

# Effect of Surface Morphology of ZnO Electrodeposited on Photocatalytic Oxidation of Methylene Blue Dye

## Part I: Analytical Study

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Photocatalysis of organic compounds by mean to semiconductors depends heavily on its structural and superficial properties. For this reason, the aim of this paper is to investigate the effect of the ratio Zn/O, grain size and grain number of zinc oxide (ZnO) on photocatalysis of methylene blue dye (MB). ZnO deposits were obtained by cathodic electrodeposition technique from an experimental design 2<sup>3</sup>. The three growth variables were voltage, temperature and time of deposition with two different levels for each variable. Our results showed that the crystallographic orientation and morphology of ZnO electrodeposited depend on different combinations of the deposit variables according to the experimental design. We also found that there is an optimum value in the ratio Zn/O, grain size and grain number of ZnO related to the higher degradation of MB.

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**Keywords:** Zinc Oxide, Electro-deposit, photo-oxidation, water treatment, texture coefficient.

## 1. INTRODUCTION

Zinc oxide is a direct wide-band-gap semiconductor with a band gap of 3.37 eV at room temperature and has been investigated extensively for its electrical, optical and photocatalytic properties. It has been used in applications such as laser diodes, solar cells, gas sensors, field effect

transistors, transparent conductive films, hydrogen production by mean to water photolysis and degradation of organic pollutants [1-5].

There have been many studies on growth factors that affect the morphology and the optical electrical properties of ZnO [6-11]. However, little research has focused the study of ZnO's morphology and its application in photocatalysis. Some of these single-factor studies have shown that the preferred orientation, size and shape of ZnO affect their photocatalytic properties.

Some of the most important parameters about growth and morphology control of semiconductor crystals by cathodic electro-deposition in an aqueous environment are: temperature, applied potential, deposit time, electrolyte's chemical composition and substrate type. According to this, Lifen Xu and colleagues reported that the ZnO acquire different morphologies ranging from the hexagonal shape until the rhombohedron shape by the change of the stabilizer agent [12]. On the other hand, Linping Xu and colleagues published the synthesis of ZnO with different morphologies by using Zinc acetylacetonate and solvents of different polarity [13]. In turn, Masanobu Izaki and Omi Takashi reported that the preferred orientation and roughness of ZnO depend on the applied potential.<sup>14</sup> Inamdar and colleagues published instantaneous or progressive growth of the grains of ZnO as function of growth temperature [1]. Wellings and colleagues found that the thickness of ZnO's film depends on the electrodeposition time, as another result, they found that there is a larger grain size with increasing time of electro-deposit [15].

The growth parameters of the cathodic electrodeposition affect to the crystallographic orientation, ratio Zn/O, grain size and grain number of ZnO. Thus, in this paper we analyze the effect of the combination of these parameters on these aspects of the morphology and on the photocatalytic process of methylene blue. The study includes an Experimental Design [16]  $2^3$  (2 levels and 3 variables), as shown in Table 1.

**Table 1.** Experimental Design

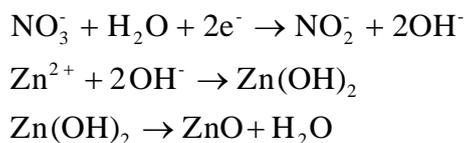
| Coded parameters | Study Parameters              | Low level (-) | High level (+) |
|------------------|-------------------------------|---------------|----------------|
| A                | Electrodeposition voltage     | -900 mV       | -850 mV        |
| B                | Electrodeposition temperature | 60 °C         | 70 °C          |
| C                | Electrodeposition time        | 5 min         | 10 min         |

The considered range of temperature variable was chosen according to reports for ZnO electro-deposits. The voltage was selected according to a previous cyclic voltammetry. With this experiment was observed that voltages below -0.9 V show hydrogen evolution on the working electrode, it implying a low adhesion of ZnO. On the other hand, at voltages higher than -0.85 V, the deposited semiconductor was too poor. The deposition times were chosen so that we could count the grain number of deposited ZnO on the substrate

The electro-deposits obtained from the experimental design were characterized by optical density, X-ray diffraction and scanning electron microscopy (SEM), while the photocatalysis was characterized by UV-Visible Spectroscopy.

## 2. EXPERIMENTAL

The electro-deposits were carried out using a bipotenciostat "Pine Instruments". We used a conventional three electrode cell, where the work electrode was indium tin oxide (ITO)-covered glass substrates with an geometric area of 0.9 cm<sup>2</sup> and resistivity between 15-25 Ω per cm<sup>2</sup>, a Ag/AgCl reference electrode and a Pt plate of 25x25 mm (Aldrich, 99.99%) was used as counter-electrode. The distance between the work electrode and counter electrode was 3 cm. As electrolyte was used an 0.1 M zinc nitrate (Zn (NO<sub>3</sub>)<sub>2</sub>) solution and the reaction was carried out as follows [17]:



Prior to electro-deposit, the ITO substrates were washed with cleaning solution and deionized water and then were rinsed with isopropyl alcohol to remove any organic residue. After deposition, the resulting films were rinsed with deionized water and dried with air at room temperature for 15 minutes. Subsequently, it was carried out the electro-deposition of ZnO in the electrochemical cell according to the experimental design presented in Table 1. Finally, the photocatalytic activity of ZnO films was characterized from MB photodegradation.

The photocatalytic tests were performed in a 6 ppm methylene blue solution in which the ZnO catalyst was submerged. This system was exposed to UV radiation from a Mineralight xenon lamp with an intensity around 10 mW/cm<sup>2</sup>.

The electro-deposits were characterized using a BRUKER D8 DISCOVER diffractometer in order to identify the crystalline phase.

The surface morphology was observed by mean to a JEOL-JSM 6610LV scanning electron microscope (SEM). Photodegradation of Methylene Blue was monitored in a UNICAM V-2 UV-Vis spectrophotometer.

## 3. RESULTS AND DISCUSSION

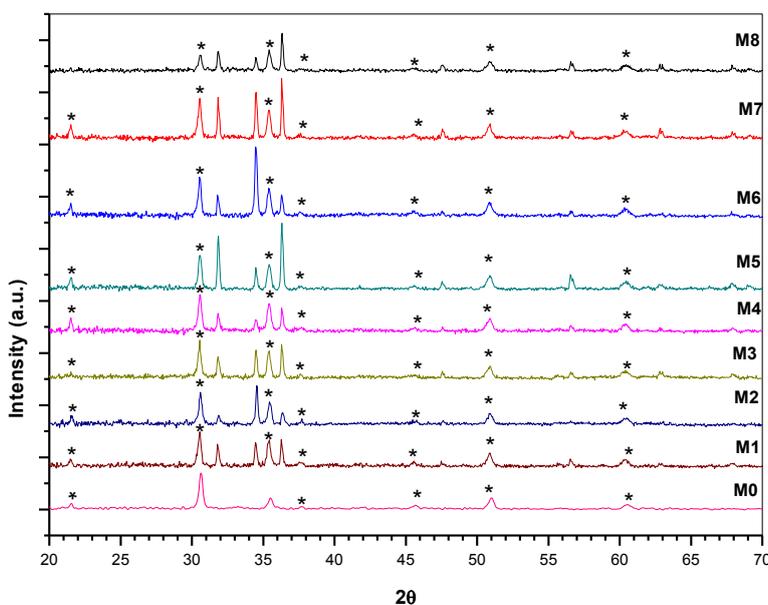
Table 2 shows the label of the samples according to the levels of the main parameters used and the results of the characterization techniques employed.

3.2 Characterization by X-ray diffraction

Figure 1 shows the characterization by X-ray diffraction for each electro-deposit developed. The diffractograms show peaks corresponding to ZnO polycrystalline in the hexagonal phase according to JCPDS crystallographic table, also other peaks were identified (labeled with an asterisk), corresponding to the ITO substrate. It is clear that the intensity of reflection peaks are different for each sample depending on growing conditions.

**Table 2.** Identification of the ZnO electro-deposits and its characterization parameters.

| ID of samples | A (V) | B (°C) | C (min) | grain number | grain size (µm) | texture coefficient in the 100 plane (T <sub>100</sub> ) | texture coefficient in the 002 plane (T <sub>002</sub> ) | ratio Zn/O | MB Degradation (%) |
|---------------|-------|--------|---------|--------------|-----------------|--|--|------------|--------------------|
| M1            | -     | -      | -       | 55           | 0.52            | 1.281  | 1.861  | 0.32       | 36.82              |
| M2            | +     | -      | -       | 65           | 0.40            | 0.688  | 1.816  | 0.27       | 29.10              |
| M3            | -     | +      | -       | 37           | 0.60            | 1.068  | 1.912  | 0.41       | 34.80              |
| M4            | +     | +      | -       | 60           | 0.51            | 1.352  | 1.213  | 0.34       | 27.50              |
| M5            | -     | -      | +       | 28           | 0.68            | 1.818  | 1.049  | 0.54       | 34.75              |
| M6            | +     | -      | +       | 33           | 0.51            | 0.863  | 2.392  | 0.39       | 28.57              |
| M7            | -     | +      | +       | 40           | 0.64            | 0.869  | 1.147  | 0.53       | 31.24              |
| M8            | +     | +      | +       | 22           | 0.56            | 0.858  | 0.551  | 0.48       | 32.50              |



**Figure 1.** Diffractograms of the polycrystalline ZnO according to experimental design

For evaluating the preferred orientation of ZnO samples, it was used texture coefficient (table 2) which it is calculated by the following equation

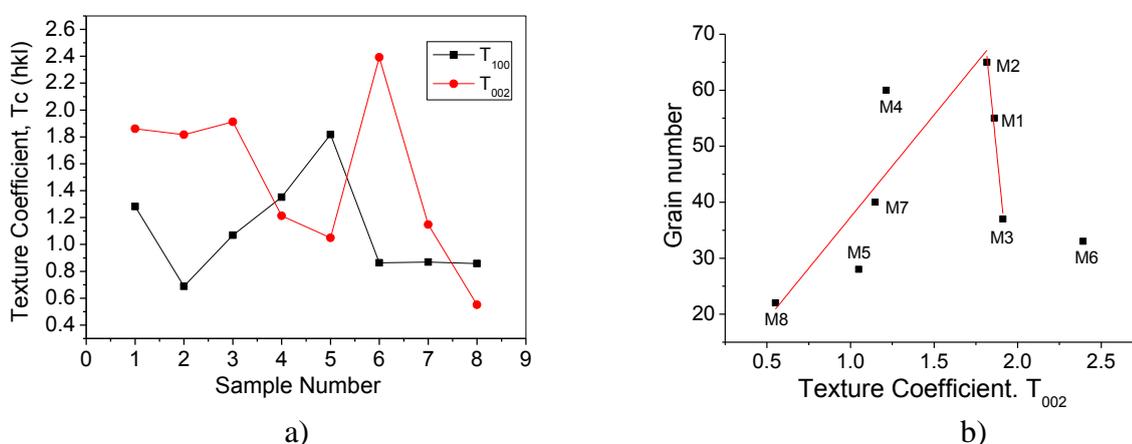
$$T_c(hkl) = \frac{I(hkl)/I_0(hkl)}{\left(\frac{1}{N}\right) \left[ \sum_N I(hkl)/I_0(hkl) \right]}$$

where  $T_c(hkl)$  is the texture coefficient of the  $(hkl)$  plane,  $I$  is the measured intensity,  $I_0$  is standard intensity JCPDS and  $N$  is the number of diffraction peaks. From the above equation,  $T_c$  is close to unity for a randomly distributed powder sample, while  $T_c$  is greater than 1 when the  $(hkl)$  plane is preferentially oriented.

The texture coefficients evaluated correspond to the  $(100)$  and  $(002)$  planes, because these indicate a change in the crystal form. Thus, a preferential orientation  $(002)$  plane indicates preferential growth of zinc oxide crystals along axis C, while the  $(100)$  preferred orientation indicates a shortening of the crystal along the axis C [18].

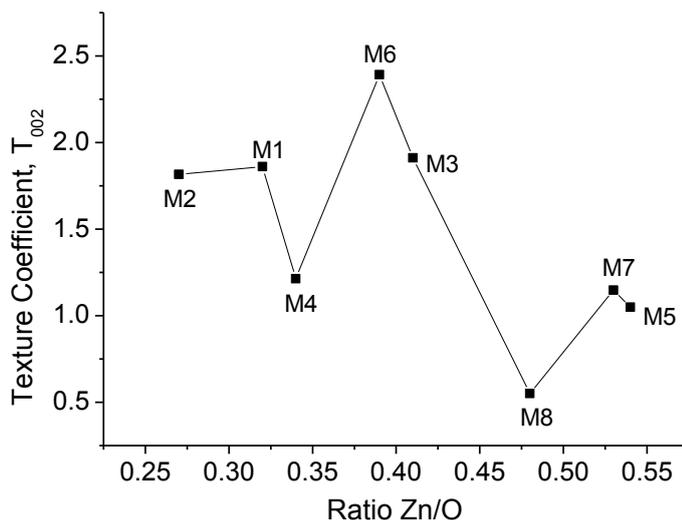
Figure 2a shows the graph of the texture coefficient as a function of sample number, it noting that most part of the texture coefficient  $T_c(002)$  are greater than the texture coefficients  $T_c(100)$ , it indicating preferential growth along the axis C.

Figure 2b shows the graph of the grain number in function of texture coefficient  $T_c(002)$ , there is an increase in the grain number as increase texture coefficient of 0.5 to 1.82, for higher values of the texture coefficient decreases grain number, which could be due to the coalition between adjacent grains. The increase in preferred orientation is attributed to the increase in the grain number in this orientation [18].



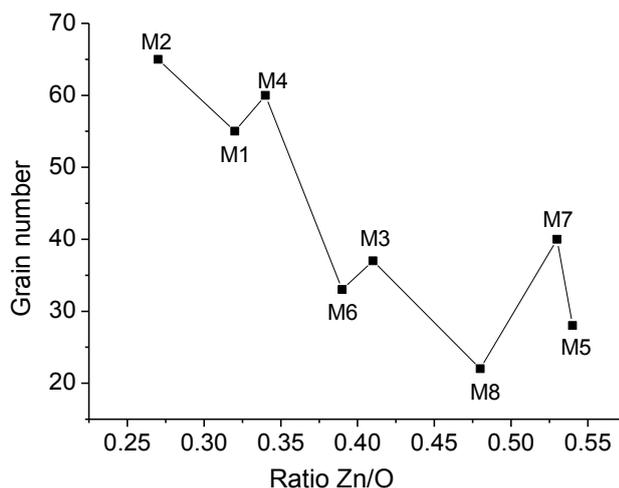
**Figure 2.** a) Texture coefficient versus sample number and b) grain number versus texture coefficient

Figure 3 shows the texture coefficient  $T_c(002)$  versus the ratio Zn / O, the trend is that lower ratio Zn / O, higher texture coefficient, this has already been noted by Yung [19],



**Figure 3.** Texture coefficient vs ratio Zn/O

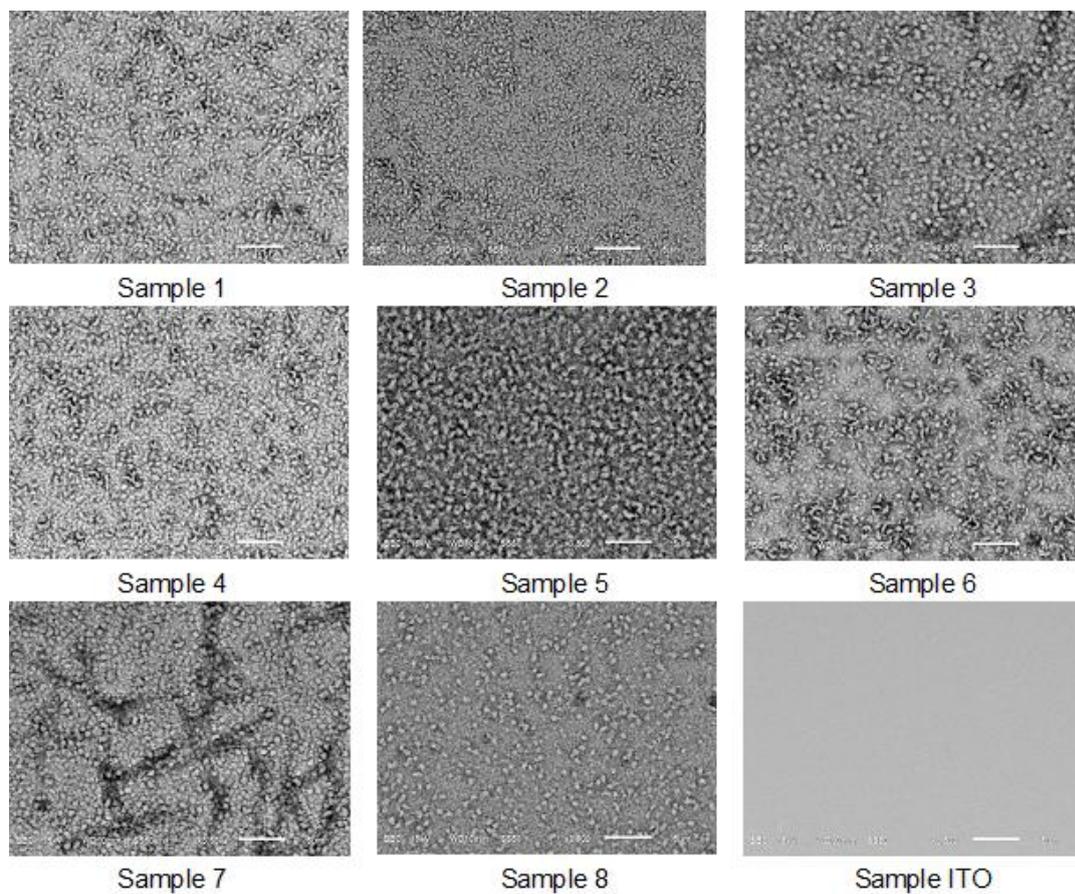
The comparison of Figures 2b and 3 show that there is a relationship between the grain number and the ratio Zn / O (Figure 4), as it can be seen, as the ratio Zn / O increases of 0.27 up to 0.48 the grain number decreases. For values greater than 0.48 in the ratio Zn / O is observed grain number increased, this is similar to those observed by Young [19]



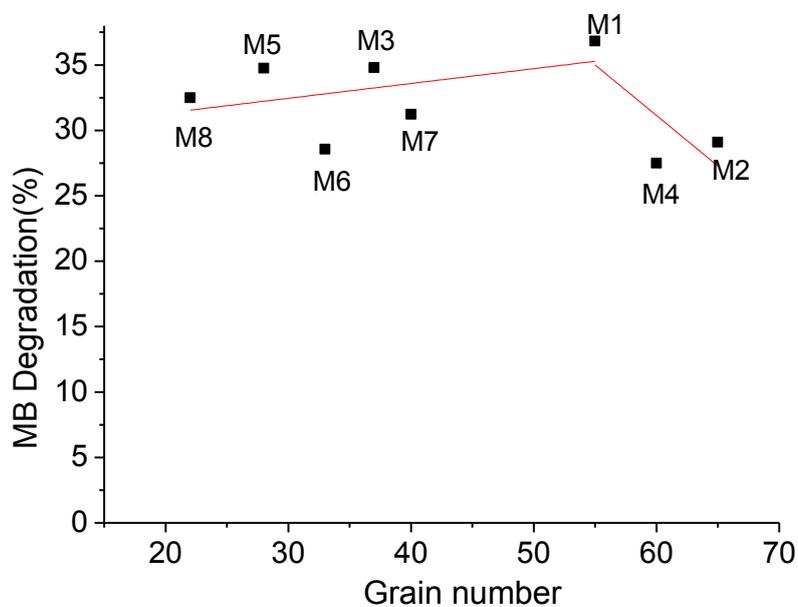
**Figure 4.** Grain number vs ratio Zn/O

### 3.4 Characterization by Scanning Electron Microscopy

Figure 5 shows the morphology of the ZnO samples obtained by SEM. In general, we see grain size and grain number different, which is typical behavior of progressive nucleation. Therefore, we can consider that the morphological structure of ZnO is affected by the combination of variables during the electrodeposition.



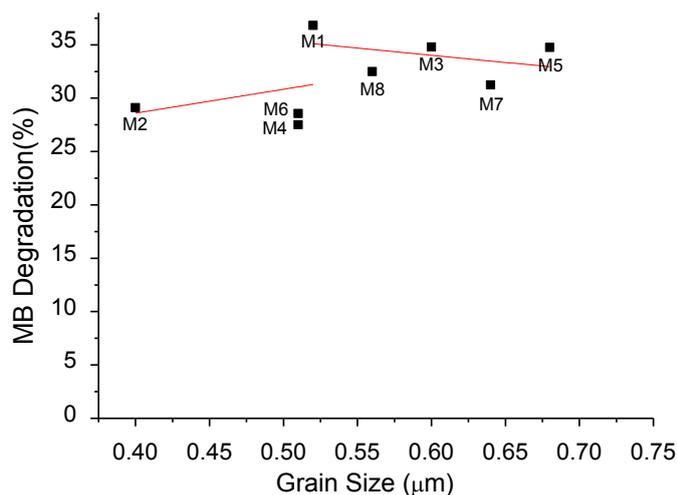
**Figure 5.** Micrographs obtained by SEM, it shows the change in grain size and grain number by variation of the deposition conditions



**Figure 6.** MB degradation versus grain number

In order to investigate how it affects the grain size and grain number on the photocatalytic efficiency of methylene blue, the grain size and grain number were obtained by SEM, see Table 2. In the Figure 6 was plotted MB degradation as a function of grain number measured in an area of  $25 \mu\text{m}^2$  for each sample, where we observed two trends. In the first trend, photocatalytic activity increased when the grain number was 22 to 55, it reaching the maximum in the latter, this likely indicates that as grain number increases also increases the surface area of ZnO having more light gathering and higher proportion active sites, it resulting in increased production of  $\text{OH}\cdot$  radicals and therefore increased degradation of MB solution during the photocatalysis [20]. In the second trend, the values of grain number over 55 generate the decrease in the degradation of MB, probably because there is decrease of grain size (see table 2), and therefore decrease the active catalytic sites

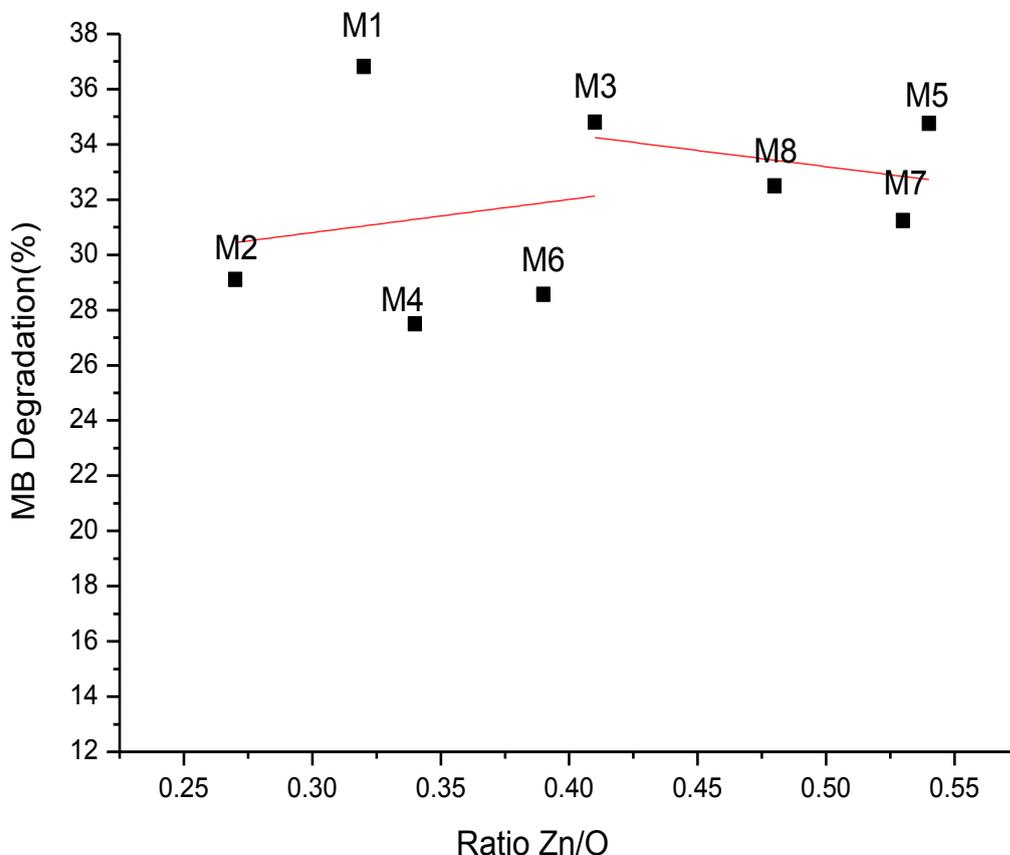
In the Figure 7 is plotted MB degradation as a function of average grain size for each sample and 2 trends can be observed again. The first trend includes the grain size range of  $0.68$  to  $0.52 \mu\text{m}$ , and shows the increase in the MB degradation with decreasing grain size, it reaching the optimum at  $0.52 \mu\text{m}$ . From Figures 6 and 7 can be inferred that for this range is true that the lower the grain size implies greater grain number and greater degradation of MB. The second covers the grain size range of  $0.52$  to  $0.40 \mu\text{m}$  and shows reduced MB degradation with decreasing grain size and from the graphs 6 and 7 it follows that for this range is true that a smaller grain size implies greater grain number and reduced degradation of MB.



**Figure 7.** MB degradation versus grain size

In the Figure 8 is represented the degradation of MB as function of the ratio Zn/O (it was obtained by EDS, Energy-dispersive *X-ray* spectroscopy, see table 2), it is clear the different effect on the ratio Zn/O for each sample according to the combination of variables during the electrodeposition. Figure 8 also shows two trends, the first spanning a range of  $0.54$  to  $0.41$  in the ratio Zn/O and shows that with decreasing the ratio Zn/O there is an increased degradation of MB and from the graphs 4 and 8 can be inferred that when the ratio Zn/O decreases there is an increased grain number and according

to Figure 6, as increases the grain number there is increased degradation of MB up to the optimum in 0.32, which it corresponds to sample 1. The second covers of 0.41 up to 0.27 and shows reduced MB degradation with decreasing ratio of Zn/O and from the graphs 4 and 8 can be inferred that when the ratio Zn/O decreases there is an increased grain number and according to Figure 6, it follows that for this range is true that as increases the grain number there is reduced degradation of MB.

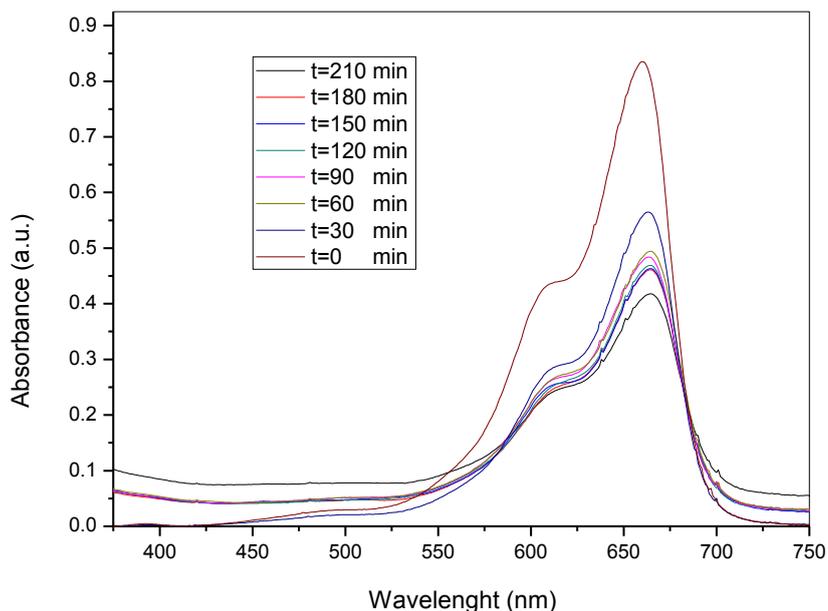


**Figure 8.** MB degradation as a function of the ratio Zn/O

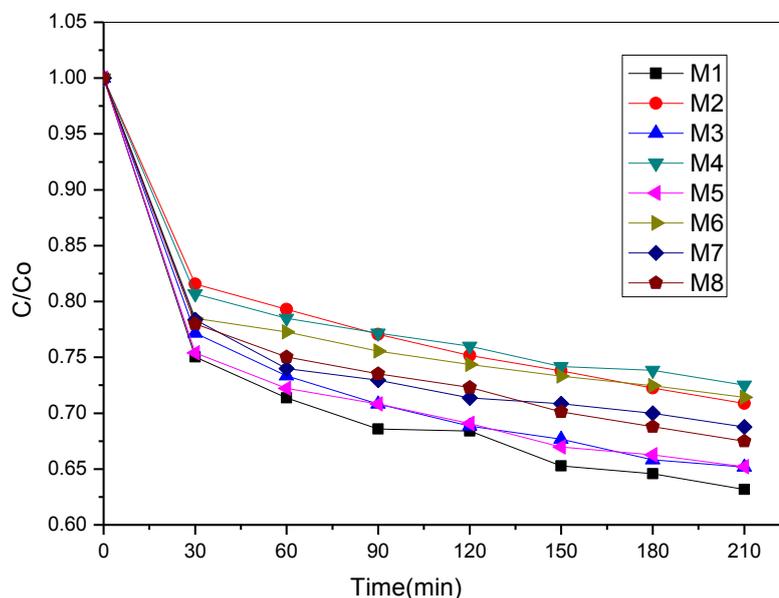
### 3.5 Photodegradation of the Methylene Blue solution

Figure 9 shows the evolution absorption spectrum of the MB with the illumination time for a representative sample. In general, it appears that as greater is the illumination time of Methylene Blue solution, the intensity of the peak located at 664 nm is reduced, which it demonstrating the MB photodegradation.

Figure 10 shows the evolution of the relative concentration of methylene blue versus illumination time for each ZnO sample electrodeposited. In this plot is remarkable the photocatalytic activity of M1 to degrade a larger amount of MB. The results of the degradation of MB are summarized in the last column of Table 2.



**Figure 9.** Variation of absorption spectrum of methylene blue with the illumination time



**Figure 10.** Evolution of the relative concentration of methylene blue solution as a function of illumination time for each sample of ZnO

#### 4. CONCLUSIONS

Based on our studies, we can conclude that the morphological structure of ZnO is affected from the combination of electrodeposition variables in experimental design. From the X-ray diffraction analysis and SEM analysis it was found preferential growth along the axis C, which it is related to grain number, grain size and ratio Zn/O. From our analytical results, we found that the ratio Zn/O, size

and number of grains are closely correlated, in turn, we found well-defined trends of these parameters with respect to the degradation of methylene blue. Also, it was found that we can achieve the greatest degradation of methylene blue dye from the electro-deposits with the grain number, grain size or ratio Zn/O appropriate.

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