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## Photo catalytic property of ZnO and Mn-ZnO nanoparticles in removal of Cibacet Turquoise blue G from aquatic solution

### ABSTRACT

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ZnO and Mn-ZnO nano powders were prepared by the sol-gel auto combustion method. The products were characterized by X-ray diffraction (XRD), energy dispersive analysis of X-ray (EDX) and scanning electron microscopy (SEM). Structural and morphological properties of nano particles were investigated and the average crystalline size of ZnO and Mn-doped ZnO was obtained 44 and 51 nm, respectively. Also, photo catalytic removal of Cibacen Turquoise Blue G dye from aqueous solution by using nano scale ZnO and Mn-ZnO powders under UV light irradiation was studied. The effect of initial dye concentrations and dosage of photo catalysts, were investigated in the photo destructive process. This is 57% of dye degraded by 0.02 mg of ZnO in 70 minutes. The degradation rate increase to 84% in the presence of 0.02 mg of Mn-ZnO in the same time.

**Keywords:** *Photo catalyst; ZnO; Mn-ZnO; Degradation; Cibacen Turquoise blue G; Sol-gel auto combustion method; Nano scale; Photo destructive.*

### INTRODUCTION

Dyes are an important class of synthetic organic compounds used in the textile industry and are therefore common industrial contamination [1]. Main pollution in textile wastewater came from dyeing processes. Every process and almost every operation within a textile dyeing has an environmental aspect that should be considered and for which the environmental performance can potentially be improved [2].

Physical methods such as adsorption, biological methods (bio-degradation) and chemical methods such as chlorination and ozonation are the most frequently used methods for the removal of the textile dyes from wastewater but only transfer the contamination from one phase to another.

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One of the attractive research fields in recent years is the synthesis of various sizes and shapes of semiconductor materials nanoparticles for removal of textile contaminants from wastewater [3-5].

Semiconductor nano particles have attracted interests of many academic and industrial researchers because of their properties based on quantum size effects and high surface area [6, 7]. Among these materials, high-quality nano powders of ZnO are currently of interest for use in a variety of technological applications, including optically transparent ultraviolet (UV) filters and photo catalysts for the destruction of chemical waste. It has been intensively studied due to its piezoelectric, pyroelectric, photocatalytic and conductive properties [8] and possesses several unique advantages such as high-specific surface area, nontoxicity, chemical stability, electrochemical activity, and high electron communication features [9-11].

Zinc oxide, is one of the most important multifunctional semiconductors commonly occurring as hexagonal wurtzite, is the n-type semiconductor with large direct band gap (~3.4 eV) and large exciton binding energy 60 meV [12-15]. ZnO has some drawbacks including the fast recombination rate of photogenerated electron-hole pair and a low quantum yield in the photocatalytic reactions in aqueous solution, which obstruct commercialization of the photocatalytic degradation process [16].

Nowadays, methods like hydrothermal [17], spray pyrolysis [18, 19], co-precipitation [20-23], organo chemical [24], sol-gel [25-27] and chemical vapour deposition (CVD) [28] methods can be used for the synthesis of nano scale ZnO.

Sol-gel auto combustion is a way with a unique combination of the chemical sol-gel process and the combustion process based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuel, giving a voluminous and fluffy product with large surface area. This process is less complicated than the others [29, 30].

In this research, sol-gel auto combustion method was applied to prepared ZnO and Mn-ZnO photo catalyst fine nanoparticles and then photocatalytic degradation of Cibacen Turquoise blue G on the surface of these nanoparticles was investigated. The structure of dye with the basic

formula of  $C_{18}H_{18}N_2O_6$  is observed in Figure 1. The dependence of several parameters such as initial dye concentrations, dosage of photocatalysts and irradiation time were also studied.

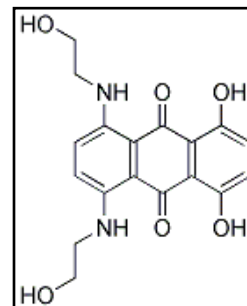


Fig. 1. Structure of Cibacen Turquoise Blue G.

## EXPERIMENTAL

### Synthesis of Nano photo catalysts

Zinc nitrate  $Zn(NO_3)_2 \cdot 6H_2O$ , Magnesium nitrate,  $Mn(NO_3)_2 \cdot 6H_2O$ , glycine,  $C_2H_5NO_2$  and ammonia were used as starting materials. All the reagents used in the experiments were analytically pure and used without further purification and treatment. Deionized water was used for the preparation of all the samples.

The mole ratio of  $Zn(NO_3)_2 \cdot 6H_2O$  to glycine was fixed at 1:2. Materials were dissolved in a minimum amount of deionized water to get a clear solution. Ammonia solution was slowly added to adjust pH to 7. The solution was allowed to evaporate on a hot plate and maintained at 60 °C under continuous stirring. After the evaporation of water, the resulting gel was ignited to form a loose powder. Finally the precursor was calcined at 600 °C for 2 hours to obtain ZnO nanoparticles.

All the above steps were repeated for preparing Mn-ZnO nano photo catalyst.

### Assessment of the photo catalytic activities of undoped and Mn-doped ZnO nanoparticles

Photo catalytic degradation of Cibacen Turquoise Blue G was used to evaluate the photo catalytic activity of synthesized ZnO and Mn-ZnO nano powders. First, the solution of 5 and 10 mg  $L^{-1}$  of dye were prepared in deionized water and then 100 ml of prepared solution are transferred in two purely clean containers. An amount of 0.01 and 0.02 mg of nano photo catalyst were added to

containers. Solutions were placed at a distance of 30 cm from UV lamp with power of 30 W for a time interval of 70 minutes. The solutions were continuously stirred throughout the whole time. Samples were taken from both solution and were filtered and centrifuged for 20 minutes to remove all nanoparticles completely. Finally, clear transparent solutions were obtained. Afterwards, samples were taken from obtained solutions and put in the double beam spectrophotometer to measure the absorbance of remained dye.

## RESULTS AND DISCUSSION

### Materials characterization

The phase identification of the nano powders was recorded by X-ray diffraction with  $Cu-K\alpha$  radiation. The crystallite powders size was also measured by X-ray line broadening technique using the Scherrer formula indicated in equation (1):

$$D = (0.9)\lambda / \beta \cos\theta$$

Where  $D$  is the grain diameter,  $\beta$  is half-intensity width of the relevant diffraction;  $\lambda$  is X-ray wavelength and  $\theta$  the diffraction angle.

A Philips XL-30 scanning electron microscope was used to characterization the morphologies and microstructure of the samples.

- **X-Ray diffractions of nanoparticles**

The phase and purity of nano powders were determined from the XRD patterns (Figure 2a & 2b). Well-defined sharp peaks indicate the good crystalline quality and confirm the formation of single-phase zinc oxide and Mn-doped ZnO nano photo catalysts. The diffraction peaks, appeared in the XRD patterns, can be indexed with the standard patterns for ZnO (JCPD 01-079-0208) and Mn-ZnO (JCPD 00-019-1461). The average crystalline size calculated from Scherrer equation were 44 and 51 nm for ZnO and Mn-ZnO, respectively.

- **EDAX analysis**

The elemental composition of nano powders is determined from the EDAX spectrum over a selected zone. Figure 3a and 3b show the EDAX spectrums of each sample. The spectrum of obtained precursor indicated the presence of Zn

(Figure 3a) and Mn-Zn (Figure 3b) as major elements in the final powders.

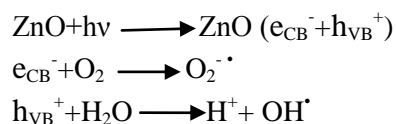
- **SEM images of nanoparticles**

An SEM image of ZnO and Mn-ZnO nano photo catalysts is shown in Figure 4 (a, b). Figure 4a shows that the ZnO nano powder contains spherical nanoparticles, whereas Figure 4b shows that ZnO on the bed of Mn for Mn-doped ZnO nano powders.

### Photo catalytic Degradation

- **Evaluation of photo catalytic of ZnO and Mn-ZnO nanoparticles**

In a photo catalytic system, photo-induced molecular transformation or reaction takes place at the surface of catalyst. A basic mechanism of photo catalytic reaction on the generation of electron-hole and its destination is as follows: when a photo catalyst is illuminated by the light stronger than its band gap energy, electron-hole pairs diffuses out to the surface of photo catalyst and participates in the chemical reaction with electron donor and acceptor. Those free electrons and holes transform the surrounding oxygen or water molecules into OH free radicals with super strong oxidization. It can oxygenolyse various kinds of organic compounds and some parts of minerals. Reactions can be shown as follows [31]:



Degradation of dye calculated from equation (2):

$$X = \frac{A_0 - A}{A_0}$$

Where  $X$  is degradation percentage,  $A_0$  is initial absorption of and  $A$  is absorption after several minutes.

The photo activities of unadoped ZnO and Mn-ZnO were carried by using UV light irradiation. Degradation can be monitored by optical absorption spectrophotometer (UNICO double beam spectrophotometer). Photo degradation of Cibacen Turquoise Blue G in a concentration of 5 and 10 mg L<sup>-1</sup> was carried with 0.02 mg ZnO and Mn-ZnO. The absorption spectrum shows in Figure 5(a-d).

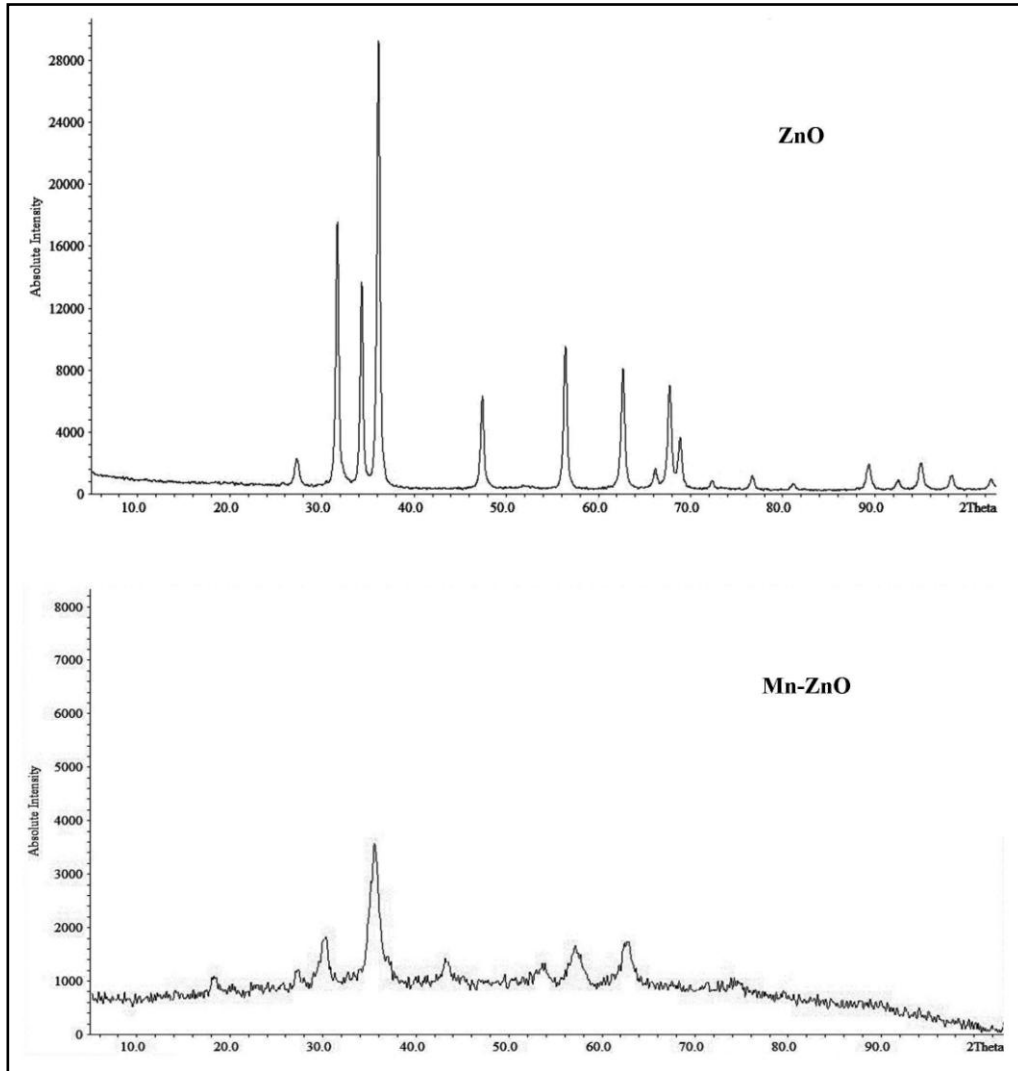


Fig. 2. XRD patterns of nanoparticles (a) ZnO and (b) Mn-ZnO

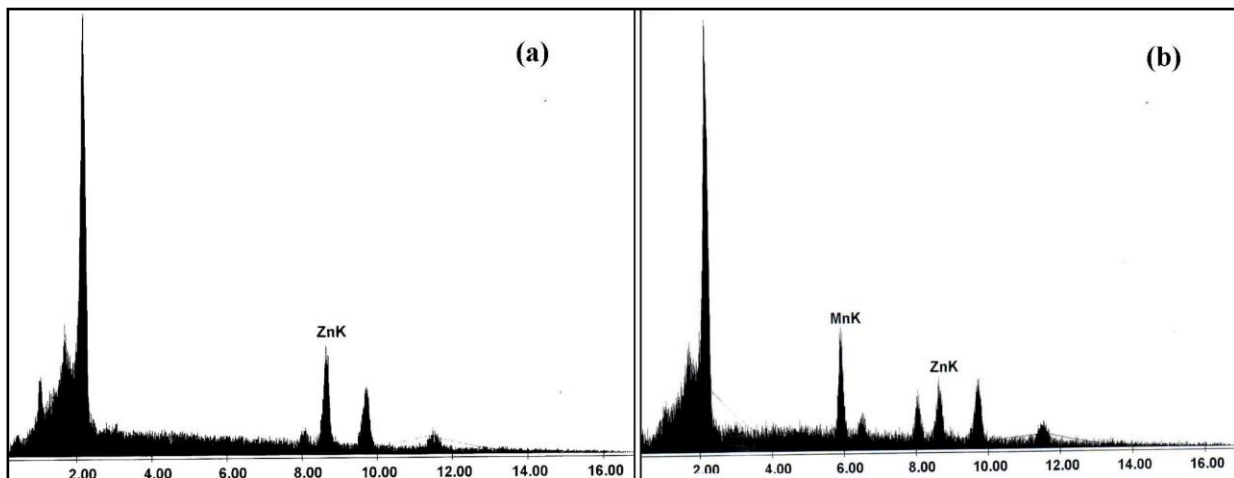


Fig. 3. EDAX analysis of nano particles (a) ZnO and (b) Mn-ZnO

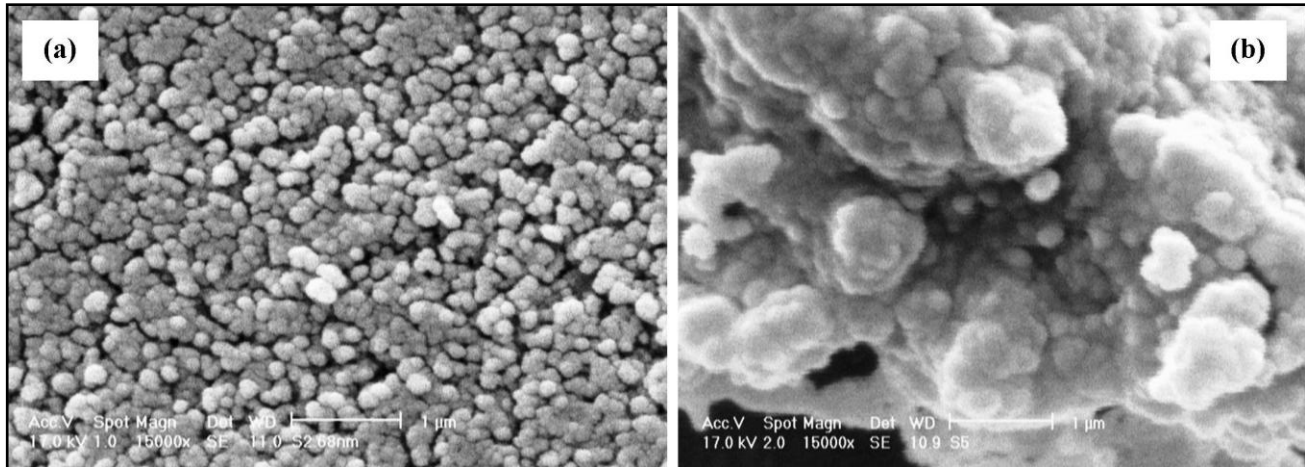


Fig. 4. SEM images of nanoparticles a) ZnO and b) Mn-ZnO

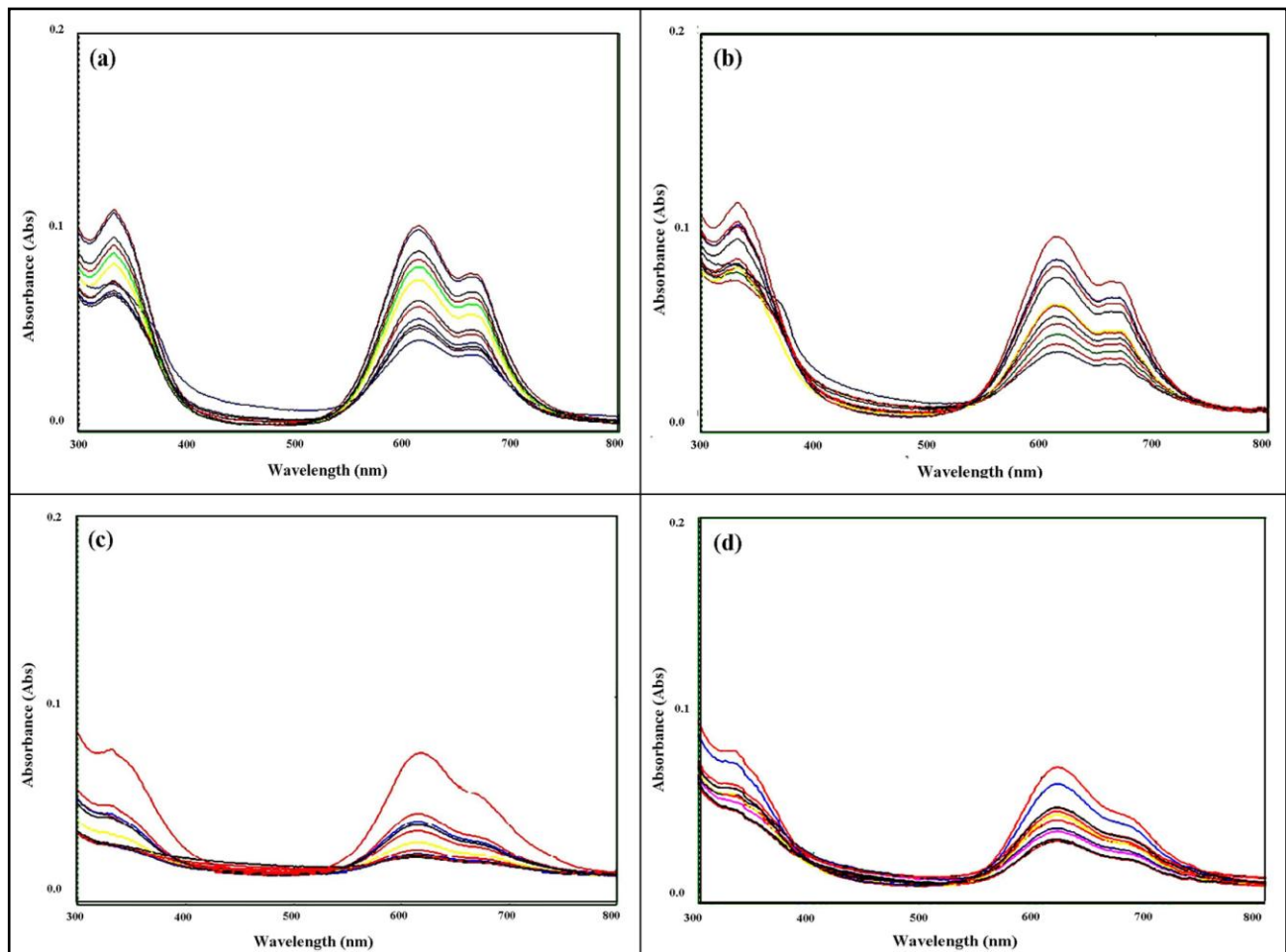


Fig. 5. Absorption spectrum of photo degradation reaction in presence of a) [Dye]= 5 mg L<sup>-1</sup>, ZnO= 0.02 mg, b) [Dye]= 10 mg L<sup>-1</sup>, ZnO= 0.02 mg, c) [Dye] = 5 mg L<sup>-1</sup>, Mn-ZnO= 0.02 mg and d) [Dye]= 5 mg L<sup>-1</sup>, Mn-ZnO= 0.02 mg



- **The Effect of Dye Concentration**

The effect of initial concentration of dye solution on its degradation, is illustrated in Figure 6 (a and b). There are 5 and 10 mg L<sup>-1</sup> from the dye, degraded in present of 0.01 mg of nano photo catalysis.

The results show that the percent of degradation decrease with increasing of initial concentration. The increasing of initial dye

concentration cause, the more dye substances are adsorbed on the surface of nanocatalysts and prevent to generate hydroxyl radicals, because of fewer active sites for adsorption of hydroxyl ions and generation of hydroxyl radicals [32]. Furthermore, with increasing dye concentration, the adsorption of photons are decreased by the catalyst, as a result, the removal percent is reduced.

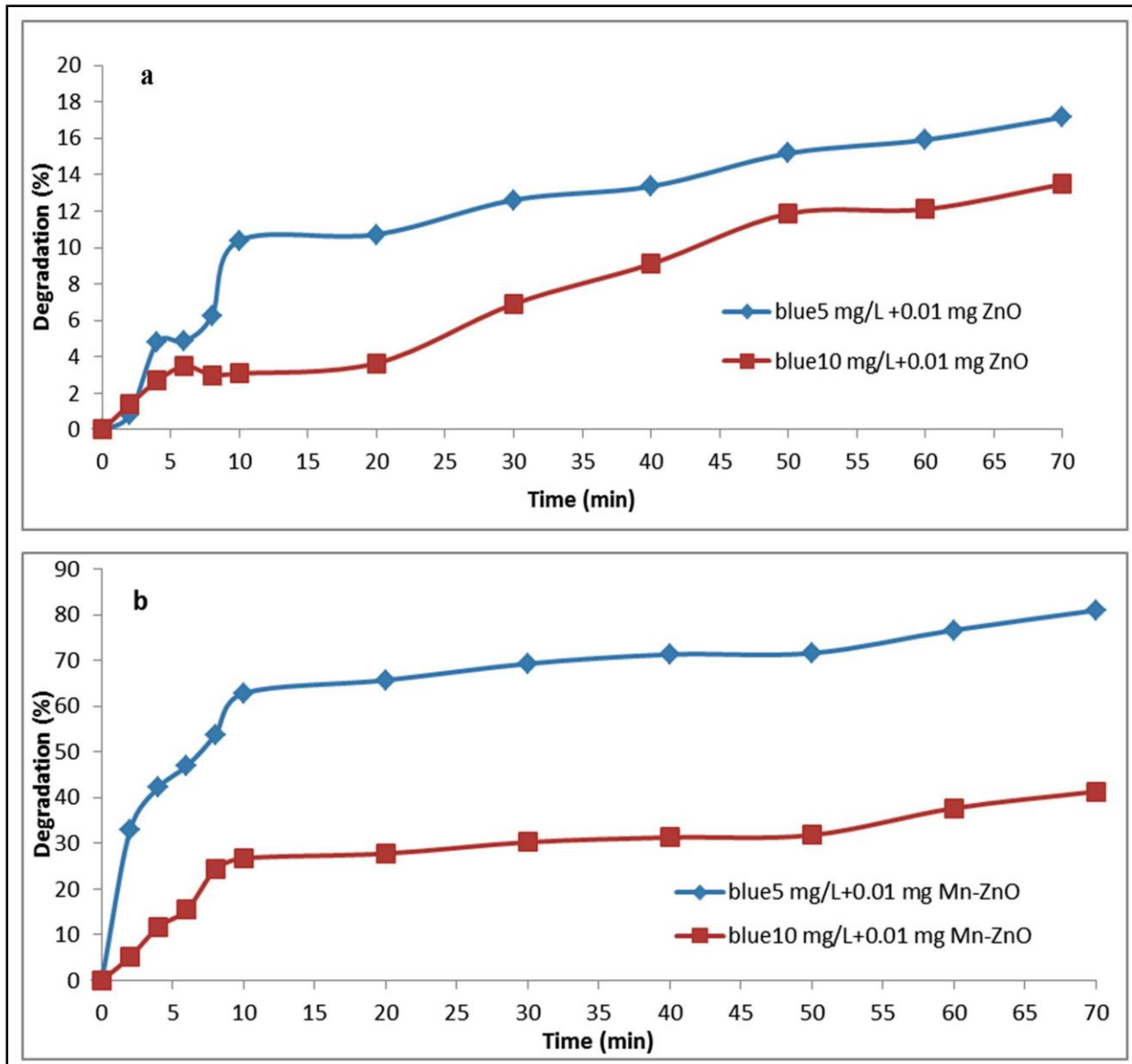


Fig. 6. Effect of dye concentration on the photodegradation reaction in the presence of a) [dye]= 5 and 10 mg L<sup>-1</sup>, ZnO= 0.01 mg b) [dye]= 5 and 10 mg L<sup>-1</sup>, Mn-ZnO= 0.01 mg

- **The Effect of Photo catalysts Concentration**

As shown in Figures 7(a and b) photo catalytic removal efficiency increases with an increase in photo catalysts concentration. The increasing of the amount of catalyst, increase the number of active sites on the photo catalyst surface,

which, increase the number of hydroxyl and superoxide radicals. Surely, increasing of catalysts concentration above the limiting value, leads to decreasing the photo degradation rate due to the interception of the light [32-34].

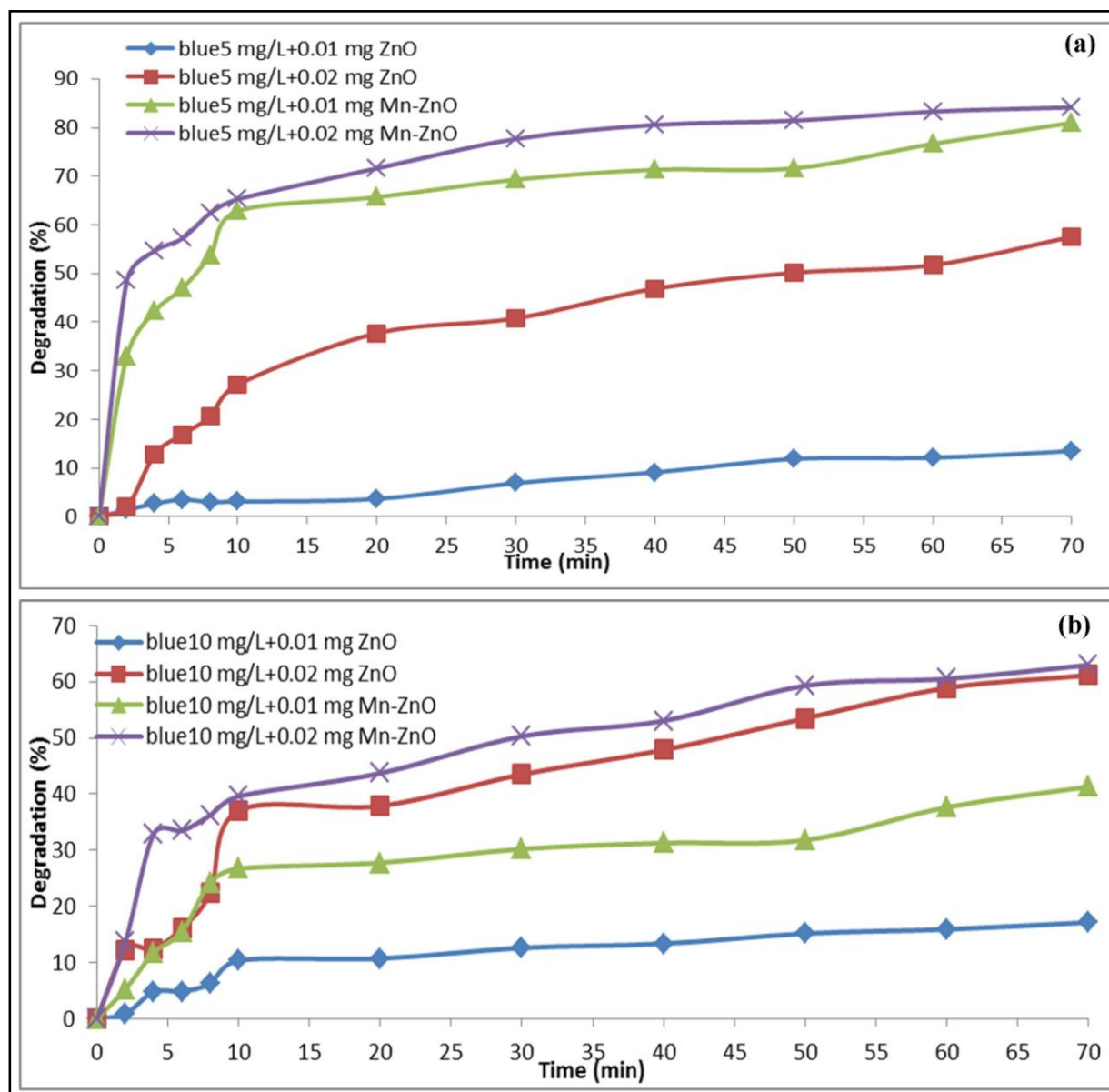


Fig. 7. Effect of photo catalyst concentration on the photodegradation reaction in the presence of a) [dye]=5 mg L<sup>-1</sup> and b) [dye]=10 mg L<sup>-1</sup>.

## CONCLUSIONS

ZnO and Mn-ZnO nano powders were synthesized by sol-gel auto combustion method. This method is simple, cost effective and high time and energy efficient process. The combustion reaction is induced anionic red-ox reaction of the gel thermally, wherein the fuel act as reductant and  $\text{NO}_3^-$  ions act as oxidant. The average particles size was determined with sherrer formula by X-ray spectrum data and estimated about 44 and 51 nm for ZnO and Mn-ZnO nanoparticles, respectively.

The photo catalytic properties of these nano structures cause to decomposition of the Cibacen Turquoise Blue G in presence of UV light irradiation. Results show, doping of ZnO nanoparticles with manganese, improve the photo catalytic properties of ZnO. The effect of different parameters such as photo catalysts concentration, type of nano photo catalyst and dye concentration is summarized in Table 1.

**Table 1.** The effect of different parameters such as photocatalysts concentration, type of nanophotocatalyst and dye concentration

Dye concentration (mg.L <sup>-1</sup> )	Type of nano	Photocatalysts Concentration (mg/L)	Photo catalytic degradation (%)
5	ZnO	100	10
		200	57
	Mn-ZnO	100	81
		200	84
10	ZnO	100	17
		200	61
	Mn-ZnO	100	37
		200	63

As results, in 5 mg/L concentration of dye, degradation percentage is 10% and 81% in presence of 100 mg L<sup>-1</sup> of ZnO and Mn-ZnO, respectively. While in presence of 200 mg L<sup>-1</sup> of ZnO and Mn-ZnO, these percentages were 57% and 84%. Therefore, increasing of concentration of

nano photo catalysts, cause with increasing in degradation percentage. Otherwise, in 10 mg L<sup>-1</sup> of dye, percentage of photo catalytic destruction is decreased to 61% and 63% for ZnO and Mn-ZnO nano powders. Moreover, the performance of Mn-doped ZnO is better than ZnO nanoparticles.

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