

## Copper-impregnated on natural material as promising catalysts for the wet hydrogen peroxide catalytic oxidation of Methyl Green

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Received 05 Aug 2020,

Revised 25 Jan 2021,

Accepted 10 Feb 2021.

### Abstract

Promising catalyst of copper impregnated on natural material (CT) synthesized via wet impregnation method, in order to enhance the catalytic wet peroxide oxidation during the degradation of organic matter in a batch reactor under mild conditions. Three different percentages of copper metal (2.5, 5 and 7.5 %) incorporated into CT material which are referred as follows 2.5% Cu-CT, 5% Cu-CT and 7.5% Cu-CT were investigated in the oxidation catalytic of methyl green (MG) dye. The chemical composition, the morphology and the structure of raw CT and all prepared samples, were investigated by X-ray fluorescence, Fourier transform infrared spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM) to get a better understand concerning the catalytic activity behavior of Cu-CT catalyst. Different variable examined the catalytic activity of the samples obtained such as initial concentrations of dye, copper (Cu) loading, temperature and H<sub>2</sub>O<sub>2</sub> effect was investigated to enhance the MG conversion. CWPO experiments showed that 2.5% Cu-CT catalysts have the maximum catalytic activity during the degradation of MG dye. The presence of copper on CT support ameliorates the hydroxyl radicals in the reaction medium after the contact with H<sub>2</sub>O<sub>2</sub> thus enhanced the catalytic conversion of the CT pristine. The optimum conditions showing an important catalytic conversion of MG dye (95 %) at 2.5% of copper loading, 139.10<sup>-3</sup> mol.L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, temperature of 40 °C and at pH 6.0 during 30 min as a reaction time.

**Keywords:** Heterogeneous catalysis (Cu-CT), Catalyst wet Oxidation, impregnation, Hydrogen Peroxide, Methyl Green dye.

# 1. Introduction

The quality of water through history has been an important factor in ensuring human well-being. Currently, one of the most serious environmental problems is the pollution of the hydrosphere, which is threatened by human activity to a large extent. Industrial activities such as painting, plastics, cosmetics and tanneries produce wastewater that contains large amounts of organic compounds that are not easily removed using traditional and biological processes [1]. Textile dyes are one of the major pollutant affect the environment due to its complex structure and its toxicity which influence the clarity and the transmittance of water [2]. Conventional treatment methods such as coagulation, flocculation, absorption and reverse osmosis are typically inadequate to degrade organic effluents, as these methods transfer pollutants from one phase to another, thus causing secondary pollution. Chlorination and ozonation are chemical processes that are also used, which require complex and expensive procedures [3]. Advanced oxidation processes are promising alternatives for wastewater treatment, including photo electrocatalysis[4], the photocatalysis [5], (CWO) catalytic wet oxidation [6], which depend on the production of highly reactive radicals such as  $\cdot\text{OH}$ ,  $\cdot\text{O}_2$ ,  $\cdot\text{OOH}$  et  $\text{SO}_4\cdot^-$  [7]. A suitable method, Catalytic Wet Peroxide Oxidation (CWPO) by adding hydrogen peroxide and a catalysts, has proven to be very effective in degrading the most complex pollutants [8], and its low cost and low energy consumption [9] are the most important advantages of this method. Heterogeneous catalysts are advantageous over homogeneous catalysts due to the difficulties of separating and recovering treated effluents. In this research, an impregnation of copper on natural material (CT) from Morocco was carried out using a metal precursor  $[\text{Cu}(\text{NO}_3)_2, 3\text{H}_2\text{O}]$ . The physicochemical properties of the support and the prepared catalysts were investigated using X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FT-IR), Fluorescence X and scanning electron microscopy (SEM) to clarify the relationship between catalyst structure and its catalytic performance. In addition, several experimental parameters were optimized during the catalytic oxidation of the green methyl (GM), such as: the catalyst mass, the copper metal loading, the initial dye concentration, the hydrogen peroxide effect (volume and concentration) and the temperature.

## 2. Materials and methods

### 2.1 Products

The raw natural material (CT) used in all CWPO experiments is from Morocco. Typical chemical composition analysis of material (80  $\mu\text{m}$  as fraction diameter) was studied via X-ray fluorescence table 1. The results obtained indicates that the predominant oxide is silica (42.6%) followed by alumina  $\text{Al}_2\text{O}_3$  (11%) and iron oxide  $\text{Fe}_2\text{O}_3$  (2.32%) associated with the material phases.

**Table 1:** Chemical composition of the row material. **L.O.I:** Loss on Ignition

<i>Component</i>	<i>SiO<sub>2</sub></i>	<i>Al<sub>2</sub>O<sub>3</sub></i>	<i>Fe<sub>2</sub>O<sub>3</sub></i>	<i>K<sub>2</sub>O</i>	<i>MgO</i>	<i>Na<sub>2</sub>O</i>	<i>CaO</i>	<i>TiO<sub>2</sub></i>	<i>P<sub>2</sub>O<sub>5</sub></i>	<i>L.O.I</i>
<i>Row material Conc %</i>	42.6	11	2.32	1.3	3.29	0.82	18.8	0.44	0.24	18.7

The material contains a high CaO amount (18.8%) indicating the abundance of calcite. L.O.I (loss on ignition) is around (18.7%) due to its calcite nature[10]. Material sample contained a molar ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  equal 3.87. Hydrogen peroxide, sodium hydroxide (NaOH), hydrochloric acid (HCl),  $\text{Cu}(\text{NO}_3)_2, 3\text{H}_2\text{O}$  and methyl green dye (MG) were bought from Sigma-Aldrich and used without further purification. Distilled water was used to prepare all solutions during all the experiment part.

## 2.2 Synthesis of the Catalyst

The heterogeneous catalyst material-Cu was synthesized using wet impregnation Fig. 1. At the first 20 g of natural material was impregnated with different wt% of copper. The mixture was constantly stirred up to the water evaporation at about 75 °C. The solids collected were dried at 100 °C overnight. Finally, the result catalyst was grinded and calcined at 500 °C for 3 h with 10 °C/min as the ramping rate.

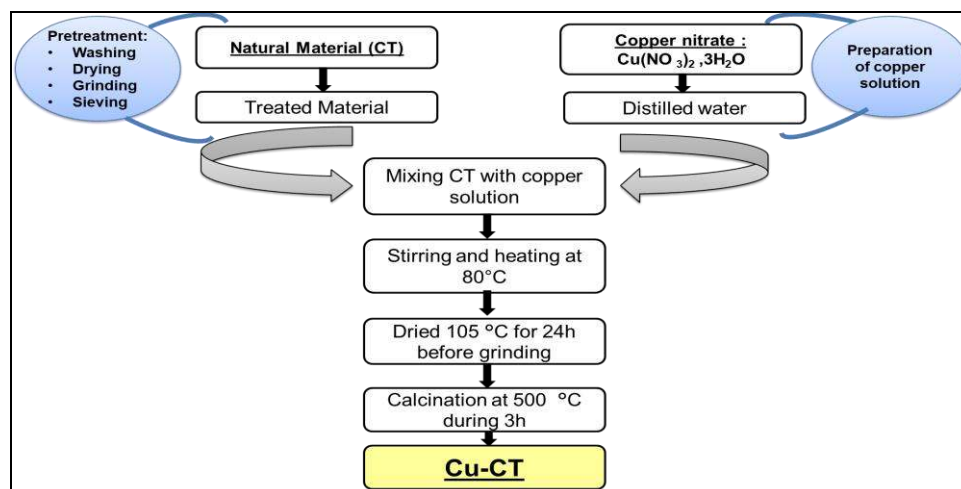


Fig. 1: Synthesis of the Catalyst Cu-CT

## 2.3 Characterization Techniques

The X-ray diffraction (XRD) analysis was studied using a diffractometer (X'Pert Pro PANalytical) equipped with a detector operating at 40 KV and 30mA with Cu K $\alpha$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ). The Fourier transform infrared spectroscopy (FTIR) was carried out using an infrared spectrometer (Bruker Vertex 70). The X-ray fluorescence (XRF) was used to explore the chemical composition of CT and scanning electron microscopy (SEM) QUANTA 200.

## 2.4 Oxidation Experiments

In order to ensure the oxidation experiment, a mass of catalyst Cu-CT was added to 200 mL of MG solution contains hydrogen peroxide. At an interval of time, samples were collected, centrifuged to separate the liquid from the catalyst for the examination. The concentration of MG was calculated by calculating the absorption intensity at its maximum absorbance wavelength of  $\lambda = 632 \text{ nm}$ , using a spectrophotometer UV-Vis (J.P.SELECTA, S.A.VR-2000) with a spectrometric quartz cell length of 1 cm, and then measured from calibration curve. The impact of different operating parameters such as selected amounts of catalyst (0.2; 0.5; 0.7; 1 g.L<sup>-1</sup>), concentration of dye (50, 75, 100 mg.L<sup>-1</sup>), hydrogen peroxide concentration and volume respectively (39.2.10<sup>-3</sup>, 97.9.10<sup>-3</sup>, 139.10<sup>-3</sup>, 196.10<sup>-3</sup> mol.L<sup>-1</sup>), (0.1, 0.3, 0.5, 1 mL) and temperature (25, 40, 60 °C) on the degradation efficiency was studied. The following equation 1 was used to determine degradation of GM dye [11][12]:

$$\text{Conversion \%} = \frac{C_0 - C_t}{C_0} \times 100 \quad (\text{equation 1})$$

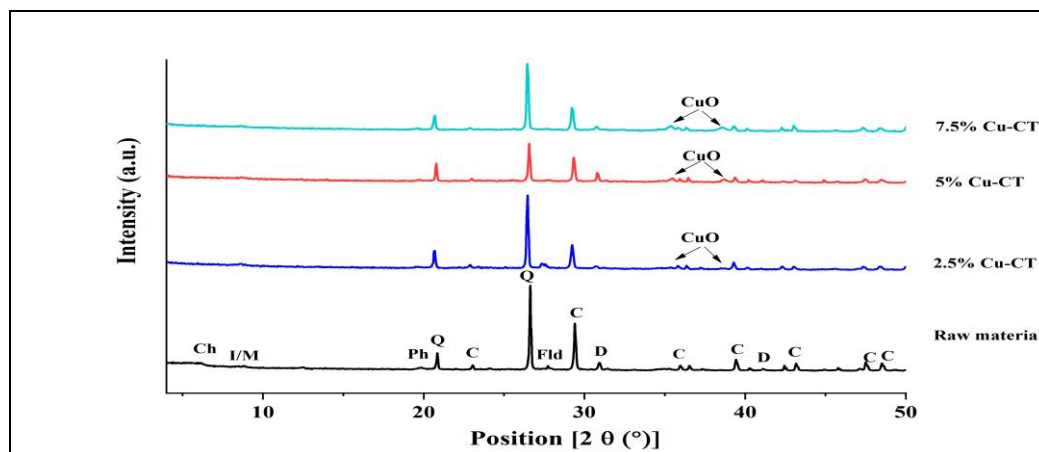
Where  $C_0$  and  $C_t$  are GM concentrations (mg.L<sup>-1</sup>) at  $t = 0 \text{ min}$  and  $t > 0 \text{ min}$  of GM dye.

## 3. Results and Discussion

### 3.1 Characterization Studies

#### 3.1.1 XRD Analysis

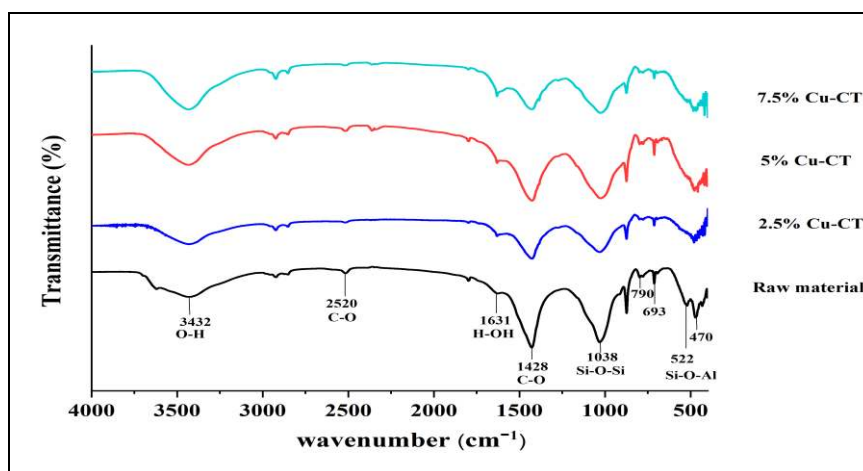
XRD analysis was used for two reasons: i) investigate all phases in the natural material, ii) analyze the CuO form the impregnation material with copper. The results are illustrated in Fig. 2. The XRD of the natural material shows that it is composed of quartz at, calcite at, dolomite at as main compound and small amount of illite, muscovite and pyrophyllite. The CuO element is indicative of the presence of copper in the impregnated catalyst (equation 2). The X ray diffractogram shows the characteristic peaks of CuO around 35.59°, 38.77° (JCPDS 01-089-2530) [13] and the peaks intensity increased with increasing copper amount. This indicates that higher loading of copper in catalyst preparation led to form the higher levels of copper oxide on the material matrix. This result confirm that copper was successfully incorporated natural material [14][15][16].



**Fig. 2:** XRD patterns of natural material (CT) before and after impregnation by cooper. **Ch** : Chlorite, **Ph** : Pyrophyllite, **Q** : Quartz, **I/M** : Illite/Muscovite, **C** : Calcite, **D** : Dolomite, **Fld** :Feldspath

### 3.1.2 Infrared

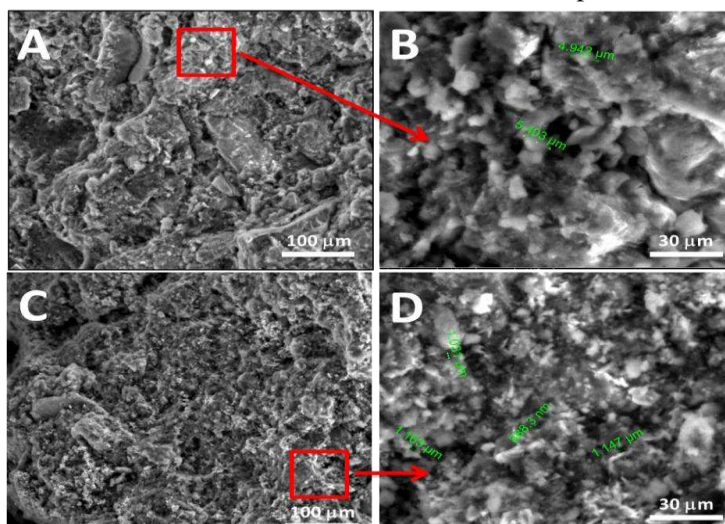
The FTIR spectra of synthesized samples were presented in Fig. 3. The band located at 3432 and 1631  $\text{cm}^{-1}$  corresponded to the stretching and vibrations bands of water absorption H-OH on the surface material [17][18], the bands at 1428 and 2520  $\text{cm}^{-1}$  are due to the presence C-O [19], the stretching vibration band of Si-O-Si was observed at 1038  $\text{cm}^{-1}$  [20], while the band at 790 and 693  $\text{cm}^{-1}$  implied quartz admixture in the samples [21][22], Bands at 470 and 522  $\text{cm}^{-1}$  correspond to the Al-O stretching and Si-O bending vibration respectively [23].



**Fig. 3:** Infrared spectra of the raw material and used catalysts.

### 3.1.3 SEM

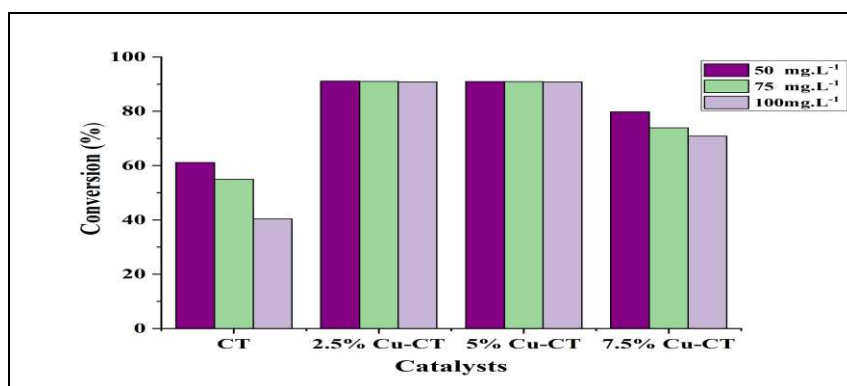
Our prepared catalysts were analyzed using Scanning Electron Microscopy (SEM) to investigate the change in morphological features of material and material impregnated by different molar ratios of copper nitrate. It can be seen from Fig. 4.a and 4.b that the surface morphology of the natural material is different from the one impregnated Fig. 4.c and 4.d: Fig. 4.a and 4.b shows the presence of several pore on the material surface that means the material become more porous and fluffier, which ameliorate the impregnation process by copper nitrate. Otherwise, SEM image of Cu-CT show that the pores diameter become more lower than CT due to the incorporation of copper [24].



**Fig. 4:** TEM images of (a and b) natural material (CT) and (c and d) natural material supported 7.5 % of cooper (7.5% Cu-CT).

### 3.1.4 Effect of copper loading and initial dye concentration

To investigate the effect of copper loading and MG initial concentration on the catalytic oxidation activity :i) a variation in the molar concentration of cooper into CT support, ii) different initial concentrations (50–100 mg.L<sup>-1</sup>) at pH of 6 with 0.139 mol.L<sup>-1</sup> of hydrogen peroxide was studied during two hours at room temperature. As estimated, the natural raw material without copper shows the lowest catalytic activity as illustrate in Fig. 5.



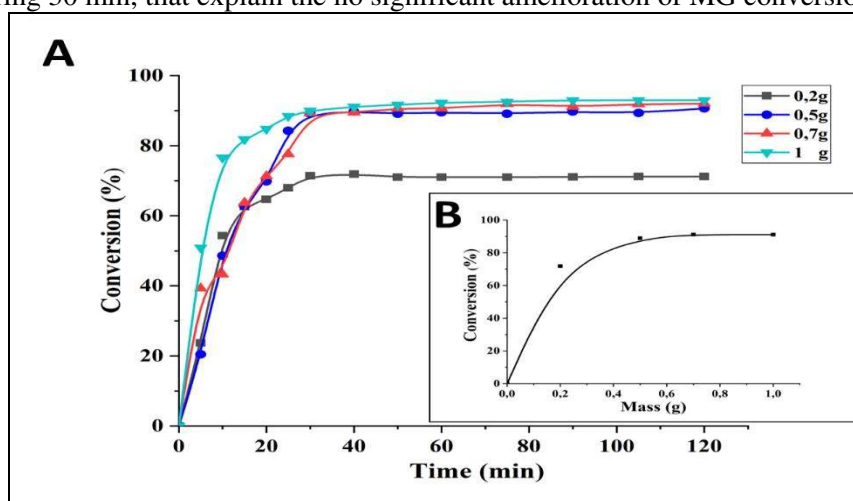
**Fig. 5:** Influence of cooper loading on the catalytic oxidation performance of CT with different initial concentrations of MG dye.

The degradation efficiency of MG by CT decreases from ~60 to 40% when the initial concentration of dye increased from 50 to 100 mg.L<sup>-1</sup>. Moreover, an increase in the copper content from 0 to 5% over the CT surface, lead to a total degradation of dye with the three dye concentrations. Contrariwise, the natural material impregnated with 7.5% of

copper showed a remarkable decrease in the dye conversion from 80 to 70%. This result may be attributed to occurrence of a sintering process with increasing content of copper to 7.5% which regroup them into porous structure of the natural material and then become inactive catalytic sites on the surface of CT support [25]. In conclusion, further catalytic wet oxidation experiments were run with the 2.5% Cu-CT catalyst

### 3.1.5 Effect of the catalyst mass

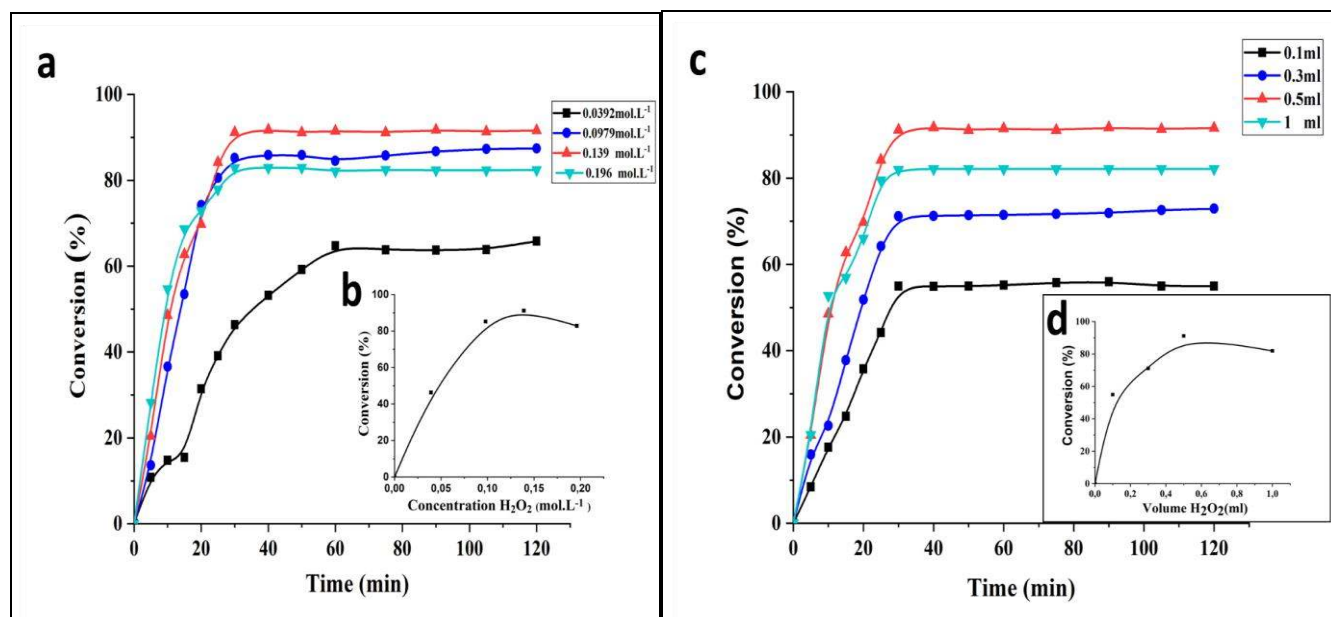
The catalyst mass plays a pivot role on the MG conversion reaction. The catalyst mass ranged from 0.2 g.L<sup>-1</sup> to 1 g.L<sup>-1</sup> in this experiment. The amelioration of the GM conversion versus catalyst mass (Fig. 6) shows that the degradation increases with increasing the catalyst mass. This rise is due to the high surface contact between Cu-CT and H<sub>2</sub>O<sub>2</sub> which enhanced the hydroxyl radicals  $\cdot\text{OH}$  production [26]. We note that 0.5 g.L<sup>-1</sup> corresponds to the better degradation (90%) during 30 min, that explain the no significant amelioration of MG conversion from 0.5 to 1 g.L<sup>-1</sup>.



**Fig. 6:** Study of catalyst amount effect.

### 3.1.6 Effect of H<sub>2</sub>O<sub>2</sub> (dose and volume)

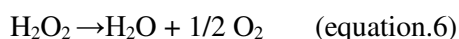
one of the critical factors influencing the CWO is hydrogen peroxide. Furthermore, different molar concentrations of H<sub>2</sub>O<sub>2</sub> were tested in MG dye degradation from aqueous solutions using 2.5% Cu-CT as the selected catalyst. Whereas catalyst mass, MG initial concentration and pH temperature were maintained at 0.5 g.L<sup>-1</sup>, 100 mg.L<sup>-1</sup>, 6 at temperature respectively. As depicted Fig. 7(a and b). It was clearly shown that there is an augmentation in the dye degradation with increasing of H<sub>2</sub>O<sub>2</sub> dose up to a 139.10<sup>-3</sup> mol.L<sup>-1</sup>. This increase explaining by hydroxyl radicals  $\cdot\text{OH}$  generation in the reaction medium between H<sub>2</sub>O<sub>2</sub> and the copper interactions (equation.3) [26]. These radicals will attack GM by converting it to intermediates products. Then, further increase in H<sub>2</sub>O<sub>2</sub> dose leads to a remarkable diminution in the degradation of MG dye. Thus 196.10<sup>-3</sup> mol.L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub> is considered as an overdose whereby some of hydroxyl radicals  $\cdot\text{OH}$  may react with hydrogen peroxide and form peroxy radicals HO<sub>2</sub> $\cdot$  (equation 4 and 5). Peroxy radicals do not contribute in the degradation of MG dye because its lower oxidation potential than that of hydroxyl radical [27][28]. Considering this result, the optimum hydrogen peroxide dose was a 0.139 mol.L<sup>-1</sup>. Fig. 7(c and d) illustrates degradation of MG dye (100 mg.L<sup>-1</sup>) in the presence of H<sub>2</sub>O<sub>2</sub> with 2.5% Cu-CT catalyst within two hours at room temperature, where the best initial concentration of hydrogen peroxide was 139.10<sup>-3</sup> mol.L<sup>-1</sup> as described later. The combination of H<sub>2</sub>O<sub>2</sub> with 2.5% Cu-CT catalyst enhanced considerably the degradation rate of MG dye until reached a full degradation at 30 min with 0.5 mL of H<sub>2</sub>O<sub>2</sub>. This result affirms that the presence of catalyst obtained promotes the formation of  $\cdot\text{OH}$  radicals. The decrease after 0.5 mL is explained by the trapping of excess  $\cdot\text{OH}$  by H<sub>2</sub>O<sub>2</sub> to produce  $\cdot\text{OOH}$  less active (equation 4).

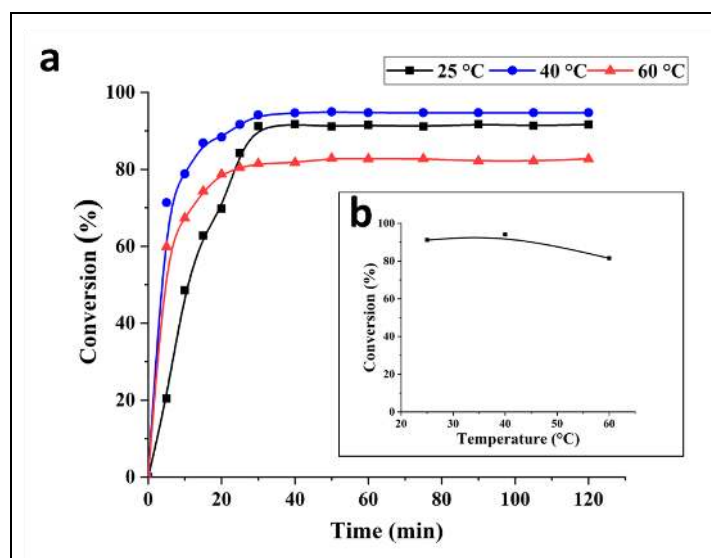


**Fig. 7:** The effect of H<sub>2</sub>O<sub>2</sub> concentration on 2.5% Cu-CT catalyst (a and b), effect of H<sub>2</sub>O<sub>2</sub> volume on 2.5% Cu-CT catalyst (c and d) during the degradation of MG.

### 3.1.7 Effect of temperature

The reaction temperature is a decisive operating factor in CWO process that influences degradation rate of dye and catalyst activity. The influence of the temperatures at 25, 40 and 60 °C on the conversion of MG dye was studied with the optimal conditions catalyst dose 0.5 g.L<sup>-1</sup>, initial dye concentration 100 mg.L<sup>-1</sup> and pH of 6 as presented in Fig. 8. At t=0 min, the conversion of dye was enhanced with increasing the temperature whereas the dye was degraded almost completely 95% at 30 min when the temperature was at either 40 or 60 °C. It is well-known that the increase in temperature accelerated the reaction rate between hydrogen peroxide and the copper catalyst on the surface of natural material to produce large amount of  $\cdot\text{OH}$  radicals during CWO process. However, an increase in temperature from 40 to 60 °C exhibited a slight decrease in the conversion efficiency of MG dye. In fact, this behavior explained on the basis that high reaction temperature improves the thermal decomposition of H<sub>2</sub>O<sub>2</sub> to O<sub>2</sub> (equation.6) [29] and thus there is no enhancement in the degradation efficiency [30][31]. Thus the optimum temperature, which is suitable for the prepared catalyst, was found at 40 °C.





**Fig. 8:** Influence of temperature on the conversion efficiency of MG dye on to 2.5% Cu-CT catalyst.

### 3.2 Comparison of the treatment efficiency with literature studies

The conversion efficiency of copper impregnated on different supports reported by some authors is illustrated in table 2 [32-37] in which we have included the results of our work as well as the situations for establishing the comparisons. As it is noticed the conversion efficiency and the optimal contact time of each treatment varies according to the synthesis process, the support used, the pollutant type, and the copper loading. But, these results show that 2.5% Cu-CT is a promising catalyst that could be used for the degradation of GM dye.

**Table 2:** Pollutants conversion efficiencies using Copper supported on natural materials obtained by reported studies.

Catalyst	Synthesis method	Oxide percentages (wt.%)	Pollutant	Efficiency	Reference
Cu/SBA-15	Impregnation method	5 wt % Cu	2-picoline	99 % (300 min)	[32]
Cu-PILC	Pillaring procedure/ Impregnation	1 wt % Cu	p-coumaric acid	98 % (50 min)	[33]
Cu-supported pillared	Solid-state reaction of Al-pillared clay	2 wt % Cu	tyrosol	80 % (60 min)	[34]
Cu-PILC	Pillaring procedure of a clay/ Impregnation	2 wt % Cu	p-hydroxybenzoic acid	98 % (60 min)	[35]
Cu-zeolite	Hydrothermal synthesis.	2 wt % Cu	olive oil mill wastewaters	97 % (180 min)	[36]
Cu (5%)/Al <sub>2</sub> O <sub>3</sub>	Wet Impregnation (WI)	5 wt % Cu	Phenol	100 % (20 min)	[15]
Cu/RC	Wet Impregnation (WI)	2.5 wt % Cu	Phenol	100 % (240 min)	[37]
Cu-CT	Wet Impregnation (WI)	2.5 wt.% Cu	Methyl Green	95 % (30 min)	Present work



## Conclusion

In summary, this work presents the preparation of an efficient Cu-CT as heterogeneous catalyst with 2.5 wt% of copper for the oxidation of MG dye. The incorporation of copper into CT matrix increased considerably the catalytic activity of CT. Hence, the CT loaded with the largest content up to 7.5 wt% exhibited the less catalytic activity because the active sites become inactive on the surface of CT support surface. The presence of H<sub>2</sub>O<sub>2</sub> in the reaction medium helps the catalyst to produce <sup>•</sup>OH up its overdose, H<sub>2</sub>O<sub>2</sub> decrease the oxidation conversion of MG by the formation of O<sub>2</sub> or <sup>•</sup>OOH. Finally, the optimum parameters for the significant effective catalytic oxidation of MG dye were found to be 2.5 percent copper load, temperature of 40 °C and 139.10<sup>-3</sup> mol.L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> at pH 6 where 95 % conversion of MG dye was achieved within 30 minutes. Since, the simplicity and flexibility of the synthetic process, we may suggest considering the instant impregnation of various metals, such as Nickel (Ni), cobalt (Co) and zinc (Zn) on others natural materials with pretreatment or without nay treatment to further enhance the CWPO effectiveness of these catalysts towards the most complex molecules.

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