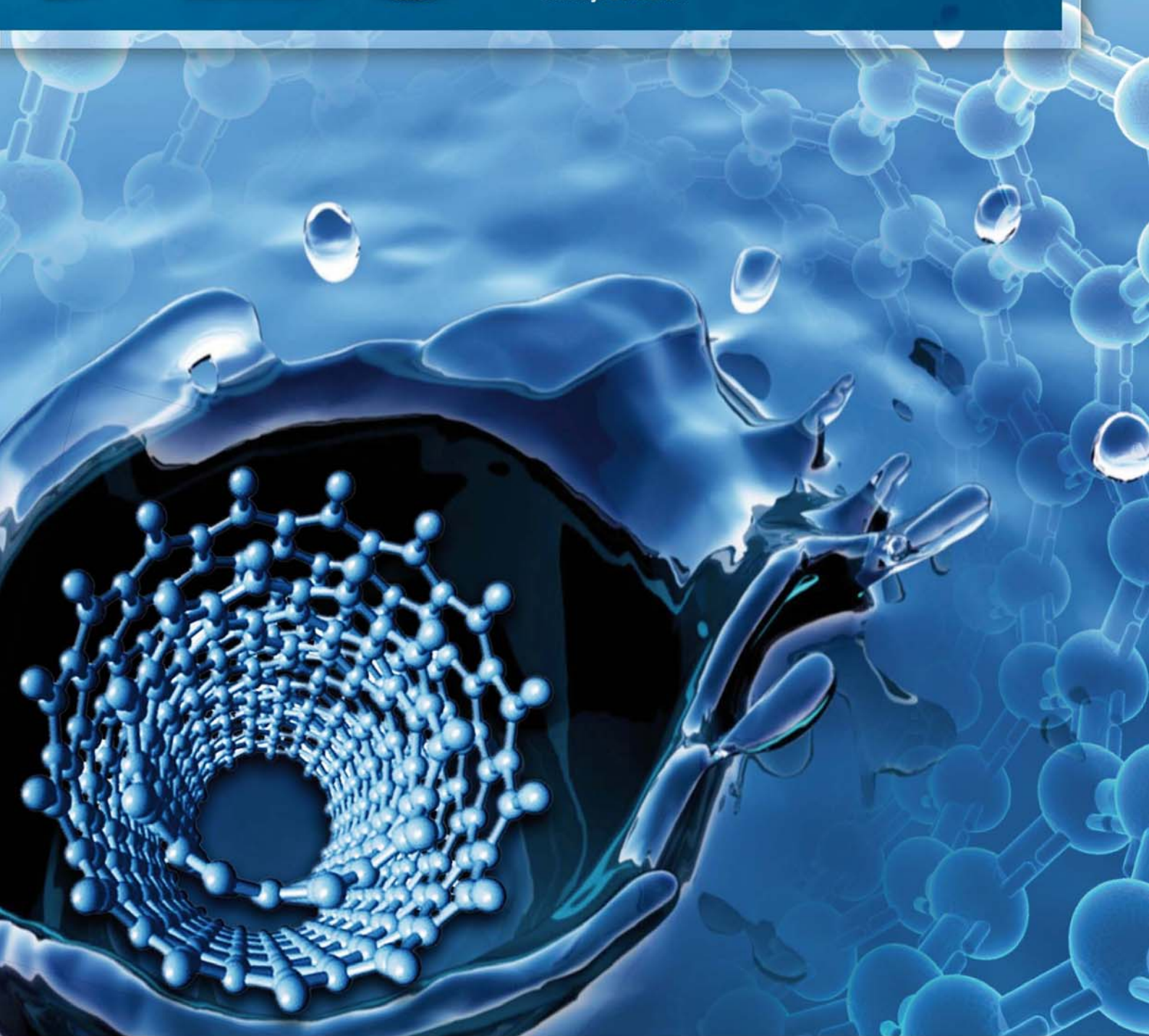


# JES

JOURNAL OF  
ENVIRONMENTAL  
SCIENCES

ISSN 1001-0742  
CN 11-2629/X

July 1, 2013 Volume 25 Number 7  
[www.jesc.ac.cn](http://www.jesc.ac.cn)



Sponsored by  
Research Center for Eco-Environmental Sciences  
Chinese Academy of Sciences

## CONTENTS

### Aquatic environment

- Application potential of carbon nanotubes in water treatment: A review  
Xitong Liu, Mengshu Wang, Shujuan Zhang, Bingcai Pan ..... 1263
- Characterization, treatment and releases of PBDEs and PAHs in a typical municipal sewage treatment plant situated beside an urban river, East China  
Xiaowei Wang, Beidou Xi, Shouliang Huo, Wenjun Sun, Hongwei Pan, Jingtian Zhang, Yuqing Ren, Hongliang Liu ..... 1281
- Factors influencing antibiotics adsorption onto engineered adsorbents  
Mingfang Xia, Aimin Li, Zhaolian Zhu, Qin Zhou, Weiben Yang ..... 1291
- Assessment of heavy metal enrichment and its human impact in lacustrine sediments from four lakes in the mid-low reaches of the Yangtze River, China  
Haijian Bing, Yanhong Wu, Enfeng Liu, Xiangdong Yang ..... 1300
- Biodegradation of 2-methylquinoline by *Enterobacter aerogenes* TJ-D isolated from activated sludge  
Lin Wang, Yongmei Li, Jingyuan Duan ..... 1310
- Inactivation, reactivation and regrowth of indigenous bacteria in reclaimed water after chlorine disinfection of a municipal wastewater treatment plant  
Dan Li, Siyu Zeng, April Z. Gu, Miao He, Hanchang Shi ..... 1319
- Photochemical degradation of nonylphenol in aqueous solution: The impact of pH and hydroxyl radical promoters  
Aleksandr Dulov, Niina Dulova, Marina Trapido ..... 1326
- A pilot-scale study of cryolite precipitation from high fluoride-containing wastewater in a reaction-separation integrated reactor  
Ke Jiang, Kanggen Zhou, Youcai Yang, Hu Du ..... 1331

### Atmospheric environment

- Effect of phosphogypsum and dicyandiamide as additives on NH<sub>3</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions during composting  
Yiming Luo, Guoxue Li, Wenhai Luo, Frank Schuchardt, Tao Jiang, Degang Xu ..... 1338
- Evaluation of heavy metal contamination hazards in nuisance dust particles, in Kurdistan Province, western Iran  
Reza Bashiri Khuzestani, Bubak Sourì ..... 1346

### Terrestrial environment

- Utilizing surfactants to control the sorption, desorption, and biodegradation of phenanthrene in soil-water system  
Haiwei Jin, Wenjun Zhou, Lizhong Zhu ..... 1355
- Detoxifying PCDD/Fs and heavy metals in fly ash from medical waste incinerators with a DC double arc plasma torch  
Xinchao Pan, Jianhua Yan, Zhengmiao Xie ..... 1362
- Role of sorbent surface functionalities and microporosity in 2,2',4,4'-tetrabromodiphenyl ether sorption onto biochars  
Jia Xin, Ruilong Liu, Hubo Fan, Meilan Wang, Miao Li, Xiang Liu ..... 1368

### Environmental biology

- Systematic analysis of microfauna indicator values for treatment performance in a full-scale municipal wastewater treatment plant  
Bo Hu, Rong Qi, Min Yang ..... 1379
- Function of *arsATorf7orf8* of *Bacillus* sp. CDB3 in arsenic resistance  
Wei Zheng, James Scifleet, Xuefei Yu, Tingbo Jiang, Ren Zhang ..... 1386
- Enrichment, isolation and identification of sulfur-oxidizing bacteria from sulfide removing bioreactor  
Jianfei Luo, Guoliang Tian, Weitie Lin ..... 1393

---

## Environmental health and toxicology

- In vitro* immunotoxicity of untreated and treated urban wastewaters using various treatment processes to rainbow trout leucocytes  
François Gagné, Marlène Fortier, Michel Fournier, Shirley-Anne Smyth ..... 1400
- Using lysosomal membrane stability of haemocytes in *Ruditapes philippinarum* as a biomarker of cellular stress  
to assess contamination by caffeine, ibuprofen, carbamazepine and novobiocin  
Gabriela V. Aguirre-Martínez, Sara Buratti, Elena Fabbri, Angel T. DelValls, M. Laura Martín-Díaz ..... 1408

## Environmental catalysis and materials

- Effect of transition metal doping under reducing calcination atmosphere on photocatalytic  
property of TiO<sub>2</sub> immobilized on SiO<sub>2</sub> beads  
Rumi Chand, Eiko Obuchi, Katsumi Katoh, Hom Nath Luitel, Katsuyuki Nakano ..... 1419
- A high activity of Ti/SnO<sub>2</sub>-Sb electrode in the electrochemical degradation of 2,4-dichlorophenol in aqueous solution  
Junfeng Niu, Dusmant Maharana, Jiale Xu, Zhen Chai, Yueping Bao ..... 1424
- Effects of rhamnolipid biosurfactant JBR425 and synthetic surfactant Surfynol465 on the  
peroxidase-catalyzed oxidation of 2-naphthol  
Ivanec-Goranina Rūta, Kulys Juozas ..... 1431

## The 8th International Conference on Sustainable Water Environment

- An novel identification method of the environmental risk sources for surface water pollution accidents in chemical industrial parks  
Jianfeng Peng, Yonghui Song, Peng Yuan, Shuhu Xiao, Lu Han ..... 1441
- Distribution and contamination status of chromium in surface sediments of northern Kaohsiung Harbor, Taiwan  
Cheng-Di Dong, Chiu-Wen Chen, Chih-Feng Chen ..... 1450
- Historical trends in the anthropogenic heavy metal levels in the tidal flat sediments of Lianyungang, China  
Rui Zhang, Fan Zhang, Yingjun Ding, Jinrong Gao, Jing Chen, Li Zhou ..... 1458
- Heterogeneous Fenton degradation of azo dyes catalyzed by modified polyacrylonitrile fiber Fe complexes:  
QSPR (quantitative structure property relationship) study  
Bing Li, Yongchun Dong, Zhizhong Ding ..... 1469
- Rehabilitation and improvement of Guilin urban water environment: Function-oriented management  
Yuansheng Pei, Hua Zuo, Zhaokun Luan, Sijia Gao ..... 1477
- Adsorption of Mn<sup>2+</sup> from aqueous solution using Fe and Mn oxide-coated sand  
Chi-Chuan Kan, Mannie C Aganon, Cybelle Morales Futalan, Maria Lourdes P Dalida ..... 1483
- Degradation kinetics and mechanism of trace nitrobenzene by granular activated carbon enhanced  
microwave/hydrogen peroxide system  
Dina Tan, Honghu Zeng, Jie Liu, Xiaozhang Yu, Yanpeng Liang, Lanjing Lu ..... 1492

Serial parameter: CN 11-2629/X\*1989\*m\*237\*en\*P\*28\*2013-7



## Degradation kinetics and mechanism of trace nitrobenzene by granular activated carbon enhanced microwave/hydrogen peroxide system

Dina Tan<sup>1,2</sup>, Honghu Zeng<sup>1,\*</sup>, Jie Liu<sup>1</sup>, Xiaozhang Yu<sup>1</sup>,  
Yanpeng Liang<sup>1</sup>, Lanjing Lu<sup>3</sup>

1. College of Environmental Science and Engineering Guilin University of Technology, Guilin 541004, China. E-mail: [dinah88@163.com](mailto:dinah88@163.com)

2. Guangxi Institute of Building Research & Design, Nanning 530011, China

3. Guangxi Polytechnic of Construction, Nanning 530003, China

Received 16 December 2012; revised 29 January 2013; accepted 01 June 2013

### Abstract

The kinetics of the degradation of trace nitrobenzene (NB) by a granular activated carbon (GAC) enhanced microwave (MW)/hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) system was studied. Effects of pH, NB initial concentration and tert-butyl alcohol on the removal efficiency were examined. It was found that the reaction rate fits well to first-order reaction kinetics in the MW/GAC/H<sub>2</sub>O<sub>2</sub> process. Moreover, GAC greatly enhanced the degradation rate of NB in water. Under a given condition (MW power 300 W, H<sub>2</sub>O<sub>2</sub> dosage 10 mg/L, pH 6.85 and temperature (60 ± 5)°C), the degradation rate of NB was 0.05214 min<sup>-1</sup> when 4 g/L GAC was added. In general, alkaline pH was better for NB degradation; however, the optimum pH was 8.0 in the tested pH value range of 4.0–12.0. At H<sub>2</sub>O<sub>2</sub> dosage of 10 mg/L and GAC dosage of 4 g/L, the removal of NB was decreased with increasing initial concentrations of NB, indicating that a low initial concentration was beneficial for the degradation of NB. These results indicated that the MW/GAC/H<sub>2</sub>O<sub>2</sub> process was effective for trace NB degradation in water. Gas chromatography-mass spectrometry analysis indicated that a hydroxyl radical addition reaction and dehydrogenation reaction enhanced NB degradation.

**Key words:** microwave; granular activated carbon; hydrogen peroxide; nitrobenzene; hydroxyl radicals

**DOI:** 10.1016/S1001-0742(12)60183-1

### Introduction

Nitrobenzene (NB) compounds are widely used as raw materials in the production of different industrial products such as pharmaceuticals, pesticides, dyes, etc. However, it also belongs to the category of highly toxic substances, being a priority pollutant (Hartter, 1985). Even at low concentrations, NB may present high risks to human health, because it is readily absorbed by contact with the skin and by inhalation of vapors (Bhatkhande et al., 2003). According to the Quality Standards for Drinking Water in China, the maximum allowable concentration of NB is 0.017 mg/L (GB5749-2006). To avoid NB pollution in water, development of techniques for NB degradation is essential.

Many conventional techniques, including physical, chemical and biological methods, have been applied for the degradation of NB in aqueous solution (Chen and Qiu, 2004). In the last decade, advanced oxidation processes

(AOPs), based on the generation of highly reactive and oxidizing hydroxyl radicals, have been shown to be effective for the destruction of refractory pollutants (ElShafei et al., 2010). These processes hold great promise to provide alternatives for NB degradation in water. According to the literature available, AOPs have included MW/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/AC, VUV/TiO<sub>2</sub>/O<sub>3</sub>, TiO<sub>2</sub>/O<sub>3</sub>, O<sub>3</sub>/UV, and Fenton processes (Zeng et al., 2012; Ma and Shi, 2002; Sui and Ma, 2001; Yin and Zhang 2009; Zhang et al., 2007; Tong et al., 2005; Jiang et al., 2011). However, the application of these methods for NB degradation has been restricted by economic consideration or stringent operating condition. For example, ozone is high in cost and difficult to operate, while TiO<sub>2</sub> is difficult to recover. Therefore, new processes for NB degradation should be developed.

In the recent years, microwave (MW) irradiation has been applied in many environmental remediation projects. A pollutant degradation process based on MW-irradiation has many advantages, such as reduced reaction time, increased selectivity of reaction, and lower activation energy (Bo et al., 2008). However, the energy of MW ( $E = 0.4$ –

\* Corresponding author. E-mail: [zenghonghu@glut.edu.cn](mailto:zenghonghu@glut.edu.cn)

40 kJ/mol at  $\nu = 1\text{--}100$  GHz) is insufficient to disrupt the chemical bonds of many organic compounds (Zhang et al., 2007). Therefore, MW has to be coupled with suitable MW absorbents such as granular activated carbon (GAC), zero-valent iron (ZVI) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to enhance the degradation efficiency. On the other hand, the energy utilization efficiency of MW-irradiation can be increased by the optimal addition of absorbents (Remya and Lin, 2011). Our previous study showed that a microwave-enhanced  $\text{H}_2\text{O}_2$ -based process was effective for the degradation of trace nitrobenzene (Zeng et al., 2012). However, this process consumes considerable  $\text{H}_2\text{O}_2$ . To reduce the consumption of  $\text{H}_2\text{O}_2$ , the MW/ $\text{H}_2\text{O}_2$  process should be improved.

Hydroxyl radicals ( $\cdot\text{OH}$ ) could be generated in aqueous solutions by MW radiation in the presence of activated carbon (Quan et al., 2007). In this system, activated carbon acted as a catalyst and could be used repeatedly; thereby it showed a great potential for removal of organic substances (Hirata et al., 2002; Kurniawan and Lo, 2009). Bo et al. (2006) reported that a MW-assisted oxidation process through a GAC fixed bed removed 90% of *p*-nitrophenol from aqueous solution, corresponding to 80% of TOC removal. In the presence of activated carbon powder, the degradation of *p*-nitrophenol and sodium dodecyl benzene sulfonate were accelerated under microwave irradiation (Zhang et al., 2007, 2009). GAC have been used in heterogeneous catalysis, due to the fact that they are able to act as a catalyst or as a catalyst support for specific applications (Oya et al., 1997). Combined use of GAC and  $\text{H}_2\text{O}_2$  enhanced the catalytic degradation rate of recalcitrant compounds and improved their biodegradability (Kurniawan and Lo, 2009). Therefore, it was hypothesized that GAC might be a good catalyst for NB degradation.

In the present study, GAC was used to improve the MW/ $\text{H}_2\text{O}_2$  system for NB degradation. The effects of pH and initial concentration of NB on NB degradation by the MW/GAC/ $\text{H}_2\text{O}_2$  process were explored and the degradation mechanism of this process was analyzed.

## 1 Materials and methods

### 1.1 Chemicals and reagents

Nitrobenzene ( $\text{C}_6\text{H}_5\text{NO}_2$ ) (> 99%, analysis purity) was obtained from Sinopharm Chemical Reagent Co., Ltd., China.  $\text{H}_2\text{O}_2$  (30%, analysis purity), methanol ( $\text{CH}_3\text{OH}$ ) (HPLC,  $\geq 99.9\%$ ), tert-butyl alcohol (analysis purity  $\geq 99.5\%$ ) and anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ , analysis purity) were purchased from Xilong Chemical Co., Ltd., China. Normal hexane ( $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ ) ( $\geq 95\%$ , HPLC) was obtained from Tanjin Guangfu Fine Chemical Research Institute, China. The GAC was granulated activated charcoal, pure grade, and supplied by Nanjing Jiali Carbon Plant, China. Sodium hydroxide (98%, analysis purity) and hydrochloric acid (analytical purity) were used for pH

adjustment.

### 1.2 Pretreatment of GAC

The GAC was immersed in 8%–10% (volume fraction) HCl for 18 hr, and rinsed with deionized water to remove oil and impurities until the pH of the washed water reached 5–6. Then the washed GAC was dried in an oven at  $105^\circ\text{C}$  for 18 hr to constant weight. Finally, the dried GAC was sieved with 20 mesh screen to obtain < 4 mm size granules (Bo et al., 2006).

### 1.3 Experimental methods

All experiments were carried out in a modified domestic MW oven (Fig. 1) at 150, 300, 450, 700, and 900 W power levels (Zeng et al., 2012). One liter of the reaction mixture (NB concentrations 200  $\mu\text{g/L}$  and  $\text{H}_2\text{O}_2$  dosage 10 mg/L) and treated GAC (4.0 g) were put into a three-neck quartz reactor. Then, the three-neck quartz reactor was installed in the modified microwave oven. The reaction temperature was controlled by a thermocouple and a cooler connected with the reactor. Every three minutes, samples were taken in a 50-mL colorimetric cylinder. The whole experiment was conducted in the dark to prevent the photolytic degradation of NB. Moreover, the collected samples at various time intervals were filtered immediately through a 0.45- $\mu\text{m}$  filter to remove suspended GAC particles. Then 3 mL extracting agent (*n*-hexane) was added (Sheng et al., 2007). The mixture was shaken in an oscillator for 15 min and left standing for 10 min. The supernatant fluid was used for the NB concentration determination. The loss of the system is about 20%, and the data from the experiment were corrected for this loss.

### 1.4 Analysis methods

The NB concentration was determined by a gas chromatograph (GC, Agilent Technologies 6890N, USA) equipped with a HP-5 column (30 m  $\times$  0.32 mm  $\times$  0.25  $\mu\text{m}$ ) and a FID detector. The carrier gas ( $\text{N}_2$ ) flow rate was 2.0 mL/min. A split-flow inlet was used and the split ratio was 1:1 with an injection volume of 1  $\mu\text{L}$ . The column temperature program was initially  $70^\circ\text{C}$  (hold 1min) and increased at the rate of  $30^\circ\text{C}/\text{min}$  to  $160^\circ\text{C}$  (hold 1 min).

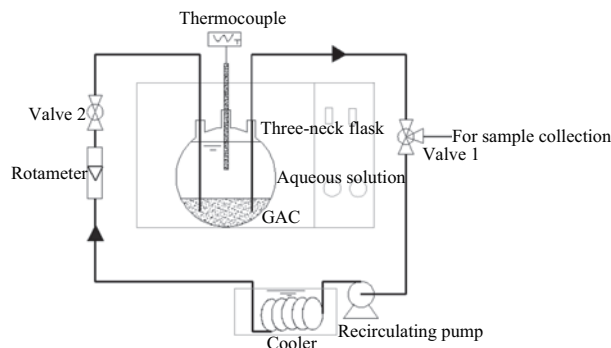


Fig. 1 Schematic diagram of the modified MW oven used in the experiments.

The injector and detector temperatures were 230°C and 280°C, respectively. Under these conditions, the retention time for NB was 3.906 min.

The intermediates were identified by GC-MS using an Agilent 6890 equipped with a 30 m length  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film, DB-5 MS column. The GC oven temperature was programmed from 70°C (1 min) to 160°C (1 min) at 25°C/min, and then raised to 250°C with a heating rate of 30°C/min. The detector and injector temperatures were 250°C and 200°C, respectively. Nitrogen was used as the carrier gas with a flow rate of 1.0 mL/min. The split-flow mode was used for injection, and the split ratio was 1:5. The MS was operated in electron ionization mode with a potential of 70 eV.

## 2 Results and discussion

### 2.1 Control experiments

The extent of NB removal/degradation in the presence of MW, GAC, and H<sub>2</sub>O<sub>2</sub> alone were quantified by conducting control experiments (Table 1). The NB concentration and the initial pH of the control experiments were kept constant at 200  $\mu$ g/L and 6.85, respectively. All the control experiments were conducted in the three-neck quartz reactor with 1 L of NB solution in quadruplicate at (60  $\pm$  5)°C, and the NB concentration was monitored for 21 min.

Poor NB degradation efficiencies were observed in the systems when MW, GAC and H<sub>2</sub>O<sub>2</sub> were used alone. Furthermore, elevation of the MW power or dosage of GAC and H<sub>2</sub>O<sub>2</sub> did not improve the NB removal effectively (Table 1). In the MW process, when MW power increased from 150 to 700 W, the removal of NB was only increased by 1.1%. As for GAC adsorption, and the maximum NB removal was 3.3% at GAC dosage of 8 g/L. The low adsorption of NB by GAC might attribute to the desorption (Sui and Ma, 2001). The NB removal in the H<sub>2</sub>O<sub>2</sub> process was investigated at different H<sub>2</sub>O<sub>2</sub> levels (5, 10, 15 and 20 mg/L). The removal of NB was very low, varying from 8%

to 18.3%. Furthermore, the removal of NB was decreased at H<sub>2</sub>O<sub>2</sub> dosage of 15 mg/L because the H<sub>2</sub>O<sub>2</sub> acted both as a hydroxyl radical initiator and inhibitors (Lu et al., 2011). The low efficiency of NB degradation when MW, GAC and H<sub>2</sub>O<sub>2</sub> were used separately implied that there were synergistic effects of MW, GAC and H<sub>2</sub>O<sub>2</sub> on degradation of NB.

### 2.2 Enhancement of MW/GAC/H<sub>2</sub>O<sub>2</sub> process for NB degradation

Figure 2 presents the degradation of NB under MW, GAC, H<sub>2</sub>O<sub>2</sub>, MW/GAC, GAC/H<sub>2</sub>O<sub>2</sub>, MW/H<sub>2</sub>O<sub>2</sub> and MW/GAC/H<sub>2</sub>O<sub>2</sub> processes. It indicates that the reaction rate data fits well to first-order reaction kinetics except for GAC adsorption and H<sub>2</sub>O<sub>2</sub> oxidation (fitting coefficient was -0.1175, 0.7881, respectively), represented by relatively high values of the goodness of fit (0.9459 > R<sup>2</sup> > 0.8644). As shown in Fig. 2, the best fit lines for lnC<sub>NB</sub> versus time have slopes that vary as a function of the degradation process, indicating that the maximum rate constant (*k*) for NB degradation was obtained for the MW/GAC/H<sub>2</sub>O<sub>2</sub> process. Therefore, the degradation rate of NB can be described by the following equation:

$$C_{NB} = C_{NB}^0 e^{kt} \quad (1)$$

The removal of NB (*E*, %) can be described by the following equation:

$$E = \frac{C_{NB}^0 - C_{NB}}{C_{NB}^0} \times 100\% \quad (2)$$

And

$$E = (1 - e^{kt}) \times 100\% \quad (3)$$

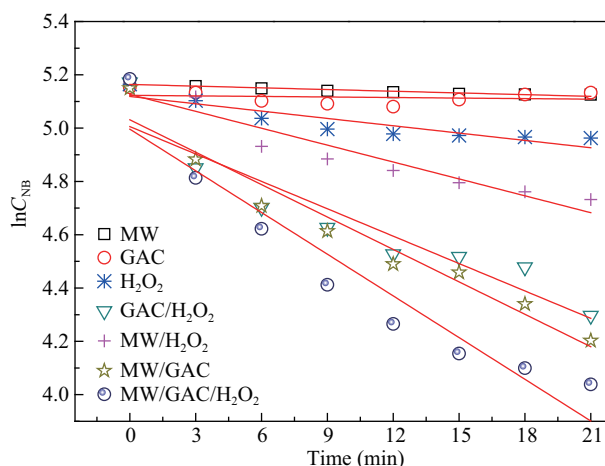
where, C<sub>NB</sub><sup>0</sup> is the initial NB concentration, C<sub>NB</sub> is the NB concentration at time *t*.

In the MW/GAC/H<sub>2</sub>O<sub>2</sub> process, the degradation rate of NB was 0.05214 min<sup>-1</sup>, which was significantly higher

**Table 1** Degradation of NB in MW, GAC and H<sub>2</sub>O<sub>2</sub> processes

Process	Dosage	NB initial concentration (μg/L)	Final NB concentration (μg/L)	NB removal (%)
MW	150 W	169.57	162.78	4.0
	300 W	170.98	163.46	4.4
	450 W	173.49	164.99	4.9
	700 W	169.55	160.90	5.1
GAC	2 g/L	179.25	176.92	1.3
	4 g/L	175.25	171.75	2.0
	6 g/L	171.23	166.95	2.5
	8 g/L	173.22	167.50	3.3
H <sub>2</sub> O <sub>2</sub>	5 mg/L	168.99	153.78	9.0
	10 mg/L	171.33	139.98	18.3
	15 mg/L	174.51	153.57	12.0
	20 mg/L	173.56	159.67	8.0

MW: microwave; GAC: granular activated carbon. Conditions: temperature (60  $\pm$  5)°C, pH = 6.85



**Fig. 2** Degradation kinetics of nitrobenzene by different processes. Conditions: initial NB = 200  $\mu$ g/L, pH = 6.85, temperature = (60  $\pm$  5)°C, MW = 300 W, GAC = 4 g/L, H<sub>2</sub>O<sub>2</sub> = 10 mg/L.

than those in the MW/H<sub>2</sub>O<sub>2</sub>, GAC/H<sub>2</sub>O<sub>2</sub> and MW/GAC processes. Compared with the MW/H<sub>2</sub>O<sub>2</sub> process (0.02112 min<sup>-1</sup>), the MW/GAC/H<sub>2</sub>O<sub>2</sub> process increased the degradation rate of NB by 0.03102 min<sup>-1</sup>. The GAC/H<sub>2</sub>O<sub>2</sub> system has exhibited high degradation rate of NB, however, the degradation rate constant (*k*) was 0.03425 min<sup>-1</sup>, which was only 0.66-fold as high as that in the MW/GAC/H<sub>2</sub>O<sub>2</sub> process. GAC is an excellent dielectric material to absorb and convert MW energy into thermal energy. The MW heat is effective in decomposing organic substances adsorbed on the carbon (Jou et al., 2010). Therefore, the high degradation rate of NB in the MW/GAC system (0.04054 min<sup>-1</sup>) without using H<sub>2</sub>O<sub>2</sub>, but the degradation rate of NB also decreased 0.01160 min<sup>-1</sup> compared with the MW/GAC/H<sub>2</sub>O<sub>2</sub> process. Moreover, the degradation rate of NB in the MW/GAC/H<sub>2</sub>O<sub>2</sub> process were larger than the sum of NB removal in GAC adsorption and the MW/H<sub>2</sub>O<sub>2</sub> process, which demonstrated that GAC not only acted as a adsorbent but also played a role in the degradation of NB.

The consumption of H<sub>2</sub>O<sub>2</sub> (CHP) per unit NB degradation showed that the CHP in the MW/GAC/H<sub>2</sub>O<sub>2</sub> process was much less in the MW/H<sub>2</sub>O<sub>2</sub> process (Fig. 3a). As shown in Fig. 3b, the GAC supply increased the degradation rate of NB greatly, indicating that GAC accelerated NB degradation and reduced the reaction time. The enhancement of NB degradation by GAC might be

ascribed to the fact that GAC enhanced the generation of HO· radicals which could increase the activity of NB molecules (Sánchez-Polo et al., 2006). In a previous study, a MW/H<sub>2</sub>O<sub>2</sub> process consumed 20 mg/L H<sub>2</sub>O<sub>2</sub> to achieve about 90% removal of NB (Zeng et al., 2012), but they did not take into account the system losses. The result indicated that the presence of GAC could reduce the consumption of H<sub>2</sub>O<sub>2</sub>. Because GAC can be easily recovered and reused, the MW/GAC/H<sub>2</sub>O<sub>2</sub> process could reduce the cost of NB removal.

Scanning electron microscopy (SEM) showed changes in the surface structure of GAC at different stages during the microwave treatment for NB degradation (Fig. 4). The process of pretreatment caused the GAC surface to graphitize, thus destroying the surface micropores and leading to a smoother surface and less micropore volume. It can be seen in Fig. 4a that the GAC particles showed obvious porosity and more slag scrap before they were pretreated. After pretreatment, the graphitization of the GAC surface and the destruction of surface pores are evidenced by the smoother surface as shown in Fig. 4b. After use of GAC, little collapses of local carbon pores during the thermal regeneration process are shown in Fig. 4c. This also shows that the GAC plays a large role in the reaction.

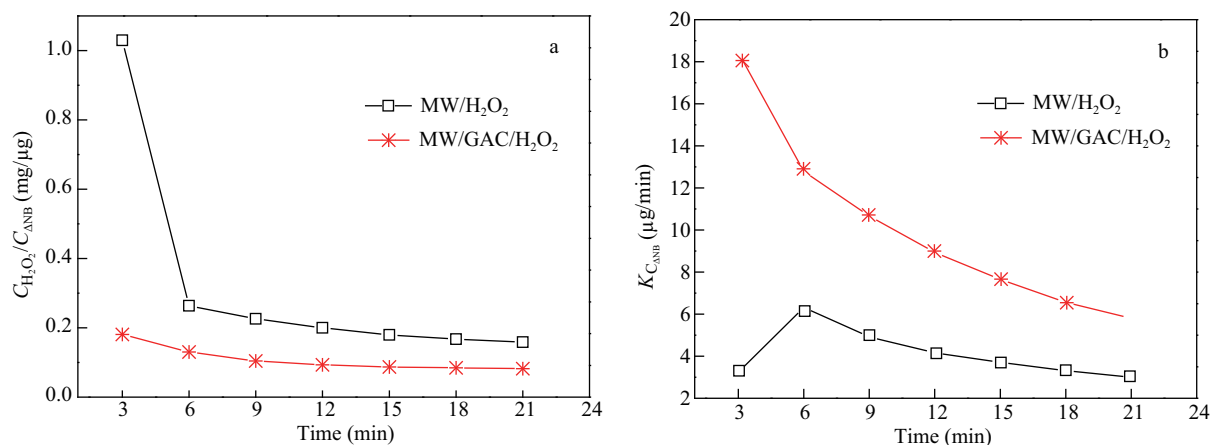


Fig. 3 Amount of H<sub>2</sub>O<sub>2</sub> consumption per unit NB degradation (a), and the degradation rate coefficient of NB as a function of time (b). Condition: initial NB = 200 μg/L, pH = 6.85, temperature = (60 ± 5)°C, MW = 300 W, GAC = 4 g/L, H<sub>2</sub>O<sub>2</sub> = 10 mg/L.

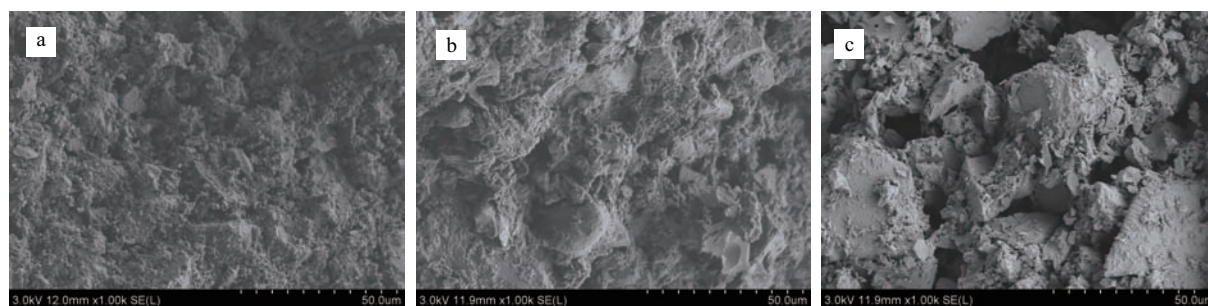


Fig. 4 SEM images of surface structure for GAC at different stages during the microwave treatment for NB degradation. (a) original GAC; (b) after pretreatment; (c) after used.

### 2.3 Effect of pH on degradation of NB

The participation of  $H^+$  in the overall reaction suggests that pH may influence the rate of nitrobenzene reduction. The results showed that pH has a significant effect on the kinetics of NB reduction (Fig. 5a).

The rate in basic and neutral solutions was faster than in acidic solution. The correlation coefficients ( $R^2$ ) of the fitting curves were 0.7762, 0.8454, 0.9077, 0.8838, 0.9013 and 0.9357 at pH 4, 6, 7, 8, 10, 12, respectively. It was noticed that the degradation rate of NB degradation were maximized ( $0.0566 \text{ min}^{-1}$ ) at pH 8 and minimized ( $0.0328 \text{ min}^{-1}$ ) at pH 4.

The effect of pH on the observed rate constant for NB reduction is depicted in Fig. 5b. The results indicated that the observed reduction rate,  $V_p$ , increased initially, then decreased after a certain pH. The average reduction rate was 4.39, 4.84, 5.50, 5.59, 5.47 and  $5.05 \text{ } \mu\text{g}/\text{min}$  for pH 4, 6, 7, 8, 10, 12, respectively.  $V_p$  can be calculated by Eq. (4):

$$V_p = \frac{C_{\text{NB}}^0 - C_{\text{NB}}}{2t} \quad (4)$$

The increase in pH from 4 to 8 increased the NB degradation rate in the MW-assisted GAC and  $H_2O_2$  systems, whereas the increase in pH from 8 to 12 decreased the NB degradation rate. Furthermore, the degradation of NB was greater in alkaline conditions than in acidic conditions. This suggested that alkaline conditions are favorable for  $H_2O_2$  dissociation into hydroxyl ion and hydroxyl radical by accepting electrons from the GAC. This radical decomposes additional hydrogen peroxide to water and peroxide radical. The dissociation of peroxide radical can be written as follows (Bach and Semiat, 2011):



The superoxide ions can decompose another hydrogen peroxide as follows:

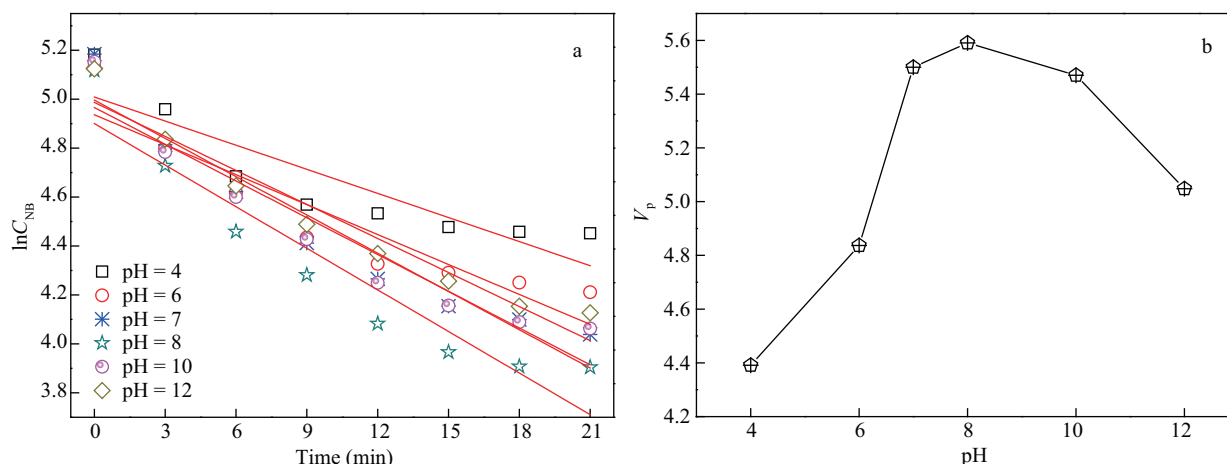
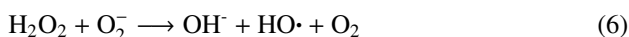


Fig. 5 Effect of pH on the kinetics (a) and the rate constant (b) of NB reduction. Conditions: initial NB =  $200 \text{ } \mu\text{g}/\text{L}$ , temperature =  $(60 \pm 5)^\circ\text{C}$ , MW = 300 W, GAC =  $4 \text{ g}/\text{L}$ ,  $H_2O_2 = 10 \text{ mg}/\text{L}$ .

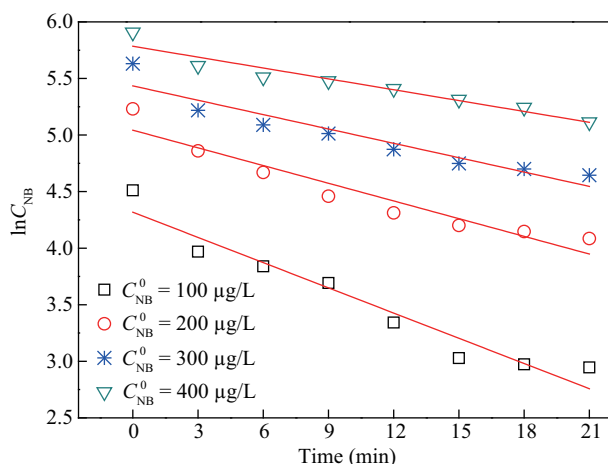
On the other hand, the increase of reaction rate in alkaline medium is probably due to the high reactivity of the anion  $\text{OOH}^-$  (from the  $H_2O_2$ ) with  $\text{HO}\cdot$  radicals as well as the transformation of this radical in its conjugated base  $\text{O}^-$  (Rivas et al., 1998). However, excessive  $\text{OH}^-$  inhibited the decomposition of hydroxyl radicals. The reason for this was still unclear. In this experiment, the optimum pH was 8. Interestingly, the NB degradation rate was  $> 0.03 \text{ } \mu\text{g}/\text{min}$  in the MW-assisted GAC and  $H_2O_2$  system under all the pH levels investigated. The oxidation properties of  $H_2O_2$  and hydroxyl radicals depend on the pH of the solution, and as a results of this fact, alkaline conditions (especially pH 8) should be applied for oxidative treatment of NB with the MW/GAC/ $H_2O_2$  process.

### 2.4 Effect of NB initial concentration on degradation of NB

It was anticipated that the NB initial concentration would also strongly influence the kinetics of NB reduction. In this study, remarkable differences in NB reduction for the four different NB initial concentration systems were observed (Fig. 6). The NB concentration varied from 100 to  $400 \text{ } \mu\text{g}/\text{L}$  while the other variables were kept constant. Clearly, the plots of  $\ln C_{\text{NB}}$  versus time were linear ( $0.89 < R^2 < 0.93$ ) under various initial NB concentrations, suggesting a first-order reaction with respect to NB. The rate of NB reduction decreased as the initial NB concentration increased. The rate constant ( $k$ ) of NB was 0.07429, 0.05214, 0.0423 and  $0.03201 \text{ min}^{-1}$  for NB initial concentration 100, 200, 300, and  $400 \text{ } \mu\text{g}/\text{L}$ , respectively. The degradation rate of NB decreased with the increase of the initial concentration. It was obvious that a low initial concentration was beneficial for the degradation of NB.

As is well known, high NB concentration inhibits the catalytic activity of GAC; consequently the amount of NB degraded by the MW/GAC/ $H_2O_2$  system is limited within a given irradiation time. In addition, in concentrated solutions, too many NB molecules may disturb the absorption





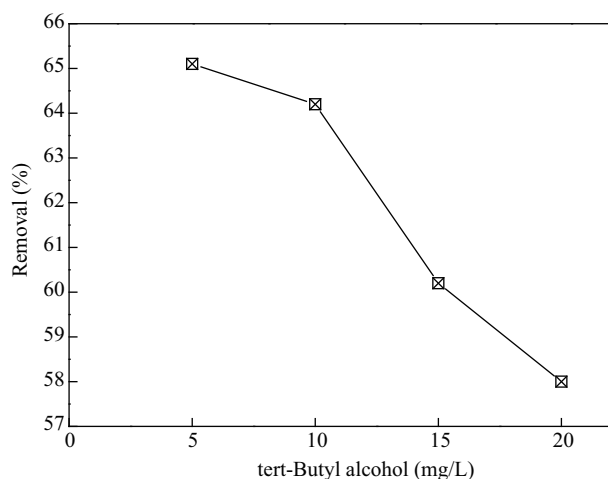
**Fig. 6** Effect of NB initial concentration on nitrobenzene reduction. Conditions: pH = 6.85, temperature =  $(60 \pm 5)^\circ\text{C}$ , MW = 300 W, GAC = 4 g/L,  $\text{H}_2\text{O}_2 = 10 \text{ mg/L}$ .

of microwave energy, which can also reduce the catalytic activity of GAC (Zhang et al., 2009).

### 2.5 Degradation mechanism analysis

The mechanism of MW-assisted NB degradation with GAC and  $\text{H}_2\text{O}_2$  was explored. *tert*-Butyl alcohol, as an inhibitor of  $\text{HO}\cdot$ , is able to consume large amounts of  $\text{HO}\cdot$  (Ma and Shi, 2002). **Figure 7** shows the effect of *tert*-butyl alcohol on MW/GAC/ $\text{H}_2\text{O}_2$  process degradation of NB for different *tert*-Butyl alcohol concentrations. The results indicated that an increase in the *tert*-Butyl alcohol concentration decreased the NB degradation efficiency in the MW-assisted GAC and  $\text{H}_2\text{O}_2$  systems. Therefore, hydroxyl radicals participated in the degradation of NB, which indicates an advanced oxidation reaction.

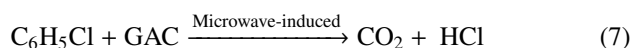
To explore the mechanism of NB degradation, the intermediates formed during the degradation by MW/GAC/ $\text{H}_2\text{O}_2$  system were identified using GC-MS. **Figure 8** demonstrates typical chromatograms of the in-



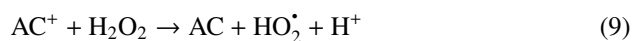
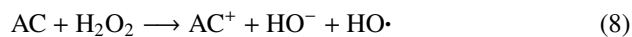
**Fig. 7** Effect of *tert*-butyl alcohol on degradation of NB. Conditions: initial NB = 200  $\mu\text{g/L}$ , pH = 6.85, temperature =  $(60 \pm 5)^\circ\text{C}$ , MW = 300 W, GAC = 4 g/L,  $\text{H}_2\text{O}_2 = 10 \text{ mg/L}$ .

termediates for the NB solutions collected after 21 min. The GC-MS analysis and the NIST library search showed that the main products were nitrophenolic compounds with benzene ring and ring opening carboxylic acid substances (**Table 2**). These intermediates might be caused by  $\text{HO}\cdot$  radicals addition reaction and dehydrogenation reaction with NB.

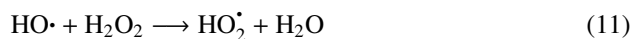
The routes of AOPs were analyzed in a number of experiments. Jou et al. (2010) reported that chlorobenzene contaminant on GAC heated by MW energy could be cracked. The reaction could be expressed as follows:



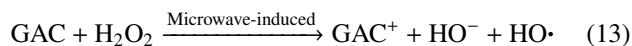
The activated carbon can act as an electron-transfer catalyst with a mechanism just like the Haber-Weiss reaction involving the reduction and oxidization of the catalyst (Reactions (8) and (9)) (Kurniawan and Lo, 2009):



The mechanism of MW decomposition of hydrogen peroxide was similar to the mechanism of UV decomposition of hydrogen peroxide. The following routes could take place in the reaction process (Ju et al., 2009).



It is envisaged that the mechanism of MW decomposition of hydrogen peroxide in the presence of the GAC catalyst was similar to the mechanism of mentioned above:



The generation rates of  $\text{HO}\cdot$  increase with the MW-assisted nitrobenzene degradation with both GAC and  $\text{H}_2\text{O}_2$ . In addition, the activated carbon with the most

**Table 2** Identified products and main fragments determined by GC-MS

Compound	Retention time (min)	Chemical formula	Matching (%)
1,2-Ethandiol,	3.78	$\text{C}_{14}\text{H}_{14}\text{O}_2$	20.5
1,2-diphenyl-( $R^*$ , $R^*$ )			
nitro-Benzene	3.95	$\text{C}_6\text{H}_5$	90
2-Hydroxy-1,1,10-trimethyl-6,9-epidioxydecalin	13.99	$\text{C}_{13}\text{H}_{22}\text{O}_3$	39.2
2-Methyl-Z-4-tetradecene	14.74	$\text{C}_{15}\text{H}_{30}$	13.3
Dodecane, 2,6,10-trimethyl-	15.55	$\text{C}_{15}\text{H}_{32}$	17.8
Phenol,2,2'-menthylenebis	16.59	$\text{C}_{23}\text{H}_{23}\text{O}_2$	94
6-(1,1-dimethylethyl)-4-methyl-			

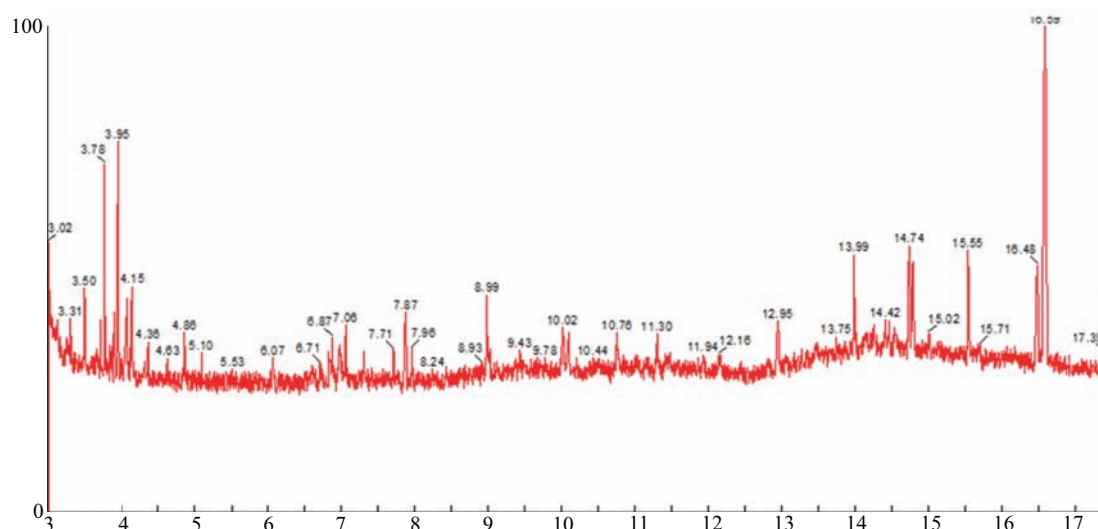


Fig. 8 GC-MS typical chromatograms of intermediates for the NB solutions collected after 21 min of MW/GAC/H<sub>2</sub>O<sub>2</sub> system degradation

disorganized structure and a highly microporous texture showed the highest catalytic activity for hydrogen peroxide decomposition (Rey et al., 2011), which made this process superior.

### 3 Conclusions

Reduction of NB was carried out with a MW/GAC/H<sub>2</sub>O<sub>2</sub> system using GAC as a catalyst. The advantage of using GAC is that it is an important enhancer of the generation of HO· radicals. The high reduction of NB concentrations by the MW/GAC/H<sub>2</sub>O<sub>2</sub> process might be due to the catalysis of MW decomposition of H<sub>2</sub>O<sub>2</sub> by GAC, and the generation of HO· radical. The degradation rate of NB was maximized at pH 8 (0.0566 min<sup>-1</sup>) and minimized at pH 4 (0.0328 min<sup>-1</sup>) in the MW/GAC/H<sub>2</sub>O<sub>2</sub> process. The increase of the initial concentration of NB decreased the degradation rate of NB. The main products were nitrophenolic compounds with a benzene ring and ring-opening carboxylic acid substances. MW-assisted trace NB degradation in the presence of GAC and H<sub>2</sub>O<sub>2</sub> was feasible. This process provides a promising way for NB degradation in a short time with reduced energy consumption.

### Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51268008, 21207024), the Key Project of Chinese Ministry of Education (No. 210170, JiaoJiSi [2010]114), the Program for Excellent Talents in the Guangxi Higher Education Institutions (No. GuiJiaoRen [2010]65) and the Guangxi Scientific Research and Technological Development Plan (No. GuiKeZhuan 1298009-17).

### References

- Bach A, Semiat R, 2011. The role of activated carbon as a catalyst in GAC/iron oxide/H<sub>2</sub>O<sub>2</sub> oxidation process. *Desalination*, 273(1): 57-63.
- Bhatkhande D S, Pangarkar V G, Beenackers A A C M, 2003. Photocatalytic degradation of nitrobenzene using titanium dioxide and concentrated solar radiation: chemical effects and scaleup. *Water Research*, 37(6): 1223-1230.
- Bo L L, Quan X, Chen S, Zhao H M, Zhao Y Z, 2006. Degradation of *p*-nitrophenol in aqueous solution by microwave assisted oxidation process through a granular activated carbon fixed bed. *Water Research*, 40(16): 3061-3068.
- Bo L L, Quan X, Wang X C, Chen S, 2008. Preparation and characteristics of carbon-supported platinum catalyst and its application in the removal of phenolic pollutants in aqueous solution by microwave-assisted catalytic oxidation. *Journal of Hazardous Materials*, 157(1): 179-186.
- Chen P, Qiu J, 2004. Study progress on nitrobenzene waste water treatment. *Guizhou Chemical Industry*, 29(2): 30-34.
- ElShafei G M S, Yehia F Z, Dimitry O I H, Badawi A M, Eshaq G, 2010. Degradation of nitrobenzene at near neutral pH using Fe<sup>2+</sup>-glutamate complex as a homogeneous Fenton catalyst. *Applied Catalysis B: Environmental*, 99(1-2): 242-247.
- Hartert D R, 1985. The use and importance of nitroaromatic chemicals in the chemical industry. In: Toxicity of Nitroaromatic Compounds (Rickert D E, ed.). Hemisphere Publishing, Washington. 1-13.
- Hirata M, Kawasaki N, Nakamura T, Matsumoto K, Kabayama M, Tamura T et al., 2002. Adsorption of dyes onto carbonaceous materials produced from coffee grounds by microwave treatment. *Journal of Colloid and Interface Science*, 254(1): 17-22.
- Jiang B C, Lu Z Y, Liu F Q, Li A M, Dai J J, Xu L et al., 2011. Inhibiting 1,3-dinitrobenzene formation in Fenton oxidation of nitrobenzene through a controllable reductive pretreatment with zero-valent iron. *Chemical Engineering Journal*, 174(1): 258-265.

- Jou C J G, Wu C R, Lee C L, 2010. Application of microwave energy to treat granular activated carbon contaminated with chlorobenzene. *Environmental Progress and Sustainable Energy*, 29(3): 272–277.
- Ju Y M, Yang S G, Ding Y C, Sun C, Gu C G, He Z et al., 2009. Microwave-enhanced  $H_2O_2$ -based process for treating aqueous malachite green solutions: Intermediates and degradation mechanism. *Journal of Hazardous Materials*, 171(1-3): 123–132.
- Kurniawan T A, Lo W H, 2009. Removal of refractory compounds from stabilized landfill leachate using an integrated  $H_2O_2$  oxidation and granular activated carbon (GAC) adsorption treatment. *Water Research*, 43(16): 4079–4091.
- Lu L J, Zeng H H, Wang B L, Tang Y F, Qiao F M, 2011. Degradation of trace nitrobenzene in water by microwave-enhanced  $H_2O_2$ -based process. *Technology of Water Treatment*, 37(8): 104–108.
- Ma J, Shi F H, 2002. Study on removal of nitrobenzene in water by  $O_3/H_2O_2$ . *Environmental Science*, 23(5): 67–71.
- Oya A, Marsh H, Heintz E, Rodriguez-Reinoso F, 1997. Introduction to Carbon Technologies. Alicante: Universidad de Alicante, Secretariado de Publicaciones, 561.
- Quan X, Zhang Y B, Chen S, Zhao Y Z, Yang F J, 2007. Generation of hydroxyl radical in aqueous solution by microwave energy using activated carbon as catalyst and its potential in removal of persistent organic substances. *Journal of Molecular Catalysis A: Chemical*, 263(1-2): 216–222.
- Remya N, Lin J G, 2011. Microwave-assisted carbofuran degradation in the presence of GAC, ZVI and  $H_2O_2$ : Influence of reaction temperature and pH. *Separation and Purification Technology*, 76(3): 244–252.
- Reya A, Zazob J A, Casasb J A, Bahamondea A, Rodriguezb J J, 2011. Influence of the structural and surface characteristics of activated carbon on the catalytic decomposition of hydrogen peroxide. *Applied Catalysis A: General*, 402(1-2): 146–155.
- Rivas F J, Kolaczowski S T, Beltrán F J, McLurg D B, 1998. Development of a model for the wet air oxidation of phenol based on a free radical mechanism. *Chemical Engineering Science*, 53(14): 2575–2586.
- Sánchez-Polo M, Salhi E, Rivera-Utrilla J, von Gunten U, 2006. Combination of ozone with activated carbon as an alternative to conventional advanced oxidation processes. *Ozone: Science and Engineering*, 28(4): 237–245.
- Sheng J, Xie L, Zhai G M, Zhang C J, Zhou Q, 2007. Liquid-liquid extraction/GC determination of nitrobenzene and its degradation products and study on its affecting factors. *Water Purification Technology*, 26(3): 69–73.
- Sui M H, Ma J, 2001. Degradation of nitrobenzene by  $O_3/AC$ . *China Water and Wastewater*, 17(10): 70–73.
- Tong S P, Zhu Y Q, Ma C A, Liu W P, 2005. The degradation of acetic acid and nitrobenzene in water by  $O_3/UV$ . *China Environmental Science*, 25(3): 366–369.
- Yin J J, Zhang P Y, 2009. Removal of trace nitrobenzene in water by VUV/TiO<sub>2</sub>/O<sub>3</sub>. *Environmental Science*, 30(1): 134–139.
- Zeng H H, Lu L J, Liang M N, Liu J, Li Y H, 2012. Degradation of trace nitrobenzene in water by microwave-enhanced  $H_2O_2$ -based process. *Frontiers of Environmental Science and Engineering*, 6(4): 477–483.
- Zhang J, Ma J, Yang Y X, Wang S J, Qin Q T, 2007. Degradation of trace nitrobenzene in aqueous solution by ozone with catalysis of nanosized TiO<sub>2</sub> supported on haydite. *Environmental Science*, 28(10): 2208–2212.
- Zhang L, Guo X J, Yan F, Su M M, Li Y, 2007. Study of the degradation behaviour of dimethoate under microwave irradiation. *Journal of Hazardous Materials*, 149(3): 675–679.
- Zhang Z H, Deng Y Q, Shen M L, Han W M, Chen Z L, Xu D P et al., 2009. Investigation on rapid degradation of sodium dodecyl benzene sulfonate (SDBS) under microwave irradiation in the presence of modified activated carbon powder with ferrous sulfate. *Desalination*, 249(3): 1022–1029.

# JOURNAL OF ENVIRONMENTAL SCIENCES

环境科学学报(英文版)  
(<http://www.jesc.ac.cn>)

## Aims and scope

*Journal of Environmental Sciences* is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

## For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via <http://www.elsevier.com/locate/jes>.

## For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: [journal@mail.sciencep.com](mailto:journal@mail.sciencep.com), or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

## Submission declaration

Submission of an article implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The submission should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

## Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The publication should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

## Editorial

Authors should submit manuscript online at <http://www.jesc.ac.cn>. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: [jesc@263.net](mailto:jesc@263.net), [jesc@rcees.ac.cn](mailto:jesc@rcees.ac.cn). Instruction to authors is available at <http://www.jesc.ac.cn>.

## Journal of Environmental Sciences (Established in 1989)

Vol. 25 No. 7 2013

<b>Supervised by</b>	Chinese Academy of Sciences	<b>Published by</b>	Science Press, Beijing, China
<b>Sponsored by</b>	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences	<b>Distributed by</b>	Elsevier Limited, The Netherlands
<b>Edited by</b>	Editorial Office of Journal of Environmental Sciences P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; <a href="http://www.jesc.ac.cn">http://www.jesc.ac.cn</a> E-mail: <a href="mailto:jesc@263.net">jesc@263.net</a> , <a href="mailto:jesc@rcees.ac.cn">jesc@rcees.ac.cn</a>	<b>Domestic</b>	Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China
<b>Editor-in-chief</b>	Hongxiao Tang	<b>Foreign</b>	Elsevier Limited <a href="http://www.elsevier.com/locate/jes">http://www.elsevier.com/locate/jes</a>
<b>CN 11-2629/X</b>	<b>Domestic postcode: 2-580</b>	<b>Printed by</b>	Beijing Beilin Printing House, 100083, China
		<b>Domestic price per issue</b>	<b>RMB ¥ 110.00</b>

ISSN 1001-0742

