Synthesis of Nanocomposite and Study Degradation of Phenol Red Dye

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Abstract. This study aims to investigate the capability of semiconductors such as titanium dioxide, copper oxide and zinc oxide, to remove a hazardous Phenol Red organic dye texture from an aqueous solution. In this sheet, (ZnO), (CuO) and (TiO₂) nanoparticles were synthesised utilise a simple chemical process. Nanocomposite has been synthesised by a physical process. The purpose of the research was to investigate semiconductors' capability, such as titanium dioxide, copper oxide, and zinc oxide, to take off a hazardous Phenol Red, a texture dye from an aqueous solution. These nanoparticles and composites' structural properties described using (XRD) and Field Emission Scanning Electron Microscope (FE-SEM). This paper describes photocatalytic degradation of Phenol Red dye solution using composite CuO/ZnO/TiO₂ nanocomposite photocatalysts, in the form of CuO/ ZnO/TiO₂ composite as a paint on the Stainless Steel cell, under ultraviolet (UV) irrations. The effect of factors affecting the reaction, such as the dye's primary concentration, the effect of temperature, and the value of the acidic function, were studied. The experimental results show that the CuO/ ZnO/TiO₂ composite can remove the Phenol Red from wastewater by X-ray diffraction (XRD) and an average volume of copper oxide molecules. The formula of Debar Shearer found that it is equal to 21.33 nm. For zinc oxide, the particle size constructed to be 18.13 nm and titanium oxide was found to be 42.63, and the particle size of the Nano chemical mixture was 20.48 nm. And CuO/ZnO/TiO₂ Nanocomposite 20.48, respectively.

Keyword: Nano oxide; Composite; ZnO; CuO; TiO₂; degradation; photocatalyst; Phenol Red dye.

1. Introduction
Research in nanomaterial synthesis methodology is generally oriented in controlling their size, shape, and composition. Each of these elements is a key factor informative the properties of materials that chief to different technological applications[1]. Nanotechnologies have become an important priority worldwide, are increasingly used in products to increased by precise exterior area and reaction, which may include chief to increased bio ability and poisoning [2]. Limitations of TiO₂ for water treatment applications are mostly due to its tiny particle size, which can become chief to expensive filtering treatment[3]. Titanium is used as sustained to copper to gives the properties of broad photochemical [4]. TiO₂ =3.2 eV [5] TiO₂ NPs have been applied wide-reaching in various areas included cosmetics, sunblock cream, soil and water[6].

Copper (II) oxide, CuO, through a bandgap of 1.2 – 1.9 eV. It is a p-type semiconductor with prospective applications in several areas like high-critical-temperature and field emission [7]. CuO NPs has widely used in batteries, and plastics, etc. Zinc oxide is an n-type semiconductor through appealing properties of excellent stability, green characteristics, and existing facile preparation routes[8].

The composition and microstructure of solid-state materials define their properties, with those favourite properties [9]. Moreover, TiO₂ and (ZnO) have shown promises as an advanced and relatively low-cost photocatalyst[10].
Additionally, stable materials such as TiO2 coupled with the CuO can advance CuO photocathodes' stability because they can protect the surface of CuO electrodes against decomposition/corrosion in the electrolyte[11]. Students have established exclusive attention in procedures that comprise stacking (CuO) upon ZnO nanoparticles' surface because the CuO is chemically established in atmospheric situations and through photocatalytic effects [12]. The poisonousness display of metal oxides was (Cu>TiO2>ZnO). The compensations of composite material above its bare components might be the increased light absorption in the visible range and other effective charge separation due to the interface incidence [13].

2. Material and Method

The main experimentation synthesis of nanoparticles and characterisation was accepted at the Department of Nano Science and Technology. The chemicals used to synthesise nanoparticle, Zinc nitrate, copper nitrate rehydrate, TiO2 pellets, NaOH and Ammonia [1].

| No | Substance             | Chemical Formula | Purity % | Suppliers |
|----|-----------------------|------------------|----------|-----------|
| 1  | Copper nitrate trihydrate | Cu(NO3)2.3H2O   | 95.0     | HIMEDIA   |
| 2  | Zinc nitrate          | Zn(NO3)2         | 98.0     | THOMAS BAKER |
| 3  | Citric acid           | C6H8O7           | 99.9     | HIMEDIA   |
| 4  | Titanium oxide pellets| TiO2             | 99.9     | HIMEDIA   |
| 5  | Ammonia               | NH3              | 25       | CDH       |
| 6  | Sodium hydroxide      | NaOH             | 10 M     | BDH       |
| 7  | deionised water       | H2O              | 99       | Lab       |

2.1 Synthesis of TiO2, CuO, ZnO Nanoparticles and Adsorbate

2.1.1 Titanium oxide nanoparticle. TiO2 NPs was integrated by dissolving 0.5 g TiO2 pellet in 30 ml of NaOH solutions (10 M) below dynamic stirring at room temperatures for 2 h. Thus, the yellow solutions were irradiated in an ultra-sonic (Sonics, VCX 1500, 20 kHz and 350 W) for 2 h in ambient temperature. The resulting precipitation was then centrifuged, washed and decant with deionised water some time and dried at 40°C for 24 h to obtain the nanoparticle[1].

2.1.2 Copper oxide nanoparticles. CuO NPs was synthesised by adding 5g of copper nitrate rehydrate Cu(NO3)2.3H2O in 50 ml of deionised water in a separate 250 ml glass beaker, and in another beaker, add 5.580 g of citric acid in 50 ml of deionised water. Then, the Cu(NO3)2.3H2O solution (50 ml) is transferred to citric acid solution and located above a magnetics stirrer with hot plates set at 45°C with high-speed stirring, then add drops wise (slowly for 40 min of NH3 solution to get sol-gel after 2 hours. Please keep it in the oven for 24 h, and finally, the powders were calcined at 400°C for 4 h to obtain the nanoparticle.

2.1.3 Zinc oxide nanoparticle. ZnO NPs were synthesised by adding 5g of zinc nitrate Zn(NO3)2 in 50 ml of deionised water taken in a separate 250 ml glass beaker, and another beaker add 5.547 g of citric acid in 50 ml of deionised water. The Zn(NO3)2 solutions (50 ml) are mixed with a citric acid solution and placed on a magnetic stirrer with a hot plate set at 90°C with high-speed stirring. Then add wise drops (slowly for 40 min of NH3 solution to get the sol-gel after 3h. Please keep it in the oven for 24 h, and finally, the precipitate was calcined at 450°C for 4 h to obtain the nanoparticle.
2.1.4 Composite nanoparticle. Prepared ZnO: CuO: TiO$_2$ with a molar ratio of 1:1:1 was taking 1/0.970 and 0.974 g of each oxide. Then dissolved in 50 ml deionised water, and the solutions were irradiated in an ultra-sonic for 1 h and keep it on the oven for 24 h at 60°C, and then the precipitated powder was calcined at 400°C for 1 h.

2.2 Adsorbate

The Phenol Red, also known as phenolsulfonphthalein, the dye was used in this experiment. (Formula $\text{C}_{19}\text{H}_{14}\text{O}_5\text{S}$, M. Wt.=354.38, $\lambda$ max= 431.4nm) was applied as adsorbates. The stock solutions were prepared by dissolving 0.1g/L of dyes in water and a stocked solution in the volumetric flask. By making 10, 20, 30, 40 ppm solution. The concentrations of the dye's solution were determined spectrophotometrically[14]. The structure of Phenol Red is given in Figure 1

![Figure 1: Structure of Phenol Red dye](image)

3. Characterisations of synthesised nanoparticle

Characterisations of the synthesised nanoparticles was performed by:

3.1 X-ray diffraction

The XRD of the sample in Figure 2 shows the formation of TiO$_2$ based on the comparison of their XRD pattern with the standard pattern of TiO$_2$ (JCPDS 21-1272) of tetragonal structure. The diffraction peaks corresponding to (110), (101), (111), (210) (211), (220), (002), (310), and (301) are quite identical to characteristic peaks of the TiO$_2$ crystal.

![Figure 2: X-ray diffraction patterns of TiO$_2$ nanoparticle.](image)
The XRD of the sample in Figure 3 shows CuO's formation based on comparing their XRD pattern with the cubic phase structure's standard CuO pattern. The diffraction peaks corresponding to (11-1), (200), (20-2), (202), (11-3), (022), and (220) are quite identical to characteristic peaks of the CuO crystal.

![X-ray diffraction patterns of CuO nanoparticle.](image3)

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

![X-ray diffraction patterns of ZnO nanoparticle.](image4)

The XRD of the sample in Figure 5 shows the CuO/ZnO/TiO2 nanocomposite formation based on comparing their XRD pattern with the standard pattern. The diffraction peaks corresponding to (110), (100), (002), (101), (111), (-125), (110), and (112) are quite identical to characteristic peaks of the ZnO /CuO/TiO2 crystal.
Figure 5 X-ray diffraction patterns of CuO/ZnO/TiO$_2$ nanocomposite

3.2 Field Emission Scanning Electron Microscope (FESEM)

The FESEM image showed the Nano oxide and composite materials in Figure 6(A-B-C-D). These Figures showed the:

(A) TiO$_2$ Nano oxide show the scanning electron microscopy images of titanium Nano oxide with a magnifying force of 200 nm and 500nm, respectively. This result explains 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 (23.79nm – 28.41nm).
(B) CuO nano oxide shows the scanning electron microscopy images of CuO with a magnifying force of 200 nm and 500 nm, respectively. This result explains that CuO was in irregular shells and compacted on top of each other. The surface of CuO is porous and contains pores and rough

![Figure (6B) \( \text{(FESEM)} \) of CuO](image)

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

![Figure (6C) \( \text{(FESEM)} \) of ZnO](image)
CuO/ZnO/TiO$_2$ Nanocomposites, material consisted of some Nanorod, some Nano squares-rod with pores inside, and some nanoparticle clusters combined Figure. (6D) show clearly Nanorod and nanosquares- rods with pores inside. The Nanorod have diameters around 50-400 nm and a few micrometres in length. We have also observed the comparing. This comparison shows that the third process's prepared product was very different, forming from the fabricated material of the first and the second process.

![Image](image-url)

**Figure (6D) (FESEM)) of nanocomposite.**

4. Results and Discussion:
4.1 Degradation:
The percentage of results pollutants degraded per unit irradiation time was calculated by Equation (1)

\[
\text{Pollutants Degradation (\%) } = \frac{(C_0 - C_t)}{C_0} \times 100
\]

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

4.2 Effects of initial concentrations:
In many cases, diffusion depends on the concentration, so the initial dye concentration was a more significant variable in the absorption process (15). To study the effects of initial dye concentrations on the degradation efficiency, the experiments are carried out using different initial concentration (10- 70) ppm at temperature (10, 20 and 30) °C, 6WVA pH=6, and in the presence of catalyst CuO/ZnO /TiO$_2$ nanocomposite. Table 2 and Figure (7) show that the higher initial dye concentration and after 15 min attains to 99.5% percentage, while for 10 ppm Phenol Red concentration after 30 min it reaches 100%. This phenomenon might be because the numbers of dye molecule are increased, but the number of OH$^-$ is still constant. With the dye's increasing initial concentration, more dye molecules are adsorbed onto the composite's surface, leading to a decrease in the oxidation process.
The effect of temperature on the degradation of phenol red dye is investigated at three different temperatures (10, 20 and 30) °C with the following condition pH=6, with different initial concentrations (10, 20, 30,40,50,60 and70) ppm of Phenol Red. The results in Table 3 and Figure (8) show that the percentage of dye removal increases when temperature increases.

**Table (3) : %Removal at different temperatures.**

| T(°C) | 10(PPM) | 20(PPM) | 30(PPM) | 40(PPM) | 50(PPM) | 60(PPM) | 70(PPM) |
|-------|----------|----------|----------|----------|----------|----------|----------|
|       | R%       |          |          |          |          |          |          |
| 10    | 97.3     | 83.35    | 60.76    | 55.8     | 40.56    | 35.03    | 21.97    |
| 20    | 97.3     | 84.43    | 50.93    | 38.95    | 33.34    | 27.35    | 23.28    |
| 30    | 97.3     | 85.2     | 54.43    | 30.32    | 34.64    | 38.43    | 24.61    |
5. Conclusions:
From the previous discussion, the following points could be taken into account:

1. CuO and ZnO were prepared by sol-gel, TiO₂ was prepared from Titanium oxide, and CuO/ZnO/TiO₂ nanocomposite was prepared from CuO, TiO₂ and ZnO as demonstrated by the results of XRD, FESEM.

2. Degradation of the (Phenol Red dye) is conducted using (CuO/ZnO/TiO₂) nanocomposite as a heterogeneous Photo-Fenton catalyst presence UV light.

3. Under optimum conditions (pH = 6, 10 ppm, and 6W UV light), 100% degradation of Phenol Red dye can be achieved in 3 hours.

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