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Effect of a modified photo-fenton procedure on the oxidative degradation of 1-naphthol in aqueous solution

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ABSTRACT/RESUME

Abstract: *The photocatalytic degradation of 1-naphthol (1-NP) using natural iron oxide (NIO) as a heterogeneous catalyst in the presence of oxalic acid was investigated under UV irradiation. The characterization of this catalyst revealed that NIOhas a mixed elemental composition and consists mainly of iron oxide (α-Fe_2O_3). This powder contains hematite as iron source and its dissolution provides Fe^{3+}cations for the photo-Fenton-like reaction in solution. The degradation rate was strongly influenced by oxygen, initial concentration of oxalic acid (C_{ox}) and 1-NP. The optimal $C_{ox}$was 1mM. The first-order kinetic constant for the degradation of 1-NP decreased with the increase in the initial concentration of 1-NP. Furthermore, the variation of pH and the concentration of Fe^{2+} during the photoreaction were also strongly dependent on the C_{ox}. The use of 1% of tertiobutanol as a scavenger confirmed the intervention of hydroxyl radicals in the photodegradation of 1 –NP. Since both oxalic acid and iron oxides are common constituents of natural waters, this investigation will give a new insight to understanding the 1-NP photodegradation in natural environment.*

I. Introduction

Water pollution by organic chemicals has been of great concern over decades [1]. 1-Naphthol, widely used as an industrial intermediate, is of a particular concern due to its acute toxicity and negative environmental impacts once released to the receiving water systems via industrial waste streams [2].Various forms of advanced oxidation processes (AOPs) have emerged as important alternatives for efficient mineralization of organic pollutants. Fenton process has its own unique advantages as an oxidizing process because its reagents are inexpensive, environmentally benign and relatively easy to transport and handle. The Fenton system involves the generation of hydroxyl radicals ($^{\bullet}OH$) which can degrade most organic compounds to carbon dioxide and water due to their high oxidation potential ($E^0 = +2.80$ V)[3].

The photochemical process that occurs with Fe^{2+}/H_2O_2/UV is called photo-Fenton and that with Fe^{3+}/H_2O_2/UV is called photo-Fenton-like. In Fenton systems, H_2O_2 is added as the direct source of $^{\bullet}OH$ [4,5].However, H_2O_2 is an acute reactive reagent and cannot stand in nature for a long time. Thisfactor limits the application of Fenton and Fenton-like systemin the remediation of organic pollutants in nature. In fact, iron oxides, oxalic acid and sunlight can form a photochemical system to give a photo-Fenton-like reaction without the addition of H_2O_2, and with much higher quantum efficiency than with $Fe(OH)^{2+}$ or iron oxides alone [6,7].

Iron oxides are a kind of natural minerals and geocatalysts, widely existing in the earth's crust and also suspending in aqueous streams, aerosol, clouds, and fogs as fine particles [8]. Major iron oxides including hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), goethite (α-FeOOH), and lepidocrocite (γ-FeOOH) show semiconductor properties with a narrow band gap of 2.0–2.3 eV and could be photoactive under solar irradiation [9]. On the other hand, oxalic acid has strong chelating ability with multivalent cations and is mainly exuded by plants in natural environment [10]. Oxalic acid is also an intermediate in the catalytic oxidation of phenol [11–14], and coumaric acid as a by-product of oil manufacturing [15].

In a word, this Fenton-like oxidation process can directly utilize natural mater (iron oxides and oxalic acid) in combination with solar energy, to decompose organic pollutants economically. It is meaningful to investigate the photodegradation of organic pollutants in the iron oxide–oxalate complex system to better understand the transformation of organic pollutants in natural surface water.In fact, the photochemistry of Fe(III)-oxalate complexes in natural aquatic environment, fog, precipitation, tropospheric aerosols and soil solution has received considerable attention over the past three decades [16–21]because iron oxide–oxalate exhibit strong ligand-to-metal charge absorption bands in the near-UV and visible region. The aims of this study were to investigate the photochemical degradation of 1-NP induced by F(III)-oxalate system and examining several factors that controlled the kinetics of 1-NP degradation.

II. Materials and methods

II.1. Reagents

All solutions were prepared with ultra-pure water (Millipore) with a resistivity of 18.2 mΩ.cm. The chemicals used in this study were 1-naphthol (99%+ Acros Organics), Oxalic acid (99.5% Prolabo), 1.10 phenantroline (Fluka analytical),sodium acetate and sulphuric acid (Panreac), Methanol (Carlo ErbaReagenti).All the chemicals were of analytical grade.

NIO is essentially constituted of hematite, it was used without any treatment; it was only washed several times with distilled water and dried at 45°C.

II.2. Irradiation procedure

The irradiation experiments were performed in a Pyrex cylindrical, reactor with a double envelopewas placed in the centre of the cylindrical stainless steel container. The photoreactor was exposed to the radiation sources composed of one low pressure mercury UV lamps type Philips HPW 125, (UV-A, λ_{max}= 365 nm). The solution was continuous magnetically stirred with a magnetic bar during irradiation to insure its homogeneity.

The reactor was first filled with the suspension containing NIOparticles. The required volume of mixed solution of 1-NP and oxalic acid were then added. The mixture was rapidly fed. The samples withdrawn at different reaction times were filtered with cellulose acetate filters (0.45 µm) to separate NIO particles. At different time intervals during the irradiation, samples were collected and analyzed by HPLC. 1-NP was monitored at 290 nm by HPLC (shimadzu). The mobile phase was a mixture of Methanol/water (60/40 v/v) was operated at a flow-rate of 1 mL min^{-1} using Supelco, C18 column (5 µm, 250 mm×4.6 mm i.d). The solution pH was measured by means of an HANNA Instruments 8521 pH-meter. The Fe(II) concentration was measured by using a complexometric method with 1,10 phenanthroline.The red-formed complex was dosed after 1 h by UV–VIS at 510 nm. The molar absorption coefficient at 510 nm ε is equal to 11153.63 M^{-1} cm^{-1}.

III. Results and discussion

III.1. Catalyst properties

The natural iron oxide (NIO) used in this work comes from a mineral in North East of Algeria. The analysis show that the NIO is not pure and contains predominantly α-Fe_2O_3 as reported in our previous paper [22]. While its composition and crystal structure was confirmed by X-ray powder diffraction (XRD). The specific surface area measured by Brunauer–Emmett–Teller (BET) method of NIO was 79.02 m^2.g^{-1} and the total pore volume was 0.0893 cm^{3}·g^{-1}.

III.2. The effect of oxalic acid concentration

The effect of initial oxalic acidconcentration (C_{ox}) on the 1-NP degradation by the photo-Fenton-like reaction with 1.5 g.L^{-1} NIO is shown in figure 1. The first-order kinetic constant (k) for 1-NP degradation increased with increasing C_{ox} from 0 to 1.5 mM (table 1).

One of the specificities of the photo-Fenton-like reaction studied in this paper is the use of oxalate (oxalic acid) that allows the forming of a photoactive complex. The Fe (III)-oxalate complex was formed according to Eq. (1). Its photolysis under UV irradiation in acidic solution form $[\equiv Fe^{II}(C_2O_4)_{(n-1)}]^{(4-2n)}$ and oxalate radical $(C_2O_4)^{\bullet-}$ as indicated by Eq. (2). In the solution, $[Fe^{III}(C_2O_4)_n]^{(3-2n)}$ could be also excited under illumination to form $[Fe^{II}(C_2O_4)_{(n-1)}]^{(4-2n)}$ and oxalate radical $(C_2O_4)^{\bullet-}$ as described by Eq. (3). The oxalate radical can be transformed to the carbon-centered radical $(CO_2)^{\bullet-}$ as described by Eq. (4), from which the excited electron is transferred to the adsorbed oxygen forming superoxide ion ($O_2^{\bullet-}$), as described byEq. (5). Fe^{3+} reacts with $O_2^{\bullet-}$ to form O_2 and Fe^{2+} as described by Eq. (7) and Fe^{2+} reacts with $O_2^{\bullet-}$ and $^{\bullet}OOH$ to form H_2O_2 in acidic solution with Fe^{3+} as described by Eq. (8). Hydroxyl radicals ($^{\bullet}OH$) and Fe^{3+} can be generated by the reaction of Fe^{2+} with H_2O_2 as described by Eq. (9).

Table 1.*The pseudo-first-order kinetic constant (k), correlation coefficient (R) and removal percentage for 1-NP photodégradation with different initials concentrations of oxalic acid.*

C_{ox}^{0} (mM)	pH	$k \times 10^{-3}$ min^{-1}	*R*	Removal percentage (%) after 2 h
0.0	4.60	7.53	0.9798	63.45
0.5	4.01	10.84	0.9353	75.35
1.0	3.00	53.26	0.9796	99.77
1.5	2.26	38.23	0.9968	98.80
5.0	2.35	12.48	0,9625	82,22

$$\text{NIO} + n\text{H}_2\text{C}_2\text{O}_4 \leftrightarrow [\equiv\text{Fe}(\text{C}_2\text{O}_4)_n]^{(2n-3)-} \quad (1)$$

$$[\equiv\text{Fe}(\text{C}_2\text{O}_4)_n]^{(2n-3)-} + h\nu \rightarrow \text{Fe}(\text{C}_2\text{O}_4)_2^{2-} \text{ (or } \equiv\text{Fe}(\text{C}_2\text{O}_4)_2^{2-}) + (\text{C}_2\text{O}_4)^{\bullet-} \quad (2)$$

$$\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_n^{3-2n} + h\nu \rightarrow [\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)_{(n-1)}]^{(4-2n)} + (\text{C}_2\text{O}_4)^{\bullet-} \quad (3)$$

$$(\text{C}_2\text{O}_4)^{\bullet-} \rightarrow \text{CO}_2 + \text{CO}_2^{\bullet-} \quad (4)$$

$$\text{CO}_2^{\bullet-} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_2^{\bullet-} \quad (5)$$

$$\text{O}_2^{\bullet-} + \text{H}^+ \rightarrow {}^{\bullet}\text{OOH} \quad (6)$$

$$\text{O}_2^{\bullet-} + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{O}_2 \quad (7)$$

$$\text{O}_2^{\bullet-}/\,{}^{\bullet}\text{OOH} + n\text{H}^+ + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 \quad (8)$$

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + {}^{\bullet}\text{OH} \quad (9)$$

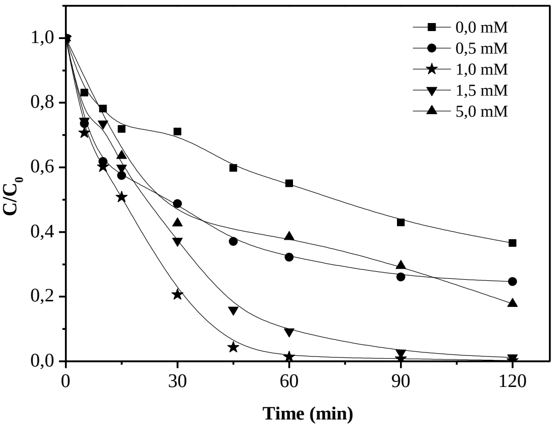

Figure 1.*The effect of initial concentration of oxalic acid on the degradation of 1-NP (10^{-4} M)under UV irradiation using 1.5 g.L^{-1}NIO.*

The increase of C_{ox} increases the production of the hydroxyl radicals. The negative effect observed at higher C_{ox} than 1 mM could be attributed to the competitive reactions between Fe(II) formed and the oxidant species generated in the ferrioxalate photolysis. The optimal C_{ox} in NIO-oxalate system was 1mM. A higher C_{ox} would lead to lower pH at the beginning of reaction which was not favorable to photo-Fenton system [23].

III.3. Fe(II) formation

The presence of Fe(II) resulting from the dissolution of α-Fe_2O_3 was checked out in the filtered aliquots by complexometry with ortho-phenantroline. Figure 2. showed the variation of Fe(II) concentration versus reaction time in the presence of different C_{ox} with 1.5 g.L^{-1} of NIO. During the photoreaction, NIO would be photo-dissolved. F(III)-oxalate complexes could generate Fe(II) species by the photo-reduction of dissolved Fe(III) species. The results indicated that generation of Fe(III)/Fe(II) under UV irradiation depended strongly on the C_{ox}. In the absence of oxalic acid, no dissolved Fe(III)/Fe(II) were found. On the other hand, higher C_{ox} led to the more Fe(II) concentration.

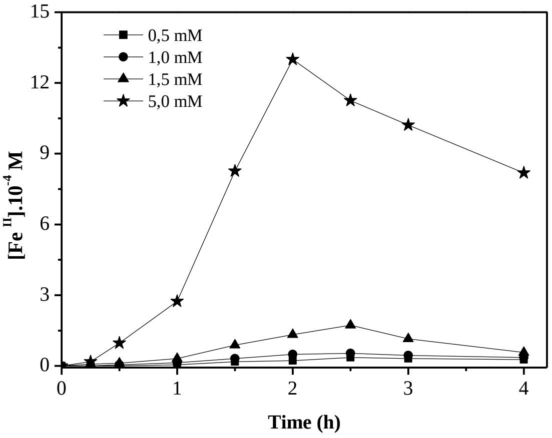

Figure 2.*The concentration of the dissolved Fe(II) vs. reaction time with different initial concentration of oxalic acid by using 1.5 g.L^{-1} NIO under UV irradiation.*

At the beginning of the photochemical process, the concentration of Fe(II) increased rapidly and attaind the peak because ≡ Fe(III)-oxalate can be easily photodissolved and reduced under irradiation

[24] and Fe(II) could be formed during this period as indicated by Eqs (3) and (7). In the late stage of the photochemical process, the formation of Fe(II) species decrease significantly with the decrease of oxalic acid which lead gradually to the increase of pH and Fe(III) precipitated as $Fe(OH)_3$.

III.4.The variation of pH value

The pH value is an important factor that influences thephoto-Fenton-like reaction. The variations of pH versus reactiontime by using 1.5 $g.L^{-1}$ of NIO with different $C_{ox}$are plotted in figure 3. It can be seen that the pH value increased gradually with the reaction time. The pH value increased significantly from 3,70 ; 3,00 ; 2,88 and 2,35 before photoreaction to 5,03 ; 5,15; 5,40 and 5,70 after 4 h photoreaction when the C_{ox} were 0,5 mM, 1 mM, 1,5 mM and 5 mM respectively.

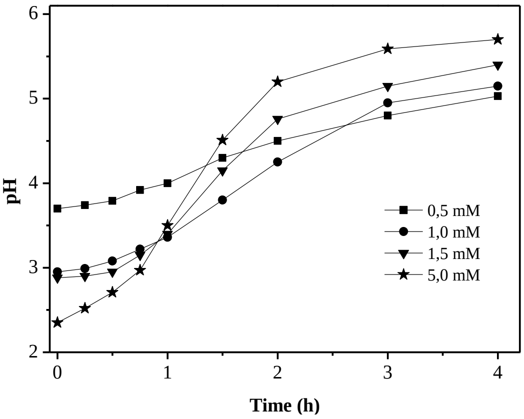

Figure 3. *The variation of pH value during 1-NP (10^{-4} M) degradation with different Cox by using 1.5 $g.L^{-1}$ of NIO under UV irradiation.*

At the beginning, a higher C_{ox} led to lower initial pH value. However, the pH in the solution increased much more slowly in the presence of a lower C_{ox} than that of the higher one. The increase of pH value was mainly attributed to the dissolution of NIO and the formation of Fe(III)-oxalate complex. A higher C_{ox}lead to more $[\equiv Fe(C_2O_4)_n]^{(2n-3)-}$ to be formed. During the photochemical process, OH^-would be generated in accompany with the generation of $HO^•$ as Eq. (10) [25,26]. More $[\equiv Fe(C_2O_4)_n]^{(2n-3)-}$in the system can generate more OH^- so as to increase the pH value more in the solution in the later stage during the photochemical process.

$$Fe^{2+} + \equiv Fe^{II}C_2O_4 + H_2O_2 \rightarrow Fe^{3+} + \equiv Fe^{III}C_2O_4^{+} + HO^{•} + HO^{-} (10)$$

III.5. The effect of initial 1-NP concentration

The effect of initial 1-NP concentrations on the rate of 1-NP degradation was performed by varying initial 1-NP concentrations from 0.5×10^{-4} to 5.0×10^{-4} M in the presence of 1.0 mM oxalic acid by using 1.5 $g.L^{-1}$ NIO under UV irradiation. A linear correlation was observed for 1-NP concentration and irradiation time (ln $[C_0/C]$vs time). Hence degradation of 1-NP by the photo-Fenton-like system followed pseudo-first order kinetics.

$$ln\frac{C_0}{C} = kt \qquad (11)$$

Where k is the pseudo-first order rate constant. The experimental results obtained (figure. 4) show that the increase of initial 1-NP concentration from 0.5×10^{-4} to 5.0×10^{-4} M decreases the degradation rate constant from 63.50×10^{-3}(R^2 = 0.9822) to 12.91×10^{-3} min^{-1}(R^2 = 0.9952), this is due to the competition between 1-NP and its reaction by-products for catalyst particles and such competitionbecomes more pronounced at higher concentrations.

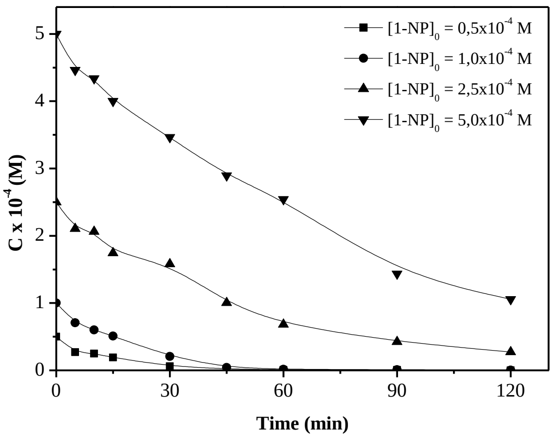

Figure 4.*The effect of initial concentration of 1-NP on photo-Fenton-like degradation of 1-NP (initial conditions: 1 mMaxalic acid, 1.5 $g.L^{-1}$ NIO) under UV irradiation.*

IV. Conclusion

The heterogeneous iron oxide–oxalate complex system, as a photo-Fenton-like system, was set up in the presence of natural iron oxide and oxalate together. 1-NP could be effectively degraded in the system under UV irradiation. The present study has demonstrated that the 1-NP degradation followed the first-order kinetics. The experimental results indicated that the photocatalytic oxidation efficiency was enhanced with a decrease in 1-NP concentration and a limited increase in the oxalate dose. The optimal (C_{ox}) was 1 mM. This factor have an impact on the concentration of Fe(II) formation and 1-NP disappearance. The good degradation of the organic contaminants is attributed to the generation of highly oxidative $^•OH$ radicals during the photo-Fenton-like reaction. This work could help us to fully understand the photoreaction process concerning F(III)-oxalate complex for the degradation of pollutants in the aquatic environment under irradiation.

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