

Synergistic effects of 4-nitrophenol degradation using gamma irradiation combined with a advanced oxidation process

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Abstract The radiation-induced degradation of 4-nitrophenol (4-NP) was performed in combination with a Fenton reagent, H₂O₂, and TiO₂ nanoparticles to investigate the synergetic effects of radiolytical degradation combined with other advanced oxidation processes. The experimental results indicated that the degradation efficiency of 4-NP was 87.5, 57.4, and 41.0 % at a dose of 20 kGy when its initial concentration was 100, 200, and 350 mg/L, respectively. Radiation combined with H₂O₂, the Fenton method, and TiO₂ remarkably increased the degradation efficiency of 4-NP, showing the synergetic effects. Radiation may enhance the biodegradability of 4-NP, suggesting that it has the potential to be used as a pretreatment method in combination with the biological method for the treatment of industrial wastewater containing toxic organic pollutants. Major intermediates during the 4-NP degradation process were identified and a possible degradation pathway was tentatively proposed.

Keywords Radiation degradation · Nitrophenol · Advanced oxidation processes · Priority pollutant · Synergistic effect

1 Introduction

Nitrophenols are anthropogenic, toxic, inhibitory, and biorefractory organic compounds, which have been widely used in the chemical industry for the manufacture of pesticides, pharmaceuticals, and synthetic dyes [1–5]. They are one of the most common organic pollutants in industrial and agricultural wastewaters. Nitrophenols including 4-nitrophenol (4-NP) are considered as priority pollutants by the U.S. Environmental Protection Agency [3]. Due to their toxicity to microorganisms, conventional wastewater treatment methods are not effective to remove them from wastewater [6–8].

Advanced oxidation processes (AOPs) have received increasing attention in the research and development of wastewater treatment technologies in the last decades [9]. These processes, including radiation, photolysis and photocatalysis, sonolysis, electrochemical oxidation technologies, Fenton-based reactions, and ozone-based processes, have been successfully applied in the removal or degradation of recalcitrant pollutants, or used as a pretreatment to convert pollutants into shorter-chain compounds that can then be treated by conventional or biological methods. Radiation technology has been applied to resolve a variety of problems of environmental interest [10, 11].

In recent years, degradation of toxic pollutants in aqueous solutions has been extensively investigated, including chlorophenols [9, 12–15], nitrophenols [1, 2, 4–8, 16–18], hexachlorobenzene [19], sulfamethazine [20–22], diclofenac [23], oxytetracycline [24], cyclohexanebutyric acid [25], landfill leachate [26], dichloroacetic acid [27], imidacloprid [28], acephate [29], ochratoxin A [30], and so on.

It is well-known that hydrogen peroxide (H₂O₂) is an efficient oxidation agent. It is widely applied in wastewater

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purification. H_2O_2 can react with hydrogen atoms ($\text{H}\cdot$), hydroxyl radicals ($\cdot\text{OH}$), and hydrated electrons (e_{aq}^-) during the radiolysis of water. Fenton's reagent, composed of H_2O_2 and Fe^{2+} , can produce high potential oxidants, hydroxyl radicals, to mineralize organic compounds to CO_2 and H_2O through chain reactions, showing an excellent effect of degrading the toxic organic pollutants.

Titanium dioxide (TiO_2) is a nontoxic and inexpensive photo-catalyst, both biologically and chemically inert. In addition, TiO_2 possesses redox properties are favorable for the oxidation of organic pollutants and have been used in a wide range of applications [4, 9, 12, 31–33].

In this study, four different oxidation technologies, including γ -ray radiation, γ - H_2O_2 , γ -Fenton reactions, and γ - TiO_2 have been used for the degradation of 4-NP. The objective of this study was to investigate the synergistic effect of 4-NP degradation when γ -ray radiation is combined with other advanced oxidation processes.

2 Materials and methods

2.1 Chemicals

4-NP was obtained from New Jersey, USA, and its purity was more than 99%. TiO_2 nanoparticles (P25, anatase, mean diameter approximately 30 nm, surface area $50 \text{ m}^2/\text{g}$) were supplied by Degussa Co. (Germany). A.R. grade hydrogen peroxide (H_2O_2 , 30%), and HPLC-grade methanol were purchased from the Beijing Chemical Plant (China). All reagents were used without further treatment. All solutions were prepared with distilled water.

2.2 Gamma-ray source

Gamma-irradiations were carried out in a ^{60}Co source at the Institute of Nuclear and New Energy Technology (INET), Tsinghua University. The dose rate is 244.5 Gy/min. The radiation dosimetry was achieved via the standard Fricke dosimeter [34].

2.3 Irradiation

For irradiation, an aqueous solution of 4-NP was prepared in gas-tight Pyrex glass vials at an initial concentration of 100, 200, and 350 mg/L. For radiation- H_2O_2 experiments, H_2O_2 was added into the vials right before irradiation, making initial H_2O_2 concentrations of 35 mg/L. For radiation- TiO_2 experiments, the TiO_2 powder was added into each vial before irradiation, making TiO_2 concentration of 1.5 g/L. The initial pH of the solution was in the range of 5.5–6.5 without adjustment. Samples were

irradiated at different doses ranging from 2 to 25 kGy. Before being analyzed, all samples were filtered through $0.45 \mu\text{m}$ filters. All operations were performed at ambient temperature.

2.4 Analytical methods

The concentration of 4-NP was analyzed using Agilent Technologies 1200 Series HPLC with a ZORBAX Eclipse XDB-C18 column ($5 \mu\text{m}$, $150 \text{ mm} \times 4.6 \text{ mm}$). The flow rate of the mobile phase was 1.0 mL/min, and the mobile phase was a mixture of methanol and water with a volumetric ratio of 70:30 (v/v).

The intermediate products of 4-NP degradation were identified by an LC/MS with a photo diode array (PDA) detection with a deuterium lamp and a tungsten lamp, and a mass spectrometric (MS) detection with an atmospheric pressure chemical ionization (APCI) source (LCMS-2010EV, Shimadzu, Japan). The PDA was set to scan from 190 to 800 nm with a slit width of 1.2 nm. The column was the same as that used in the HPLC above. The cell temperature was set to 40°C . The positive ions were scanned from 10 to 400 m/z at 500 amu/s by a detector set to 1.4 kV with an event time of 1.5 s. The negative ions were scanned from 10 to 400 m/z at 1000 amu/s by a detector set to 1.5 kV with an event time of 1 s. The nebulizing gas was 99.999% nitrogen at a flow rate of 1.5 L/min. The curved desolvation line (CDL) temperature was set to 250°C . The heat block temperature was set to 250°C . The injection volume was set to $50 \mu\text{L}$ using an auto sampler.

3 Results and discussion

3.1 Effect of 4-NP initial concentration

The influence of the initial concentration of 4-NP on its degradation using γ -ray irradiation was investigated when its initial concentration was 100, 200, and 350 mg/L, respectively. The removal efficiency of 4-NP (saturated with air, initial pH 5.25) at different absorbed doses was calculated and depicted in Fig. 1.

From Fig. 1, it can be seen that the removal efficiency of 4-NP was 87.49, 57.42, and 41.04%, respectively, when its initial concentration was 100, 200, and 350 mg/L and its absorbed dose was 20 kGy. When the absorbed dose increased to 25 kGy, the removal efficiency of 4-NP increased to 95.78% at an initial concentration of 100 mg/L.

The removal efficiency of 4-NP decreased with an increase in the initial concentration. This is because the intermediates competing with 4-NP for the reactive radicals, and with a decrease of 4-NP concentration, the

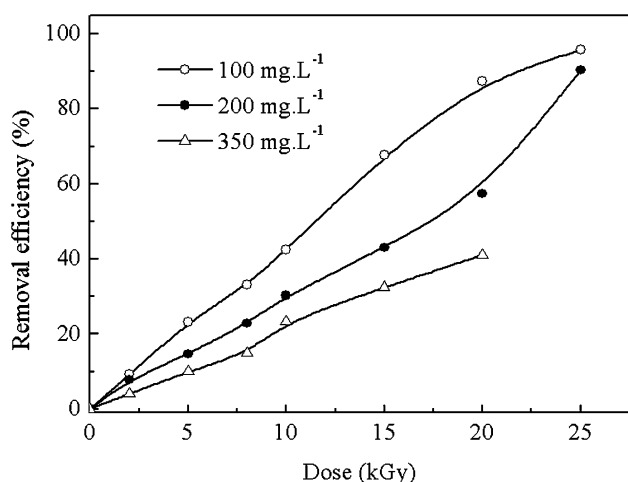


Fig. 1 Degradation of 4-NP at different initial concentrations as a function of absorbed dose

probability of reactive radicals attacking 4-NP became less and more reactive radicals recombine. It was obvious that at a higher 4-NP concentration, the time course of the degradation process was somewhat longer, but the absolute sum of the 4-NP degraded was higher. Also, with a decrease in the 4-NP concentration, the dose needed for complete degradation was strongly reduced.

3.2 Effect of pH

The influence of the pH value on irradiation-induced degradation of 4-NP was investigated when the initial pH of the 4-NP solution was 2.5, 5.25, and 11.0, mainly in order to compare the effect of acidic and alkaline reaction conditions on 4-NP degradation. The pH of the solution was adjusted using 0.1 M NaOH and 0.1 M H₂SO₄. The influence of pH on 4-NP degradation is shown in Fig. 2.

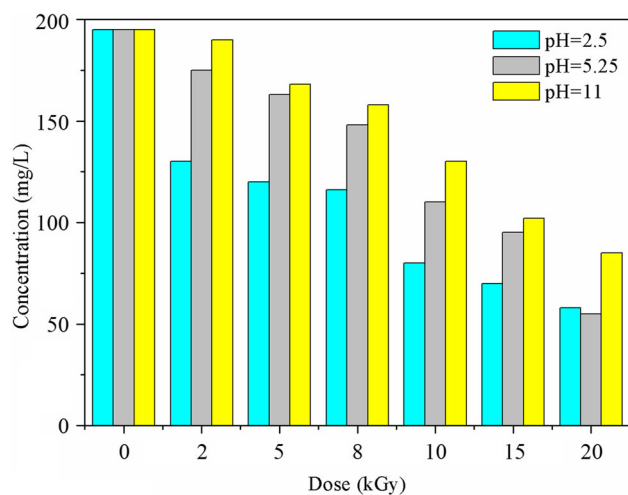


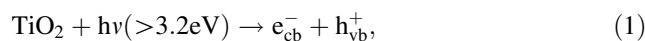
Fig. 2 (Color online) Effect of pH on 4-NP degradation

From Fig. 2, it can be seen that the degradation efficiency of 4-NP at pH 5.25 was lower than that at a pH of 2.5, but higher than that at a pH of 11.0. At a dose of 10 kGy, the degradation of 4-NP at pH 2.5 and pH 5.25 were 53 and 41 %, respectively. However, the degradation efficiency of 4-NP in alkaline condition (pH 11.0) only reached 31 % at the same dose. The results revealed that 4-NP degradation was more effective at acidic or neutral conditions than alkaline conditions. This is mainly because that the H_{aq}⁺ left, while the e_{aq}⁻ was consumed. The accumulation of soluble carboxylic acids produced during the radiation also had a contribution.

3.3 Combination of radiation with other advanced oxidation processes

In this study, a 200 mg/L 4-NP solution was treated by single γ -radiation, radiation-H₂O₂, radiation-Fenton agent, and radiation-TiO₂, respectively, to investigate the synergistic effect of combining the γ -radiation method with other advanced oxidation processes. The results are shown in Fig. 3.

From Fig. 3, it can be seen that the combination of radiation with H₂O₂, radiation with the Fenton method, and radiation in the presence of TiO₂ nano-particles showed a synergistic effect, which can remarkably increase the degradation efficiency of 4-nitrophenol. When combined with irradiation, TiO₂ in the aqueous solution directly absorbs gamma-rays [19], where valence band electrons of the semiconductor are promoted to conduction band electrons (e_{cb}⁻), leaving positive holes (h_{vb}⁺) in the valence band (Eq. 1).



The holes and electrons can either recombine with or migrate to the surface of the nanoparticles of TiO₂

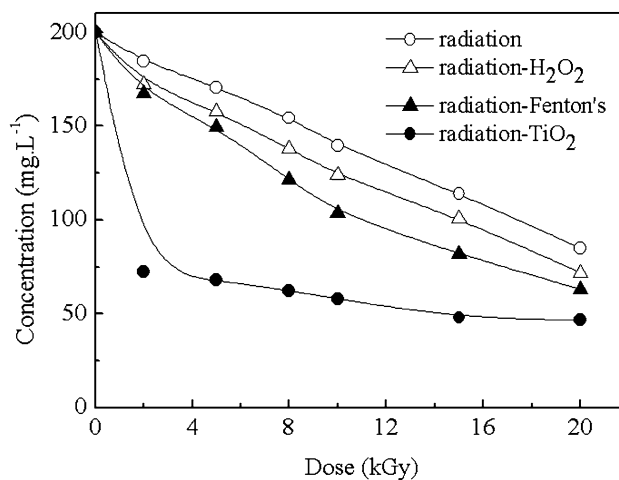
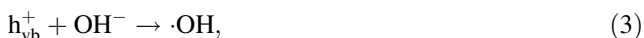


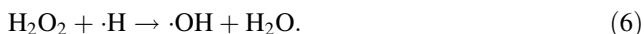
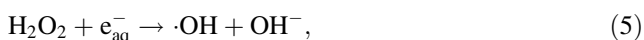
Fig. 3 Degradation of 4-NP by different oxidation processes

separately, where the holes react with adsorbed water or hydroxyl groups to form adsorbed $\cdot\text{OH}$ (Eqs. 2, 3).



Therefore, $\cdot\text{OH}$ becomes the primary oxidant in aqueous solutions with TiO_2 nanoparticles, promoting the degradation of 4-NP.

Hydrogen peroxide molecules can be split into hydroxyl radicals ($\cdot\text{OH}$) by ^{60}Co -ray, which can react with $\cdot\text{H}$ and e_{aq}^- produced by water radiolysis, converting them into much more reactive $\cdot\text{OH}$ (Eqs. 4–6). As a result, the degradation of 4-NP was promoted, showing an obvious synergetic effect by combining H_2O_2 and gamma irradiation.



Xiang et al. [35] found that sludge protein foaming solution could be effectively decolorized and deodorized by gamma irradiation in the presence of hydrogen peroxide. The color, odor, and foamability of irradiated samples under hydrogen peroxide oxidation were significantly improved. Zhang and Yu investigated the radiation-induced degradation of polyvinyl alcohol in aqueous solutions [36]. The degradation efficiency of PVA was influenced by several factors, such as initial PVA concentration, dose rate, pH, and the addition of H_2O_2 . Iqbal and Bhatti [37] studied the gamma radiation/ H_2O_2 treatment of nonylphenol polyethoxylates (NPEO), their results indicated that the NPEO sample irradiated to the absorbed dose of 15 kGy/4.58% H_2O_2 had more than 90% degradation. Gamma radiation/ H_2O_2 treatment revealed a considerable reduction in cytotoxicity and mutagenicity.

As expected, radiation combined with other advanced oxidation processes resulted in an increase in 4-NP removal efficiency. The synergic effect of 4-NP degradation was in the following order:

Radiation- TiO_2 > radiation-Fenton reagent
> radiation- H_2O_2 > radiation

Although all these processes led to the degradation of 4-nitrophenol, the radiation in the presence of TiO_2 nanoparticles was found to be the most promising method for the destruction of 4-nitrophenol.

3.4 Biodegradability evaluation of 4-NP in aqueous solution

4-NP is a toxic pollutant and is difficult to biodegrade. To improve its biodegradability, the 4-NP solution was

treated by gamma irradiation. Figure 4 presents the variation in the specific oxygen uptake rate (SOUR) when 4-NP irradiated aqueous solutions (initial concentration of 100 mg/L) were utilized by aerobic microorganisms in the activated sludge. It can be seen that the SOUR curve of the 4-NP aqueous solution was lower than the SOUR curve of endogenous respiration before gamma irradiation, which suggesting that 4-NP inhibited the microbial metabolism. After irradiation, SOUR curves were not enhanced at the first stage. Oppositely, when the absorbed dose was 1 kGy, SOUR values decreased to be lower than that without irradiation, suggesting that some intermediates produced during 4-NP radiolysis inhibited the activity of aerobic microorganisms. However, with an increase in dose, the toxic intermediates could be decomposed to the lower toxic or non-toxic products. Therefore, the SOUR curves increased stably and reached above the endogenous respiration curve when the absorbed dose increased to 6 and 9 kGy, revealing that the inhibition of the aerobic microorganisms of the 4-NP solution was partially eliminated. The biodegradability of the 4-NP solution was improved by ionizing radiation pretreatment significantly.

Radiation can achieve partial destruction of the parent compound. It is thought that these chemical transformations may reduce the toxicity of nitroaromatic compounds and enhance their biodegradability. The results obtained in this study suggest that radiation technology could be used as a pretreatment process in combination with biological process for the treatment of industrial wastewater containing toxic compounds.

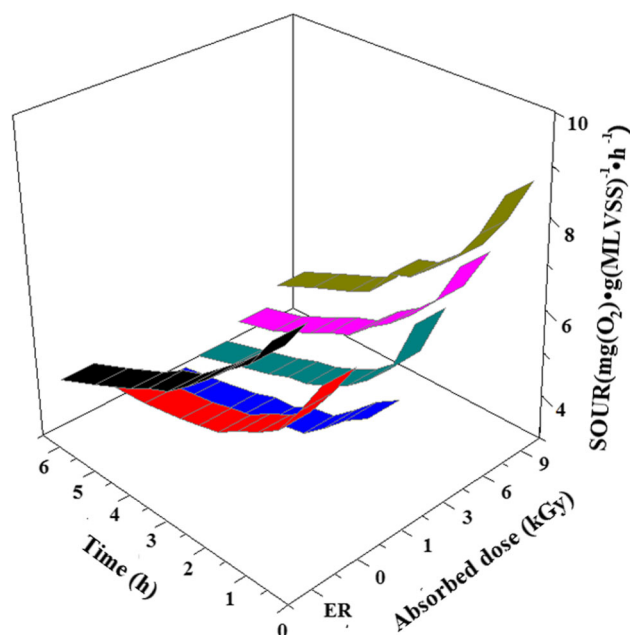


Fig. 4 (Color online) Variation of specific oxygen uptake rate with time and absorbed dose

3.5 Degradation pathways

The irradiated solutions of 4-NP were analyzed by LC/MS to detect the formation of organic intermediates during the degradation process. The results showed that hydroquinone, benzoquinone, 4-nitropyrogallol, and 4-nitrocatechol were identified as major aromatic intermediates for the radiation-induced degradation of nitrophenol.

Radiolytic degradation of organic pollutants could be initiated by OH· radicals, as well as other oxidizing radicals (e.g. HO₂·/O₂·, etc.). For the degradation of aromatic compounds, hydroxyl radicals preferentially attack the benzene ring to form OH-adducts. In the case of 4-nitrophenol degradation, the attack spots of the electrophilic radical ·OH occurred at aromatic ring position. As the –NO₂ of 4-NP is present at the *p*-position of –OH, the ·OH attack will occur preferentially in the *o*-position with respect to –OH, resulting in *ortho* OH-adducts. The OH-adducts could obtain oxygen to form the corresponding peroxy-radicals, which are rather unstable, releasing HO₂· or leading to ring cleavage.

Zhang et al. studied the kinetics and mechanisms of the radiolytic degradation of nitrobenzene (NB) in aqueous solutions through analyzing the radiolytic products of NB under various conditions using FTIR and GC-MS analyses. They proposed the mechanisms behind the radiolytic degradation of NB under both oxidative and reductive conditions in light of the degradation products observed [38].

Aromatic ring cleavage could lead to the formation of different organic intermediates, which then could be converted into low molecular organic acids, such as formic acid and oxalic acid, and finally mineralized to CO₂ and H₂O. Nitrites could be formed from the release of the –NO₂ group, it could be then oxidized to a nitrate by the ·OH radical.

4 Conclusion

Gamma irradiation of 4-NP could lead to its degradation in different conditions. The combination of radiation with H₂O₂, the Fenton method, and TiO₂ nanoparticles showed obvious synergetic effects, which can remarkably increase the degradation efficiency of 4-nitrophenol. Radiation may enhance the biodegradability of 4-NP, suggesting that radiation technology has the potential to be used as a pretreatment process in combination with biological treatment.

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