Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20524

70 (2017) 311–321
April

Photocatalytic degradation of 2,4-dichlorophenol using natural iron oxide and carboxylic acids under UV and sunlight irradiation: intermediates and degradation pathways

W. Remache, S. Belaidi, L. Mammeri, H. Mechakra, T. Sehili*, K. Djebbar

Laboratoire des Sciences et Technologies de l'Environnement, Université des Frères Mentouri Constantine 1, Constantine, Algeria,
Tel. +213 (0) 770740136; email: tsehili@yahoo.fr (T. Sehili), Tel. +213 (0) 774609553; email: remache.wassila@umc.edu.dz (W. Remache),
Tel. +213 (0) 553894820; email: belaidi_siham@yahoo.fr (S. Belaidi), Tel. +213 (0) 551894492;
email: l_mammeri@yahoo.fr (L. Mammeri), Tel. +213 (0) 550262253; email: mechakra_hind@umc.edu.dz (H. Mechakra),
Tel. +213 (0) 774821717; email: kedjebbar@yahoo.fr (K. Djebbar)

Received 7 September 2016; Accepted 17 January 2017

ABSTRACT

The photocatalytic degradation of 2,4-dichlorophenol (2,4-DCP) has been studied using natural iron oxide (NIO) as a heterogeneous catalyst under various conditions. NIO was found to be inactive for 2,4-DCP degradation under UV irradiation (wavelength 365 nm); however, it was very effective under solar light. 2,4-DCP was nearly completely removed with solar light in about 6 h. This can be due to the higher absorptivity of NIO in the solar system. The dependence of 2,4-DCP photodegradation on carboxylic acids in NIO–carboxylate–UV systems was investigated. The presence of oxalic acid allows the highest photocatalytic oxidation rates than other carboxylic acids such as citric, tartaric, malic and malonic acid. The results demonstrated that the 2,4-DCP photodegradation using NIO in the presence of oxalic acid followed the first-order kinetic $k = 3.270 \times 10^{-2}$ min^{-1}. The optimal content of the NIO and oxalic acid concentration were found to be 1.0 g L^{-1} and 5.0 mM, respectively. The use of 2.0% of isopropanol as a scavenger confirmed the intervention of hydroxyl radicals in the photodegradation of 2,4-DCP. The reaction intermediates were identified by an ultrahigh performance liquid chromatography coupled high-resolution mass spectrometry analysis and a reaction mechanism was proposed. Complete mineralization has been confirmed by chemical oxygen demand analysis. A series of experiments were also carried out with solar light in order to compare the results with those obtained with UV irradiation. The process NIO–carboxylate (oxalate, citrate, tartrate and malate) shows good efficiency under solar light, it is an economically viable method for pretreating wastewaters containing recalcitrant pollutants such as chlorophenolic compounds.

Keywords: Natural iron oxide; 2,4-Dichlorophenol; Photodegradation; Solar light; Hydroxyl radicals

1. Introduction

Chlorophenols have been used extensively in many industrial products such as petrochemicals, pharmaceuticals, dyes, pulp industries, pesticides and paint [1–3]. They are recalcitrant to biodegradation and consequently persistent in the environment. The production of 2,4-dichlorophenol (2,4-DCP), which is largely used in the field of herbicides and fungicides overpass 100,000 tons a year. It is involved in the synthesis of the 2,4-dichlorophenoxyacetic acid of "oxadiazon" and of "Dowco 118", which is a phosphorated herbicide. It appears also in the degradation of these compounds [4]. Therefore, it is important to find innovative and economical methods for the safe and complete destruction of chlorophenols. Advanced oxidation processes constitute a promising technology for the treatment of wastewaters

---

* Corresponding author.

containing recalcitrant organic pollutants. These processes involve the generation of non-selective and highly reactive hydroxyl radical ($HO^•$), which is one of the most powerful oxidation agents [5]. In recent years, various iron systems have been attracting extensive attention due to generating $HO^•$ in photochemical process. Iron oxides (including oxyhydroxides) should be a kind of natural minerals and geocatalysts. The iron oxides are found in soils and rocks, lakes and rivers, on the seafloor, in air and organism [6]. Major iron oxides including goethite(α-FeOOH), hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), lepidocrocite (γ-FeOOH) and magnetite (Fe_3O_4) show semiconductor properties with a narrow band gap of 2.0–2.3 eV and could be photoactive under solar irradiation [7]. The use of iron oxides as photocatalysts is recommended due to their abundance on earth. In fact, photocatalytic degradations induced by iron oxides have been extensively studied [8–12]. Unfortunately, the photochemical transformation rate for recalcitrant organic compounds on the surface of iron oxides was very slow. To be more important, iron oxides and polycarboxylic acids can form a photochemical system to give a photo-Fenton-like system [13–16]. Organic carboxylic acids, mainly exuded by plants in soil, have strong chelating ability with multivalent cations [17]. In nature, this photochemical oxidation process can directly utilize iron oxide, polycarboxylic acids and sunlight to decompose organic pollutants economically. It has been reported that Fe(III) coordinated with some carboxylates and formed various complexes such as Fe(III)–tartrate and Fe(III)–oxalate [18,19]. Under irradiation, many kinds of active radicals ($ROO^•$, $O_2^{•-}$, $HO_2^•$, $^•OOH$) are generated in the solution through a ligand-to-metal charge transfer path [20]. In the presence of dissolved oxygen, hydrogen peroxide (H_2O_2) is formed from the photodegradation of organic carboxylic acid. The Fe(II) and H_2O_2 so produced may react via the so-called Fenton reaction to produce hydroxyl radicals $HO^•$, which eventually degraded the organic pollutants present in the system [19]. Carboxylic acids are able to extract iron from natural iron oxides (NIOs) or hydroxides [21,22]. Oxalic acid was found to be the most promising source because of its acid strength, good complexing characteristics and high reducing power, compared with other organic acids. Concerning photodegradation studies, it was found that bisphenol A could be photodegraded efficiently in the presence of oxalic acid than other carboxylic acids such as citric, tartaric, malonic, malic and succinic acid [23]. The use of iron oxide–oxalate in photodegradation processes is due to its high absorption in the UV and visible region. This feature favors its application for wastewater treatment using solar energy as source of irradiation decreasing the costs.

In this study, 2,4-DCP was selected as a model organic pollutant because of its persistence in the environment and high toxicity due to the two chlorine atoms in its structure.

So, its removal from environment has caused for much concern [2,24,25]. But the photodegradation of 2,4-DCP and mechanisms in the iron oxide–carboxylate complex system have not been described in previous studies.

The objectives were first to test the photocatalytic activity of NIO on 2,4-DCP photodegradation under UV and solar light, second to determine the enhancement effect of carboxylic acids and NIO on the photocatalytic degradation of 2,4-DCP in the NIO–carboxylate complexes system, third to identify the main intermediates and propose possible photodegradation pathways based on identified by-products.

2. Experimental setup

2.1. Chemicals

2,4-DCP was supplied by Riedel-de Haën (purity >99%). Sodium hydroxide (98%) and acetonitrile (99%) was provided by Carlo Erba Reagents. Ammonium acetate (98%), sodium acetate (99%), acetic acid (99.5%) and sulfuric acid (98%) were provided by Panreac. 1,10-Phenanthroline (>99%) and perchloric acid (60%) were purchased from Fluka and Prolabo, respectively. Oxalic, citric, malonic and tartaric acids (99.5%) were obtained from Prolabo. Malic acid (99%) from Biochem Chemopharma. All aqueous solutions were prepared with ultrapure water obtained from a Milli-Q ultrapure water purification system (Millipore, Bedford, MA, USA).

2.2. Irradiation procedure

The reaction suspension was formed by adding given dosage of NIO powder into 50 mL of aqueous 2,4-DCP solution or mixed 2,4-DCP and carboxylic acid solution (initial concentration of 2,4-DCP = 10^{-4} M) with a predetermined pH value. The pH of the sample solution of the photochemical reactor was adjusted with $HClO_4$ and/or NaOH solution and measured by means of an HANNA Instruments 8521 pH-meter. Prior to the photoreaction, the suspension was magnetically stirred in the dark for 1 h to establish adsorption/desorption equilibrium. The various aqueous suspensions were then illuminated by UV or solar radiation while being magnetically stirred. Experiments under UV radiation were performed in a Pyrex cylindrical reactor (diameter of 3 cm) with a cooling water jacket placed in an elliptical stainless steel chamber. A high pressure mercury UV lamp (Philips HPW 125), which dominantly emits radiation at 365 nm was used. Light intensity (I = 1.6 mW cm^{-2}) was measured using a radiometer type VLX 3W. The lamp and the reactor are on both focal axes of the elliptical chamber. The reaction temperature was kept at 20°C ± 1°C by cycling water.

Experiments under solar light were carried out in the University of Mentouri (GPS coordinates: N = 36°20′, E = 6°37′), Constantine, using a Pyrex cylindrical reactor containing 50 mL of the system solution. The solar intensity (sunny days in August 2014) was 0.98 W cm^{-2} measured with a SOLAR LIGHT radiometer PMA2100 positioned to sample height. The samples taken from the solution at certain time intervals were filtered through 0.45 μm membrane filters to separate NIO particles from the solutions. All solutions were prepared with ultrapure water (Millipore).

2.3. Analytical methods

At different time intervals during the irradiation, samples were collected and analyzed by high performance liquid chromatography (HPLC). 2,4-DCP was monitored at 284 nm by HPLC (Shimadzu) equipped with a controller model SCL-10A VP, photodiode-array UV–Vis detector model SPD-M10A VP and two pumps model LC8A. The system is controlled by software "Class VP5" for storing and processing of chromatograms. The mobile phase was a mixture of acetonitrile/water (60/40 v/v) was operated at a flow rate of 1.0 mL min^{-1} using Supelco, C18 column (5 μm, 250 mm × 4.6 mm inner diameter (i.d.)). The UV–Vis absorption spectra were recorded employing a Unicam "Helios α" spectrophotometer controlled by software "Vision". The ferrous ion can easily be determined by the formation of a red complex with 1,10-phenanthroline. The molar absorption coefficient at 510 nm of the complex Fe(II) phenanthroline is equal to 1,1180 L mol^{-1} cm^{-1} [26]. Chemical oxygen demand (COD) was obtained according to the method presented by Thomas and Mazas [27], using the dichromate as the oxidizer in a strong acid medium. The sample was digested at 150°C for 2 h in a WTW CR 3200 thermoreactor. The optical density for the color change of dichromate solution was determined with a UV–Vis spectrophotometer.

The ultrahigh performance liquid chromatography (UHPLC; Dionex 3000, Thermo Scientific, USA) coupled to a Q-Exactive Hybrid Quadrupole-Orbitrap Mass Spectrometer (Thermo Scientific, USA) was employed to identify the intermediates. The electrospray ionization source was operated in a negative mode. Separation was carried out using a Waters Acquity HSS T3 column (1.8 μm, 100 Å × 2.1 mm) at a flow rate of 0.3 mL min^{-1}. Mobiles phases were 0.1% formic acid in water (A) and 0.1% formic acid in acetonitrile (B). A 22 min gradient was applied: the concentration of eluent B was initially kept at 1% for 2 min, then increased to 100% in 11 min, kept at 100% for 2 min, then decreased to 1% in 0.1 min, and kept at 1% for 6.9 min.

3. Results and discussion

3.1. Properties of NIO

The catalyst (NIO) used in this study was obtained from the iron deposits which is located in North-East Algeria. The collected powder was washed and dried at 45°C before using for photocatalysis treatment. The NIO has already been characterized by X-ray powder diffraction (XRD), X-ray fluorescence, surface area, scanning electron microscopy and Raman analyses in previous works of our group [10,28,29]. XRD results revealed that iron deposits are mostly composed of hematite (Fe_2O_3). The specific surface area was measured to be 79.015 m^2 g^{-1} and the total pore volume was 0.0892 cm^3 g^{-1} [10]. The Raman analysis of NIO indicates that the major component in the natural powder is hematite. No signal from other iron oxide phases was observed [29].

The chemical composition of NIO fractions is summarized in Table 1 [10]. NIO is mostly composed of hematite (Fe_2O_3: 76.06%), other elements were also determined in lesser percentages such as CaO, MgO, Cl, K_2O and SO_3. Silicate and alumina constitute 4.75% and 0.38%, respectively, of the NIO. Li et al. [30] reported that silicate and alumina are not photoactive under light irradiation at a wavelength of longer than 200 nm owing to their wide band gaps.

3.2. Photocatalytic degradation kinetics

The first step to study in these processes is to check the influence of direct photolysis. It can be seen from Fig. 1 that the direct photolysis of 2,4-DCP was about 39% in 360 min, under UV light irradiation (λ = 365 nm), however, as NIO with concentrations from 0.5 to 2 g L^{-1} was added, the degradation rate was lower, which means that at pH 8.4 (native pH value of 2,4-DCP with NIO), the presence of NIO itself could not help enhancing the 2,4-DCP degradation due to the screen effect of NIO particles in solution, and hence resulted in the lower absorption of UV light by 2,4-DCP.

3.3. Effect of the light source

To test the photocatalytic activity of NIO under solar light and UV irradiation (λ = 365 nm and 300 nm < λ < 450 nm), the experiments were carried out in the suspension with an initial concentration of 10^{-4} M 2,4-DCP and NIO 1 g L^{-1}. It is well known that the intensity of a light source and the wavelength of irradiation play very important role in photocatalytic process. Generally, higher light intensity can lead to a higher degradation rate for organic pollutants in photochemical reaction (because the number of the produced photons becomes higher). The results are given in Fig. 2. The direct photolysis of 2,4-DCP in aqueous solution irradiated by polychromatic light (300 < λ_{irr} < 450 nm) was about 41% in 360 min. When NIO was added 2,4-DCP concentration decreased by 26% in the same time.

39% degradation of 2,4-DCP was achieved when solution was irradiated under 125 W UV lamp (λ_{irr} = 365 nm) in the absence of NIO. However, degradation under UV_{365nm} + NIO

Table 1
Chemical composition of NIO fractions obtained by X-ray fluorescence [10]

Compounds formula	Composition (%)
SiO_2	4.75
Al_2O_3	0.38
Fe_2O_3	76.06
CaO	2.64
MgO	0.17
Cl	0.008
Na_2O	0.000
K_2O	0.026
SO_3	0.004

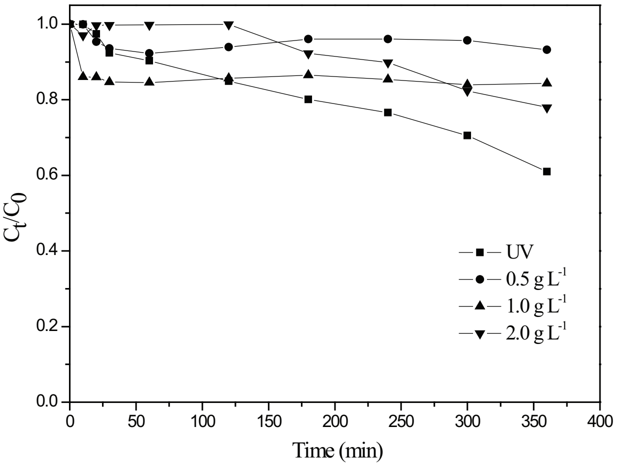


Fig. 1. The effect of NIO dosage on the photodegradation of 10^{-4} M 2,4-DCP under UV irradiation at pH 8.4.

was seen to be 16% in 360 min. For the two systems of radiation it is deduced that NIO was practically inactive as catalyst for degradation of 2,4-DCP. The addition of NIO would retard the reaction due to light attenuation.

Using solar light only as source of photons, it was found that, 2,4-DCP was photolyzed by 59% in 360 min due to the maximum absorbance wavelengths of 2,4-DCP 284 nm. The wavelength of solar radiation received by the earth is above 290 nm. In the presence of solar light and 1.0 g L^{-1} of NIO, the degradation efficiency of 2,4-DCP was significantly increased as compared with photolysis. More than 90% of 2,4-DCP was removed after 360 min of reaction time. The photoinduced degradation is due to the reaction with hydroxyl radicals.

Although the light sources differ in irradiation intensities, wavelengths and irradiation ways that cannot be compared directly, However, the photodegradation of 2,4-DCP by solar light was confirmed by these results. The band gap of NIO is 2.2 eV which corresponds to a wavelength of 560 nm. Thus, NIO absorbs light in the visible part of the solar spectrum (wavelength < 560 nm). Excitation of NIO by solar radiation may generate electron–hole pairs by promotion of an electron from the valence to conduction band [7,31]. The excited electrons are further transferred to oxygen to form hydroxyl radicals as described by Eqs. (1)–(3). 2,4-DCP in the reaction solution is then attacked by the hydroxyl radicals to be degraded. The absence of adsorption of 2,4-DCP on the surface of NIO eliminates the possibility of the direct oxidation by surface generated holes h$^+$.

$$\mathrm{Fe_2O_3} + h\nu \rightarrow \mathrm{h}^+ + \mathrm{e}^- \tag{1}$$

$$\mathrm{O_2} + \mathrm{e}^- \rightarrow \mathrm{O}_2^{\bullet -} \tag{2}$$

$$\mathrm{O}_2^{\bullet -} + 2\mathrm{H}^+ \rightarrow 2\mathrm{HO}^{\bullet} \tag{3}$$

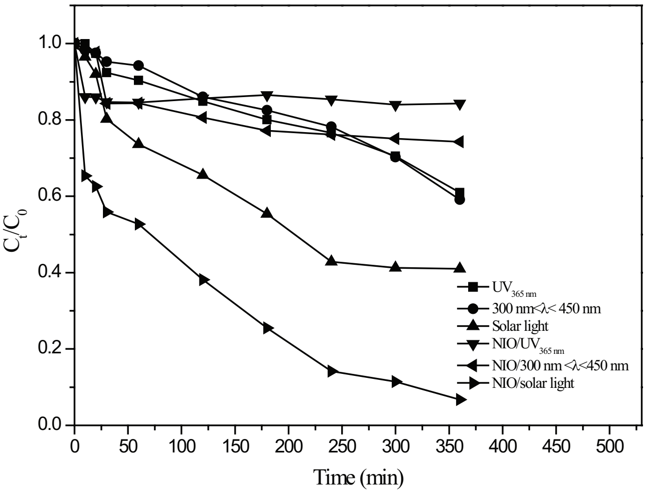


Fig. 2. The effect of light source on the photodegradation of 10^{-4} M 2,4-DCP by using 1.0 g L^{-1} NIO at pH 8.4.

3.4. Effect of carboxylic acids on 2,4-DCP degradation rate by NIO/UV-A system

The simultaneous presence of iron oxides, UV-A radiation and carboxylic acids is known to accelerate the degradation of organics in water [14,32–34]. Heterogeneous photodegradation of 2,4-DCP using NIO (1 g L^{-1}) combined with five carboxylic acids under UV-A irradiation was conducted. The initial concentration of 2,4-DCP was 10^{-4} M and that of all carboxylic acids was 5 × 10^{-3} M.

It could be seen from Fig. 3 that the presence of oxalic acid allows the highest photocatalytic oxidation rates and total conversion of 2,4-DCP was achieved in about 150 min when oxalic acid was present. The adsorption of oxalic acid contributes to the photodegradation of 2,4-DCP because the photoactive Fe(III)–oxalate complexes that leads the generation of active species (H_2O_2 and HO$^\bullet$) are formed by the oxalic acid adsorption process [13]. A slight positive effect on 2,4-DCP removal when citric acid was present. On the other hand the addition of malic, malonic and tartaric acid did not cause any effect on 2,4-DCP degradation nor Fe(II) formation. This means that Fe(III)–carboxylate complexes do not absorb in the UV region and, as a consequence the photo-Fenton reaction cannot generate enough hydroxyl radicals because Fe(II) and oxidants like H_2O_2 are not produced in our experimental conditions. Safarzadeh-Amiri et al. [35] reported that Fe(III)–oxalate has a high molar absorption coefficient for wavelengths above 200 nm, absorbs light strongly at longer wavelengths up to 500 nm. The absorption of light by Fe(III)–oxalate complexes results in the electron transfer from the oxalate to the central ferric and produces a ferrous ions, H_2O_2 and hydroxyl radicals with a high quantum. Other Fe(III)–polycarboxylate complexes may not have spectral characteristics similar to those of ferrioxalate, and generally have much lower and wavelength dependent quantum yields as compared with ferrioxalate [36]. The influence of these ligands on initial velocity V_0 (2,4-DCP) in the Fe(III)–carboxylate/UV systems followed the sequence of oxalate > without ligand >

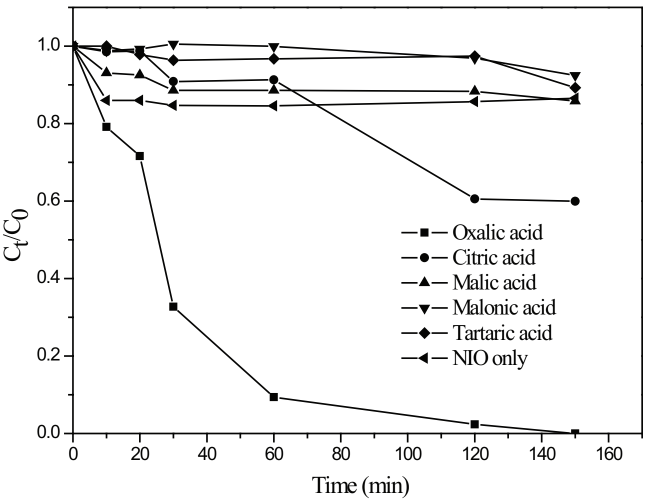


Fig. 3. The effect of 5 × 10^{-3} M oxalic, citric, malic, malonic and tartaric acids on the degradation of 2,4-DCP with an initial concentration of 10^{-4} M, in the presence of NIO with the dosage of 1.0 g L^{-1} under UV irradiation.

malate > tartrate > malonate > citrate. The initial velocities are displayed in Table 2.

For a photochemical process involving iron oxide and polycarboxylate, formation of Fe–carboxylate complexes on the surface of iron oxide and in the solution is indispensable to the final formation of •OH. Iron oxides and polycarboxylic acids can form complexes on the surface of iron oxides via ligands [37]. Rodríguez et al. [38] reported that the effect of the different carboxylic acids can be explained taking into account their acidity and their capacity of forming Fe(III) complexes. The acidity constants (pKa_1) were 1.23, 3.09, 3.4, 2.85 and 3.03, while pKa_2 constants were 4.19, 4.75, 5.11, 5.69 and 4.45 for oxalic, citric, malic, malonic and tartaric acid, respectively. Fe(II) dissolved from the Fe(III)–carboxylate complexes might be an indicator of the interaction of iron oxide and polycarboxylic acids. The studies of Li et al. [23] suggested that short-chain dicarboxylic acids are able to coordinate easily with iron oxide to form Fe(III)–carboxylate complexes with a higher photochemical activity than that with a longer carbon chain.

Fig. 4 shows the variation of Fe(II) concentration vs. reaction time. The results indicated that generation of Fe(II) depended on the kind of polycarboxylic acids. As shown in Fig. 4, NIO was photodissolved and the concentration of Fe(II) was increased on prolonging the reaction time for oxalic acid. By contrast, no iron ion was detected in the presence of citric, tartaric, malonic and malic acid.

3.5. Effect of carboxylic acids on 2,4-DCP degradation rate by NIO/solar light system

When both 5 × 10^{-3} M carboxylic acids and 1.0 g L^{-1} NIO were added into the 2,4-DCP solution to form the photo-Fenton-like system under solar light (Fig. 5), the removal percentage of 2,4-DCP was achieved by 53%, 73%, 90%, 96% and 100% after 240 min reaction. The efficiency of the iron–carboxylate complex to remove 2,4-DCP presents the following order: Fe(III)–oxalic > Fe(III)–citric > Fe(III)–tartaric > Fe(III)–malic > Fe(III)–malonic. The results showed that NIO, carboxylic acids and solar light all play most important roles in the 2,4-DCP degradation reaction. The 2,4-DCP photodegradation should be greatly enhanced in the cooperation of NIO, carboxylate and solar light. This improvement in efficiency was mainly due to the fact that Fe(III)–carboxylate complex formed could absorb solar light and rapidly photolyze, generated hydroxyl radicals $HO^{\bullet}$ by the Fenton process.

Fig. 6 showed the variation of Fe(II) concentration vs. reaction time. During the photoreaction, NIO would be

Table 2
Initial velocity of 2,4-DCP disappearance ([2,4-DCP] = 10^{-4} M, [carboxylic acids] = 5 × 10^{-3} mol L^{-1}, [NIO] = 1 g L^{-1}), rate percentage (obtained for a reaction time of 150 min)

Carboxylic acids	Rate (%)	V_0 (mol L^{-1} min^{-1})
Oxalic acid	100	2.087 × 10^{-6}
NIO only	16	1.399 × 10^{-6}
Malic acid	15	6.903 × 10^{-7}
Tartaric acid	11	2.144 × 10^{-7}
Citric acid	40	1.471 × 10^{-7}
Malonic acid	7	1.143 × 10^{-7}

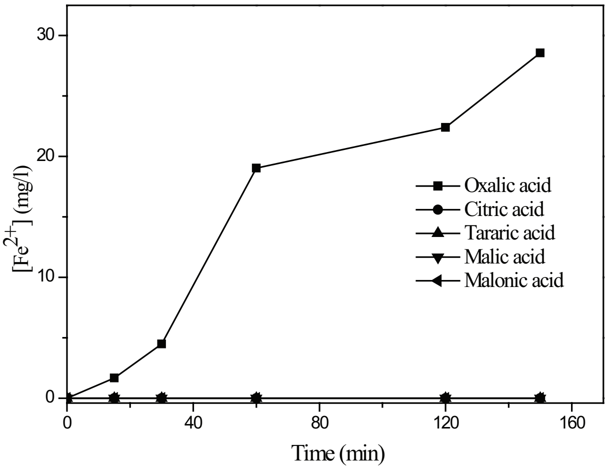


Fig. 4. The concentration of Fe(II) vs. reaction time in NIO–carboxylic acid system under UV irradiation.

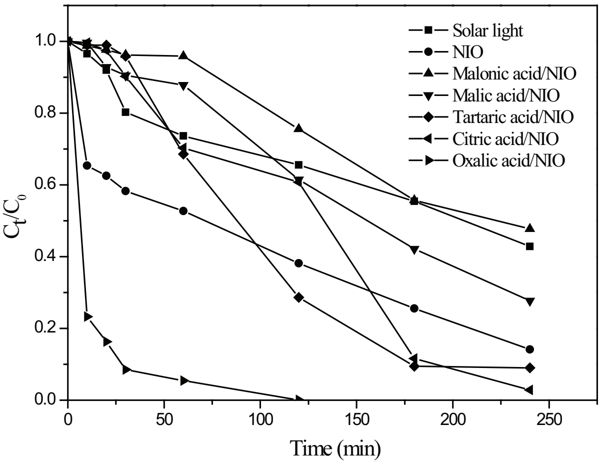


Fig. 5. The effect of 5 mM oxalic, citric, malic, malonic and tartaric acids on the degradation of 2,4-DCP with an initial concentration of 10^{-4} M, in the presence of NIO with the dosage of 1.0 g L^{-1} under solar light.

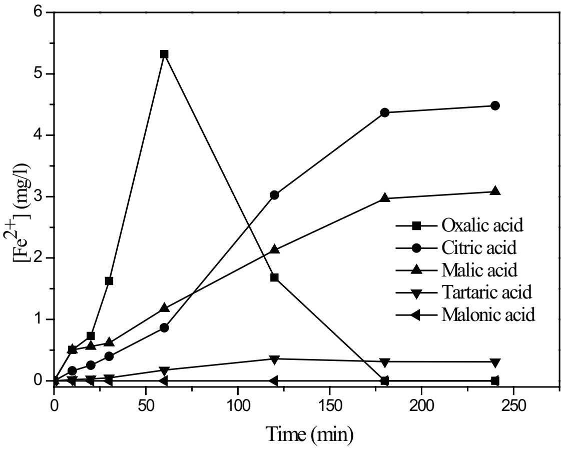


Fig. 6. The concentration of Fe(II) vs. reaction time in NIO–carboxylic acid system under solar light.

photodissolved with the 2,4-DCP degradation. Dissolved iron was increased gradually from 0 to 60 min and then decreased along with reaction time when oxalic acid was added. By contrast, the concentration of Fe(II) was increased greatly on prolonging the reaction time for citric, tartaric and malic acid. NIO did not generate Fe(II) with malonic acid due to different complexation abilities. For the NIO–carboxylic acids system the positive effect of solar light to increase iron leaching can be explained through the formation of Fe(III)–carboxylate (malate, citrate, tartrate and oxalate) complexes that photoreduce to yield radicals and Fe(II). The importance of iron leaching has been considered to explain the photodegradation of 2,4-DCP.

Iron oxides and polycarboxylic acids can form Fe(III)–carboxylate complex on the surface or in the solution. Photolysis of Fe(III)–polycarboxylate complexes may result in oxidative degradation of the carboxylate ligand and reduction of the metal center to Fe(II) [20]. In the presence of dissolved oxygen, H_2O_2 is formed from the photodegradation of organic carboxylic acid [13,19].

The photochemical process in the presence of iron oxide and oxalate together has been described in detail [15,19,39]. Generally, oxalic acid is first adsorbed on the surface of iron oxide to form iron oxide–oxalate complexes of $[\equiv Fe(III)(C_2O_4)_n]^{3-2n}$ (Eq. (4)), which can be excited to form a series of radicals including oxalate radical $(C_2O_4)^{\bullet-}$, carbon-centered radical $(CO_2)^{\bullet-}$, superoxide ion $(O_2^{\bullet-})$, $^{\bullet}OOH$. In acidic solution Fe^{2+} reacts with $O_2^{\bullet-}$ to form H_2O_2 and Fe^{3+} as described by Eq. (10). Fe^{2+} reacts with H_2O_2 to form Fe^{3+} and hydroxyl radical $HO^{\bullet}$ as described by Eq. (11).

$$\text{Iron oxide} + nH_2C_2O_4 \rightarrow \equiv Fe[C_2O_4)_n]^{(2n-3)-} \tag{4}$$

$$\equiv Fe[C_2O_4)_n]^{(2n-3)-} + hv \rightarrow Fe(C_2O_4)_2^{2-} / \equiv Fe(C_2O_4)_2^{2-} + C_2O_4^{\bullet-} \tag{5}$$

$$Fe^{III}[C_2O_4)_n]^{3-2n} + hv \rightarrow Fe^{II}[C_2O_4)_{(n-1)}]^{4-2n} + C_2O_4^{\bullet-} \tag{6}$$

$$C_2O_4^{\bullet-} \rightarrow CO_2 + CO_2^{\bullet-} \tag{7}$$

$$CO_2^{\bullet-} + O_2 \rightarrow CO_2 + O_2^{\bullet-} \tag{8}$$

$$O_2^{\bullet-} + Fe^{3+} \rightarrow Fe^{2+} + O_2 \tag{9}$$

$$O_2^{\bullet-} + nH^+ + Fe^{2+} \rightarrow Fe^{3+} + H_2O_2 \tag{10}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet} \tag{11}$$

The above experimental results confirmed that the Fe(III)–oxalate complex had a higher photochemical activity under UV and solar light than other Fe(III)–carboxylate complexes. This carboxylic acid was then applied in this work to evaluate the photochemical activities of the photo-Fenton-like system and the effect of Fe(III)–oxalate species on the degradation of 2,4-DCP.

3.6. *2,4-DCP photodegradation in NIO–oxalic acid systems*

3.6.1. *The effect of NIO dosage*

Since the photoreaction of 2,4-DCP was carried out in suspension of NIO powder, the oxide content is thought to be an important experimental parameter because it will influence the penetration of the UV light into the sample. Fig. 7 shows the dependence of 2,4-DCP degradation on the dosage of NIO in the presence of oxalic acid with an initial concentration of 5×10^{-3} M and pH 2.2.

The combination of NIO with 5.0 mM oxalate solution without UV illumination (in the dark) produced only 2% degradation of 2,4-DCP after 150 min of reaction. UV illumination of an oxalate solution with different dosages of NIO showed very fast 2,4-DCP photodegradation. It can be observed that the photodegradation of 2,4-DCP in NIO–oxalate system depended strongly on the dosage of NIO and an optimal dosage of NIO was 1.0 g L^{-1}, at which the first-order kinetic constant (k) reached the maximal value of 3.27×10^{-2} min^{-1}. However, an increase in photocatalyst dose leads to decrease in the removal percentage of the 2,4-DCP. More $[\equiv Fe(III)(C_2O_4)_n]^{(2n-3)-}$ or $[Fe(III)(C_2O_4)_n]^{(2n-3)-}$ will be formed in the presence of more NIO and eventually more radicals $HO^{\bullet}$ can be produced to lead to a higher degree of 2,4-DCP degradation [40]. On the other hand, excessive dosage of NIO will limit the penetration of UV light in the solution and decrease the formation of $HO^{\bullet}$.

3.6.2. *The effect of initial concentration of 2,4-DCP*

To investigate the effect of initial concentration of 2,4-DCP on its degradation, a set of experiments were carried out with initial concentration of 2,4-DCP varying from 10^{-4} to 5×10^{-4} M in the presence of oxalic acid with an initial

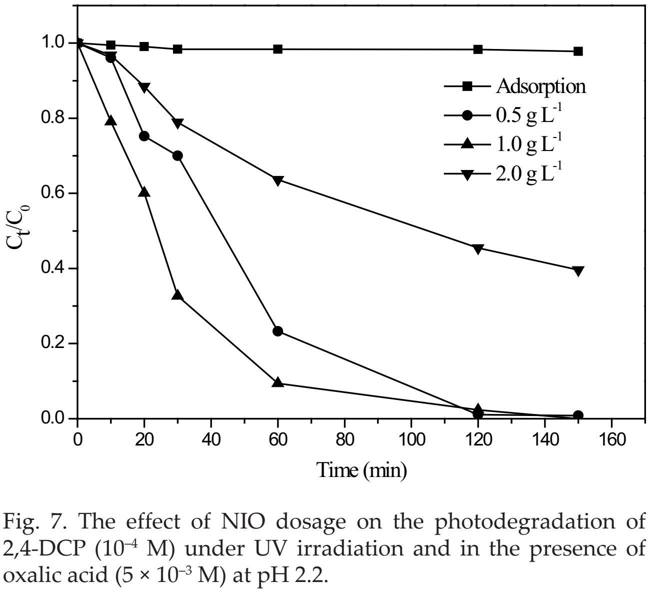


Fig. 7. The effect of NIO dosage on the photodegradation of 2,4-DCP (10^{-4} M) under UV irradiation and in the presence of oxalic acid (5×10^{-3} M) at pH 2.2.

concentration of 5 × 10^{-3} M by using NIO with the dosage of 1.0 g L^{-1} under UV irradiation. The results are shown in Fig. 8. The photocatalytic degradation of 2,4-DCP by hydroxyl radical was described as first-order kinetic model, which is expressed as $k = -\ln(C_t/C_0)$, where C_0 and C_t are the concentration of 2,4-DCP at time 0 and t, respectively.

The pseudo-first-order degradation rate constant of 2,4-DCP decreased when the initial concentrations of 2,4-DCP increased from 10^{-4} to 5 × 10^{-4} M, this is due to the competition between 2,4-DCP and its reaction by-products for generated hydroxyl radical and such competition becomes more pronounced at higher concentrations. This can be justified by the oxidative intermediates that have been identified in the ultrahigh performance liquid chromatography coupled high-resolution mass spectrometry (UPLC–HR/MS) analysis (to be discussed later in the section on the reaction mechanism). The dependence of first-order kinetic constant (k) on the initial concentration of 2,4-DCP is listed in Table 3. The k values were 3.27 × 10^{-2} (R^2 = 0.970), 1.2 × 10^{-2} (R^2 = 0.990) and 0.38 × 10^{-2} (R^2 = 0.987) min^{-1} when the initial concentration of 2,4-DCP were 10^{-4}, 2 × 10^{-4} and 5 × 10^{-4} M, respectively.

3.6.3. The effect of the initial concentration of oxalic acid

It is believed that the initial concentration of oxalate (C_0^{ox}) should be a key factor to affect the degradation of 2,4-DCP in aqueous suspension under UV light. To study the effect of the (C_0^{ox}) on 2,4-DCP photodegradation, the first set of experiments with initial 2,4-DCP concentration of 10^{-4} M and NIO dosage of 1 g L^{-1} was carried out, followed by the experiments on different initial concentrations of oxalate in the range of 10^{-3}–7 × 10^{-3} M under UV light irradiation. The results in Fig. 9 show that the degradation of 2,4-DCP was very strongly accelerated by oxalic acid. The optimal concentration for the enhancement was about 5 × 10^{-3} M. At higher concentrations the rate of degradation of 2,4-DCP decreased.

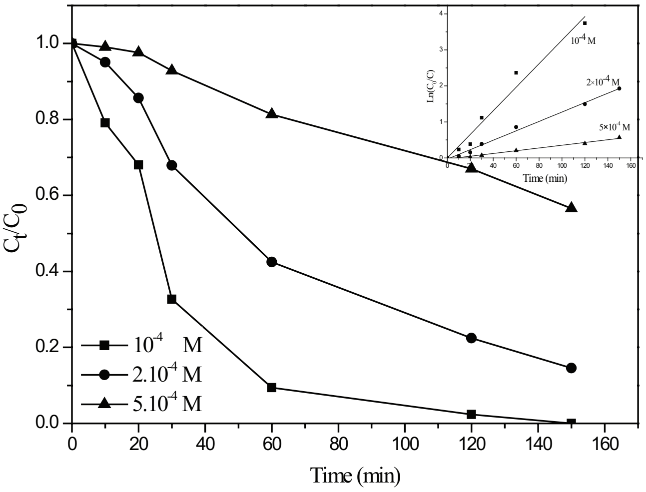


Fig. 8. Effect of initial concentration of 2,4-DCP on the photodegradation of 2,4-DCP (initial conditions: 5 × 10^{-3} M oxalic acid, 1 g L^{-1} NIO) under UV irradiation.

Table 3
Dependence of first-order kinetic constant (k) on the initial concentration of 2,4-DCP

Initial concentration of 2,4-DCP (M)	k (min^{-1})	R^2
10^{-4}	3.27 × 10^{-2}	0.970
2 × 10^{-4}	1.22 × 10^{-2}	0.990
5 × 10^{-4}	0.38 × 10^{-2}	0.987

The first-order kinetic constant (k) for 2,4-DCP degradation increased with increasing (C_0^{ox}) from 0.0 to 5 × 10^{-3} M, at which k reached 3.27 × 10^{-2} min^{-1}. However, the first-order kinetic constant for 2,4-DCP degradation decreased when the (C_0^{ox}) was 7 × 10^{-3} M and the k value was 1.27 × 10^{-2} min^{-1}.

These results clearly show that the presence of high concentration of oxalic acid has a negative effect on the photodegradation of 2,4-DCP. This may be attributed to the competitive reaction of oxalic acid with generated hydroxyl radical $^{\bullet}$OH together with 2,4-DCP [14,41]. Thus, less of the generated $^{\bullet}$OH would be available for 2,4-DCP photodegradation.

3.6.4. The effect of isopropanol

In order to determine if hydroxyl radicals are involved in the photodegradation of the 2,4-DCP, 2.0% of isopropanol was added to NIO–2,4-DCP suspension in the presence of oxalate and under light irradiation. Actually, isopropanol is usually used as a hydroxyl radicals scavenger, the rate constant of reaction of these radicals on isopropanol being close to 2 × 10^9 M^{-1} s^{-1} [42]. The results showed that the photodegradation of 2,4-DCP can be directly attributed to the attack of $^{\bullet}$OH radicals as demonstrated by the inhibition of the degradation during irradiation at 365 nm in the presence of isopropanol compared with the photodegradation of 2,4-DCP in the absence of this alcohol (Fig. 10).

3.6.5. The effect of initial pH value

To investigate the effect of initial pH value on the photodegradation of 2,4-DCP, a set of experiments were

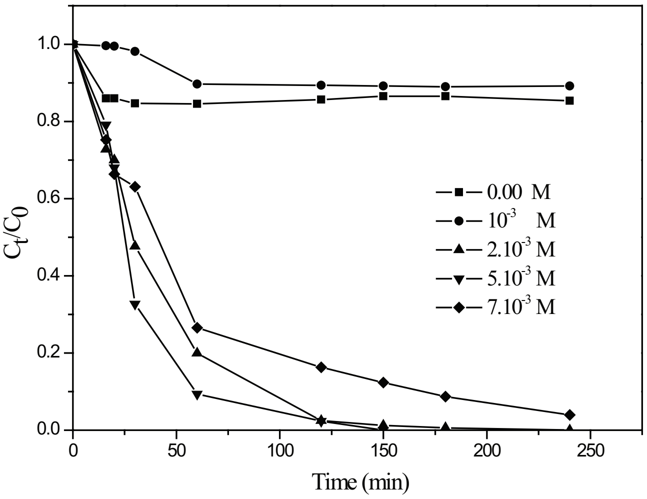


Fig. 9. Effect of the initial concentration of oxalic acid on the 2,4-DCP degradation with the initial concentration of 10^{-4} M under UV irradiation by using NIO.

carried out under different initial pH, which was adjusted by titrating NaOH or $HClO_4$ before reaction, with initial concentration of 2,4-DCP of 10^{-4} M and NIO dosage of 1.0 g L^{-1} and the optimal initial concentration of oxalic acid was 5 × 10^{-3} M. The results showed (Fig. 11) that 2,4-DCP photodegradation should depend strongly on pH in the NIO–oxalate system. The optimal initial pH value for the photodegradation was at 2.2–3.5. No degradation occurred at pH higher than 6.

The iron species in solution are strongly dependent on pH. When pH was up to 6, the Fe^{3+} and Fe^{2+} almost cannot exist in the solution and the predominant Fe(III) and Fe(II) species were $Fe(OH)_2$ and $Fe(OH)_3$ as the precipitate, which might hardly be photoactive. As a result, the generation of active species, such as H_2O_2 and $HO^{\bullet}$, is inhibited at higher initial pH.

Balmer and Sulzberger [19] reported that the effect of pH can be explained by the type of Fe(III)–oxalate complexes. At an initial pH of 3–4, $[Fe(III)(C_2O_4)_2]^-$ and $[Fe(III)(C_2O_4)_3]^{3-}$ are the main Fe(III)–oxalate species and are highly photoactive, generating more $HO^{\bullet}$. So the initial pH of the oxalate solution was concluded to be a very important factor in the photodegradation of 2,4-DCP.

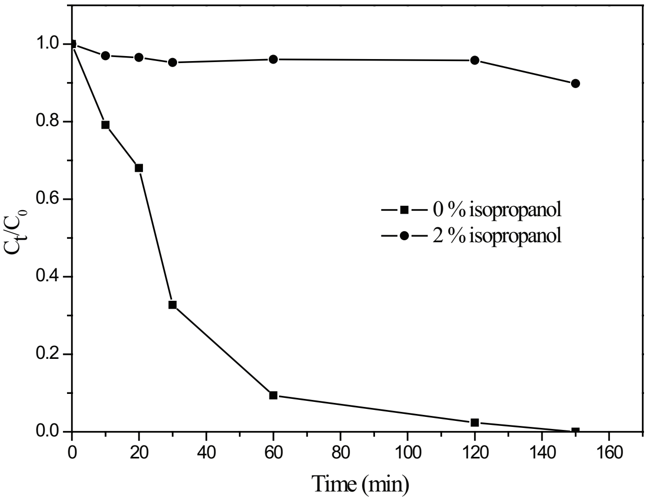


Fig. 10. Effect of isopropanol on the photodegradation of 2,4-DCP in the presence of NIO (1 g L^{-1}) and oxalic acid (5 × 10^{-3} M).

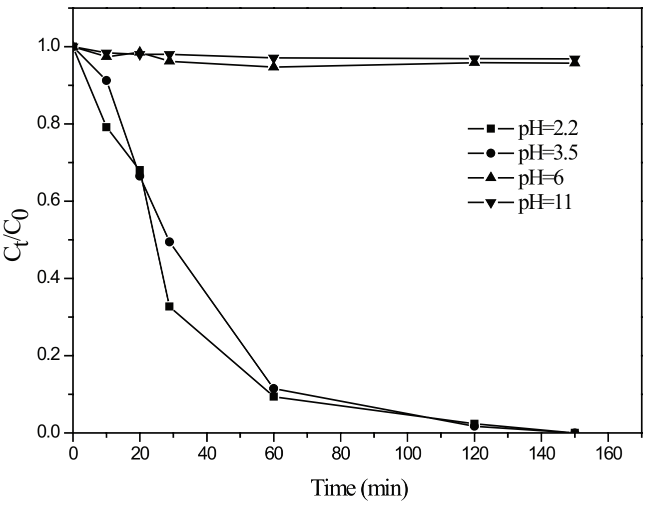


Fig. 11. Effect of pH on the photodegradation of 2,4-DCP in the presence of NIO (1 g L^{-1}) and oxalic acid (5 × 10^{-3} M).

3.6.6. Proposed reaction mechanism

As a result of UV-irradiation of 2,4-DCP in NIO–oxalate system, several aromatic intermediates were detected.

According to UPLC–HR/MS analyses, the detected aromatic intermediates were found to be chlorohydroquinone, 3,5-dichlorocatechol, 4,6-dichlororesorcinol, 3,5-dichloro-2-hydroxy-1,4-benzoquinone, 2-chloro-6-hydroxy-1,4-benzoquinone and some other trace substances. The mass spectra of all identified intermediates were summarized in Table 4. All of them appeared at lower retention times than 2,4-DCP, which means that they had a more hydroxylated structure than the original molecule after photocatalytic degradation. The orientation of hydroxylation is consistent with the directing influence of phenol function [4].

Hydroxyl radical produced from photolysis of Fe(III)–oxalate complex are responsible for the transformation of 2,4-DCP by attacking 2,4-DCP in the following ways.

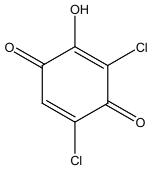
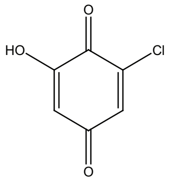
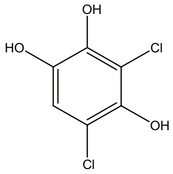
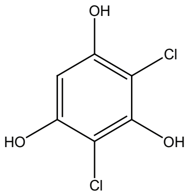
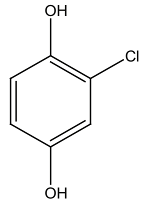
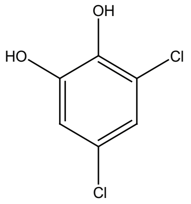
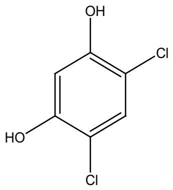
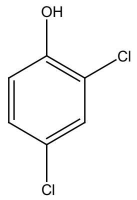
3.6.6.1. By substituting an chlorine atom The hydroxyl radical may replace the chlorine atom of 2,4-DCP at the para-position to form 2-chlorohydroquinone (P1), as indicated by two peaks exhibiting a 3:1 cluster at $m/z = 143$ $[M-H]^-$, 145 $[M+2-H]^-$, in the chromatograph under negative ionization. The para site was the preferred location for radical collisions on the 2,4-DCP because of the steric effect [43,44]. The resulting 2-chlorohydroquinone may dissociate two hydrogen atoms to yield 2-chloro-1,4-benzoquinone, but this intermediate was not detectable because hydroxyl radical attacks it rapidly at the ortho site to form 2-chloro-6-hydroxy-1,4-benzoquinone (P2) $m/z = 159$ $[M-H]^-$, 161 $[M+2-H]^-$).

3.6.6.2. By hydroxylation of the aromatic ring 2,4-DCP can be hydroxylated by HO• addition reaction onto the aromatic ring, leading two isomers of 3,5-dichlorocatechol (P3), and 4,6-dichlororesorcinol (P4) as indicated by three peaks exhibiting a 9:6:1 cluster at $m/z = 177$ $[M-H]^-$, 179 $[M+2-H]^-$ and 181 $[M+4-H]^-$ which have also been observed in several researches [4,44]. P3 and P4 would then undergo further hydroxylation to form 3,5-dichloro-2-hydroxy-1,4-hydroquinone (P5), 4,6-dichloro-5-hydroxy-resorcinol (P6) as detected at $m/z = 193$ $[M-H]^-$, 195 $[M+2-H]^-$ and 197 $[M+4-H]^-$.

P5 (3,5-dichloro-2-hydroxy-1,4-hydroquinone) may separate two hydrogen atoms to yield its corresponding 3,5-dichloro-2-hydroxy-1,4-benzoquinone (P7) as detected at $m/z = 191$ $[M-H]^-$, 193 $[M+2-H]^-$ and 195 $[M+4-H]^-$. The formation of P7 in a photo-Fenton-like oxidation was also observed by Chu et al. [24].

Based on the experimental results analyzed above and taking into account the information reported in the literature [24,44], we can propose a photodegradation mechanism of 2,4-DCP in the presence NIO–oxalate (Fig. 12).

Table 4
Intermediates detected in photodegradation of 2,4-DCP

Retention time (min)	Intermediate	Detected mass (*m*/*z*)	Structure
6.33	3,5-Dichloro-2-hydroxy-1,4-benzoquinone	191/193/195	
6.81	2-Chloro-6-hydroxy-1,4-benzoquinone	159/161	
6.9	3,5-Dichloro-2-hydroxy-1,4-hydroquinone	193/195/197	
8.15	4,6-Dichloro-5-hydroxy-resorcinol	193/195/197	
8.23	2-Chlorohydroquinone	143/145	
8.93	3,5-Dichlorocatechol	177/179/181	
9.32	4,6-Dichlororesorcinol	177/179/181	
10.16	2,4-Dichlorophenol	161/163/165	

3.6.7. Mineralization

Complete degradation of 2,4-DCP does not imply that the 2,4-DCP was completely oxidized into CO_2, H_2O and inorganic ions. It is known that reaction intermediates can form during the oxidation of pollutant and some of them could be long-lived and even more toxic than the parent compounds. Therefore, it is necessary to realize the mineralization of 2,4-DCP. In this study, the mineralization of 2,4-DCP was investigated by COD analysis. The experiments were performed under the standard experimental conditions (2,4-DCP concentration = 10^{-4} M, oxide content = 1 g L^{-1}, oxalic acid concentration = 5 × 10^{-3} mol L^{-1} and pH = 2.2) under UV-A light irradiation. Fig. 13 shows that complete mineralization of 2,4-DCP was achieved in 11 h. The improvement of COD removal can be understood by the higher production of $HO^\bullet$ radicals due the photo-Fenton-like reaction.

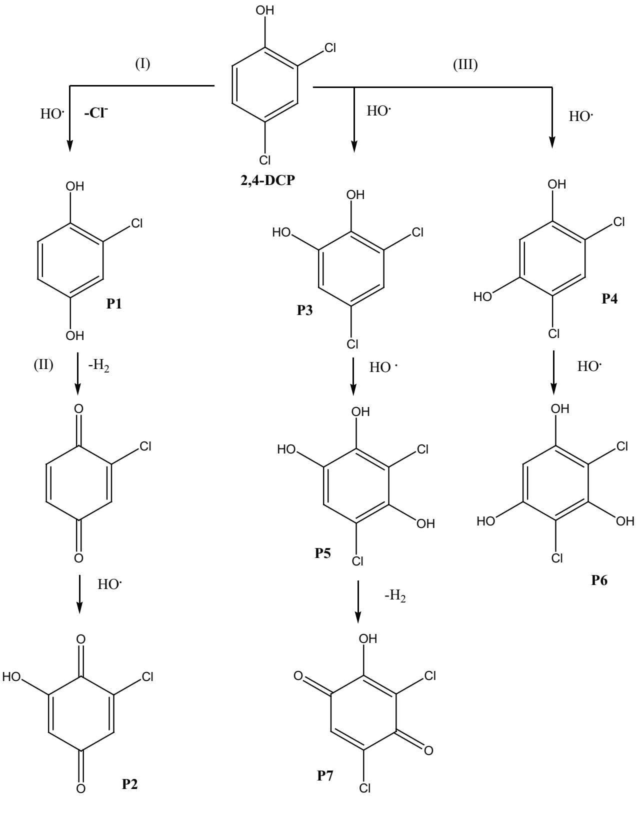


Fig. 12. Proposed mechanism and degradation pathway of 2,4-DCP in NIO/oxalate/UV system.

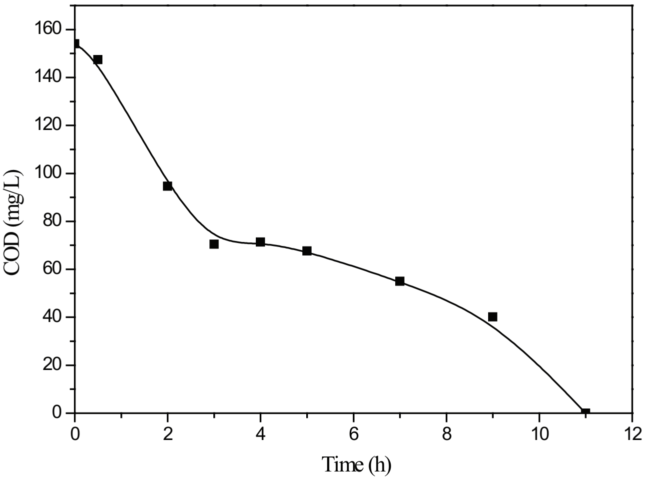


Fig. 13. Effect of NIO and oxalic acid on COD removal of 2,4-DCP under UV radiation.

Zhang et al. [45] reported that the aromatic intermediates would be further oxidized to organic acids by $HO^\bullet$ such as oxalic, acetic and formic acids until mineralize to CO_2 completely.

$$HO^\bullet + 2,4 - DCP \rightarrow \text{intermediates} \tag{12}$$

$$HO^\bullet + \text{intermediates} \rightarrow CO_2 + H_2O + HCl \tag{13}$$

4. Conclusions

Results of the present work suggest that the photodegradation of 2,4-DCP induced by an NIO was strongly wavelength dependent. Photocatalytic property of NIO was evaluated by degradation of 2,4-DCP under solar light. 2,4-DCP was not removed under the condition of using only NIO at 365 nm.

The NIO–oxalic acid system showed the highest photochemical efficiency under UV irradiation and solar light compared than other carboxylic acids used. 2,4-DCP degradation depended significantly on various factors including the dosage of NIO, initial concentration of oxalic acid, initial concentration of 2,4-DCP and initial pH value in NIO–oxalate system under UV-A light irradiation.

The application of solar light allowed degradation rates higher than UV-A radiation in NIO–carboxylic acid system. This can be due to the higher absorptivity of Fe(III)–carboxylate (oxalate, citrate, tartrate and malate) complexes in the solar system. Considerable photodecomposition ability by solar light is an advantage of this system under practical conditions.

Acknowledgment

The authors appreciate the financial support of the Ministry of Higher Education and Scientific Research of Algeria.

References

[1] Z. Zhang, Q. Shen, N. Cissoko, J. Wo, X. Xu, Catalytic dechlorination of 2,4-dichlorophenol by Pd/Fe bimetallic nanoparticles in the presence of humic acid, J. Hazard. Mater., 182 (2010) 252–258.

[2] L. Liu, F. Chen, F. Yang, Y. Chen, J. Crittenden, Photocatalytic degradation of 2,4-dichlorophenol using nanoscale Fe/TiO_2, Chem. Eng. J., 181 (2012) 189–195.

[3] L. Ren, J. Zhang, Y. Li, C. Zhang, Preparation and evaluation of cattail fiber-based activated carbon for 2,4-dichlorophenol and 2,4,6-trichlorophenol removal, Chem. Eng. J., 168 (2011) 553–561.

[4] T. Sehili, P. Boule, J. Lemaire, Photocatalysed transformation of chloroaromatic derivatives on zinc oxide IV: 2,4-dichlorophenol, Chemosphere, 22 (1991) 1053–1062.

[5] W.H. Glaze, J.W. Kang, D.H. Chapin, The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation, Ozone Sci. Eng., 9 (1987) 335–352.

[6] U. Schwertmann, R.M. Cornell, Iron Oxides in the Laboratory: Preparation and Characterization, Wiley–VCH, Weinheim, 1991.

[7] J.K. Leland, A.J. Bard, Photochemistry of colloidal semiconducting iron oxide polymorphs, J. Phys. Chem., 91 (1987) 5076–5083.

[8] C. Kormann, D.W. Bahnemann, M.R. Hoffmann, Environmental photochemistry: is iron oxide (hematite) an active photocatalyst? A comparative study: α-Fe_2O_3, ZnO, TiO_2, J. Photochem. Photobiol., A, 48 (1989) 161–169.

[9] K.M. Cunningham, M.C. Goldberg, E.R. Weiner, Mechanisms for aqueous photolysis of adsorbed benzoate, oxalate, and succinate on iron oxyhydroxide (goethite) surfaces, Environ. Sci. Technol., 22 (1988) 1090–1097.

[10] S. Belaidi, T. Sehili, L. Mammeri, K. Djebbar, Photodegradation kinetics of 2,6-dimetylphenol by natural iron oxide and oxalate in aqueous solution, J. Photochem. Photobiol., A, 237 (2012) 31–37.

[11] Y. Mameri, N. Debbache, M.e.m. Benacherine, N. Seraghni, T. Sehili, Heterogeneous photodegradation of paracetamol using Goethite/H_2O_2 and Goethite/oxalic acid systems under artificial and natural light, J. Photochem. Photobiol., A, 315 (2016) 129–137.

[12] C.L. Hsueh, Y.H. Huang, C.Y. Chen, Novel activated alumina-supported iron oxide-composite as a heterogeneous catalyst for photooxidative degradation of reactive black 5, J. Hazard. Mater., 129 (2006) 228–233.

[13] P. Mazellier, B. Sulzberger, Diuron degradation in irradiated, heterogeneous iron/oxalate systems: the rate-determining step, Environ. Sci. Technol., 35 (2001) 3314–3320.

[14] X. Wang, C. Liu, X. Li, F. Li, S. Zhou, Photodegradation of 2-mercaptobenzothiazole in the γ-Fe_2O_3/oxalate suspension under UVA light irradiation, J. Hazard. Mater., 153 (2008) 426–433.

[15] C. Siffert, B. Sulzberger, Light-induced dissolution of hematite in the presence of oxalate. A case study, Langmuir, 7 (1991) 1627–1634.

[16] C. Liu, F. Li, X. Li, G. Zhang, Y. Kuang, The effect of iron oxides and oxalate on the photodegradation of 2-mercaptobenzothiazole, J. Mol. Catal. A: Chem., 252 (2006) 40–48.

[17] T. Kayashima, T. Katayama, Oxalic acid is available as a natural antioxidant in some systems, Biochim. Biophys. Acta, 1573 (2002) 1–3.

[18] X. Feng, S. Ding, F. Xie, Photochemical degradation of dimethyl phthalate by Fe(III)/tartrate/H_2O_2 system, Bull. Korean Chem. Soc., 33 (2012) 3686–3690.

[19] M.E. Balmer, B. Sulzberger, Atrazine degradation in irradiated iron/oxalate systems: effects of pH and oxalate, Environ. Sci. Technol., 33 (1999) 2418–2424.

[20] T.D. Waite, F.M. Morel, Photoreductive dissolution of colloidal iron oxides in natural waters, Environ. Sci. Technol., 18 (1984) 860–868.

[21] W. Miller, L. Zelazny, D. Martens, Dissolution of synthetic crystalline and noncrystalline iron oxides by organic acids, Geoderma, 37 (1986) 1–13.

[22] S.O. Lee, T. Tran, B.H. Jung, S.J. Kim, M.J. Kim, Dissolution of iron oxide using oxalic acid, Hydrometallurgy, 87 (2007) 91–99.

[23] F.-b. Li, J.-j. Chen, C.-s. Liu, J. Dong, T.-x. Liu, Effect of iron oxides and carboxylic acids on photochemical degradation of bisphenol A, Biol. Fertil. Soils, 42 (2006) 409–417.

[24] W. Chu, C. Kwan, K. Chan, S. Kam, A study of kinetic modelling and reaction pathway of 2,4-dichlorophenol transformation by photo-Fenton-like oxidation, J. Hazard. Mater., 121 (2005) 119–126.

[25] R.F. Pupo Nogueira, J.R. Guimarães, Photodegradation of dichloroacetic acid and 2,4-dichlorophenol by ferrioxalate/H_2O_2 system, Water Res., 34 (2000) 895–901.

[26] J. Demas, W. Bowman, E. Zalewski, R. Velapoldi, Determination of the quantum yield of the ferrioxalate actinometer with electrically calibrated radiometers, J. Phys. Chem., 85 (1981) 2766–2771.

[27] O. Thomas, N. Mazas, La mesure de la demande chimique en oxygène dans les milieux faiblement pollués, Analusis, 14 (1986) 300–302.

[28] H. Mechakra, T. Sehili, M. Kribeche, A. Ayachi, S. Rossignol, C. George, Use of natural iron oxide as heterogeneous catalyst in photo-Fenton-like oxidation of chlorophenylurea herbicide in aqueous solution: reaction monitoring and degradation pathways, J. Photochem. Photobiol., A, 317 (2016) 140–150.

[29] M.E.A. Kribéche, H. Mechakra, T. Sehili, S. Brosillon, Oxidative photodegradation of herbicide fenuron in aqueous solution by natural iron oxide α-Fe_2O_3, influence of polycarboxylic acids, Environ. Technol., 37 (2016) 172–182.

[30] F. Li, X. Li, C. Liu, T. Liu, Effect of alumina on photocatalytic activity of iron oxides for bisphenol A degradation, J. Hazard. Mater., 149 (2007) 199–207.

[31] B.C. Faust, M.R. Hoffmann, D.W. Bahnemann, Photocatalytic oxidation of sulfur dioxide in aqueous suspensions of α-Fe_2O_3, J. Phys. Chem., 93 (1989) 6371–6381.

[32] Q. Lan, F. Li, C. Liu, X.Z. Li, Heterogeneous photodegradation of pentachlorophenol with maghemite and oxalate under UV illumination, Environ. Sci. Technol., 42 (2008) 7918–7923.

[33] L. Mammeri, T. Sehili, S. Belaidi, K. Djebbar, Heterogeneous photodegradation of 1-naphthol with natural iron oxide in water: influence of oxalic acid, Desal. Wat. Treat., 54 (2015) 2324–2333.

[34] J. Lei, C. Liu, F. Li, X. Li, S. Zhou, T. Liu, M. Gu, Q. WU, Photodegradation of orange I in the heterogeneous iron oxide–oxalate complex system under UVA irradiation, J. Hazard. Mater., 137 (2006) 1016–1024.

[35] A. Safarzadeh-Amiri, J.R. Bolton, S.R. Cater, Ferrioxalate-mediated photodegradation of organic pollutants in contaminated water, Water Res., 31 (1997) 787–798.

[36] V. Balzani, V. Carassiti, Photochemistry of Coordination Compounds, Chapter 10, Academic Press, London, 1970, pp. 145–192.

[37] J.D. Filius, T. Hiemstra, W.H. Van Riemsdijk, Adsorption of small weak organic acids on goethite: modeling of mechanisms, J. Colloid Interface Sci., 195 (1997) 368–380.

[38] E.M. Rodríguez, B. Núñez, G. Fernández, F.J. Beltrán, Effects of some carboxylic acids on the Fe(III)/UVA photocatalytic oxidation of muconic acid in water, Appl. Catal., B, 89 (2009) 214–222.

[39] B.C. Faust, R.G. Zepp, Photochemistry of aqueous iron (III)-polycarboxylate complexes: roles in the chemistry of atmospheric and surface waters, Environ. Sci. Technol., 27 (1993) 2517–2522.

[40] S. Wei, L. Liu, H. Li, J. Shi, Y. Liu, Z. Shao, Photodecolourization of orange II with iron corrosion products and oxalic acid in aqueous solution, Appl. Catal., A, 417 (2012) 253–258.

[41] F. Gulshan, S. Yanagida, Y. Kameshima, T. Isobe, A. Nakajima, K. Okada, Various factors affecting photodecomposition of methylene blue by iron-oxides in an oxalate solution, Water Res., 44 (2010) 2876–2884.

[42] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\bullet$OH/$O^{\bullet-}$) in aqueous solution, J. Phys. Chem. Ref. Data, 17 (1988) 513–886.

[43] L. Xu, J. Wang, Fenton-like degradation of 2,4-dichlorophenol using Fe_3O_4 magnetic nanoparticles, Appl. Catal., B, 123 (2012) 117–126.

[44] C. Kwan, W. Chu, A study of the reaction mechanisms of the degradation of 2,4-dichlorophenoxyacetic acid by oxalate-mediated photooxidation, Water Res., 38 (2004) 4213–4221.

[45] C. Zhang, M. Zhou, G. Ren, X. Yu, L. Ma, J. Yang, F. Yu, Heterogeneous electro-Fenton using modified iron–carbon as catalyst for 2,4-dichlorophenol degradation: influence factors, mechanism and degradation pathway, Water Res., 70 (2015) 414–424.