

## Remarkable CWPO of crystal violet dye removal using the fishbone doped of copper synthesized by impregnation method

Fatiha Mejbar <sup>(a)\*</sup>, Youssef Miyah <sup>(a)</sup>, Anissa Lahrichi <sup>(b)</sup>, Salma Ssouni <sup>(b)</sup>, Aniss Khalil <sup>(a)</sup>, Loubna Nahali <sup>(a)</sup>, Mohammed Benjelloun <sup>(a)</sup>, Ghita El Mouhri <sup>(b)</sup>, Farid Zerrouq <sup>(a)</sup>

<sup>(a)</sup> Laboratory of Materials, Processes, Catalysis, and Environment, University Sidi Mohamed Ben Abdellah, Higher School of Technology, Post office Box 2427 Fez, Morocco.

<sup>(b)</sup> Laboratory of Biochemistry, Faculty of Medicine and Pharmacy, University Sidi Mohamed Ben Abdellah Fez-Morocco.

\* Corresponding author:  
[Fatihamejbar2@yahoo.fr](mailto:Fatihamejbar2@yahoo.fr)

Received 3 Jan 2021,

Revised 12 Oct 2021,

Accepted 22 Oct 2021

### Abstract

This work aimed to study the remarkable catalytic performance of fishbone (FB) doped copper (Cu) synthesized by the impregnation method for crystal violet (CV) dye's catalytic wet hydrogen peroxide oxidation (CWPO). The catalysts (x%Cu-FB) prepared were characterized by several techniques such as the X-ray diffraction (XRD), the Fourier transformed infrared spectroscopy (FTIR), the zero point charge measurement ( $\text{pH}_{\text{zpc}}$ ), and the scanning electron microscopy (SEM) coupled by the energy-dispersive X-ray spectroscopy (EDX). In addition, this catalysis (x%Cu-FB) was employed as heterogeneous catalysts for CWPO of crystal violet dye removal using different parameters effects in particular the percentage of metallic precursor Cu, the catalyst amount, the concentration of CV dye, the hydrogen peroxide  $\text{H}_2\text{O}_2$  concentration, the temperature, the pH solution. The discolorization rate efficiency was boosted from 98% for 1% Cu-FB after only 35 min of reaction with the optimum conditions namely  $\text{pH}=10$ ,  $[\text{CV}] = 20 \text{ mg L}^{-1}$ ,  $[\text{H}_2\text{O}_2] = 0.048 \text{ mol L}^{-1}$ ,  $W_{\text{Cu-FB}} = 2 \text{ g L}^{-1}$  and  $T=50^\circ\text{C}$ . Finally, it can be seen from this study that the oxidation process by a fishbone catalyst could be economical and effective in removing a large part of the textile pollutants (CV dye) existing in industrial wastewater. The scope of the study makes this method a clean alternative that fits into a perspective of sustainable development.

**Keywords:** Catalysis, Fishbone, Impregnation, Discolorization rate, Metallic precursor.

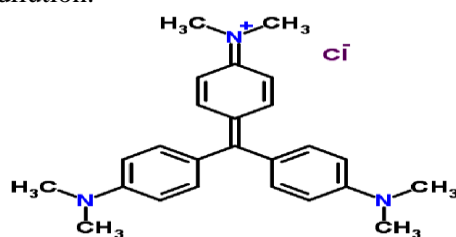
## 1. Introduction

The evolution of legislation on liquid discharges, the sustained increase in the demand for drinking water, and the universal awareness of the need to preserve the environment make wastewater treatment a rapidly expanding investigation field [1]. The impact of the increased toxicity of water laden with organic pollutants such as textile dyes and its consequences on the environment stimulates research on innovative methods to preserve our ecosystem and fight against its pollution and degradation [2–8]. Indeed, dyes are known for their stability and their recalcitrant capacity, their carcinogenic and toxic powers make them very dangerous for human health and living aquatic organisms [9–18]. However, faced with the complexity of industrial textile effluents, physicochemical, biological and incineration treatments are no longer sufficient. The use of oxidizing compounds such as oxygen, hydrogen peroxide, or ozone, in addition to conventional processes, improves the performance of the various processes [19,20]. Note that oxidation by molecular oxygen using high temperatures and pressures (250 to 300 ° C and 50 to 150 bar) leads to yields greater than 90%, for a residence time of approximately one hour [21]. However, the operating pressure and temperature generate significant investment and unusual constraints in the pollution control field [22]. Hydrogen peroxide seems to be the best suited for wastewater treatment [23]. Indeed, it is easy to use, has an acceptable cost and it is not likely to create secondary pollution of the treated flow [24]. In addition, it has bleaching, disinfectant, and deodorant action [25]. Wet oxidation using hydrogen peroxide combined with a solid catalyst (CWPO: Catalytic Wet Peroxide Oxidation) is an effective method of treating organic waste in a dilute aqueous medium [26]. Its preferred application field is that of waste that is difficult to biodegrade or toxic and insufficiently concentrated to be incinerated [20,27]. Recently, in the context of waste recovery, several researchers have reported that biomaterials have been used as catalytic support such as tannin materials, date, and olive kernels, egg and snail shells, lignin, banana, and orange peels, chitin/chitosan, dead biomass, algae, bone gelatin, leaf mold, modified wool and modified cotton [12,28–31]. This work aims to develop new catalysts for the crystal violet's (CV) heterogeneous catalytic oxidation by hydrogen peroxide in aqueous media. Dyes oxidation was chosen as a model reaction to test the prepared catalysts. We have prepared catalysts series with different copper contents supported on the fishbone powder. Several characterization techniques have been used in particular: X-ray diffraction (XRD), Scanning electron microscopy (SEM) coupled by EDX, and Fourier transform infrared (FTIR).

## 2. Materials and methods

### 2.1. Dye's preparation

The cationic dye used is Crystal violet with a purity of 99% and chemical formula  $C_{25}N_3H_{30}Cl$  and a molar mass of  $407.979 \text{ g mol}^{-1}$ . Figure 1 shows the Crystal violet structure. The stock solution is prepared by dissolving 1g of pure Crystal violet dye powder in 1L of distilled water. The solutions used in the tests of the catalysis process are obtained by the Crystal violet (CV) stock solution dilution.



**Figure 1.** Structure of the Crystal Violet dye.

### 2.2. Catalyst synthesis

The catalyst used in this study was prepared by the two-step impregnation method, namely:

1) Support's preparation: the support chosen is the fishbone (FB); the latter is washed with soda and hydrogen peroxide to remove impurities, then dried in an oven at 105 °C for 24 h then crushed and sieved to obtain the fraction less than 90 µm.

2) Support's impregnation: a hydrated copper nitrate metal salt solution is added to the quantity of previously wet support. The suspension is stirred magnetically in a water bath until evaporation and a powder are obtained. The latter is dried in an oven for 20 hours and then crushed, calcined at 500 °C under an air constant flow for 5 hours.

Thus, a series of the catalyst with different copper content supported by FB was prepared 1% Cu-FB, 2% Cu-FB and 3% Cu-FB.

### 2.3. *Catalysis procedure*

Different characterization techniques were used to identify and evaluate the catalysts main constituents composition, namely:

- X-ray diffraction (XRD) from the Panalytical company using Cu K<sub>α</sub> radiation ( $\lambda = 1.54060$  nm), operating at 40 kV and 30 mA and  $2\theta = 10^\circ$ - $80^\circ$ .

- Fourier transform infrared spectroscopy (FTIR), from the company BRUKER and with a wavelength range of 400-7500 cm<sup>-1</sup>.

- Scanning electron microscopy (SEM) (Quanta 200 FEI equipped with EDAX probe for microanalysis of surfaces). The elemental composition quantitative analysis was investigated by X-ray energy dispersive spectroscopy (EDX).

The CV dye oxidation is carried out at room temperature and atmospheric pressure. During the experiment, 200 ml of Crystal violet solution are put under magnetic stirring in a 500 ml beaker, then add the amount of catalyst thereafter the volume H<sub>2</sub>O<sub>2</sub>. Samples of 5 ml are taken every 5 min and then filtered through a syringe filter (45 µm in diameter). The absorbance of each sample is measured with a UV-visible spectrophotometer at wavelength 589 nm. This operation continues until the absorbance value stabilizes.

We are interested in the optimization of the main factors influencing the Crystal violet oxidation reaction, namely: the dye's initial concentration, the catalyst mass, the metal precursor percentage in the support, the hydrogen peroxide volume, the pH initial solution, and temperature.

To achieve this we have kept all parameters constant except for the optimized parameter. The study concerns the determination of the Crystal violet decolorization efficiency and which is given by the following equation 1 :

$$\text{Dye removal rate (\%)} = \left( \frac{C_0 - C_e}{C_0} \right) 100 \quad (1)$$

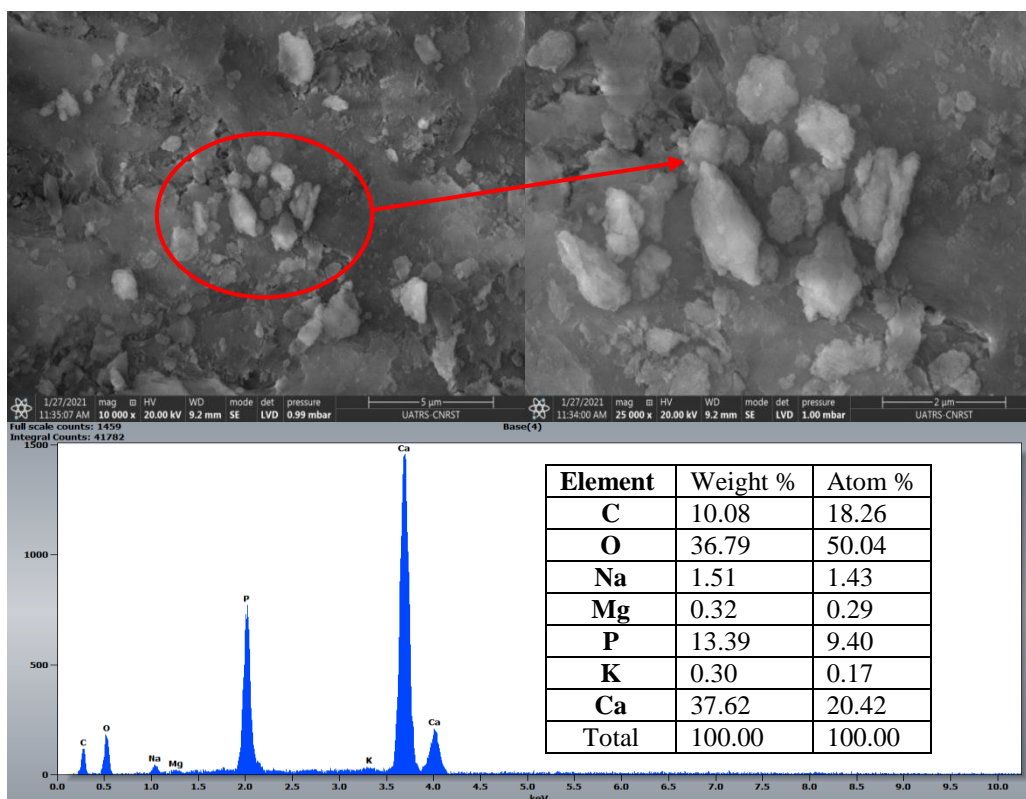
Where C<sub>0</sub> is the dye initial concentration and C<sub>e</sub> is the dye's concentration at equilibrium.

## 3. Results and Discussion

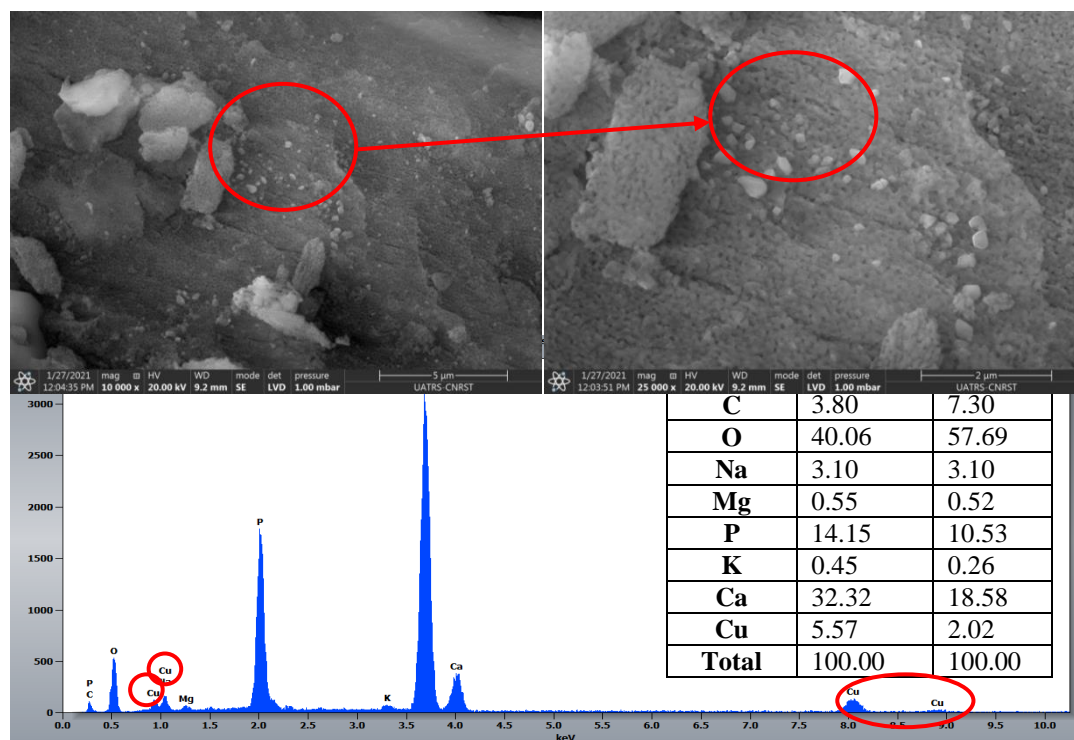
### 3.1. *Catalyst's characterization*

Our catalysts samples were analyzed by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). The application of these techniques made it possible to visualize the surface morphology of the catalysts studied. The fishbone powder support presented in Figure 2, shows that it is characterized by a regular and homogeneous shape. Chemical analysis by EDX shows the presence of elements such as calcium (Ca), sodium (Na), potassium (K), and Magnesium (Mg) which confirms the crystalline nature of our support [32]. The catalyst prepared based on the fishbone powder impregnated with copper (Cu-FB) presented in Figure 3 indicates the presence of copper spots well distributed on our FB support surface. Moreover, the EDX analysis indicates the presence of copper peaks of

significant intensity. These results confirm that our Metal precursor (Copper) was well fixed to our support surface (FB biomaterial)

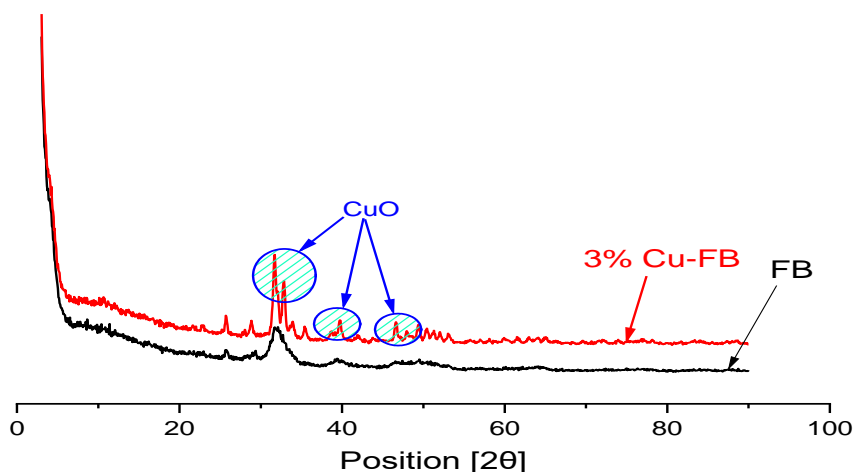


**Figure 2.** SEM analysis coupled by EDX of the fishbone (FB) support



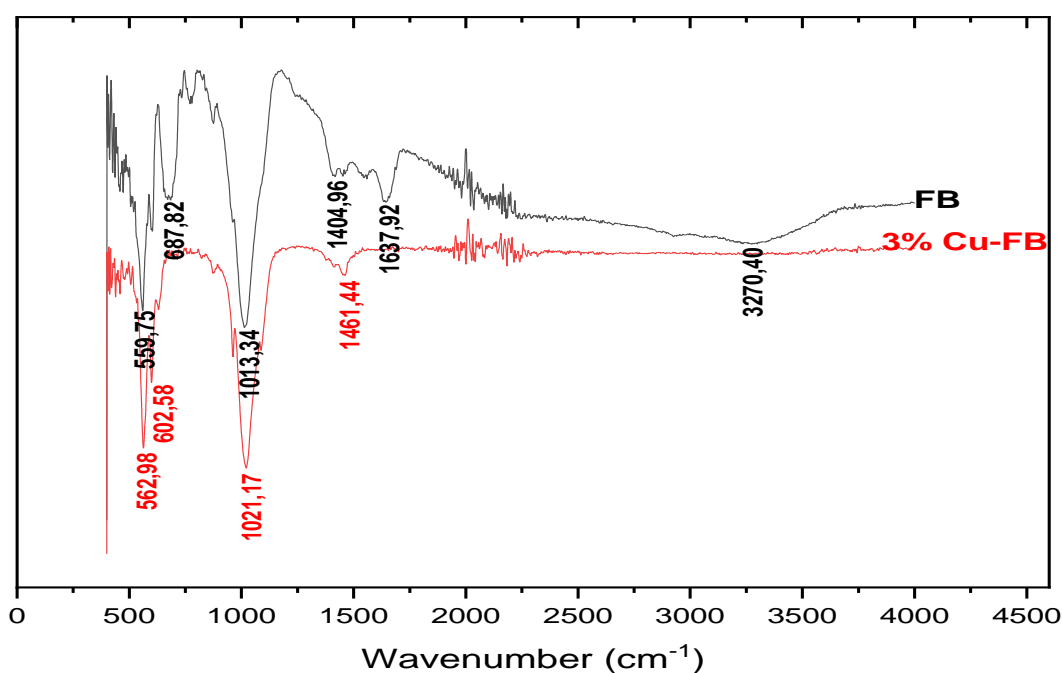
**Figure 3.** SEM analysis coupled by EDX of the 3% Cu-FB catalyst

Figure 4 illustrates the X-ray diffractometric analyzes which were carried out to determine the FB support and the 3% Cu-FB catalyst crystalline composition. The diagram obtained from the XRD mineral analysis revealed that the FB sample studied mainly contains hydroxyapatite and after impregnation with the hydrated copper nitrate precursor, the presence of copper oxide peaks is observed which shows that the latter has been well impregnated on our Fishbone support surface [33].



**Figure 4.** Diffractometric analysis (XRD) of the FB support and the 3% Cu-FB catalyst.

Figure 5 represents the Fourier transform infrared spectrum which makes it possible to determine the fishbone (FB) and the catalyst (3% Cu-FB) characteristic bands specific groupings. Spectrometric adsorption bands observation confirms the presence of specific bonds of hydroxyapatite and the metal precursor (copper nitrate). The band located at  $3270.40\text{ cm}^{-1}$  and corresponds to the elongation vibration of the constitution water OH group; the bands located at  $1021.17$ ,  $1013.34$ , and  $1404.96\text{ cm}^{-1}$  are attributed to the carbonate groups  $\text{CO}_3^{2-}$  vibrations; the band located at  $1461.44\text{ cm}^{-1}$  corresponds to the formation of the Cu-O bond; the band at  $1637.92$  corresponds to the carbonyl  $\text{-CO}$  groups; The bands  $562.98$ ,  $559.75$ ,  $602.58$  and  $687.82\text{ cm}^{-1}$  are attributed to the vibrations of the phosphate groups  $\text{PO}_4^{3-}$  [34–37].

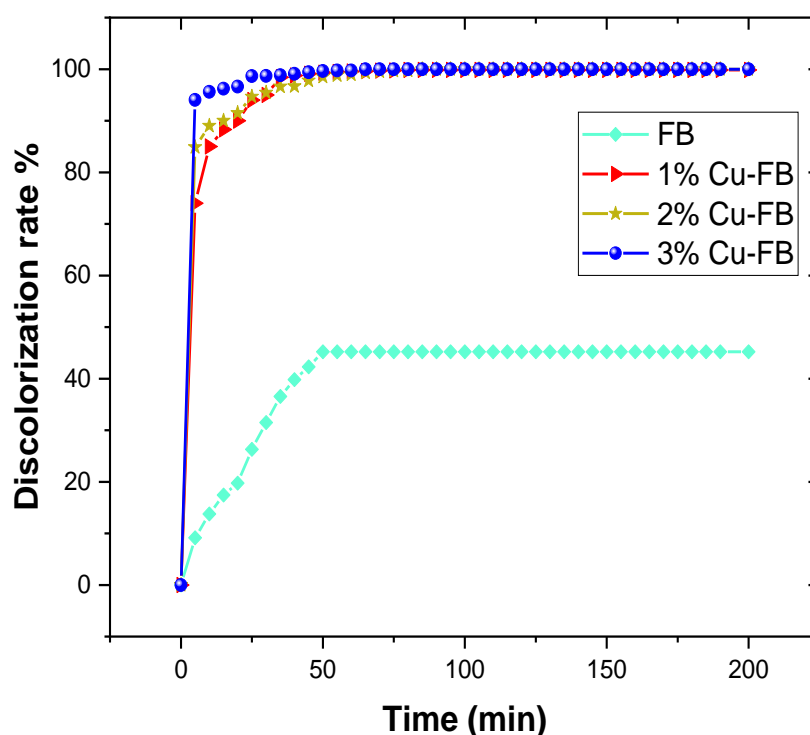


**Figure 5.** FTIR Spectra of FB support and 3% Cu-FB catalyst

### 3.2. Effect of several oxidation parameters

#### 3.2.1. Effect of Cu metal precursor content

The discoloration performance of the Crystal Violet (CV) aqueous solution by copper-impregnated fish skeleton powder (Cu-FB) was examined over time [0; 200 min] as shown in Figure 6. The discoloration rate of the solution in the presence of the non-copper impregnated FB catalyst was found to increase slowly during the first 40 minutes to a maximum of 44% above 50 minutes. On the other hand, when the percentage of copper FB impregnation increases from 1% to 3%, the rate, and the CV discoloration rate increase rapidly within the first 10 minutes of the oxidation reaction to more than 80%, beyond 30 minutes the abatement percentage exceeds 95% for the three copper precursor levels studied. In light of these results, it is found that the catalyst with the 1% copper FB impregnation rate offers a considerable rate and removal rate, which will then be recommended for further study.

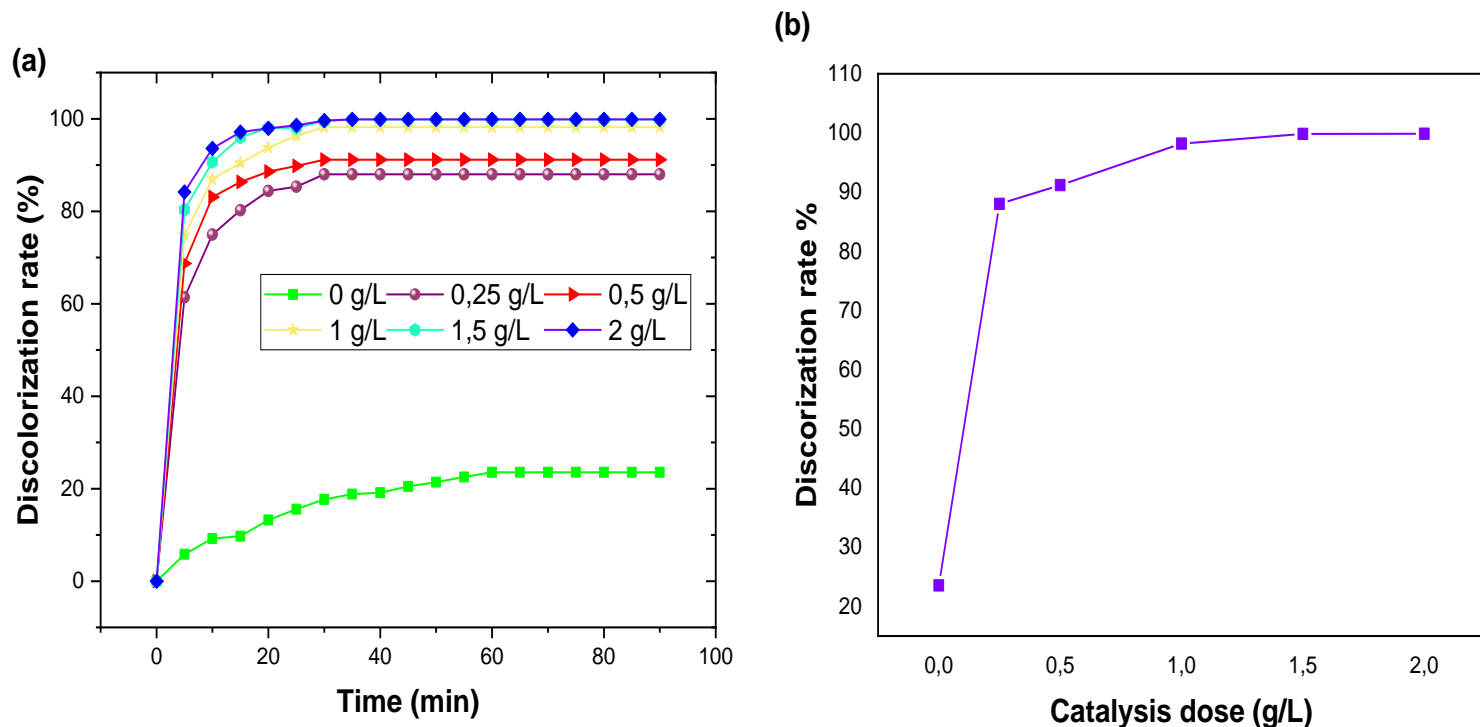


**Figure 6.** Effect of the FB impregnation rate by copper.

#### 3.2.2. Effect of catalyst amount's

The 1% Cu-FB catalyst amount's effect on the CV oxidation reaction by  $\text{H}_2\text{O}_2$  has been studied for 1% Cu-FB catalyst amounts between 0 and  $2\text{ g L}^{-1}$  (Figure 7). It is noted that the percentage reduction in the CV in the absence of the catalyst did not exceed 23% during the first 90 minutes and that the introduction of increasing catalyst amounts ( $0.25$  to  $2\text{ g L}^{-1}$ ) in the oxidation solution accelerated the reaction for the first 10 minutes and increased the dye reduction percentage from 82 to 98%, respectively; beyond 15 minutes. The figure shows that the CV disappearance kinetics increases with the catalyst amount. This can be attributed to the fact that the increase in the catalyst quantity from  $0\text{ g L}^{-1}$  to  $2\text{ g L}^{-1}$  should be accompanied by an increase in the adsorption sites number, therefore by an increase in the dye disappearance rate. Indeed, adsorption to the surface of the catalyst is the essential initial step in the heterogeneous catalysis process, requiring contact between the molecule to be degraded and the catalyst at the adsorption sites. This interaction between the solid catalyst and the organic molecule in the aqueous phase plays a very important role in the mechanisms of catalytic degradation [38].

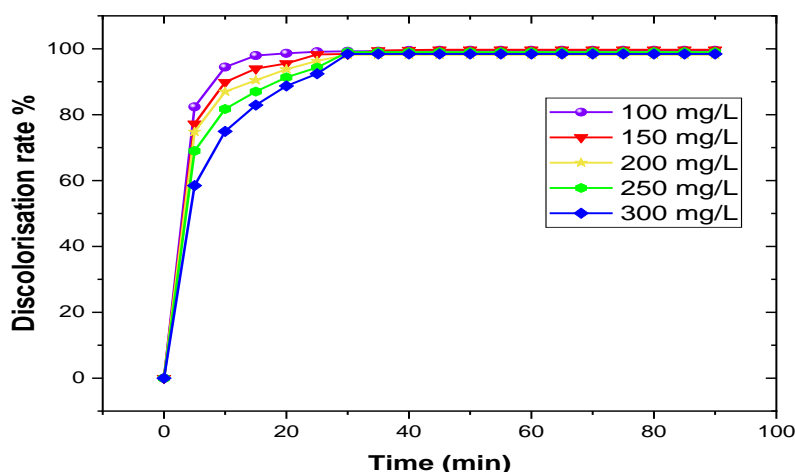




**Figure 7.** 1% Cu-FB mass's effect

### 3.2.3. Effect of Crystal Violet concentration

The influence of the initial concentration of the CV dye on its catalytic degradation by  $\text{H}_2\text{O}_2$  was studied for a concentration range going from 100 to 300  $\text{mg L}^{-1}$  by fixing the quantity of catalyst 1% Cu-FB at 1  $\text{g L}^{-1}$  and the volume 30%  $\text{H}_2\text{O}_2$  at 2  $\text{ml L}^{-1}$  (Figure 8). It is found that increasing the CV solution concentration from 100 to 300  $\text{mg L}^{-1}$  is accompanied by a decrease in the CV elimination percentage during the first 25 minutes; a maximum elimination of 99% is reached after 30 minutes for all concentrations studied. The latter has generally been interpreted by strong adsorption of the dye which then covers a considerable part of the active sites and reduces the hydroxyl radicals formation rate [39].

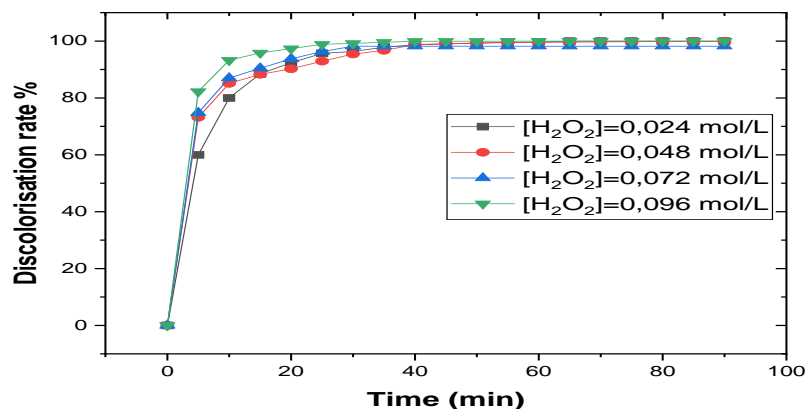


**Figure 8.** Effect of Crystal Violet (CV) Concentration on Discolorization Rate

### 3.2.4. Effect of hydrogen peroxide concentration

The effect of the variation in the hydrogen peroxide concentration on the CV disappearance kinetics at 200  $\text{mg L}^{-1}$  and catalyzed by 1  $\text{g L}^{-1}$  of 1% Cu-FB was studied for the series ranging from 0.024 to 0.096  $\text{mol L}^{-1}$  (Figure 9). The results of the figure illustrate that the elimination percentage increases proportionally with the increase in the hydrogen peroxide concentration until reaching a maximum of 99% after 30 min. Indeed; the hydrogen peroxide addition in heterogeneous

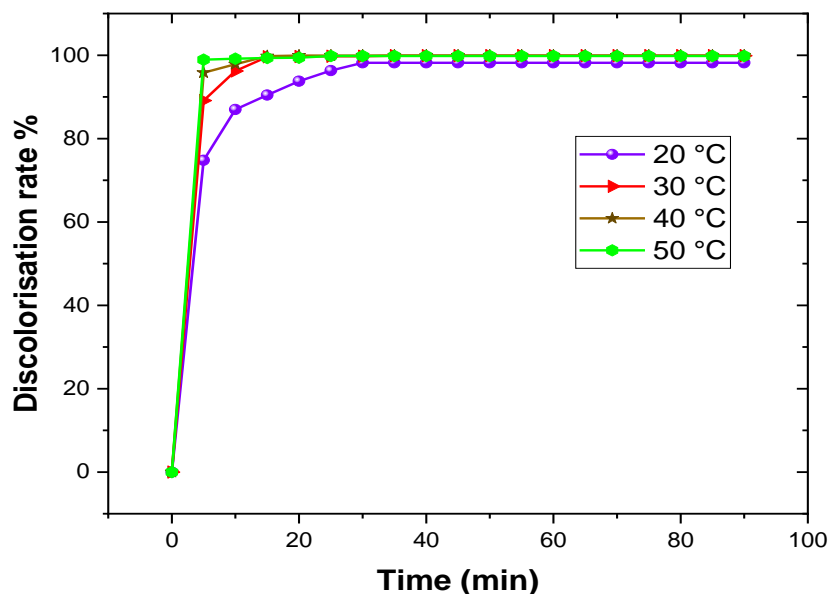
catalysis accelerates the CV degradation reaction, this acceleration is due to greater participation of OH radicals existing in the reaction medium. These very reactive entities participate in the dye degradation by a radical process [40].



**Figure 9.** Effect of H<sub>2</sub>O<sub>2</sub> concentration on Discolorization Rate

### 3.2.5. Effect of temperature

The temperature's influence on the elimination of CV (200 mg L<sup>-1</sup>) by H<sub>2</sub>O<sub>2</sub> (0.5ml) and catalyzed by 1% Cu-FB (1 g L<sup>-1</sup>) was studied by varying the temperature by 20 at 50 °C. The results are given in (Figure 10). Obtained results analysis shows that the temperature significantly influences the CV degradation reaction kinetics. This is because oxidation is faster and reaches equilibrium after 10 minutes for a temperature above 40 °C. On the other hand, for temperatures below 40 °C, the reduction rate only reaches equilibrium after 30 minutes. The elimination rate at equilibrium is independent of temperature and reaches almost 100%. So, we can say that the ambient temperature is sufficient to have a maximum reduction rate. Indeed, a higher temperature increased the rate of reaction between the hydrogen peroxide and the catalyst, by increasing the oxidizing species such as OH• radicals or high valence copper species generation rate [41].

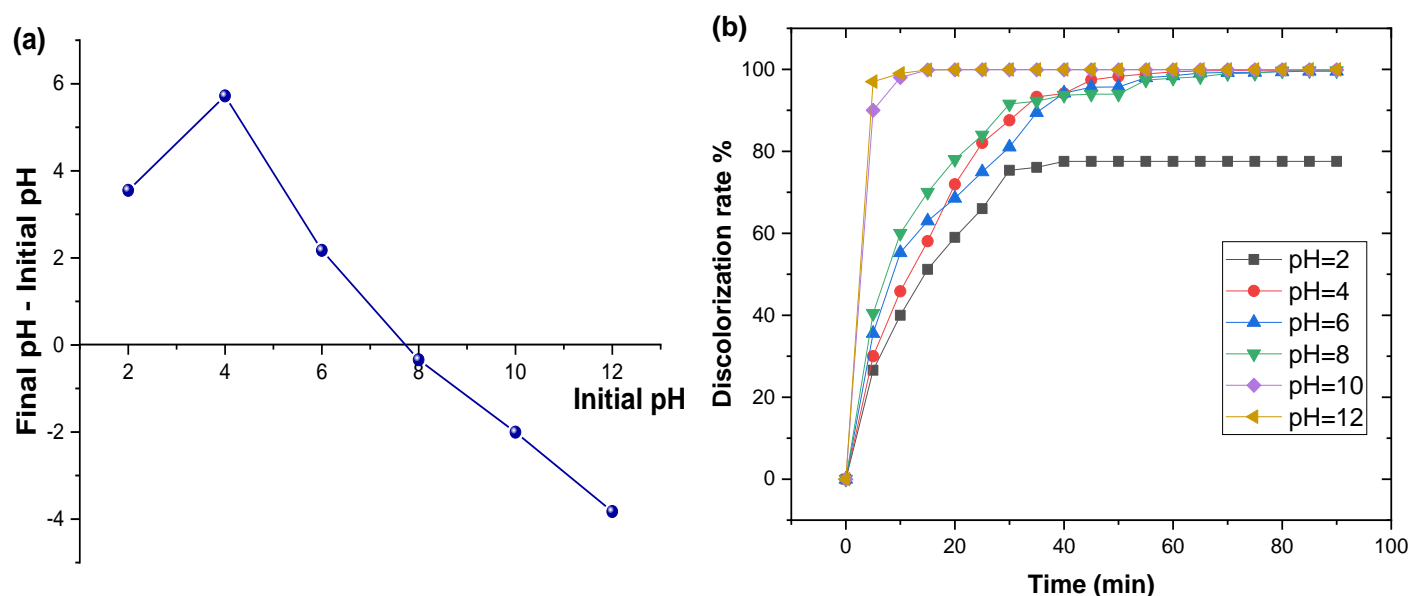


**Figure 10.** Effect of Temperature on Discolorization Rate



### 3.2.6. Effect of pH solution

The pH's effect on the CV removal ( $200 \text{ mg L}^{-1}$ ) by  $\text{H}_2\text{O}_2$  (0.5ml) catalyzed by 1% Cu-FB ( $1 \text{ g L}^{-1}$ ) has been examined in a wide pH range from 2 to 12. The pH of the solution is adjusted by adding a few drops of HCl or NaOH. The zero load point of the 1% Cu-FB catalyst is around 7.8 (Figure 11a). The results obtained show that at basic pH 10 and 12 the CV disappearance is very fast (98 and 99% of discoloration at 5 min), this result can be explained by the force of attraction between the dye and the catalyst surface charge increases the probability of encountering the catalyst (Figure 11b). At acidic pH 2, a relative drop in catalytic activity is observed (77% reduction at 30 min), this is due to repulsive interactions between the dye and the catalyst surface charge reducing the probability of meeting with the catalyst [42].



**Figure 11.** Zero-point charge of the 1% Cu-FB catalyst (a), the pH's effect on the discolorization rate (b).

### 3.3. Bibliographic results

As most of the existing research in the bibliographic literature uses purely chemical catalysts and which however require expensive processes, our research team looked at the use of fish bones, which are found in large quantities, and the final destination is the landfill discharge, as much as support in which we have impregnated the copper as a metallic precursor to making an efficient, ecological, and economical natural biocatalyst for the wet peroxide oxidation that is rival of synthetic materials whose harmfulness could result in the short or long term. The wet peroxide catalytic oxidation results we obtained using copper-fishbone for the crystal violet dye removal as well as bibliographic results on the synthetic catalysts use have been mentioned and collected in **Table 1**.

**Table 1.** CWPO Experimental Results summary and bibliographic results

Catalyst	Catalyst preparation method	Dyes	Discoloration rate	References
Copper-Fishbone	Impregnation	Crystal Violet	98%	This Work
Manganese-Copper-Oxides	Autocombustion	Crystal Violet	100%	[43]
Peroxo and gold modified titanium nanotubes	Hydrothermal synthesis	Methyl orange	50%	[26]
Peroxo titanium nanotubes	Hydrothermal synthesis	Methyl orange	93%	[44]
Copper-containing magnetic-activated carbon	Chemical impregnation	Direct Violet	90.16%	[45]
Nickel-doped carbon xerogels	wet impregnation-reduction	Methyl orange	90%	[46]
Aluminium-iron pillared bentonite	Pillaring	Tartrazine	71.5%	[47]
Cu-loaded MgAl hydrotalcite	Impregnation	Methyl orange	99.2%	[48]
Iron-impregnated 13X	Impregnation	Methyl orange	99.4%	[49]
Activated carbon fiber supported nanoscale zero-valent iron	Liquid-phase reduction	Methyl orange	99.2%	[50]
Delafossite-Alumina	Precipitation	Reactive red 195	99.75%	[51]
Rare-earth doped nickel spinel ferrites	sol-gel autocombustion	Orange II azo-dye	90.6%	[23]

#### 4. Conclusion

This study carried out on the valuation of biomaterial FB doped with 3 copper contents (1, 2, and 3% Cu-FB) in the advanced oxidation process of the cationic dye CV by H<sub>2</sub>O<sub>2</sub> showed that this process is effective and that the hydroxyl radicals produced in a catalytic medium have a very high oxidizing power and are capable of degrading almost all of the CV. The 3 catalysts, showed a good capacity to eliminate 98% of the CV in less than 35 min. Subsequently, the study of some parameters' effect on the process efficiency shows that the pH, the CV solution concentration, the oxidant volume, the temperature as well as time can be optimized. The highest yield obtained is of the order of 98% with the following conditions: pH: 10 (basic), [CV]: 20mg L<sup>-1</sup>, V<sub>H<sub>2</sub>O<sub>2</sub></sub>: 2ml, catalyst mass: 2 g L<sup>-1</sup>, Time: 10 minutes, and Temperature: 50°C. We can conclude that the oxidation process by a catalyst based on FB is economical and efficient. The scope of the study to remove other organic pollutants existing in industrial wastewater may prove cost-effective and make this method a clean alternative that fits into a sustainable development perspective.

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