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# Study the effect of crystallite size for Cu NPs on the degradation of methylene blue dye under the sun light illumination

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**ABSTRACT**

In the present work, the colloidal nanoparticles were prepared from a bulk metal by laser ablation technique. Copper thin films were fabricated via a simple deposition method (drop casting method). This study focuses on degradation efficiency of methylene blue dye (MB). The films were analyzed by using X- ray diffraction pattern and scanning electron microscope (SEM). We found from results of X- ray and SEM decrease the crystallite size from (39 to 31 nm) with increase pulse numbers, also the grain size decrease and surface homogeneity increased when the pulses number increases from (1500 to 2500). The copper nanoparticles (Cu NPs) shown Photo-catalytic activity in different irradiation time. Photocatalytic properties were evident on the absorption of methylene blue dye (MB) increase when increases irradiation time and add Cu NPs. Degradation efficiency of MB dye increases progressively with longer irradiation times and decreases grain size of CuNPs, so that the relationship between crystallite size and degradation efficiency was inversely. Found from results two factors effect on the Degradation efficiency, first the irradiation time, second the crystallite size.



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## 1. INTRODUCTION

The use of various synthesis techniques to control the size and shape of nanoparticles enhances their physicochemical properties [1]-[2]. The pulsed laser ablation (PLA) method is employed to synthesize high-purity nanoparticles (NPs) with a narrow size distribution [3]-[5]. PLA, being an eco-friendly technique, allows the production of NPs in a single step [6]-[7]. Pulsed laser ablation in liquid (PLAL) provides the ability to prepare a wide range of materials [8]-[11]. Various methods have been used to synthesize CuO nanoparticles, such as chemical deposition, sol–gel routes, and others [12]. Cu nanoparticles (CuNPs) have also been synthesized using PLA [13], with the smallest and most uniform particle sizes observed when prepared in aqueous media [14]. Nanomaterials offer a new approach to convert bulk materials into particles at the nanoscale [15]. The optical and electronic properties of materials change significantly when particle sizes are below 100 nm [16]-[17]. One important development in catalysis is photocatalysis, which uses light and a catalyst to enhance the rate of chemical reactions [18]. Semiconductor compounds have shown promising results as catalysts in physical and chemical photocatalytic processes, particularly for the removal of hazardous environmental pollutants [19]. CuO has been widely employed as a photocatalyst due to its excellent photoelectric properties and narrow band gap [20]-[21]. CuO (cupric oxide) is a p-type semiconductor with a bandgap of approximately 1.3 eV [22]-[25]. Photocatalysis is an eco-friendly and simple technique [26]. The decomposition of methylene blue (MB) depends on both the illumination time and the structural properties of the catalyst [27].

The optimal absorption peak of MB occurs at 666 nm, which is used to monitor the residual dye concentration [28]. The aim of this work is the preparation of CuNPs, which is particularly challenging due to their tendency to oxidize in the presence of air.

## 2. METHODS AND MATEREALS

In the present study, CuNPs were prepared using a Nd:YAG pulsed laser to copper plate targets (purchased from Sigma Aldrich, with 99.9% purity) immersed in distilled water to a depth of 3 cm. A laser wavelength of 532 nm, a repetition rate of 1 Hz, pulse numbers of 1500 and 2500, and a laser energy of 900 eV were employed. The set-up used to preparation the colloidal shown in Figure 1.

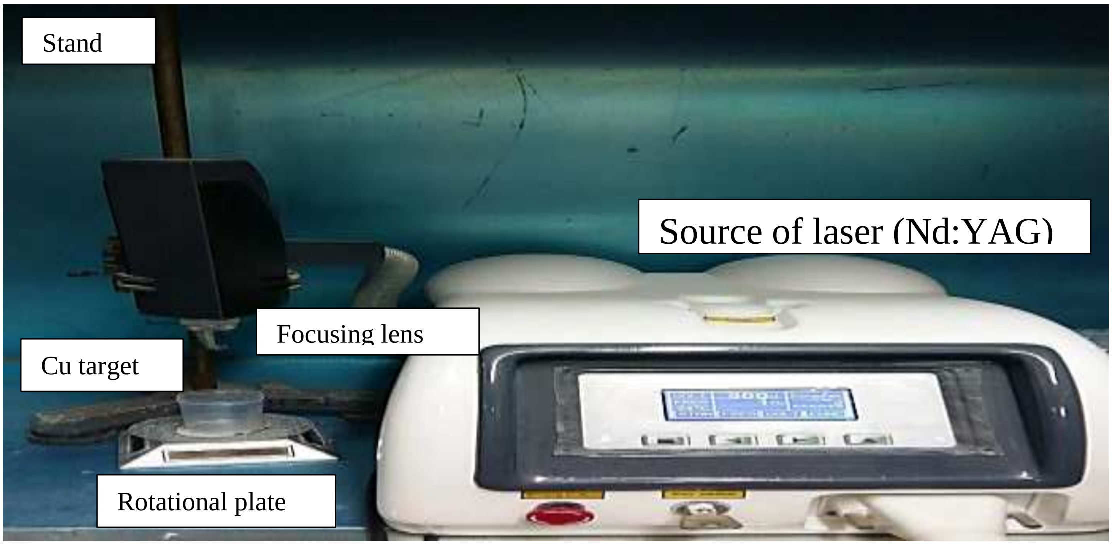


Figure 1. show set-up of PLA use to preparation the colloidal in liquid.

The resulting colloidal nanoparticles were deposited onto glass substrates using the drop-casting method to study their structural properties (XRD and SEM), the advantages of drop casting method are uniform surfaces coverage on a large area, high preparation speed, good control on thickness of the film, low cost and wastage of materials. Debye– Scherrer Equation used to calculate the average crystallite size [29]. Additionally, the colloidal solution was mixed directly to (0.002 g) of MB dye for 30 mints, after that let the mixed in the dark for 60 mints before it exposes to sun light to investigate the dye degradation efficiency. The degradation of the dye was calculated using equation (1) [28],[30] under sunlight irradiation (without heat treatment) for different exposure times of 1, 2, and 3 hours, the set-up used to study the degradation of MB shown in Figure 2 and the schematic diagram showing in Figure 3.

$$D(\%) = (A0 - At / A0) \times 100 = (C0 - Ct / C0) \times 100 \quad (1)$$

Where $A_0$, $C_0$, $A_t$, and $C_t$ are the absorbance and concentration values initially before radiation exposure and after exposure time (t), respectively.
Then, if the plot of ln ( $C_0$ /$C_t$ ) versus (t) for the experimental data gives a good fit, correlation coefficient (R2 ) is close enough to 1 [28].

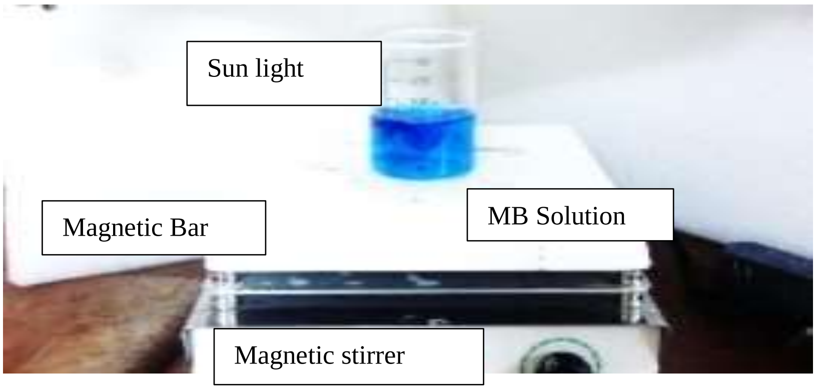


Figure 2. explain the degradation of MB using colloidal of Cu NPs

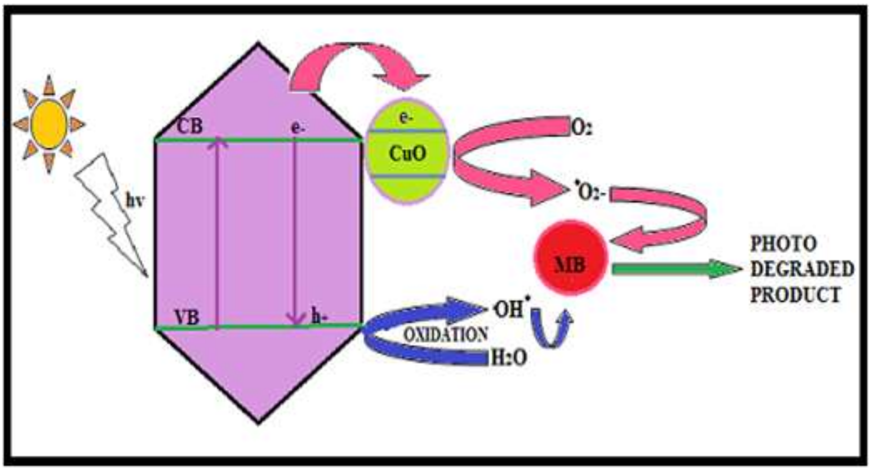


Figure 3. Schematic diagram showing the degradation of methylene blue dye using CuNPs [33].

## 3. RESULTS AND DISCUSSION

### 3.1. X- ray diffraction

The X-ray diffraction (XRD) patterns of the CuNPs exhibited three main peaks corresponding to the (111), (200), and (220) planes, as shown in Figure 4. The diffraction peaks match well with the standard reference patterns, indicating that the prepared samples possess a face-centered cubic (FCC) structure, the standard cared number (No.04-0836), this result agree with [31]. The strong intensity of the (111) peak may be attributed to preferential growth along this plane. The average crystallite size was calculated to be 31 nm for samples prepared with 2500 pulses. This value is smaller than the average crystallite size of 39 nm observed for samples prepared with 1500 pulses under the same conditions, except for the difference in pulse numbers [13].

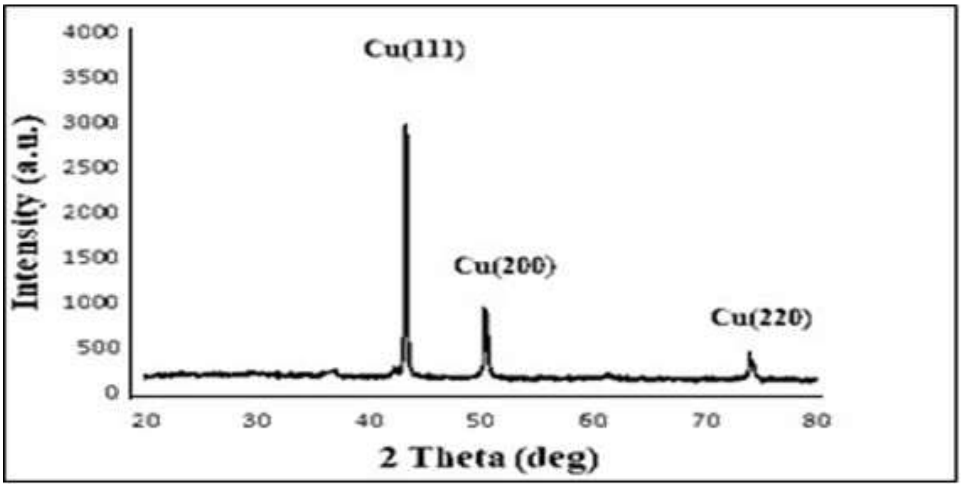


Figure 4. XRD diffraction patterns of Cu nanoparticles preparing at 2500 pulses.

Table 1. explain some parameters effect on the crystallite sizes of Cu NPs.

| Pulses | h k l | 2 Theta (deg) | Crystallite size (nm) |
|---|---|---|---|
| 1500 | 111 | 50.4 | 39 |
| 2500 | 111 | 43.31 | 31 |

### 3.2. Sem analyses

SEM analyses were employed to compare the morphology of the prepared samples. Figure 5 shows SEM images of CuNPs prepared using the PLA technique with different pulse numbers (1500 and 2500). SEM images showed the pulses numbers played crucial roles in the morphology of the prepared samples, Figures 5(a,b) and (c,d) illustrate the effect of pulse number on the structural properties of the samples, including surface morphology and grain size. An increase in the number of pulses resulted in a more homogeneous surface and a reduction in grain size.

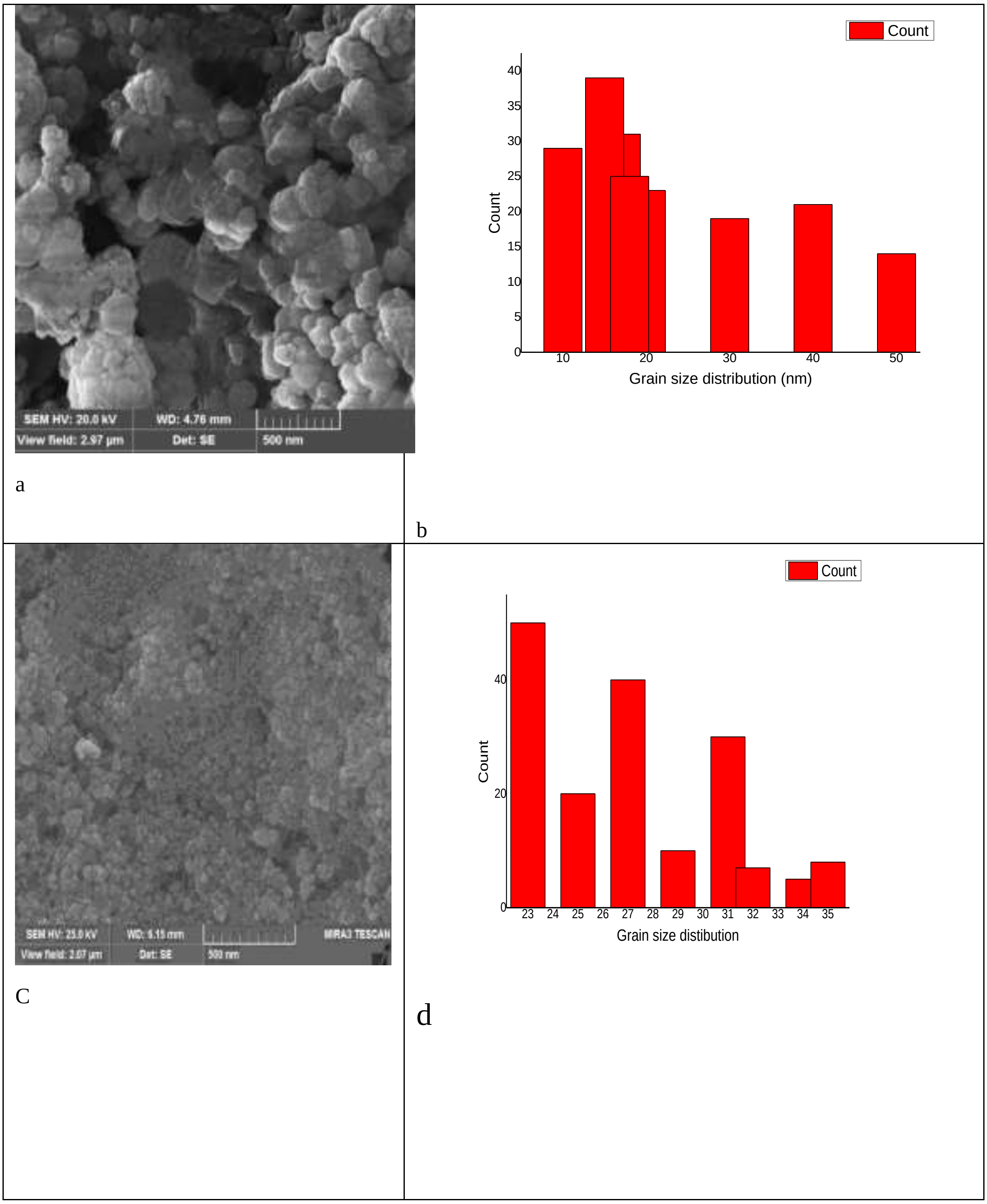


Figure 5. SEM image for Cu NPs at different pulses number (1500, 2500)

### 3.3. Photo-catalyst properties

Figures 6 and 7 show the effect of irradiation time, crystallite size, and grain size of CuNPs on the degradation of methylene blue (MB), compared to the degradation of MB without nanoparticles. The curves in these figures indicate that the absorption increases as the crystallite size decreases for samples prepared with pulse numbers of 2500 and 1500, respectively. Spherical shape of CuNps with the particles size played roles in the degradation of MB dye.

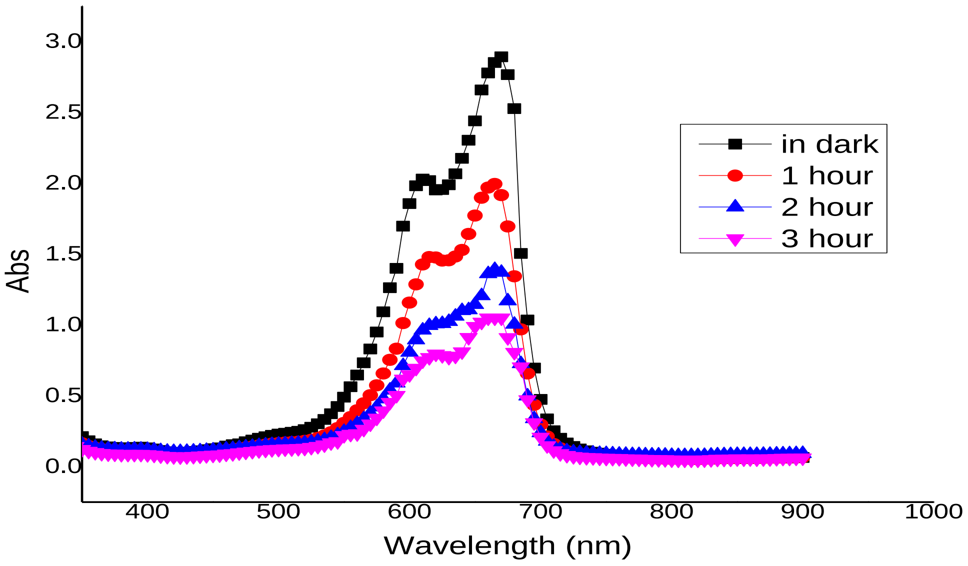


Figure 6. explain the effect of crystallite size on the absorption values for sample prepared with pulses number 2500 pules .

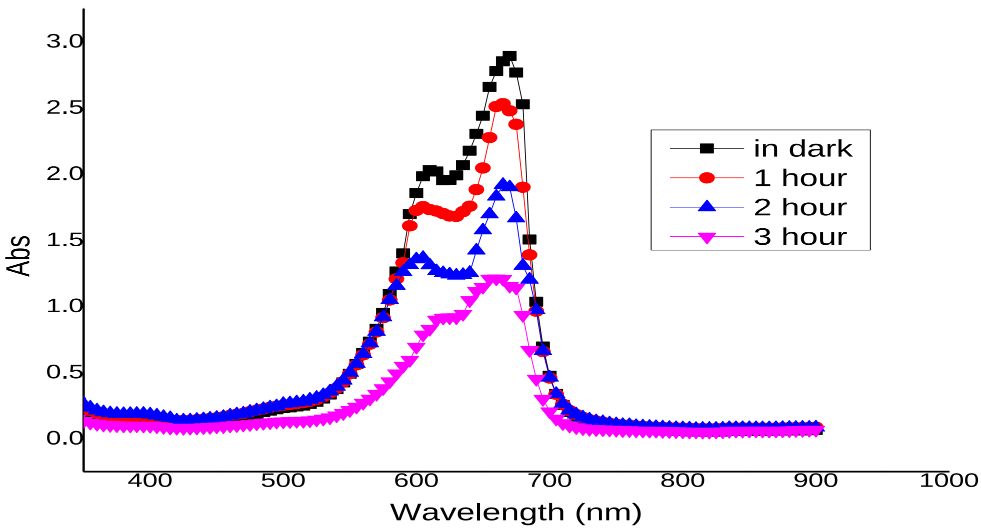


Figure 7. explain the effect of crystallite size on the absorption values for sample prepared with pulses number 1500 pules.

The time-dependent photodegradation of methylene blue (MB) dye is illustrated in Figure 8 for CuNPs prepared with different pulse numbers (1500 and 2500) and corresponding crystallite sizes. The degradation of MB ($C/C_0$) increases with increasing pulse number, which corresponds to a decrease in crystallite and grain size, as well as with longer irradiation times, this result agree with [32]. CuNps nanoparticles act as catalysts, for that accelerating the degradation processing and reducing reaction time, this result agree with [34]. Figure 9 illustrates the decomposition efficiency of the dye using CuNPs with different crystallite sizes, showing an inverse and relationship between crystallite size and degradation efficiency. The relationship is complex the results indicating that smaller crystallite sizes can lead to higher efficiency due to increased surface area and increase catalytic reactions

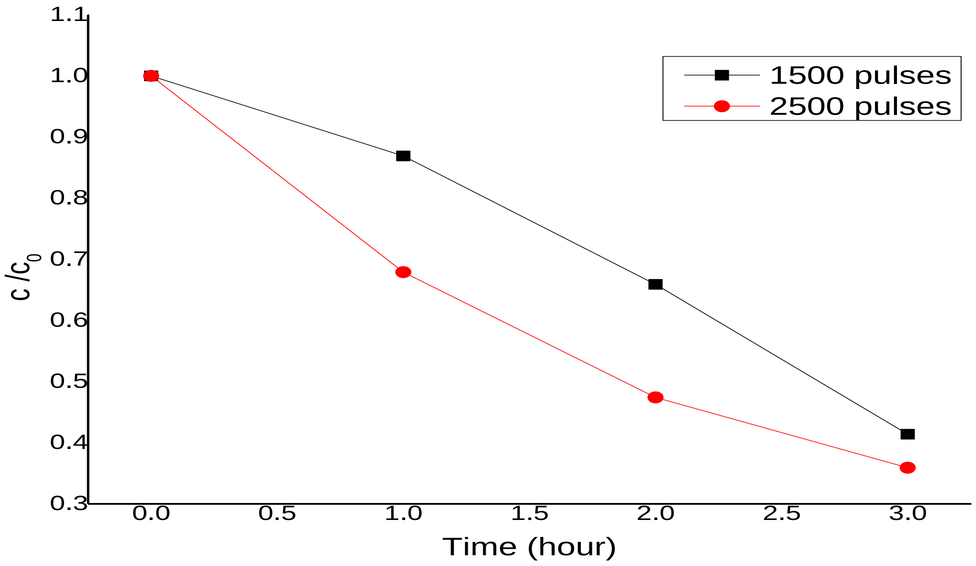


Figure 8. Time dependent photodegradation of MB under UV irradiation

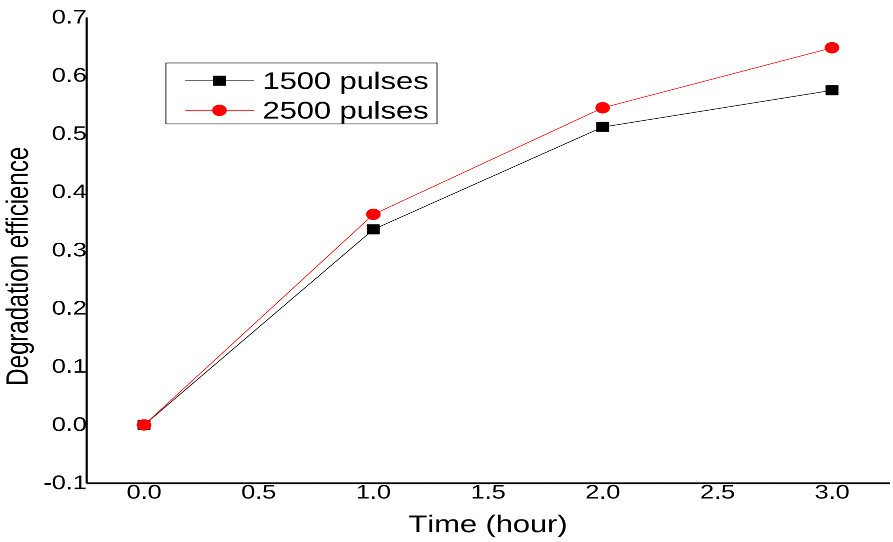


Figure 9. Degradation efficiency of MB using CuNPs.

## 4. CONCLUSION

In this work, it was concluded that the crystallite size and grain size of CuNPs depend on the number of laser pulses, with an inverse relationship between them. The laser ablation technique proved to be an effective method for producing nanoparticle structures. As the number of pulses increases, both the crystallite size and grain size decrease. The efficiency of CuNPs in the decomposition of methylene blue (MB) dye is influenced by the grain size and irradiation time, showing an inverse proportionality.

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