

## Research Article

# 4-Nitroaniline Degradation by TiO<sub>2</sub> Catalyst Doping with Manganese

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Stainless steel anode covered with layer film of TiO<sub>2</sub> doped with manganese was utilized to decompose 4-nitroaniline in rectangular borosilicate glass reactor, while stainless steel mesh was chosen as cathode; the anode and cathode were connected to the direct-current power; meantime two 60 W ( $\lambda_{\max} = 365$  nm) UV lamps were used as light source. The microstructures on TiO<sub>2</sub> before and after being doped with manganese were analyzed by energy disperse X-ray (EDX) and X-ray diffraction (XRD). The performance of degradation of 4-nitroaniline was evaluated by analyzing cracking ratio of 4-nitroaniline ring, the chemical oxygen demand (COD), and total organic carbon (TOC) in remaining solution. Monitored parameters during all the photocatalytic reaction including dissolved oxygen, direct voltage, and radiation dosage of ultraviolet rays were investigated. When dissolved oxygen concentration, direct voltage, and radiation dosage of ultraviolet rays were, respectively, equivalent to 9 mg/L, 24 V, and 1200  $\mu\text{W}/\text{cm}^2$ , the degradation ratio of 4-nitroaniline reached maximum. The experimental results indicated that cracking ratio of 4-nitroaniline ring and the removal ratio of COD and TOC were, respectively, more than 99%, 85%, and 80% when reaction was run for 10 hours. The values of COD and TOC were, respectively, less than 16 mg/L and 8 mg/L while the experiment was finished.

## 1. Introduction

4-Nitroaniline, important aromatic compounds, has been widely used as precursor in chemical synthesis of various azo dyes, antioxidants, pesticides, antiseptic agents, poultry medicines, fuel additives, and important corrosion inhibitors [1]. However, the chemical stability and toxicity also make it hazardous [2]. The treatment and disposal of wastewater containing 4-nitroaniline have emerged as an important environmental concern. Furthermore, it shows toxicity, mutagenicity, and carcinogenicity towards different experimental model organisms [3, 4]. Consequently, many developed and developing countries have enlisted 4-nitroaniline as priority pollutant and imposed restriction on its production, usage, and disposal [1]. 4-Nitroaniline metabolites are considered to be nonbiodegradable or only slowly degradable [5] and have varying toxicities to aquatic life and higher organisms [6, 7].

The photocatalytic degradation of organic environmental pollutants in the presence of a semiconductor such as TiO<sub>2</sub>, ZnO, and Fe<sub>2</sub>O<sub>3</sub> has become interesting enormously over the last 10 years [6–11]. Partly it is of reason that it may completely mineralize a variety of aliphatic and aromatic compounds under suitable conditions and it may be less expensive. However, much attention in this area has focused on the use of slurry system, thus causing a series of trouble, such as the need of separating the spent catalysts particles and need of continuous stirring to keep the semiconductor suspended. Therefore, a photocatalytic technique without filtration and suspension is desirable. Recently, different suitable materials matrix has been chosen to be immobilized support, such as glass [12], conductive glass [11], and stainless steel [12].

This study aimed to improve the catalyzing performance by preparing the 20–50  $\mu\text{m}$  film whose main component was TiO<sub>2</sub> doped with manganese in the surface of stainless steel.

This technique can enhance the degradation efficiency of 4-nitroaniline by means of irradiation of ultraviolet rays and imposing 24 V voltage. During the whole degradation, the ratio of crackling of aromatic cycle and the removal ratio of COD and TOC were kept almost at the same level because of the synergistic effect between modified catalyst and the good operational condition. The effects of external potential and radiation dosage of ultraviolet rays on the photocatalytic reaction efficiency were investigated in detail. The quantum analysis of 4-nitroaniline concentration and the values of COD and TOC were also determined.

## 2. Experiments

**2.1. Samples Preparation.** The 25 g  $\text{TiCl}_4$  (purity 99%) was added to 2 L demonized water with 2 mL concentrated sulfuric acid; after the  $\text{TiCl}_4$  was completely hydrolyzed, the 0.75 g manganese oxalate dissolved in 100 mL 10% oxalic acid was slowly added to above-mentioned solution. Then about 130 to 160 mL 17% ammonia was slowly added to ensure the mixture pH value was between 7.0 and 7.5. The mixture was filtrated and rinsed with deionized water to remove the  $\text{NH}_4\text{Cl}$  until the leaching liquid cannot form white precipitation with 0.2 mmol/L  $\text{Ag}_2\text{SO}_4$ . The filtrated residue successively underwent desiccation at 373 K for 2 hours and vacuum drying at 353 K under pressure of  $10^{-1}$  Pa for 3 hours; finally the  $\text{Ti}(\text{OH})_4$  doped manganese oxalate was obtained.

The anatase crystal form  $\text{TiO}_2$  doped with manganese was achieved by incinerating  $\text{Ti}(\text{OH})_4$  doped with manganese oxalate at 830 K for 5 hours. The rutile crystal phase  $\text{TiO}_2$  doped with manganese was gained by incinerating  $\text{Ti}(\text{OH})_4$  doped with manganese oxalate at 1080 K for 5 hours.

**2.2. X-Ray Diffraction (XRD).** The  $\text{TiO}_2$  crystal form was determined by (XRD) using a D/max 2500VL/PC diffractometer with  $\text{Cu}/\text{K}\alpha$  radiation (Rigaku Corporation, Japan).

**2.3. Energy Dispersive X-Ray (EDX).** The constitution of  $\text{TiO}_2$  doped with manganese was determined by analyzing the data of EDX (JSM-5610LV/NORAN-VANTAGE; Japan Electron Optics Laboratory Limited Corporation, Japan; Thermo Electron, America). The testing parameters on energy dispersion of X-ray included  $25.6934^\circ$  taking-off angle, 15 KeV accelerating voltages, and 100-second live time.

**2.4. Catalytic Experiments.** The catalytic experiments were performed in a rectangular quartz reactor dissolved 2.5 g of catalyst and 8 L of 4-nitroaniline solution. The original concentration of 4-nitroaniline was chosen as 100 mg/L. A 120 W medium pressure Hg lamp (Philip) was utilized and the mean value of radiation power, determined using an UV radiometer (Digital, UVX36), was  $1200 \mu\text{W}/\text{cm}^2$ ; oxygen was continuously bubbled into the stirred suspension to maintain DO (dissolved oxygen) in solution being more than 9 mg/L.

Samples of 10 mL volume were withdrawn at fixed intervals. After centrifugation,  $0.45 \mu\text{m}$  microfiltration, the concentration of the 4-nitroaniline was determined by

measuring its absorbance in the wavelength of 380 nm with the help of UV spectrophotometer (UNICO (Shanghai) Instruments Limited Corporation, China). TOC determinations were carried out by using a Vario TOC analyzer (Element Corporation, Germany).

## 3. Results and Discussions

**3.1. Analysis of XRD on Anatase  $\text{TiO}_2$  Doped with Manganese Oxalate.** As can be seen from Table 1 and Figure 1 prepared  $\text{TiO}_2$  doped with manganese appeared single and strong peak at maximum diffraction angles at  $25.3^\circ$  and  $48.2^\circ$ ; triple peak at  $36.9^\circ$ ,  $37.8^\circ$ , and  $38.61^\circ$ ; and double and medium peak at maximum diffraction angles at  $54^\circ$  and  $55.3^\circ$ . It can be easily observed that the characteristics that  $\text{TiO}_2$  doped with manganese exhibited are almost the same as those of the anatase  $\text{TiO}_2$  standard card (PDF number 00-002-0387). Analyzed results further certified that prepared  $\text{TiO}_2$  doped with manganese was of anatase crystal form.

Besides, Figure 1 showed that a peak around  $32.5^\circ$  was attributed to  $\text{Mn}_3\text{O}_4$  according to JCPDS cards (NO75-1560).

**3.2. Analysis of XRD on Rutile  $\text{TiO}_2$  Doped with Manganese Oxalate.** As can be seen from Table 2 and Figure 2 prepared  $\text{TiO}_2$  doped with manganese appeared single and strong peak at maximum diffraction angles at  $25.44^\circ$ ,  $36.08^\circ$ , and  $54.34^\circ$ ; medium and single peak at  $41.26^\circ$  and  $56.68^\circ$ ; and weak and single peak at maximum diffraction angles at  $39.22^\circ$  and  $44.08^\circ$ . It can be easily observed that the characteristics that  $\text{TiO}_2$  doped with manganese exhibited are almost the same as those of the rutile  $\text{TiO}_2$  standard card (PDF number 00-001-1292). The data from comparing their diffraction angle and intensity indicated that  $\text{TiO}_2$  doped with manganese oxalate still keeps the rutile crystal phase.

**3.3. Analysis of EDX on Anatase and Rutile  $\text{TiO}_2$  Doped with Manganese Oxalate.** The statistical analyzing results were listed in Tables 3 and 4. The data from Tables 3 and 4 indicated that the ratio of  $\text{Ti}^{4+}$  and  $\text{Mn}^{2+}$  almost equaled 50 : 1 among the matrices of anatase crystal phase  $\text{TiO}_2$  doped with manganese and rutile crystal phase  $\text{TiO}_2$  doped with manganese, which certified that  $\text{TiO}_2$  doped with manganese could not alter the microstructure of  $\text{TiO}_2$ .

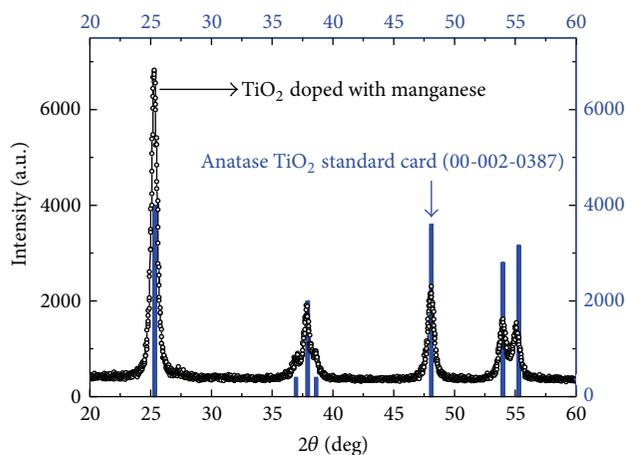
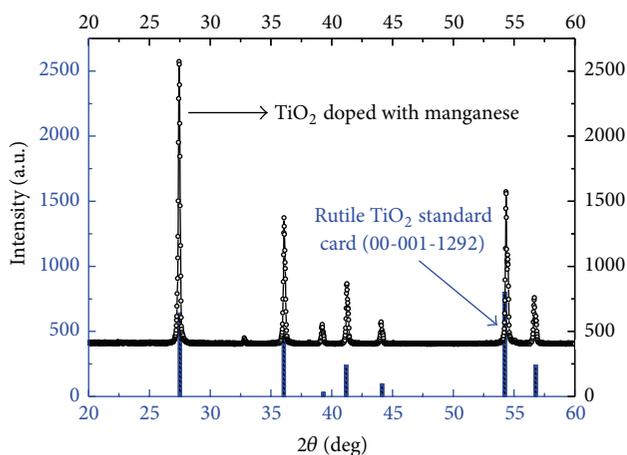
**3.4. The Relationship between Removal Ratio of COD and Removal Ratio of 4-Nitroaniline.** The ionic radius of  $\text{Mn}^{2+}$  (0.80 Å) is quite similar to that of host  $\text{Ti}^{4+}$  (0.68 Å). Hence,  $\text{Mn}^{2+}$  ions can easily substitute  $\text{Ti}^{4+}$  ion in  $\text{TiO}_2$  lattice without distorting the pristine crystal structure; thus it can stabilize the anatase crystal phase over a range of doping concentrations. The doped  $\text{Mn}^{2+}$  can reduce the band gap of semiconductor  $\text{TiO}_2$ . The band gap can be achieved by CB (conduction band) subtracting VB (valence band). The photogenerated charge carriers such as  $\text{h}^+$  and  $\text{e}^-$  whose function motivated hydroxyl radical may be recombined and this may lead to producing electron accumulating phenomenon. Thus this could low catalytic activity. Thus  $\text{TiO}_2$  doped with manganese can overcome above-mentioned

TABLE 1: Comparing diffraction angle and intensity of anatase TiO<sub>2</sub> standard card and TiO<sub>2</sub> doped with manganese.

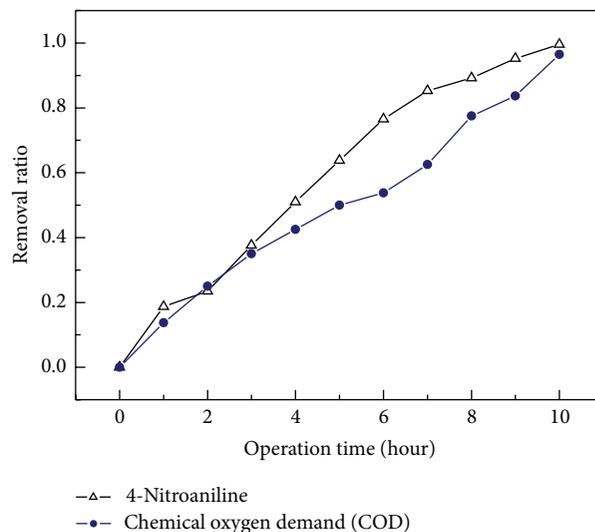
Anatase TiO <sub>2</sub> standard card (00-002-0387)	Angle (°)	25.25	36.96	37.93	38.61	48.1	53.89	55.30
	Intensity (a.u.)	100	10	50	10	90	70	79
Prepared TiO <sub>2</sub> doped with manganese	Angle (°)	25.3	36.9	37.8	38.61	48.2	54	55.30
	Intensity (a.u.)	6820	806	1906.7	953	2153	1613.3	1226.7

TABLE 2: Comparing diffraction angles and intensity of rutile TiO<sub>2</sub> standard card and prepared TiO<sub>2</sub> doped with manganese.

Rutile TiO <sub>2</sub> Standard card (00-001-1292)	Angle (°)	27.51	36.06	39.31	41.19	44.14	54.23	56.78
	Intensity	80	60	4	30	12	100	30
Prepared TiO <sub>2</sub> doped with manganese	Angle (°)	25.44	36.08	39.22	41.26	44.08	54.34	56.68
	Intensity (a.u.)	2572	1371.7	552.5	864.2	571.7	1570.8	757.5

FIGURE 1: Comparison of XRD pattern of anatase standard card (00-002-0387) and TiO<sub>2</sub> doped with manganese oxalate.FIGURE 2: Comparison of XRD pattern of rutile TiO<sub>2</sub> standard card (PDF number 00-001-1292) and TiO<sub>2</sub> doped with manganese oxalate.

shortcoming and catalytic performance of TiO<sub>2</sub> doped with manganese can be improved. Figure 3 indicated that the hydroxyl radicals produced by photochemical reaction could

FIGURE 3: The relationship between removal ratio of 4-nitroaniline and COD removal ratio during the reaction ( $c$  (4-nitroaniline) = 100 mg/L; voltage = 12 V; ultraviolet ray dosage = 1200  $\mu\text{W}/\text{cm}^2$ ).TABLE 3: Statistical results of metal on anatase TiO<sub>2</sub> doped with manganese by EDX.

Element	K-ratio (calculation)	Atom (%)	Element weight (%)
Ti-K	0.9756	97.73	97.41
Mn-K	0.0221	2.27	2.59

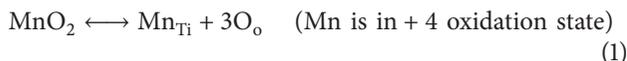
rapidly strike the ring of 4-nitroaniline and result in the ring cracked out; finally the cracked ring can be converted into inorganic substance with reductive property.

**3.5. Induced Defect States by Doped with Manganese in the Pristine TiO<sub>2</sub>.** The variable oxidation states and their ionic radii of manganese are Mn<sup>2+</sup> (0.80 Å), Mn<sup>3+</sup> (0.66 Å), or Mn<sup>4+</sup> (0.60 Å). Probable defect states can be represented using Kroger and Vink notation [11, 12].

TABLE 4: Statistical results of metal on rutile TiO<sub>2</sub> doped with manganese by EDX.

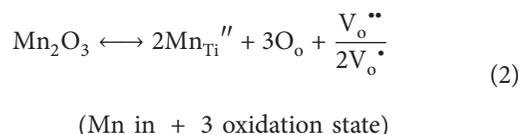
Element	K-ratio (calculation)	Atom (%)	Element weight (%)
Ti-K	0.9699	97.20	96.80
Mn-K	0.0273	2.80	3.20

Assume Mn<sup>4+</sup> occupying the lattice of Ti<sup>4+</sup> in TiO<sub>2</sub> matrix:

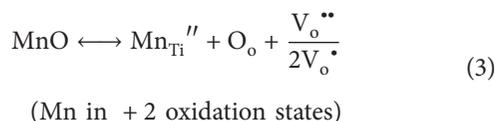


When the manganese of MnO<sub>2</sub> may be present as tetravalent state, tetravalent titanium in TiO<sub>2</sub> can be replaced by tetravalent manganese. Because the ionic radius of Ti<sup>4+</sup> was 0.72 Å is bigger than that of tetravalent manganese (0.60 Å); thus the replacing process can produce 3O<sub>o</sub>. Meantime because the Mn<sup>4+</sup> of MnO<sub>2</sub> and Ti<sup>4+</sup> of TiO<sub>2</sub> may be all present as tetravalent, the ionized oxygen vacancy does not produce.

Assuming Mn<sup>3+</sup>/Mn<sup>2+</sup> occupying the lattice of Ti<sup>4+</sup> in TiO<sub>2</sub> matrix, it induces doubly ionized/two single ionized oxygen vacancies:



When the manganese of Mn<sub>2</sub>O<sub>3</sub> may be present as trivalent state, tetravalent titanium in TiO<sub>2</sub> can be replaced by trivalent manganese. Because the ion radius of Ti<sup>4+</sup> was 0.72 Å is bigger than that of trivalent manganese (0.66 Å); thus the replacing process can produce O<sub>o</sub>. Meantime the Mn<sup>3+</sup> of Mn<sub>2</sub>O<sub>3</sub> and Ti<sup>4+</sup> of TiO<sub>2</sub> may be present as different valence states; thus doubly ionized/two single ionized oxygen vacancies may be produced:



When the manganese of MnO may be present as bivalent state, tetravalent titanium in TiO<sub>2</sub> can be replaced by bivalent state manganese. Because the ion radius of Ti<sup>4+</sup> was 0.72 Å which is smaller than that of bivalent manganese (0.80 Å), the replacing process can produce O<sub>o</sub>. Meantime the Mn<sup>2+</sup> of MnO and Ti<sup>4+</sup> of TiO<sub>2</sub> may be present as different valence states; doubly ionized/two single ionized oxygen vacancies may be produced.

The notations V<sub>o</sub>, V<sub>o</sub><sup>•</sup>, and V<sub>o</sub><sup>••</sup> represent neutral, single, and doubly ionized oxygen vacancies. O<sub>o</sub> is oxygen occupying oxygen lattice. Mn<sub>Ti</sub> is manganese ion at titanium lattice and the (') represents the deficiency in the charge.

3.6. *The Removal of Total Organic Carbon (TOC) during the Photochemical Reaction.* As can be seen in Figure 4 TOC removal ratio almost keeps the same pace with 4-nitroaniline removal ratio during all the degradation. This is mainly attributed to synergistic effect between high efficient catalyst and the direct-current electric field. During the whole reaction, the dissolved oxygen and electric field could make the system mix up better; meantime, the produced hydroxyl radicals can be swiftly transferred to the surface of catalyst with the help of electric field. Thus the catalyzing efficiency can be greatly enhanced. By means of availing of this kind of method, 4-nitroaniline can be converted into harmless inorganic substance. Besides, enhanced activity of TiO<sub>2</sub> doped manganese was mainly attributed to the bicrystalline framework of anatase and rutile which suggests the synergistic effect between the mixed polymorphs. It is well known that TiO<sub>2</sub> with bicrystalline framework of anatase-rutile can effectively reduce the recombination of photogenerated charge carrier [13–15].

As can be seen in Figure 5, photochemical reaction accompanying with electric field and UV light without photocatalyst only can produce about 10% cracking ratio of 4-nitroaniline ring. But, it was observed from Figure 4 that when the TiO<sub>2</sub> doped with manganese was used as catalyst under the same conditions, the cracking ratio of 4-nitroaniline ring and removal ratio of TOC were, respectively, equivalent to 99% and 97%, which further proved that photochemical reaction accompanying with electric field, UV light, and catalyst (TiO<sub>2</sub> doped with manganese) can rapidly decompose 4-nitroaniline. The above-mentioned experimental results indicated that the TiO<sub>2</sub> doped with manganese mainly plays an important role, while electric field and UV light play a minor role during the process of degradation of 4-nitroaniline.

As can be seen in Figure 6 photochemical reaction by means of TiO<sub>2</sub> without doping manganese can only decompose about 30% of 4-nitroaniline; meantime the removal of TOC only reaches 20% within ten hours. But, it can be observed from Figure 6 that the cracking ratio of 4-nitroaniline and removal ratio of TOC were, respectively, equivalent to 99% and 97% when the TiO<sub>2</sub> doped with manganese was utilized to decompose the 4-nitroaniline. These data further proved that manganese mainly plays an important role during the process of decomposing 4-nitroaniline by photochemical reaction with 12 V voltages and 1200 μW/cm<sup>2</sup> dosage ultra violet ray.

3.7. *Analyzing the Byproduct by IR (Infrared).* After finishing degradation of the 4-nitroaniline by catalytic reaction, the byproduct of reaction was gained by filtering the solution and the product was sandy beige. The dried residue was analyzing by infrared spectrometer. As can be seen in Figure 7 the characteristic peaks of 4-nitroaniline disappeared and appeared to be the characteristic peaks of alkyne and ester. The analyzed results indicated that the byproducts of degradation 4-nitroaniline were not harmful to water body and human beings.

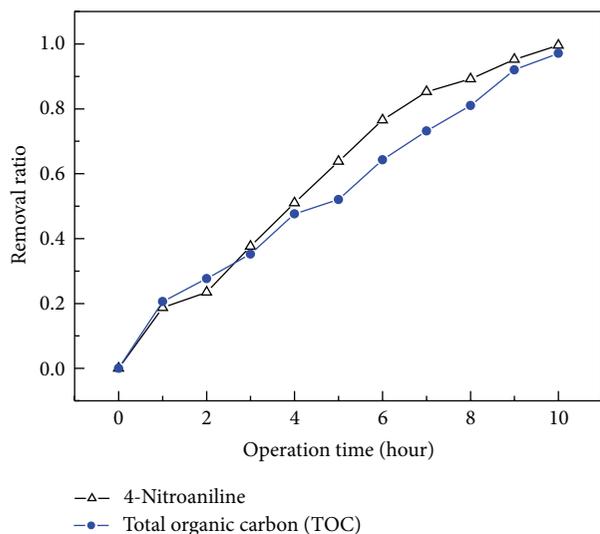


FIGURE 4: The relationship between TOC removal ratio and 4-nitroaniline removal ratio during the reaction ( $c$  (4-nitroaniline) = 100 mg/L; voltage = 12 V; ultraviolet ray dosage =  $1200 \mu\text{W}/\text{cm}^2$ ).

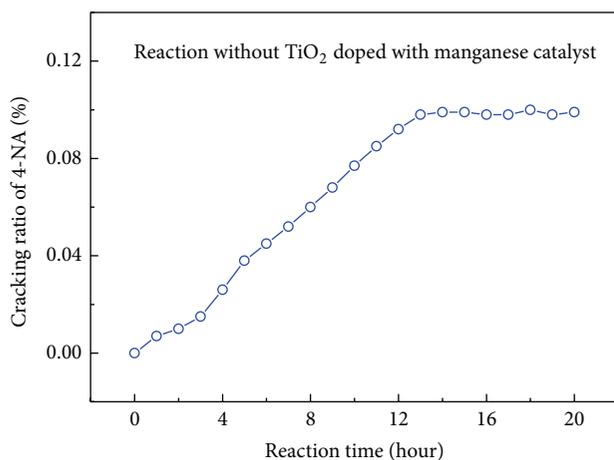


FIGURE 5: The relationship between cracking ratio of 4-nitroaniline ring and operation time during reaction ( $c$  (4-nitroaniline) = 100 mg/L; voltage = 12 V; ultraviolet ray dosage =  $1200 \mu\text{W}/\text{cm}^2$ ).

Figure 7 showed that the characteristic peaks at wavenumbers  $842.83 \text{ cm}^{-1}$  ( $\delta_{\text{C-H}}$ ) which represented the para-substitution of benzene ring and peaks at wavenumbers  $2177.63 \text{ cm}^{-1}$  ( $\nu_{\text{C=N}}$ ) disappeared completely. Meantime, the characteristic peaks at wavenumbers between  $1200$  and  $1700 \text{ cm}^{-1}$  belonging to  $\nu_{\text{nitro}}$  appeared weak peaks, and the most part of peaks disappeared. The results indicated that the byproducts of degradation of 4-nitroaniline cannot contain the ring of benzene, alkenes. The weak peaks appearance near the wavenumbers  $2000 \text{ cm}^{-1}$  from IR of byproducts indicated the existence of alkynes groups. This further certified that the 4-nitroaniline was completely decomposed during the whole reaction. The byproducts only contained little inorganic compounds containing nitrogen.

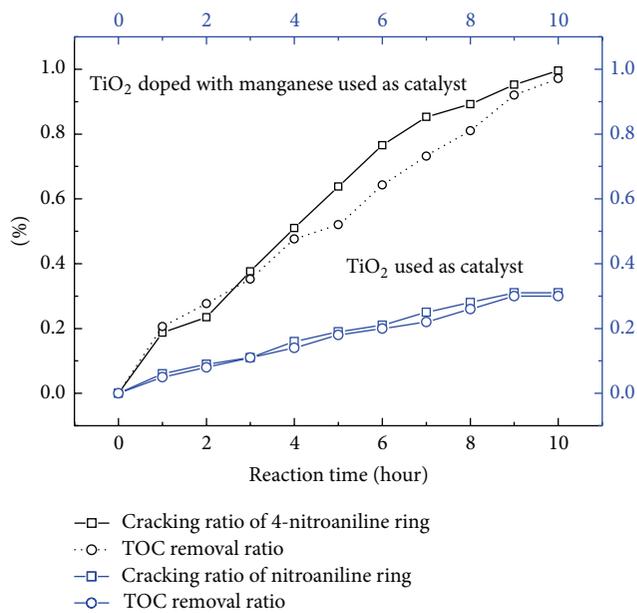


FIGURE 6: Comparison the performance of degradation of 4-nitroaniline on  $\text{TiO}_2$  and  $\text{TiO}_2$  doped with manganese ( $c$  (4-nitroaniline) = 100 mg/L; voltage = 12 V; ultraviolet ray dosage =  $1200 \mu\text{W}/\text{cm}^2$ ).

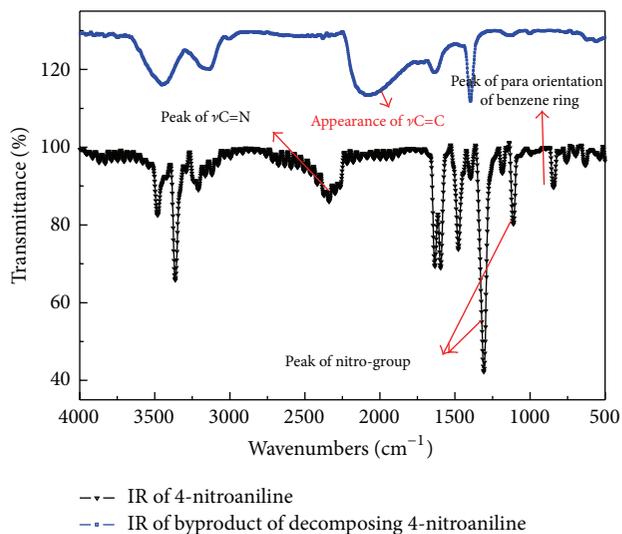


FIGURE 7: The infrared spectrometer on byproduct after finishing degradation of the 4-nitroaniline.

**3.8. Analyzing the Byproducts by Elemental Analysis (EA).** The elemental analyzing data on byproducts produced during decomposing 4-nitroaniline were listed in Table 5. The analyzed result showed that the byproducts contained eleven point zero percent carbon, two point forty-two percent hydrogen, one point ninety percent nitrogen, and eighty-four point sixty-eight percent oxygen. The carbon and hydrogen element were derived the trace conjugated alkenes and the nitrogen was derived from the inorganic nitrogen oxides by analyzing those data from Figure 7 and Table 5.

TABLE 5: Elemental analysis results on byproduct during decomposing the 4-nitroaniline.

Element	Carbon	Hydrogen	Nitrogen	Oxygen
Mass percent (%)	11.0	2.42	1.90	84.68

#### 4. Conclusions

- (1) Anatase and rutile TiO<sub>2</sub> doped with manganese oxalate exhibited strong performance of decomposing 4-nitroaniline when they were mixed up according to fixed ratio 9 : 1.
- (2) During the process of degradation of 4-nitroaniline, the TiO<sub>2</sub> doped with manganese plays an important role, while the electron field and UV light play a weak and synergistic role.
- (3) During the whole degradation, the cracking ratio of ring of 4-nitroaniline, the removal ratio of COD and the removal ratio of TOC were kept almost at the same pace. The cracking ratio of 4-nitroaniline ring, the removal ratio of COD, and TOC were, respectively, more than 99%, 85%, and 80% when reaction was run for 10 hours.
- (4) The values of COD and TOC were, respectively, less than 16 mg/L and 8 mg/L while the experiment was finished within 10 hours. The final concentrations in effluent on COD and TOC met the Discharge Standard of the National Primary Standard.
- (5) The invented method can completely solve the problem of treating waste water on 4-nitroaniline whose concentration was below 100 mg/L.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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