

Reactivity of Cu_2O -Cu in the Discoloration of Methylene Blue via a Heterogeneous Fenton-Like Process

Hamidani, Meriem; Djerad, Souad[†]; Tifouti, Lakhdar*

Laboratory of Environmental Engineering, Department of Process Engineering, Faculty of Engineering, Badji Mokhtar - Annaba University, P.O. Box 12, 23000 Annaba, ALGERIA

ABSTRACT. *In this study, copper particles were synthesized by using sodium ascorbate as a green reducing agent under atmospheric conditions. The product was micron-sized and mainly formed by metallic copper Cu with a minor presence of Cu_2O . The product was used as a catalyst in the discoloration of methylene blue in a heterogeneous Fenton-like process in which H_2O_2 was produced in situ. The effect of different parameters such as copper loading, dye concentration, pH of the solution, and the temperature was studied. The total discoloration was achieved after 42 min with 30 mg of copper at 60 °C and pH= 3. The amount of H_2O_2 produced in situ during methylene blue discoloration was evidenced by the permanganate method. It was found the formation of 110 μM after 40 min. The external addition of H_2O_2 at 0.001 M reduced the time for total discoloration to 10 min and the application of 40 kHz ultrasounds reduced the time further to 6 min.*

KEYWORDS: Copper; Ascorbate; Green process; Dye discoloration; Heterogeneous Fenton-like; Advanced oxidation process.

INTRODUCTION

Industrial effluents have been under extensive research by the scientific community because they present serious dangers to the aquatic, air, and soil environments [1-4].

Pollution of water by industries is an issue of major concern. Nowadays, huge amounts of dyes are discharged by industries in an environment that poses a direct and long-term toxic threat to aquatic lives and humans [5, 6]. About 15% of the total world production of dyes is lost during the dyeing processes [7]. Methylene Blue (MB), an aromatic heterocyclic compound is broadly used in different fields of chemistry, textile, biology, and medicine [8]. Due to its

high solubility in water causes contamination in local aquatic systems when it is discharged directly without prior treatment. For humans, methylene blue has been reported to cause nausea, abdominal pain, cyanosis, ethaemoglobinaemia, sweating, headache, and confusion [8]. Its high stability makes it hard to degrade by traditional methods [9]. For this reason, highly efficient techniques such as Advanced Oxidation Processes (AOPs) are employed successfully for the treatment of such persistent compounds. AOPs generate hydroxyl radicals ($\cdot\text{OH}$), a kind of green oxidants with the oxidation potential of 2.8 eV [10, 11], known as non-selective

* To whom correspondence should be addressed.

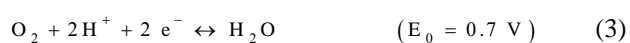
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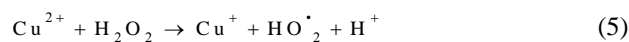
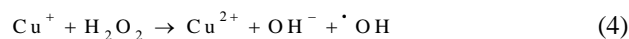
and highly efficient oxidizing species [12]. AOPs are successfully used for the treatment of wastewaters from textile [13], petrochemical [14], and pharmaceutical industries [15]. One of the most frequently used AOPs is the Fenton process. Traditional Fenton involves the reaction between hydrogen peroxide and ferrous ion which generates hydroxyl radicals in a homogeneous system. Fe²⁺ is used as catalyst and H₂O₂ as oxidant. This system has many advantages such as its high performance, simplicity, and its non-toxicity since H₂O₂ can break down into environmentally safe species like H₂O and O₂ [16]. Nevertheless, various factors that hinder the efficacy of the process such as the high cost of hydrogen peroxide, hazards associated with its transport, handling, and storage have made the process unsafe and economically challenging. These drawbacks may be avoided by producing H₂O₂ in situ.

In the metal/O₂ system, the in situ formation of the oxidant H₂O₂ occurred via the reduction of oxygen by metals, and H₂O₂ is subsequently transformed into reactive oxygen species by Fenton reaction [17]. In-situ H₂O₂ production by the metal-catalyzed process has the advantage of forming a Fenton oxidation system in itself. Economically, it is a suitable alternative for the classical Fenton process as the operating costs are greatly reduced. In this study, Cu₂O-Cu was prepared and used for the generation of H₂O₂/[•]OH.

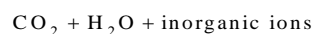
In the literature, copper was less used because of its higher reduction potential (+0.337 V, Cu²⁺/Cu) providing the weaker driving force for electron transfer compared to that of iron (-0.44 V, Fe²⁺/Fe) and aluminum (-1.67 V, Al³⁺/Al), but the reaction is still thermodynamically possible to reduce oxygen to H₂O₂ (0.7 V, O₂/H₂O₂), especially in acidic conditions [17]. In this case, metal dissolution and oxygen reduction occurred simultaneously as follows [17].



The formation of H₂O₂ catalyzed by Cu⁺/Cu²⁺ redox couple allows a Fenton-like process to take place generating hydroxyl radicals [17]:



Hydroxyl radical reacts with a wide variety of organic contaminants, producing shorter and simpler organic compounds, or in case of full mineralization, carbon dioxide, water, and inorganic salts:



In this study, the discoloration of Methylene blue *via* a heterogeneous Fenton-like process is reported. The heterogeneous catalyst (Cu₂O-Cu) was synthesized in the laboratory *via* a green process using sodium ascorbate as a reducing agent. In the literature, only metallic copper (Cu) was tested in a heterogeneous Fenton-like process [17], and few works about the activity of a solid formed by copper and its oxides have been reported [18].

Sodium ascorbate is found mainly in fresh fruits and vegetables. It is an important water-soluble antioxidant (reductant) and enzyme cofactor in various hydroxylation reactions [19]. It is also a renewable, inexpensive, and nontoxic product [20]. In the literature, the synthesis of copper is usually carried out under drastic conditions to produce pure Cu particles. However, from economical and efficacy points of view, this is questionable since copper oxides when present with pure metallic copper may increase the effectiveness of heterogeneous Fenton-like process [18]. In this study, we followed a simple way to synthesize copper under air and without the addition of protective agents. The synthesis and application of copper were expressively chosen to be economical and eco-friendly to respond to the increased demand for green chemistry and the implementation of sustainable processes.

EXPERIMENTAL SECTION

Solutions of copper cations and sodium ascorbate were prepared by dissolving CuSO₄ · 5H₂O (99 wt%, Sigma-Aldrich) and C₆H₇NaO₆ (100 wt%, Riedel de Haën) separately in deionized water.

Copper particles were synthesized by adding 50 mL of sodium ascorbate at 0.5 M to the same volume and concentration of CuSO₄ at 60 °C and 250 rpm. The mixture produced instantaneously an orange suspension which turned to pink-brown with the progress of the reaction. After 1 h, the experiment was stopped and the product was

washed several times with deionized water and acetone after which it was dried under air at room temperature and stocked for characterization and further use. X-ray diffraction patterns were obtained with a Rigaku-Ultima IV X-ray diffractometer and the surface morphology was examined by FEI Quanta 250 FEG Scanning Electron Microscope. The elemental content was evidenced by the Energy Dispersive X-ray (EDX) spectroscopy EDAX X1 analyzer (Ametek).

The obtained product was tested in the discoloration reaction of Methylene blue (100% Fluka).

The concentration of the dye was determined by using a Jenway 6705UV/VIS spectrometer at 665 nm. Samples of MB solution at different time intervals were measured in an optical quartz cell. The discoloration efficiency of MB was calculated from the difference of initial absorbance (A_0) and the absorbance at different time intervals (A_t):

$$\text{Discoloration efficiency (\%)} = \left(\frac{A_0 - A_t}{A_0} \right) \times 100 \quad (7)$$

In a typical experiment, a definite mass of copper was added to 100 mL of Methylene Blue (MB) at 3.10×10^{-5} mol/L (≈ 10 mg/L) under heating (60°C). The solution was kept under agitation at a moderate speed (100 rpm) to maintain the uniformity of the system.

The effects of different parameters on the discoloration of Methylene blue such as copper loading, dye concentration, pH of the solution, and temperature were studied. Hydrogen peroxide was externally added and ultrasounds were applied in order to reduce at minimum the reaction time.

RESULTS AND DISCUSSION

Copper characterization

The product obtained was formed by fine particles ($0.5 \mu\text{m}$ - $1.5 \mu\text{m}$) agglomerated into greater ones with a size of about $8 \mu\text{m}$ (Fig. 1a). The agglomeration was a consequence of the absence of the dispersion agent. XRD analysis (Fig. 1b) shows peaks at ($2\theta = 43.3^\circ, 50.4^\circ, 74.1^\circ$) indexed to pure copper [JCPDS 04-0836] with crystallite size (calculated with Scherrer method) of 652.4 nm and peaks at ($2\theta = 29.6^\circ, 36.5^\circ, 42.4^\circ, 61.4^\circ$) indexed to Cu_2O [JCPDS 05-0667] with crystallite size of 102.82 nm. Elemental analysis (EDX) shows the presence of 37.69% (wt %) of oxygen and 62.31% (wt %) of copper. The presence of Cu_2O was expected and wanted since copper was synthesized without special protection from the air. To get pure Cu the reaction has to be realized under inert

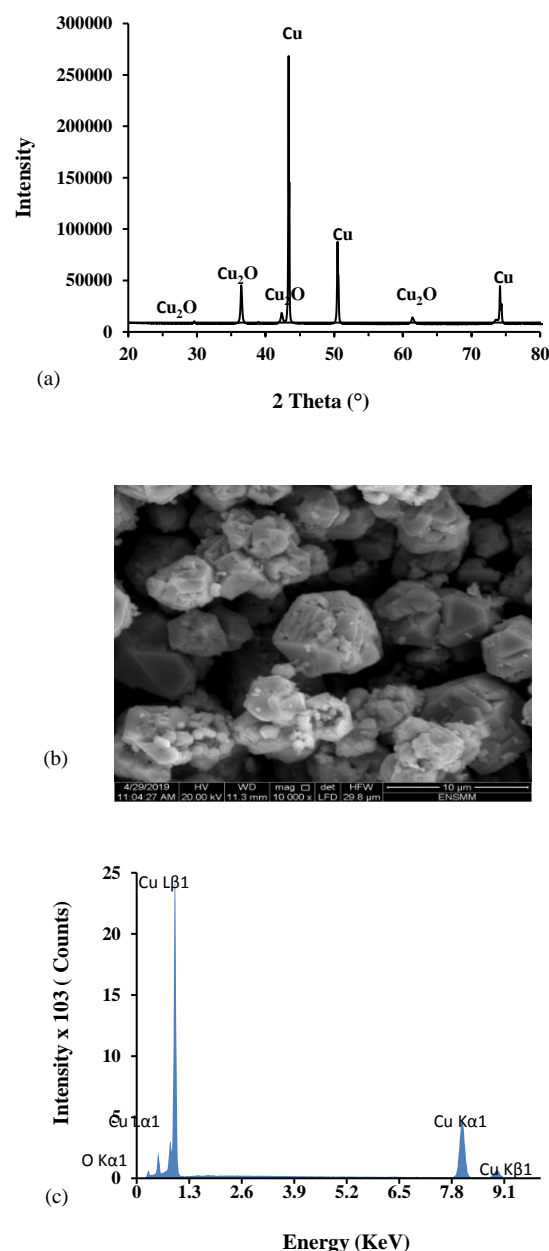


Fig. 1: XRD pattern (a) SEM image (b), and EDX analysis (c) of copper particles.

atmosphere or under strong reducing conditions or in nonaqueous media, but this was not the aim of this study.

The activity of copper in Methylene blue discoloration

Preliminary experiments were carried out to test the feasibility of the discoloration of MB in the presence of copper at different pHs. The results have shown that at neutral and alkaline pH the discoloration of MB

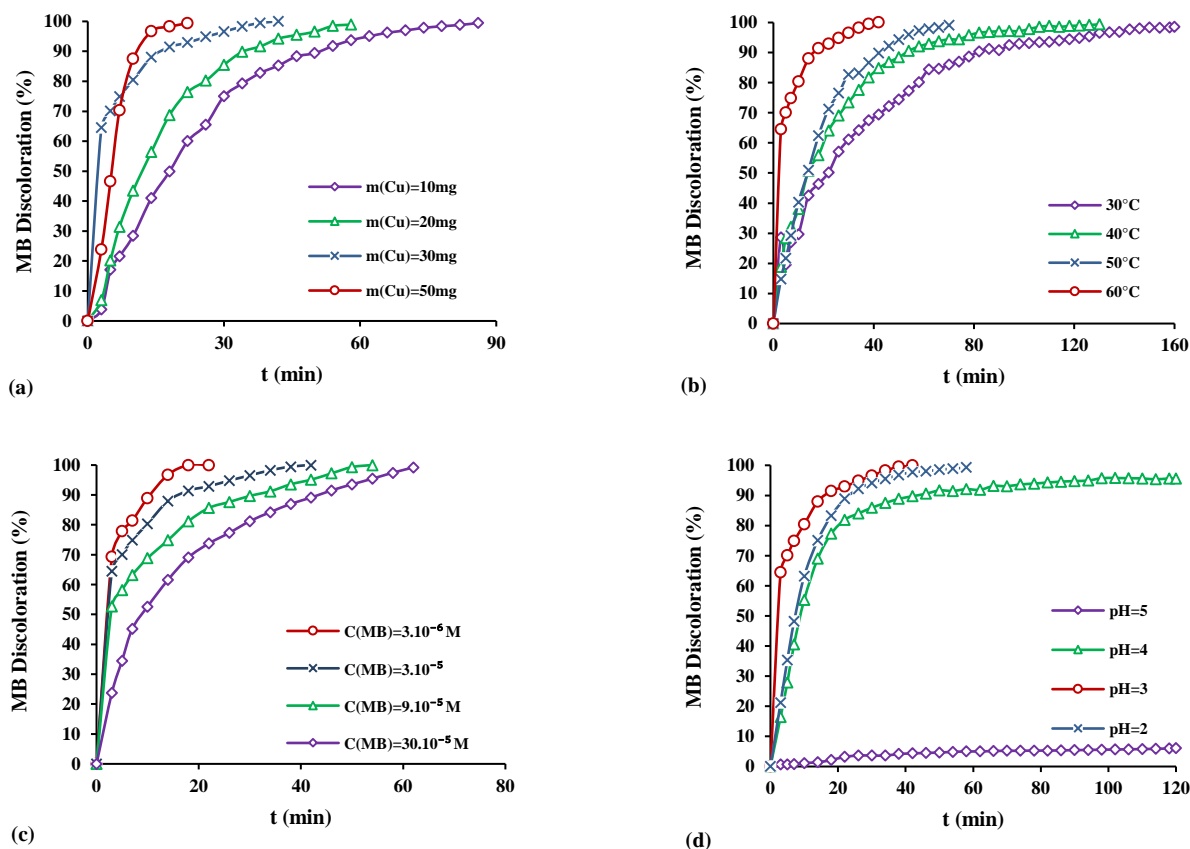


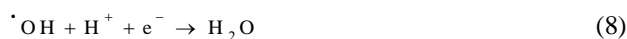
Fig. 2: Effect of the parameters on the discoloration of Methylene Blue by copper: copper loading (a), temperature (b), initial dye concentration (c), and pH of MB solution (d).

was not significant even after a prolonged reaction time and that only in an acidic medium that was possible. The discoloration of MB was thus an acid-driven process.

The effect of copper loading was investigated by maintaining constant the following conditions: 100 mL of MB at 3.10^{-5} M (≈ 10 mg/L), 100 rpm, 60 °C, and pH= 3 and varying the amount of copper from 10 mg to 50 mg (Fig. 2a). The results show that the discoloration rate of MB increased with copper loading and reached 100% after 86 min with 10 mg and after 24 min with 50 mg. The amount of 30 mg was selected to investigate the other parameters because at high copper loading (50 mg) spectrometry analysis of MB was somewhat disturbed.

The effect of temperature was investigated in the range 30-60 °C by maintaining the other parameters constant: 30 mg of copper, pH= 3, 100 rpm, and $C_{MB}=3.10^{-5}$ M. The results show that total discoloration was attained after 160-130-66 and 42 min at 30-40-50 and 60 °C respectively (Fig. 2b). The results also show that increasing the concentration of MB from 3.10^{-6} M to 3.10^{-4} M (100 X)

prolonged the reaction time at which total discoloration was reached (Fig. 2c). The discoloration of MB seems to be favored by the acidic medium. In fact, at pH= 2 and 3, the reaction was sufficiently rapid when compared to pH= 4 while at pH= 5 no significant discoloration was observed (Fig. 2d). It should be noted that at pH= 2 the results were slightly less efficient than those obtained at pH= 3. This is because the scavenging effect of $\cdot\text{OH}$ radicals by H^+ became stronger at $\text{pH}<3$ as reported in the literature [16]:



The disappearance of color during the discoloration of methylene blue could be described as a pseudo-first-order reaction kinetics for which the following equation could be used:

$$\text{Ln} \left(\frac{A}{A_0} \right) = -k \cdot t \quad (9)$$

Equation (9) was applied to the results of the effect of temperature (in Fig. 2b) in order to determine the activation

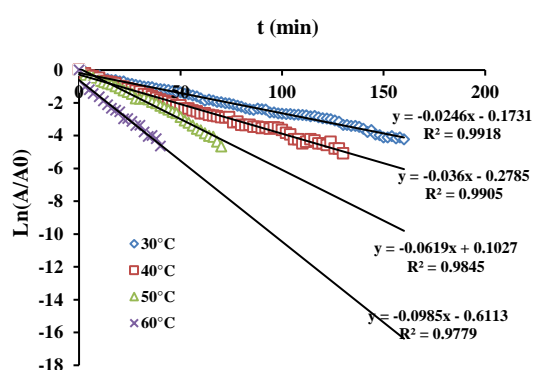


Fig. 3: Pseudo-first order plots of Methylene blue discoloration in the function of temperature.

energy. From the slopes of the straight lines in Fig. 3 the apparent rate constants, k were evaluated. Arrhenius equation $k = k_0 e^{-E_a/RT}$ was plotted as $\ln k$ vs. $(1/T)$ for each temperature and the activation energy was calculated from the slope $-E_a/R$. The activation energy was determined to be equal to 39.62 kJ/mol.

The in situ formation of H_2O_2 started with the corrosive dissolution of copper and the concomitant reduction of oxygen. In this study, the formation of H_2O_2 was evidenced by using the permanganate method [21]. It was found the formation of 32 μM of H_2O_2 after 2 min of reaction which increased to 75 μM , 95 μM , and 110 μM after 10, 25, and 40 min respectively.

In addition, $\cdot OH$ radicals produced by the decomposition of H_2O_2 were detected with 2-propanol used as a scavenger of hydroxyl radicals (2-propanol presents high reactivity with $\cdot OH$: $k_{\cdot OH, 2\text{-propanol}} = 3 \times 10^9 M^{-1} s^{-1}$) [22]. For this task 1 mL of pure 2-propanol was added to MB solution prior to the reaction with copper. No discoloration of MB was observed over 1 h of the experiment confirming the involvement of hydroxyl radicals in the reaction with the alcohol. Both results (H_2O_2 dosage and $\cdot OH$ radicals detection) enable the identification of the Fenton-like process.

The agglomeration of the particles due to the absence of dispersive agents did not prevent them to be active in the discoloration process of methylene blue. This fact was likely due to the presence of Cu_2O which was found to be decisive in the improvement of the effectiveness of metallic copper in the heterogeneous Fenton-like process [18].

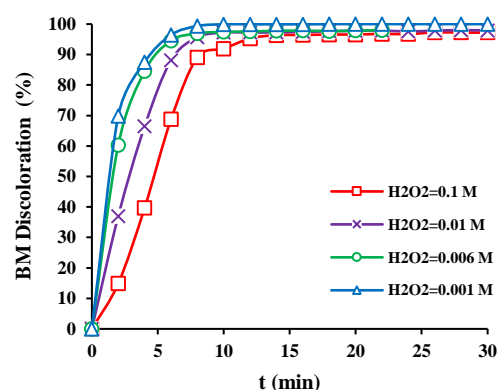
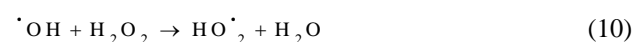


Fig. 4: Effect of the addition of H_2O_2 in acidic medium on the activation of the discoloration reaction of MB by copper.

External addition of H_2O_2 and application of cavitation

H_2O_2 concentration is a vital parameter since the Fenton system is directly influenced by the number of $\cdot OH$ radicals. In order to increase the number of generated $\cdot OH$ and reduce the time for total MB discoloration, H_2O_2 was externally added at different concentrations ranging from 0.001 M to 0.1 M while the other conditions were maintained constant: 30 mg of copper, 60 $^\circ C$, 100 rpm, MB at $3.10^{-5} M$ and $pH = 3$ (Fig. 4).

The results show that the presence of H_2O_2 improved the discoloration rate compared to the system without it. However, the reaction time for complete discoloration of MB extended when the concentration of H_2O_2 increased. For example, when H_2O_2 at 0.1 M was used, only 39.73% of MB was removed after 4 min, while with H_2O_2 at 0.001 M, the value increased to 87.52% after the same reaction time. This behavior may be due to the fact that increasing the concentration of H_2O_2 solution led to self-quenching of $\cdot OH$ radicals and the formation of $(HO_2\cdot)$ which are less effective oxidant than $\cdot OH$ radicals [23, 24]:



Hence, high H_2O_2 concentration should be avoided to keep the contribution of reactions 10 and 11 as small as possible. To show the impact of the external addition of H_2O_2 on the course of the discoloration reaction, two UV-Vis spectra were recorded in the absence (Fig. 5a) and the presence of H_2O_2 at 0.001 M (Fig. 5b). The total discoloration was reached after 10 min in the presence of H_2O_2 while in its absence it was attained after 42 min.

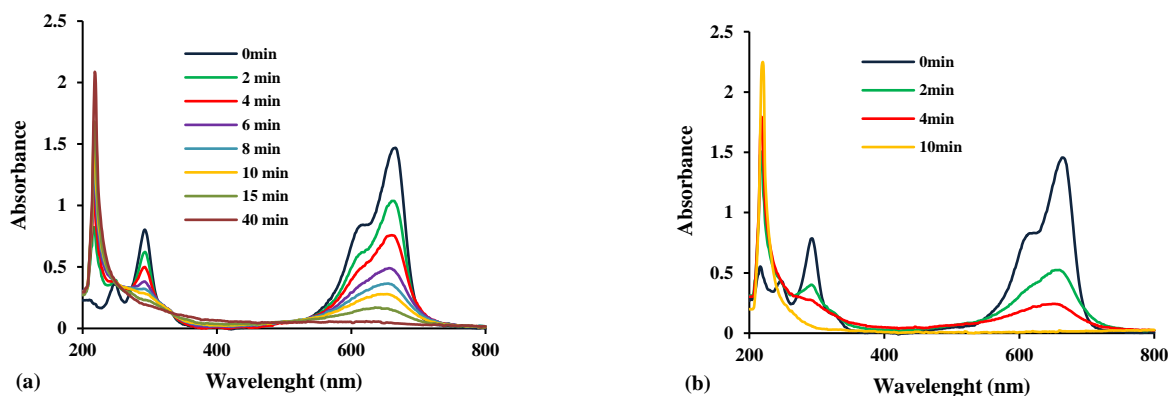


Fig. 5: Spectra of MB discoloration without H₂O₂ feeding (a), and with H₂O₂ feeding at 0.001 M (b).

The same experiments were repeated with a neutral solution of MB at pH=6 (solution original pH, not adjusted). On the contrary to the results obtained in acidic media, increasing the concentration of H₂O₂ led to an increase in the discoloration rate (Fig. 6). In fact, 90.85% were registered with H₂O₂ at 0.001 M after 60 min while total discoloration was obtained after 35 min with H₂O₂ at 0.1 M. This behavior was likely due to the fact that in this case hydrogen peroxide had replaced protons in the leaching process of copper (as it can corrode the solid surface) and obviously increasing the concentration of H₂O₂ produced more Cu²⁺ necessary to initiate the Fenton process (Cu²⁺/H₂O₂). During the reactions in neutral media, great ebullition was visually observed. This was likely due to H₂O₂ decomposition favored by the presence of copper. Under the same conditions in acidic media, no ebullition was observed. Hydrogen peroxide is known to be less stable in a neutral medium than in an acidic one.

On the other hand, the discoloration reaction in neutral media showed 2 stages which are composed of an induction period (first stage) and a followed rapid discoloration (second stage). The induction period is defined as a period of time during which no measurable reaction occurs [25] but which is considered also as an activation process of the solid surface. In our case, the induction period did not greatly vary with the concentration of H₂O₂. It was about 4 min with H₂O₂ concentration ranging from 0.001 to 0.01 M while at 0.1 M it was about 2 min.

Hydrogen peroxide is a weak acid with relatively high oxidation potential ($E^0 = 1.77$ V) which alone, does not lead to the generation of hydroxyl radicals. However, it may

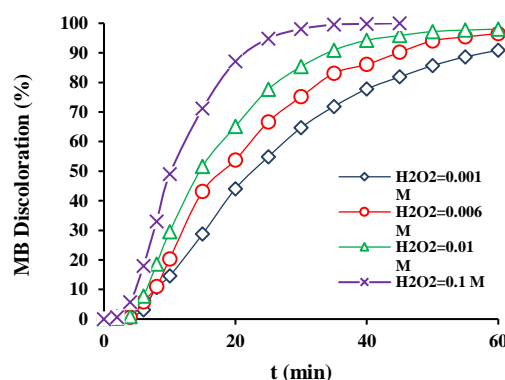
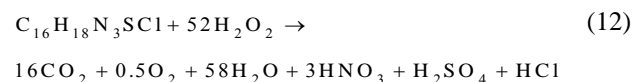


Fig.6: Effect of the addition of H₂O₂ in the neutral medium in the presence of copper.

react with the organic molecules in homogeneous systems via direct electron transfer. In the case of methylene blue the reaction may be written according to the following reaction:



To distinguish the contribution of homogeneous and heterogeneous reactions in acidic and neutral media, the same experiments were repeated with H₂O₂ but in the absence of copper (i.e. MB/H₂O₂ only) at the concentrations that gave the best results (0.1 M in neutral medium and 0.001 M in acidic medium). The results show that the discolorations occurred in both cases but were weak compared to the reactions in the presence of copper. In fact, in the acidic medium in the presence of 30 mg of copper and H₂O₂ at 0.001 M (MB/Cu/H₂O₂/H⁺), total

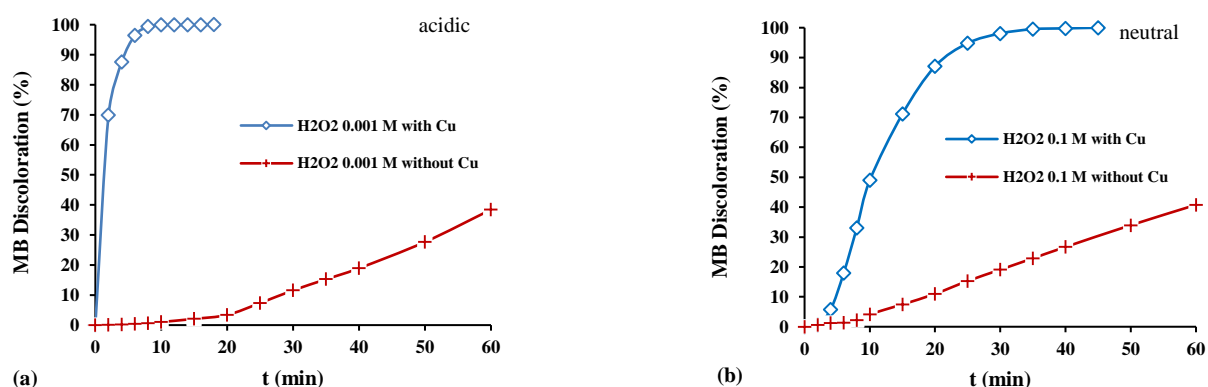


Fig. 7: Effect of the addition of H_2O_2 in acidic (a) and neutral (b) media in the presence and absence of copper.

the discoloration was obtained after 10 min. In homogeneous system ($MB/H_2O_2/H^+$) with the same concentration of H_2O_2 , only 1.04% of discoloration was registered (Fig. 7a). This means that under acidic and heterogeneous conditions the homogeneous reaction occurring simultaneously was not significant because of the rapidity of the heterogeneous process. On the contrary, in neutral media, it reached 100% after 35 min in the presence of copper with H_2O_2 at 0.1 M and 22.39% with H_2O_2 alone after the same reaction time (Fig. 7b). In this case, the part of the homogeneous reaction was more important. It can be concluded that prolonging the reaction time during MB discoloration in a heterogeneous and neutral system allows the homogeneous reaction (MB/H_2O_2) to take place. In homogeneous systems, induction periods were observed in both cases (acidic and neutral conditions). It took a long time for the reaction to start in an acidic medium than in a neutral one, the concentration of hydrogen peroxide was probably the cause.

On the other hand, the reaction (12) shows that one mol of MB needs 52 mol of H_2O_2 to be totally oxidized ($n_{H_2O_2}/n_{MB}=52$). The ratio $n_{H_2O_2}/n_{MB}$ used in the acidic medium in homogeneous system was 33.33 which is lower than the stoichiometry while that used in the neutral medium was higher (3333.33) and despite that, the oxidation of methylene blue was not better than that in acidic medium. Two parameters favored the instability of hydrogen peroxide; increasing its pH value and its concentration. Both conditions were present in a neutral medium which may explain the slight effect on MB oxidation [26].

In the presence of more recalcitrant pollutants, H_2O_2 alone can be totally ineffective. For this reason, it is considered

in AOP only when combined with other agents such as catalyst, UV, or visible light.

It should also be noted that the discoloration of methylene blue in homogeneous systems followed a pseudo-zero order ($A=A_0-kt$) since straight lines were obtained in both cases. The calculation of constant rates gave $k=0.012 \text{ min}^{-1}$ for the acidic condition with H_2O_2 at 0.001 M and $k=0.011 \text{ min}^{-1}$ for the neutral condition with H_2O_2 at 0.1 M. In the presence of copper under the same conditions the kinetic followed a pseudo-first-order ($\ln A=\ln A_0-kt$) with constant rates $k=0.611 \text{ min}^{-1}$ for the reaction in an acidic medium and $k=0.177 \text{ min}^{-1}$ in a neutral one. In both cases, the presence of copper had increased the reaction rate but the improvement was more remarkable (51 times) in the acidic medium (from 0.012 min^{-1} to 0.611 min^{-1}) than in the neutral one (15 times) (from 0.011 min^{-1} to 0.177 min^{-1}). The leaching process of copper and the stability of hydrogen peroxide were more important in an acidic medium so that their effect on MB degradation was more significant.

Ultrasonic cavitation has been applied for the degradation of a multitude of organic molecules [27-29]. In the literature, the phenomena occurring during the ultrasonic process were widely described. The formation of cavitation microbubbles can grow continuously until they reach a critical size, which can cause a violent implosive collapse. The rapid implosion of cavitation bubbles is followed by a localized extremely high temperature and high pressure for a shorter time [29]. Under these conditions, water can be transformed into different oxidizing species *via* pyrolyzes such as $\cdot OH$, $H\cdot$, $HO\cdot_2$, and H_2O_2 [30, 31]. In this study, a Branson B200 device was used generating 40 kHz of ultrasonic frequency. The ultrasonic process was

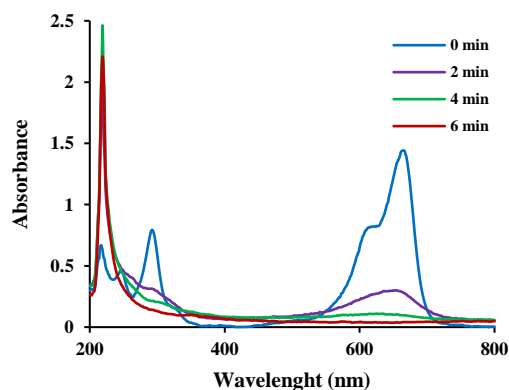


Fig. 8: UV-Vis spectra of MB discoloration in the presence of copper, H₂O₂ and ultrasounds in acidic medium.

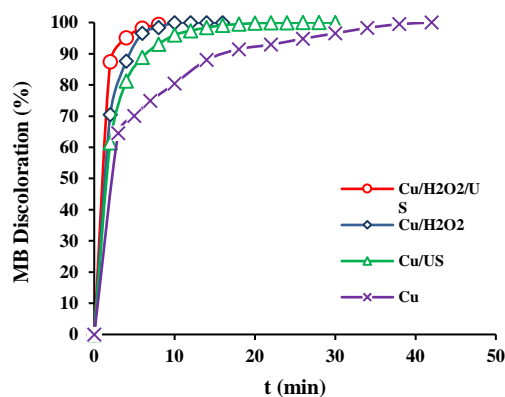


Fig.9: Comparison between the results obtained in acidic media (pH= 3) with copper alone (30 mg), copper (30 mg) in the presence of ultrasounds at 40 kHz, copper (30 mg) with H₂O₂ at 0.001 M, and the three parameters together.

applied to the system containing 30 mg Cu, and MB acidified at pH= 3 (Cu/US/H⁺). In this case, the magnetic stirring could not be applied (because of the construction of the US device which has a very thick basis). Despite that, the discoloration of MB was improved in the presence of ultrasounds. After 10 min, it registered 96% versus 80.4% obtained with copper alone. If magnetic agitation was applied, we expect total discoloration to occur in a shorter time. This result may be explained by the fact that in a solid/liquid system, the cavitation bubbles when they collapse near the solid may hit the surface resulting in its activation [32]. When the ultrasonic process was applied on the system containing 0.001 M H₂O₂, 30 mg Cu, and MB acidified at pH= 3 (Cu/H₂O₂/US/H⁺), the reaction rate was further increased since after just 2 min 87.38% of MB

were discolored and after 6 min the solution was already transparent (Fig. 8). In the presence of copper, the reaction followed a pseudo-first-order regardless of the conditions used (addition of US or H₂O₂). The constant rate calculated for the system Cu alone gave a value of $k = 0.091 \text{ min}^{-1}$, it increased to 0.41 min^{-1} , 0.611 min^{-1} and 0.69 min^{-1} for the systems Cu/US, Cu/H₂O₂, and Cu/H₂O₂/US respectively (all in acidic conditions).

The system (Cu/H₂O₂/US) is called “sono-Fenton” process. In this process, ultrasonic dissociation of water and molecular oxygen enhances not only the generation of $\cdot\text{OH}$ (Eqs. (13-14)) but also generates H₂O₂ in situ (Eq. (15)) [33].



This may explain the rapid increase in the reaction rate when ultrasounds were applied since a supplement of oxidants has been added.

It should be noted that the degradation obtained with the system Cu/H₂O₂ was slightly faster than that with the system Cu/US. It's because in Cu/H₂O₂ system, magnetic stirring was used and the oxidant was externally fed while in the system Cu/US only ultrasonic agitation was present and the oxidant species were produced in situ. The most efficient system is that combining Cu/US/H₂O₂ in which the discoloration reaction was very fast.

CONCLUSIONS

In this study, Cu₂O-Cu was synthesized via a green process using sodium ascorbate as the natural reducing agent. The solid has proved to be effective in the discoloration of MB through a heterogeneous Fenton-like process in which H₂O₂ was produced in situ.

Total discoloration of MB at 3.10^{-5} M ($\approx 10 \text{ mg/L}$) was achieved after 42 min with 30 mg of copper, at pH= 3 and 60 °C. The external addition of hydrogen peroxide at 0.001 M and the application of cavitation at 40 kHz have drastically reduced the reaction time of total discoloration to 6 min. Nevertheless, from the practical and economical point of view, the external addition of hydrogen peroxide can be avoided because it is unsafe to handle while producing it in situ offers the easiness of implementation. Cu₂O-Cu catalyzed in-situ production of H₂O₂/HO \cdot is cost

effective because a single solid can be used for oxidant production as well as for degradation of dyes molecules. Nevertheless, if we have to add another AOP process to improve the effectiveness of copper in MB discoloration, ultrasounds are the most judicious choice because Cu/US process is easier and safer to handle compared to Cu/H₂O₂ process in addition to the fact that the efficiencies of both processes are not greatly different.

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