Enhanced photocatalytic oxidation of humic acids using Fe^{3+} - Zn^{2+} co-doped TiO_2 : The effects of ions in aqueous solutions

Rongfang Yuan, Dan Liu, Shaona Wang, Beihai Zhou, Fangshu Ma[†]

Beijing Key Laboratory of Resource-oriented Treatment of Industrial Pollutants, Department of Environmental Engineering, School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China

ABSTRACT

Photocatalytic oxidation in the presence of Fe-doped, Zn-doped or Fe-Zn co-doped TiO_2 was used to effectively decompose humic acids (HAs) in water. The highest HAs removal efficiency (65.7%) was achieved in the presence of 500°C calcined 0.0010% Fe-Zn co-doped TiO_2 with the Fe:Zn ratio of 3:2. The initial solution pH value, inorganic cations and anions also affected the catalyst photocatalytic ability. The HAs removal for the initial pH of 2 was the highest, and for the pH of 6 was the lowest. The photocatalytic oxidation of HAs was enhanced with the increase of the Ca^{2+} or Mg^{2+} concentration, and reduced when concentrations of some anions increased. The inhibition order of the anions on TiO_2 photocatalytic activities was $\text{CO}_3^{2-} > \text{HCO}_3^- > \text{Cl}^-$, but a slightly promotion was achieved when SO_4^{2-} was added. Total organic carbon (TOC) removal was used to evaluate the actual HAs mineralization degree caused by the 500°C calcined 0.0010% Fe-Zn (3:2) co-doped TiO_2 . For tap water added with HAs, the UV_{254} and TOC removal rates were 57.2% and 49.9%, respectively. The UV_{254} removal efficiency was higher than that of TOC because of the generation of intermediates that could significantly reduce the UV_{254} , but not the TOC.

Keywords: Fe^{3+} - Zn^{2+} co-doped TiO_2 , Humic acids, Inorganic ions, Photocatalytic oxidation

1. Introduction

Humic acids (HAs), a major fraction of natural organic matter (NOM) in surface water, are notoriously known for their detrimental effects in water [1], including turning the water into brown [2], generating complex metals and organic pollutants [3], and reacting with active chlorine during water disinfection, resulting in the formation of trihalomethanes [4]. Therefore, HAs removal is an important task during water treatment.

Nowadays, several techniques have been developed for the treatment of HAs [1]. Removal of HAs by various adsorbents has been studied [5]. However, many of these adsorbents need to be either disposed of or regenerated via a high temperature/acid addition process before reuse, creating a substantial amount of waste containing HAs and spent adsorbent in high concentrations [6]. Recently, removal of NOM from drinking water by advanced oxidation processes (AOPs) has been studied [7]. Extensive research has been devoted to the removal of HAs by photocatalyzed oxidation processes using semiconducting

metal oxide nanoparticles like TiO_2 [7]. The research efforts in this area are mainly based on assessing the factors that describe the kinetics and mechanistic pathways of photocatalytic removal of HAs.

However, TiO_2 has relatively wide band gap of 3.2 eV, which limits the efficiency of photocatalytic reactions, due to the high recombination rate of photogenerated electrons (e^-) and holes (h^+) [8]. Various metal ions (Zn, Cu, Cr, Mn, Fe, and so on) have been doped into TiO_2 to narrow the E_g of TiO_2 [7]. In addition, it has been reported that simultaneously doping of two dopants could enhance the photocatalytic activity of TiO_2 as compared to the enhancement through single element doping [9, 10]. Studies were focused on the rare-earth metals, such as Sr, Er and Ce [8, 10, 11], which are harmful for human bodies. The metals of Fe and Zn are more suitable to be used in organic matter photodegradation [12].

In addition, the efficiency of the photocatalytic oxidation of water can be influenced by many parameters. Radical scavenging and catalyst inactivation induced by inorganic substances present in water can affect the photocatalytic oxidation process [13].

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[†] Corresponding author

Email: mfsustb@sina.com

Tel: +86-10-62332465 Fax: +86-10-62333757

The main goal of this paper is to optimize the preparation method of Fe-Zn co-doped TiO₂ catalyst, as well as to study the effect of the following parameters on the photocatalytic oxidation: (a) pH, (b) some natural anions including HCO₃⁻, CO₃²⁻, SO₄²⁻ and Cl⁻, (c) some cations including Mg²⁺ and Ca²⁺, and (d) the effect of tap water compared to Milli-Q water as solvent.

2. Methods

2.1. Equipment

The photocatalytic reactor was a cylindrical glass column with a diameter and height of 60 and 850 mm, respectively. A 37 W low-pressure mercury vapor lamp (Φ22 mm × 790 mm; Beijing Haili Lighting Equipment Company, China) with UV wavelength of about 254 nm and UV radiation intensity of about 110 μW/cm² was found inside the column. The O₂ gas, which was prepared by an oxygenerator (Beijing North Star Yaaoo Scitech Co., Ltd., China), was fed into the reactor through a porous glass core aeration plate (pore size 4-7 μm).

2.2. Preparation of TiO₂

Tetrabutyl orthotitanate (analytical reagent, Tianjin) of 68 mL was dissolved in 120 mL ethylalcohol, and the obtained mixed solution was stirred for 2 h. Afterward, a series of FeCl₃ or ZnCl₂ solutions with different concentrations (atomic ratios of Fe/Zn to Ti of 0.0000% - 0.0100%), glacial acetic acid (80 mL), ethylalcohol (120 mL) and Milli-Q water (30 mL) were mixed together and added to the mixed solution in drops. The final mixed solution was placed at 30°C for 7 d, dried at 105°C and heated at 400-600°C. The nanometer-sized TiO₂ was obtained after adequate mulling.

2.3. Characterization of TiO₂

Scanning electron microscopic (SEM) images were obtained with an EVO18 electron microscope (Carl Zeiss, Germany). X-ray diffraction (XRD) patterns were collected in a Rigaku Dmax-RB diffractometer (Tokyo, Japan). The BET surface areas (S_{BET}) of the samples were determined by Quadrasorb SI-MP apparatus (Quantachrome Instrument, USA). Diffuse reflectance spectroscopy (DRS) was performed using a HITACHI U-3010 UV-Vis scanning spectrophotometer (Tokyo, Japan).

2.4. Photocatalytic Activity Tests

The aqueous slurry of 1,500 mL (pH 7), with 50 mg/L HAs (chemical purity, Tianjin) and 0.1 g/L TiO₂, was stirred and bubbled with O₂ (1.0 L/min) for 30 min prior to irradiation using the UV lamp. The reaction was stopped at 5 min intervals, and clear solution was obtained after centrifugation at 2,000 r/min. The HAs concentrations were determined using a UV-Vis spectrophotometer (Hach DR5000, USA) at 254 nm. The tests were repeated 3 times to minimize the errors.

2.5. Effects of the pH Value, the Inorganic Ions and the NOM

In a supplementary experiment, the initial solution pH value

was adjusted at the beginning of the oxidation by addition of HCl or NaOH to the HAs solution. The HAs removal efficiencies for the initial pH value of 2, 4, 6, 8, 10 and 12 in the presence of the optimized catalyst were determined.

The influence of inorganic anions, including HCO₃⁻, CO₃²⁻, SO₄²⁻ and Cl⁻, and cations including Mg²⁺ and Ca²⁺, were also investigated using the optimized catalyst. Different concentrations (0.5, 1.0, 1.5, 2.0 and 2.5 mmol/L) of NaHCO₃, Na₂CO₃, Na₂SO₄, NaCl, MgCl₂ and CaCl₂, similar with the concentration level in natural water, were added into the water with the initial pH value of 7.0, and the HAs concentrations were determined every 5 min.

In order to obtain the NOM removal efficiency, the tap water with UV₂₅₄ of 0.036 /cm and total organic carbon (TOC) of 5.5 mg/L was used. HAs of 50 mg/L was added in to the tap water, and the UV₂₅₄ and TOC were measured to be 1.272 /cm and 16.5 mg/L, respectively. TOC measurements were performed by the spectrophotometer using low-range TOC ampoules (Hach Chemical, USA).

3. Results and Discussion

3.1. HAs Removal

3.1.1. Single ion-doped TiO₂

Fig. 1 shows the influence of Fe or Zn dopants in the catalyst on the degradation of HAs. It can be seen that Fe doping increased the photocatalytic activity of TiO₂. That was because the ionic radii of Fe³⁺ (55 pm) was smaller than that of Ti⁴⁺ (60.5 pm); therefore, Fe³⁺ could replace Ti⁴⁺, and highly disperse in TiO₂ lattice, resulting in the improvement of the photocatalytic activity [7].

For Zn-doped TiO₂, Zn²⁺ ions (ionic radii of 74 pm, a little larger than that of Ti⁴⁺) were partially dispersed in the bulk of TiO₂; ZnO might be formed on the surface of TiO₂, and inhibiting the growth of TiO₂ [14]. In addition, the e⁻ and h⁺ transfer occur between the conduction band of ZnO and the conduction band of TiO₂. This efficient charge separation increases the photocatalytic activity of TiO₂/ZnO composite [15].

The optimal calcination temperature was 500°C for both Fe-doped and Zn-doped TiO₂, and the best photocatalytic activities were achieved when the Fe³⁺ or Zn²⁺ doping amount was 0.0010%, corresponding to the HAs removal efficiencies of 57.4% and 53.7%, respectively. The photocatalytic activities of Fe-doped or Zn-doped TiO₂ depended on the calcination temperature and the dopant concentration which affected the S_{BET} , E_g and crystallinity of the catalysts [10]. The SEM morphology of un-doped TiO₂ calcined at 500°C is shown in Fig. 2, and the characteristics of the catalysts are shown in Table 1.

The SEM morphology of un-doped TiO₂ calcined at 500°C indicates that the TiO₂ nanoparticles are globular and agglomerated. The diameter of TiO₂ was in the range of 10-50 nm.

The S_{BET} of the TiO₂ decreased as the calcination temperature increase because of the aggregation of the nanoparticles (Table 1). In addition, the doping amount can also affect the S_{BET} values of the ion-doped TiO₂. For the catalysts calcined at 400-500°C, the S_{BET} increased with an increase in the content of the dopant.

Fig. 1. Photocatalytic oxidation of 50 mg/L HAs in the presence of TiO_2 .

Table 1. BET Surface Areas and Energy Band Gaps of TiO_2

Doping amount (%)	BET surface area (m^2/g)					Energy band gap (eV)				
	400°C	450°C	500°C	550°C	600°C	400°C	450°C	500°C	550°C	600°C
Un-doped	81	68	60	23	1.2	3.11	3.06	3.02	2.98	2.92
Fe-	0.0005	86	72	64	23	8.9	3.10	3.04	3.00	2.95
	0.0010	90	73	67	57	15	3.08	3.00	2.95	2.89
	0.0050	92	78	78	32	1.4	3.05	2.96	2.88	2.83
	0.0100	94	79	81	34	1.1	3.03	2.91	2.82	2.75
Zn-	0.0005	112	97	96	52	13	3.10	3.05	3.00	2.97
	0.0010	126	95	93	76	29	3.10	3.05	2.99	2.95
	0.0050	135	101	97	69	16	3.08	3.01	2.95	2.91
	0.0100	137	104	95	67	2.8	3.06	2.99	2.93	2.89
Fe-Zn co-doped (500°C, 0.0010%)	BET surface area (m^2/g)					Energy band gap (eV)				
	1:4	2:3	1:1	3:2	4:1	1:4	2:3	1:1	3:2	4:1
	95	103	106	115	101	2.95	2.93	2.93	2.93	2.91

This can be attributed to the segregation of the dopant cations at the grain boundary, which inhibits grain growth by restricting the coalescence of some smaller neighboring grains [16]. For the catalysts calcined at 550-600°C, when the doping amount increased, the S_{BET} increased at first, and then decreased. The reduction in the S_{BET} may be due to blocking of fine capillaries of parent TiO_2 surface by metal film islands [17].

A larger S_{BET} indicates a larger amount of active sites on the catalyst surface. Therefore, the photocatalyst with lower calcination temperature and larger dopant amount may have a better catalytic activity when only S_{BET} is considered.

The TiO_2 calcined at higher temperatures showed a tendency to red shift, which resulted from the narrower E_g of rutile TiO_2

compared with that of anatase TiO_2 . By increasing the content of the dopants, the E_g were hence decreased because of a charge-transfer transition between the new dopant level near the valence band and the conduction band of the TiO_2 [17]. The reduction in the E_g of TiO_2 indicated that more light energy could be used during the photocatalytic degradation process, and therefore the photocatalytic activity of the catalyst was enhanced.

As it is known that TiO_2 in anatase phase shows better photocatalytic activity, the XRD analysis was conducted. With increasing doping amount of Fe^{3+} or Zn^{2+} , the diffraction peaks belonging to the (101) peak of anatase phase (2θ at about 25.3°) in Fe/Zn-doped TiO_2 powder increased at first, and then decreased; meanwhile,

Fig. 2. Scanning electron microscopic images of un-doped TiO₂ calcined at 500°C.

the intensity of the (110) peak of rutile phase (2θ at about 27.4°) increased after doping. This was because the phase transformation temperature reduced after doping [18]. In addition, with the increase of the calcination temperature, the diffraction peak of anatase appeared stronger and sharper, indicating that better crystallites were formed, and the intensity of the rutile phase increased when the calcination temperature increased because of the transformation of TiO₂ from anatase phase to rutile phase.

Moreover, the crystallites sizes of the TiO₂ catalysts can be calculated by Scherrer Formula [19] according to the XRD results. The particle diameters of the (101) peak of anatase phase for ions-doped TiO₂ were in the range of 10-50 nm, which can be confirmed by the SEM analysis (Fig. 2). Differences of the crystallites sizes among the catalysts with diffident dopant amount were not obvious. The most important factor for the crystallites sizes was the calcinations temperature. When the calcination temperature and the dopant amount changed, the variation tendency of the particle diameters for the catalysts was same with that of the S_{BET} .

According to the abovementioned results, the calcination temperature, as well as the dopant amount, can affect the photocatalytic activity of the catalyst by change the characteristics of TiO₂. Although the 0.0010% ions-doped TiO₂ calcined at 500°C had neither the largest S_{BET} , nor the narrowest E_g , it had a higher catalytic activity for HAs photocatalytic oxidation compared with the other catalysts because of the combined action of the crystallinity, S_{BET} and E_g .

3.1.2. Fe-Zn co-doped TiO₂

The HAs removal efficiencies in the presence of the Fe-Zn co-doped TiO₂ were higher than those in the presence of single ion-doped TiO₂, which could be attributed to the synergetic co-doping effects of Fe and Zn into TiO₂. Firstly, the S_{BET} for the 0.0010% Fe-Zn co-doped TiO₂ were larger than those of the Fe-doped or Zn-doped TiO₂. Doping of a second metal can change the catalyst surface structure because of the conservation of a large number of micropores, and therefore enhances the S_{BET} of the

co-doped catalyst [7]. Secondly, the E_g of the co-doped TiO₂ was between those of the Fe-doped and Zn-doped TiO₂, and was not considerably wider than that of the Fe-doped one. Thirdly, for the Fe-Zn co-doped TiO₂, the effect of the dopant type on the anatase peak intensities was not significant when the total doping concentration was conserved; only the anatase phase was found in the co-doped TiO₂. Therefore, higher photocatalytic activity was achieved.

The 500°C calcined 0.0010% Fe-Zn co-doped TiO₂ with the Fe:Zn ratio of 3:2 showed the highest catalytic activity, with the HAs removal efficiency of 65.7%. It was reported by Yang and Lee that 65% of HAs (10 mg/L) was removed after 120 min using the UV/TiO₂ system with the TiO₂ amount of 2 g/L [20]. Although there was a lower HAs concentration and a higher TiO₂ amount, the HAs removal efficiency in this research was a little lower, indicating that higher photocatalytic activity could be achieved when Fe³⁺ and Zn²⁺ ions were doped in TiO₂. Also, about 50% of HAs can be decomposed by the same process, except that Al³⁺-Fe³⁺ co-doped TiO₂ was used as the catalysts [9], showing that the Fe³⁺-Zn²⁺ TiO₂ synthesized by sol-gel method is better for the catalytic reaction.

High removal efficiency of the pollutant through photocatalytic oxidation process can be obtained because of the generation of H₂O₂ and ·OH [7]. In addition, Fe³⁺ and Zn²⁺ in the co-doped TiO₂ act as shallow trapping sites for charge carriers (e⁻ and h⁺) (Eq. (1) and Eq. (2)), and then react with H₂O₂ and OH⁻ in water to generate ·OH (Eqs. (3)-(6)) [21]. Zn²⁺ can react with Fe³⁺ in water, and therefore reduce the recombination rate of photogenerated e⁻ and h⁺.

where X^{n+} represents Fe³⁺ or Zn²⁺.

3.2. Effects of Inorganic Ions in Aqueous Solutions

In this study, the optimized photocatalyst (500°C calcined 0.0010% Fe-Zn co-doped TiO₂ with the Fe:Zn ratio of 3:2) was used, and the HAs removal efficiencies at different pH value, cation or anion concentrations were detected.

3.2.1. Initial solution pH value

It can be seen from Fig. 3 that the HAs removal efficiencies for the initial pH of 2, 4, 6, 8, 10 and 12 were 83.7%, 75.8%, 64.4%, 71.6%, 77.6% and 79.7%, respectively. At acidic conditions (pH increased from 2 to 6), the HAs photocatalytic oxidation

Table 2. Peak Intensities and Particle Diameters of TiO₂

Doping amount (%)	Peak intensity (anatase/rutile, a.u.)					particle diameter of (101) peak (nm)					
	400°C	450°C	500°C	550°C	600°C	400°C	450°C	500°C	550°C	600°C	
Un-doped	2,770/-	3,301/-	3,312/-	4,834/78	6,311/581	12.1	13.7	15.2	21.3	46.0	
Fe-	0.0005	2,659/-	3,388/-	3,415/-	5,299/105	7,087/1,685	13.1	14.1	15.9	20.5	44.0
	0.0010	3,155/-	3,686/-	4,677/-	5,702/192	7,850/2,402	13.5	13.9	15.6	20.0	37.7
	0.0050	3,186/-	4,016/-	4,712/-	7,181/199	7,152/2,500	13.6	14.4	16.0	31.8	41.4
	0.0100	1,925/-	3,389/-	4,348/-	6,241/411	7,001/3,962	13.8	14.4	16.3	32.4	43.2
		0.0005	2,436/-	3,277/-	3,598/-	4,676/-	7,535/680	11.0	12.2	13.3	19.0
Zn-	0.0010	2,367/-	2,352/-	3,619/-	4,445/-	6,858/964	11.3	12.4	13.8	17.0	35.4
	0.0050	2,195/-	2,271/-	3,517/-	3,614/-	6,600/1,380	11.5	13.2	14.7	22.4	33.9
	0.0100	1,978/-	2,065/-	3,283/-	3,466/54	6,378/1,512	11.8	13.3	14.8	21.6	44.5
Fe-Zn co-doped (500°C, 0.0010%)	Peak intensity (anatase/rutile, a.u.)					particle diameter of (101) peak (nm)					
	1:4	2:3	1:1	3:2	4:1	1:4	2:3	1:1	3:2	4:1	
	3,826/-	3,878/-	3,982/-	4,027/-	4,185/-	13.5	13.2	12.8	12.2	13.3

Fig. 3. Effect of pH on photocatalytic oxidation of 50 mg/L HAs in the presence of Fe-Zn co-doped TiO₂.

efficiency decreased as the pH increased. However, the HAs removal efficiency increased with the solution pH increased from 8 to 12).

Changes in the pH values can affect the photocatalytic degradation rates of HAs because the initial pH value influences the zero-point charge (ZPC) of TiO₂. The pH_{ZPC} for TiO₂ is widely reported between 6 and 7 [22]. Because the doping amount of metal ions was extremely low, the pH_{ZPC} for Fe-Zn co-doped TiO₂ was detected to be about 6, similar with that for the pure TiO₂. When the pH value of the solution was close to 6, the aggregation of the co-doped TiO₂ occurred, resulting in the reduction of the *S*_{BET} of the catalysts. Therefore, the HAs removal for the initial pH of 6 was the lowest.

The surface of the Fe-Zn co-doped TiO₂ tends to be positive charged for pH < pH_{ZPC}, and becomes negatively charged for pH > pH_{ZPC} [23]. The HAs in solution is negatively charged. Due to the electrostatic attraction, the acidic solution favors adsorption of HAs onto TiO₂ surface, and the HAs removal efficiency increases accordingly. Besides, at acidic condition, H⁺

could react with O₂ more easily, and more H₂O₂ would form to promote the photocatalytic oxidation of HAs.

At alkaline condition, OH⁻ can be adsorbed on the surface of the catalysts, and react with the transitional metals (Fe⁴⁺ and Zn³⁺), resulting in the production of ·OH (Eq. (4)).

3.2.2. Cations

Fig. 4 shows that a beneficial effect of cations in water on the degradation of HAs was achieved. At time of 120 min of irradiation, 72.1%, 75.5%, 78.1%, 81.9% and 83.5% of degradations with Fe-Zn co-doped TiO₂ were observed for 0.5, 1.0, 1.5, 2.0 and 2.5 mmol/L of Ca²⁺ in neutral medium, whereas 65.7% degradations occurred in medium without Ca²⁺. The HAs removal efficiencies were 70.4%, 73.0%, 74.9%, 76.7% and 79.5% for the medium with Mg²⁺ concentration of 0.5, 1.0, 1.5, 2.0 and 2.5 mmol/L, respectively. The photocatalytic oxidation of HAs was enhanced with the increase of the Ca²⁺ or Mg²⁺ concentration.

The enhancement of degradation by addition of these ions is due to increase of charge separation by accepting the conduction band electron [23]. In addition, the addition of Ca²⁺ or Mg²⁺ in the solution can affect the adsorption of HAs on the surface of TiO₂. For solution without Ca²⁺ or Mg²⁺, the pH value of the solution is 7, close to the pH_{ZPC} of TiO₂ (pH of 6). The adsorption of OH⁻ is a little stronger than that of H⁺, and the adsorption of HAs with negatively charged is weak. When Ca²⁺ or Mg²⁺ ions were added, reactions in Eqs. (7)-(10) occurred.

where M²⁺ represents Ca²⁺ or Mg²⁺.

Ca^{2+} or Mg^{2+} shows bridging behavior between TiO_2 and HAs (Eq. (9)). Besides, the cations can react with A^- ions, resulting in the growing of HAs molecular chain. The longer molecular chain makes it easier for HAs to be adsorbed on the surface of TiO_2 , and the HAs removal efficiency increases.

3.2.3. Anions

Inorganic anions, including HCO_3^- , CO_3^{2-} , SO_4^{2-} and Cl^- , are common in drinking water. The effects of these inorganic anions on HAs photocatalytic oxidation were determined (Fig. 5). When

HCO_3^- with the concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5 mmol/L were added in the solution, the HAs removal efficiencies were 63.3%, 61.8%, 59.8%, 58.0% and 55.8%, respectively. The figures were 61.4% (64.8%), 58.2% (64.1%), 54.5% (64.0%), 52.1% (63.5%) and 48.2% (63.1%) when CO_3^{2-} (Cl^-) with the above-mentioned concentrations were added. The photocatalytic activities were inhibited when these anions were added, and the order of inhibition were $\text{CO}_3^{2-} > \text{HCO}_3^- > \text{Cl}^-$. However, when SO_4^{2-} was added at the concentrations of 0.5, 1.0, 1.5, 2.0 and

Fig. 4. Effects of cations on photocatalytic oxidation of 50 mg/L HAs in the presence of Fe-Zn co-doped TiO_2 .

Fig. 5. Effects of anions on photocatalytic oxidation of 50 mg/L HAs in the presence of Fe-Zn co-doped TiO_2 .

2.5 mmol/L, a slight increase for HAs removal was observed, and the HAs removal efficiencies were 66.8%, 67.6%, 68.2%, 69.0% and 69.6%, respectively.

The CO_3^{2-} , HCO_3^- and Cl^- can be adsorbed by the catalyst and result in TiO_2 contamination [24]. The inhibition of CO_3^{2-} , HCO_3^- and Cl^- on photocatalytic activity can be explained with the scavenging of h^+ and $\cdot\text{OH}$ radicals by ions [25]. The reactions of the ions with h^+ and $\cdot\text{OH}$ are given in Eqs. (11)-(12) [13, 25].

where Y^{n-} represents CO_3^{2-} , HCO_3^- , Cl^- or SO_4^{2-} , and $\cdot\text{Y}^{(n-1)-}$ represents $\cdot\text{CO}_3^-$, $\cdot\text{HCO}_3^-$, $\cdot\text{Cl}$ or $\cdot\text{SO}_4^-$, respectively.

Although $\cdot\text{CO}_3^-$, $\cdot\text{HCO}_3^-$ and $\cdot\text{Cl}$ can react with HAs, their oxidizabilities are limited. As the concentrations of CO_3^{2-} , HCO_3^- or Cl^- increase, the effect becomes increasingly significant.

CO_3^{2-} has a higher inhibiting capacity of TiO_2 than HCO_3^- in the photocatalytic degradation of organic compounds. However, the pH value of the 2.5 mmol/L Na_2CO_3 solution was 11.0, while that of the 2.5 mmol/L NaHCO_3 solution was 8.5; it is shown that for alkaline solution, the HAs removal efficiency increased with the solution pH increased. The lower removal efficiency in the presence CO_3^{2-} was attributed to the weaker oxidizing ability of $\cdot\text{CO}_3^-$ than that of $\cdot\text{HCO}_3^-$.

The HAs removal efficiency in the presence of Cl^- was not decreased significantly, because $\text{Ti}-\text{O}$ is predominant in neutral water, and the adsorption of Cl^- can be ignored [24].

The presence of SO_4^{2-} slightly promoted the reactions of HAs removal because of the elimination of negative ion adsorption and a small extent of the participation of $\cdot\text{SO}_4^-$ (Eq. (11) and Eq. (12)) [24]. As a strong oxidizing agent, $\cdot\text{SO}_4^{2-}$ can accelerate the reaction.

3.3. HAs Removal in Tap Water

TOC removal was used to evaluate the actual HAs mineralization degree in tap water caused by the 500°C calcined 0.0010% Fe-Zn (3:2) co-doped TiO_2 (Fig. 6). The UV_{254} removal efficiency increased rapidly during the first 100 min and then became stable because of the degradation of HAs into intermediate molecules during the photocatalysis. Meanwhile, the TOC rapidly decreased all along the 2 h.

For the HAs solution, the characteristic absorption peaks at 254 nm and 400 nm are attributed to benzene components and chromophore groups, respectively [3]. The absorbances of the original HAs at 254 and 400 nm were 0.735 and 0.093, respectively. The HAs absorbance at 254 nm (400 nm) after treatment decreased by 42.8% (40.9%). The TiO_2 photocatalytic oxidation effectively destroyed both the benzene components and the chromophore groups. However, the benzene components were a little more difficult to destroy than the chromophore groups.

The TOC removal rate was 49.9%, which indicates that 49.9% of HAs was mineralized into CO_2 and H_2O . The UV_{254} removal efficiency (57.2%) was higher than that of TOC because of the generation of intermediates that could significantly reduce the UV_{254} , but not the TOC.

Fig. 6. TOC and UV_{254} removal for tap water by Fe-Zn co-doped TiO_2 photocatalytic oxidation.

4. Conclusions

HAs were effectively degraded in the presence of Fe-doped, Zn-doped or Fe-Zn co-doped TiO_2 under irradiation with UV light. The HAs removal efficiencies were affected by the S_{BET} , E_g and crystallinity of the catalysts. Highest HAs removal efficiency was achieved in the presence of 500°C calcined 0.0010% Fe-Zn co-doped TiO_2 with the Fe:Zn ratio of 3:2.

Changes in the initial solution pH values can affect the photocatalytic degradation rates of HAs. The HAs removal for the initial pH of 2 was the highest, and for the pH of 6 was the lowest.

The inorganic cations and anions also affect the photocatalytic activity of the co-doped TiO_2 . The photocatalytic oxidation of HAs was enhanced with the addition Ca^{2+} or Mg^{2+} ions. The photocatalytic activities were inhibited when CO_3^{2-} , HCO_3^- or Cl^- was added, and the order of inhibition was $\text{CO}_3^{2-} > \text{HCO}_3^- > \text{Cl}^-$; but the removal of HAs was slightly promoted when SO_4^{2-} was added.

For tap water added with HAs, the UV_{254} removal efficiency was higher than that of TOC because of the generation of intermediates that could significantly reduce the UV_{254} , but not the TOC.

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