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Effects of nitrate on the UV photolysis of H_2O_2 for 2,4-dichlorophenol degradation in treated effluents

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ABSTRACT

The major objective of this study was to delineate the effect of nitrate on the UV oxidation of 2,4-DCP by conducting a bench-scale operation at various reaction times, and initial concentrations of H_2O_2 and NO_3^-. 2,4-DCP (20±5 μg/L) was oxidized in very limited amounts through direct UV photolysis, without additional oxidation by hydroxyl radicals. However, it was completely oxidized with an initial H_2O_2 concentration of 20 mg/L at a reaction time of 1.0 min under the operating conditions described below. The practical reaction time for 80% oxidation turned out to be 2.0 min (with a high UV dose) with an initial H_2O_2 concentration of 10 mg/L. Nitrate enhanced the 2,4-DCP oxidation by the hydroxyl radicals produced from nitrate photolysis with the relatively low initial H_2O_2 concentrations of 0.0 to 5 mg/L, but hindered the oxidation, when an initial H_2O_2 concentration in the reactor was less than or around about 10 mg/L. The adverse effect of nitrate on the 2,4-DCP oxidation was not observed with a relatively high initial H_2O_2 concentration of 20 mg/L at the reaction times of 1.0 to 2.0 min. The scavenging effect of nitrate on the 2,4-DCP oxidation was generally limited with the concentration ranges tested in this study.

Keywords: 2,4-dichlorophenol; UV oxidation; Nitrate; Nitrite; UV/H_2O_2 process

1. Introduction

The UV oxidation process is being increasingly used to oxidize complex organic constituents in the treated effluents from domestic wastewater treatment plants, for water reuse. The UV oxidation process typically involves the generation and use of hydroxyl radicals, one of the most active oxidants known. Hydroxyl radicals, unlike other oxidants, are capable of oxidizing almost all the reduced materials present in treated effluents, without restriction to specific classes or groups of compounds [1]. The typical concentrations of NO_3^--N range from 3 to 5 mg/L in the biologically well-treated effluents. However, the nitrate ion, NO_3^- , is a well-known strong absorber of UV light in the case of wavelengths generally below 250 nm [2,3]. NO_2^- from NO_3^- photolysis may hinder the degradative oxidation reactions of organic chemicals enhanced by hydroxyl radicals. Low-pressure, high-intensity UV lamps, manufactured in a mercury-indium amalgam, are continuously being developed. Studies should be conducted to investigate the adverse effects of nitrate on the UV oxidation of 2,4-dichlorophenol (2,4-DCP) using these new and efficient monochromatic lamps.

It is known that nitrate photolysis has three distinct mechanisms, which result in the formation of nitrite

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(NO_2^-), peroxynitrite (ONO_2^-), and nitrogen dioxide radical ($\bullet NO_2$), respectively. One of these mechanisms is the direct route to NO_2^- formation from NO_3^- photolysis, with a low quantum yield [3,4]. A significant production of NO_2^- can be expected via the two other reactions which produce the intermediates ONO_2^- and $\bullet NO_2$, which in turn eventually undergo thermal reactions to form NO_2^- as a stable product [3,5]. The formation of hydroxyl radicals ($\bullet OH$) can be also expected, together with one of the intermediates, $\bullet NO_2$, from nitrate photolysis. As NO_2^- accumulates, it can react with $\bullet OH$, and acts as an $\bullet OH$ scavenger.

The mechanisms involving H_2O_2 photolysis were also critically reviewed [6]. Hydrogen peroxide (H_2O_2) also influences NO_2^- production. Since H_2O_2 photolysis provides another source of hydroxyl radicals, it might be expected to decrease NO_2^- production. H_2O_2, however, appears to act in part as a scavenger of hydroxyl radicals. Peroxynitrite ions and their conjugate acid, peroxynitrous acid (ONO_2H), are strong oxidants. Hydroxyl radicals are also produced from the decomposition of peroxynitrous acid. Nitrite and oxygen can be formed from the reaction between peroxynitrous acid and hydrogen peroxide [5,7,8]. The literature review conducted on the reactions related with the UV photolysis of hydrogen peroxide in the presence of nitrate revealed that both nitrate and hydrogen peroxide appear to act either as an $\bullet OH$ producer or, at some time, as an $\bullet OH$ scavenger, in an aqueous solution.

The UV photolysis or UV oxidation (i.e., photolysis of hydrogen peroxide in the H_2O_2/UV process) has recently been increasingly applied to the oxidation of trace organic chemicals found in water and treated water. These processes were studied for the removal of atrazine, trichloroethylene (TCE), methyl tertiary butyl ether (MTBE), 1,4-dioxane, pesticides, taste- and odor-causing compounds such as MIB and geosmin, N-nitrosodimethylamine (NDMA), and a variety of pharmaceuticals [1,9–15]. There was only one study, though, in which the effects of nitrate in an aqueous solution were systematically determined for the H_2O_2/UV process [16]. In their study, the UV oxidation for EDTA degradation was studied with wavelengths of 222 and 254 nm in NO_3^- solutions, in the presence and absence of H_2O_2. The effects of the NO_3^- concentrations 0, 10, 20, 50, and 100 mg/L were investigated where the NO_3^- concentration range studied was quite different from that in this study. Nitrate was reported to have caused a significant "inner filter" effect by reducing the absorption of UV by H_2O_2.

Studies have been conducted on the UV oxidation of 2,4-DCP dissolved in aqueous solutions [17–19]. However, no studies were conducted for the effect of nitrate on the UV oxidation of 2,4-DCP, especially dissolved in around or less than 20 μg/L. The major objective of this study was to delineate the effects of nitrate on the UV oxidation of 2,4-DCP by conducting a bench-scale operation at various reaction times, and initial concentrations of H_2O_2 and NO_3^--N. The identification of the intermediates from 2,4-DCP oxidation was not within the scope of this study.

2. Materials and methods

All the experiments were carried out in an 8.4 L jacketed brown-glass reactor equipped with a 3.6 L stainless-steel reaction chamber. The UV lamp in the chamber (Trojan Logic™ LF18), with a nominal power of 67 W, emitted radiation at 254 nm. The inner surfaces of all the tubes were made of Teflon, and all headspaces inside the reactors and tubes were completely eliminated during the experiments [20]. All the experiments were performed in batch mode, and the pHs in the reactors were not controlled.

The influent solution (12 L) to be poured into the reactor was prepared by dissolving 15 mL of the 2,4-DCP (99%, Sigma) stock solution (0.016 g 2,4-DCP/1 L methanol) and 0.362 g $NaNO_3$ (98%, Shinyo) in 11 L of double-distilled water. The mixture was carefully poured in the reactor, and was circulated with the use of an installed peristaltic pump for 3 min, to completely mix the solution. Aliquots (342.83 μg/L) of H_2O_2 (35%, Showa) were then injected into the mixture, and the reactor was filled with additional double-distilled water in order to avoid any headspace inside it (for an H_2O_2 concentration of 10 mg/L as an example). This influent solution was completely mixed again with the use of the recirculation pump for the first min, without any UV irradiation, and the UV lamp in the chamber was then turned on to initiate oxidation reaction. Samples (40 mL) were regularly collected according to the pre-determined schedule, and were analyzed for 2,4-DCP using the solid phase micro-extraction process [21]. The concentrations of 2,4-DCP were measured by using GC/MS (Varian Saturn 2000 Ver. 6.41) equipped with a PTE-5, 30 m × 0.25 mm ID, 0.25 μm film column. The flow rate of the carrier gas (helium) was set 40 cm/s at 40°C. The injector temperature was 280°C. The oven temperature was initially set to 40°C and kept up to 260°C at 12°C/min [22].

3. Results and discussion

As shown in Fig. 1(a), 2,4-DCP was rapidly degraded for the first 0.5 min of UV exposure, and was completely oxidized at a reaction time of 1 min with nitrate addition and without it. It is noted that this complete degradation was observed with a relatively high initial H_2O_2 concentration of 20 mg/L in the reactor. The adverse effect of NO_3^- on 2,4-DCP degradation could not clearly be

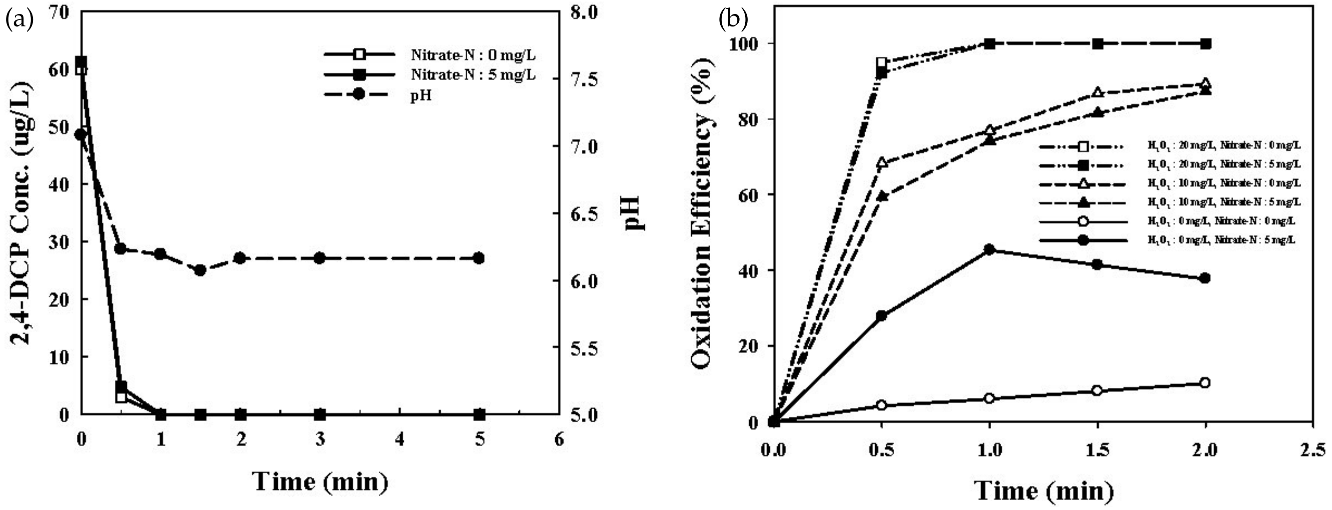

Fig. 1. (a) Profiles of 2,4-DCP concentration and pH (in the absence of nitrate) as functions of reaction time with respect to different initial conc. of NO_3^--N; initial conc. of 2,4-DCP: 64 µg/L, initial conc. of H_2O_2: 20 mg/L. (b) Profiles of oxidation efficiencies (%) of 2,4-DCP as functions of reaction time with respect to different initial conc. of H_2O_2 and NO_3^--N; initial conc. of 2,4-DCP: 20±5 µg/L.

shown under this operating conditions. The pH slightly decreased and ranged from 7.08 to 6.16 in the absence of nitrate. The overall pattern of pH decrease in the presence of nitrate showed trends very similar to that in the absence of it [not shown in Fig. 1(a)]. The pH ranged from 6.41 to 6.07 with the initial NO_3^--N concentration of 5 mg/L. Fig. 1(b) shows the profiles of oxidation efficiencies (%) of 2,4-DCP as functions of reaction time with respect to different initial concentrations of H_2O_2 and NO_3^- at an initial 2,4-DCP concentration of 20 ± 5 µg/L. The removal of 2,4-DCP was generally rapid for the first 1 min of UV oxidation and gradually increased after that. It also shows that 2,4-DCP was degraded by UV irradiation in the reactor without adding H_2O_2 and NO_3^-. The removal efficiencies in the absence of H_2O_2 and NO_3^- were only about 6% at a 1 min reaction time and about 10% at a 2 min reaction time. This indicates that 2,4-DCP can be oxidized in very limited amounts through direct UV photolysis, without additional oxidation by hydroxyl radicals

It is quite interesting to compare the oxidation in the two reactors, into which H_2O_2 was not supplied. NO_3^-, however, was added into the one reactor as an initial NO_3^--N concentration of 5 mg/L, and no NO_3^- was added into the other reactor [Fig. 1(b)]. The oxidation efficiencies in the reactor where NO_3^- was present were higher than those in the reactor where NO_3^- was absent, possibly due to the oxidation of 2,4-DCP by hydroxyl radicals. NO_3^- can be attributed to the OH radical production from the NO_3^- absorption of UV [8], even when no H_2O_2 dissolved in the solution was present in the reactors. The results indicate that NO_3^- clearly has enhanced the 2,4-DCP oxidation through the following nitrate photolysis [2,3,9]:

$$NO_3^- + h\nu + H^+ \rightarrow \bullet NO_2 + \bullet OH \qquad (1)$$

The adverse effect of nitrate on the oxidation of 2,4-DCP was clearly shown when the oxidation efficiencies in one reactor where nitrate was added were compared with those in the reactor where nitrate was not added. The initial H_2O_2 concentration was 10 mg/L for both reactors [Fig. 1(b)]. The differences in oxidation efficiencies caused by NO_3^- in the reactor were relatively small, and ranged only about 2 to 9%. This might be because the photolysis of NO_3^- produced NO_2^- ions which were accumulated during the reaction, as mentioned above [2,9]. The observed oxidation efficiencies consequently decreased due to OH radical scavenging by photochemically generated NO_2^-, as shown in the following chemical reactions [5]. NO_3^- was also reported to have caused a significant "inner filter" effect by reducing the absorption of UV by H_2O_2, which resulted in a significant reduction in the efficiency of UV/H_2O_2 system [2]:

$$NO_2^- + \bullet OH \rightarrow \bullet NO_2 + OH^- \qquad (2)$$

$$H_2O_2 + \bullet OH \rightarrow H_2O + H^+ + \bullet O_2^- \qquad (3)$$

The differences in the oxidation efficiencies caused by NO_3^- were a little larger in the reactor at the initial H_2O_2 concentration of 10 mg/L than those at the initial H_2O_2 concentration of 20 mg/L, as the NO_3^- photolysis and scavenging hydroxyl radicals by nitrite ions were rather limited at this high H_2O_2 concentration. The adverse effect

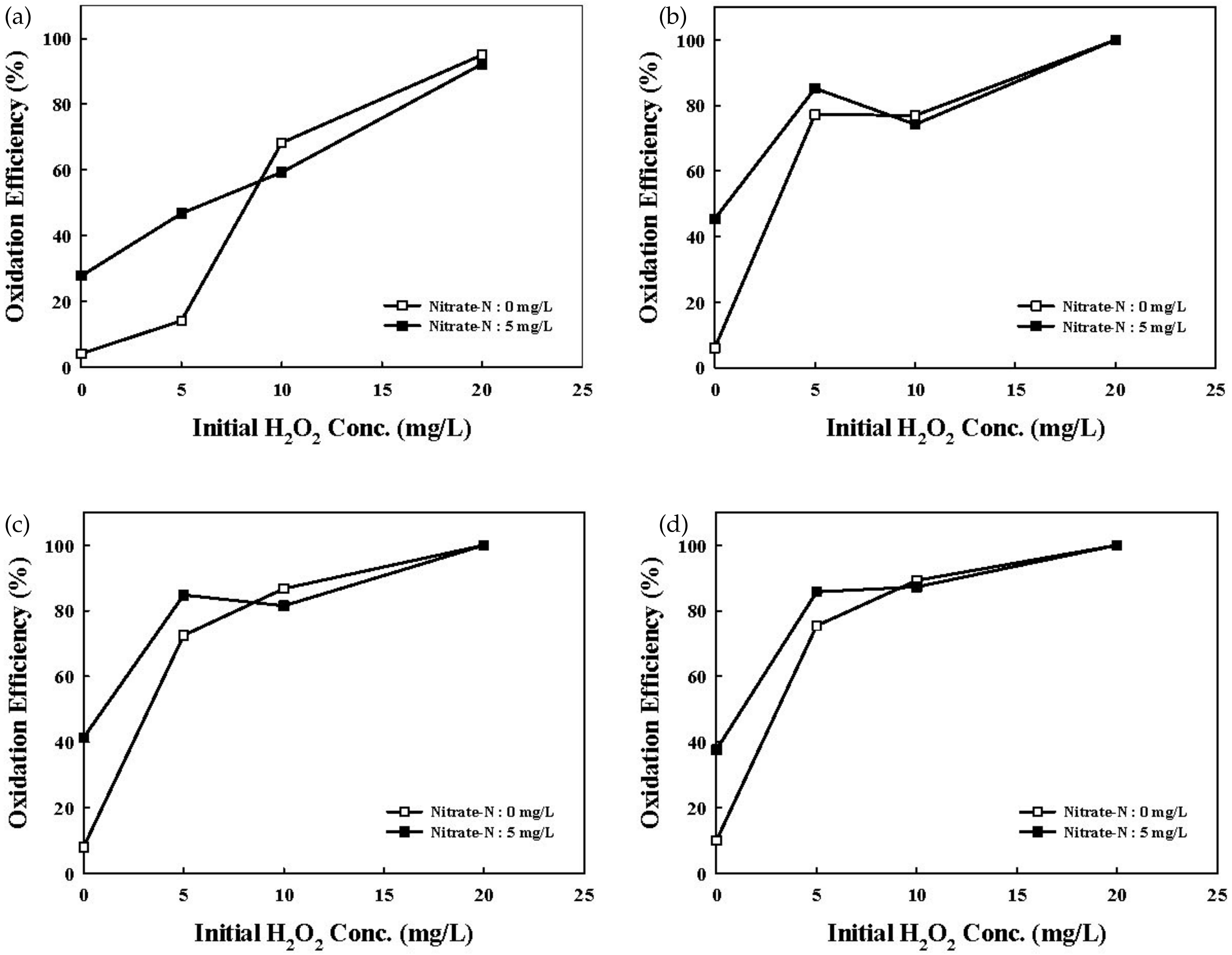

Fig. 2. Oxidation efficiencies (%) of 2,4-DCP as functions of initial conc. of H_2O_2 with respect to the different initial conc. of NO_3^--N at the reaction times of (a) 0.5 min, (b) 1.0 min, (c) 1.5 min, and (d) 2.0 min. Initial conc. of 2,4-DCP: 20±5 µg/L.

was clearly reduced at the short reaction time of 0.5 min, and disappeared at the long reaction times of 1.0, 1.5 and 2.0 min with the initial H_2O_2 concentration of 20 mg/L. The results indicate that 2,4-DCP can be completely oxidized with an initial H_2O_2 concentration of 20 mg/L at a reaction time of 1.0 min under the operating conditions described above. It is noted that the 0.5, 1.0, 1.5 and 2.0 min of UV exposure accounted for 238, 477, 715 and 954 mJ/cm^2 as an UV dose, respectively, considering the reaction times and UV intensities applied under the operating conditions described above.

The effects of the reaction times on the 2,4-DCP degradation are shown in Fig. 2. The oxidation of 2,4-DCP was not limited by nitrate with the initial H_2O_2 concentrations of 0.0 and 5 mg/L at any reaction time, and was rather enhanced by nitrate in the reactors. The 2,4-DCP oxidation was hindered in very limited amounts with the initial H_2O_2 concentrations of 10 mg/L at all reaction times, but was not hindered with the initial H_2O_2 concentrations of 20 mg/L at the relatively long reaction times of 1.0, 1.5 and 2.0 min, except at the short reaction time of 0.5 min. It is interesting that the oxidation efficiencies with the initial H_2O_2 concentrations of 5 mg/L was rather higher than those with the initial H_2O_2 concentrations of 10 mg/L at the reaction time of 1 min. The results show that the practical reaction time for the 80% oxidation turned out to be 2.0 min with an initial H_2O_2 concentration of 10 mg/L. However, when a reaction time of 1 min is considered for 2,4-DCP oxidation, the desirable initial H_2O_2 concentration can be 5 mg/L rather than 10 mg/L in the reactor for high removal efficiency.

Fig. 3 shows that the UV photolysis of H_2O_2 was the most effective method for 2,4-DCP degradation among the three options considered for this study, as the scavenging effect of nitrate ion on the 2,4-DCP oxidation was rather limited with the concentration ranges tested in this study.

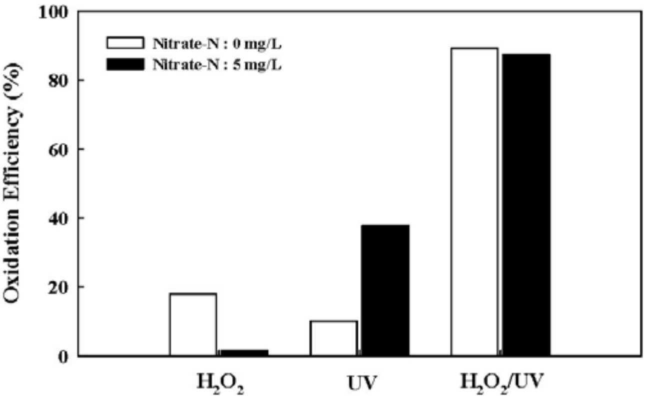

Fig. 3. Profile of removal efficiencies (%) of 2,4-DCP with respect to the different initial concentration of NO_3^--N with the initial H_2O_2 concentration of 10 mg/L and at the reaction time of 2 min; H_2O_2: H_2O_2 addition without UV irradiation, UV: UV irradiation without H_2O_2 addition, and H_2O_2/UV: UV oxidation; initial concentration of 2,4-DCP: 20±5 µg/L.

It is noted that 18% oxidation of 2,4-DCP, initiated by H_2O_2 alone in the solution, was observed without any UV irradiation under the operating conditions. The reason for this relatively high oxidation is, so far, unknown, even if hydrogen peroxide itself is one of the strong oxidants. This might be possible because H_3O^+, produced from the reaction of H_2O_2 with H_2O, caused the additional 2,4-DCP oxidation. The oxidation efficiencies in the reactor where NO_3^- was present were higher than those in the reactor where NO_3^- was absent, possibly due to the oxidation of 2,4-DCP by hydroxyl radicals. NO_3^- could be attributed to the OH radical production from the NO_3^- absorption of UV, even when no dissolved H_2O_2 in the solution was present in the reactors, previously discussed above.

4. Conclusions

It was found that 2,4-DCP (20 ± 5 µg/L) was oxidized in very limited amounts through the direct UV photolysis, without additional oxidation by hydroxyl radicals. However, it was completely oxidized with an initial H_2O_2 concentration of 20 mg/L at a reaction time of 1.0 min under the operating conditions described above. The practical reaction time for the 80% oxidation turned out to be 2.0 min (with a high UV dose) with an initial H_2O_2 concentration of 10 mg/L. Nitrate enhanced the 2,4-DCP oxidation by the hydroxyl radicals produced from nitrate photolysis with the relatively low initial H_2O_2 concentration of 0.0 to 5 mg/L, but hindered the UV oxidation when the initial H_2O_2 concentration in the reactor was less than or around about 10 mg/L. The 2,4-DCP oxidation was not clearly hindered by nitrate with a relatively high initial H_2O_2 concentration of 20 mg/L at the long reaction times of 1.0 to 2.0 min. The scavenging effect of nitrate on the 2,4-DCP oxidation was generally limited with the concentration ranges tested in this study. It is noted that about 18% oxidation of 2,4-DCP, initiated by H_2O_2 alone in the solution, was observed without any UV irradiation under the operating conditions. The reason for this relatively high oxidation should be further investigated, even if hydrogen peroxide itself is one of the strong oxidants. This may be possibly because H_3O^+, produced from the reaction of H_2O_2 with H_2O, resulted in the additional 2,4-DCP oxidation.

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