EFFECT OF A MODIFIED PHOTO-FENTON PROCEDURE ON THE OXIDATIVE DEGRADATION OF 1-NAPHTHOL IN AQUEOUS SOLUTION

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Abstract:
A heterogeneous photo-Fenton-like degradation process of 1-naphthol (1-NP) promoted by natural iron oxide (NIO) in the presence of oxalic acid was studied under artificial irradiation (365 nm). This is an important reaction for the environment since both oxalic acid and iron oxides are common constituents of natural waters. 1-NP was selected as a model pollutant, while the NIO used in this work comes from a mineral in Algeria. The NIO was characterized by X-ray diffraction (XRD), X-ray fluorescence and Brunauer-Emmett-Teller (BET) methods to disclose the crystal composition and surface area. The analysis revealed that the NIO has a mixed elemental composition that consists mainly of iron oxide. The effect of the dosage of NIO and initial concentration of oxalic acid on 1-NP degradation was investigated in the NIO/oxalate suspension under UVA light irradiation. The phototransformation experiment of 1-NP shows that the NIO alone could play an important role in its degradation at 365 nm. The additional oxalic acid could significantly accelerate 1-NP degradation. The optimal initial concentration of oxalic acid was found to be 1 mM. This investigation will give a new insight to understanding the 1-NP photodegradation in natural environment.

Keywords: 1-Naphthol; Natural mineral; Oxalic acid; degradation; photo-Fenton-like; hydroxyl radicals.
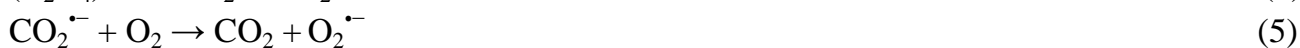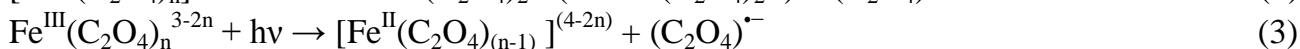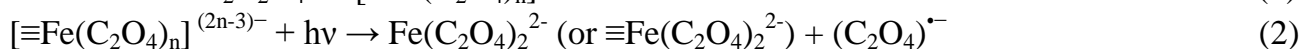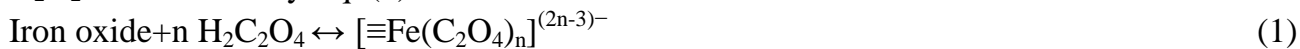
1. INTRODUCTION

Fenton reaction is known to be a very effective way in the removal of organic pollutants for wastewater treatment [1–3]. Hydroxyl radicals ($^{\bullet}$OH) with high reactivity can form during Fenton reaction and degrade most of organic compounds with second-order rate constants of $10^8 –10^{10}$ M^{-1} s^{-1} [4–6]. When light was introduced into Fenton or Fenton-like system, as called photo-Fenton and photo-Fenton-like reactions, more $^{\bullet}$OH could be generated [7]. In Fenton and Fenton-like systems, hydrogen peroxide (H_2O_2) is the most important factor because it is the direct source of $^{\bullet}$OH [8]. Sufficient hydrogen peroxide has to be added so as to make the system be efficient [1,9]. However, H_2O_2 is an acute reactive reagent and cannot stand in nature for a long time. This factor limits the application of Fenton and Fenton-like system in the remediation of organic pollutants in nature.

In nature, iron, oxalic acid and sunlight can establish a homogeneous photo-Fenton-like system where iron exists in a dissolved form or a heterogeneous photo-Fenton-like system where iron is in solid form [10]. The heterogeneous Fe(III)–oxalate system should be more applicable to the natural environment, because the iron species are mostly present as amorphous or (hydr)oxides [10].

The photochemical process in the presence of iron oxide and oxalate together has been described in detail [11–13]. In this suspension, oxalic acid is first adsorbed on the surface of the iron oxide forming $[\equiv Fe^{III}(C_2O_4)_n]^{(3-2n)}$ as described by Eq. (1). This complex can be excited to 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 by Eq. (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).

$$\text{Iron oxide} + n\,H_2C_2O_4 \leftrightarrow [\equiv Fe(C_2O_4)_n]^{(2n-3)-} \tag{1}$$

$$[\equiv Fe(C_2O_4)_n]^{(2n-3)-} + h\nu \rightarrow Fe(C_2O_4)_2^{2-}\ (or \equiv Fe(C_2O_4)_2^{2-}) + (C_2O_4)^{\bullet-} \tag{2}$$

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

$$(C_2O_4)^{\bullet-} \rightarrow CO_2 + CO_2^{\bullet-} \tag{4}$$

$$CO_2^{\bullet-} + O_2 \rightarrow CO_2 + O_2^{\bullet-} \tag{5}$$

$$O_2^{\bullet-} + H^+ \rightarrow {}^{\bullet}OOH \tag{6}$$

$$O_2^{\bullet-} + Fe^{3+} \rightarrow Fe^{2+} + O_2 \tag{7}$$

$$O_2^{\bullet-}/\,{}^{\bullet}OOH + nH^+ + Fe^{2+} \rightarrow Fe^{3+} + H_2O_2 \tag{8}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \tag{9}$$

2. EXPERIMENTAL

2.1. Reagents

The natural iron oxide (NIO) was washed several times with distilled water and dried at 45°C. 1-naphthol (99%+ Acros Organics), Oxalic acid (99.5%) from Prolabo and Methanol (99% VWR Prolabo) were used without further purification. Deionized water (18.2mΩ.cm) from an ultrapure water system (Simplicity UV, MILLIPORE) was used in all experiments.

2.2. 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 NIO particles. 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).

3. RESULTS AND DISCUSSION

3.1. 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 Fe_2O_3 as reported in our previous paper [14]. 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 $cm^{3.}g^{-1}$.

3.2. Photodecomposition of 1-NP in the Fe_2O_3/oxalate suspension

Fig. 1 showed the photodegradation of 1-NP with the initial concentration of 10^{-4} M under different conditions. The combination of 1 $g.L^{-1}$ NIO with 1 mM oxalic acid without UV light (in the dark) produced 22.5% degradation of 1-NP after 2 h of reaction; this is due to adsorption on the surface of iron oxide (curve a). UV illumination of an oxalate solution without NIO results in 32.4% degradation of 1-NP after 2 h, corresponding to the photodegradation of 1-NP by UV illumination (curve b). Without oxalic acid but only with 1 $g.L^{-1}$ NIO under UV light irradiation at pH 3 (curve c), the removal percentage of 1-NP was at 39% level. However, when both 1 mM oxalic acid and 1 $g.L^{-1}$ NIO were added in to the reaction suspension to form the photo-Fenton-like system under UV irradiation (curve d), the removal percentage of 1-NP was significantly increased up to 99.1% after 2 h reaction and its first-order kinetic constant was determined to be 4.5×10^{-2} min^{-1}. The results indicate that the combination of NIO, oxalate and UV light is essential for 1-NP photodegradation.
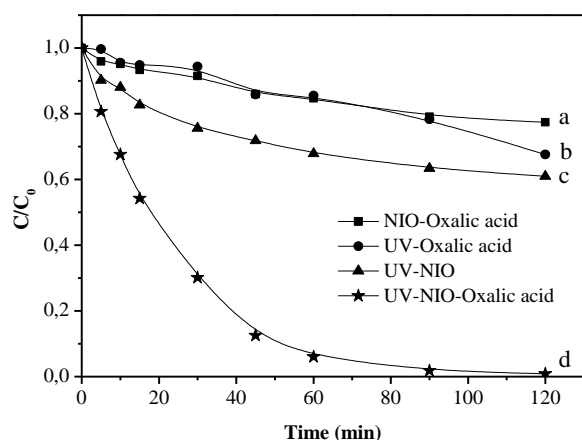

Fig. 1. Photodegradation of 1-NP (10^{-4} M) under different conditions.
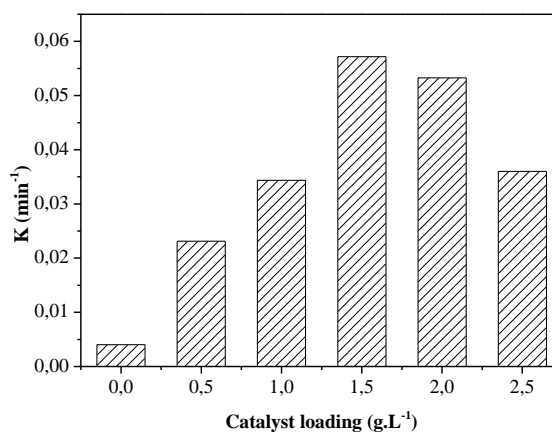

Fig. 2. The effect of NIO dosage on the degradation of 1-NP (10^{-4} M) under UV irradiation in the presence of 1 mM oxalic acid.

3.3. Effect of catalyst dosage

The influence of the iron oxide dosage on the photodecomposition kinetics of 1-NP in the presence of oxalic acid was investigated using different dosages of NIO varying from 0.0 to 2.5 $g.L^{-1}$. It could be seen from (Fig. 2) that there should be an optimal dosage of 1.5 $g.L^{-1}$. In fact, excessive dosage of iron oxide will lead to the obstruction in the penetration of UV light in the solution.

3.4. Effect of oxalic acid concentration

Fig. 3 showed the dependence of 1-NP photodegradation on the initial concentration of oxalic acid (C_{ox}) with 1.5 g.L^{-1} NIO under UV irradiation and the inserted figure presented the dependence of the first-kinetic constant (k) on the C_{ox}. The results showed that in the absence of oxalic acid at pH 4.6, 1-NP degraded at a low k value of 7.53×10^{-3} min^{-1}. Iron oxides acted as a photocatalyst and could be excited to generate electron-hole pairs [15] in the absence of oxalate. However, in the presence of oxalic acid, an iron oxide-oxalate complex formed and a photo-Fenton-like system was set up. The experimental results obtained show that the k values of 1-NP degradation were 7.53×10^{-3}, 10.84×10^{-3}, 53.26×10^{-3} and 38.23×10^{-3} min^{-1} when the C_{ox} was 0.0, 0.5, 1.0 and 1.5 mM, respectively. This result clearly shows the enhancement of 1-NP degradation in oxalate solution. The optimal C_{ox} is 1.0 mM under these experimental conditions. While, any excess oxalic acid will occupy the adsorption sites on the surface of iron oxide and also react competitively with generated $^{\bullet}$OH together with 1-NP. Furthermore, excessive oxalate would lead to the formation of a large quantity of Fe^{3+}, which would inhibit the formation of H$_2$O$_2$, as described in Eq. (8). On the other hand a higher C_{ox} would lead to lower pH which was not favourable to photo-Fenton system [16].
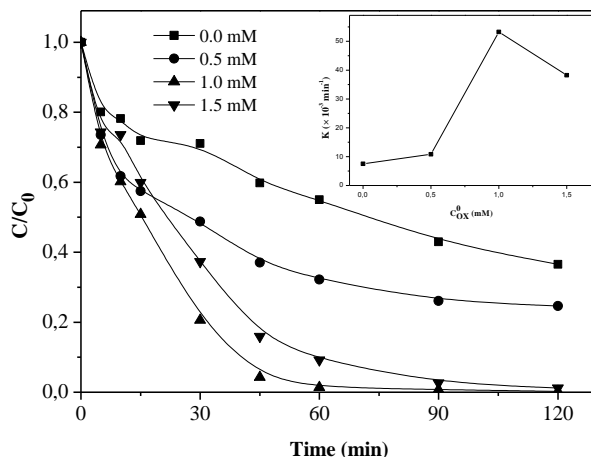

Fig. 3. The effect of initial concentration of oxalic acid on the degradation of 1-NP (10^{-4} M) under UV irradiation by using 1.5 g.L^{-1} NIO.

4. CONCLUSION

The heterogeneous iron oxide–oxalate complex system, as a photo-Fenton-like system, was set up in the presence of iron oxide and oxalate together. 1-NP could be effectively degraded in the system under UVA irradiation. The photodegradation of 1-NP depended strongly on the dosage of iron oxide and the initial concentration of oxalate. The optimal (C_{ox}) was 1 mM. The good degradation of the organic contaminants is attributed to the generation of highly oxidative $^{\bullet}$OH radicals during the photo-Fenton_like reaction. The NIO catalysts would be of great importance for industrial use due to their high photoactivity, high photocatalytic stability, little iron leaching, easy physical separation , no need to be regeneration and low cost.

5. REFERENCES

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