



Synthesis, characterization and degradation activity of Methyl orange Azo dye using synthesized CuO/ α -Fe₂O₃ nanocomposite

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ABSTRACT

This study investigated the photo-degradation of methyl orange (MO) as a type of azo dye using a CuO/ α -Fe₂O₃ nanocomposite. A CuO/ α -Fe₂O₃ powder with a crystalline size in the range of 27-49 nm was successfully prepared using simple co-precipitation along with a sonication method. The characterization of the synthesized sample was done via XRD, FE-SEM, EDS, FTIR and DRS analyses. The Tauc equation revealed that the band gap of the nano composite in the direct mood was 2.05 eV, which is in the visible light range. The effect of operating factors containing dye concentration, photocatalyst dosage and pH on dye degradation efficiency was measured. Response Surface Method (RSM) was employed to specify the parameter effects. The photocatalytic activity of the CuO/ α -Fe₂O₃ nanocomposite was evaluated by degradation of MO under visible light irradiation. The results showed that the pH value played a very effective role in the dye degradation process efficiency. Also, the photocatalytic degradation of MO obtained was equal to 88.47% in the optimal values.

1. Introduction

Nowadays, water pollution has become an environmental crisis facing society, thus increasing the requirement for clean water. Removing organic pollutants from wastewater is an important step in environmental protection [1-3]. In recent years, the textile industry uses about 12-20% of synthetic dyes to color a variety of textiles. Due to incomplete use and washing operations, the untreated dyes are discharged into the environment. The discharged effluents contain dyes which cause environmental problems and are potentially carcinogenic for humans. Therefore, the removal of dyes from wastewater is highly regarded matter. Many techniques such as adsorption, electrochemical oxidation, ozonation, membrane filtration and biological treatment have been widely used to remove the dye components from polluted wastewater. These methods generally suffer from disadvantages including complicated processes, need for special operating

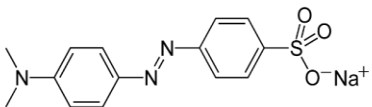
conditions, high equipment cost, energy intensive time consuming operations, finite versatility and lower adaptability to the extensive range of dye wastewaters. Therefore, the development of an effective process to degrade the dye solution is very important. In this regard, attempts have been made to access other types of efficient treatment processes, including advanced oxidation processes (AOPs). In this method, the metal oxide semiconductors convert the organic pollutants to non-dangerous components such as water and carbon dioxide [4]. Among the iron oxide semiconductors, hematite (α -Fe₂O₃) has the most stable phase. This is a result of its high photo corrosion resistance, high efficiency, nontoxic nature, low-cost and eco-friendly characteristics [5, 6]. The α -Fe₂O₃ has a narrow band gap (2.2 eV) that is suitable in visible light and the solar spectrum region. Its conduction band edge is rather less than the H₂/H₂O redox potential [7]. Copper oxide is a P-type semiconductor metal oxide with a limited band gap of 1.2-1.5 eV [8]. Thus, it could have great

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potential for improvement in photocatalytic efficiency. The suitable composition of oxides may be due to the formation of very effective photocatalysts [9]. Methyl orange dye belongs to the azo dye (N=N) class and is a toxic dye. Table 1 shows the characteristics and chemical structure of MO. This dye is widely used in the textile industry. MO causes health risks like breathing difficulties, diarrhea, vomiting and nausea. It has a weak acid-base index with potential toxic and carcinogenic factor. Therefore, its removal from wastewater is required. In this research, a co-precipitation and sonication method was employed for the synthesis of the CuO/ α -Fe₂O₃ composite. The photocatalytic activity was appraised on the base of methyl orange degradation under visible light in an almost neutral situation without enhancing every radical initiator. It was found that adding CuO modified the photocatalytic property of α -Fe₂O₃ nanoparticles; we also observed high photocatalytic activity for the degradation of methyl orange as a type of azo dye.

Table 1. Characteristics and Chemical Structure of MO

Molar mass	327.349 g/mol
Hill Formula	C ₁₄ H ₁₄ N ₃ NaO ₃ S
Absorption maximum ($\lambda_{\max}$)	465 nm
Structure	

2. Materials and Method

2.1. Materials

All chemicals used were of analytical grade. Ferric chloride hexahydrate (FeCl₃·6H₂O) with a purity of 99.9%, copper sulfate pentahydrate (CuSO₄·5H₂O) with a purity of 99.9%, ammonia solution of 25% and methyl orange were purchased from the Merck Company of Germany. Quadruple distilled water was used in every photocatalytic experiment.

2.2. Photocatalytic reactor design

In this study, a semi-batch photocatalytic reactor with 1 liter volume was used. The designed reactor consisted of a double cylindrical chamber of Pyrex glass material. The Teflon reactor cap was equipped with four quartz glass tubes and 60 W halogen lamps. In order to create uniform irradiation in the reactor, the quartz tubes were placed symmetrically on the cap. To increase the contact area between the pollutant and photocatalyst particles, the reactor was equipped with a rotary agitator with 100 rpm of power. In addition, the aeration process was carried out using an air pump to mixing the solution and also dissolving the oxygen. The temperature was controlled in the solution using a cool water jacket and circulation. Finally, in order to

prevent acts of environmental irradiation, the reactor was placed in box covered with aluminum foil. Figure 1 shows a reactor schematic and its components during the degradation process.

2.2.1. Preparation of CuO/ α -Fe₂O₃ nanocomposite

The CuO/ α -Fe₂O₃ nano photocatalyst was prepared as follows: FeCl₃·6H₂O and CuSO₄·5H₂O were used as the starting material. The molar ratio of Fe to Cu was 3:1. The solution was stirred at ambient temperature for 15 min with drop-wise adding the ammonia solution until the pH reach to 9. The obtained sediment was centrifuged and washed with quadruple distilled water until all the chloride ions belonging to the iron precursors were washed from the sediment. Then, the wet material was dried in an oven for 2 h at 100 °C and calcined at 450 °C for 2 h [10].

3. Results and discussion

3.1. Characterization

The Fourier transform infrared spectra (FTIR) were studied via a FTIR-8400S spectrophotometer (Shimadzu, Japan). The crystal phases were examined by a D8-Advance X-Ray diffractometer (XRD) (Bruker, Germany) using Cu K α radiation. The FE-SEM measurements were analyzed using a Mira3-XMU field emission scanning electron microscope (TESCAN, Czech Republic) to obtain the surface morphology of the prepared sample. The energy dispersive X-Ray spectroscopy (EDS) was conducted using a scanning electron microscope to analyze the elements. The UV-Vis diffuse reflectance (DRS) was carried out by Avaspace-2048-TEC (Avantes, Nederland).

3.1.1. XRD

Figure 2 shows the X-Ray diffraction pattern of CuO/ α -Fe₂O₃ in the range of $2\theta=10-90^\circ$; the crystalline peaks were detected for α -Fe₂O₃ at $2\theta= 24.1, 33.2, 35.6, 40.9, 49.5, 54.1, 57.3, 62.4$ and 64.1 respectively that ascribed to the (012), (104), (110), (113), (024), (116), (118), (214) and (300) the existence of alpha phase with hexagonal structure [11]. Also, the two main peaks for CuO at $2\theta= 36.1$ and 38.8° ascribed to (-111) and (111) with monoclinic structure [12]. The average crystallite size was calculated by the Debye-Scherrer equation [13]:

$$\tau = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where τ is mean size of the crystalline, λ is the wavelength of X-Ray, K is a shape factor, β is the line broadening at half the maximum intensity (FWHM) and θ is the Bragg angle. The average crystalline size of the CuO/ α -Fe₂O₃ composite was found to be 31 nm using Equation (1).

3.1.2. FE-SEM and EDS

Figure 3 indicates the FE-SEM image of the CuO/ α -Fe₂O₃ nanocomposite in different scales. These images show that

the particle size is in the range of 27-49 nm with a sphere-like morphology. The EDS analysis was applied to recognize elements that exist in the CuO/ α -Fe₂O₃ composite (Figure 4). The results confirmed that all elements were present at their corresponding keV values.

3.1.3. Uv-Vis DRS

The results of the Uv-Vis DRS analysis of CuO/ α -Fe₂O₃ are shown in Figure 5. The results showed that the adsorption edge was extended toward the visible region for CuO/ α -Fe₂O₃. This phenomenon was caused due to the charge transition of CuO to the conduction (valance) band of α -Fe₂O₃. Therefore, this work increased absorption in visible light and improved the photocatalyst activity. The CuO/ α -Fe₂O₃ band gap in the direct path was obtained via the Tauc equation by drawing a Tauc curve of the DRS data near the band edge (Figure 6) [14, 15]. This equation was given here.

$$[F(R_{\infty})hv]^{\frac{1}{n}} = (hv - E_g) \quad (2)$$

where $h\nu$ is the photon energy, E_g is the band gap, $n=0.5$ for allowed direct transition and $F(R_{\infty})$ is the Kubelka-Munk function where $R_{\infty}=R_{\text{sample}}/R_{\text{standard}}$ [16]. The band gap of CuO/ α -Fe₂O₃ was found to be 2.05 eV; the reported values of the direct band gap of pure α -Fe₂O₃ was the in the 2.2-2.67 eV range [17-19]. The E_g decrement value can improve the photocatalytic activity in the visible light radiation zone.

3.1.4. FTIR

Figure 7 shows the FTIR spectra of the CuO/ α -Fe₂O₃ composite in the range of 400-4000 cm⁻¹. Metal oxide generally has absorption bands under 1000 cm⁻¹ [20]. The characteristic peaks of CuO stayed in the range of 984-426 cm⁻¹ [21]. The peaks at 538, 607 and 869 cm⁻¹ were attributed to Cu-O vibration [20-22]. The peaks at 473 and 597 cm⁻¹ corresponded to Fe-O vibration. The peak at 3352 cm⁻¹ was attributed to water hydration [23]. The peak at 1361 cm⁻¹ corresponded to (COO⁻) and the peak at 1128 cm⁻¹ corresponded to the presence of O-H stretching [21].

3.1.5. Photocatalytic activity

The evaluation of photocatalytic activity was investigated by the degradation of a model compound. Methyl orange

with concentrations of 25, 15, and 5 mg/L and a photocatalyst with the amount of 0.5, 0.75, and 1 g/L were used under visible light radiation for duration of 2 hours in reactor. In each experiment, the pH of solution was adjusted using 0.1N HCl or 0.1N NaOH. Before starting the visible light irradiation, the suspensions were stirred in the dark for 30 min to get the adsorption-desorption equilibrium between the MO and photocatalyst. Four 60 W halogen lamps were used as the light source to enable visible light irradiation. At the beginning of the photocatalytic reaction, sampling was taken at 15 min intervals for 2 h. This sample was centrifuged to separate the photocatalyst powder nanoparticle. The remaining concentration of MO was measured to determine the absorbance of MO by using the Uv-Vis spectrophotometer at a maximum absorption of 465 nm. The photocatalytic activity of CuO/ α -Fe₂O₃ was investigated by the degradation of the methyl orange. According to previous studies, three key factors including photocatalyst dosage, dye concentration and PH value were selected as variables [24-27]. Design expert software (Version 7) was used to design the experiments. All designed experiments were performed in 120 min under four 60 W halogen lamps irradiation. The degradation results of all tests are shown in Table 2. In the best case scenario, the degradation of MO was 88.47%. Figure 8 shows the methyl orange degradation process under optimized condition. The rate of photocatalytic degradation can be measured by the following formula [28]:

$$D\% = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (3)$$

where D is the photocatalytic degradation while C_0 and C_t are the MO concentrations (mg/L) at the time 0 and t. A photograph of the degradation of MO in different irradiation times under optimized condition is shown in Figure 9.

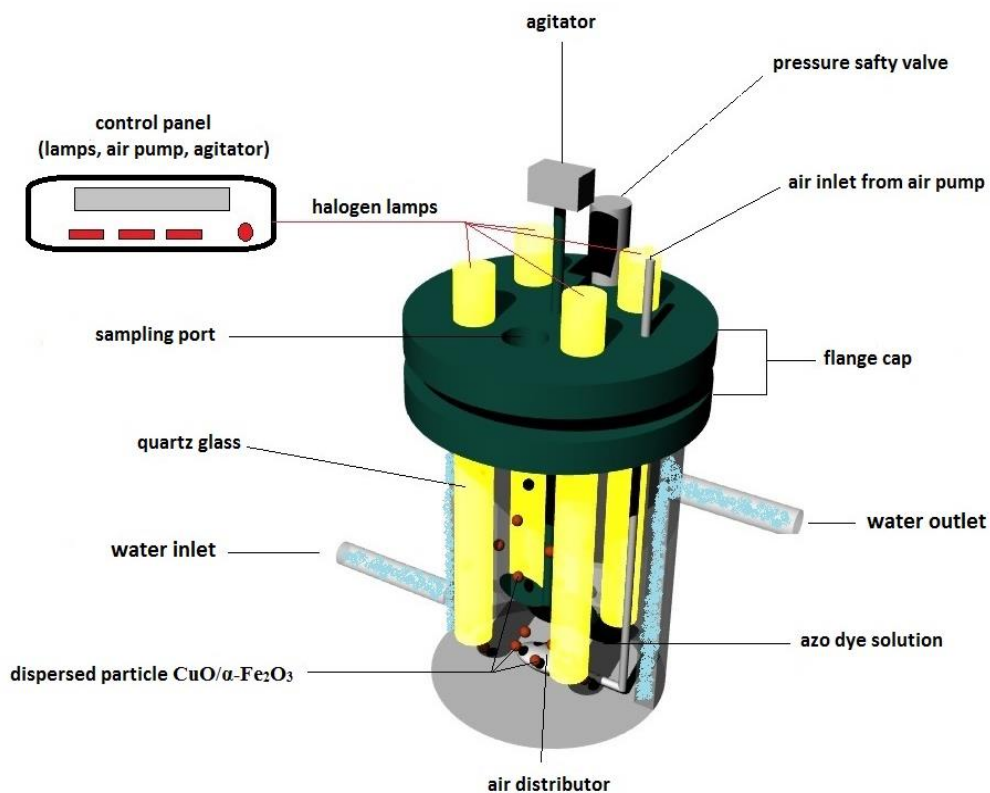
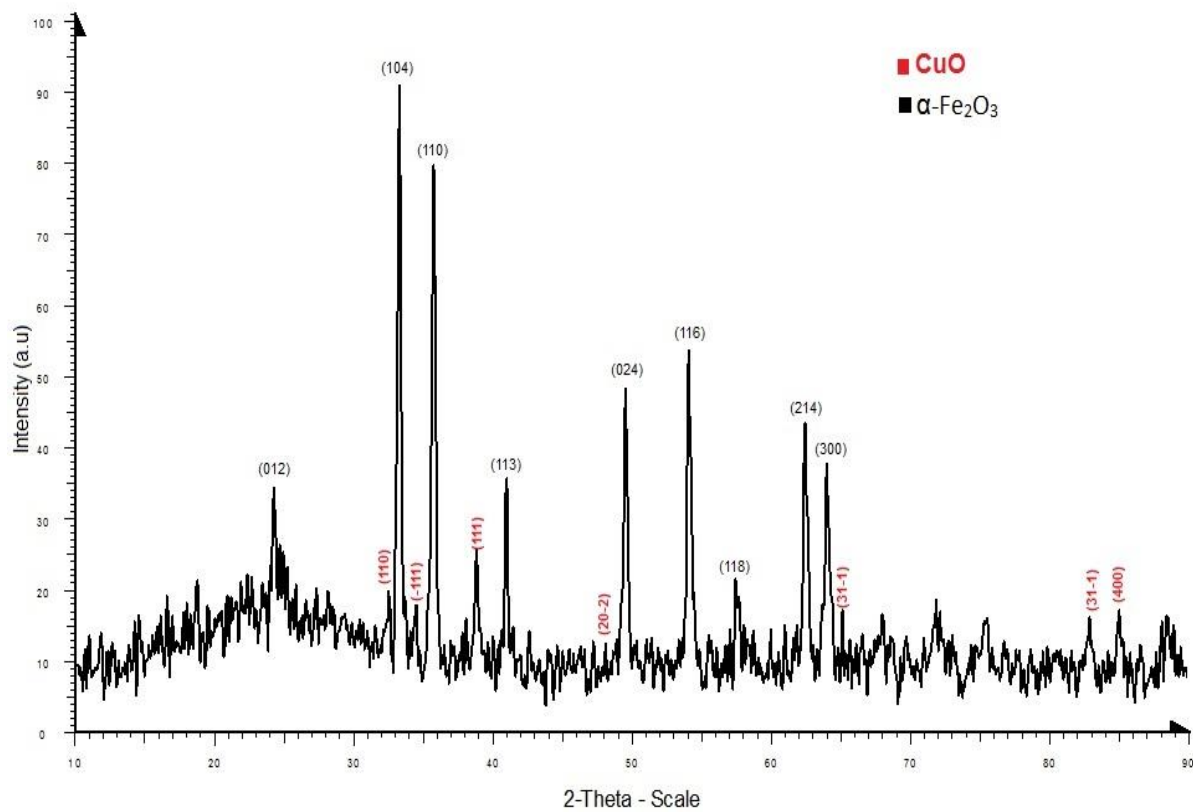


Fig.1. The photocatalytic reactor schematic

Fig. 2. XRD pattern of $\text{CuO}/\alpha\text{-Fe}_2\text{O}_3$

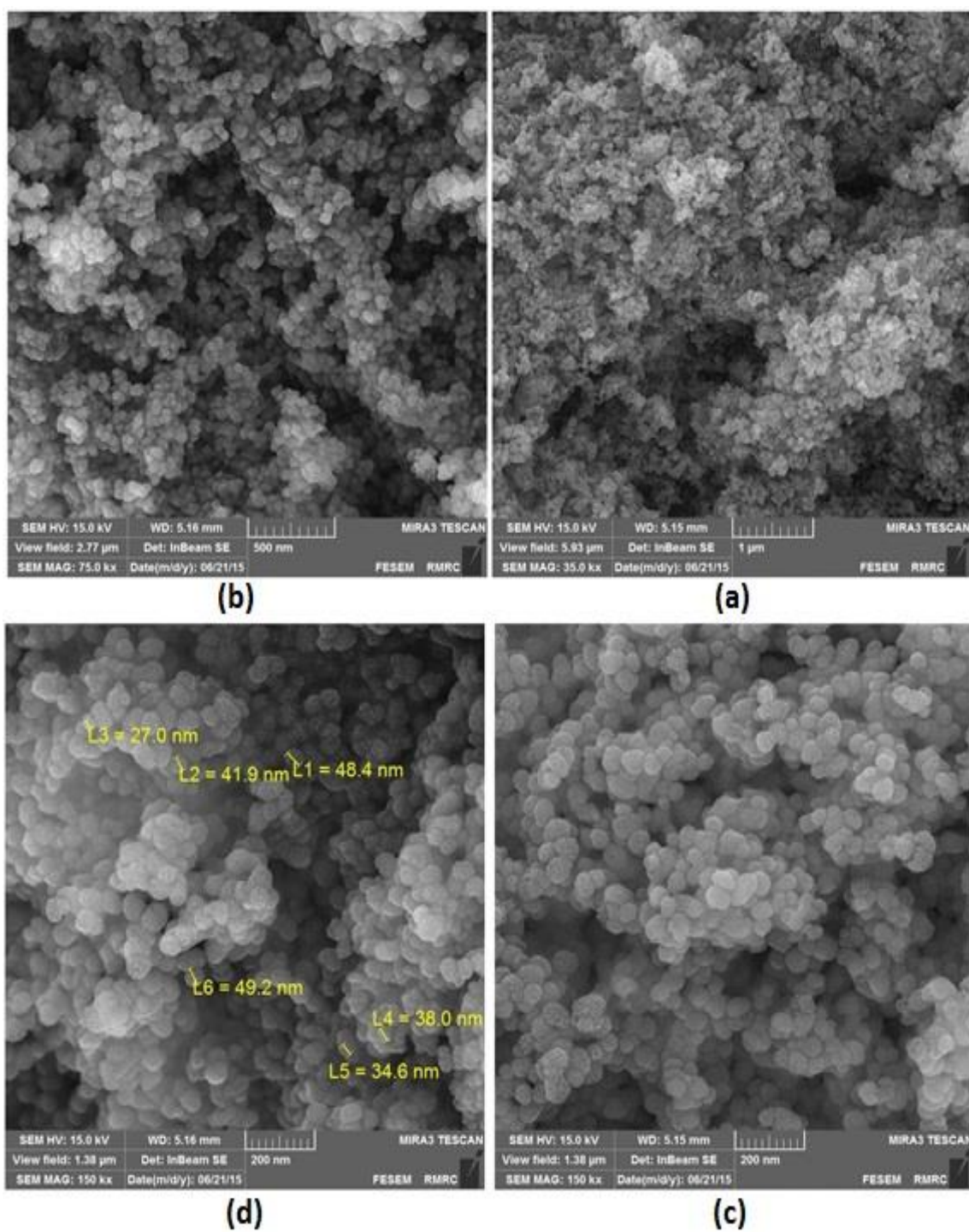


Fig. 3. FE-SEM images of CuO/ α -Fe₂O₃ in different scale (a) 1 μ m (b) 500 nm (c) 200 nm (d) 200 nm along with particle size

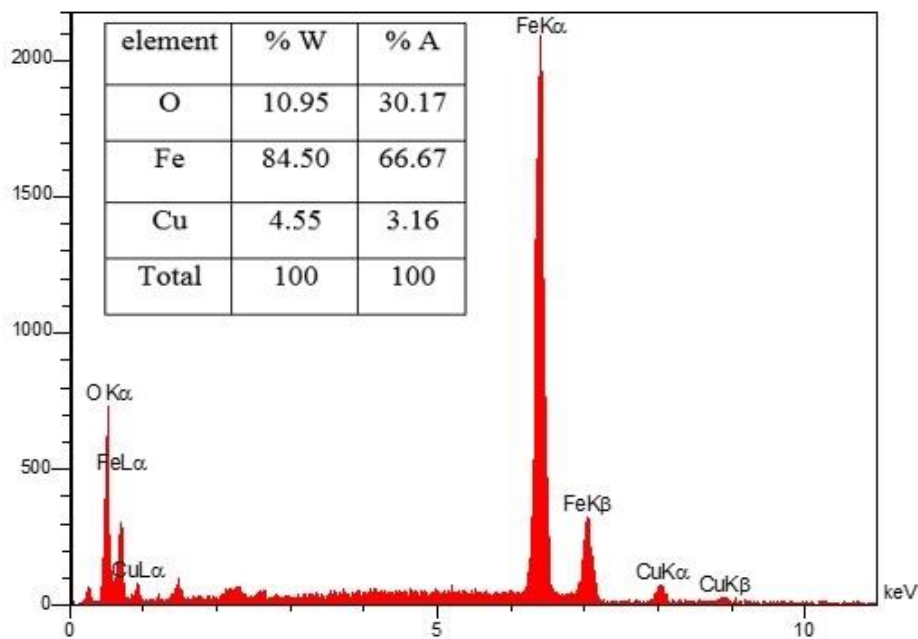
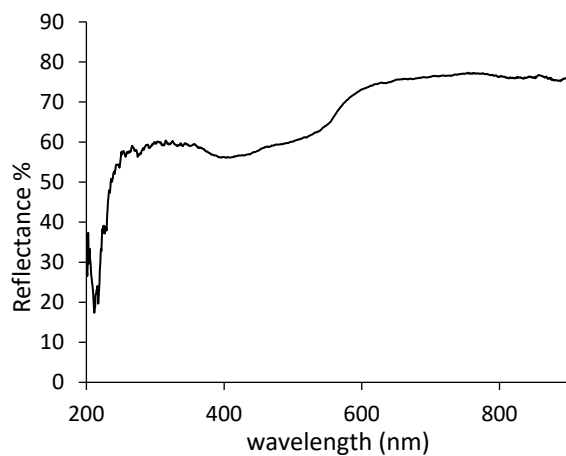
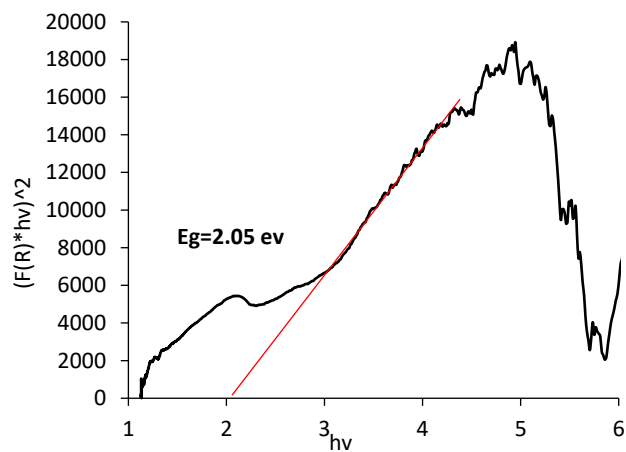
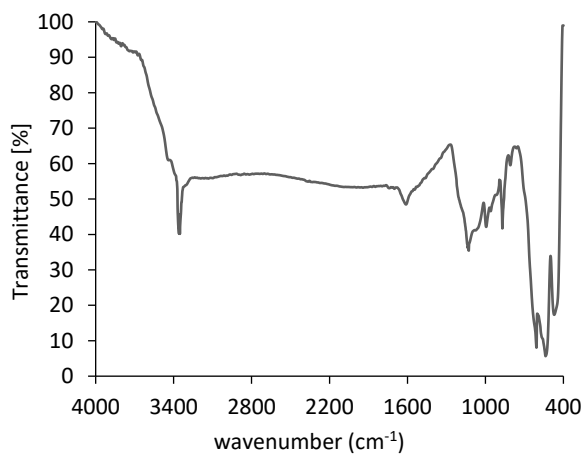
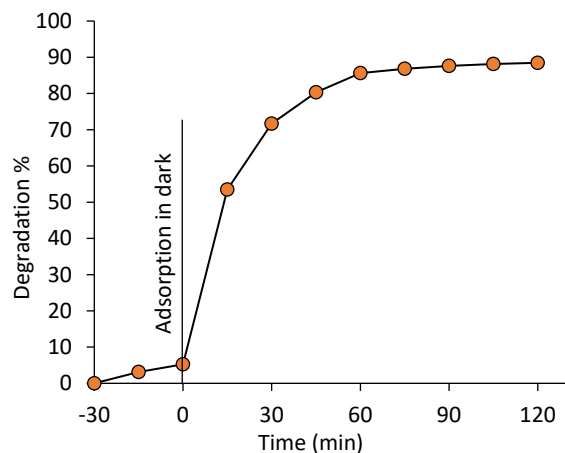
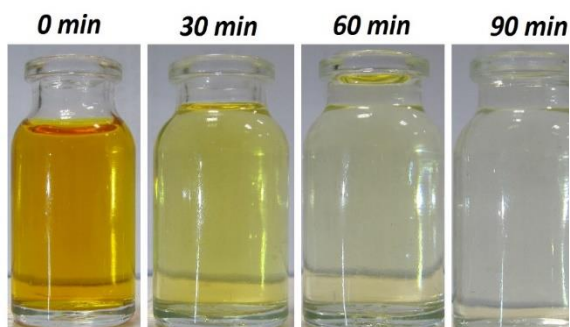
Fig. 4. EDS Analysis of CuO/α-Fe₂O₃Fig. 5. DRS chart of CuO/α-Fe₂O₃Fig. 6. Tauc curve of CuO/α-Fe₂O₃Fig. 7. FTIR spectra for CuO/α-Fe₂O₃ composite

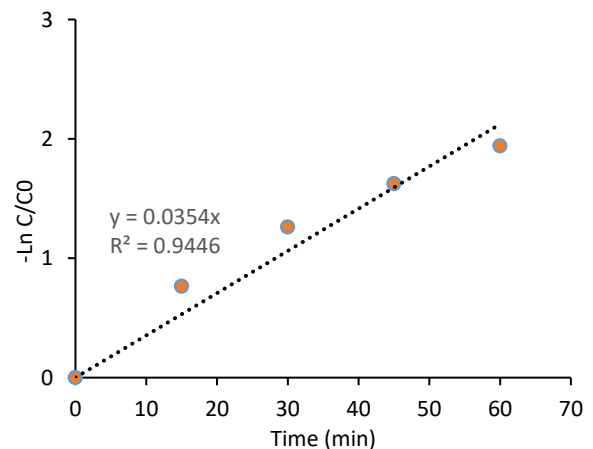
Table 2. Designed experiments for methyl orange degradation by software design expert

Run #	PH value	Dye Concentration (mg/L)	Photocatalyst Dosage (gr/L)	Dye Degradation %
1	6	25	1.5	76.32
2	9	15	1.5	5.41
3	6	5	1.5	70.02
4	9	15	0.5	6.57
5	6	5	0.5	73.82
6	3	5	1	47.23
7	6	15	1	87.41
8	3	15	0.5	65.34
9	9	5	1	4.38
10	6	15	1	88.47
11	6	15	1	88.12
12	6	15	1	87.94
13	6	15	1	88.33
14	3	25	1	62.23
15	3	15	1.5	59.29
16	6	25	0.5	78.63
17	9	25	1	4.93

**Fig. 8.** Photo-degradation of MO using CuO/ α -Fe₂O₃ under optimized condition**Fig. 9.** A photograph of degradation MO by CuO/ α -Fe₂O₃ in different irradiation times

3.1.6. Photo-degradation kinetics of MO

The photo-degradation kinetics of MO was studied in optimum condition ($C_{CAT}=1\text{gr/L}$, $C_{dye}=15\text{ mg/L}$ and $\text{PH}=6$). In the first 60 minutes of Reaction, the relationship of $(-\ln C/C_0)$ vs time was linear. Therefore, photo-degradation followed the pseudo first-order kinetics [29]. The kinetics of MO photo-degradation by CuO/ α -Fe₂O₃ is shown in Figure 10. The observed constant rate of MO photo-degradation using CuO/ α -Fe₂O₃ at 60 min reaction time was 0.0354 min^{-1} .

**Fig. 10.** Kinetics of MO degradation by CuO/ α -Fe₂O₃

4. Conclusions

A CuO/ α -Fe₂O₃ nanocomposite with a particle size in the range of 27-49 nm and sphere-like agglomerates were synthesized using co-precipitation and a sonication method. The synthesized powders were characterized with FE-SEM, EDS, XRD, FTIR and DRS techniques. The photo-degradation results showed that CuO/ α -Fe₂O₃ was a suitable photocatalyst for the degradation of methyl orange (MO) under visible light irradiation. The degradation of MO was almost 88.5% at 120 min under the conditions of $C_{cat}=1$ gr/L, $C_{MO}=15$ mg/L, and pH=6. The kinetic data at 60 min after the start of the photo-degradation reaction was well fitted with the pseudo first-order model. The calculated constant rate of the reaction was 0.0354 min^{-1} .

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