J Biochem Tech (2019) (4): 69-75
ISSN: 0974-2328

Synthesis of Nanocomposite and Studying the Degradation of Alizarin Dye

Ola A. Nasief and Ahmed N. Abd

Received: 19 July 2019 / Received in revised form: 23 November 2019, Accepted: 04 December 2019, Published online: 27 December 2019

Abstract

This study aimed to evaluate the ability of semiconductors such as TiO_2, CuO, and ZnO that are utilized to remove the hazardous Alizarin organic dye of textile from aqueous solution. In this paper, Zinc oxide (ZnO), Copper oxide (CuO), and Titanium oxide (TiO_2) nanoparticles were synthesized through a simple chemical process. In this study, the nano-powder of copper oxide was synthesized by the reaction of copper nitrate and citric acid, zinc oxide was synthesized by the reaction of citric acid and zinc nitrate by the sol-gel, and titanium oxide was synthesized by the reaction of industrial titanium dioxide with sodium hydroxide and finally, CuO/ZnO/TiO_2 nanocomposite was synthesized by physical process. The structural properties of these nanoparticles and composite were characterized using X-ray diffraction (XRD), and Field Emission Scanning Electron Microscope (FE-SEM). We described the photocatalytic degradation of Alizarin dye solution using CuO/ZnO/TiO_2 nanocomposite photocatalysts in the form of CuO/ZnO/TiO_2 composite as a paint on the Stainless Steel cell, under ultraviolet (UV) irradiations. The effect of factors affecting the reaction such as the initial concentration of the two dyes, the effect of temperature, and the value of the acidic function was studied. The experimental results demonstrated that CuO/ZnO/TiO_2 composite can remove the Alizarin red from wastewater by XRD and an average volume of copper oxide molecules by the formula of Debar Shearer found that it is equal to 21.33 nm. The particle size was found to be 18.13, 42.63, 20.48, and 20.48 nm for zinc oxide, titanium oxide, nano chemical mixture, and CuO/ZnO /TiO_2 nanocomposite, respectively.

Key words: Nano oxide, Composit; ZnO, CuO, TiO_2, degradation, photocatalyst, Alizarin dye

Introduction

Research on the synthesis method of nanomaterials was generally oriented in the control of their size, shape, and composition. Each of these elements is a critical factor that gives information about the properties of materials that are used in different technological applications (Kharissova et al., 2013; Dubey and Singh, 2019). Nanotechnologies have become an urgent priority worldwide that are progressively to the increased precise surface area and reactivity, which can lead to increased bioavailability and toxicity (Shaimaa Hamed, 2017; Jaleel et al., 2018). The limitations of TiO_2 for applications in water treatment are mostly due to its tiny particle size, which may require expensive filtering treatment (Kahru et al., 2008). Titanium is utilized with copper to give the properties of broad photochemical (Al-Dhahir, 2013; Mahmoud et al., 2018). TiO_2 with a band gap of =3.2 eV (Naika et al., 2015) TiO_2 NPs are used in diverse areas including cosmetics, sunblock lotions, soil, and water (Fatin et al., 2012).

Copper (II) oxide (CuO) with a bandgap of 1.2-1.9 eV is a p-type semiconductor that has potential applications in various areas including field emission and high-critical-temperature (Wong. H. Liang, 2016). CuO NPs have full applications in batteries, plastics, etc. Zinc oxide as an n-type semiconductor. Also, it is distinguished through appealing properties of excellent stability, green characteristics, and existing facile preparation routes (Hailemicheal et al., 2018).

The composition and microstructure of solid-state materials determine their properties (Teng, 2017). Moreover, TiO_2, ZnO it is a photocatalyst. In addition, has shown promises as an advanced and relatively cheap (Mohammadi-Aloucheh, 2018).

Additionally, stable materials such as TiO_2 coupled with the CuO can increase the stability of CuO photocathodes because they can protect the surface of CuO electrodes against decomposition/corrosion in the electrolyte (Kubacka et al., 2013). Researchers have developed an exclusive interest in techniques that contain loading copper oxide (CuO) onto the surface of ZnO nanoparticles because CuO is chemically established in atmospheric conditions and photocatalytic reactions (Lu et al., 2008). The toxicity of metal oxides is Cu>TiO_2>ZnO.

Materials and Methods

The first experiment was carried out at the Department of Nano Science and Technology to synthesize nanoparticles and characterize them. The chemicals used for the synthesis of nanoparticles included zinc nitrate, copper nitrate trihydrate, TiO_2 pellets, NaOH, and Ammonia (Kharissova et al., 2013).

Synthesis of TiO_2, CuO, ZnO Nanoparticles and Adsorbate

Titanium oxide nanoparticles

TiO_2 NPs were synthesized by dissolving 0.5g TiO_2 pellets in 30ml NaOH solution (10 M) under vigorous stirring at room

Ola A. Nasief and Ahmed N. Abd

Department of Chemistry, College of Science, University of Diyala, Baquba City, Diyala governorate, Iraq.

temperature for 2 hours. It was irradiated in an ultra sonicator at room temperature for 2 h. The resulting precipitate was then centrifuged, washed, and decanted with deionized water several times and dried at 60°C for 24h in order to obtain the nanoparticles (Kharissova et al., 2013).

Copper oxide nanoparticles

5g copper nitrate trihydrate was added into 50ml distilled water and in another beaker, 5.580 g citric acid was added into 50ml distilled water. Then the $Cu(NO_3)_2.3H_2O$ solution (50ml) was transferred to the citric acid solution on a magnetic stirrer with a hot plate set at 280°C with high-speed stirring. After a while, NH_3 was added dropwise (slowly for 40 min). After 2 h, the solution was subjected to sol-gel and then kept in an oven for 24 h. Finally, the precipitated powder was dried at 400°C for 4h to obtain the nanoparticles.

Zinc oxide nanoparticles

5g zinc nitrate ($Zn(NO_3)_2$) was dissolved in 50ml distilled water in a 250ml-glass beaker and in another beaker, 5.547 g citric acid was dissolved in 50ml distilled water. Then the $Zn(NO_3)_2$ solution (50ml) was transferred into the citric acid solution on a magnetic stirrer with hot plate set at 280°C with high-speed stirring. After a while, NH_3 was added dropwise (slowly for 40 min). After 3 h, the solution was subjected to sol-gel and then kept in an oven for 24 h. Finally, the precipitated powder was dried at 450 °C for 4 hours to obtain the nanoparticles.

Composite nanoparticles

Preparation the composite is percentage molarity 1:1:1 of every one oxide ZnO, CuO, and TiO_2 take a weight (1,0.970 and 0.974 g of them. Then each of them was dissolved in 50ml deionized water and the solutions were irradiated in an ultrasonic for 1 h and kept on the oven at 120°C for 24 h. The precipitated powder was dried at 400°C for 1 h.

Adsorbate

In this experiment, the Alizarin dye (M. formula $C_{14}H_8O_4$, M. Wt.=240.21, λmax= 421.5nm) was used as the adsorbate. The stock solution was made by dissolving 0.1g/L of dye in water with the final concentrations of 10, 20, 30, and 40-ppm in the volumetric flask. The concentration of the dye solution was determined spectrophotometrically. The structure of Alizarin is given in Figure 1.

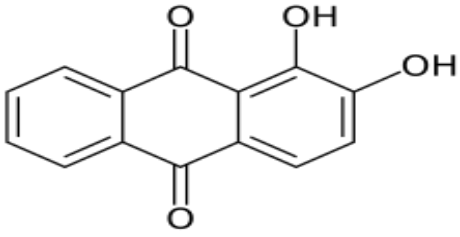

Figure 1: The structure of Alizarin dye.

Characterization of the synthesized nanoparticles

Characterization of the synthesized NPs was performed using the following techniques.

X-ray diffraction

As shown in Figure (2), the XRD of the sample shows the formation of TiO_2 based on the comparison of their XRD patterns with the standard patterns of TiO_2 (JCPDS 21-1272) with tetragonal structure. The diffraction peaks related to (110), (101), (111), (210) (211), (220), (002), (310), and (301) are quite identical to characteristic peaks of the TiO_2 crystal.

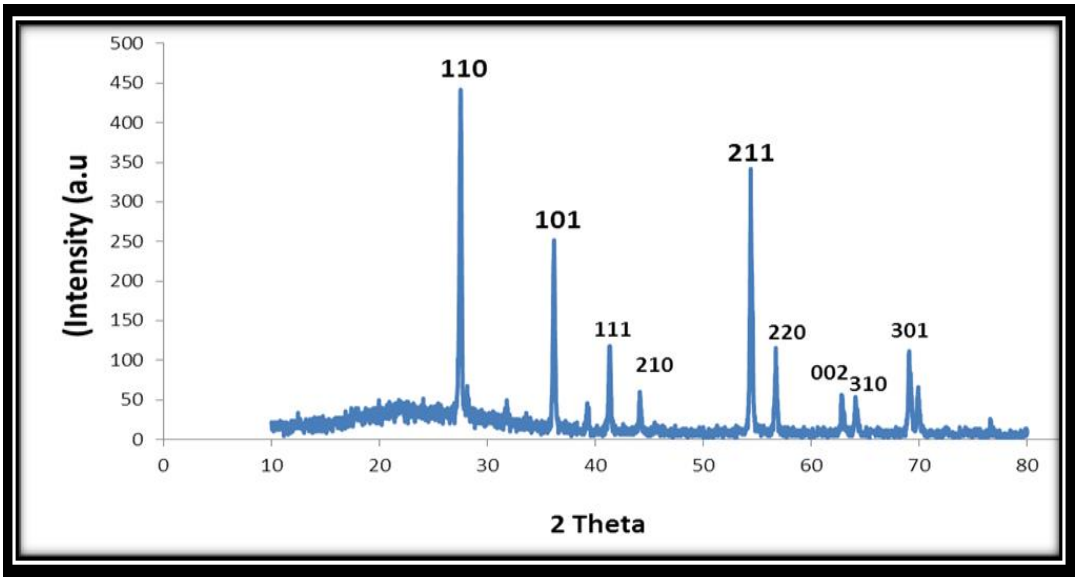

Figure 2: XRD patterns of **TiO_2** nanoparticle.

The XRD of the samples in Figure (3) shows the formation of CuO based on the comparison of their XRD patterns with the standard patterns of CuO with a cubic phase structure. The diffraction peaks corresponding to (11-1), (200), (20-2), (202), (11-3), (022), and (220) are quite identical to the characteristic peaks of CuO crystal.

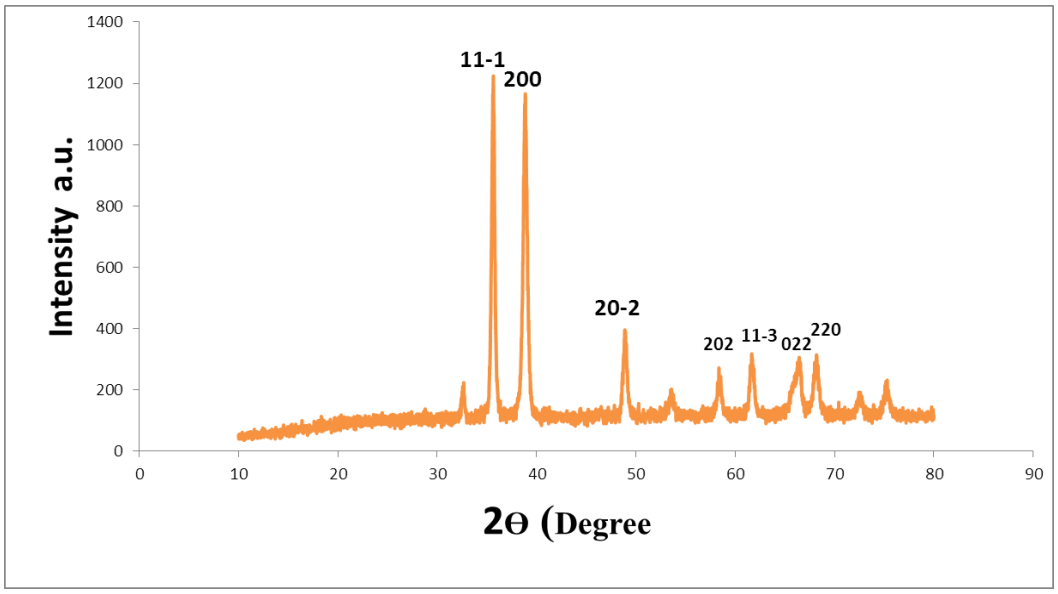

Figure 3: XRD patterns of **CuO** nanoparticle

The XRD of the sample in Figure (4) shows the formation of ZnO based on the comparison of their XRD patterns with the standard patterns of ZnO with a cubic phase structure. The diffraction peaks corresponding to (101), (110), (110), (103), and (201) are quite identical to the characteristic peaks of the ZnO crystal.

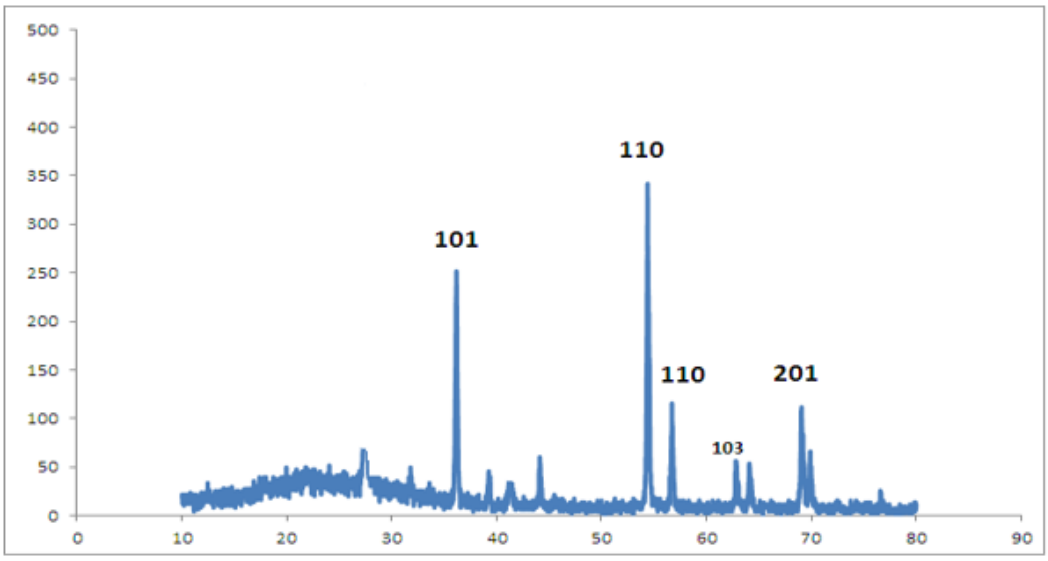

Figure 4: XRD patterns of **ZnO** nanoparticle.

The XRD of the sample in Figure (5) shows the formation of $CuO/ZnO/TiO_2$ nanocomposite based on the comparison of their XRD patterns with the standard patterns. The diffraction peaks corresponding to (110), (100), (002), (101), (111), (-125), (110), and (112) are quite identical to characteristic peaks of the $ZnO/CuO/TiO_2$ crystal.

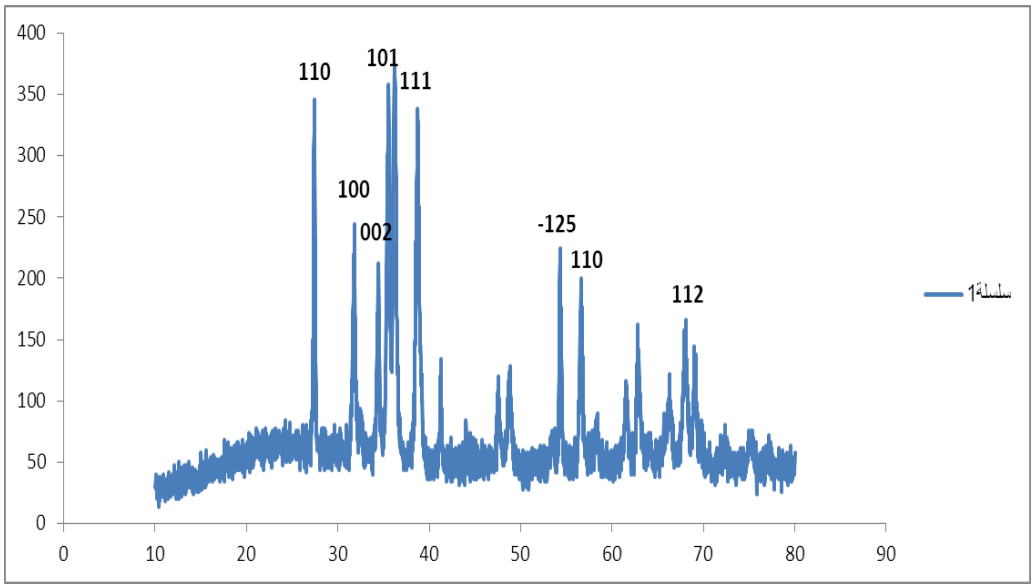

Figure 5: XRD patterns of CuO/ZnO/TiO2 nanocomposite

Field Emission Scanning Electron Microscope (FESEM)

The FESEM image showed nano oxide and composite materials. In Figure 6 (A-B-C-D), **(A)** shows the scanning electron microscopy image of titanium nano oxide with the magnification of 200 nm and 500nm. This demonstrates that TiO_2 was in the form of irregularly-shaped nanoparticles with various small and large grain sizes, and the particle size is in the range of 23.79nm – 28.41nm.

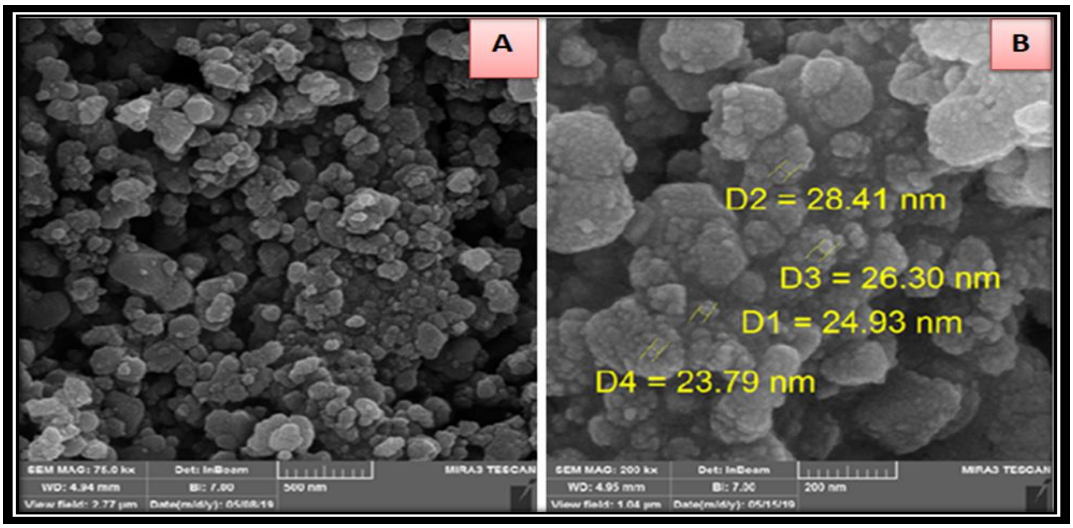

Figure (6A): (FESEM)) of TiO_2

(B) shows the scanning electron microscopy images of CuO nano oxide with the magnification of 200 nm, and 500 nm. This explains that Cuo was in the form of irregular shells, compacted on top of each other. The surface of Cuo is porous and contains pores and rough.

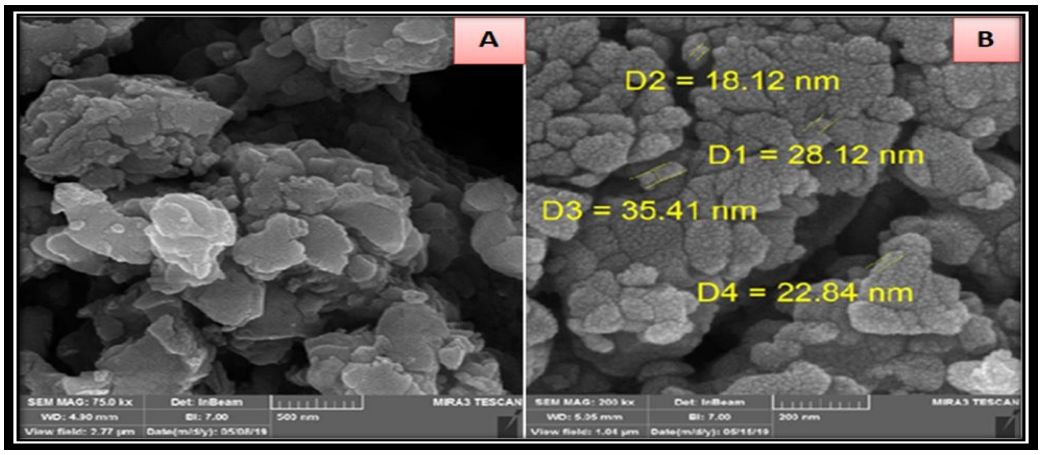

Figure (6B): \ (FESEM)) of CuO

(C) ZnO nano oxide with the magnification of 200 nm and 500 nm. It seems that ZnO is irregular in shape, and the particle size is in the range of 32–43nm. The surface of nanoparticles is porous and contains pores and bumps, as well as particle distribution, which is heterogeneous.

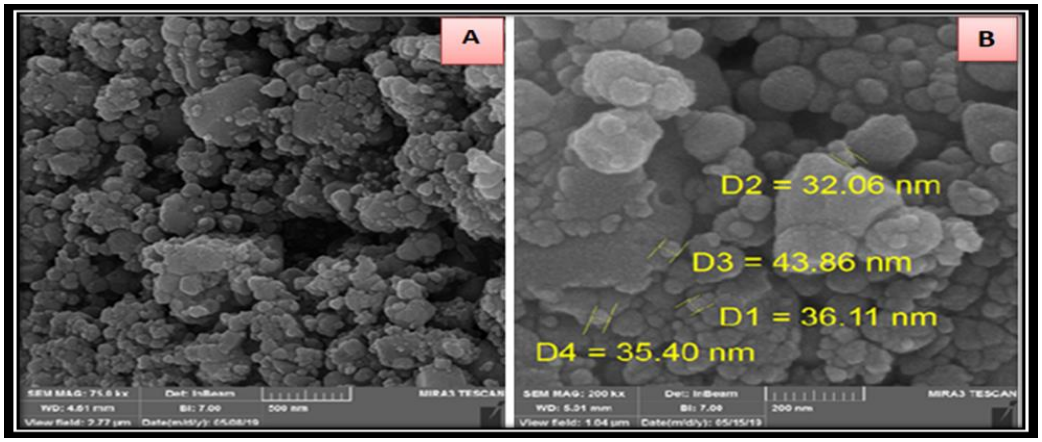

Figure (6C): FESEM of ZnO

(D) CuO/ZnO/TiO_2 nanocomposite, materials consisted of some nanorods, some nano square-rods with pores inside, and some cluster of nanoparticles combined together; Figure. (6D) clearly shows nanorods and nanosqure-rods with pores inside. The nanorods have a diameter of around 50-400 nm and a few micrometers in length. We also observed the comparison. This comparison showed that the prepared products of the third process were very different in terms of the structure from the fabricated materials of the first and the second processes.

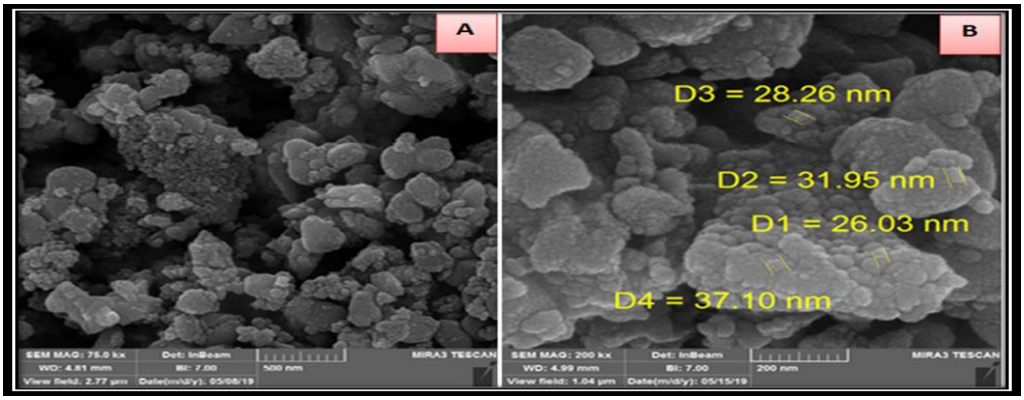

Figure (6D): FESEM of the nanocomposite.

Results and Discussion:

Degradation:

The percentage of results pollutants degraded per unit irradiation time was calculated by Equation (1)

Pollutants Degradation (%) = $(C_o - C_t)/ C_o \times 100$ **(1)**

Where C_0 is the initial concentration of pollutants and *Ct* is the concentration (ppm) of pollutants at the irradiation time.

Effect of initial concentration:

To assess the effect of initial dye concentration on the degradation efficiency, the experiments were done by using different initial concentrations (10 - 70 ppm) at the temperature of 10° C, pH= 6, and in the presence of catalyst (CuO/ZnO /TiO_2 nanocomposite) and 6W UV, as shown in figure (7). As the concentration of alizarin decreases, the percentage of degradation increases and reaches the highest value of 100% at 10 ppm Alizarin dye concentration. Table (1) shows that the higher initial dye concentration after 15 min leads to 26.32% degradation, while for 10ppm Alizarin concentration after 3 h it reaches 100%. This may be because the number of dye molecules increases but the number of OH is still constant. On the other hand, with the increase in the initial concentration of the dye, more dye molecules were adsorbed on to the surface of the catalyst.

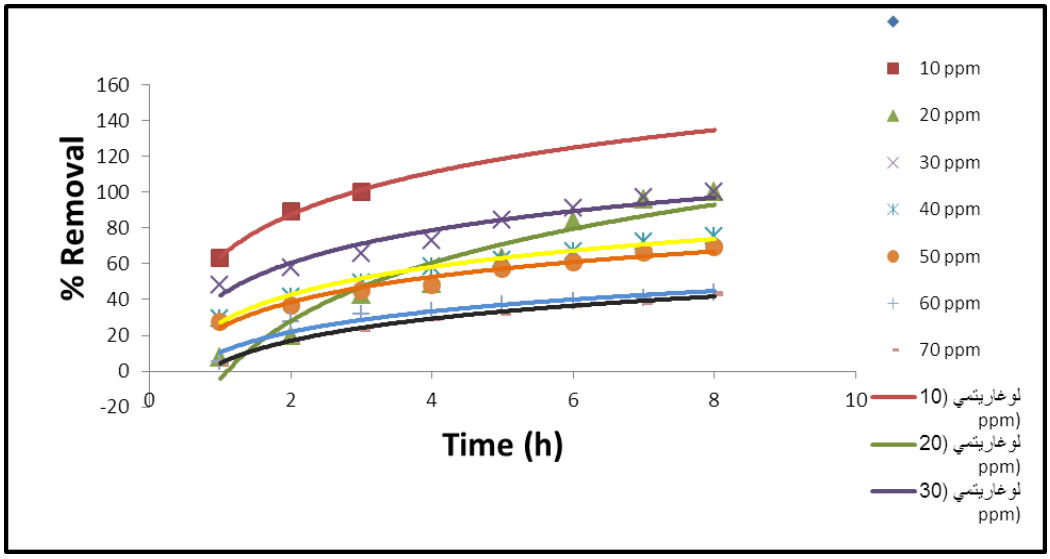

Figure 7: Variation of percentage Removal (R %)

Table 1: Degradation percentage (R%) of Alizarin dye

Time(h)	10(PPM)	20(PPM)	30(PPM)	40(PPM)	50(PPM)	60(PPM)	70(PPM)
	R%						
1	63.16	7.9	48.1	29.22	27.58	5.45	4.77
2	89.48	19.5	57.9	41.6	36.64	27.55	17.6
3	100	42.65	65.63	49.47	45.28	31.58	23.31
4		48.45	73	58.42	48.44	33.86	29.48
5		63.2	84.23	62.10	57.06	37.03	32.48
6		83.7	90.9	66.85	61.06	38.95	36.7
7		95.8	97.2	72.12	66.32	40.71	38.35
8		100	100	75.27	69.06	43.7	43.31

Effect of temperature on Alizarin dye degradation process:

The effect of temperature on the degradation of Alizarin dye was investigated at three different temperatures (10, 20, and 30 °C) in the following condition; pH=6, with different initial concentrations (10, 20, 30, 40, 50, 60, and 70 ppm) of Alizarin. The results in Figure (8) show that dye removal percentages for 10, 20, 30, 40, 50, 60, and 70 ppm increase with increasing temperature.

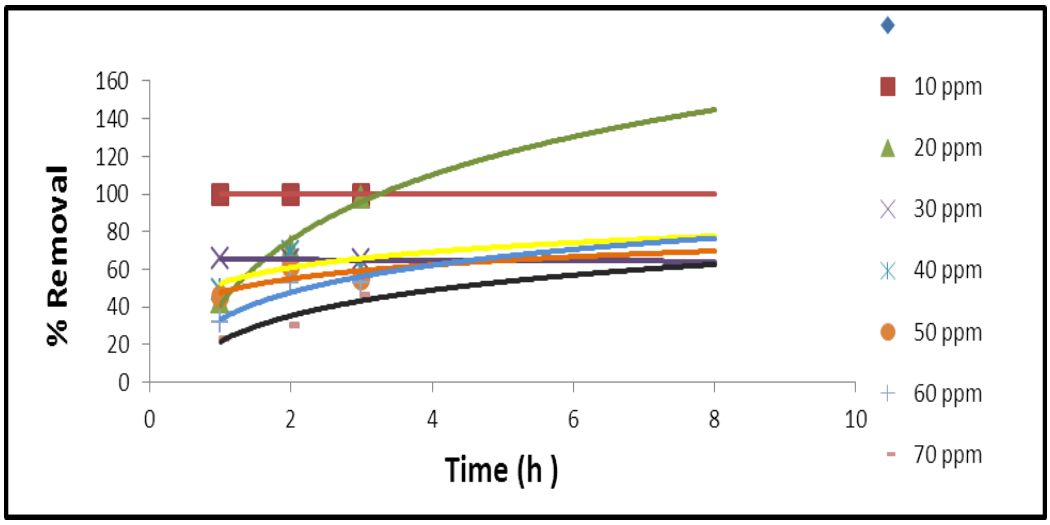

Figure 8: Effect of % Removal at different temperatures

Table 2: Value of %Removal at different temperatures

T(°C)	10(PPM)	20(PPM)	30(PPM)	40(PPM)	50(PPM)	60(PPM)	70(PPM)
	R%						
10	100	42.65	65.63	49.47	45.28	31.58	23.31
20	100	71.6	65.1	69.22	61.28	52.63	30.68
30	100	98.45	64.93	60.55	55.28	53.1	46.17

Conclusions:

From the previous discussion, the following points could be drawn into account:

1. CuO and ZnO were prepared by sol-gel, TiO_2 was prepared from Titanium oxide and CuO/ZnO/TiO_2 nanocomposite was prepared from CuO, TiO_2, and ZnO as demonstrated by the results of FESEM and XRD.
2. Degradation of the Alizarin dye was conducted by using CuO/ZnO/TiO_2 nanocomposite as a heterogeneous photo-Fenton catalyst in the presence of UV light.
3. Under optimum conditions (pH = 6, 10 ppm, and 6W UV light), 100% degradation of Alizarin dye could be achieved in 3 hours.

References

Al-Dhahir, T. A. (2013). Quantitative phase analysis for titanium dioxide from X-ray powder diffraction data using the Rietveld method. *Diyala Journal For Pure Science*, *9*(2), 108-119.

Dubey J., & Singh A. (2019). Green Synthesis of TiO2 Nanoparticles Using Extracts of Pomegranate Peels for Pharmaceutical Application, *International Journal of Pharmaceutical and Phytopharmacological Research*, *9*(1):85-87.

Fatin, S. O., Lim, H. N., Tan, W. T., & Huang, N. M. (2012). Comparison of photocatalytic activity and cyclic voltammetry of zinc oxide and titanium dioxide nanoparticles toward degradation of methylene blue. *International Journal of Electrochemical Science*, *7*(10), 9074-9084.

Hailemicheal, A., Lineo F. M., Himanshu N., (2018). Synthesis and Characterization of Copper Oxide Nanoparticles and their Application as Electrode Modifiers.

Jaleel EA, Abd AN, & Juad HH. (2018). Preparation Nanocomposite Cuo-Attapulgite, Used as Catalyst in Photo Degradation of Methyl Orange. *World.* *7*(1):104-9.

Kahru, A., Dubourguier, H. C., Blinova, I., Ivask, A., & Kasemets, K. (2008). Biotests and biosensors for ecotoxicology of metal oxide nanoparticles: a minireview. *Sensors*, *8*(8), 5153-5170.

Kharissova, O. V., Dias, H. R., Kharisov, B. I., Pérez, B. O., & Pérez, V. M. J. (2013). The greener synthesis of nanoparticles. *Trends in biotechnology*, *31*(4), 240-248.

Khoshnood, R., Jaafarzadeh, N., Jamili, S., Farshchi, P., & Taghavi, L. (2017). Acute toxicity of TiO2, CuO and ZnO nanoparticles in brine shrimp, Artemia franciscana. *Iranian Journal of Fisheries Sciences*, *16*(4), 1287-1296.

Kubacka, A., Munoz-Batista, M. J., Ferrer, M., & Fernández-García, M. (2013). UV and visible light optimization of anatase TiO2 antimicrobial properties: Surface deposition of metal and oxide (Cu, Zn, Ag) species. *Applied Catalysis B: Environmental*, *140*, 680-690.

Lu, F., Cai, W., & Zhang, Y. (2008). ZnO hierarchical micro/nanoarchitectures: solvothermal synthesis and structurally enhanced photocatalytic performance. *Advanced Functional Materials*, *18*(7), 1047-1056.

Mahmoud, Z. H., Falih, M. S., Khalaf, O. E., Farhan, M. A., & Ali, F. K. (2018). Photosynthesis of AgBr Doping TiO2 Nanoparticles and degradation of reactive red 120 dye. *Journal of Advanced Pharmacy Education & Research*| *Oct-Dec*, *8*(4).

Mohammadi-Aloucheh, R., Habibi-Yangjeh, A., Bayrami, A., Latifi-Navid, S., & Asadi, A. (2018). Green synthesis of ZnO and ZnO/CuO nanocomposites in Mentha longifolia leaf extract: characterization and their application as anti-bacterial agents. *Journal of Materials Science: Materials in Electronics*, *29*(16), 13596-13605.

Naika, H. R., Lingaraju, K., Manjunath, K., Kumar, D., Nagaraju, G., Suresh, D., & Nagabhushana, H. (2015). Green synthesis of CuO nanoparticles using Gloriosa superba L. extract and their antibacterial activity. *Journal of Taibah University for Science*, *9*(1), 7-12.

Shaimaa Hamed J. (2017). Synthesis of TiO_2 and Cu_2O nanoparticles and TiO_2/Cu_2O nanocomposite and study the ability to remove pollutants from aqueous solution. The Fifth Scientific Conference of the College of Science University of Kerbala.

Teng, L. H. (2017). *Fabrication and Characterization of Copper Oxide Thin Film by Thermal CVD for Ethanol Sensor Application* (Doctoral dissertation, Universiti Tun Hussein Onn Malaysia).

Wong. H. Liang. (2016). Green Synthesis, Characterization of Zinc Oxide Nanoparticles and Their Photocatalytic Activity. a project report submitted to the Department of Chemical Science, Faculty of Science, Universiti Tunku Abdul Rahman.