# Synthesis of $TiO_2$ and $Cu_2O$ nanoparticles and $TiO_2/Cu_2O$ nanocomposite and study the ability to remove pollutants from aqueous solution

# تخليق جسيمات $Cu_2O,TiO_2$ النانوية ومتراكباتها $Cu_2O/TiO_2$ ودراسة قابليتهم لازالة الملوثات من محاليلها المائية

Shaimaa hamed jaber

The University of AL-Mustansiriya,College of Science, Department of Chemistry

## Abstract

$TiO_2$,$Cu_2O$ nanoparticles and $TiO_2/Cu_2O$ nanocomposite have been synthesized by electrochemical deposition method. The synthesized nanoparticles and nanocomposite characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM).

Results showed that $TiO_2$ nanoparticles have average size of (8-14)nm, $Cu_2O$ nanoparticles have average size of (11-15)nm and $TiO_2/Cu_2O$ nanocomposite have average size of (13-20)nm.

The synthesized nanoparticles were applied to remove 1-nitroso-2-naphthol from aqueous solution. UV-vis spectra results indicate that the percentage of degradation with the sequence $TiO_2/Cu_2O$= 89% > $TiO_2$= 68% > $Cu_2O$= 42% .

**Keywords:** $TiO_2$ nanoparticles, $Cu_2O$ nanoparticles, $TiO_2/Cu_2O$ nano composite, photocatalysis.

**الخلاصة**

تم تخليق اوكسيد التيتانيوم النانوي($TiO_2$)،اوكسيد النحاس النانوي ($Cu_2O$) والمتراكب النانوي من جسيمات $Cu_2O/TiO_2$ بطريقة الترسيب الكهروكيميائي وبفرق جهد مقداره 3 فولت. شخصت هذه الجسيمات النانوية باستخدام تقنية حيود الاشعة السينية، المجهر الالكتروني النافذ والمجهر الالكتروني الماسح . حيث كان متوسط الحجم للجسيمات النانوية لاوكسيد التيتانيوم nm(14-8)، ولاوكسيد النحاسnm( 15-11) وللمتراكب nm( 20-13).

أظهرت نتائج طيف الاشعة الفوق البنفسجية والمرئية فعالية عالية في التحفيز الضوئي للجسيمات النانوية $Cu_2O,TiO_2$ وجسيمات النانو $Cu_2O/TiO_2$ المتراكب في معالجة الماء المتلوث بمادة 1-nitroso-2-naphthol حيث كانت النسب المئوية للازالة بالتسلسل :

$TiO_2/Cu_2O$= 89% > $TiO_2$= 68% > $Cu_2O$= 42% .

## Introduction

Nanoparticles, involved $TiO_2$ and $Cu_2O$ used widely in many fields, including medical and industrial as well as in environmental decontamination applications due to these particles possess characteristics such as abundance, low cost, have good electrical, high optical absorption coefficient and low band gap energies[1-2]. $TiO_2$ played a major role in the treatment of pollutant water contaminated with mineralization of organic pollutants like aliphatic and aromatics components, dyes, pesticides[3]. In Photocatalytic reactions hydroxyl radicals and superoxide anions ($OH^{\bullet}$ and $O^{\bullet-}_2$) are generated when a photon is absorbed by semicondition as shown in the mechanism follows [4]:

$Sem.+ h\nu \rightarrow M \quad (e^- + h^+)$ (1)

$H_2O + Sem.(h^+) \rightarrow M + OH^{\cdot} + H^+$ (2)

$O_2 + Sem.(e^-) \rightarrow M + O^{\cdot -}_2$ (3)

where, Sem. are $TiO_2$, $Cu_2O$ and $TiO_2/Cu_2O$

GUPTA Shipra & TRIPATHI Manoj reported that the studied metals including Pt, Ag, Au, Pd, Ni, Rh and Cu have been very effective in improving photocatalysis by $TiO_2$[5].

Titanium is used as supported to copper to gives the properties of wide photochemical[6] , this agree with Pasini et al [7], and Liu et al[8]. $TiO_2$ has band gap (~3.2 eV) respond to UV light only and limited absorption capacity in the visible region, thus it can be modified surface with $Cu_2O$ which has narrow band gap (1.9-2.2eV) that can facilitate the absorption in the visible region. subsequently, the electrons excited by visible light transfer from the conduction band of $Cu_2O$ to that of $TiO_2$ since reducing the recombination rate of photo-induced charge carriers and improving the photocatalytic of $TiO_2/Cu_2O$ nanocomposite [9-10].

In this work, $Cu_2O$ nanoparticles, $TiO_2$ nanoparticles and $Cu_2O/TiO_2$ composite were prepared by electrochemical deposition method and characterized by X-ray diffraction (XRD), Transmission electron microscopy(TEM) and Scanning electron microscopy (SEM) . In addition, prepared 1-nitroso2-naphthol as an organic pollutant for water .

## Materials and Method

- **Synthesis of $TiO_2$ nanoparticles**

All chemicals were reagent grade or the highest available commercial grade and were used as received.

$TiO_2$ nanoparticles have been synthesized by electrolysis using 100 ml of (0.03M) $NH_4Cl$ at 23 °C as electrolyte. A rectangular Ti plate (3 cm x 2 cm x 0.1 cm) was used as anode. Graphite rode (0.4 x 4 cm) was used as the counter electrode cathode. Befor mountiy the substrate in the cell, they were cleaned sonically using aqueous and organic cleaner solvents (acetone, ethanol, chloroform and de-ionized water). The applied D.C voltage was 3V with current density of $2.1 \times 10^{-3}$ $mA/cm^2$ for 45 minute. $TiO_2$ nanoparticle were obtained and washed by de-ionized water.

- **Synthesis of $Cu_2O$ nanoparticles**

The same procedure of $TiO_2$ nanoparticles synthesis was used to prepare $Cu_2O$ nanoparticles using Cu plate (3 cm x 2 cm x 0.1 cm) as anode with current density of $1.7 \times 10^{-3}$ $mA/cm^2$ for 45 minute.

- **Synthesis of $TiO_2/Cu_2O$ nanocomposite**

The same procedure of $TiO_2$ nanopaticles synthesis was used to prepare $TiO_2/Cu_2O$ nanocomposite . using Cu plate (3 cm x 2 cm x 0.1 cm ) as cathode with current density $4.4x10^{-3}$ $mA/cm^2$ for 45 minute often then, the two electrode were replaced where Ti plate became as cathode and Cu plate became as anode for 45 minute. $TiO_2/Cu_2O$ nanocompsition was obtained anode washed by de-ionized water.

- **Preparation of pollutant water**

  0.001 gm of organic pollutant (1-nitroso-2-naphthol) dissolved in 75 ml of water. Added to:

  A- 0.001 gm of $Cu_2O$ nanoparticles to 25 mL of prepared pollutant water .

  B- 0.001 gm of $TiO_2$ nanoparticles to 25 mL of prepared pollutant water .

  C- 0.001 gm of $TiO_2/Cu_2O$ nanocomposite to 25 mL of prepared pollutant water .

- **Irradiation cell**

  The cell consist of UV (125 W mercury medium pressure lamp), quartz tube, Pyrex tube was used as a reactor. Pyrex tube was cooled by ice to prevent the rising temperature resulting from UV irradiation.

Fig. (1) Irradiation cell

## Results and Discussion

The structure of the various samples was investigated by X-ray diffraction (XRD) shown in Figures (2), (3) and (4) respectively. All the scans were recorded by SHIMADZU XRD -6000. The XRD use (Cu radiation line of wavelength of 1.54 $A^o$ in 2 Θ from 10 to 80).

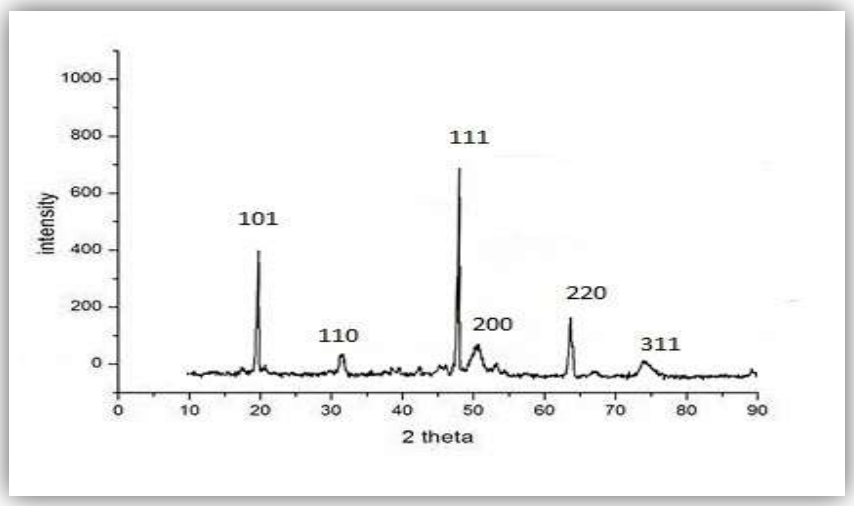


Fig (2) X-ray diffraction patterns of $Cu_2O$ nanoparticle

The XRD of sample in fig.(2) shows the formation of $Cu_2O$ based on the comparison of their XRD patterns with the standard patterns of $Cu_2O$ (JCPDS 05-667) of cubic phase structure. The diffraction peaks corresponding to (101) ,(110), (111), (200),(220), (311), and (222) are quite identical to characteristic peaks of the $Cu_2O$ crystal.

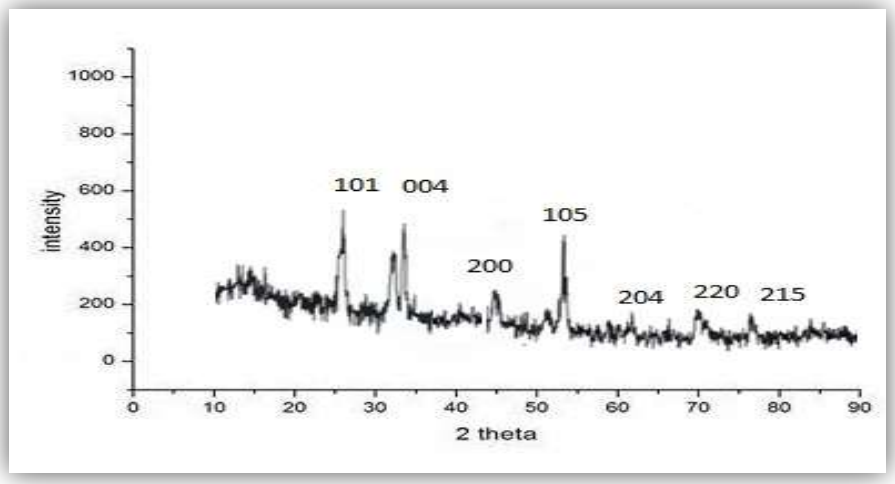


Fig (3) X-ray diffraction patterns of $TiO_2$ nanoparticle

The XRD of sample in fig.(3) shows the formation of $TiO_2$ based on the comparison of their XRD patterns with the standard patterns of TiO2 (JCPDS 21-1272) of tetragonal structure.

The diffraction peaks corresponding to (101), (004), (200), (105) (204), (220) and (215) are quite identical to characteristic peaks of the $TiO_2$ crystal.

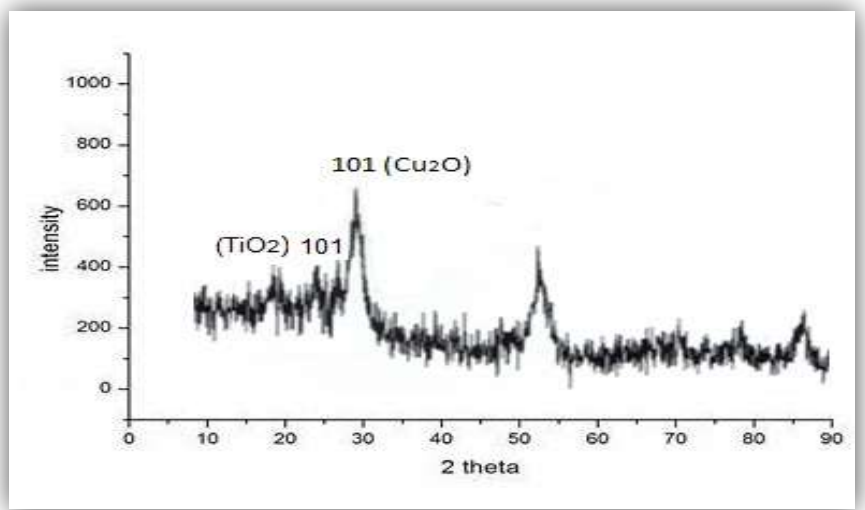


Fig. (4) X-ray diffraction patterns of $TiO_2/Cu_2O$ nanocomposite

The XRD pattern shows a significant amount of broadening line which are characteristic of nanoparticles the crystal size can be calculated according to Debye - Scherrer formula:[11]

$$D = \frac{\kappa \lambda}{\beta \cos\theta} \qquad (1)$$

where K=0.9 scherrer constant , λ is the wavelength of the cu-kα radiation, β is the full width at half maximum and θ is the angle obtained from 2θ values corresponding to maximum intensity peak in XRD pattern. The mean crystal size of nanoparticles which obtained in table (1).

**Table (1) the mean crystal size and 2θ of $Cu_2O$, $TiO_2$ nanoparticles and $TiO_2/Cu_2O$ nanocomposite**

| sample | 2θ | Crystal size(nm) |
|---|---|---|
| $Cu_2O$ | 31.5 | 14.7 |
| $TiO_2$ | 28 | 12.3 |
| $TiO_2/Cu_2O$ | 31 | 18.9 |

The average particles size and distribution were determined randomly on the Transmission Electron Microscopy( TEM) images. Fig.( 5) to (7) show TEM of the samples.

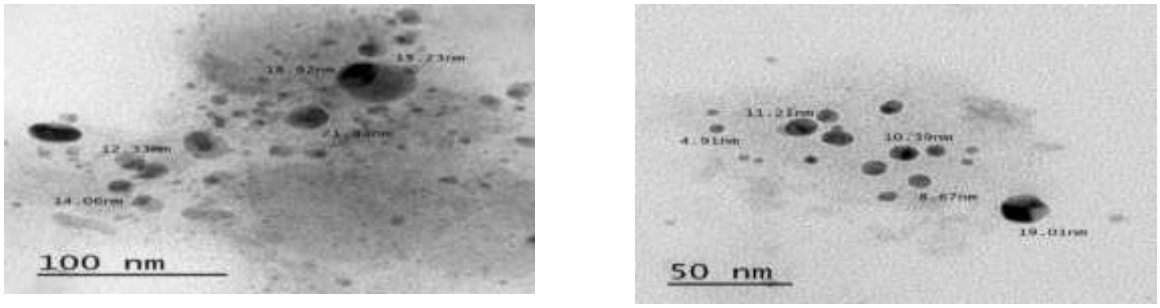


Fig.( 5) TEM of $TiO_2$ nanoparticle

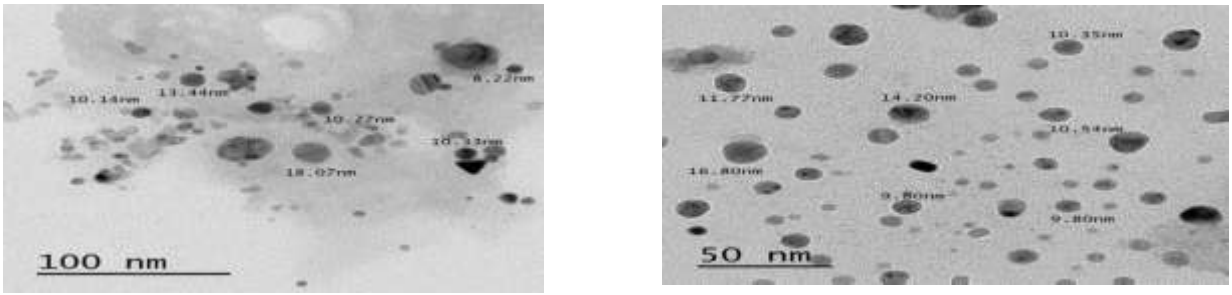


Fig.(6) TEM of $Cu_2O$ nanoparticle

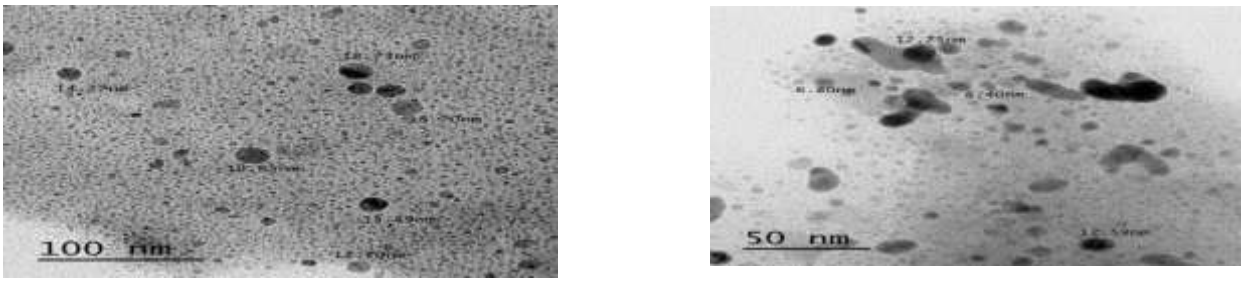


Fig.( 7) TEM of $TiO_2/Cu_2O$ nanocomposite

The Average Particles size of $Cu_2O$, $TiO_2$ nanoparticles and $TiO_2/Cu_2O$ nanocomposite particles that estimated from the TEM graph was 11.6,8.3 and 13 nm respectively, which agrees with that obtained from XRD analysis. As shown in table (2).

Scanning Electron Microscopy (SEM) images, Fig. (8),( 9) and (10) show the morphology and size distribution of different sample. The surface of nanoparticles sample is smooth with good crystal linty. The average particle size and distribution were determined randomly on SEM images.

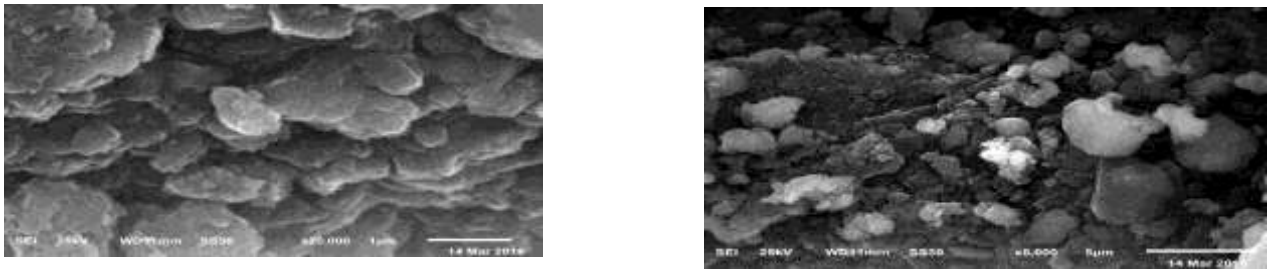

Fig. (8) SEM of $TiO_2$ nanoparticle

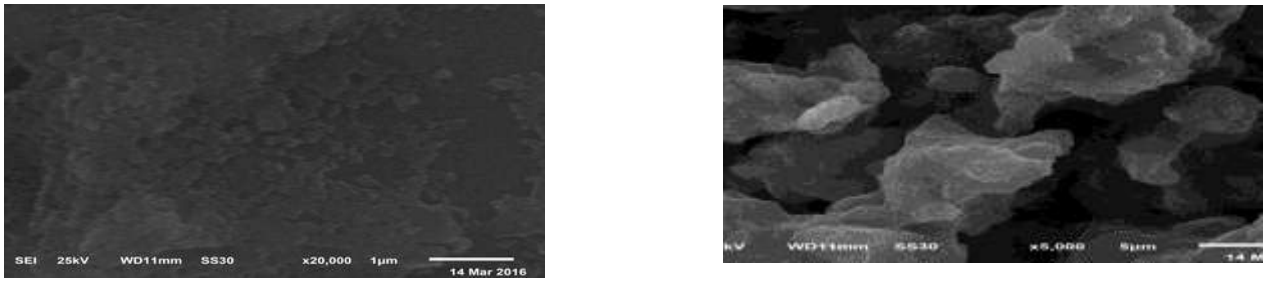

Fig. (9) SEM of $Cu_{2O}$ nanoparticle

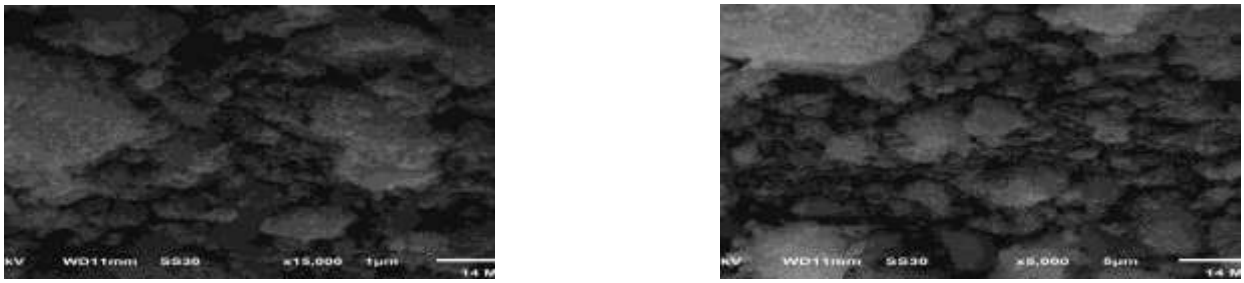

Fig. (10) SEM $TiO_2/Cu_2O$ nanocomposite

**Table (2) Average particles size of TEM and SEM of $Cu_2O$, $TiO_2$ nanoparticles and $TiO_2/Cu_2O$ nanocomposite**

| TEM | | SEM | |
|---|---|---|---|
| **sample** | **Average Particles size** | **Sample** | **Average Particles size** |
| $Cu_2O$ | 11.6 | $Cu_2O$ | 15.2 |
| $TiO_2$ | 8.3 | $TiO_2$ | 14.3 |
| $TiO_2/Cu_2O$ | 13 | $Cu_2O/TiO_2$ | 20.1 |

- **Photocatalytic activity studies**

Nanoparticles and nanocomposite have several applications important such as photocatalytic degradation to various kinds of organic and inorganic pollutants in water due to they have high photocatalytic activity and high photochemical stability [12,13].

In this research $TiO_2$, $Cu_2O$ nanoparticles and $TiO_2/Cu_2O$ nanocomposite were used as photocatalytic degradation of contaminated water was contaminated by organic material called 1-nitroso-2-naphthol which prepared previous and chosen to study the photocatalytic activity for those nanoparticles.

Figures (11, 12 and 13) show the UV-Vis of aqueous solution of 1- Nitroso-2-naphthol with copper oxide, titanium oxide nanoparticles and $TiO_2/Cu_2O$ nanocomposite before and after irradiation process respectively, observed decrease in the absorbency of 1- Nitroso-2-naphthol presented in water after the addition of nanoparticles and irradiation of contaminated water compared to absorbance of 1- Nitroso-2-naphthol before addition of nanoparticles.

The electrons was irritation and transport from valance band to conduction band where oxidation and reduction reactions occur, and free radicals such as $OH^{\cdot}$, $OH_2$ and $H_2O_2$ is created free radicals oxidize the organic material (1-nitroso-2-naphthol). Through our study shows that $TiO_2/Cu_2O$ nanocomposite better and more effective to degradation the pollutant than titanium oxide nanoparticles and copper oxide nanoparticles. UV-vis spectra results indicates that the percentage of degradation with the sequence $TiO_2/Cu_2O$= 89% > $TiO_2$= 68% > $Cu_2O$= 42% .

The hetero-interface between $Cu_2O$ and $TiO_2$ facilitates the separation and transmission of the photo induced charge carriers, with greatly enhanced photocatalytic activity.In addition, $OH^{\cdot}$ reactive species were found in aqueous $TiO_2/Cu_2O$ suspension under visible light irradiation[14].

In this research, the $TiO_2/Cu_2O$ nanocomposite shawed not only absorption in the UV region but also absorption in the visible region in facilitating the photo degradation efficiency.

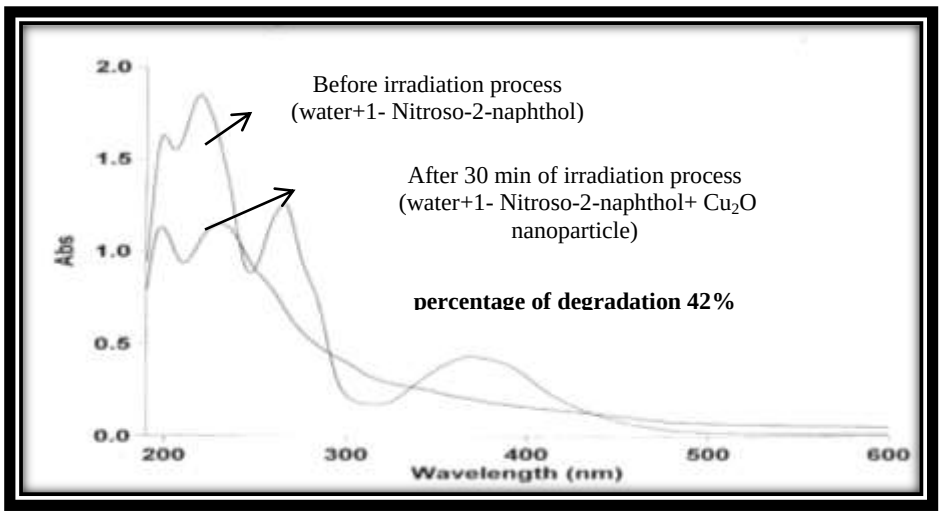


Fig. (11) UV-Vis of pollutant water before irradiation process and UV-Vis of pollutant water after irradiation process with $Cu_2O$ nanoparticles

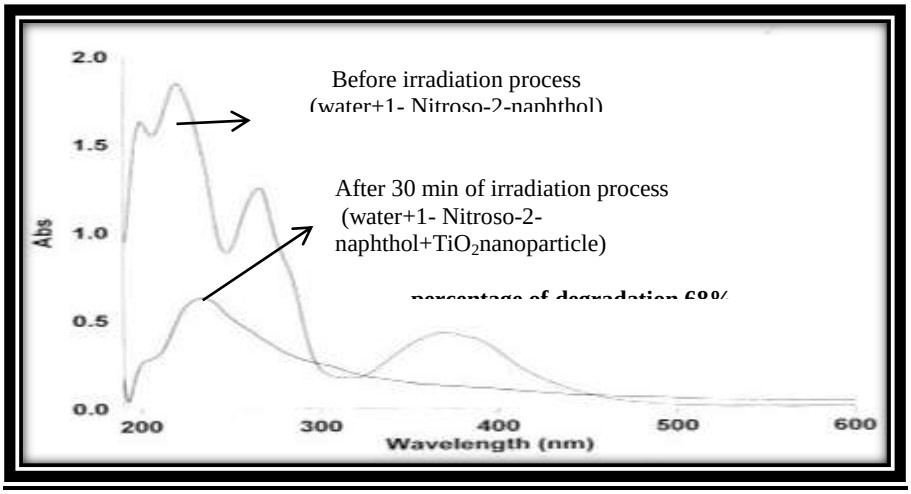


Fig. (12) UV-Vis of pollutant water before irradiation process and UV-Vis of pollutant water after irradiation process with $TiO_2$ nanoparticles

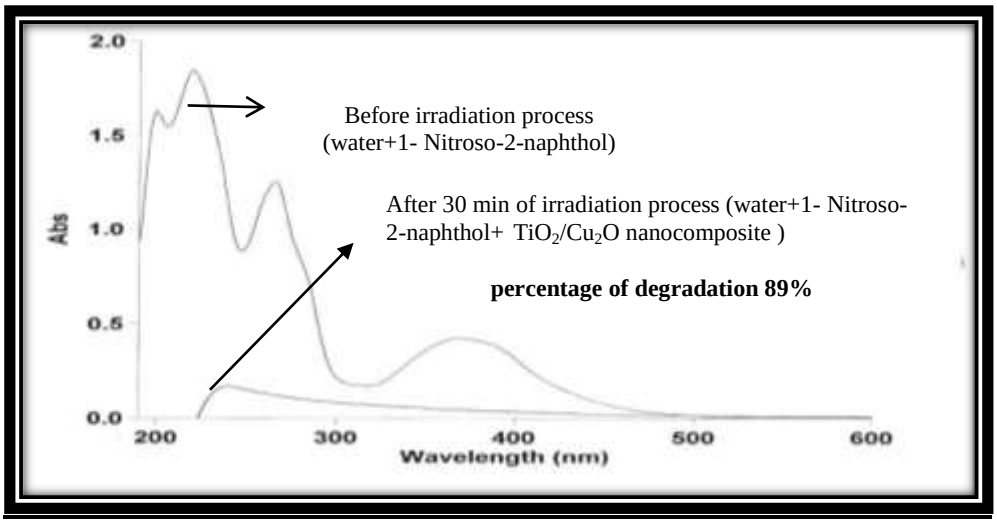


Fig. (13) UV-Vis of pollutant water before irradiation process and UV-Vis of pollutant water after irradiation process with $TiO_2/Cu_2O$ nanocomposite

## Conclusions

$TiO_2$,$Cu_2O$ nanoparticles and $TiO_2/Cu_2O$ nanocomposite were synthesized by electrochemical deposition method . The UV–vis absorption spectra reported that the catalytic activity of $Cu_2O/TiO_2$ composite is more than the catalytic activity of $TiO_2$,$Cu_2O$ nanoparticles. The interface between $Cu_2O$ and $TiO_2$ facilitates the separation and transmission of the photo induced charge carriers, with greatly photocatalytic activity. This study provides photocatalyst $TiO_2/Cu_2O$ composite nanoparticles that can work under UV light irradiation as well as for promising applications in photocatalysis fields for the treatment of organic contaminated water.

## References

1-Amedea B. S and Nelson D.( Nanotoxicology of Metal Oxide Nanoparticles ). Metals.2015, 5, : 934-975.

2- Sayed M. B , R.A. El Khashab, A.A. Nayl.( Synthesis, Characterization and Catalytic Activity of $Cu/Cu_2O$ Nanoparticles Prepared in Aqueous Medium). Bulletin of Chemical Reaction Engineering & Catalysis. 2015, 10 (2): 169-174.

3- Mohamed A. B.( Photocatalysis for Wastewater Purification over $TiO_2$ Nanoparticles). J Powder Metall Min. 2014, 3 (1):1-2.

4- Muneer M. B, Abdul Amir H.K, Abu Bakar M, Mohd S. T and Kamaruzzaman S.( Synthesis and Catalytic Activity of $TiO_2$Nanoparticles for Photochemical Oxidation of Concentrated Chlorophenols under Direct Solar Radiation). Int. J. Electrochem. Sci. 2012, (7):4871 -4888.

5- GUPTA S. M and TRIPATHI M.( A review of $TiO_2$ nanoparticles). Chinese Sci Bull. 2011, 56(16): 1639−1657.

6-Manoj B. G, Anandarup G, Francois-Xavier F, Tewodros A, Xiaoxi H, Rafael S, Xiaoxin Z, Radek Z, and Rajender S. V. (Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis). Chem.Rev. 2016, 116(6): 3722−3811.

7-Thomas P, Marco P, Magda B, Rosa B, Stefania A, Nikolaos D, Jose A.L. Meenakshisundaram S, Qian H, Christopher J. K, Graham J. H and Fabrizio C. (Selective oxidation of 5-Hydroxymethyl-2-Furfural using Supported Gold-Copper Nanoparticles).Green Chem.2011,13, 2091−2099.

8- Liu N, Jha H, Hahn R, Schmuki P.( Palladium Activated Decoration of $TiO_2$Nanotubes by Copper Nanoparticles and Enhanced Photocatalytic Properties).ECS Electrochem. Lett.2012,1 (16): 29-31.

9- Xinwen H and Zongjian L .( Heterogeneous Deposition of $Cu_2O$ Nanoparticles on $TiO_2$ Nanotube Array Films in Organic Solvent). Journal of Nanomaterials. 2013 (2013):1-8 .

10- Peter A, Mihaly-Cozmuta L, Mihaly-Cozmuta A, Nicula C,Tudoran.B.L and Baia L. (Efficiency of $Cu/TiO_2$to remove salicylic acid by photocatalytic decomposition: kinetic modeling). Materials Technology: Advanced Performance Materials.2014,29 (3):129-133 .

11- Dongfang Z.( Synergetic effects of $Cu_2O$ photocatalystwith titania and enhanced photoactivityunder visible irradiation). Acta Chimica Slovaca. 2013,6(1): 141-149.

12- Habib M.A, Shahadat M.T, Bahadur N.M.( Synthesis and characterization of ZnO-$TiO_2$ nanocomposites and their application as photocatalysts). Int Nano Lett. 2013, 3 (5):1-8.

13- Sayan B, Indranil S,Aniruddha M.( Role of nanotechnology in water treatment and purification: Potential applications and implications). International Journal of Chemical Science and Technology. 2013, 3(3): 59-64.

14- Zongjie Liu, Chungen Zhou,( improved photocatalytic activity of nano CuO-incorporated $TiO_2$ granules prepared by spray drying). Progress in Natural Science: Materials International. 2015,25( 4): 334–341.