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TREATMENT OF 2-DIAZO-4,6-DINITRO-PHENOL WASTEWATER USING TiO2/SiO2 COMPOSITE FILM IN A PHOTOCATALYTIC REACTOR

Article Highlights  
• Photocatalytic activity of filter media modified by TiO2/SiO2 was evaluated using DDNP wastewater  
• By modified filter media, removal rates of chroma and COD separately reached 70.00 and 60.85%  
• Optimal working parameters were: 59:1 of Ti/Si, pH 1, 7 ml L⁻¹ H2O2, and 3000 times chroma  
• Under optimal condition, decolorization and COD removal rate separately reached 98.50 and 92.50%  

Abstract  
TiO2/SiO2 composite film was used to modify the surface of the filter media sintered by coal refuse. 2-Diazo-4,6-dinitrophenol (DDNP) wastewater was used as the response substrate to test its photocatalytic activity in the self-made photocatalytic reactor. The influencing factors of the photocatalytic activity of the modified filter media were studied. When the modified filter media was used, the decolorization rate and COD removal rate of DDNP wastewater reached 70.00 and 60.85%, respectively. But unmodified filter media almost had no photocatalytic activity. The orthogonal test showed that the optimal working parameters separately were: 59:1 of Ti/Si in the TiO2/SiO2 composite film, pH 1, 7 ml L⁻¹ H2O2 and 3000 times chroma (equivalent initial concentration of DDNP wastewater). Under the above condition, the decolorization rate and COD removal rate separately reached 98.50 and 92.50% after 1 h photocatalytic reaction. They were far higher than those in the reaction catalyzed by pure TiO2. Furthermore, under the condition of illumination and aeration, the photocatalytic activities were obviously higher than those under only illumination or aeration.  

Keywords: TiO2/SiO2, photocatalysis, modification, DDNP, decolorization rate, COD.

2-Diazo-4,6-dinitrophenol (DDNP) has been widely used as an important and effective explosive [1]. It is an energetic compound and a very promising initiator [1-4]. But in the producing process of DDNP, the accompanying DDNP wastewater contained many toxic substances such as two nitro diazo phenol, nitro compounds, sulfide, phenol, etc. DDNP wastewater had the characteristics of higher chroma, higher COD, higher toxicity, and complicated composition, etc. [5,6]. If untreated DDNP wastewater was discharged into river, it would severely pollute the environment and threaten the health of people [7]. This problem has attracted the researchers’ extensive attention. At present, the main methods of treating DDNP wastewater are adsorption method, microelectrolysis/H2O2 method, and biochemistry method [7,8]. But the cost of these methods was high. And some methods are in the period of exploration, and it is difficult for them to be applied and promoted [9,10]. Photocatalytic oxidation was a newly developed techno-
logy. Sunlight was used as a potential radiation source. It could stimulate the generation of the hole-electron pairs. So strong redox occurred in this method. Many pollutants could be treated by this method.

Coal gangue is the largest solid waste in our country. Its emission and accumulation not only take up a large number of cultivated land, but also cause great pollution and endanger people’s health. It has become a public nuisance. The comprehensive development and utilization of coal gangue are urgent and imperative in our country. As the main component of sintered filter material, coal gangue would not only satisfy the basic requirement of water treatment, but also have obvious mineralogy characteristics of crystal. It was widely used in wastewater treatment because of its many surface pores, large roughness, and more stable performance. Coal gangue and its sintered products often contain a lot of quartz and scale quartz. So their surface and photocatalytic activity can be increased by nano modification.

As a kind of typical nanomaterials, titanium dioxide (TiO2) was widely used in pollutants processing due to its non-toxicity, high-stability, and photo-electric properties [11-16]. Despite many good properties, there were certain problems associated with nano- metric TiO2. Such problems included nanoparticles agglomeration [17], phase transformation [18,19], decrease in surface area upon thermal treatment [19,20], recombination of photogenerated electron-hole pair [21], lack of visible light photo activity due to its wide band gap (Eg = 3.2 eV), etc. [21]. Furthermore, the photocatalytic efficiency of pure TiO2 in photocatalytic reactions was found to be limited in our previous study [16]. To solve most of these problems, many TiO2-based composite photocatalysis have been prepared to enhance the photocatalytic activity [11,12]. In comparison to those single-phase titania materials, these composites tend to show higher photocatalytic activity. Although the surface of the unmodified filter media was very rough and there were many irregular holes, its particle surface was smoother. There were a large number of small bumps and uniform distribution on the particle surface of the modified filter media.

Preparation of the filter media modified by TiO2/SiO2

Firstly, the modified filter media was prepared by the liquid phase deposition method [16]. (NH4)2TiF6, (NH4)2SiF6 and H3BO3 were used as the precursors. The mole ratio of (NH4)2TiF6 + (NH4)2SiF6 and H3BO3 was 1:3. The molarity of (NH4)2TiF6 was 0.1 mol L\(^{-1}\) and the used concentrations of H3BO3 were 0.2, 0.3, and 0.4 mol L\(^{-1}\). The distilled water was used as the solvent of the coating solution. The other steps were same as the reference [16]. After certain time, the sintered filter media modified by the TiO2/SiO2 composite film was obtained.

Characterization of the modified filter media

Particle morphology and physico-chemical properties of the filter media modified by TiO2/SiO2 were characterized by the same methods in the reference [16]. The background of surface of the modified filter media was bright. This was due to the reflection because of the presence of TiO2 thin film. And light was reflected on uneven surface many times. This would inevitably increase the absorption and utilization of light. It would be advantageous to the catalytic reaction. Although the surface of the unmodified filter media was very rough and there were many irregular holes, its particle surface was smoother. There were a large number of small bumps and uniform distribution on the particle surface of the modified filter media. They were TiO2 grains (30-50 nm). These particles plindged up in together in different ways. This made the micro-structure of the surface of modified filter media change. The specific surface area of the modified filter media was greatly improved. It was advantageous to the adsorption of more ultraviolet light. In our previous study we found that the main components of the unmodified filter media were silicon, aluminum, oxygen, carbon, calcium, and iron. Titanium elements existed in the energy spectr um diagram of modified filter media. And they existed in the form of TiO2 compounds. The weight percentage and atomic percentage of titanium were 0.99 and 0.40%, respectively. There were a large number of alpha-quartz crystal, scale quartz and calcium feldspar in the mineral phase structure. TiO2 crystal could not be found in unmodified filter media. But new TiO2 crystal was found in XRD atlas of modified filter media. The superposition phenomenon existed in the diffraction peaks of TiO2 crystals and calcium feldspar crystal.
Photocatalytic reactor

The photocatalytic reactor was same as the one used in our previous work [16]. The interlayer was the photocatalytic reaction unit filled with the sintered filter media modified by the TiO\textsubscript{2}/SiO\textsubscript{2} composite film. The reactor had already been described in details elsewhere [16].

Orthogonal test design

The orthogonal test design is a method that utilizes an orthogonal test table to organize the tests and to scientifically analyze the test results before decision-making. This paper firstly analyzed the main parameters that affected the photocatalytic activity of TiO\textsubscript{2}/SiO\textsubscript{2} composite film and their respective levels and then discussed the conducted orthogonal test to optimize the parameters of the photocatalytic system.

Based on the effects of varied factors on DDNP wastewater degradation, the mole ratio of Si and Ti in the TiO\textsubscript{2}/SiO\textsubscript{2} composite film, chroma (initial concentration), pH and addition amount of H\textsubscript{2}O\textsubscript{2} were selected as the orthogonal test factors. Each factor was taken three levels. There were 27 combinations to be tested in the orthogonal test L\textsubscript{9} (3\textsuperscript{4}). We applied the orthogonal array to select nine representative combinations to be tested. The factors and levels were shown in Table 1.

<table>
<thead>
<tr>
<th>Level</th>
<th>Factor</th>
<th>Mole ratio of Ti and Si (A)</th>
<th>Initial chroma (B) (C)</th>
<th>pH (C)</th>
<th>H\textsubscript{2}O\textsubscript{2} addition amount, ml L\textsuperscript{-1} (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39:1</td>
<td>5000</td>
<td>1</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>59:1</td>
<td>3250</td>
<td>3</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>79:1</td>
<td>3000</td>
<td>5</td>
<td>11</td>
<td></td>
</tr>
</tbody>
</table>

Analysis method

In the process, COD removal rate and decolorization rate were evaluated. The COD values were determined by the potassium dichromate method. The variation of absorbency was characteristic of the decolorization efficiency. The variation of absorbency was calculated by the formula [16].

RESULTS AND DISCUSSION

Influencing factors of the photocatalytic activity of the modified filter media

Under the condition of neutral and room temperature, the photocatalytic degradation experiment of DDNP wastewater with 5000 times chroma (initial concentration) was conducted. The decolorization rate and COD removal rate of unmodified filter media reached 18.00 and 22.64%, respectively. But after the filter media was modified by the TiO\textsubscript{2}/SiO\textsubscript{2} composite film, the decolorization rate and COD removal rate reached 70.00 and 60.85%, respectively. They were far higher than those in the reaction catalyzed by pure TiO\textsubscript{2} [16]. This indicated that the modified filter media had better photocatalytic degradation activity.

Then, a series of photocatalytic reactions were conducted to further improve the photocatalytic activity of the modified filter media. DDNP wastewater of 3250 times chroma and 317.99 mg L\textsuperscript{-1} COD was treated and different influencing factors were analyzed.

Influence of mole ratio of Ti and Si

The experiments without irradiation had been done in previous study reported in the China Water and Wastewater. The decolorization rates were all very small (< 7%) [30]. In present study, the decolorization rates of 24 h were also very small (< 2%) and the results had no significant difference. So the adsorption of the composite films of different Ti/Si was neglected in further study.

In present study, when the mole ratio of Ti and Si in the TiO\textsubscript{2}/SiO\textsubscript{2} composite film was 59:1, the photocatalytic activity of the modified filter media was best (Figure 1). The decolorization rate and COD removal rate were 70.00 and 60.85%, respectively.

In TiO\textsubscript{2}/SiO\textsubscript{2} composite film, the Si-O-Ti bond formed between SiO\textsubscript{2} and TiO\textsubscript{2}, and then SiO\textsubscript{2} with net structure entered into the compound [31]. SiO\textsubscript{2} net inhibited the TiO\textsubscript{2} mass transport and reduced the growth rate of crystal particle. So the TiO\textsubscript{2} particle size in TiO\textsubscript{2}/SiO\textsubscript{2} compound with uniform composition could be well controlled. The reduction of particle size increased the width of the forbidden band, and the effect of quantum size was significant. This caused the energy increase of band gap. The time that carrier
was diffused from interior to surface of catalyst shortened in photocatalytic reaction, and the separation efficiency of photo-generated electron and hole was improved. So the photocatalytic degradation activity was enhanced. However, SiO₂ did not have photocatalytic activity. So, when TiO₂ surface was occupied by more SiO₂, its effective surface reduced. Under the condition, it was not easy for the photo-generated electron and the hole to produce [32]. Hence, if the content of SiO₂ in the TiO₂/SiO₂ composite film was too high, the photocatalytic activity of composite film would decline.

**Influence of chroma**

When the chroma of DDNP wastewater was 3250 times, the decolorization rate and COD removal rate reached the highest value (Figure 2). The higher the initial concentration of solution was, the weaker the penetrating ability of ray was, and the lower the amount of photons which participated in photocatalytic reaction was. More solute was adsorbed on the surface of catalyst, and the active site reduced [31]. These inhibited the catalyst to absorb the ultraviolet and produce the •OH. So the photocatalytic efficiency reduced. Though the decolorization rate was high when the initial concentration was too low, the amount of treated DDNP wastewater was low. The degradation ability of photocatalytic reaction could not be fully exerted. In the experiment, the surface adsorption of the TiO₂/SiO₂ composite film reached saturation because of overhigh concentration wastewater. Most active sites of the TiO₂/SiO₂ composite film surface were occupied due to surplus organic molecular. And the absorption of ultraviolet and the production of •OH were influenced. But the photocatalyst could not be fully applied because of overlow concentration wastewater, which affected the degradation efficiency.

**Influence of reaction time**

When the reaction time was more than 60 min, the efficiencies of photocatalytic degradation tend to be steady (Figure 3). And the decolorization rate and COD removal rates were 73.85 and 65.17%, respectively. The oxidation reaction incompletely happened when illumination time was too short, so the removal was not good. Too long illumination time had no significant effect on the removal of pollutant.

**Influence of pH**

Under the acidic condition, the decolorization rate and COD removal rate both reached the maximum which were 81.54 and 72.34%, respectively (Figure 4). When pH was more than 7, the decolorization rates declined with the rising of pH. The variation of pH would impel the change of electrification state of TiO₂ surface. When pH was below 3.5, the particle surface took positive charge. And it was beneficial for the photo electron to migrate to the surface of catalyst. And the electron reacted with O₂ adsorbed by catalyst, so the combination of E⁻ and H⁺ was inhibited. Furthermore, pH of solution directly affected the surface state, interfacial potential, surface charge, and aggregation of TiO₂ [33]. The isoelectric point of TiO₂ was about 6.5. When pH was more than 6.5, the surface charge was negative and the main form was TiO⁻. And when pH was below 6.5, the surface charge was positive and the main form was TiOH₂⁺. The characteristic of surface charge affected the TiO₂ surface adsorption of organic molecules, and affected the migration of photo electron and hole from the interior to the surface of TiO₂ [31-33]. Due to different surface morphology and surface charge, the adsorption ability of catalyst was significantly different, so the process of photodegradation was affected.
Influence of H\textsubscript{2}O\textsubscript{2} addition amount

The optimal addition amount of H\textsubscript{2}O\textsubscript{2} was 9 ml L\textsuperscript{-1} (Figure 5). When the addition amount was more than 9 ml L\textsuperscript{-1}, there was not direct relationship between two rates and H\textsubscript{2}O\textsubscript{2} addition amount. This indicated that H\textsubscript{2}O\textsubscript{2} not only was the generating agent of •OH but also the scavenger of •OH. The addition amount of H\textsubscript{2}O\textsubscript{2} influenced the yield of •OH and the removal of pollutant. Only in certain range, there was direct relationship between the yield of •OH and H\textsubscript{2}O\textsubscript{2} amount, and too much H\textsubscript{2}O\textsubscript{2} could promote the clearance of •OH [34]. And the redundant H\textsubscript{2}O\textsubscript{2} would enhance the effluent COD. So it was very necessary for wastewater to find the optimal addition amount of H\textsubscript{2}O\textsubscript{2}.

Orthogonal test of optimal process parameters

Based on the effects of varied factors on DDNP wastewater degradation, the mole ratio of Si and Ti in the TiO\textsubscript{2}/SiO\textsubscript{2} composite film, chroma (initial concentration), pH, and H\textsubscript{2}O\textsubscript{2} addition amount were selected as the orthogonal test factors. Each factor was taken three levels in the orthogonal test L\textsubscript{9} (3\textsuperscript{4}). The range analysis was shown in Table 2.

<table>
<thead>
<tr>
<th>Number</th>
<th>Mole ratio of Ti and Si (A)</th>
<th>Initial chroma (B)</th>
<th>pH (C)</th>
<th>H\textsubscript{2}O\textsubscript{2} addition amount (D)</th>
</tr>
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<tbody>
<tr>
<td>K1</td>
<td>85.23</td>
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<td>82.76</td>
<td>82.26</td>
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<tr>
<td>K2</td>
<td>85.71</td>
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<td>79.71</td>
<td>80.41</td>
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<tr>
<td>K3</td>
<td>66.36</td>
<td>80.19</td>
<td>74.83</td>
<td>74.64</td>
</tr>
<tr>
<td>R</td>
<td>19.35</td>
<td>2.60</td>
<td>7.92</td>
<td>7.62</td>
</tr>
</tbody>
</table>

Table 2. Range analysis of orthogonal test
Table 2 is the result of range analysis of orthogonal test, and the decolorization rates were calculated. The primary and secondary orders of different factors were defined by different range values in each column. The best level of each factor was determined by the maximum value of K (total of Kn of each factor at the same level). As a result, the optimum process parameters were determined. As could be seen from Table 2, the mole ratio of Ti and Si in the TiO2/SiO2 composite film had more impact on decolorization rate, whereas the initial chroma of DDNP wastewater had less impact on decolorization rate. The order of the effects of varied factors on photocatalytic degradation is A > C > D > B. The optimal parameter was A2B3C1D1. Namely, the optimal parameters were 59:1 of mole ratio of Ti and Si, pH 1, 7ml L–1 H2O2 addition amount, and 3000 times chroma of DDNP wastewater. Under the optimal condition, the decolorization rate and COD removal rates were 98.50 and 92.50%, respectively. They were higher than any group. And they were far higher than those in the reaction catalyzed by pure TiO2 [16].

CONCLUSIONS
Many factors affected the photocatalytic activity of the filter media modified by TiO2/SiO2. The mole ratio of Ti and Si, pH, H2O2 addition amount and chroma of DDNP wastewater were researched. Under the optimal condition, the decolorization rate and COD removal rates are 98.50 and 92.50%, respectively. They were far higher than those in the reaction catalyzed by pure TiO2. The chroma and COD of effluent were 45 times and 22.89 mg L–1, which could meet the first class standard in the national Sewage Comprehensive Discharge Standard (GB8978-1996). This demonstrated that higher catalytic activity existed in the photocatalytic reaction under the optimal conditions determined by orthogonal test.

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REFERENCES
TRETMAN OTPADNE VODE SA 2-DIAZO-4,6-DINITROFENOLOM POMOĆU TiO2/SiO2 KOMPOZITNOG FILMA U FOTOKATALITIČKOM REAKTORU

TiO2/SiO2 kompozitni film je korišćen za modifikaciju površine filtra koji je sinterovan otpadnim ugljem. Otpadna voda koja sadrži 2-diazo-4,6-dinitrofenol (DDNP) je korišćena za testiranje njegove fotokatalitičke aktivnosti u fotokatalitičkom reaktoru. U radu je ispitana uticaj odgovarajućih faktora na fotokatalitičku aktivnost modifikovanog filera. Korišćenjem modifikovanog filera postiže se stepen dekolorizacije od 70% i stepen smanjenja hemijske potrošnje kiseonika (HPK) merena preko DDNP od 60,85%. Nemodifikovani filter skoro da nema fotokatalitičku aktivnost. Ortogonalni eksperiment je pokazao da su optimalni operativni parametri: odnos Ti/Si u kompozitnom filmu TiO2/SiO2 59:1, pH 1, 7 ml L⁻¹ H2O2, i hroma 3000 puta (ekivalentno početnoj koncentraciji DDNP u otpadnoj vodi). Pod ovim optimalnim uslovima posle 1 h fotokatalitičke reakcije, stepen obezbojenja i stepen uklađivanja HPK odstranjivanja su dostigli vrednosti 98,50 i 92,50%, redom. Ako se primene iluminacija i aeracija, fotokatalitička aktivnost je veća nego pri primeni samo iluminacije ili samo aeracije.

Ključne reči: TiO2/SiO2, fotokataliza, modifikacija, DDNP, stepen dekolorizacije, HPK.