Effect of ion (Al, Fe and Zn) co-doped TiO2 nanotubes on photocatalytic degradation of humic acids under UV/ozonation for drinking water purification

Rongfang Yuan and Beihai Zhou

ABSTRACT

O3/UV/TiO2 was used to effectively decompose humic acids (HAs) in drinking water. A series of Al-doped, Fe-doped, Zn-doped and co-doped TiO2 nanotubes were successfully synthesized by a hydrothermal method. According to the characterization of ion-doped TiO2 nanotubes, Al3+ and Fe3+ ions occupied substitutional positions in the crystal lattice, and Zn2+ ions were partially dispersed in the bulk of the TiO2 nanotubes, with ZnO formed on the surface of the TiO2. The calcination temperature and doping concentration could affect the anatase phase weight fractions, average crystallite sizes, Brunauer–Emmett–Teller (BET) surface area, bandgap energy, and photocatalytic activity of the catalysts. For single ion-doped TiO2 nanotubes, the best photocatalytic activities were achieved when the ion-doping amount was 1.0%, and the optimal calcination temperatures for Al-, Fe- or Zn-doped TiO2 were 600 °C, 550 °C and 550 °C, respectively. The highest HA removal efficiency of 80.1% was achieved in the presence of 550 °C calcined, 1.0% co-doped TiO2 nanotubes with an Fe:Zn ratio of 1:1 (atomic percent), with second-order rate constant of 0.0394 L/(min·mg). The addition of a third ion had little effect on the photocatalytic activity. The pollutants in filter influent from No. 9 waterworks in Beijing could be efficiently removed, with UV254 and total organic carbon (TOC) removal efficiencies of 57.2% and 44.7%, respectively.

Key words | Al-Fe-Zn co-doping, drinking water, humic acids, TiO2 nanotubes

INTRODUCTION

Humic acids (HAs) are notorious because they turn water brown, form complexes with metals and organic pollutants, and react with active chlorine during water sterilization in plants, resulting in the formation of trihalomethanes (Wei et al. 2011).

Several techniques have been developed to treat HAs. O3 can reduce color, UV254 and total organic carbon (TOC), and decrease high apparent molecular weight fractions. UV photocatalytic oxidation, which is characterized by the generation of highly reactive -OH, has emerged as a highly efficient method for decomposing pollutants. Therefore, O3/UV/TiO2 was chosen to generate -OH in the present study.

TiO2 was the most promising catalyst for eliminating contaminants because of its low cost, long-term stability and nontoxicity (Hao & Zhang 2009). However, the relatively wide bandgap of TiO2 limits the photocatalytic efficiency because of the high recombination rate of photogenerated e− and h+ (Pang & Abdullah 2012a). Therefore, ion-doped TiO2 nanotubes have been studied (Yuan et al. 2014). Al, Fe or Zn ions could enhance the catalytic activity of TiO2 (Yuan et al. 2015). However, researchers have seldom considered Al, Fe and Zn co-doped TiO2 nanotubes for UV photocatalytic ozonation.

In this study, a UV/TiO2 photocatalytic ozonation method was used. The photocatalytic activities of Al-, Fe-, Zn- and co-doped TiO2 nanotubes with different doping concentrations and at different calcination temperatures were investigated. In order to obtain the removal efficiency of natural organic matter (NOM), the filter influent from No. 9 waterworks in Beijing was used, and the UV254 and TOC of the water were determined.

doi: 10.2166/ws.2015.130
METHODS

Materials

P-25 TiO₂, which has an S_{BET} of 50 m²/g, an average crystal-lite size of 21 nm, and a crystal structure of 80% anatase and 20% rutile, was provided by the Degussa Corporation (Richfield Park, New Jersey). HAs (content ≥ 99%, formula weight 600–1000), AlCl₃, Fe(NO₃)₃·9H₂O and ZnCl₂ were purchased from Beijing Chemical Reagent Company.

The major photocatalytic reactor was a cylindrical glass column (φ 60 mm × 750 mm). The light source in the reaction column was a 37 W low-pressure mercury vapor lamp (φ 22 mm × 793 mm) with a wavelength of 254 nm and intensity of 110 μW/cm². O₃-containing gas which was produced by an O₃ generator (maximum output of 3 g/h, Beijing Tonglin Scitech Co., Ltd, China) was inlet into the reactor through a porous glass core aeration plate (pore size 4–7 μm) situated at the bottom of the reactor.

Preparation of TiO₂ nanotubes

One gram of P-25 TiO₂ was added into 16 mL of 10 mol/L NaOH solution in a Teflon vessel. The mixture was stirred for 2 h at 20 °C to form a suspension, heated at 110 °C for 24 h, and cooled to room temperature in air. The precipitates were washed with distilled water to pH 7 and subsequently dispersed in 0.1 mol/L HCl solution for 30 min. After washing to pH 7 and drying at 60 °C, the titanic acid nanotubes were obtained. TiO₂ nanotubes were prepared by calcining at 400–600 °C for 2 h.

Al-, Fe-, Zn- and co-doped TiO₂ nanotubes were prepared following the aforementioned procedure in the presence of AlCl₃, Fe(NO₃)₃·9H₂O or ZnCl₂ with doping levels of 0.1%–5.0%. All dopant concentrations mentioned in this work are the nominal atomic ones.

Characterization of TiO₂ nanotubes

X-ray diffraction (XRD) patterns were collected in a Rigaku Dmax-RB diffractometer (Tokyo, Japan). Transmission electron microscopy (TEM) images were acquired with a HITACHI HT-7700 electron microscope (Tokyo, Japan). The S_{BET} of the samples were determined on a Quadrasorb SI-MP apparatus (Quantachrome Instrument, USA). Diffuse reflectance spectroscopy (DRS) was performed using a HITACHI U-3010 UV-vis scanning spectrophotometer (Tokyo, Japan).

Photocatalytic activity tests

Catalysts of 0.1 g/L were added into the water. The aqueous slurries (1.5 L) were stirred and bubbled with O₃ (0.7 mg/min) for 30 min prior to UV irradiation. When the UV lamp was turned on, HA solution was poured into the slurries immediately, and the initial HA concentration was 10 mg/L. The reaction was stopped at 5 min intervals by adding 0.5 mL of 0.001 mol/L Na₂S₂O₃ solution into a 10 mL sample. The suspension was filtered through 0.45-μm-pore-size microporous membranes to separate the photocatalyst particles. HA concentrations were determined using a UV-vis spectrophotometer (Hach DR5000, USA) operated at 254 nm. All the tests were repeated three times to minimize the errors.

In order to obtain the removal efficiency of NOM, the filter influent from No. 9 waterworks in Beijing (TOC 3.8 mg/L, UV₂₅₄ 0.078/cm, permanganate index 1.62 mg/L, turbidity 0.2 NTU, and pH value 7.5) was used, UV₂₅₄ was determined using a UV-vis spectrophotometer operated at 254 nm, and TOC measurements were performed by the spectrophotometer using low-range TOC ampoules (Hach Chemical, USA).

RESULTS AND DISCUSSION

Characterization of photocatalysts

Morphology

TEM morphologies of 550 °C calcined 1.0% Al-Fe-Zn (1:1:1) co-doped TiO₂ nanotubes (Figure 1(a)) indicate that the TiO₂ nanotubes exhibited hollow, open-ended structures with a diameter of 6–8 nm, and the tube wall thickness was approximately 1 nm. The Ti, Al, Fe, Zn and O elements are involved in the energy dispersive X-ray (EDX) spectra of ion-doped TiO₂.
XRD analysis

Figure 1(b) shows that the crystallite phase containing Al, Fe and Zn metal oxides was not observed in the XRD patterns. The ionic radii of $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ were smaller than that of $\text{Ti}^{4+}$. Therefore, the dopant ions could be highly dispersed in the TiO$_2$ nanotubes (Pang & Abdullah 2012a). Zn ions were partially dispersed in the bulk of the TiO$_2$ nanotubes. ZnO might be formed on the surface of TiO$_2$ because the radius of the $\text{Zn}^{2+}$ ion is 74 pm, a little larger than that of $\text{Ti}^{4+}$. However, these oxides were not observed in the XRD patterns because their metal sites were expected to be below the visibility limit of X-ray analysis (Ravichandran et al. 2013).

The anatase phase exhibited a higher photocatalytic activity than the other phases (Pang & Abdullah 2012b). The titanate/amorphous phase transformed into the anatase phase as the calcination temperature increased. When the calcination continuously increases, the rutile phase is formed. Only the anatase phase was found in most of the TiO$_2$ nanotubes, except for the 600°C calcined TiO$_2$, which exhibited both the anatase and rutile phases. Meanwhile, the diffraction peaks of the anatase phase became weaker after ion-doping.

The Bragg angles decreased when ions were added because the crystallite could not be considered as an ideal crystal, suggesting that the $\text{Al}^{3+}$, $\text{Fe}^{3+}$ and $\text{Zn}^{2+}$ ions could replace $\text{Ti}^{4+}$ in the TiO$_2$ nanotube lattice (Deng et al. 2013) and disrupt the arrangement of the TiO$_2$ basic octahedral units, hence distorting the overall crystallite structure (Bokhimi et al. 2003). As a result, broadening diffraction peaks and decreasing peak intensities were observed.

Brunauer-Emmett-Teller (BET) surface area analysis

The $S_{\text{BET}}$ values of the TiO$_2$ nanotubes (shown in Table 1) were significantly higher than that of P-25 TiO$_2$ because of the inner and outer surfaces of the layered tubular structure (Pang & Abdullah 2012b). The $S_{\text{BET}}$ of the TiO$_2$ nanotubes decreased as the calcination temperature increased, which is attributed to nanotube aggregation (Zhang et al. 2012).
The $S_{\text{BET}}$ values of ion-doped TiO$_2$ nanotubes were smaller than those of un-doped samples, and the $S_{\text{BET}}$ decreased as the concentration of the dopant increased (Pang & Abdul- lah 2012a), which was because of partial pore blockages and framework defects.

The $S_{\text{BET}}$ values of co-doped catalysts were higher than those of single ion-doped catalysts. When a second metal was doped into the crystal lattice, the catalyst surface structure changed because of the conservation of a large number of micropores (Thirupathi & Smirniotis 2011). However, the $S_{\text{BET}}$ of Al-Fe-Zn (1:1:1) co-doped TiO$_2$ was not much higher than those of the co-doped TiO$_2$ catalysts which were doped by only two dopants.

A larger $S_{\text{BET}}$ value indicates more pollutant could be adsorbed on the surface of the catalyst, and therefore affects the photocatalytic activities.

**UV-vis DRS analysis**

The $E_g$ of the catalysts were calculated based on the UV-vis DRS analysis by the method given in the literature (Yuan et al. 2020), and the relationships between the $E_g$ and the type and concentration of the doped ions are shown in Figure 1(c) and Table 1. The $E_g$ of TiO$_2$ calcined at higher temperatures were wider than those calcined at lower temperatures. This tendency results from the narrower $E_g$ of rutile TiO$_2$ (3.0 eV) compared with that of anatase TiO$_2$ (3.2 eV).

The $E_g$ of undoped TiO$_2$ nanotubes ranged from 3.23 to 3.26 eV, corresponding to the absorption of 384–381 nm. The reflectance spectra of ion-doped TiO$_2$ nanotubes (Al-doped 383–407 nm, Fe-doped 391–456 nm, and Zn-doped 383–403 nm) slightly shifted toward longer wavelengths compared with those of un-doped specimens, and the $E_g$ of ion-doped TiO$_2$ nanotubes were visibly narrower. These results revealed that the dopant elements were successfully incorporated into the TiO$_2$ nanotube lattice and changed its crystal and electronic structures (Yu et al. 2009). The $E_g$ decreased as the concentration of dopant increased because of a charge-transfer transition between the new dopant level near the valence band and the conduction band of the TiO$_2$ nanotubes (Pang & Abdullah 2012a). The reduction in the $E_g$ of the TiO$_2$ nanotubes allowed the excitation of the catalyst under a lower irradiation power and thus enhanced its photocatalytic activity (Pang & Abdullah 2013).

Moreover, the $E_g$ of 1.0% co-doped TiO$_2$ calcined at 550 C was between those of single ion-doped TiO$_2$. The $E_g$ of Al-Zn co-doped TiO$_2$ was the widest because the $E_g$ increased.

---

**Table 1** | Some catalytic properties and photocatalytic activities of Al-, Fe-, Zn- and co-doped TiO$_2$ nanotubes

<table>
<thead>
<tr>
<th>Properties</th>
<th>BET surface areas (m$^2$/g)</th>
<th>Indirect energy bandgap (eV)</th>
<th>HAs removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500</td>
<td>550</td>
<td>600</td>
</tr>
<tr>
<td>Un-doped</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-doped</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1%</td>
<td>175</td>
<td>133</td>
<td>101</td>
</tr>
<tr>
<td>0.5%</td>
<td>172</td>
<td>135</td>
<td>98</td>
</tr>
<tr>
<td>1.0%</td>
<td>156</td>
<td>134</td>
<td>91</td>
</tr>
<tr>
<td>5.0%</td>
<td>82</td>
<td>70</td>
<td>53</td>
</tr>
<tr>
<td>Fe-doped</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1%</td>
<td>173</td>
<td>136</td>
<td>114</td>
</tr>
<tr>
<td>0.5%</td>
<td>147</td>
<td>123</td>
<td>105</td>
</tr>
<tr>
<td>1.0%</td>
<td>143</td>
<td>120</td>
<td>87</td>
</tr>
<tr>
<td>5.0%</td>
<td>132</td>
<td>112</td>
<td>81</td>
</tr>
<tr>
<td>Zn-doped</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1%</td>
<td>170</td>
<td>135</td>
<td>111</td>
</tr>
<tr>
<td>0.5%</td>
<td>167</td>
<td>132</td>
<td>112</td>
</tr>
<tr>
<td>1.0%</td>
<td>155</td>
<td>134</td>
<td>110</td>
</tr>
<tr>
<td>5.0%</td>
<td>116</td>
<td>97</td>
<td>72</td>
</tr>
<tr>
<td>Al:Fe:Zn (1.0% co-doped)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1:0</td>
<td>153</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:0:1</td>
<td>172</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0:1:1</td>
<td>157</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1:1</td>
<td>175</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of Al-doped and Zn-doped TiO₂ was wider than that of the Fe-doped TiO₂.

Photocatalytic activities

The photocatalytic activities of TiO₂ nanotubes were determined from the UV photocatalytic ozonation of HAs in the presence of the catalysts (Figure 2 and Table 1). The HA concentration decreased rapidly in the first 10 min, and then tended to be stable because the concentrations of O₃ and HAs reduced significantly as the time went on, and the HA degradation during the first 10 min was consistent with second-order reaction.

A smaller SBET value indicates a smaller amount of adsorbed pollutant on the catalyst surface that can affect the photocatalytic activity. The reduction in the $E_g$ of ion-doped TiO₂ enhanced the photocatalytic activity. The HA removal efficiency in the presence of P-25 TiO₂ (39.2%) was lower than that in the presence of ion-doped TiO₂ nanotubes because the SBET values of the TiO₂ nanotubes were larger, and the $E_g$ were narrower.

Single ion-doped TiO₂

The best photocatalytic activities were achieved when the ion-doping amount was 1.0%. The optimal calcination temperatures for Al-, Fe- or Zn-doped TiO₂ were 600 °C, 550 °C and 550 °C, corresponding to HA removal efficiencies of 76.7%, 77.4% and 73.2%, respectively. Another test showed that only approximately 1%–2% of HAs was adsorbed by the catalysts, indicating that the differences between the HA removal efficiencies were owing to the photocatalytic activities of the diverse catalysts. The SBET and $E_g$ decreased as the calcination temperature and dopant concentration increased (Table 1). The photocatalytic activities are attributed to the SBET, $E_g$ and crystalline phases of the catalysts (Zhang et al. 2000) which are dependent on the calcination temperature and the dopant concentration.

There are different reasons for the improvement of the photocatalytic activities of TiO₂ after Al-, Fe- or Zn-doping. The ionic radii of Al³⁺ (53.5 pm) and Fe³⁺ (55 pm) are slightly smaller than that of Ti⁴⁺ (60.5 pm). After two doping ions replace two Ti⁴⁺ ions, one O₂⁻/C₀ hole appears. This phenomenon alters the crystal shape and promotes the generation of e⁻/h⁺ pairs, which results in increased photocatalytic activity (Yuan et al. 2013, 2014). The ionic radius of Zn²⁺ is slightly larger than that of Ti⁴⁺. ZnO might be formed on the surface of TiO₂. In the TiO₂/ZnO composite, the e⁻ transfer occurs from the conduction band of light-activated ZnO to the conduction band of light-activated TiO₂ and, conversely, h⁺ transfer can take place from the valence band of TiO₂ to the valence band of ZnO (Sukharev & Kershaw 1996). This efficient charge separation increases the photocatalytic activity of the TiO₂/ZnO composite. In addition, as the Zn²⁺ ions can be partially doped into the TiO₂ lattices, the photogenerated e⁻ can be effectively scavenged by Zn²⁺ ions (Zang et al. 1995).

Co-doped TiO₂

The 550 °C calcined 1.0% Fe-Zn co-doped TiO₂ nanotubes (Fe:Zn = 1:1) showed the highest catalytic activity (80.1%...
HA removal), and the rate constant was 0.394 L/(min·mg). The addition of a third metal ion had little effect on HA removal. $S_{BET}$ values increased when two or more metal ions were used as dopants (Table 1). The rutile phase was not found in the co-doped TiO$_2$ (Figure 1(b)), which subsequently promoted the HA removal. The doped Fe$^{3+}$ dissolved in TiO$_2$ changed the color of Fe-doped and co-doped TiO$_2$ nanotubes from white to orange, and the $E_g$ of Fe-doped and co-doped samples decreased compared with that of un-doped TiO$_2$. The $E_g$ of 550°C calcined TiO$_2$ containing 1:1 of Al:Fe and Fe:Zn were narrower than that of Al-Zn co-doped TiO$_2$. The $E_g$ of Fe-Zn co-doped TiO$_2$ was not considerably wider than that of Fe-doped TiO$_2$. Therefore, the highest photocatalytic activity that was achieved depended on all of the abovementioned reasons.

A red shifting tendency was observed for the doped catalysts compared with the un-doped samples. Given that the reactor was not protected from light during the experiments, the UV and part of the visible light in the laboratory would have promoted the degradation of HAs in the presence of ion-doped TiO$_2$.

**Mechanism of co-doped TiO$_2$ photocatalytic process**

The Fe-Zn co-doped TiO$_2$ nanotubes exhibited high photocatalytic activity. A valence band $e^-$ was promoted to the conduction band and left $h^+$ which reacts with H$_2$O (Equations (1)–(3)) (Pang & Abdullah 2013):

$$\text{TiO}_2 + h\gamma \rightarrow \text{TiO}_2(e^- + h^+)$$  
(1)

$$h^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+$$  
(2)

$$e^- + \text{O}_2(\text{ads}) \rightarrow \text{O}_2^{\cdot\bullet}$$  
(3)

Fe$^{3+}$ in the ion-doped TiO$_2$ acted as shallow trapping sites for $e^-$ and $h^+$ (Equations (4) and (5)) and formed Fe$^{2+}$ and Fe$^{4+}$. The unstable Fe$^{2+}$ and Fe$^{4+}$ reacted with H$_2$O, OH$^-$ and O$_2$ and subsequently transformed into Fe$^{3+}$ (Equations (6)–(10)) (Wei et al. 2011). Similarly to Fe$^{3+}$, the inclusion of Zn$^{2+}$ ions as dopants in TiO$_2$ also generate ·OH and O$_2^{\bullet\bullet}$ radicals (Equations (11)–(17)) (Rauf et al. 2011):

$$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$$  
(4)

$$\text{Fe}^{3+} + h^+ \rightarrow \text{Fe}^{4+}$$  
(5)

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^-$$  
(6)

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(OH)}^{2+} + \cdot\text{OH}$$  
(7)

$$\text{Fe(OH)}^{2+} + h\gamma \rightarrow \text{Fe}^{2+} + \cdot\text{OH}$$  
(8)

$$\text{Fe}^{4+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \cdot\text{OH}$$  
(9)

$$\text{Fe}^{3+} + O_2(\text{ads}) \rightarrow \text{Fe}^{3+} + O_2^{\bullet\bullet}$$  
(10)

$$\text{Zn}^{2+} + e^- \rightarrow \text{Zn}^+$$  
(11)

$$\text{Zn}^{2+} + h^+ \rightarrow \text{Zn}^{3+}$$  
(12)

$$\text{Zn}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Zn}^{2+} + \cdot\text{OH} + \text{OH}^-$$  
(13)

$$\text{Zn}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Zn(OH)}^+ + \cdot\text{OH}$$  
(14)

$$\text{Zn(OH)}^+ + h\gamma \rightarrow \text{Zn}^+ + \cdot\text{OH}$$  
(15)

$$\text{Zn}^{3+} + \text{OH}^- \rightarrow \text{Zn}^{2+} + \cdot\text{OH}$$  
(16)

$$\text{Zn}^+ + \text{O}_2(\text{ads}) \rightarrow \text{Zn}^{3+} + \text{O}_2^{\bullet\bullet}$$  
(17)

The combination of TiO$_2$ with the doped ions resulted in the generation of Ti$^{3+}$ (Equations (18) and (19)). Zn$^{3+}$ could also react with $e^-$ and Fe$^{3+}$ (Equation (20)):

$$\text{Fe}^{2+} + \text{Ti}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ti}^{3+}$$  
(18)

$$\text{Zn}^+ + \text{Ti}^{4+} \rightarrow \text{Zn}^{2+} + \text{Ti}^{3+}$$  
(19)

$$\text{Fe}^{3+} + \text{Zn}^+ \rightarrow \text{Fe}^{2+} + \text{Zn}^{2+}$$  
(20)
Treatment of filter influent through O₃/UV/co-doped TiO₂ process

In order to obtain the removal efficiency of NOM, the filter influent from No. 9 waterworks in Beijing was used, and the UV₂₅₄ and TOC of the water were determined. The UV₂₅₄ was attributed to aromatic compounds and other compounds containing C=C and C=O bonds in the water, and the TOC removal efficiency was used to evaluate the actual degree of HA mineralization caused by the co-doped TiO₂ nanotubes. Figure 3 shows the changes in UV₂₅₄ and TOC removal efficiency for the filter influent that was photocatalyzed in the presence of 550 °C calcined TiO₂ with an ion-doping concentration of 1.0% (Fe:Zn = 1:1).

The UV₂₅₄ removal efficiency increased obviously during the first 5 min, and then the removal rate slowed down in the period of 5–15 min. The UV₂₅₄ became stable after 15 min because of the degradation of aromatic compounds into intermediate molecules during photocatalysis, and the UV₂₅₄ removal efficiency was 57.2%. As the photocatalytic reaction proceeded, an increasing number of intermediates were produced and may have hindered the adsorption process, eventually leading to the termination of the degradation of the pollutants on the surface of the co-doped TiO₂ (Jiang et al. 2012). Meanwhile, the TOC rapidly decreased during the first 15 min of the reaction, and then the removal rate slowed down in the period of 15–20 min. When the reaction time exceeded 20 min, the TOC remained constant. The TOC removal rate was 44.7%, indicating that 44.7% of the pollutants were mineralized into CO₂ and H₂O. The second-order rate constants of UV₂₅₄ and TOC were 1.4426 cm/min and 0.0162 L/(min·mg), respectively.

The removal efficiency of UV₂₅₄ was higher than that of TOC because of the generation of intermediates that could significantly reduce the UV₂₅₄, but not the TOC. The pH of water before and after the reaction was also measured. The results show that the pH decreased from 7.5 to 5.6, indicating the formation of carboxylic acids, which are oxidation-resistant compounds (Yuan et al. 2013). In the period between 15 and 20 min, the UV₂₅₄ removal stopped but TOC removal continued because of the mineralization of intermediates. The TOC removal efficiency was lower than that of UV₂₅₄ because of the presence of intermediates.

CONCLUSIONS

A series of Al-doped, Fe-doped, Zn-doped and co-doped TiO₂ nanotubes were successfully synthesized by a hydrothermal method. Results of various characterization techniques, including XRD and UV-vis DRS, show that Al³⁺ and Fe³⁺ ions occupied substitutional positions in the crystal lattice, and Zn²⁺ ions were partially dispersed in the bulk of the TiO₂ nanotubes, while ZnO might be formed on the surface of the TiO₂. As the calcination temperature and ion doping concentration increased, the S₇BET decreased, and the S₇BET of co-doped catalysts were higher than those of single ion-doped catalysts. The E₇ of ion-doped TiO₂ nanotubes were narrower than those of undoped TiO₂ nanotubes.

![Figure 3](https://iwaponline.com/ws/article-pdf/16/1/237/413036/ws016010237.pdf)
HA degradation by the O$_2$/UV/ion-doped TiO$_2$ process followed second-order kinetics. The catalytic activities of the catalysts were affected by the $S_{BET}$, $E_g$ and the crystalline phases of the catalyst. For single ion-doped TiO$_2$ nanotubes, the best photocatalytic activities were achieved when the ion-doping amount was 1.0%, and the optimal calcination amount was 1.0%, and the optimal calcination temperature for Al-, Fe- or Zn-doped TiO$_2$ were 600 °C, 550 °C and 550 °C, respectively. The highest HA removal efficiency was obtained in the presence of 1.0% co-doped TiO$_2$ nanotubes containing Fe:Zn of 1:1 and calcined at 550 °C. The addition of a third ion had little effect on HA removal.

The filter influent from No. 9 waterworks in Beijing was used to obtain the removal efficiency of NOM. The pollutants in the water could be efficiently removed. About 44.7% of the pollutants were mineralized into CO$_2$ and H$_2$O. The TOC removal efficiency was lower than that of UV$_{254}$ because of the presence of intermediates.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (51178043).

REFERENCES


