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The degradation and mineralization of 4-chlorophenol in aqueous solutions by electron beam irradiation in the presence of TiO_2 nanoparticles

Ruiyuan Yang[a], Min Wang[a,*], Zhongqun Shen[a], Wenfeng Wang[a], Hongjuan Ma[a], Jianzhong Gu[b]

[a]*Shanghai Institute of Applied Physics, Chinese Academy of Sciences, P.O. Box 800-204, Shanghai 201800, PR China*
[b]*Applied Radiation Institute, Shanghai University, Shanghai 201800, PR China*

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Abstract

In this study, the effect of TiO_2 nanoparticles on radiation-induced degradation and mineralization of 4-chlorophenol in aqueous solutions was investigated. Solutions of 4-chlorophenol with different contents of TiO_2 nanoparticles were irradiated by electron beam with absorbed doses up to 35.2 kGy. The changes of absorption spectra, pH, total organic carbon (TOC), 4-chlorophenol and Cl^- concentrations were examined.

The absorbencies of characteristic peaks of 4-chlorophenol decreased distinctly with increasing TiO_2 nanoparticle contents at the same absorbed dose. Although the addition of TiO_2 nanoparticles changed the initial pH, pH values of the solutions with different contents of TiO_2 nanoparticles were almost equal and diminished smoothly with increasing absorbed dose after 3 kGy absorbed dose of irradiation. The TiO_2 nanoparticles had little influence on the degradation of 4-chlorophenol but dramatically promoted the mineralization of 4-chlorophenol. It is suggested that TiO_2 nanoparticles affect the intermediate degradation products during the decomposition of 4-chlorophenol.

Keywords: Electron beam irradiation; 4-chlorophenol; TiO_2; Degradation and mineralization

1. Introduction

Organic contaminants present in industrial wastewater are of major concern with respect to the health of the general public. The chlorophenols are important xenobiotic pollutants of the aquatic environment, originating from different branches of the chemical industry. Several ways have been studied for the removal of chlorophenol compounds under different conditions.

Radiolytic techniques have been found to be convenient in elucidating radical reaction mechanisms. Free radicals are formed when water is irradiated with ionizing radiation, such as γ-rays or a high-energy electron beam (Pikaev and Skubin, 1984; Lawless et al., 1991; Terzian et al., 1991). The majority of these radicals are hydroxyl radicals (•OH) and hydrated electrons (e^-_{aq}), although smaller quantities of other radicals such as •H are also formed. In recent years, much attention has been paid to photocatalysis as an alternative technique, where the pollutants are degraded by UV irradiation of a semiconductor suspension such as titanium dioxide or zinc oxide based on the formation of pairs of electron/positive holes (e^-/$h+$), when the photocatalyst is subjected to UV light. Positive holes oxidize adsorbed organic substrates or react with water leading to the formation of hydroxyl radicals, which are very efficient oxidizing agents (Al-Sayyed et al., 1991; Augugliaro et al., 1991).

In this paper, the effect of TiO_2 nanoparticles on the degradation and mineralization of 4-chlorophenol in aqueous solution were studied using electron beam irradiation. Solutions of 4-chlorophenol with different

*Corresponding author. Tel.: +862159554934; fax: +862159555351.
E-mail address: wangmin@sinap.ac.cn (M. Wang).

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contents of TiO_2 nanoparticles were irradiated by electron beam with absorbed doses up to 35.2 kGy. The changes of absorption spectra, 4-chlorophenol and Cl^- concentrations, total organic carbon (TOC) and pH value were examined.

2. Experimental

2.1. Materials

$Ce(SO_4)_2$, $Ce_2(SO_4)_3$, H_2SO_4, 4-chlorophenol, dichloromethane, hydrochloric acid, methanol, sodium sulfate and 2,5-dibromotoluene are AR grade and used without further purification. TiO_2 nanoparticles were supplied by Degussa (P25, anatase, surface area $50\,m^2\,g^{-1}$, mean diameter approximately 30 nm). Triple distilled water was used in the determination of absorbed doses and deionized water was used in the preparation of 4-chlorophenol solutions.

2.2. Facility and methods

The high-voltage type electron accelerator in Radiation Application Insitute of Shanghai University was used as electron beam irradiation facility. The energy and beam current of electron beams were 1.5 MeV and 1 mA, respectively, during the experiment. The calibration of absorbed doses was the same as described elsewhere (Wang et al., 2006). The concentrations of 4-chlorophenol were determined by gas chromatography (Shimadzu GC2010). TOC values were measured by a TOC analyzer (Shimadzu TOC 5000). The absorption spectra and absorbance were analyzed by a UV–vis spectrophotometer. The pH values of the solutions were measured with a PHSJ-4A model pH meter. The concentrations of chloride ions formed during irradiation were determined by ion selective electrode.

2.3. Experimental procedures

Deionized water was used to prepare the 4-chlorophenol solution with a concentration of $1\,mmol\,L^{-1}$. The contents of TiO_2 nanoparticles in the 4-chlorophenol solutions were 0, 0.5, 1.0, 2.5 and $5.0\,g\,L^{-1}$. In all, 30 ml of the solution was irradiated with different irradiation times of 10, 20, 40, 70, 120 and 200 s. After irradiation, 4-chlorophenol solutions were filtered by a 0.25 μm Millipore membrane filter prior to analyses.

3. Results and discussion

3.1. Changes of absorption spectra

The absorption spectra of $1\,mmol\,L^{-1}$ 4-chlorophenol solutions with different TiO_2 contents at the absorbed dose of 12.3 kGy are shown in Fig. 1, 4-chlorophenol has a strong absorption band in ultraviolet area with the wavelength of 198, 225 and 280 nm. The characteristic peak value of 4-chlorophenol decreased markedly with

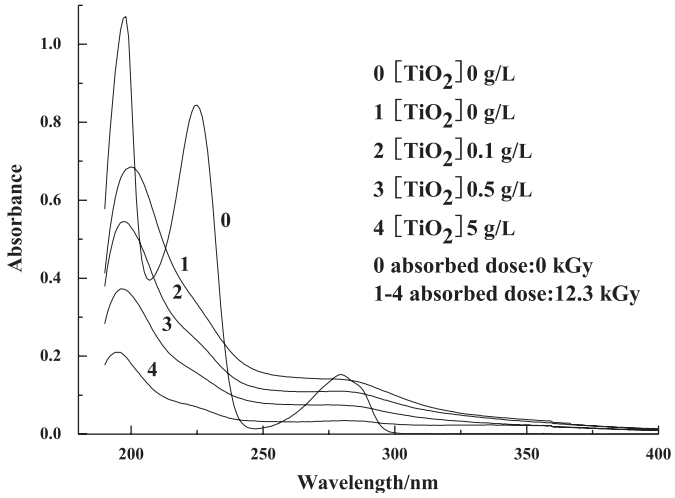


Fig. 1. Absorption spectra of $1\,mmol\,L^{-1}$ 4-chlorophenol aqueous solutions with different TiO_2 contents by 12.3 kGy electron beam irradiation (curve 0 before irradiation). $[TiO_2](g\,L^{-1})$: 0 (curves 0 and 1), 0.1 (curve 2), 0.5 (curve 3) and 5 (curve 4).

increasing TiO_2 contents from 0 to $0.5\,g\,L^{-1}$. After 12.3 kGy electron beam irradiation, the absorbance at 198 nm of 4-chlorophenol aqueous solution with $0.5\,g\,L^{-1}$ TiO_2 nanoparticles decreased 65% compared with the solution without TiO_2 nanoparticles. The experimental results indicated that TiO_2 had a positive influence on the degradation of 4-chlorophenol. The absorption peak of 280 nm diminished and finally disappeared with increasing TiO_2 contents from 0 to $5\,g\,L^{-1}$. This is in marked contrast to the degradation of 4-chlorophenol without TiO_2 under γ irradiation, in which the absorption peak of 280 nm increased slowly with increasing absorbed dose from 0 to 7.5 kGy and then decreased appreciably at 14.9 kGy absorbed dose.

3.2. Degradation and mineralization of 4-chlorophenol solutions

The concentrations and TOC values of 4-chlorophenol solutions with different TiO_2 contents under electron beam irradiation are shown in Figs. 2 and 3. The initial concentration and TOC of 4-chlorophenol solutions decreased with increasing TiO_2 contents, which implied that there was a little absorption of 4-chlorophenol on TiO_2 nanoparticles. No new peak appeared in the GC chromatographic analysis in the 4-chlorophenol aqueous solution containing TiO_2 before irradiation, which indicated that no degradation occurred without irradiation. Table 1 lists the change of chloride ion concentration in 4-chlorophenol solutions with different TiO_2 contents under electron beam irradiation. The chloride ion concentration increased along with the absorbed dose and TiO_2 contents, and almost all organic chlorine can be removed from 4-chlorophenol to form chloride ions.

It can be clearly observed in Fig. 2 that 4-chlorophenol concentration decreased rapidly with increasing absorbed

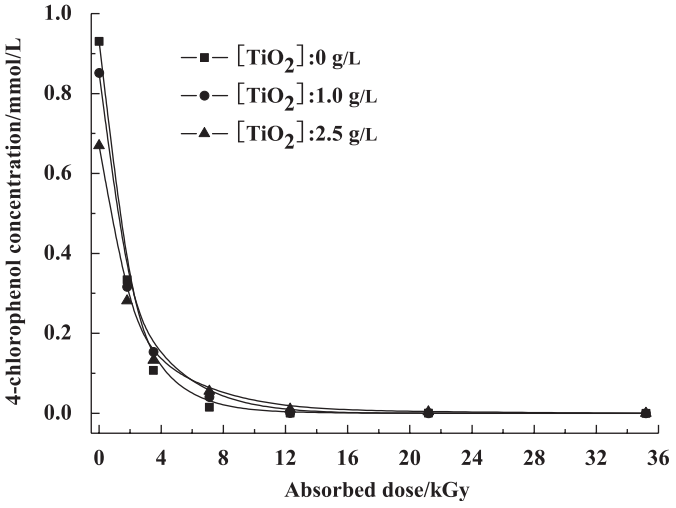


Fig. 2. The relationship between 4-chlorophenol concentration and absorbed doses with different TiO_2 contents.

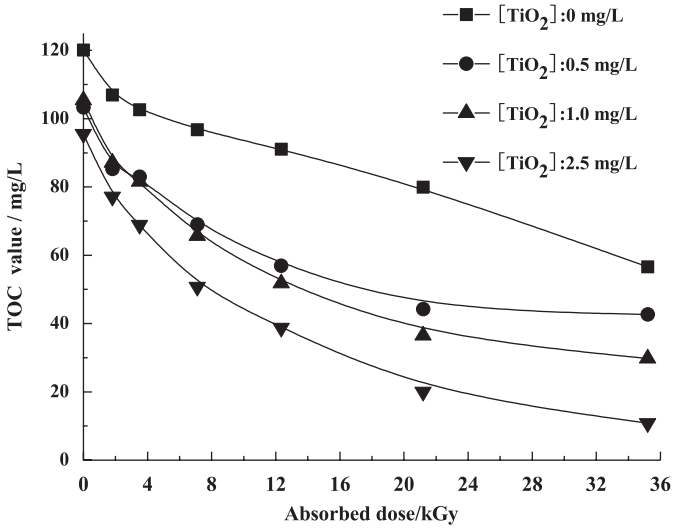
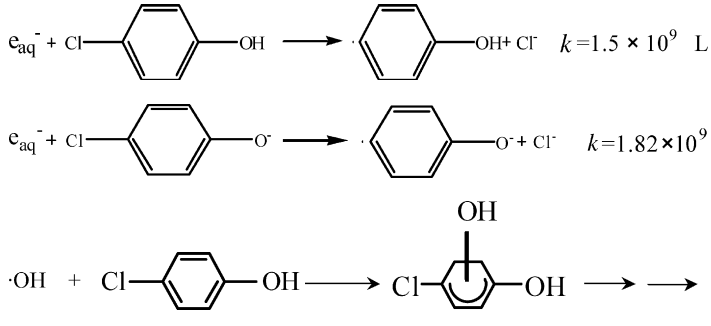


Fig. 3. The relationship between TOC value and absorbed dose with different TiO_2 contents.

dose from 0 to 5 kGy and then decreased slowly while the absorbed dose continued to increase. Oppositely, TOC decreased smoothly along with the augment of absorbed dose as illustrated in Fig. 3. The degradation efficiencies of 4-chlorophenol were almost same with different TiO_2 contents from 0 to 2.5 g L^{-1}, but TOC removal enhanced greatly with increasing TiO_2 contents. When the absorbed dose was 3.5 kGy, 4-chlorophenol concentrations were 0.11, 0.15 and 0.13 mmol L^{-1} with TiO_2 contents of 0, 1.0 and 2.5 g L^{-1}, respectively. However, TOC values were 103, 82 and 69 mg L^{-1} with the absorbed dose of 3.5 kGy and 57, 30 and 11 mg L^{-1} with the absorbed dose of 35.2 kGy. The experimental results showed that the addition of TiO_2 nanoparticles had little influence on the degradation of 4-chlorophenol, but dramatically promoted the mineralization of 4-chlorophenol solutions. The presence of TiO_2 played a positive role in mineralization of 4-chlorophenol, which was in agreement with the conclusion obtained in phenol degradation experiment (Chitose et al., 2003). The change of chloride ion concentration was different from the change of 4-chlorophenol concentration and TOC. The concentration of chloride ions in the solution without TiO_2 was much higher than with 0.5 and 1.0 g L^{-1} TiO_2 contents under the same irradiation condition. The chloride ion concentration in the solution increased dramatically when TiO_2 content increased to 5.0 g L^{-1} under different absorbed doses. Taking research results concerning chloride ions into consideration, it is suggested that TiO_2 nanoparticles affect the intermediate degradation products during the decomposition of 4-chlorophenol.

The result of pulse radiolysis of 4-chlorophenol aqueous solution showed that the degradation of 4-chlorophenol can be concluded from formulas (1)–(3) (Stafford et al., 1994). It is obvious that radiation-induced degradation of 4-chlorophenol and the formation of chlorine ions can be attributed to two opposing paths: reduction of 4-chlorophenol (Formulas (1) and (2)), and oxidation of 4-chlorophenol (Formula (3)). In aerated solutions, e^-_{aq} and H atoms are scavenged by oxygen to form O_2^-• and HO_2• radicals through reactions (4) and (5) that have low reactivity with organic compounds.



$$e^-_{aq} + O_2 \rightarrow O_2^-\bullet \quad k = 1.9 \times 10^{10}\ \mathrm{L\,mol^{-1}\,s^{-1}}, \tag{4}$$

$$H + O_2 \rightarrow HO_2\bullet \quad k = 1.2 \times 10^{10}\ \mathrm{L\,mol^{-1}\,s^{-1}}. \tag{5}$$

The main degradation intermediates formed as a result of •OH attack on different positions were identified as 4-chlorocatechol, 4-chlororesorcin and hydroquinone and can be decompounded ulteriorly into inorganic compound

Table 1
Cl-concentration (10^{-4} mol l^{-1}) with different absorbed dose and TiO_2 content

Absorbed dose (kGy)	$[TiO_2]$ (g/L)			
	0	0.5	1.0	5.0
1.8	3.74	2.40	2.48	4.09
3.5	4.78	2.97	3.28	5.45
12.3	5.57	5.38	4.76	6.97
35.2	6.48	6.33	6.18	9.21

with increasing absorbed doses. It was suggested that the holes and •OH radicals on the particle surface are the strong oxidant and the free •OH radicals in the solution are not the important oxidants according to the reaction of •OH radicals with the TiO_2 particles using pulse radiolysis (Lawless et al., 1991). It is probable that the addition of TiO_2 promoted the proportion of the oxidation degradation and decreased the proportion of the reducing degradation. In the GC/MS analysis of 4-chlorophenol, 4-chlorocatechol and small quantities of other compounds such as phenol and 4-chlororesorcin were observed with 1.0 g L^{-1} TiO_2 at the absorbed dose of 3.5 kGy. At the same content of TiO_2, the concentration of the intermediate degradation products decreased with increasing absorbed doses. No intermediate degradation products were detected in the GC chromatographic analysis of 4-chlorophenol solutions with 35.2 kGy electron beam irradiation. The experimental results of chloride ions indicated that the intermediates are not degraded drastically under lower absorbed doses and lower TiO_2 content, and then the intermediates can be decomposed ulteriorly into inorganic compound with increasing absorbed dose and increasing TiO_2 content. And the organic chlorine can be removed subsequently.

3.3. The change of pH value

The change of pH values of 4-chlorophenol solutions with different TiO_2 contents under electron beam irradiation is illustrated in Fig. 4. The figure shows that pH values of 4-chlorophenol solutions decreased dramatically once the solutions were irradiated by electron beam. Then the pH values decreased smoothly with increasing absorbed dose. The reason for the change of pH value could be attributed to two factors. H^+ is formed when water is irradiated by electron beam. The above disscussion suggested the chlorine ions were formed during radiation degradation process. It is obvious that the decrease of the pH value could be attributed to the formation of hydrochloric acid. The amount of organic Cl decreases with increasing of absobed dose and thereby the HCl formation rate also decreases. In the figure, the pH is a logarithmic scale, while the dose is plotted on a linear scale.

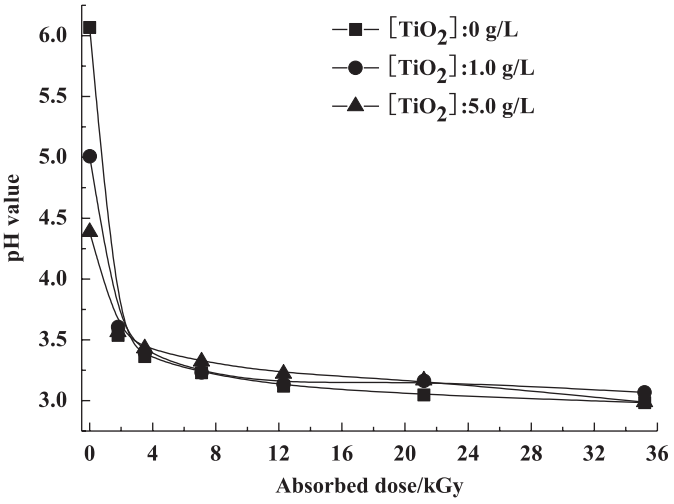


Fig. 4. The change of pH value with absorbed dose with different TiO_2 contents.

Considering this, the pH value decreased smoothly along with the augment of absorbed dose actually.

4. Conclusion

The degradation and mineralization of 4-chlorophenol aqueous solutions in the presence of TiO_2 nanoparticles by electron beam irradiation were investigated. The experimental results showed that TiO_2 nanoparticles had little influence on the change of 4-chlorophenol concentration but dramatically promoted the mineralization of 4-chlorophenol solutions. It is suggested that TiO_2 nanoparticles affect the degradation pathway of 4-chlorophenol.

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