

Degradation of nitrobenzene in wastewater by γ -ray irradiation

ZHANG Shu-juan¹, FENG Shao-hong¹, YU Han-qing^{1,*}, LI Qian-rong²

(1. Department of Chemistry, University of Science & Technology of China, Hefei 230026, China. E-mail: hqyu@ustc.edu.cn; 2. Research Center for Physics & Chemistry, University of Science & Technology of China, Hefei 230026, China)

Abstract: The degradation of nitrobenzene (NB) by γ -ray irradiation was studied. The influences of dose rate and initial NB concentration were investigated in details. At a dose rate of 55 Gy/min, the degradation kinetics was pseudo-first-order at NB concentrations from 0.2 mmol/L to 4.0 mmol/L. At an initial NB concentration of 0.8 mmol/L, the degradation of NB at various dose rates also followed pseudo-first-order kinetics. Dissolved oxygen was found to have a positive effect on NB degradation. The degradation products were identified as nitrophenol, nitrosobenzene, and hydroquinone, and so on. Based on the product analysis, possible degradation pathways of nitrobenzene were proposed.

Keywords: degradation; irradiation; nitrobenzene (NB); kinetics

Introduction

Nitrobenzene (NB), a highly toxic compound, is widely presented in various industrial wastewaters. The strong electron-deficient character of its nitro-group causes NB resistant to bio-oxidation (Mackey, 1995). Therefore, effective alternative methods for the removal of NB from wastewater, either by mineralization or by chemical transformation, should be pursued. During the last two decades, photocatalytic degradation has been applied to convert NB to nitrophenol isomers (Berge, 1994; Rodriguez, 2000). Some other researchers used elemental iron (Fe^0) to reduce nitroaromatic compounds (NACs) to anilines (Johnson, 1996). However, there are disadvantages in these techniques considering the reclamation of catalysts, the light absorbing efficiency and the efficiency in generating of hydroxyl radicals.

Ionizing radiation is a promising method for the treatment of wastewaters. During the action of ionizing radiation with dilute solutions, hydrated electrons, hydrogen atoms and hydroxyl radicals are formed. These primary species are active, especially hydroxyl radicals, which can initiate the degradation of many types of pollutants in wastewaters. Utilization of ionizing radiation to treat wastewaters has a major advantage: a complete degradation of pollutants can be achieved without consumption of any chemicals and resulting in no further pollution (Sakumoto, 1984; Getoff, 1999). However, information about the radiation-induced degradation of NB in wastewater is still sparse. Hence, in this work, effects of the initial NB concentration and dose rate on the degradation kinetics were evaluated, and the degradation products were identified by GC/MS analysis.

1 Materials and methods

1.1 Materials and irradiation experiments

NB and ethyl acetate, both purchased from Shanghai Chemical Reagent Company, were of analytical grade. NB was used without further purification, while ethyl acetate was

redistilled before use. Throughout the experiments, the samples were prepared with doubly distilled water in Pyrex glass vessels and irradiated by a ^{60}Co - γ -source. The irradiated solutions were sampled at certain time intervals.

1.2 Analytical methods

NB concentration was determined using a High Performance Liquid Chromatography (HPLC) (Agilent 1100, VWD detector) with an ODS column. A GC system (Agilent 6890) coupled to an MS (Micromass) through an EI interface was used to identify the degradation products. A 30 m \times 0.25 mm \times 0.25 μm DB-5 column was used. The samples before subject to GC-MS analysis were extracted by ethyl acetate, and then dehydrated by anhydrate magnesium sulfate for 24 h. Thereafter, the filtrate was concentrated to 1 ml using a spin evaporator.

2 Results and discussion

2.1 Effect of initial NB concentration on the degradation of NB

Fig. 1 illustrates the degradation of NB with irradiation time at different initial NB concentrations. The degradation of NB at a certain dose rate was dependent upon the initial NB concentration. For the degradation of NB, the reactions between NB and hydroxyl radicals were predominant. The kinetic model of these reactions can be described as following equation:

$$r = k \cdot C_a \cdot C_b,$$

where C_a and C_b are the concentration of NB and hydroxyl radical, respectively; k is the rate constant; r is the reaction rate.

During the irradiation processes, the yield of hydroxyl radicals is kept constant and the item C_b can be integrated into k . When the NB concentration was lower than 4.0 mmol/L, the degradation of NB was only influenced by the concentration of NB and followed pseudo-first-order kinetics. On the other hand, as the initial NB concentration was higher, the influence of NB concentration could be neglected. As a result, the degradation kinetics of NB should be pseudo-zero-order.

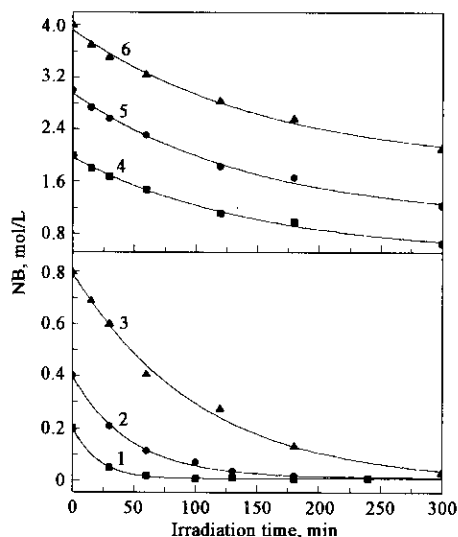


Fig.1 The degradation of NB with irradiation time at different initial NB concentrations: 1. 0.2 mmol/L; 2. 0.4 mmol/L; 3. 0.8 mmol/L; 4. 2.0 mmol/L; 5. 3.0 mmol/L; 6. 4.0 mmol/L, at a dose rate of 55 Gy/min

The kinetic data of NB degradation at different initial NB concentrations are listed in Table 1. The effect of initial NB concentration on the degradation behavior was significant. The degradation rate constant increased with decreasing initial NB concentration. The decrease of correlation coefficient (R value) with the increase of initial NB concentration was in good agreement with the above analysis that degradation kinetics of NB should be pseudo-zero-order at high NB concentrations.

Table 1 The degradation kinetic data at different initial NB concentrations (dose rate: 55 Gy/min, pH = 6.3, air saturated)

NB, mmol/L	Reaction order	Rate constant, min ⁻¹	R
4.0	$n = 1$	0.0021	0.9880
3.0	$n = 1$	0.0029	0.9882
2.0	$n = 1$	0.0037	0.9926
0.8	$n = 1$	0.0113	0.9945
0.4	$n = 1$	0.0175	0.9978
0.2	$n = 1$	0.0396	0.9980

2.2 Effect of dose rate on the degradation of NB

The degradation of NB with irradiation time at different dose rates is shown in Fig. 2. At 0.8 mol/L, the NB degradation followed first-order at various dose rates. Furthermore, a higher dose rate led to a greater degradation rate. The results in Fig. 3 provide further support for this conclusion. Under the same irradiation dose of 7.2 kGy, the degradation of NB was more efficient at higher dose rates than at lower dose rates. The kinetic data of NB degradation at different dose rates are presented in Table 2.

Table 2 The degradation kinetic data at different dose rates (initial NB concentration: 0.8 mmol/L, pH = 6.3, air saturated)

Dose rate, Gy/min	Reaction order	Rate constant, min ⁻¹	R
15.75	$n = 1$	0.0038	0.9985
20.2	$n = 1$	0.0041	0.9964
39.8	$n = 1$	0.0065	0.9996
64.9	$n = 1$	0.0103	0.9997
104.9	$n = 1$	0.0141	0.9997

2.3 Effect of dissolved oxygen on the degradation of NB

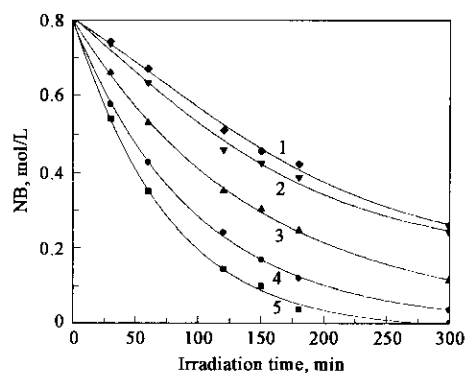


Fig.2 The degradation of NB with irradiation time at different dose rates: 1. 15.8 Gy/min, 2. 20.2 Gy/min, 3. 39.8 Gy/min, 4. 64.9 Gy/min, 5. 104.9 Gy/min, at an initial NB concentration of 0.8 mmol/L

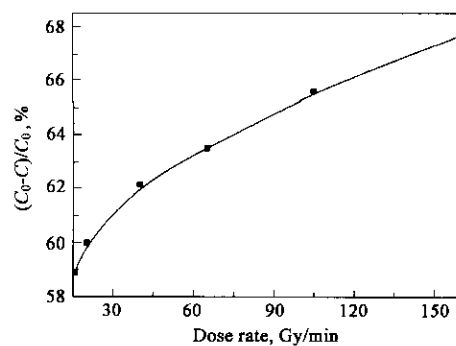


Fig.3 Effect of dose rate on the degradation efficiency of NB at a same dose of 7.2 kGy (initial NB concentration: 2.0 mmol/L)

The degradation efficiencies of NB under different atmospheres are presented in Table 3. At both low and high initial NB concentrations, e.g., 0.8 mmol/L and 2.0 mmol/L, respectively, the increase of dissolved oxygen in irradiation solutions enhanced the degradation of NB, whereas the exhaust of oxygen from solutions reduced the NB degradation. This result indicates that O_2 played an important role in the degradation of NB.

Table 3 Effect of dissolved oxygen on NB degradation (irradiation time: 100 min, dose rate: 55 Gy/min, pH = 6.3)

Initial [NB], mmol/L	Degradation, %		
	Air saturated	N_2 saturated	O_2 saturated
0.8	58.4	53.9	68.7
2.0	35.7	21.3	42.6

2.4 FT-IR analysis of the degradation products of NB

FT-IR spectra of NB and the degradation products after 5 h irradiation are illustrated in Fig. 4. The asymmetrical stretching vibration (ν_{as} , 1525 cm^{-1}) and symmetrical stretching vibration (ν_s , 1348 cm^{-1}) of nitro-group were strong in the spectrum of neat NB (spectrum 1), whereas those in spectrum 2 were considerably weak, indicating the elimination of nitro-group of NB. On the other hand, the peaks at wavenumbers of 1290 cm^{-1} and 740 cm^{-1} in spectrum 2 were much stronger than those in spectrum 1. These two peaks are attributed to nitroso-dimers and δ_{C-N-O} .

respectively. Furthermore, the characteristic absorption peaks of aromatic skeletal vibration at the band 1600–1450 cm^{-1} weakened, indicating the destruction of aromatic ring.

2.5 GC-MS analysis of the degradation products of NB

In order to clarify the pathways of NB degradation, the final products were analyzed by GC-MS (spectra not shown). The analytical results in Table 4 show that nitrophenol, nitrosobenzene, and hydroquinone, etc. were the main products of NB degradation by γ -ray irradiation. Based on the product analysis, possible pathways are proposed in Fig. 5.

Irradiation of dilute NB aqueous solutions produces several reactive species, $\cdot\text{OH}$, e_{aq}^- and $\text{H}\cdot$. Due to the high redox potential of $\cdot\text{OH}$ ($E^0 = 2.80 \text{ V}$), the role of $\cdot\text{OH}$ was

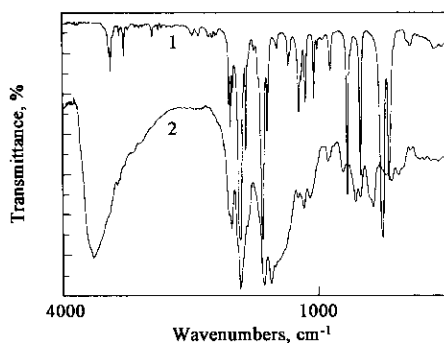


Fig. 4 FT-IR spectra of initial NB sample (spectrum 1) and the sample irradiated 5 h (spectrum 2) [initial NB concentration: 2.0 mmol/L, dose rate: 55 Gy/min, pH = 6.3]

Table 4 GC-MS analysis results (initial NB concentration: 2.5 mmol/L, irradiation time: 5 h, dose rate: 55 Gy/min, pH = 6.3, air saturated)

t_R , min	MIP	BP	Fragments	MM	CM	Compound
1.89	102	43	73, 61, 57, 29	102.0687	102.0681	Cyclopentane-diol
2.75	107	77	64, 51, 50, 38	107.0395	107.0371	Nitrosobenzene
4.38	139	139	109, 81, 65, 53, 39	139.0289	139.0269	<i>o</i> -nitrophenol
5.28	110	54	108, 82, 80, 39	110.0397	110.0368	Hydroquinone, quinone
6.70	139	139	93, 81, 65, 53, 39	139.0263	139.0269	<i>m</i> -nitrophenol
7.02	155	53	153, 107, 93, 79, 39	155.0268	155.0219	4-nitrocatechol
7.12	139	139	109, 93, 81, 65, 53, 39	139.0277	139.0269	<i>p</i> -nitrophenol

Notes: t_R : retention time on the GC chromatogram; MIP: Molecular ion peak in the MS spectra; BP: Base peak in the MS spectra; MM: measured mass; CM: calculated mass

3 Conclusions

Experimental results demonstrated that both the initial NB concentration and dose rate had a substantial effect on the kinetic behavior of NB degradation induced by γ -ray irradiation. The degradation kinetics of NB followed pseudo-first-order at NB concentrations from 0.2 mmol/L to 4.0 mmol/L at various dose rates. GC-MS analysis showed that the dominant degradation products of NB were nitrophenol, nitrosobenzene, and hydroquinone, etc. In the light of this investigation, it can be concluded that γ -ray irradiation is a promising pre-treatment method for NB-rich wastewaters.

References:

Berge D, Ratnaweera H, Efrainsen H, 1994. Degradation of recalcitrant

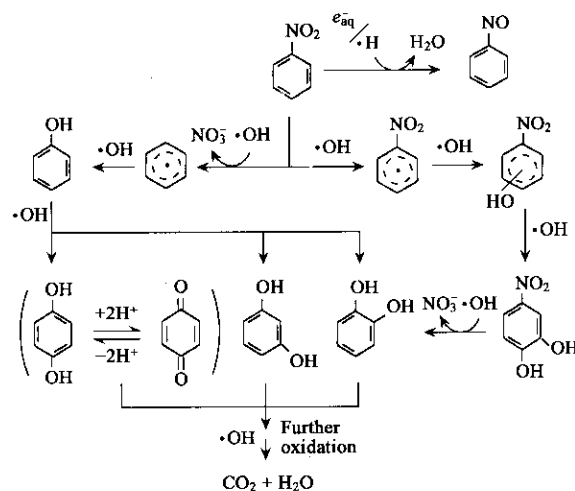


Fig. 5 Possible pathways of NB degradation induced by γ -ray irradiation

predominant in the NB degradation. Initiated by $\cdot\text{OH}$, electron transfer and denitration occurred, leading to the formation of phenyl radicals and nitrophenyl radicals. The addition of $\cdot\text{OH}$ to those intermediates resulted in the formation of phenol, hydroquinone, quinone, *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, and 4-nitrocatechol. Finally, carbon dioxide and water formed after further oxidation. On the other hand, the reductive species e_{aq}^- ($E^0 = -2.9 \text{ V}$) and $\text{H}\cdot$ ($E^0 = -2.1 \text{ V}$) eliminated the oxygen of nitro-group and resulted in the formation of nitrosobenzene.

chlorinated organics by radiochemical and biochemical oxidation [J]. Water Sci Tech, 29: 219–228.

Getoff N, 1999. Radiation chemistry and the environment [J]. Radiat Phys Chem, 54: 377–384.

Johnson T L, Scherer M P, Tratnyek G, 1996. Kinetics of halogenated organic compound degradation by iron metal [J]. Environ Sci Technol, 30: 2634–2640.

Mackey Q D, Shin W Y, Ma K C, 1995. Illustrated handbook of physical properties and environmental fate for organic chemical [M]. Boca Raton, FL: Lewis.

Rodriguez M, Kichner A, Contreras S et al., 2000. Influence of H_2O_2 and Fe^{2+} in the photodegradation of nitrobenzene [J]. J Photochem Photobiol A: Chem, 133: 123–127.

Sakumoto A, Miyata T, 1984. Treatment of waste water by a combined technique of radiation and conventional method [J]. Radiat Phys Chem, 24(1): 99–115.

(Received for review March 17, 2003. Accepted May 30, 2003)