Activation of oxygen by copper coupled with ascorbic acid under solar and artificial light for Orange G oxidation

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ABSTRACT

This study aims at providing a new method for effective decontamination of organic pollutants in the field of water treatment. This study shows that using advanced oxidation processes in particular the photocatalytic oxidation of L-ascorbic acid (H_2A) by molecular oxygen in the presence of copper (Cu(II)), hydroxyl radicals ($^•OH$) are generated thus enabling the degradation of organic pollutants. The oxidation of H_2A by oxygen with Cu(II) as catalyst to stimulate the degradation of orange G (OG) dye in aqueous solution was investigated in the absence (Cu(II)/H_2A) and presence of artificial and natural light (Cu(II)/H_2A/$UV_{310 nm}$ or sunlight, respectively). All the decolorization experiments were performed at room temperature (20°C) within 300 min and with initial OG concentration of 0.05 mM. The effect of different parameters such as dosages of H_2A, dosage of Cu(II) and solution pH on the degradation efficiency of the processes were also investigated. The results show that the optimal degradation condition was selected at an initial pH of 4.5, H_2A dosage of 5 mM and Cu(II) dosage of 1 mM. The use of a radical scavenger, tert-butanol, confirmed the involvement of $^•OH$ in OG degradation in both systems. Likewise, the addition of hydrogen peroxide (H_2O_2) in the previous systems leads to $^•OH$ radicals formation via the Fenton-like and photo-Fenton-like systems. The influence of solar light was also studied showing a significant enhancement in the photodegradation efficiency of OG. In the Cu(II)/H_2A/sunlight system, OG degradation of 93.6% was achieved after 2 h of reaction time compared with 100% degradation when using the Cu(II)/H_2A/H_2O_2/sunlight. These results show that the photo-oxidation of H_2A with Cu(II) open a new pathway in the degradation of refractory pollutants by a natural processes.

Keywords: Orange G; Ascorbic acid; Oxygen; Copper (II); Hydrogen peroxide; Hydroxyl radicals

1. Introduction

Many recent research works focusing on the development of new methodologies for the degradation of toxic water pollutants, lead to a main conclusion that the most effective technique for degrading organic pollutants is achieved when powerful oxidizing agents such as $^•OH$ or other radicals, are generated. Since some of these radicals are naturally produced in the environment by several catalytic processes, it has become important to understand the effect of these radicals on the abiotic transformations of organic pollutants naturally occurring in the environment. These radicals especially the hydroxyl radical ($^•OH$) may play a vital role in the process of decontamination and mineralization under natural condition.

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One way of generating ·OH radicals is by oxidizing L-ascorbic acid or vitamin C (H_2A), which is a water-soluble vitamin that is involved in many biochemical reactions. L-Ascorbic acid is naturally found in a wide variety of animals and plants. H_2A exists in nature in two forms: the reduced (L-ascorbic acid) and oxidized (dehydroascorbic acid) forms. Trace levels of transition metals such copper (Cu) and iron (Fe), which are naturally present in aquatic environment, can participate in the metal-catalyzed Haber–Weiss reaction (superoxide-driven Fenton reaction) [1] and catalyze the oxidation of H_2A by molecular oxygen to produce ·OH [2–4]. Although copper has higher potential toxic properties than iron, Cu has a faster H_2O_2 decomposition rate than Fe in a Fenton reaction, which could be carried out under more nearly neutral conditions, because copper salts are more soluble at neutral pH [5]. Generally H_2A is considered as an excellent reducing agent and can serve as a donor antioxidant in free radical-mediated oxidative processes. As a reducing agent, it is able to reduce redox-active metals such as copper and iron, thus increasing their pro-oxidant chemistry [6]. In addition, the ene-diol group of H_2A on carbons 2 and 3 enable oxidization through one or two electron transfers, thereby allowing it to scavenge oxygen [7]. Therefore, in aquatic ecosystems, H_2A can play an important role in a variety of chemical and biological processes relevant to the transformation of organic compounds.

The catalytic process in the presence of H_2A and copper together has been studied extensively in biological systems and described in detail [8–10]. In the presence of dioxygen, the first step in the reaction is the formation of an intermediate complex which undergoes a transfer of two electrons to produce dehydroascorbic acid (DHA) and hydrogen peroxide as described by Eq. (1).

$$H_2A + O_2 \rightarrow DHA + H_2O_2 \qquad (1)$$
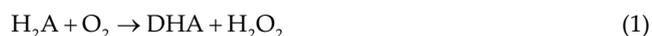
In the presence of hydrogen peroxide formed, ascorbic acid can recycle Cu(II) to Cu(I) facilitating further generation of reactive oxygen species by subsequent Fenton cycles producing hydroxyl radicals. These radicals can then quickly and non-selectively mineralize a broad range of organic contaminants present in the medium by a conventional redox reaction.

$$HA^- + Cu(II) \rightarrow Cu(I) + A^{\bullet-} + H^+ \qquad (2)$$

$$Cu(I) + H_2O_2 \rightarrow Cu(II) + OH^- + HO^{\bullet} \qquad (3)$$
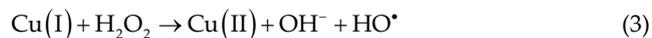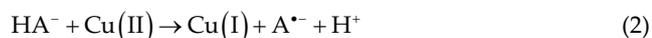
This system is of significant relevance to metal cycling and self-cleaning processes naturally occurring in the environment.

In this study, orange G (OG) dye was selected as a model recalcitrant organic compound due to its high aqueous solubility (5 g/100 mL) and persistence in the environment. Its removal from the environment has caused much concern [11–14]. The H_2A/Cu(II) system described above was introduced in recent research studies as a new AOP method used for the purification of many types of wastewater [15,16]. However, no studies reported using the oxidation of H_2A catalyzed by Cu in the presence of light. To the best of our knowledge, this

work is the first to utilize H_2A/Cu(II)/UV system in treating a persistent azo dye (OG) using simulate and solar light. The objectives of this work are to understand: (1) the transformations of pollutants in aquatic environments in the presence of H_2A and copper, (2) the effect of various factors, such as pH, dosages of H_2A and Cu(II) on the kinetics of OG degradation, (3) the influence of H_2O_2 and light on the degradation of OG.

2. Materials and methods

2.1. Chemicals

The model Orange G (OG) pollutant was obtained from Alfa Aesar (Germany), the L-ascorbic acid (H_2A, 99.6%) from Mallinckrodt and copper sulfate pentahydrate ($CuSO_4.5H_2O$, 99%) from Riedel-de HaËn. Tert-butanol (t-BuOH, 99%), perchloric acid ($HClO_4$, 60%), sodium hydroxide (NaOH, >97%), hydrogen peroxide (H_2O_2, 30%), sulfuric acid (97%) were supplied by VWR Chemicals Prolabo (Spain) and $TiCl_4$ (98%) by Fluka. All chemicals were of analytical grade and used without further purification. The solutions were prepared with ultra-pure water (Millipore) with a resistivity of 18.2 mΩ.cm.

2.2. Experimental setup and procedure

All experiments were performed using a batch system in the dark in a 150 mL jacketed cylindrical glass reactor placed in a stainless steel container and open to air. The solution was kept at a constant room temperature of 20°C ± 1°C using a thermostat circulating water bath. A magnetic stirrer was located at the base of the reactor to ensure the uniformity of solutions. After the calculation of the concentrations required for each experiment, an appropriate volume of OG is taken from the stock solution. The reagents H_2A and Cu(II) are added to the solution containing the pollutant one after the other. The reaction reference time t = 0 is determined when the second reagent (Cu(II)) is added after completing the volume with ultrapure water and homogenization of the solution. Samples were, respectively, taken at fixed intervals and mixed immediately with appropriate amounts of tert-butanol to quench the reaction before analysis. The solution pH was adjusted by 1.0 M of $HClO_4$ or NaOH and measured using HANNA Instruments 8521 pH-meter (Germany).

When conducting experiments in the presence of light, the solution was irradiated by 3 UV lamps (Duke Sun Lamp GL 20 W, λ_{max} = 310 nm) placed inside the stainless steel container. Light intensity (I = 0.18 mW cm^{-2}) was measured using UVP Model UVX Digital Radiometer.

The tests under natural solar radiation were carried out during the month of June 2017 during a sunny day in Constantine, Algeria (latitude 36°20′N, longitude 6°37′E). Experiments were conducted in the same cylindrical Pyrex reactor, placed vertically. The light intensity was 2.14 mW cm^{-2} measured by UVP Model UVX digital radiometer positioned to the sample height.

2.3. Analytical methods

The decolorization of OG was quantified spectrophotometrically. The concentration of OG was monitored by measuring the absorbance at λ_{max} = 478 nm, using a UV–Visible

spectrophotometer (Thermo Scientific) controlled by software Thermo Insight. Hydrogen peroxide was measured using a colorimetric method based on photoelectric measurement of the color intensities of hydrogen peroxide solutions treated with $TiCl_4$ reagent, according to the reaction in Eq. (4). The molar absorption coefficient at 410 nm is 720 $M^{-1} cm^{-1}$ [17]. The yellow color produced in the reaction is due to the formation of pertitanic acid (H_2TiO_4).

$$Ti^{4+} + H_2O_2 + 2H_2O \rightarrow H_2TiO_4 + 4H^+ \qquad (4)$$
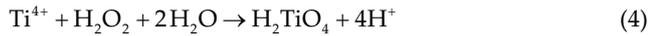
3. Results and discussion

3.1. Generation of H_2O_2 in the $H_2A/Cu(II)$ process

To confirm that H_2O_2 is generated during the oxidation of H_2A by molecular oxygen (open to the atmosphere) with Cu(II) as catalyst, a spectral study of the oxidation process was performed and the formation of the H_2O_2 was monitored.

The UV-visible absorption spectrum is reported in Fig. 1a. Since there are significant differences among the spectrums of H_2A at different times, we can deduce that a transformation has occurred. As reported by Zhou et al. [15], the oxidation of H_2A catalyzed by Cu(II) leads to the formation of reactive species via reactions shown in Eqs. (2)–(9). Primarily, HA^- reduces Cu(II) to Cu(I) through a one-electron oxidation as described by Eq. (2). Subsequently, the Cu(I) generated reduces O_2 into H_2O_2 by two single-electron transfer reactions (Eqs. (5) and (6)) [18]. Finally, the reaction of Cu(I) with H_2O_2 (the Fenton-like reaction; Eq. (3)) produces reactive oxidants such as $^\bullet OH$, which reacts rapidly and non-selectively on most of the organic compounds.

$$Cu(I) + O_2 \rightarrow Cu(II) + O_2^{\bullet-} \qquad 3.1 \times 10^4 M^{-1} s^{-1} \qquad (5)$$

$$Cu(I) + O_2^{\bullet-} \xrightarrow{2H^+} Cu(II) + H_2O_2 \qquad 2.0 \times 10^9 M^{-1} s^{-1} \qquad (6)$$

$$O_2^{\bullet-} + H^+ \leftrightarrow HO_2^\bullet \qquad (pK_a = 4.8) \qquad (7)$$

$$Cu(II) + O_2^{\bullet-} (HO_2^\bullet) \rightarrow Cu(I) + O_2 (O_2 + H^+) \qquad 6.6 \times 10^8 M^{-1} s^{-1} \quad (8)$$

$$Cu(II) + H_2O_2 \rightarrow Cu(I) + HO_2^\bullet + H^+ \qquad < 1 M^{-1} s^{-1} \qquad (9)$$
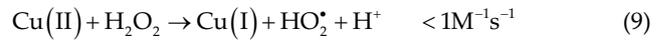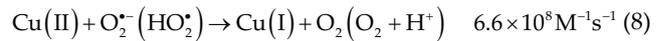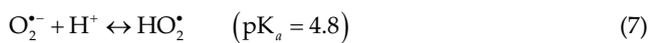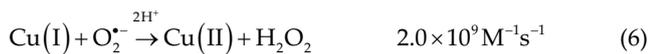
Fig. 1b shows the concentration of H_2O_2 generated with respect to time during the oxidation of 5 mM of H_2A catalyzed by 1 mM Cu(II). Hydrogen peroxide concentration was determined by the formation of a yellow complex with $TiCl_4$. As shown in Fig. 1b, the concentration of H_2O_2 increases rapidly with time in the first 30 min of the process and reached its peak with a concentration of 0.18 mM. In the late stages of the process, the formation of H_2O_2 decreases significantly due to the decrease of H_2A concentration. In addition, hydrogen peroxide is consumed by a Fenton-like reaction of Cu with H_2O_2 to produce hydroxyl radicals as shown by Eq. (3). The same analysis was performed in the presence of UV light. Similar results were observed with an acceleration of the H_2A transformation and H_2O_2 generation. This acceleration can be explained by the photolysis process of ascorbic acid at 310 nm in addition to its oxidation by O_2 as shown by Eq. (1).

3.2. Degradation of OG induced by Cu(II)/H_2A system

The removal of OG with an initial concentration (C_{OG}) 0.05 mM at pH 3 under different reaction conditions is displayed in Fig. 2. Neither Cu(II) nor H_2A alone changed the concentration of OG in 300 min, suggesting that both Cu(II) and H_2A alone are unreactive toward OG. To eliminate the possibility of the oxidation of OG by H_2O_2, a controlled experiment was also conducted in the dark using H_2O_2 at 0.2 mM (the concentration formed during H_2A oxidation). As shown in Fig. 2, no degradation was observed. Similar results are reported in Divya et al. [19]. However, the combination of Cu(II) with H_2A (open to atmosphere) degraded OG by more than 49% after 300 min of reaction time. The positive effect of the Cu(II)/H_2A system can be attributed to the in situ generation of Cu(I) and hydrogen peroxide (Fig. 3b) by the oxidation of H_2A catalyzed by Cu(II), giving rise to the
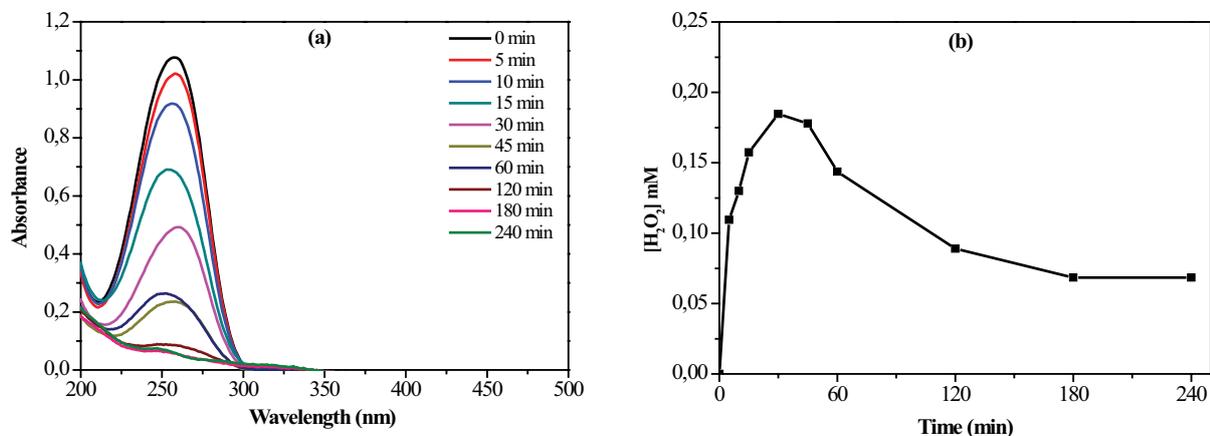
Fig. 1. (a) Spectral evolution of H_2A diluted in 25 mL and (b) formation of H_2O_2 in Cu(II)/H_2A system ($[Cu(II)]_0$ = 1 mM, $[H_2A]_0$ = 5 mM, pH = 3 ± 0.1, T = 20°C).

formation of hydroxyl radicals (Eqs. (2), (5) and (6)) capable of degrading OG. We can also see that OG disappears rapidly at the start of the reaction and greatly slows down after 120 min of treatment. This is due to the slow generation of H_2O_2, which is necessary during a Fenton's reaction. These results are consistent with the kinetics of formation of H_2O_2 obtained after 120 min as shown in Fig. 3b.

On the other hand, almost no degradation of OG was observed in the $Cu(II)/H_2A/N_2$ system (Fig. 3a). Likewise H_2O_2 was not produced (data not shown), indicating that the dissolved oxygen has an important role in the degradation of OG by the $Cu(II)/H_2A$ system. Fig. 3a also shows that the $Cu(II)/H_2A/O_2$ system exhibited similar degree of OG degradation to that with $Cu(II)/H_2A$ system open to the atmosphere.
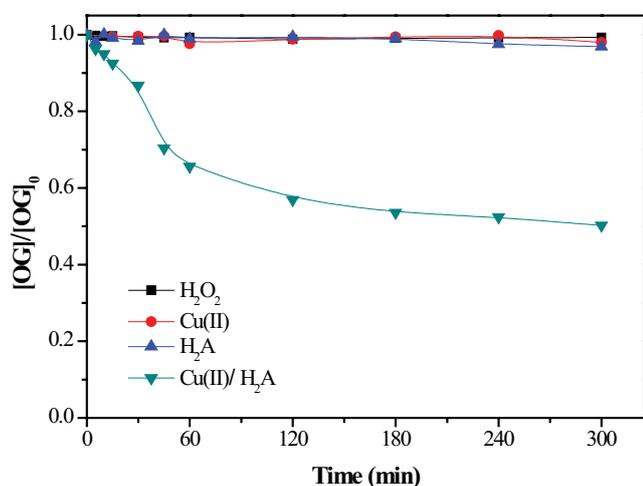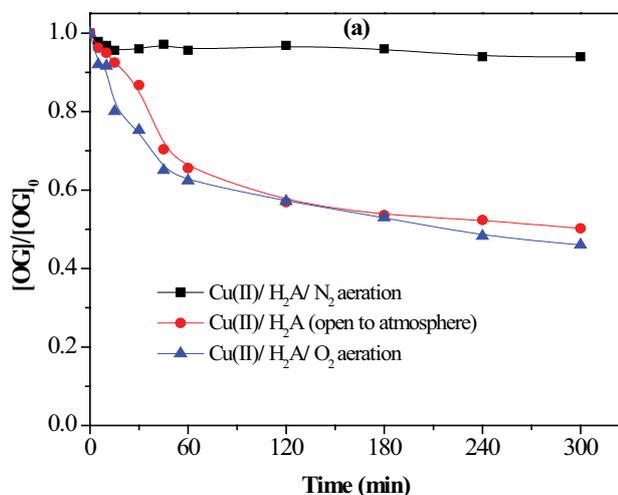
The concentration of H_2O_2 was monitored in the $Cu(II)/H_2A$ and $Cu(II)/H_2A/O_2$ systems. Fig. 3b shows that the excessive O_2 reacts with HA^- producing higher concentration of H_2O_2 (0.27 mM) than that when open to atmosphere but did not make a commensurate difference in OG degradation. This can be related to the low concentration of Cu(I), which is decreased by excessive O_2 as suggested by Eqs. (5) and (6), indicating that Cu(I) is responsible for the activation of H_2O_2.

In order to give evidence for the formation of $^•OH$ radicals, 2% (v/v) t-BuOH was added to $Cu(II)/H_2A$ system. t-BuOH is used as hydroxyl radicals scavenger, the rate constant of the reaction between $^•OH$ and t-BuOH is $6 \times 10^8 M^{-1} s^{-1}$ [20]. As shown in Fig. 4, the degradation of OG was significantly inhibited in the presence of t-BuOH. Therefore, it can be deduced that the primary reactive oxidant was $^•OH$ in the $Cu(II)/H_2A$ process.

3.3. Degradation of OG induced by $Cu(II)/H_2A/UV$ system

To investigate the influence of UV irradiation on the $Cu(II)/H_2A$ process, the photodegradation of OG in $Cu(II)/H_2A/UV$ system was studied. We conducted controlled experiments with 1 mM Cu(II), 5 mM H_2A and 0.2 mM H_2O_2, varying reaction conditions and comparing the results of the following systems UV only, H_2O_2/UV, $Cu(II)/UV$, H_2A/UV and $Cu(II)/H_2A/UV$. The obtained results are presented in Fig. 5.

We monitored the degradation of OG under UV irradiation of 310 nm. This wavelength was chosen because it is present in the solar spectrum that reaches earth ($\lambda \geq 290$ nm) and has enough energy to cause the redox reactions leading to the degradation of the pollutant. The irradiation experiments were carried out immediately after mixing the reactants, making the contribution of the thermal process ($Cu(II)/H_2A$ in the dark) negligible.

As depicted in Fig. 5a, the degradation of OG in the single system (direct UV irradiation) is negligible, indicating that UV irradiation alone is insufficient to decompose OG. Likewise, in the $Cu(II)/UV$ and H_2A/UV systems, the

Fig. 2. Compared degradation of OG by H_2O_2 alone, Cu(II) alone, H_2A alone and $Cu(II)/H_2A$ processes. Conditions: $[OG]_0 = 0.05$ mM, $[H_2O_2]_0 = 0.2$ mM, $[Cu(II)]_0 = 1$ mM, $[H_2A]_0 = 5$ mM, pH = 3 ± 0.1, $T = 20°C$.
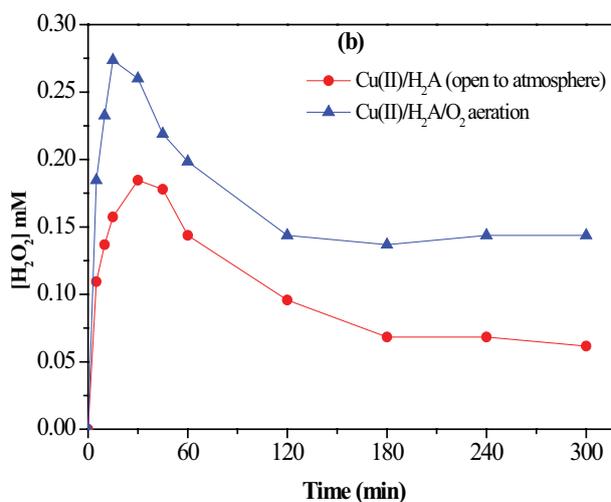
Fig. 3. (a) Decolorization of OG and (b) formation of H_2O_2 in the $Cu(II)/H_2A$ system under different aeration conditions ($[OG]_0 = 0.05$ mM, $[Cu(II)]_0 = 1$ mM, $[H_2A]_0 = 5$ mM, pH = 3 ± 0.1, $T = 20°C$).

degradation of OG was also negligible. This means that both Cu(II) and H_2A, even in the presence of UV light, are not capable of decomposing OG when present independent of each other. The H_2O_2/UV system exhibited noticeable degradation rate because $^\bullet$OH was produced by the direct photolysis of H_2O_2 (Eq. (10)) and then the OG is oxidized by $^\bullet$OH.

However, in the Cu(II)/H_2A/UV that forms a photo-Fenton-like system, OG was significantly decomposed up to 57% after 5 h of reaction time. At the beginning of the reaction, OG degrades rapidly then after 15 min of irradiation it starts decomposing with moderate rate until 5 h of reaction time.

Fig. 5b also shows that the concentration of H_2O_2 formed during the irradiation of the OG/Cu(II)/H_2A mixture as a function of the irradiation time reaches a maximum after 15 min with a concentration of 0.20 mM. However for longer times it decreases to reach a relatively stationary value. This correlates with the maximum degradation of OG obtained after 15 min as shown in Fig. 5a.
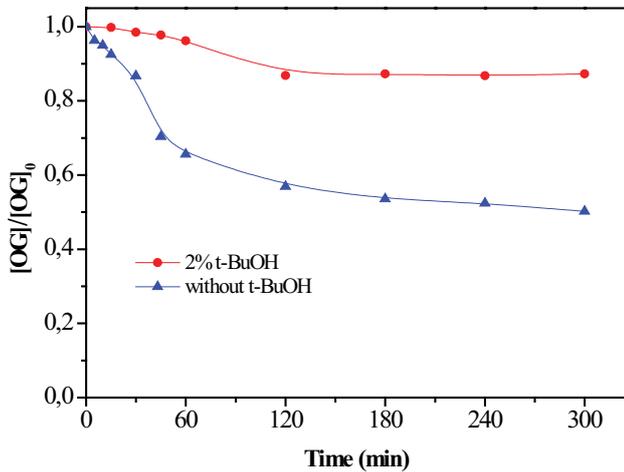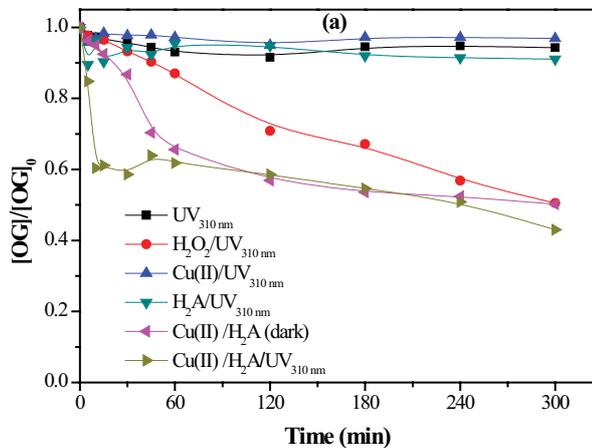
The photo-Fenton-like system Cu(II)/H_2A/UV is effective in degrading OG, however to determine the influence of UV light we compare it with Cu(II)/H_2A process conducted in the dark. As depicted in Fig. 5a, UV light accelerates the degradation of OG significantly but the overall gain is pretty much similar to that in the dark. This acceleration can be explained by an increase in the generation of Cu(I), which is produced not only by recycling Cu(II) in the presence of ascorbic acid (Eq. (2)) but also by the reduction of Cu(II) to Cu(I) enhanced by the presence of $HO_2^\bullet$ (Eq. (8)), which is formed by the further reaction of $HO^\bullet$ with H_2O_2 according to Eq. (11). The $HO^\bullet$ are in turn generated during the photolysis of H_2O_2, according to Eq. (10) and as shown in Fig. 5a. These results are in good agreement with Lee et al. [21] who explain this phenomenon by generation of reactive oxygen species in aqueous solutions in the presence of UV light. The formation of H_2O_2 results in quite similar concentrations of 0.18 and 0.20 mM in Cu(II)/H_2A and Cu(II)/H_2A/UV, respectively (Fig. 5b), which can explain the negligible difference in the overall gain of the two systems [22].

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet \quad (<380\,nm) \tag{10}$$

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \tag{11}$$
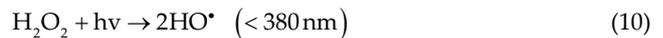
As before, the addition of t-BuOH to Cu(II)/H_2A/UV system, inhibited the photo-Fenton-like reaction in the presence of UV light (Fig. 6), confirming that $^\bullet$OH radicals are responsible for decomposing OG.

3.4. Effect of H_2A and Cu(II) concentration

Optimal degradation of the pollutant can be achieved by producing the hydroxyl radicals by the reagents themselves, that is, by H_2A and Cu(II). This implies that neither the acid nor Cu(II) should be overdosed, so that the maximum amount of these radicals is available to oxidize the organic pollutants. Based on this, we have experimented with the concentrations of H_2A and Cu(II) with the aim of getting

Fig. 4. Degradation of OG in the presence and in the absence of t-BuOH by the Cu(II)/H_2A system ($[OG]_0$ = 0.05 mM, $[Cu(II)]_0$ = 1 mM, $[H_2A]_0$ = 5 mM, pH = 3 ± 0.1, T = 20°C).
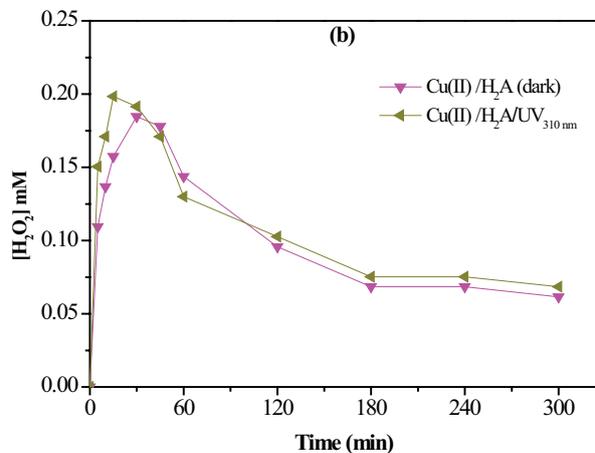
Fig. 5. (a) Photodegradation of OG in different systems upon irradiation at $\lambda_{irradiation}$ = 310 nm and (b) the formation of H_2O_2 with time in Cu(II)/H_2A/UV system. ($[OG]_0$ = 0.05 mM, $[H_2O_2]_0$ = 0.2 mM, $[Cu(II)]_0$ = 1 mM, $[H_2A]_0$ = 5 mM, pH = 3 ± 0.1, T = 20°C).

their optimal concentrations. The experimental results are illustrated in Fig. 7.

The increase in the concentration of H_2A or Cu(II) in the solution increases the production rate of $^{\bullet}OH$ radicals and therefore the rate of the decomposition of OG. In fact, Fig. 7 shows that the degradation efficiency in both processes Cu(II)/H_2A and Cu(II)/H_2A/UV improves with increasing

initial doses of H_2A or Cu(II) introduced in the solution. However, it should be noted that the efficiency decreases at higher concentrations. The best results obtained are with concentrations of 5 mM for H_2A and 1 mM for Cu(II). These concentrations were considered as our optimal concentrations.

In the case of overdosing H_2A, the decrease in the efficiency at higher concentrations could be attributed to the scavenging of $^{\bullet}OH$ radicals by the excess of H_2A [15,23]. Similarly, an overdose of Cu(II) leads to an excessive generation of Cu(I), which can decrease these same active entities following the reduction of Cu(I) to Cu(II) as described by Eq. (12).

$$Cu(I) + HO^{\bullet} \rightarrow Cu(II) + OH^{-} \quad 2 \times 10^{10} \ M^{-1} s^{-1} \tag{12}$$
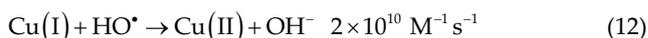
3.5. Effect of pH

Since the pH influences the speciation of acids, we have undertaken a study to see if a modification of this parameter has an effect on our processes in the absence and presence of light. Solutions of OG (0.05 mM), H_2A (5 mM) and Cu(II) (1 mM) were studied at different pH levels of 2, 3 and 4.5 adjusted by diluted NaOH or $HClO_4$ before reaction (Fig. 8). We were limited to a maximum pH value of 4.5, because beyond this value a precipitate (copper oxide) is formed halting our Fenton-like reaction.

Fig. 8 shows that the degradation of OG was significantly influenced by pH. In fact, at pH = 3 and pH = 4.5 we obtained

Fig. 6. Photodegradation of OG in the presence and in the absence of t-BuOH by the Cu(II)/H_2A/$UV_{310 \ nm}$ system ([OG]$_0$ = 0.05 mM, [Cu(II)]$_0$ = 1 mM, [H_2A]$_0$ = 5 mM, pH = 3 ± 0.1, T = 20°C).
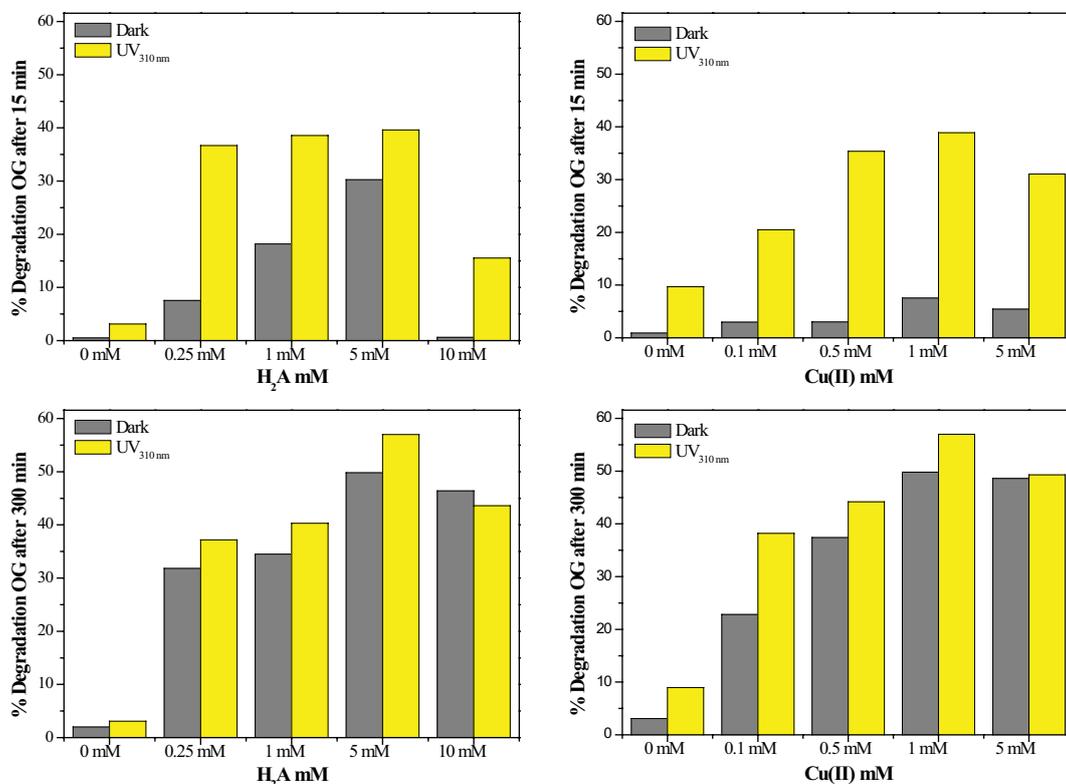
Fig. 7. Effect of H_2A and Cu(II) concentrations on the degradation of OG by the Cu(II)/H_2A system in the absence and presence of $UV_{310 \ nm}$ irradiation ([OG]$_0$ = 0.05 mM, [H_2A]$_0$ = 0–10 mM, [Cu(II)]$_0$ = 0–5 mM, pH = 3 ± 0.1, T = 20°C).

degradation percentages of 49.8% and 51.3%, respectively, after 300 min of reaction time in the absence of light. At the same pH levels, degradation percentages of 57% and 64.5% were obtained in the presence of light. The results at pH = 3 and pH = 4.5 were pretty much similar because at this pH range the active species are the same.

However, the degradation after 300 min of reaction time at pH = 2 was only 34% in the dark and 36.7% in the presence of light. In fact, the oxidation rate of H_2A depends not only on the concentrations of both H_2A and metal ion but also on the H^+ content of the medium. Indeed, at a very low pH levels close to 1, H_2A is completely protonated and hardly oxidized than at higher pH levels. This explains the low degradation percentage obtained at pH = 2.

The influence of pH can also be attributed to the amount of H_2O_2 generated during the oxidation of H_2A, which depends on the pH of the medium [16]. The amount of H_2O_2 can be increased if part of the concentration of H_2A is replaced by the monoanion (HA^-). It should be noted that about 68% of H_2A exists at a pH around 4 in the monoanion form with a pK_{a1} of 4.1 [24]. This is confirmed by the results depicted in Fig. 9, showing that the amount of H_2O_2

generated reached a top peak of 0.25 mM at pH = 4.5 in the dark and a top peak of 0.27 mM at the same pH in the presence of light. As a result our optimal pH level for OG degradation is 4.5 for both systems. In conclusion, the pH level influences both the speciation of ascorbic acid and the amount of H_2O_2 generated in the oxidation of H_2A.

3.6. Effect of H_2O_2

Since the in situ generation of H_2O_2 in both Cu(II)/H_2A and Cu(II)/H_2A/UV systems was low, the degradation of OG was investigated by adding a supplementary dose of H_2O_2 with the purpose of improving its performance.

The decomposition of OG in the dark was examined at different H_2O_2 concentrations in the range of 1–100 mM. Fig. 10a shows that the degradation of OG increases with increasing H_2O_2 concentrations from 1 to 50 mM and starts decreasing for concentrations above 100 mM. In fact, after 5 h reaction, 54.4%, 65.3%, 81% and 81.9% of the OG had disappeared in the solution with 1, 5, 10 and 50 mM of H_2O_2, respectively. It is apparent that the increase in the disappearance of OG was roughly proportional to the concentration of
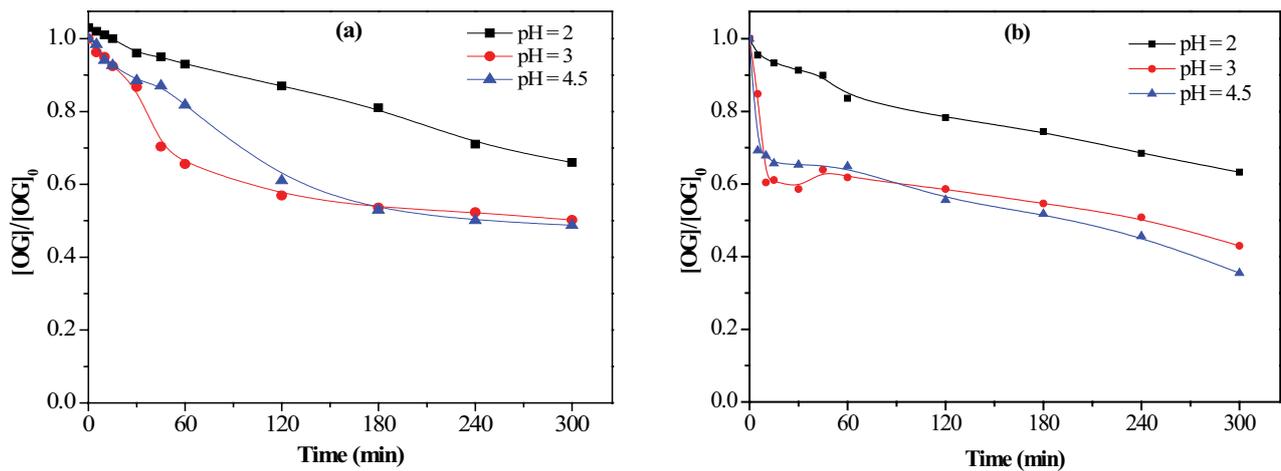
Fig. 8. Effect of pH on the degradation of OG by the Cu(II)/H_2A (a) in the dark and (b) under $UV_{310\,nm}$ irradiation ([OG]$_0$ = 0.05 mM, [Cu(II)]$_0$ = 1 mM, [H_2A]$_0$ = 5 mM, T = 20°C).
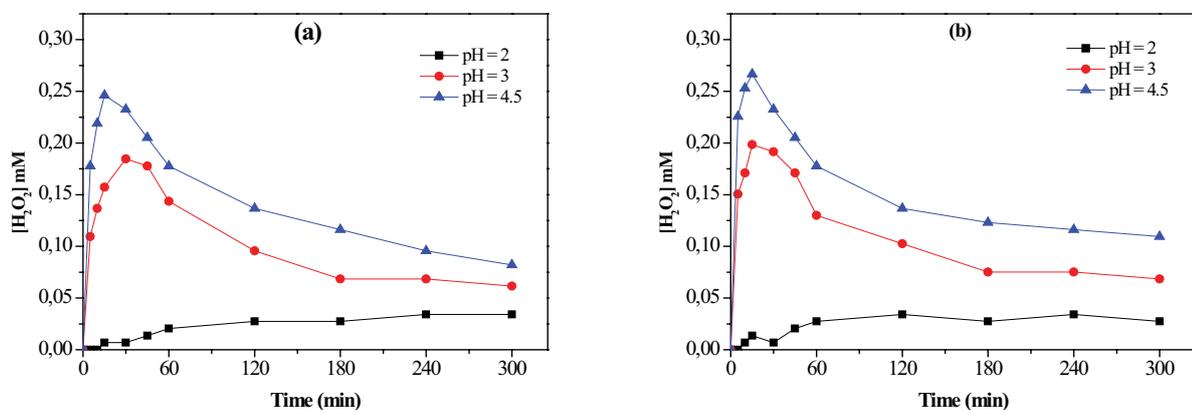
Fig. 9. Formation of H_2O_2 at different pH values by the Cu(II)/H_2A (a) in the dark and (b) under $UV_{310\,nm}$ irradiation ([OG]$_0$ = 0.05 mM, [Cu(II)]$_0$ = 1 mM, [H_2A]$_0$ = 5 mM, T = 20°C).
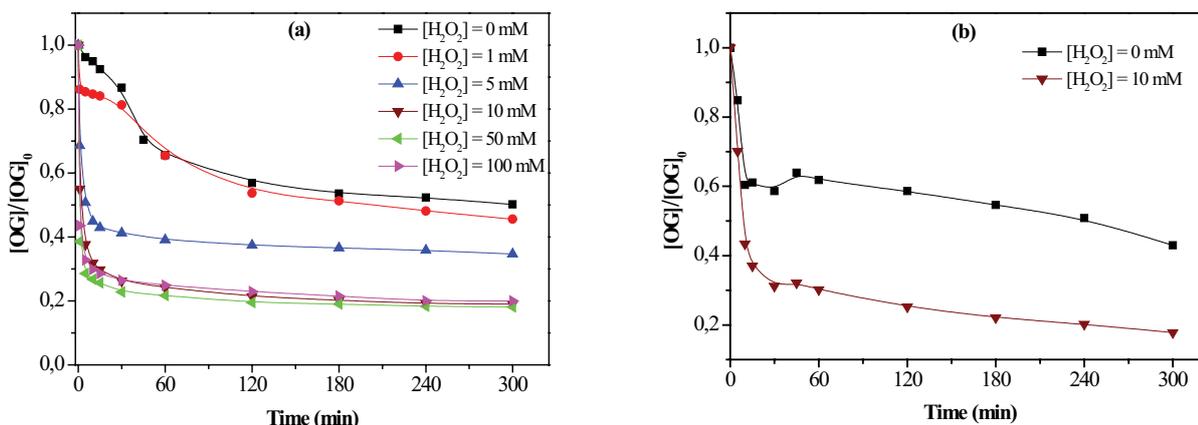
Fig. 10. Effect of H_2O_2 concentration on the degradation of OG by (a) Cu(II)/H_2A and (b) Cu(II)/H_2A/$UV_{310\ nm}$ ([OG]$_0$ = 0.05 mM, [Cu(II)]$_0$ = 1 mM, [H_2A]$_0$ = 5 mM, pH = 3 ± 0.1, T = 20°C).

H_2O_2, because the increase of H_2O_2 concentration would lead to more hydroxyl radicals produced. However, the excess H_2O_2 could act as a HO• scavenger resulting in the generation of $HO_2^•$ (Eq. (11)) that is less active than the hydroxyl radical, explaining the decrease in degradation efficiency above 100 mM.

$$HO^• + HO_2^• \rightarrow O_2 + H_2O \qquad (13)$$

Fig. 10a also shows that there was no further improvement in OG degradation as the H_2O_2 concentration is increased above 10 mM. As a result, this concentration was chosen as our optimal concentration used when degrading our pollutant in the presence of UV light as depicted in Fig. 10b.

As before we obtained similar results when using UV light (Cu(II)/H_2A/ H_2O_2/UV) with slight improvement in the percentage of OG degradation 82.2% compared with that in the dark 81.9% (Cu(II)/H_2A/H_2O_2).

3.7. Effect of the solar irradiation

In nature, copper in its dissolved form, ascorbic acid and solar light can potentially form a homogeneous photo-Fenton-like system. To study such a concept, we exposed an OG/Cu(II)/H_2A system (0.05, 1, 5 mM) to sunlight with the aim of investigating the influence of natural irradiation on OG degradation. We exposed the system to natural sunlight during a sunny day at Constantine (Algeria) and compared its photodegradation results with a system exposed to artificial light.

Fig. 11 presents the photodegradation of OG using UV and solar light under different reaction conditions. It can be seen that both systems solar only and H_2A/solar are inefficient in degrading OG. However, the Cu(II)/H_2A/solar and Cu(II)/H_2A/UV systems are capable of OG decomposition with percentages of 93.84% and 57%, respectively. The degradation is much higher when using solar light than when using artificial light. The presence of 10 mM H_2O_2 has similar effect as that obtained when using UV light (Fig. 10b), nevertheless the reaction is faster and the percentage of OG degradation reaches 100%. This can be due to the high-energy
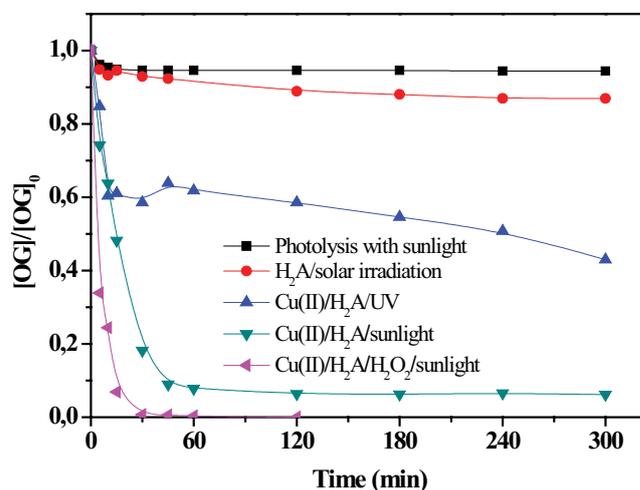
Fig. 11. Photodegradation of OG in the Cu(II)/H_2A system under natural and artificial irradiation ([OG]$_0$ = 0.05 mM, [Cu(II)]$_0$ = 1 mM, [H_2A]$_0$ = 5 mM, pH = 3 ± 0.1, T = 20°C).

of solar light, especially at lower wavelengths, enhancing the efficiency of the photodegradation process where Cu(II) can be reduced to Cu(I) by reacting with photo-generated reactive oxygen species [25]. Therefore, the use of solar light could be a good alternative in organic pollutants degradation especially from the economical point of view.

3.8. Comparison of the studied processes performances

In order to compare the performances of different methods used in this study for the degradation of the OG in a homogeneous medium, all our experiments were carried out with the same dose of Cu(II) (1 mM), H_2A (5 mM) and H_2O_2 (10 mM) taking the decomposition rates after 5 h of reaction time. The results obtained are shown in Fig. 12.

Under the conditions of our experiments, the Cu(II)/H_2A/H_2O_2/sunlight process is the most effective among all systems, resulting in a 100% degradation of OG just after 2 h of reaction time.
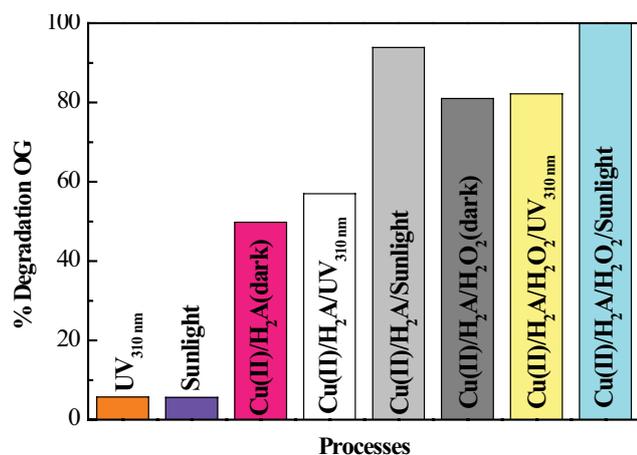
Fig. 12. Comparison of the performances of the different processes studied in a homogeneous medium [OG] = 0.05 mM, [Cu^{2+}] = 1 mM, [H_2A] = 5 mM, [H_2O_2] = 10 mM.

4. Conclusion

This study investigated the degradation of OG by Cu(II)/H_2A and Cu(II)/H_2A/UV processes. The obtained results report that the combination of Cu(II) with ascorbic acid (H_2A) generates H_2O_2 by reducing dissolved oxygen, subsequently activated by the intermediate Cu(I) to induce the production of hydroxyl radicals ($^\bullet$OH), thus resulting in a significant degradation of OG. However, the Cu(II)/H_2A/UV system degraded the OG faster than the Cu(II)/H_2A system, which is attributed to the enhanced reduction of Cu(II) by $HO_2^\bullet$ (or $O_2^{\bullet-}$), which was additionally produced during the photodecomposition of H_2O_2.

In both Cu(II)/H_2A and Cu(II)/H_2A/UV systems, the degradation rate and efficiency can be improved by an increasing the initial concentrations of Cu(II) and ascorbic acid; concentrations of 1 mM of Cu(II) and 5 mM of the acid are sufficient to induce the reactions. The optimal degradation of OG was achieved at pH 4.5 in both systems. The radicals $^\bullet$OH are the main actors of the degradation of OG whatever the system used. The external supply of H_2O_2 to the above systems (i.e., the Cu(II)/H_2A/H_2O_2 and Cu(II)/H_2A/H_2O_2/UV) was found to further enhance the OG degradation.

Under natural irradiation, the experiments highlight the efficiency of the previous systems on the OG degradation. It can be deduced that in natural environments with sunlight, the transformation cycle of Cu(II) to Cu(I) occurs when Cu(II) and ascorbic acid coexist together with higher efficiency as compared with artificial irradiation induction. The comparison of the performances of the different processes used for the degradation of OG showed that the Cu(II)/H_2A/H_2O_2/sunlight process is the most efficient.

This study confirms that both the Cu(II)/H_2A and Cu(II)/H_2A/UV systems are effective methods for reducing OG from water. In natural conditions during night time, the Cu(II)/H_2A can be effective in degrading OG from water and during daytime the degradation efficiency is further enhanced in the presence of sunlight using the Cu(II)/H_2A/sunlight process.

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