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NATURAL IRON OXIDE AS A HETEROGENEOUS PHOTO-FENTON-LIKE CATALYST FOR THE DEGRADATION OF 1-NAPHTHOL UNDER ARTIFICIAL AND SOLAR LIGHT

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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 H_2O_2 was studied under artificial (365 nm) and solar irradiation. This is an important reaction for the environment since both H_2O_2 and iron oxides are common constituents of natural waters. Furthermore, iron oxides function as catalysts in chemical oxidation processes used with H_2O_2 for treatment of contaminated waters. The NIO used in this study was characterized by X-ray diffraction (XRD), X-ray fluorescence and Brunauer–Emmett–Teller (BET) methods. The results show that the NIO is a composite material that contains predominantly crystalline hematite particales (Fe_2O_3). The Fe_2O_3 in NIO was able to initiate the Fenton-like and photo-Fenton-like reactions. The effects of initial pH, catalyst dosage, H_2O_2 concentration and the wavelength of the light source (UV and solar) on the photodegradation of 1-NP were investigated. The optimal content of the NIO was 1 g L^{-1} and the optimal H_2O_2 concentration was 10 mM. The degradation could occur efficiently over a wide pH range of 3-8.3. Furthermore, an important effect of light was observed. The photo-oxidation of 1-NP in NIO-H_2O_2 system under solar light was significantly accelerated in comparison with artificial irradiation at 365 nm.

Keywords: *1-Naphthol; Natural iron oxide; hydrogen peroxide; photo-oxidation; Solar light.*

Résumé

Le procédé photo-like -Fenton utilisé pour la dégradation du 1-NP par un oxyde de fer naturel (NIO) en présence de H_2O_2 a été étudié sous irradiation artificielle (365 nm) et solaire. Les oxydes de fer agissent comme catalyseurs dans des procédés d'oxydation chimiques utilisés avec le H_2O_2 pour le traitement des eaux contaminées. NIO utilisé dans cette étude a été caractérisé par diffraction des rayons X (XRD), la fluorescence des rayons X et le Brunauer- Emmett -Teller (BET). Les résultats montrent que NIO est composé en majeure partie d'hématite (80%). Le Fe_2O_3 initie les réactions de like-Fenton et photo-like-Fenton. Les effets du pH initial, la masse du catalyseur, la concentration de H_2O_2 et de la longueur d'irradiation (UV et solaire) sur la photodégradation du 1-NP ont été étudiés. La teneur optimale de NIO est de 1 g L^{-1} et la concentration de H_2O_2 optimale est de 10 mM. La dégradation peut se produire de manière efficace sur une large gamme de pH de [3- 8,3]. En outre, un effet important de la lumière a été observée. La photo-oxydation du 1-NP dans le système NIO-H_2O_2 en présence de la lumière solaire a été considérablement accélérée par rapport à l'irradiation artificielle à 365 nm.

Mots clés: *1-Naphtol; oxyde de fer naturel; peroxyde d’hydrogène; photo-oxidation; lumière Solaire.*

ملخص

تمت دراسة عملية تفكك النافتول (1-NP) في وسط غير متجانس حسب مفاعل (photo-Fenton-like) في وجود أكسيد الحديد الطبيعي (NIO) مع وجود بيروكسيد الهيدروجين (H_2O_2) تحت الإشعاع الاصطناعي (365 نانومتر) و الشمسي. هذا النظام مهم بالنسبة للبيئة لأن H_2O_2 وأكاسيد الحديد موجودة في المياه الطبيعية. علاوة على ذلك، أكاسيد الحديد تعمل كحافز في عمليات الأكسدة الكيميائية مع H_2O_2 لمعالجة المياه الملوثة. تم تحليل NIO المستخدم في هذه الدراسة من خلال الطرق التالية : (DRX)، (FX) و(BET). أظهرت النتائج أن NIO هوعبارة عن مادة مركبة أغلبيتها بلورات Fe_2O_3. ان Fe_2O_3 في NIO قادرة على الشروع في حدوث معادلات Fenton-like و photo-Fenton-like. وقد تم دراسة تأثير درجة الحموضة الأولية، تركيزالمحفز(NIO)، تركيز H_2O_2 و الطول الموجي لمصدر الضوء (الأشعة فوق البنفسجية و الأشعة الشمسية) على التفكك الضوئي ل 1-NP . كان تركيز NIO الأمثل 1 g L^{-1} و كان تركيز H_2O_2 الأمثل 10 ميلي مول . التفكك يحدث بكفاءة على نطاق واسع من درجة الحموضة 3-3.8 . علاوة على ذلك، لوحظ تأثير مهم للضوء. الأكسدة الضوئية ل 1-NP في النظام NIO-H_2O_2 تحت أشعة الشمس أسرع بشكل ملحوظ مقارنة مع الأشعة الاصطناعية.

الكلمات المفتاحية : 1- نافتول؛ أكسيد الحديد الطبيعي؛ بيروكسيد الهيدروجين ؛ الأكسدة الضوئية ؛ ضوء الشمس .

1. Introduction

In recent years, advanced oxidation processes (AOPs) which are characterized by the formation of highly reactive and nonselective hydroxyl radicals ($^{\bullet}$OH, $E^0 = 2.8$ V) for the mineralization of recalcitrant organic contaminants, have been widely applied for wastewater treatment [1-4]. The $^{\bullet}$OH for AOPs can be produced in a system with dissolved iron (Fe^{2+}/ Fe^{3+}) and hydrogen peroxide in acid medium (homogeneous Fenton reaction) as shown in Equations (1) and (2):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\bullet} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \quad (2)$$

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 the presence of UV light (<320 nm), additional reactions of the hydroxyl radical production can occur as follows [5]:

$$H_2O_2 + h\upsilon \rightarrow 2\ HO^{\bullet} \quad (3)$$

In the photo-Fenton-like process, UV light irradiation increases the $^{\bullet}$OH formation rate and the efficiency via photoreduction of Fe^{3+} to Fe^{2+} and by photochemical reactions of complexes formed with the ferric ions because the reduction of Fe^{3+} by H_2O_2 in non-irradiated systems is slow and thus ineffective [6-8]:

$$Fe(III)OH^{2+} + h\upsilon \rightarrow Fe^{2+} + HO^{\bullet} \quad (4)$$

$$Fe^{3+}(L^-) + h\upsilon \leftrightarrow Fe^{2+} + L^{\bullet} \quad (5)$$

The main shortcomings of the homogeneous Fenton process are: (i) the recovery of dissolved iron ions from the treated solution requires additional treatments makes the process laborious and non-economical [9-10], (ii) Fenton catalytic cycle is restrained by the formation of stable iron complexes with phosphates anions or generated carboxylic acids and (iii) the necessity of working at low pH (~3) for preventing precipitation of Fe^{2+} and Fe^{3+} ions and the formation of iron oxide sludge. In order to extend its operation pH values, research has focused on the idea of replacing dissolved iron with solid catalyst (such as iron oxides/oxyhydroxides) in so-called heterogeneous Fenton-like process.

Iron oxides can be used as iron sources Fenton-like processes, and their ability to oxidize organic compounds with high efficiency have been reported in the literature [11–16]. In comparison with the classic Fenton process, the use of solid iron oxides has advantages related to the easiness in the separation of the catalyst after treatment of the effluent and no rigid control of the pH during the reactions [11, 17-23].

The purpose of this study is to investigate the using of a natural iron oxide (NIO) in heterogeneous photo-Fenton-like process for the degradation of 1-naphthol under UV and solar illumination. Several key factors such as the amount of the photocatalyst, initial concentration of hydrogen peroxide and initial pH value were studied to provide a better knowledge of this photochemical process. The photo-oxidation of 1-NP was also compared in the presence of solar irradiation.

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), sodium hydroxide (NaOH, 98% Carlo Erba Reagenti), hydrochloric acid (HCl, 37% Merck), perchloric acid (98%), hydrogen peroxide (30%) 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.

2.3. Photodegradation experiments

The irradiation experiments were performed in a Pyrex cylindrical reactor with a double envelope with about 2 cm in diameter, open to air, was 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 lamp type Philips HPW 125, (UV-A, $\lambda_{max} = 365$ nm). Light intensity ($I = 2.01$ mW cm^{-2}) was measured using a radiometer type VLX 3W. The solution (usually 50 ml) 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 H_2O_2 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. All experiments were performed at $T = 293 \pm 1$°K by cycling water. The solution pH was adjusted by 1.0 M of HCl or NaOH and measured by means of an HANNA Instruments 8521 pH-meter.

2.4. Analysis

1-NP was determined by HPLC (Shimadzu) equipped with a controller model SCL-10A VP, photodiode-array UV-Vis detector model SPD-M10A VP and two pumps model LC 8A. The system is controlled by software "Class VP5" for storing and processing of chromatograms. The analytical column is a C18 Supelco (5µm, 250 mm x 4.6 mm i.d). The methanol-ultrapure water mixture (60:40) was used at mobile flow rate of 1 mL min^{-1} at room temperature. The detection wavelength was at 290 nm. The UV-Vis absorption spectra were recorded employing a Unicam «Heλios α» spectrophotometer controlled by software "Vision".

3. Results and discussion

3.1. Catalyst characterization

The natural iron oxide (NIO) used in this work comes from a mineral in Chaabet-El-Ballout, which is located in Souk-Ahras, 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 [24]. 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. Characterization of 1-NP

The UV-visible spectra of 1-NP (10^{-4} M) in aqueous solution at experimental pH (pH = 6.5) pointed up in Fig. 1 shows a maximum absorption at λ_{max} = 290 nm ($\varepsilon = 4560 \pm 200$ L mol^{-1} cm^{-1}) and a shoulder around 320 nm. For pH values above the pK_a of 1-naphthol (pK_a = 9.3), the shape of the UV-Visible spectrum substrate changes because the anionic form is predominant. The absorption spectrum of the anionic form, as shown in Fig. 1, has two strips at 245 nm and the other at 332 nm. There was a band shift of 42 nm. We can note the good recovery of UV absorption spectrum substrate and the solar emission spectrum. Thus, it may undergo a phototransformation in the aquatic environment.

3.3. Photodegradation of 1-NP under different reaction conditions

The degradation of 1-NP (10^{-4} M) versus time under different conditions is shown in Fig. 2. The photocatalytic ability of NIO in presence of H_2O_2 (curve 4) showed a significant 1-NP reduction achieving a conversion rate of 94.6% after 3 h reaction and its pseudo-first-order kinetic constant was determined to be 29.75x10^{-3} min^{-1} (R^2 = 0.991). In absence of H_2O_2 in analogous reaction condition (curve 2) it led to a conversion rate of 72.1% and k value was determined to be 12.16x10^{-3} min^{-1} (R^2 = 0.983). 1-NP reduction was also observed in dark Fenton-like reaction only in presence of NIO and H_2O_2 (curve 1); the removal percentage of 1-NP after 3 h was 35.1% and its k value was determined to be 3.54x10^{-3} min^{-1} (R^2 = 0.995). The small extent degradation in dark Fenton reaction may be due to the formation of hydroxyl radical by thermal decomposition of H_2O_2 [25]. The photolysis in presence of H_2O_2 (curve 3) yielded an enhanced rate of 1-NP degradation with a conversion rate of 86.7% (k = 11.11x10^{-3} min^{-1}, R^2 = 0.992), which showed that H_2O_2 also could go upon photolysis yielding hydroxyl radicals under 365 nm light irradiation [26].

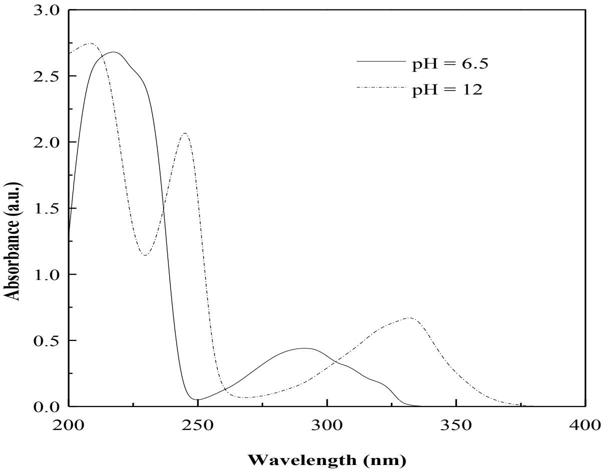

Fig. 1. UV-Visible spectrum of 1-NP (10^{-4} M) in aqueous solution.

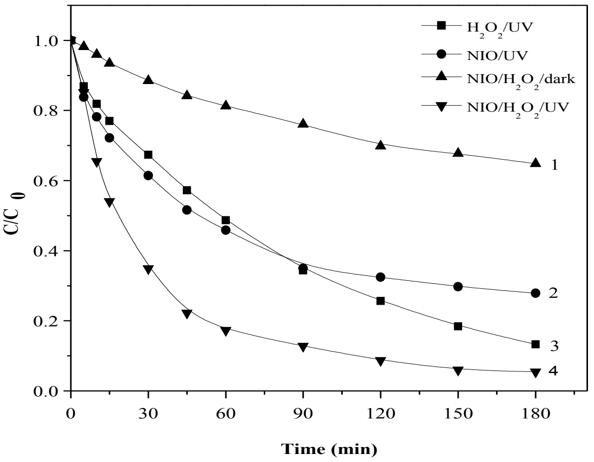

Fig. 2. Degradation of 1-NP under different conditions. $[1\text{-}NP]_0 = 10^{-4}$ M; [NIO] = 1 g L^{-1}; $[H_2O_2]$ = 10 mM; T = 20°C.

3.4. Effect of catalyst dosage

The effect of catalyst dosage on the degradation of 1-NP in NIO/H_2O_2/UV system was assessed by irradiating 10^{-4} M 1-NP solutions containing 0-1.5 g L^{-1} NIO. As shown in Fig. 3, increasing the dosage of NIO to 1 g L^{-1} could increase the degradation of 1-NP. However, with the NIO further increased to1.5 g L^{-1}, the degradation efficiency of 1-NP decreased. The result could be attributed to that the higher concentration of Fe_2O_3 could lead to the scavenging of $^{\bullet}OH$ radicals by iron ions and induce the decrease in degradation of 1-NP [27]. According to the corresponding photocatalytic activities, the optimized dosage of the catalyst was 1 g L^{-1}.

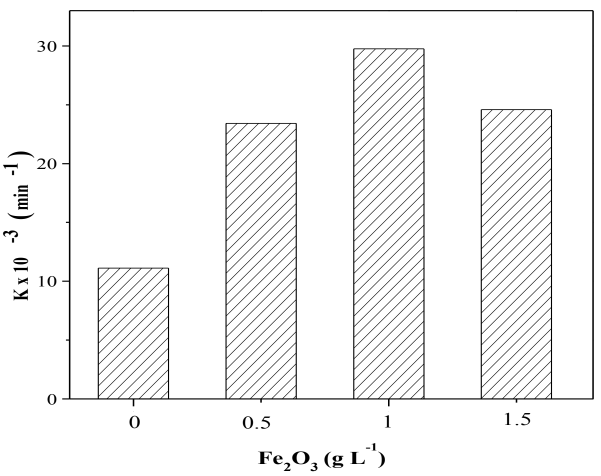

Fig. 3. The effect of catalyst dosage on the degradation of 1-NP in NIO/H_2O_2/UV system. $[1\text{-NP}]_0 = 10^{-4}$ M; $[H_2O_2] = 10$ mM; T = 20°C.

3.5. Effect of initial H_2O_2 concentration

The photodegradation of 1-NP was performed at different H_2O_2 concentrations (Fig. 4). Within the range of 0.1-50 mM H_2O_2, the rate of 1-NP degradation increased with increasing initial H_2O_2 concentration.

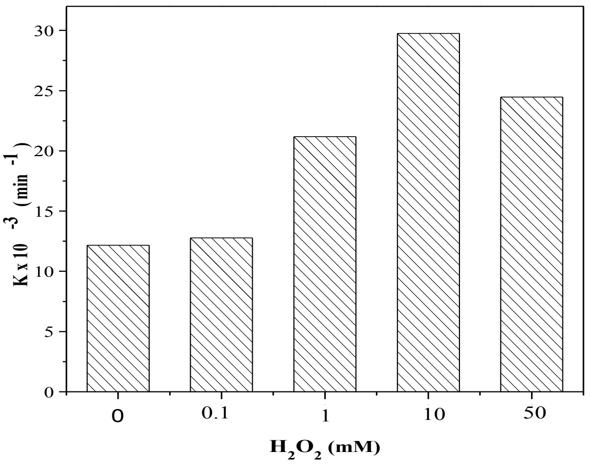

Fig. 4. The effect of initial H_2O_2 concentration on the degradation of 1-NP in NIO/H_2O_2/UV system. $[1\text{-NP}]_0 = 10^{-4}$ M; [NIO] = 1 g L^{-1}; T = 20°C.

Being similar to general Fenton-like degradation, H_2O_2 was decomposed at the surface of catalysts to generate hydroxyl radicals. The increase of H_2O_2 concentration would lead to more hydroxyl radicals produced. However, further increase in H_2O_2 resulted in a decrease of degradation efficiency. The excess H_2O_2 could act as a $HO^\bullet$ scavenger resulting in the generation of $HO_2^\bullet$ that is less active than the hydroxyl radicals [28].

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \quad (6)$$

$$HO^\bullet + HO_2^\bullet \rightarrow O_2 + H_2O \quad (7)$$

3.6. Effect of pH on the degradation of 1-NP in NIO/H_2O_2/UV system

It is well established that pH shows significant effect on the hydroxyl radical oxidation in various advanced oxidation technologies involving Fenton reagent [29]. Therefore, Effect of initial pH on the degradation of 1-NP was also investigated here. As shown in Fig. 5, the reaction could occur efficiently over a wide pH range of 3–8.3, which solved one of the critical drawbacks of the homogeneous Fenton system, i.e., working well only under highly acidic conditions pH 2–3 [30]. The result is consistent with that of some previous reports which showed that the pillared clays could extend the range of pH values for Fenton-like oxidation [31, 32].

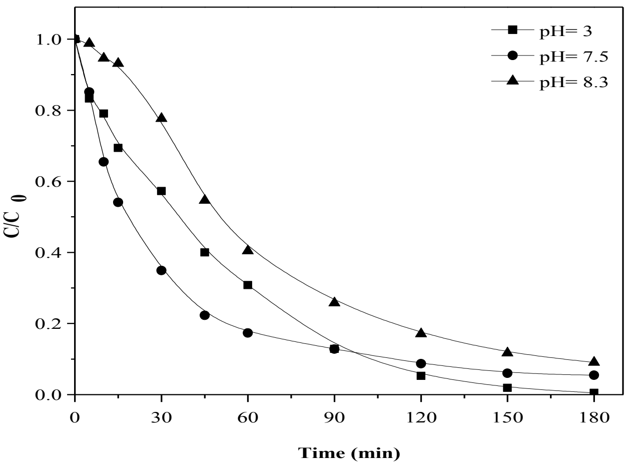

Fig. 5. Effect of pH on the degradation of 1-NP in NIO/H_2O_2/UV system. $[1\text{-NP}]_0 = 10^{-4}$ M; [NIO] = 1 g L^{-1}; $[H_2O_2] = 10$ mM; T = 20°C.

3.7. Effect of the solar irradiation

In order to test the efficiency of 1-NP removal from the water, when the degradation is photoinduced by NIO and H_2O_2 in environmental conditions, a comparative study in term of the kinetic and the pathway of photodegradation process in natural and artificial media was performed. The process was experienced by using solar light irradiation where mixture of 1-NP-NIO-H_2O_2 (10^{-4} M; 1 g L^{-1}, 1 mM) was exposed to natural sunlight during a sunny day at Constantine (Algeria). The average of solar irradiance in the experiment was 37 mW cm^{-2}. Fig. 6 presents the 1-NP degradation with NIO/H_2O_2/UV and NIO/H_2O_2/solar light processes. As could be seen, 1-NP degradation is much higher in photo-Fenton-like/solar light than in photo-Fenton-like/UV processes, 94.6% and 93.6%, respectively. So, from this analysis it is evident that both NIO/H_2O_2/UV and NIO/H_2O_2/solar light has the capacity of eliminate 1-NP. However, the employment of solar light benefits the 1-NP degradation when compared to the UV lamp. Although from the economical point of view, the use of solar light could be a good alternative in organic pollutants degradation.

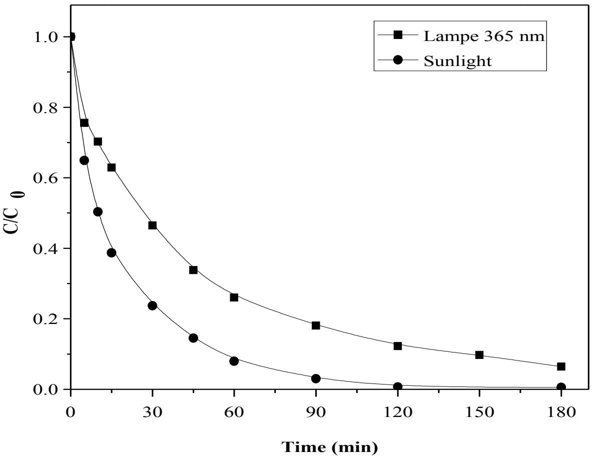

Fig. 6. 1-NP degradation in the mixture 1-NP/NIO/H_2O_2 during natural and artificial irradiation. $[1\text{-NP}]_0 = 10^{-4}$ M; [NIO] = 1 g L^{-1}; $[H_2O_2]$ = 1 mM; T = 20°C.

3.8. Comparison of various processes studied in degradation of 1-NP

In order to evaluate the efficiency of the Fenton-like reagent and the beneficial effect of solar irradiation on the removal of 1-NP in aqueous solution, the following experiments were performed: (i) NIO + H_2O_2 (dark Fenton-like), (ii) photolysis (only solar irradiation), (iii) solar irradiation + NIO, (iv) solar irradiation + H_2O_2 (photo-bleaching), and (v) solar irradiation + NIO + H_2O_2 (solar photo-Fenton-like). The concentrations of NIO and H_2O_2 used were 1.5 g L^{-1} and 1 mM. Fig. 7 shows the 1-NP removal of the above processes.

Dark Fenton experiments were conducted to assess the oxidation power of the Fenton reagent in the absence of solar light. Dark Fenton achieved a reduction of the order of 35.1% after 3h of the treatment. It is widely known that the active oxidants in dark Fenton systems are also the hydroxyl radicals [33].

The solar irradiation alone (photolysis) produced 80% degradation of 1-NP after 3h of irradiation; this is thought to be due to the good recovery of UV absorption spectrum substrate and the solar emission spectrum. Thus, it may undergo a phototransformation in the aquatic environment.

The combination of solar irradiation and catalyst (NIO) alone results in 99.06% degradation of 1-NP after 3h because the aqueous suspension of NIO (Fe_2O_3) strongly absorbs light up to 600 nm and then can behave as photocatalyst even though a very efficient positive holes-electrons recombination takes place.

Additional experiments were also performed to assess the contribution of photo-bleaching in the presence of H_2O_2. The 1-NP removal due to photo-bleaching (solar irradiation + H_2O_2) was 89.12% after 3h of treatment. The increased removal compared to solar irradiation alone (photolysis) can be attributed to the formation of some extra hydroxyl radicals from the irradiation of H_2O_2 [34].

However, the removal percentage of 1-NP was significantly increased up to 99.43% by solar photo-Fenton process after 3h of treatment. The high efficiency of solar photo-Fenton process is due to the formation of more $HO^•$ than during the other processes (dark Fenton, photo-bleaching, solar irradiation + NIO, photolysis) [34], as well as the regeneration of Fe^{2+} from the photolysis of the complex $Fe(III)OH^{2+}$ in solution (Eq. (4)) [35].

Hence, the relative efficiencies of the above processes can be given in the following order: solar photo-Fenton (solar irradiation + NIO + H_2O_2) > solar irradiation + NIO > photo-bleaching (solar irradiation + H_2O_2) > photolysis (only solar irradiation) > Dark Fenton (NIO + H_2O_2).

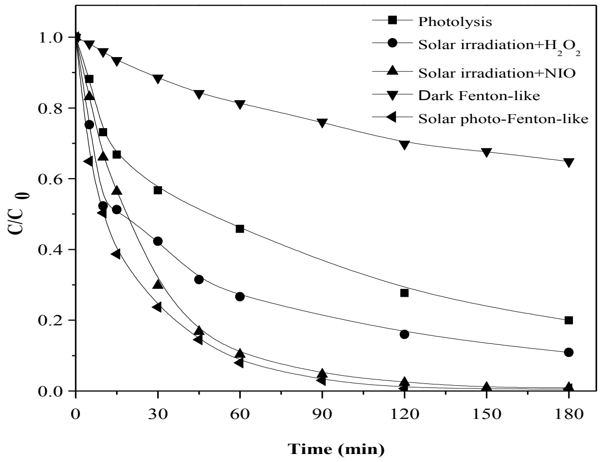

Fig. 7. 1-NP degradation under different processes during natural irradiation. $[1\text{-NP}]_0 = 10^{-4}$ M; [NIO] = 1.5 g L^{-1}; $[H_2O_2]$ = 1 mM; T = 20°C.

4. Conclusion

In this study, we report the use of a natural iron oxide (Fe_2O_3) for the heterogeneous photo-Fenton-like oxidation of 1-NP in the presence of hydrogen peroxide. NIO could be a highly efficient catalyst to reduce 1-NP concentration from aquatic environment. 1-NP in aqueous was decomposed by NIO under UV irradiation within a wide pH range. Solar photo-Fenton-like was proved to be very efficient for the treatment of the 1-NP, reaching a removal of approximately 99.43%. The good degradation of the organic contaminants is attributed to the generation of highly oxidative $^•OH$ 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.

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