 2). The filling rate of the filter media was 50% and the volume was about 250 ml. 50 cm length quartz glass tube was placed in the internal device of the photocatalytic reactor. 25 W ultraviolet illumination tube was placed in the quartz glass tube. Glass tube mouths of 1 cm inner diameter were set in each side of the reactor, and water inflow from upper orifice. Oxygen was generated by air pump. The reactor was washed with the original solution, and timing began when appropriate solution was taken into the reactor.

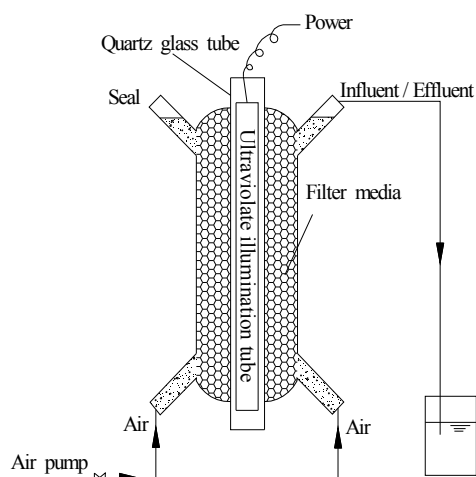


Figure 2. The test device of photocatalytic reaction.

Water samples and analysis method

Heavy nitrogen wastewater was used as the target degradation substrate and COD removal rate and decolorization rate were evaluated. The COD value was

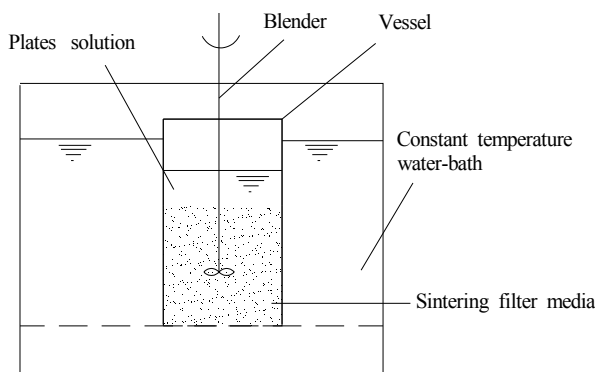


Figure 1. The device for the preparation of the modified filter media.

measured by the potassium dichromate method. The decolorization rate was used to measure the degradation effect of the modified filter media. And the variation of absorbency was characteristic of decolorization efficiency. The computation formula was as follows:

$$\eta = 100 \frac{A_0 - A}{A_0} \quad (1)$$

where A_0 and A are the absorbency of wastewater at the initial time and t time, respectively. Absorbency was determined by 722 s visible spectrophotometer. And the wavelength value was 420 nm.

RESULTS AND DISCUSSION

Particle morphology and physicochemical properties of TiO₂ film

SEM. Figure 3 shows that the SEM images of the modified and unmodified filter media under different magnification. Figure 3c and d were the corresponding enlarged images of Figure 3a and b, respectively. Figure 3b shows that the surface of modified filter media had brighter background. As TiO₂ thin film had reflection, and light left the uneven surface after multiple reflections. The absorption and utilization of light would inevitably increase. It was good for the catalytic reaction. Although the surface of unmodified filter media was

very rough, and there were large irregular holes in the surface. But the surface of particle was smoother. Figure 3d shows that many evenly distributed 30–50 nm bumps existed in the surface of the modified filter media. They were TiO₂ grain particles and these particles piled up in together in different ways. This made the microstructure of the surface of the modified filter media change. And the specific surface area of the modified filter media was greatly improved. It was good for the particle to be adsorbed on the surface. Then more ultraviolet light was adsorbed. So TiO₂ film had good photocatalytic performance [20].

EDS. Figure 4 shows the EDS electron energy spectrum diagram of the modified and unmodified filter media. From the diagram we can see that the main components of the unmodified filter media were silicon, aluminum, oxygen, carbon, calcium and iron. Titanium element was found in the energy spectrum diagram of the modified filter media and existed in the form of TiO₂. The weight percentage and atomic percentage of the titanium were 0.99 and 0.40%, respectively (Figure 4b).

XRD. In order to further research the crystallography characteristics of modified and unmodified filter media, XRD was conducted. The results were shown in Figure 5. By the qualitative analysis, a great quantity of alpha quartz crystal, calcium scale quartz, and feldspar existed in the mineral phase structure of the filter media. TiO₂ crystal did not be found in the unmodified

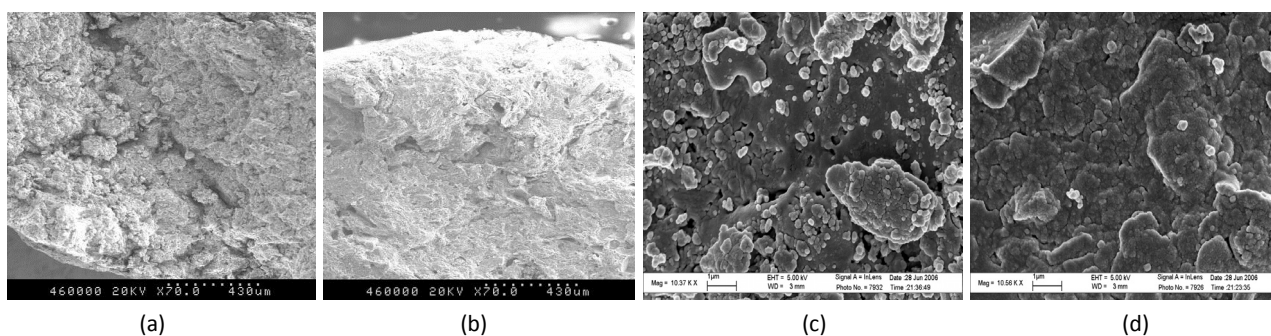


Figure 3. Image of SEM (unmodified and modified).

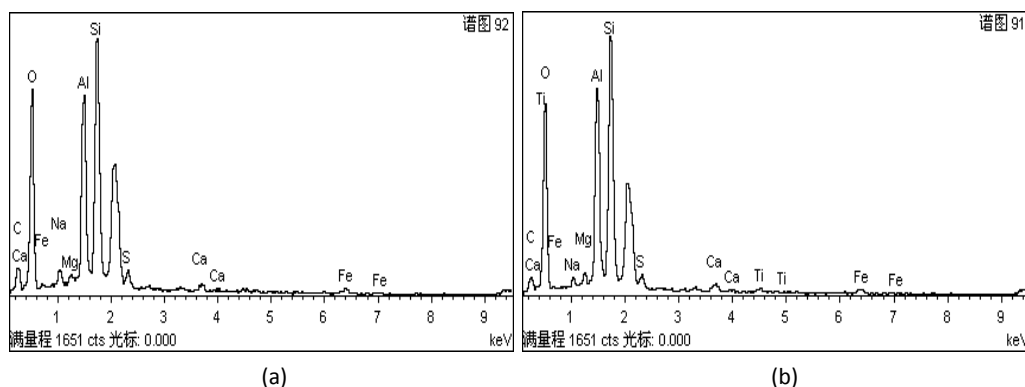


Figure 4. Image of EDS (unmodified and modified).

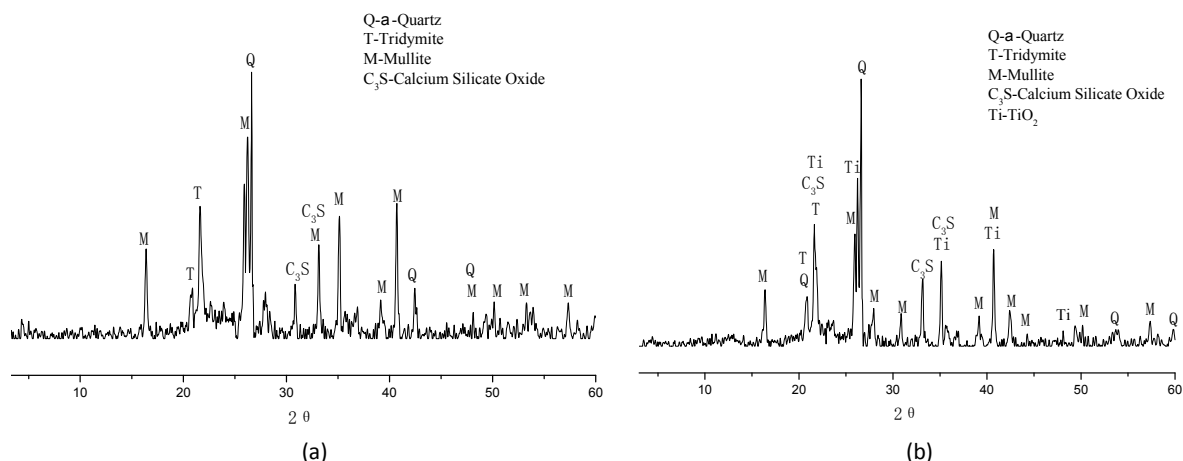


Figure 5. Image of XRD.

filter media. New TiO₂ crystal was found in the modified filter media. The superposition phenomenon was found in the diffraction peak of TiO₂ crystals and calcium feldspar crystal.

Specific surface area and void fraction. The specific surface area and void fraction of modified and unmodified coal gangue filter media were shown in Table 1. The specific surface area of the modified filter media has been increased by 70%. The main reason was that the microstructure was formed because of the high dispersion degree of nano TiO₂ at the surface of the filter media. After the treatment of high temperature, amorphous TiO₂ was transformed into the anatase phase. Specific surface area significantly increased owing to the crystallization of the element and the formation of microporous [21]. According to the physical and chemical theory, the solid with big specific surface area often was in the unstable state and its surface always tended to become smooth [22]. Such surface had good adsorption performance and could provide more catalytic activity center for the reaction, and the catalytic reaction could smoothly happen.

Table 1. Specific surface area and void fraction of modified and unmodified filter media

Filter media	Specific surface area m ² /g	Void fraction %
Unmodified	4.6	48.51
Modified	7.8	49.63

Analysis of influence factors of modification

In this paper, the heavy nitrogen wastewater of 18750 times chroma and 1589.94 mg/L COD was treated by the filter media modified by TiO₂. And the photocatalytic activity of the modified film was investigated. All photocatalytic reaction times were setting for 1h. In the process of TiO₂ film preparation, its photocatalytic performance was influenced by many

factors. In this study, the mole ratio of initial solution, deposition temperature, deposition time, heat treatment temperature, and heat preservation time were studied.

Mole ratio of initial solution. H₃BO₃ and (NH₄)₂TiF₆ of different mole ratios were mixed and stirred at 80 °C for 5 h, and then were heated at 450 °C for 1 h. Under this condition, the modified film was obtained and its photocatalytic performance was studied.

Figure 6 shows the composition of the plating solution obviously affected the photocatalytic activity. The decolorization rate and COD removal rate increased at first and then declined. When the mole ratio of H₃BO₃ and (NH₄)₂TiF₆ was 3:1, the decolorization and COD removal rates reached the maximum which are 46.67 and 28.90%, respectively. The transparency of the deposition film was determined by the composition of reaction solution. When the concentration of (NH₄)₂TiF₆ was higher, the speed of the hydrolysis and the film formation grew faster. When large amount grain deposited in very short time, the film was thick and opaque. But when the concentration of (NH₄)₂TiF₆ was lower, the film formation was slow. So film was transparent. If the concentration of (NH₄)₂TiF₆ was too lower, it was difficult for the film to form because it was difficult for [TiF₆]²⁻ to hydrolyze [11,23]. Meantime, the pH value of the initial solution effected the dehydration, polymerization, and TiO₂ phase [24–27].

The pH value of the precursor solution is a decisive factor in controlling the final particle size [28], shape [29], phase [30] and agglomeration [31] due to its influence on the relative rates of hydrolysis and polycondensation. The coordination Ti⁴⁺ and OH⁻ depended of the pH [24]. In the pH 2 solutions ([Ti(OH)₂(H₂O)₄]²⁺), rod-like rutile formed. In the pH 4 solutions ([Ti(OH)₄(H₂O)₂]⁰), the skewed chains of the anatase structure formed. And small quantities of the rutile structure existed in the precursor species and decreased the critical size of anatase-to-rutile transfor-

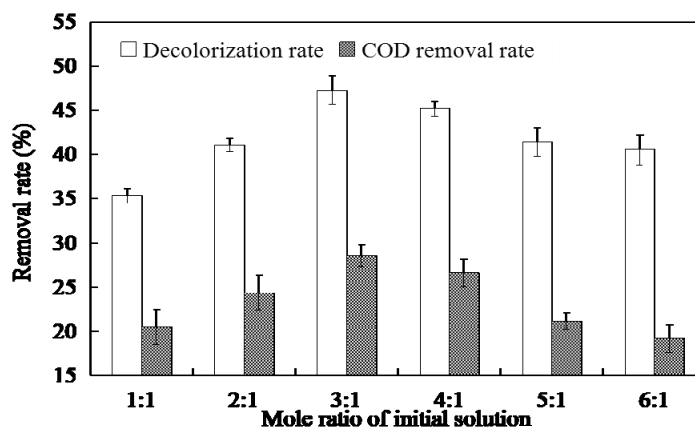


Figure 6. Effect of the mole ratio of initial solution on removal rate.

mation [24]. The probabilities of polycondensation occurred in the pH 7 solutions ($[\text{Ti}(\text{OH})_6]^{2-}$). So anatase and rutile cocrystallized from the solutions. In the pH 9 solutions ($[\text{Ti}(\text{OH})_7]^{3-}$), much structural and free water in the netlike precursor structure was involved during the process of polymerization. The presence of excessive OH^- would hinder the orientation movement of crystal nucleus. Thus, the disordered precursor structure would easily crystallize into the anatase phase. These provided a deep insight into the formation mechanism of anatase or rutile at different pH values [24].

H_3BO_3 did not affect the film thickness but the speed of film formation. When H_3BO_3 content was too low, the mixed solutions was not stable and tended to hydrolyze. So the speed of $[\text{TiF}_6]^{2-}$ hydrolysis was very rapid. While H_3BO_3 content was too high, the hydrolysis of $[\text{TiF}_6]^{2-}$ was inhibited. So the film formation was hard. When the concentrations of $(\text{NH}_4)_2\text{TiF}_6$ and H_3BO_3 were in the range of 0.08–0.20 mol/L and 0.10–0.50 mol/L, respectively, the optimal condition of film formation reached [32]. When the mole ratios of H_3BO_3 and $(\text{NH}_4)_2\text{TiF}_6$ were from 2 to 4, the transparent film

could be obtained. Therefore, 0.10 mol/L $(\text{NH}_4)_2\text{TiF}_6$ and the mole ratios 2, 3, and 4 of H_3BO_3 and $(\text{NH}_4)_2\text{TiF}_6$ were chosen in this study.

Water bath temperature. Due to the endothermic process of the film formation, temperature effected the formation of film. When temperature was higher, the speed of the film formation was quicker. But too high temperature would cause the evaporation of the plating solution. So the spot existed in the surface of the film and it was not suitable for the film formation. When $C_{\text{H}_3\text{BO}_3}:C_{(\text{NH}_4)_2\text{TiF}_6}$ was 3:1, the mixed solution was deposited for 5 h and then heated at 450 °C for 1 h. Under this condition, the modified film was obtained and its photocatalytic performance was studied.

Figure 7 shows TiO_2 film had certain catalytic activity when water bath temperature is from 50 to 90 °C. Hence, the temperature range of the liquid phase deposition film is wide. With the rising of water bath temperature, the decolorization rate and COD removal rose at first and then declined. When water bath temperature was 70 °C, the removal rates reached the highest values which are 52.00 and 34.45%, respect-

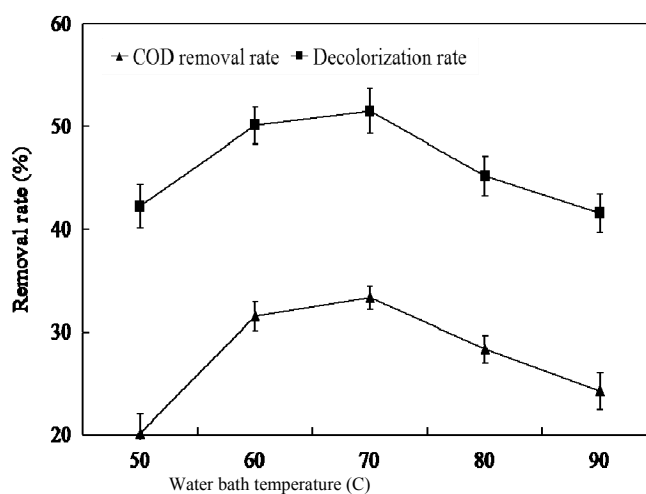


Figure 7. Effect of water bath temperature on removal rate.

ively. With the rising of temperature, the time that the turbid phenomenon emerged in the plating solution obviously reduced. According to the collision theory of chemical reaction, at lower temperature, $[\text{Ti}(\text{OH})_6]^{2-}$ and $-\text{OH}$ at the surface of the filter media would fully contact and collide. And the dehydration and the polymerization reaction happened [33,34]. TiO_2 film generated at the surface. With the rising of temperature, the thermodynamic movement of molecular sped up and the dehydration and polymerization of $[\text{Ti}(\text{OH})_6]^{2-}$ and $-\text{OH}$ sped up. Therefore, with the rising of temperature in low temperature range, COD removal rate also increased. But when temperature continued to rise, the speed of the dehydration and polymerization of $[\text{Ti}(\text{OH})_6]^{2-}$ was higher than that of $[\text{Ti}(\text{OH})_6]^{2-}$ and $-\text{OH}$. Dehydration and polymerization of $[\text{Ti}(\text{OH})_6]^{2-}$ might be the main process of film formation. The polymer chains emerged in this process covered the surface of matrix, and the dehydration and polymerization of $[\text{Ti}(\text{OH})_6]^{2-}$ and $-\text{OH}$ was impeded. This caused the reduction of film adhesion. Hence, when temperature rose to the critical value, the removal rates declined. Based on above analysis, water bath temperature effected the deposition and the adhesion of film. The optimal temperature was 70 °C in this study.

Deposition time. At certain water bath temperature, the thickness of photocatalytic film changed with the variation of deposition time. In this study, the conditions of $c_{\text{H}_3\text{BO}_3}:c_{(\text{NH}_4)_2\text{TiF}_6}$ of 3:1 and 80 °C water bath were chosen, the solution was deposited for different time and then heated at 450 °C for 1h. The photocatalytic performance of the modified film obtained under above condition was studied.

Figure 8 shows TiO_2 film had photocatalytic activity when the deposition time was from 3 to 6 h. The decolorization rate and COD removal rate rose at first and then decreased with the rising of deposition time. When deposition time was 5 h, the removal rates reached the maximum which were 52.00 and 34.45%,

respectively. At certain water bath temperature, when deposition time increased, film became thicker. Its photocatalytic activity has been increased. But when the film thickness was out of certain range, its photocatalytic activity would decline because certain depth existed both in the illumination of ultraviolet and in the photocatalytic reaction of film [11]. Meanwhile, deposition temperature affected the deposition time. Generally, the higher the temperature was, the greater the deposition rate was, the shorter the film formation time of certain thickness was. So there was close relationship between deposition time and film thickness. In this study, the optimal deposition time was 5 h.

Calcination temperature. During the preparation of TiO_2 photocatalyst, heat treatment temperature was an important parameter. Under the conditions of 5 h deposition time, $c_{\text{H}_3\text{BO}_3}:c_{(\text{NH}_4)_2\text{TiF}_6}$ of 3:1, and water bath temperature of 80 °C, the mixed solution was treated at different calcination temperature for 1 h. The effects of calcination temperature on the photocatalytic activity of TiO_2 film were studied.

Figure 9 shows the decolorization rate and COD removal rate rose at first and then declined with the rising of calcination temperature. When calcination temperature was 500 °C, the decolorization rate and COD removal rate reached the maximum which were 58.40 and 36.97%, respectively. Before sintering, TiO_2 existed in amorphous state. Anatase phase TiO_2 could be obtained by heat treatment. With the rising of sintering temperature, the anatase phase gradually transformed into the rutile phase. Calcination effected not only the physical and chemical properties of nanocrystal of titanium oxide but also the size of grain. When calcination temperature was from 300 to 500 °C, catalyst had the best photocatalytic activity [35–37]. Because calcination could let the gel become dense at above temperature, and the particle size of micropore increased with the enlargement of sintering grain. So the crystallinity of dried anatase phase and mixed

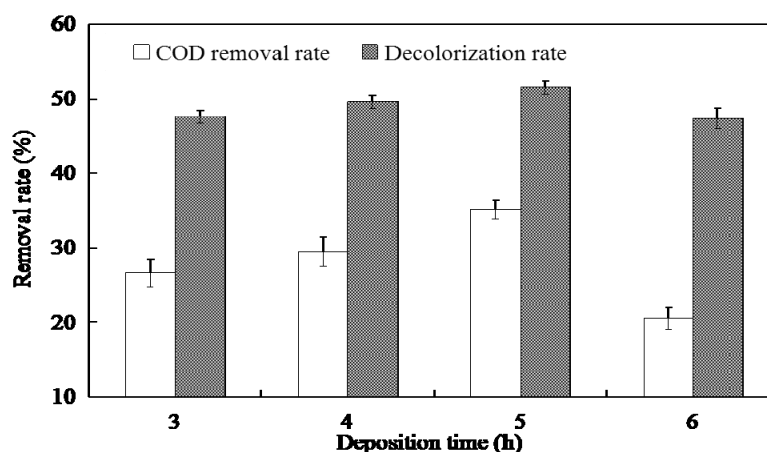


Figure 8. Effect of deposition time on removal rate.

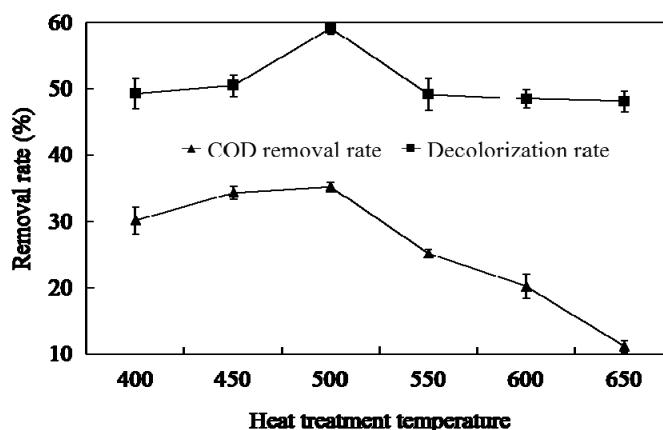


Figure 9. Effect of heat treatment temperature on removal rate.

phases was obviously improved. When calcination temperature was less than 550 °C, anatase phase mainly existed [37]. When calcination temperature was 550 °C, the rutile phase mainly existed and its proportion gradually increased with the rising of temperature. When calcination temperature was more than 700 °C, rutile phase mainly existed. The photocatalytic performance of TiO₂ strongly depended on its crystal phase and surface area [37]. The pure rutile phase TiO₂ hardly had catalytic activity. But the anatase phase of higher surface area had better photocatalytic activity. When small amount anatase phase transformed into the rutile phase, the catalytic activities of mixed phases were higher than those of pure anatase phase TiO₂ [35–37]. In this study, the optimal temperature of heat treatment was 500 °C.

Heat preservation time of calcination. According to the optimal conditions of single factor experiment, when the ratio of C_{H3BO3} and C_{(NH4)2TIF6} was 3:1, the deposition time was 5 h, and the water bath temperature was 70 °C, the plating solution was treated at 500 °C for different time. The photocatalytic performance of

the modified film obtained under above conditions was studied.

Figure 10 shows the heat preservation time affected the photocatalytic activity of modified filter media. The decolorization rate and COD removal rate increased at first and then declined with the rising of time, and the photocatalytic activity was highest when the heat treatment time was 2 h. The decolorization rate and COD removal rate were 63.73 and 41.84%, respectively. Anatase phase TiO₂ gradually transformed the rutile phase with the increasing calcination time. With the increasing proportion of rutile phase, the photocatalytic performance of TiO₂ film would be significantly affected. So the heat preservation time of calcination should be controlled. The optimal heat treatment time was 2 h in this study.

Orthogonal experiment of optimal process parameters

To determine the optimal parameters of the gangue filter media modified by TiO₂, the decolorization rate was evaluated. C_{H3BO3}:C_{(NH4)2TIF6} of plating solution, water

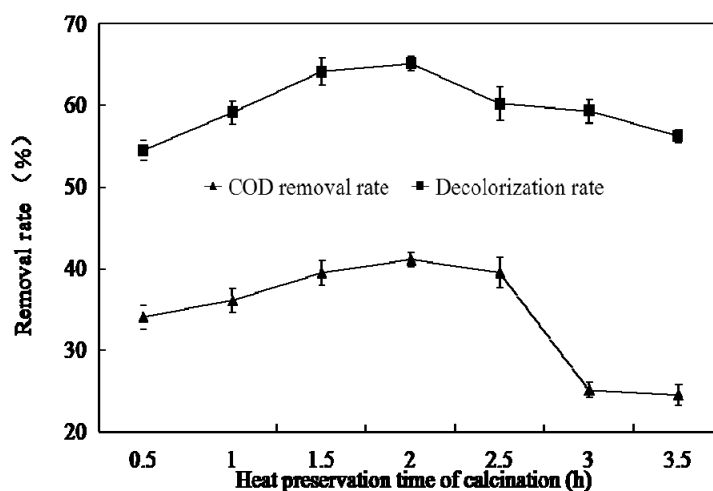


Figure 10. Effect of heat preservation time of calcination on removal rate.

bath temperature, calcination temperature, and heat preservation time of calcination were chosen, each factor taking three levels. The orthogonal experiment of four factors and three levels was arranged (Table 2). The concerned results are shown in Tables 3 and 4.

died. The results showed that the filter media hardly had photocatalysis before it was modified. But after it was modified by TiO₂, the decolorization rate and COD removal rate increased in different degree. The morphology of the modified filter media was examined by

Table 2. Factors and levels of orthogonal experiment

Level	Factor			
	C _{H3BO3} :C _{(NH4)2TIF6}	Reaction temperature, °C	Calcination temperature, °C	Calcination heat preservation time, h
	A	B	C	D
1	2:1	60	450	1
2	3:1	70	500	2
3	4:1	80	550	3

Table 3. Schemes and results of orthogonal experiment

Number	A	B	C	D	COD removal, %
1	2:1	60	450	1	42.63
2	2:1	70	500	2	45.76
3	2:1	80	550	3	43.52
4	3:1	60	500	3	37.64
5	3:1	70	550	1	35.79
6	3:1	80	450	2	37.85
7	4:1	60	550	2	28.40
8	4:1	70	450	3	33.70
9	4:1	80	500	1	36.74

Table 4 shows the effect order of each factor on the photocatalytic activity of the filter media modified by TiO₂ is A > C > B > D in the heavy nitrogen wastewater. The optimal parameters were C_{H3BO3}:C_{(NH4)2TIF6} of 2:1 (0.1 mol/L (NH₄)₂TiF₆), water bath temperature of 80°C, calcination temperature of 500 °C, and heat preservation time of 1 h. When the filter media was modified under above conditions, the decolorization rate and COD removal reached 65.89 and 47.87%, respectively. The rates were higher than any group of the orthogonal experiment.

CONCLUSION

The sintering filter media was modified by TiO₂ and its photocatalytic performance was preliminary stu-

SEM, EDS and crystallite structure by XRD. The SEM, EDS, and XRD data showed that new TiO₂ crystal was found in the modified filter media. And the specific surface area of the modified filter media greatly increased. So it was an important method for the sintering filter media to be modified by TiO₂ to improve its photocatalytic activity. And it also showed that TiO₂ was an excellent photocatalyst.

Many factors affected the modification of the filter media modified by TiO₂. The orthogonal experiment showed that the optimal preparation parameters of the sintering filter media modified by TiO₂ separately were the ratio of H₃BO₃ and (NH₄)₂TiF₆ for 2:1, water bath temperature for 80 °C, deposition time for 5 h, calcination temperature for 500 °C, and heat preservation time of calcination for 1 h. The heavy nitrogen wastewater of 1589.94 mg/L COD and 18750 times chroma was treated by the filter media modified by TiO₂ under above technological conditions. And the decolorization rate and COD removal rate were 65.89 and 47.87%, respectively.

Acknowledgements

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Table 4. Range analysis of orthogonal experiment

Number	C _{H3BO3} :C _{(NH4)2TIF6}	Water bath temperature, °C	Calcination temperature, °C	Calcinations heat preservation time, min
K1	131.91	108.67	114.18	115.16
K2	111.28	115.25	120.14	112.01
K3	98.84	118.11	107.71	114.86
K1/3	43.97	36.22	38.06	38.39
K2/3	37.09	38.42	40.05	37.34
K3/3	32.95	39.37	35.90	38.29
R	11.02	3.15	4.14	1.05

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IZVOD

ISPITIVANJE FAKTORA KOJI UTIČU NA FOTOKATALITIČKU AKTIVNOST FILTERA MODIFIKOVANIH TiO₂

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(Naučni rad)

Gangue filter je modifikovan pomoću titan-dioksida (TiO₂) metodom depozicije u tečnoj fazi. Ispitivani su neki činioci koji utiču na fotokatalitičku aktivnost, kao što je molarni odnos početnog rastvora, temperatura vodenog kupatila, vreme depozicije, temperatura kalcinacije i dužina kalcinacije. Morfologija filma je ispitivana pomoću SEM i EDS, a kristalna struktura pomoću difrakcije X-zraka (XRD). Podaci dobijeni pomoću SEM, EDS i XRD su pokazali da je u modifikovanom filteru pronađena nova TiO₂ kristalna faza. Specifična površina modifikovanog filtera je značajno povećana. Kod vertikalnog eksperimenta optimalni parametri modifikacije su: (NH₄)₂TiF₆:H₃BO₃ = 1:2, temperatura vodenog kupatila 80 °C, vreme depozicije 5 h, temperatura kalcinacije od 500 °C i dužina kalcinacije 1 h. Pod pomenutim uslovima, otpadna voda teškog azota od 1589,94 mg/L COD i 18750 puta veće koncentracije hroma tretirana je pomoću modifikovanog filtera. Posle 1 h katalitičke reakcije, brzina obezbojavanja i brzina COD odstranjivanja je dostigla 65,89 i 47,87%, redom.

Ključne reči: TiO₂ • Depozicija u tečnoj fazi • Teški azot • Brzina obezbojavanja • COD