

THE EFFECT OF IRON OXIDE AND POLYCARBOXYLIC ACIDS ON THE PHOTODEGRADATION OF 2,6-DIMETHYLPHENOL

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Abstract

A natural iron oxide (NIO) was applied for the photodegradation of 2,6-dimethylphenol in presence of polycarboxylic acids under UV irradiation. The dependence of 2,6-DMP degradation was attributable to the formation of dissolved Fe-polycarboxylate in the solution and adsorbed on the surface of natural iron oxide. The results showed that the photodegradation of 2,6-DMP could be enhanced greatly in the presence of oxalate. The variables studied were the aqueous pH, the presence of hydrogen peroxide and temperature in NIO / oxalate / UV system. The optimal pH value was found to be in the range of 3–4. It was found that the formation of Fe (II) in NIO / oxalate system occurred more vigorously at the initial stage and gradually became moderate. Furthermore, the formation of H₂O₂ during the photoreaction was studied to explore its relationship with the photodegradation efficiency and the iron cycling process. The use of 2.0% of isopropanol as a scavenger confirmed the intervention of hydroxyl radicals in the degradation of 2,6-DMP.

Keywords: Natural iron oxide (NIO), 2,6-DMP, Fe – polycarboxylate, H₂O₂, hydroxyl radicals.

Résumé

Un oxyde de fer naturel a été utilisé pour la photodégradation du 2,6-diméthylphénol (2,6-DMP) en présence des acides polycarboxyliques sous irradiation UV. La dépendance de la dégradation du 2,6-DMP est attribuée à la formation des complexes Fe - polycarboxylate dissous dans la solution et adsorbés sur la surface de l'oxyde de fer naturel. Les résultats ont montré que la photodégradation du 2,6-DMP pourrait être considérablement améliorée en présence d'oxalate. Les variables étudiées étaient le pH de la solution, la présence du peroxyde d'hydrogène et la température dans le système oxyde de fer naturel / oxalate / UV. La valeur du pH optimale s'est révélée être dans l'intervalle de 3-4. Il a été constaté que la formation de Fe (II) dans le Système oxyde de fer naturel / oxalate a été plus vigoureuse à la phase initiale et devient progressivement modérée. En outre, la formation de H₂O₂ pendant la photoréaction a été étudiée pour monter sa relation avec l'efficacité de la photodégradation du 2,6-DMP et le processus de cycle du fer. L'utilisation de 2,0% d'isopropanol en tant que piège a confirmé l'intervention des radicaux hydroxyle dans la dégradation du 2,6-DMP.

Mots clés : Oxyde de fer naturel, 2,6-DMP, Fe – polycarboxylate, H₂O₂, radicaux hydroxyle.

ملخص

تم تطبيق أكسيد حديد طبيعي (NIO) للتفكك الضوئي للمركب 2,6-diméthylphénol (2,6-DMP) في وجود الأحماض الكاربوكسيلية تحت الأشعة فوق البنفسجية. وكان اعتماد تفكك 2,6-DMP إلى تشكيل المعقدات Fe – polycarboxylate في المحلول و المدمصة على سطح أكسيد الحديد الطبيعي. أظهرت النتائج أن التفكك الضوئي للمركب 2,6-DMP يمكن ان يتعزز بشكل كبير في وجود الأوكسالات. تمت دراسة المتغيرات مثل pH ، وجود بيروكسيد الهيدروجين و درجة الحرارة في النظام NIO / أوكسالات / الأشعة فوق البنفسجية. تم العثور على قيمة pH الأمثل في المجال 3-4. كما تبين أن تشكيل الحديد الثنائي في النظام NIO / oxalate يتم بسرعة أكبر في المرحلة الأولى، ويصبح تدريجيا معتدل. علاوة على ذلك، تمت دراسة تشكيل H₂O₂ خلال التفاعل الضوئي لاكتشاف علاقتها مع فعالية التحلل الضوئي و دورة الحديد. استخدام 2.0 ٪ من الأيزوبروبانول أكد تدخل جذور الهيدروكسيل في تفكك 2,6-DMP.

الكلمات المفتاحية: أكسيد حديد طبيعي (NIO)، 2,6-diméthylphénol، Fe – polycarboxylate، H₂O₂، جذور الهيدروكسيل.

1. Introduction

Advanced oxidation processes (AOPs) have been applied for degradation and mineralisation of organic pollutants such as phenolic compounds [1, 2], pharmaceuticals [3], agrochemicals [4], landfill leachate [5] and also for feasible and enhanced treatment of decentralised wastewaters [6]. These processes were found to be environmentally sustainable if the process energy consumption was low [7]. Fenton process is a strong oxidation system amongst advanced oxidation processes and has been successfully put into use for removal of recalcitrant organic contaminants [2, 5]. This process is known as the reaction between hydrogen peroxide as an oxidant and iron ions as a catalyst to produce highly active species, mainly non-selective $\cdot\text{OH}$ radicals with oxidation potential of 2.8 V [8]. Photo-Fenton reaction is a combination of Fenton reagents and UV-Vis light that brings about additional $\cdot\text{OH}$ radicals via (i) photoreduction of ferric ions to ferrous ions and (ii) hydrogen peroxide photolysis [9].

In nature, iron, polycarboxylic acids 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]. Environmental applications of heterogeneous photocatalysis, using titanium dioxide (TiO_2) and iron oxides have been extensively investigated to remove organic pollutants in aqueous solution. Iron oxides are abundantly available minerals present in the earth crust. Out of the sixteen known iron oxides and hydroxides [11], magnetite (Fe_3O_4), goethite ($\alpha\text{-FeOOH}$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) are widely used in heterogeneous catalysis processes and have been attractive alternatives for remediation of polluted soil, groundwater [12] and wastewater. Different physico-chemical characteristics of these oxides make them more or less favourable for oxidative reactions. From these features, surface area, pore size/volume and the crystalline structure have principal effects on their activities [13, 14].

Polycarboxylates such as citrate, malonate, and oxalate are common constituents of precipitation, fog, surface waters and soil solutions. Polycarboxylates can form strong complexes with Fe^{3+} and enhance the dissolution of iron in natural water through photochemical processes. Moreover, such polycarboxylate complexes undergo rapid photochemical reactions under sunlight irradiation leading to the formation of oxidative species.

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 [15]. In the 1990s several research groups [16–20] studied the mechanisms of iron (hydr)oxides dissolution in aqueous oxalate

solution. The chemical adsorption of oxalic acid first occurs on the surface of iron oxide leading to the formation of Fe –oxalate complexes, and simultaneously the non-reductive/reductive dissolution of iron oxide takes place [21–25]. Light irradiation can greatly enhance the reductive dissolution of Fe(III) –oxalate complexes, yielding Fe(II) and oxalate radical (C_2O_4) $^{\cdot-}$ [18–25].

In this work, 2,6-dimethylphenol (2,6-DMP) or 2,6-xyleneol was selected as a model pollutant. The xyleneols represent 35% in weight of this mixture (the mixture being composed of 85% of polycyclic aromatic hydrocarbons, of 10% of phenolic compounds and 5% of heterocyclic compounds of nitrogen, sulfur or oxygen) [26]. They are thus likely to be in considerable quantity in the environment. The investigation of viable methods of treatment of polluted waters containing trace amounts of xyleneols is, therefore, of environmental interest. We have used a natural iron oxide (NIO) which is provided from the iron deposits from Chaabet-El-Ballout which is located in North-East Algerian. The analysis of iron deposits revealed that they are mostly composed of hematite.

In this study, the enhancement effects of polycarboxylic acids (oxalic, citric, succinic, malonic, tartaric and malic acids) on the phototransformation of 2,6-DMP reacting with natural iron oxide (NIO) was studied. The results showed that the photodegradation of 2,6-DMP could be enhanced greatly in the presence of oxalate. In order to further understand the degradation of 2,6-DMP by natural iron oxide, the influencing factors as pH of the solution, H_2O_2 and temperature were also studied. Furthermore, the experiments were conducted to evaluate the photochemical activities of the Photo-Fenton-like system and the effect of Fe(III) – oxalate species on the degradation of 2,6-DMP.

2. Experimental

2.1. Materials

The NIO was washed several times with distilled water and dried at 45 °C. 2,6-dimethylphenol was supplied by Reidel-de Haën (purity greater than 99%), sodium hydroxide (NaOH , 98% Carlo Erba Reagenti), perchloric acid (HClO_4 , 98% Prolabo), acetate sodium (99%), acetic acid (99.5%), and sulphuric acid (98%) were provided by Panreac. 1,10 O-phenantroline (>99% Fluka), titanium (IV) oxysulfate solution (Sigma Aldrich, Fluka analytical). Hydrogen peroxide (30%), oxalic acid (99%) and citric acid (99.5%) from Prolabo. Malic acid from (99% Biochem, chemopharma) and methanol (99% VWR Prolabo) were used without further purification. Deionized water from an ultrapure water system (Simplicity UV, MILLIPORE) was used in all experiments.

2.2. Experimental setup and procedure

Degradation experiments were performed in container made up of stainless steel, built upon an elliptical base. The solution was irradiated in a Pyrex glass tube. It was placed vertically in the center of the cylinder and irradiated by a fluorescent lamp (Philips TLAD 15W/05), which dominantly emits radiation at 365 nm. Light intensity ($I = 0.45 \text{ mW cm}^{-2}$) was measured using a radiometer type VLX 3W. The photoreactor tube was placed in a Pyrex glass jacket of a slightly larger diameter flushed by water; thus providing cooling and keeping constant temperature of the irradiated solution. The irradiated solutions and suspensions were magnetically stirred during whole experiments. The suspensions of 2,6-dimethylphenol ($5 \times 10^{-4} \text{ M}$) and 1 g L^{-1} of iron oxides were stirred in the dark for 30 min before irradiation to establish adsorption/desorption equilibrium. The samples withdrawn at different reaction times were filtered with cellulose acetate filters ($0.45 \mu\text{m}$) to separate NIO particles. All experiments were performed at $T = 20 \pm 2^\circ\text{C}$. The solution pH was adjusted by 1 M of HClO_4 or NaOH and measured by means of an HANNA Instruments 8521 pH meter.

2.3. Analytical methods

The remaining 2,6-DMP during the photodegradation 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 ($5 \mu\text{m}$, $250 \times 4.6 \text{ mm i.d.}$). The methanol ultrapure water mixture (55 / 45) was used at mobile flow rate of 1 mL min^{-1} at room temperature. The detection wavelength was at 270 nm. 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 $\text{Fe(II)} - \text{phenanthroline}$ is equal to $11.180 \text{ mol}^{-1} \text{ L cm}^{-1}$ [27]. Hydrogen peroxide was determined using titanium (IV) oxysulfate according to DIN 38402H15.

3. Results and discussion

3.1. Properties of natural iron oxide

The natural iron oxide sample was examined by X-ray diffraction (XRD) to determine its crystal structure as reported in our previous paper [28]. The specific surface area measured by Brunauer-Emmett-Teller (BET) method was $79.015 \text{ m}^2\text{g}^{-1}$ and the total pore volume was $0.0892 \text{ cm}^3\text{g}^{-1}$.

3.2. Phototransformation of 2,6-DMP by polycarboxylic acids on natural iron oxide

The effects of polycarboxylic acids on the transformation of 2,6-DMP with natural iron oxide and under UV irradiation were presented in Fig. 1.

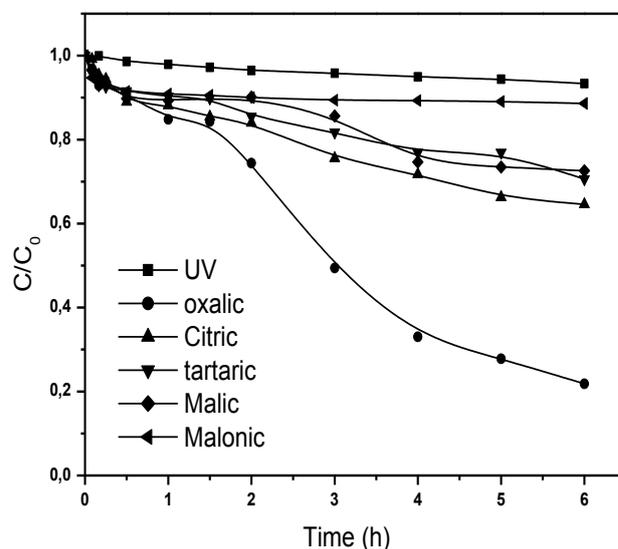


Fig.1. Effect of carboxylic acids ($5 \times 10^{-3} \text{ M}$) on the photodegradation of 2,6-DMP ($5 \times 10^{-4} \text{ M}$) under UV irradiation by using 1 g L^{-1} NIO.

2,6-DMP degradation occurred slowly in the absence of polycarboxylic acids. In comparison, the transformation was promoted in the case of adding of oxalic, citric, malic, tartaric, and malonic acids respectively. The photocatalytic degradation of 2,6-DMP followed the first-order reaction kinetics with the first-order kinetics constants (k) for 2,6-DMP degradation as 0.262, 0.072, 0.050, 0.049, 0.034 h^{-1} in the presence of oxalic, citric, malic, tartaric, and malonic acids respectively. The results showed that the photodegradation rate of 2,6-DMP in presence of oxalic acid was the highest, presumably due to the sufficient amount of Fe(II) leached from natural iron oxide.

From Fig. 2 it is apparent that oxalic acid is the only carboxylic acid which leads to higher amounts of leached iron. We were unable to detect any release of iron (II) in the suspension of the other carboxylic acids.

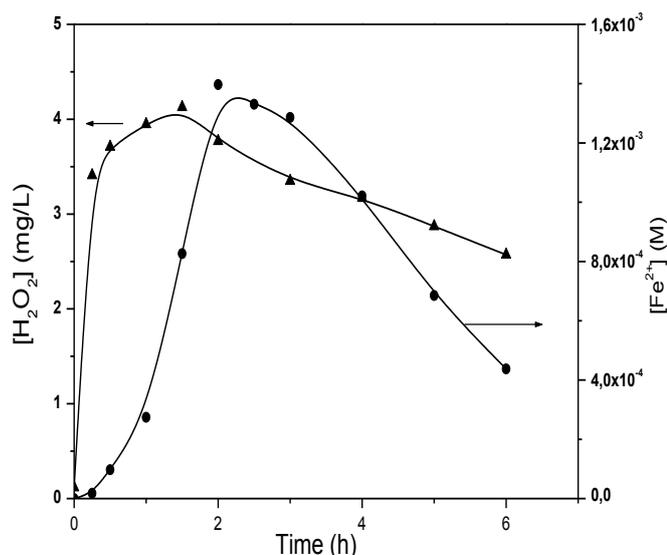
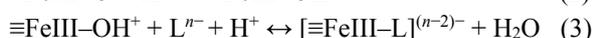
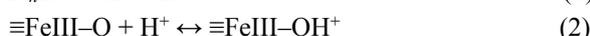
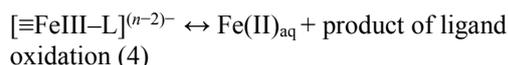


Fig. 2. The variation of dissolved Fe²⁺ and H₂O₂ during 2,6-DMP photodegradation under an initial concentration of 5×10⁻³ M oxalic acid and 1 g L⁻¹ of natural iron oxide.

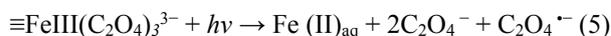
The effect of the different carboxylic acids can be explained taking into account their acidity and their capacity of forming Fe(III)-complexes. Thus, according to the literature, the ideal agent for iron(III) oxides ligand promoted dissolution should be a strong acid of an anion which is a good ligand for Fe(III) [29]. A compound that comes close to these requirements is oxalic acid that presents a moderate acid strength (pK_{a1} = 1.25; pK_{a2} = 4.27) and forms Fe(III)-complexes of high stability (being log of stability constants β₁ = 7.53; β₂ = 13.64 and β₃ = 18.49) [30,31]. However, the extents of hydrolysis and reductive dissolution of iron oxides by H₂O alone were low. Polycarboxylic acids have strong complexation abilities. They can react with iron oxides to form surface-bound Fe(II) species, *i.e.* ≡Fe(II) – polycarboxylate, on the surface of iron oxides with three distinct steps: (i) adsorption of organic ligands on the iron oxide surface, (ii) non-reductive complexation, and (iii) reductive complex [32,33]. When iron oxide particles suspend in polycarboxylic acid solution, an electrical double layer is established at the interface by acid ionization and protonation of oxygen as shown in Eqs. (1) and (2). The formed surface hydroxyl groups become active sites for subsequent adsorption of organic ligands as described by Eq. (3).



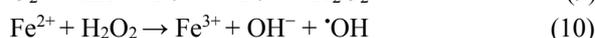
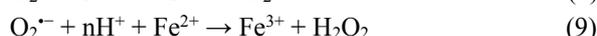
Some authors have pointed out that during the leaching process, Fe(III) reduces to Fe(II) on the oxide surface due to electron transfer from the adsorbed carboxylic acid [34]. The reduction of structural Fe(III) to Fe(II) destabilizes the coordination sphere of the iron both as a result of the loss of charge and because of the larger size of the Fe(II) and thus induces detachment of iron as Fe(II) Eq. (4). Also Fe(II) ions accelerate the reductive dissolution of iron oxides. Fe(II) ions when present in the solid iron oxide network, can be transferred to the water.



When UV-A radiation is applied and in the case of iron oxide – oxalic acid system Eq. (4) can be written as Eq.(5):



The oxalate radical can be transferred into carbon-centered radical CO₂^{•-} as described by Eq. (6), and the excited electron is transferred from carbon-centered radical into adsorbed oxygen and superoxide ion O₂^{•-}, as described by Eq. (7). H₂O₂, thought to be formed from O₂^{•-} Eqs. ((8) and (9)) participates in a classical Fenton reaction with Fe(II), formed by photo-reduction of Fe(III), producing [•]OH (Eq. (10)).



In order to elucidate the formation of H₂O₂, as showed in Eq. (9), Hydrogen peroxide was determined by the formation of a yellow complex with titanium (IV) oxysulfate in the NIO (1 g L⁻¹) and oxalic acid suspensions with initial concentration of oxalic acid of 5×10⁻³ M under UV light illumination. The results showed that H₂O₂ was detected at a significant level about 4 mg L⁻¹(Fig. 2). Its concentration in the system depends on both the rates of its generation and consumption. Hydrogen peroxide is an important intermediate in the aqueous iron oxide and oxalate suspension by irradiating with UV light.

The Fenton reaction, utilizing [•]OH for the degradation of organic chemicals, is hampered by the presence of an [•]OH scavenger. This is important since wastewater usually contains various types of [•]OH scavenger. 2.0 % of isopropanol was added to NIO – 2,6-DMP suspension in the presence of oxalate and under light irradiation. The results showed that the photodegradation of 2,6-DMP was totally inhibited compared to the photodegradation of 2,6-DMP in absence of isopropanol (Table 1). It can be seen that

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the rate kinetic of 2,6-DMP in presence of 2.0 % of isopropanol was similar to the rate kinetic obtained from UV direct photolysis of 2,6-DMP at 365 nm.

Table. 1 The pseudo- first-order kinetic constant (k) for photodegradation of 2,6-DMP in different systems.

Reaction	k (h^{-1})
photolysis	9.3×10^{-3}
With isopropanol	5.3×10^{-3}
Without isopropanol	$26,2 \times 10^{-2}$

3.3. Effect of pH

To study the effect of pH on the photocatalytic degradation of 2,6-DMP (5×10^{-4} M) in NIO – oxalate suspensions ($1 \text{ g L}^{-1} - 5 \times 10^{-3}$ M), six sets of experiments under UV irradiation were performed by means of different initial pH from 2 to 11. Fig. 3 showed the change of the pseudo-first-order kinetic constant (k) values for 2,6-DMP degradation on the initial pH values.

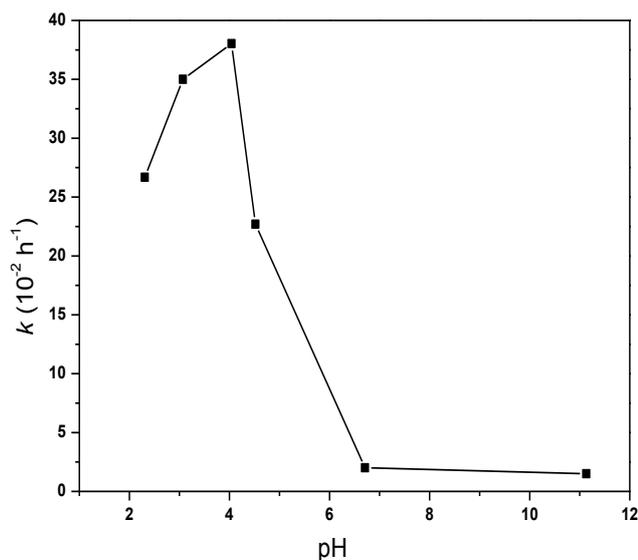


Fig. 3. The pseudo-first-order kinetic constant (k) versus the initial pH value for the photodegradation of 2,6-DMP (5×10^{-4} M) by using 1.0 g L^{-1} NIO in the presence of oxalic acid (5×10^{-3} M).

The photodegradation of 2,6-DMP is seen to depend strongly on pH in the iron oxide–oxalate system. pH 4 was the optimal one and the maximal k value was determined to be $38.04 \times 10^{-2} \text{ h}^{-1}$. It can be seen from Fig. 3 that when pH was beyond the range of about 3–4, the degradation of 2,6-DMP would be inhibited considerably. Balmer and Sulzberger [35] had reported that the most important Fe(III) – oxalate species were $\text{Fe(III)(C}_2\text{O}_4)_2^-$ and $\text{Fe(III)(C}_2\text{O}_4)_3^{3-}$, which are highly photoactive when the pH was at

around 4. In our study, the $\text{Fe(III)(C}_2\text{O}_4)_2^-$ and $\text{Fe(III)(C}_2\text{O}_4)_3^{3-}$ species might exist in a higher concentration in the solution and on the surface. The k value was decreased when the pH value was increased to 4–5, because of the low photoactivity of $\text{Fe(III)(C}_2\text{O}_4)^+$ and $[\text{Fe(III)(C}_2\text{O}_4)]^+$ species which are predominant at this interval of pH [22,24,36,37]. When pH was beyond 6, the predominant Fe(III) species were Fe(OH)_2 and Fe(OH)_3 as the precipitate and the photodegradation of 2,6-DMP was inhibited. The initial pH of the oxalate solution was concluded to be an important factor to affect such a photo-Fenton reaction.

3.4. Effect of additional H_2O_2

During the photoreaction, H_2O_2 could be formed and then decomposed by reacting with Fe^{2+} species, simultaneously. It was found in the experiment that its concentration was at 4 mg L^{-1} (1.2×10^{-4} M) as shown in Fig. 2 (section 3.2). In order to estimate the optimum concentration of H_2O_2 in the natural iron oxide – oxalic acid ($1 \text{ g L}^{-1} - 5 \times 10^{-3}$ M) system and under UV irradiation, a series of experiments were established in the presence of various H_2O_2 concentrations ranging from 10^{-3} M to 10^{-2} M (Fig. 4).

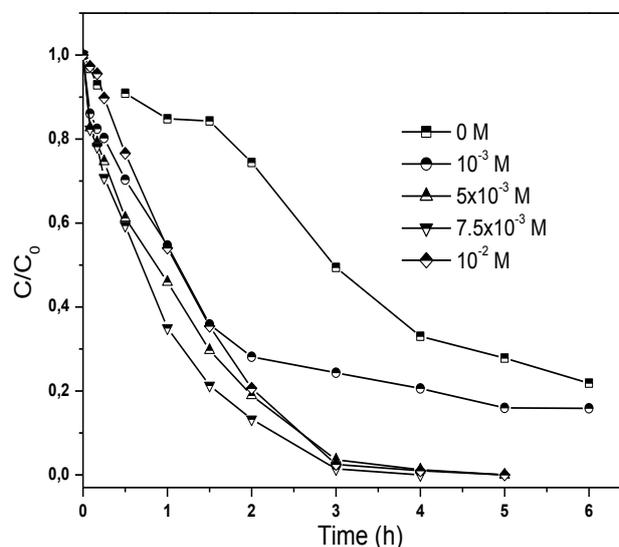
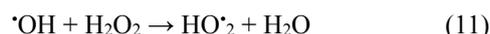


Fig. 4. Effect of additional H_2O_2 on the degradation of 2,6-DMP in presence of 1 g L^{-1} NIO and 5×10^{-3} M oxalic acid under UV irradiation.

The photocatalytic ability of NIO in presence of H_2O_2 showed a significant enhancement in the degradation of 2,6-DMP. It is noted that the concentration of H_2O_2 generated by natural iron oxide – oxalate system is not sufficient for the complete degradation of 2,6-DMP. A net acceleration is observed for $[\text{H}_2\text{O}_2] = 10^{-3}$ M and increases slightly with increasing the concentration of

H₂O₂. Indeed, this elimination occurred over a reaction time of 4 hour for [H₂O₂] = 7.5×10⁻³ M, the overall rate of 2,6-DMP degradation in NIO/oxalate/H₂O₂/UV ($k = 1.27 \text{ h}^{-1}$) was about five time faster than by NIO/oxalate/UV ($k = 0.266 \text{ h}^{-1}$). This velocity, in terms of hydrogen peroxide concentration, reaches a maximum. Effectively, a large hydrogen peroxide concentration reduces perceptibly the 2,6-DMP degradation rate. The decrease in the rate to high concentrations of H₂O₂ can be explained by an increased importance of interception of radicals by H₂O₂ Eq. (11).



It has been reported that the rate of formation of $\cdot\text{OH}$ radicals depends on the concentration of H₂O₂, the nature of iron oxide [38, 39] and pH [40].

3.5. Effect of temperature

With the aim of development of an industrial photocatalytic process, it is useful to know if the temperature of the effluent to be purified may have an impact on the physico-chemical processes involved in its treatment. Should in this case, include a system of heating or cooling to the final process. The study of the influence of the temperature is therefore necessary. The effect of temperature value on the photodegradation of 2,6-DMP with NIO/oxalate system was determined with the temperature range of 20-50 °C (Fig.5). As expected temperature has a clear positive effect on the degradation of 2,6-DMP.

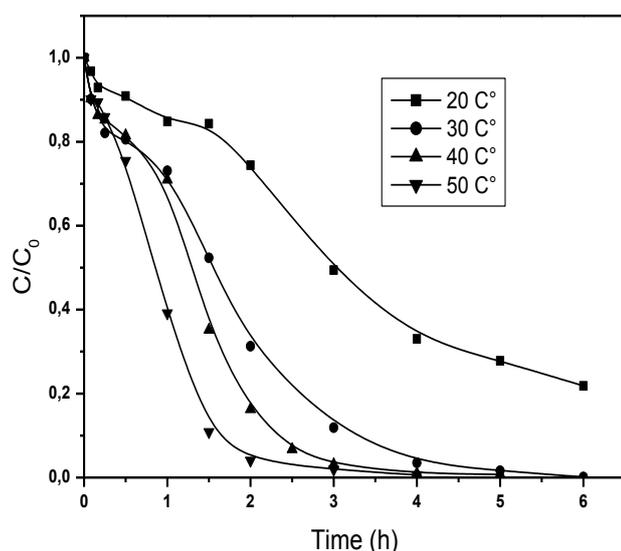


Fig. 5. Influence of temperature on photo-Fenton-like degradation of 2,6-DMP (initial conditions: 5×10⁻³ M oxalic acid, 1 g L⁻¹ (NIO) under UVA irradiation.

These results can be explained by considering that higher temperatures favor the decomposition of H₂O₂. Lee *et al.* [41] studied the decomposition of H₂O₂ at different temperatures and have found that the rate of decomposition increases exponentially from 30°C to 50°C. Furthermore, in most chemical reactions, an increase in temperature produces an increase in the reaction rate constant and the acceleration of the production of free radical species and their reaction with the molecules in the medium.

4. Conclusion

Phototransformation of 2,6-DMP at the iron oxide – water interface can be promoted effectively with added polycarboxylic acids. Among carboxylic acids studied, oxalic acid was found as the most active to dissolve iron from the natural iron oxide and also for degradation of 2,6-DMP. The photodegradation of 2,6-DMP depended strongly on the initial pH, it was found that the optimal range of initial pH value in the iron oxide–oxalate system was at about 3–4. The contribution of $\cdot\text{OH}$ radicals has been proved by adding 2% of isopropanol as a scavenger. Application of UV-A/NIO/oxalic acid/H₂O₂ system allows total degradation of 2,6-DMP in less than four hours. An important effect of temperature was observed. The results indicated that in the meantime, oxalate, pH, the formation of hydrogen peroxide and Fe-oxalate species play the important roles in the reaction.

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