

Short communication

Photocatalytic degradation of methyl orange using CuO/Al₂O₃ nanocomposite obtained by microwave-assisted thermal decomposition route

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ABSTRACT

Aluminum oxide (Al₂O₃) and copper oxide (CuO) are known to exhibit very exceptional properties including high thermal and chemical properties that promise a wide area of applications. In this paper, we report the microwave-assisted thermal decomposition route to CuO/Al₂O₃ nanocomposite and its application as a photocatalyst for methyl orange (MO) degradation. Al₂O₃ was first prepared at different temperatures of 900, 1000, and 1100 °C, denoted as Al₂O₃(1), Al₂O₃(2), and Al₂O₃(3). Subsequently, the best temperature (1000 °C) was selected for the synthesis of CuO/Al₂O₃ nanocomposite. XRD analysis confirmed the hexagonal crystal structure for all the Al₂O₃ and the monoclinic phase for the CuO within the composite. The crystallite sizes of the alumina increased with temperature and a similar growth pattern occurred in the entire samples. Scanning electron microscopy and transmission electron microscopy (SEM and TEM) show clear spherical morphology for all the samples with obvious agglomeration as temperature increases. Optical characterization displayed decreasing band gap energies with increasing temperature, implying size increase due to particle interaction, boundary energy reduction, and grain boundary migration. The photocatalytic performance of the CuO/Al₂O₃ under visible light was evaluated on methyl orange (MO), and the degradation was studied with some process parameters such as the effect of catalysts dosage and initial concentration of MO. Results showed that the CuO/Al₂O₃ exhibited about 94.2 % efficiency within 3 h using an optimum dose of 2.0 g/L and an initial MO concentration of 20 mg/L. However, the use of CuO/Al₂O₃ nanocomposites to remove other organic pollutants could confirm the robustness of this catalyst.

1. Introduction

The release of hazardous waste, particularly from textile and other chemical industries, into water streams poses significant risks to both the environment and human health. These wastes often contain toxic substances and chemicals that are harmful and non-biodegradable [1]. Dyes represent one of the most perilous contaminants found in water sources. Within the industrial sector, textile processes including dyeing, printing, finishing, and washing account for 85 % of total water usage

and 65 % of chemical consumption in the textile supply chain [2]. Approximately 7.5 metric tons of pollutants are discharged annually solely from dyeing processes. The intricate molecular structures of dyes, consisting of aromatic rings linked with various functional groups carrying π -electrons, enable them to absorb light within the 380–700 nm spectra, resulting in coloration owing to the presence of chromogens and chromophores. Among both natural and synthetic dyes, the prevalence of azo compounds has raised concerns due to their highly carcinogenic nature, primarily emanating from amine and benzidine emissions.

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Moreover, the non-biodegradable nature of dye molecules contributes to their prolonged persistence in the environment, escalating associated hazards [3].

Methyl orange, also known as dimethylaminoazobenzenesulfonate, is a prevalent azo-anionic dye. This synthetic organic dye is soluble in water, demonstrates remarkable color intensity, and exhibits a vibrant orange colour upon dissolution in water [4]. Typical of all Azo dyes, methyl orange is known to be a major human carcinogen apart from being a water pollutant. Its presence in the environment remains a cause for concern especially in the developing nations where their usage seems to be unrestricted. Hence, the need to remove methyl orange from aqueous systems continues to generate research interest. Different methods of MO removal have been reported such as coagulation-flocculation ultra-filtration [5,6], electrochemical degradation [7,8], and advanced oxidation processes such as non-thermal plasma advanced oxidation process [9], and photocatalytic degradation [10–14]. One of the critical factors considered in the adoption of pollutant removal methods is cost efficiency and complete mineralization of pollutants. To this end, photocatalytic degradation of waste presents significant potential as a sustainable and effective oxidation method, particularly in the field of wastewater treatment [15]. The low operational expenses, rapid mineralization of specific pollutants, and the absence of the necessity for high pressure and temperature make photocatalytic oxidation particularly advantageous [16].

Semiconductor metal oxides have been widely utilized as photocatalysts in dye degradation [17–19] and due to the challenges of the recombination process, the use of heterojunction systems has been considered one of the ways to address this shortcoming [20,21]. The compatibility of the electronic structure of the compositing semiconductor materials is very important, hence TiO_2/ZnO [22], CuO/CeO_2 [23], $\text{SnO}_2\text{-ZnO}$ [24], $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ [25], $\text{Ag}_2\text{O}/\text{MoS}_2$ [26], WO_4/TiO_2 [27], Fe_2O_3 on NCQDs-MgO [28], GO on $\text{Mn}_3\text{O}_4/\text{TiO}_2$ [29], Bi_2O_3 QDs on TiO_2 [30], $\text{Cu}_2\text{O-BiVO}_4\text{-WO}_3$ [31], and $\text{Fe}/\text{ZnO}/\text{SiO}_2$ [32] nanostructured photocatalysts have been reported for water remediation. Alumina coupled to other metal oxide nanoparticles has been used as heterojunction photocatalyst system [33–36]. The combination of CuO and Al_2O_3 proves effective in eliminating pollutants because of the low conductivity, high surface area, low dielectric constant, low thermal expansion, and chemical stability associated with the composite [37–39]. Furthermore, Al_2O_3 showcases an abundance of defect sites, which not only positions it as an exceptional electron acceptor but also significantly bolsters overall efficiency as a photocatalyst to remove dyes from aqueous system [39,40]. In this context, $\text{CuO}/\text{Al}_2\text{O}_3$ nanocomposites prepared by different processes have been reported. For example, Sridevi *et al* prepared $\text{CuO}/\text{Al}_2\text{O}_3$ by hydrothermal treatment for enhanced visible-light driven photocatalytic activity [41], sol-gel method has been adopted by Marulasiddeshi *et al* to prepare $\text{CuO}/\text{Al}_2\text{O}_3$ [42], and the pressureless sintering method using CuO and calcined white Al_2O_3 have also been reported [43]. $\text{CuO}/\text{Al}_2\text{O}_3$ and ternary composites such as $\text{CuO}/\text{CeO}_2\text{-Al}_2\text{O}_3$, and $\text{CuO}/\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalysts have been prepared by an impregnation method [44]. $\text{Al}_2\text{O}_3\text{:CuO}$ synthesized by the polymeric precursor method by varying the pH of the precursor solution has been presented [45].

Microwave irradiation synthesis method is one of the approaches used for the preparation of metal oxide [46,47] and complex metal oxide nanoparticles [48,49]. The generated microwave impacts reaction processes due to its ability to generate high-frequency waves that heat up reactants within a short time. Similarly, calcination temperature influences the structure, morphology, and particle size of the nanomaterials. In this current study, $\text{Al}_2\text{O}_3/\text{CuO}$ nanocomposite was synthesized by microwave-assisted thermal decomposition route and its application in the degradation of methyl orange was evaluated.

2. Experimental

2.1. Materials

Analytical grades of aluminum acetate, zinc acetate, ethylene glycol, methyl orange, NaOH and HCl (32 %), were purchased from Merck. They were used as received without additional purification.

2.2. Characterization techniques

X-ray powder diffractometer was recorded at room temperature in conjunction with a $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) to measure the diffraction patterns. Morphological analysis of the samples was measured using a JEOL 5600LV scanning electron microscope (SEM) and Hitachi HF-2000 transmission electron micrographs (TEM). Prove 300 UV-visible spectrophotometer was used for the measurement of the Absorption spectroscopy.

2.3. Method of synthesis

The synthesis of Al_2O_3 and $\text{CuO}/\text{Al}_2\text{O}_3$ was conducted according to the following procedure: Firstly, 1.5 g of aluminium acetate was dispersed in 25 mL ethylene glycol and the solution was thoroughly stirred at 40°C for 1 h. This was followed by a dropwise addition of 1 M sodium hydroxide to adjust the pH of the stirred solution to 10. The solution was subsequently poured into a microwave vessel lined with PTFE and resistant to pressure, where it was allowed to undergo a reaction through cyclic microwave radiation at 800 W. After 5 min, the microwave heating was stopped, and the solution was cooled to ambient temperature and centrifuged. The resulting precipitate was rinsed thrice with ethanol and left to air dry. Finally, the product was divided into 3 portions and each portion was transferred to a crucible and calcinated in a furnace for 2 h at different temperatures of 900, 1000, and 1100°C .

$\text{CuO}/\text{Al}_2\text{O}_3$ nanocomposite was prepared by mixing an equal amount of aluminium acetate and copper acetate (0.5 g) dissolved in 20 mL ethylene glycol and vigorously stirred at 40°C for 1 h. A solution of 1 M sodium hydroxide was added in dropwise to the mixture to adjust the pH to 10 and the solution was then poured into a microwave vessel lined with PTFE and resistant to pressure, where it was allowed to undergo a reaction through cyclic microwave radiation at 800 W. The microwave heating was stopped after 5 min and the solution was to cool to ambient temperature and centrifuged. The resulting precipitate was rinsed thrice with ethanol and left to air dry. Finally, the product was transferred to a crucible and calcinated in a furnace for 2 h at 1000°C .

2.4. Photocatalysis studies

The photocatalytic activity of the synthesized $\text{CuO}/\text{Al}_2\text{O}_3$ nanocomposite was evaluated by studying its photocatalytic potency on an aqueous solution of MO under visible light irradiation. The photocatalytic reactor is equipped with a 250-W Xe discharge lamp and a reactor vessel which has an inbuilt recirculating water source. The vessel was charged with a specific dye solution and a known concentration of catalyst. The photocatalytic experiment proceeds with stirring the mixture of the dye solution and catalyst in the dark for about 20–30 min to allow equilibration, followed by the irradiation by the light from the Xenon lamp. During this process, the solution was constantly agitated under the lamp and aliquots were drawn from the system every 15 min, filtered and measure using UV-visible spectroscopy. This process was allowed to run over a period of 3 h [13].

3. Results and discussion

3.1. XRD studies

X-ray diffraction patterns of the Al_2O_3 nanoparticles calcinated at

900, 1000, and 1100 °C are depicted in Fig. 1a-c, and demonstrates a successful synthesis of the nanoparticles. Similar patterns occurred in the three samples prepared at different calcination times. However, the XRD results also exhibit the effect of calcination time on the crystallinity and crystal size.

The sample calcined at 900 °C (Fig. 1 (a)) displays low intensities

peaks which are relatively broad and are attributed to the (012), (104), (110), (113), (024), (116), (211), (018), (214), (300), (1010), (220), (223), (312), and (0210) of α - Al_2O_3 and corresponds to JCPDS file no. 71-1123 with space group $R\bar{3}c$ [50]. It can be observed that a more crystalline phase of α - Al_2O_3 phase is formed after 1000 °C as presented in Fig. 1 (b and c). The samples prepared at 1000 and 1100 °C

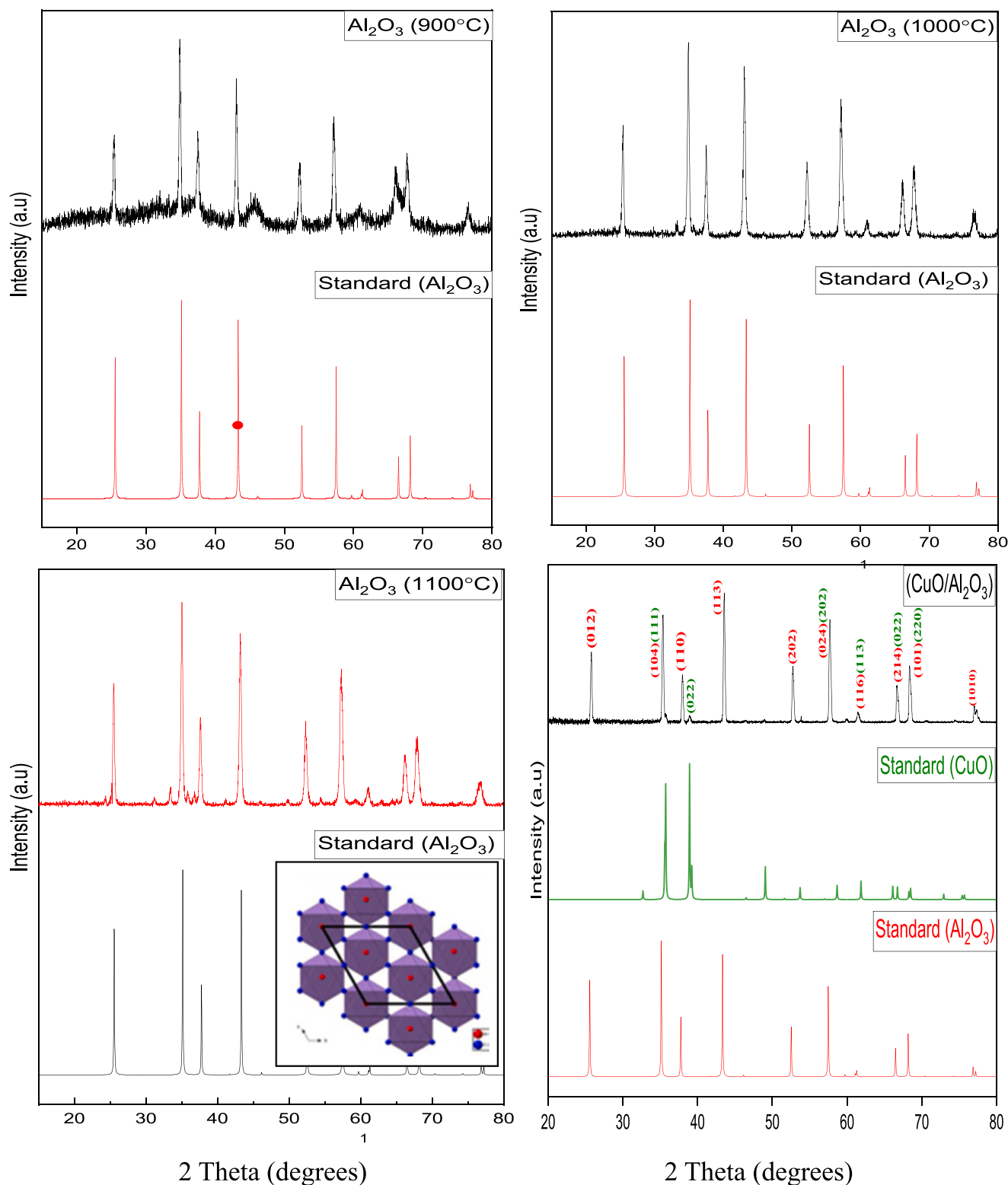


Fig. 1. XRD patterns of Al_2O_3 NPs synthesized at different calcination temperatures of (a) 900, (b) 1000, and (c) 1100 °C (inset is the packing diagram of α - Al_2O_3 nanoparticles). (d) XRD patterns of $\text{CuO}/\text{Al}_2\text{O}_3$.

have more intense and narrower peaks that suggest larger crystal sizes. Beyond 1000 °C, the Al₂O₃ samples not only increased in crystallite size as indicated in the sharp peaks, but also a reduction in the background noise occurred. α phase of Al₂O₃ is the most stable form and has been reported to be formed only at temperatures beyond 1000 °C. The formation of this phase at 900 °C could be related to the synthesis procedure, which is different from other reported processes involving a combustion agent such as citric acid [51–53].

The diffraction patterns of the CuO/Al₂O₃ nanocomposite show that the sample has been obtained from two components of CuO and Al₂O₃. The diffraction peaks due to the CuO could be identified at 2θ of 35.63, 38.80, 53.34, 58.23, 61.62, and 66.35, which are assigned to the (1 1 1), (0 2 2), (0 2 0), (2 0 2), (1 1 3), and (2 2 0) planes of monoclinic CuO (JCPDS 45–0397), and patterns ascribed to the Al₂O₃ agree very well with the hexagonal α -alumina phase. There was no change in the crystalline phase of the alumina emanating from the incorporation of a secondary semiconductor metal oxide to form a composite system. CuO/Al₂O₃ nanocomposite synthesized by the conventional methods [54,55], also indicated the formation of the monoclinic phase for the CuO. However, γ -Al₂O₃ crystalline phase was reported with standard alumina card (JCPDS files no. 29.0063) and JCPDS No. 10–425) respectively.

The average crystalline size was estimated using the Scherrer equation (1)[56], where D is the average crystal size, K is known as Debye–Scherrer's constant, and it is given as 0.89 for spherically shaped samples, λ denotes the X-ray radiation wavelength (often given as $\lambda = 1.54$ for CuK α Å), β is the width of the peak at half-maximum intensity (FWHM) of the sample (radian) and θ is the diffraction angle [57,58]. The estimated crystalline sizes of 45.2, 48.4 and 56.8 nm for Al₂O₃ (1), Al₂O₃ (2), and Al₂O₃ (3) are in line with the crystal growth that takes place with temperature.

3.2. Morphological analysis

Fig. 2(a–c) present the external morphology of the Al₂O₃ nanoparticles synthesized at different temperatures, 900, 1000, and 1100 °C respectively. The SEM images show particles with nearly spherical shapes and agglomeration with no distinct edge. The micrographs show that temperature increases the agglomeration, causing the particles to form crumps at 1100 °C. The temperature change leads to significant morphological changes in the structure of the nanoparticles. With enhanced calcination temperatures, a variation occurs in the size and shape of the nanoparticles and increased agglomeration may also be due to the improved surface forces among the particles [59]. Larger particles and large pores have been located at different agglomeration junctions [60].

The transmission electron microscopy images (Fig. 3) give NPs of similar shape and the size estimation using image J shows sizes of 42.8, 44.4 and 58.5 nm for the samples obtained at 900, 1000 and 1100 °C respectively. These are close to the sizes calculated from their XRD patterns and it could be observed that apart from the size increment, agglomeration of the particles increases as the temperature increase which has been attributed to surface reactivity.

The surface morphology of the composite has been visualized using Scanning Electron Micrographs (SEM) and presented in Fig. 4a. From

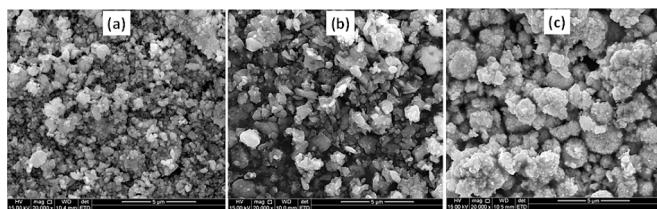


Fig. 2. SEM micrographs of Al₂O₃ NPs synthesized at different calcination temperatures of (a) 600, (b) 800, and (c) 1000 °C.

the figure, the external surface morphology of the CuO/Al₂O₃ nanoparticles depict spherical morphology with a slight agglomeration of nanoparticles that is expected for such a high-temperature calcination process. TEM images of CuO/Al₂O₃ show spherical morphology whose average particle size is about 52.4 nm, and this agrees well with the calculated crystallite size using Scherrer's equation. The HR-TEM images are depicted in Fig. 4(c), showing lattice fringes with interplanar spacing of 0.23 and 0.26 nm corresponding to (1 1 0) and (–1 1 1) planes of Al₂O₃ and CuO, respectively [61,62]. Both the XRD and EDX (presented in Fig. 4c) analyses were confirmatory of the successful formation of a pure phase composite of CuO/Al₂O₃.

3.3. Optical absorption properties

The UV–Vis spectra of the different samples of the γ -Al₂O₃ NPs and the composite with CuO are shown in Fig. 5(a–d). The sharp absorption edge exhibited by all the spectra around 280 nm is ascribed to the photoexcitation of electrons causing migration from the valence band to the conduction band [63]. In addition, the absorption spectrum of CuO/Al₂O₃ nanocomposite (Fig. 6d) shows a broad absorption band in the spectral range of 385 to 410 nm attributed to the photoexcitation of electrons in the CuO.

The optical band gap of the Al₂O₃ nanoparticles at varying calcination temperatures has been calculated using the Tauc relation given in Equation 1 [64]:

$$(h\nu\alpha) = (h\nu - E_g)^n \quad (1)$$

where, α represents the absorption coefficient, ν denotes the frequency, h is the Planck's constant, E_g is the value for the absorption band gap energy and n is a constant that is related to the different types of electronic transitions whereby the direct allowed, indirect allowed, direct forbidden, indirect forbidden transitions are associated with $n = 1/2, 2, 3/2$ or 3 respectively).

The linear part of the $(\alpha h\nu)^2$ vs photon energy ($h\nu$) curves is shown in Fig. 6. The values of the band gap decreased from 4.4 to 3.8 eV with increasing calcination temperature from 900 to 1100 °C. The existence of impurities and structural defects like oxygen vacancies and interstitials could influence the measurements of the energy band gap. Therefore, the decrease in band gap values could be due to the diffusion of aluminum and oxygen atoms that occupy interstitial sites between Al₂O₃ lattices, which resulted in the decrease in the band gap energies. The band gap energy of the composite was obtained as 4.3 eV. Table 1 summarises the values of the optical band gap of the Al₂O₃ nanoparticles for varying calcination temperatures (900, 1000, and 1100 °C).

3.4. Photodegradation of methyl orange

The generation of conduction band electrons (e^-) and valence band holes (h^+) upon the irradiation of CuO/Al₂O₃ nanocomposite is significant for the degradation of the methyl orange. The photo-generated electrons could react with electron acceptors such as O₂, adsorbed on the surface of the catalyst to form a superoxide radical anion O₂ $^{\bullet-}$. Concomitantly, photogenerated holes oxidize the organic molecules and react with OH $^-$ or H₂O which oxidizes them into OH $^{\bullet}$ radicals. The generated radicals together with other highly oxidant species (peroxide radicals) are responsible for the photodecomposition of MO into less harmful mineral end-products [65]. The recombination of electron-hole pairs has the potential to generate energy through fluorescence emission. Nevertheless, a reduced emission intensity extends the duration of electron-hole recombination and promotes the rate of photocatalytic activity. [66,67]. Therefore, using a 250–W Xe lamp as an excitation source for the heterogeneous CuO/Al₂O₃, electrons and holes could have a longer lifetime and may form a higher number of active radicals [10,66]. Fig. 6 illustrates the absorption spectra depicting the degradation of MO at 15-minute intervals under visible light. The findings

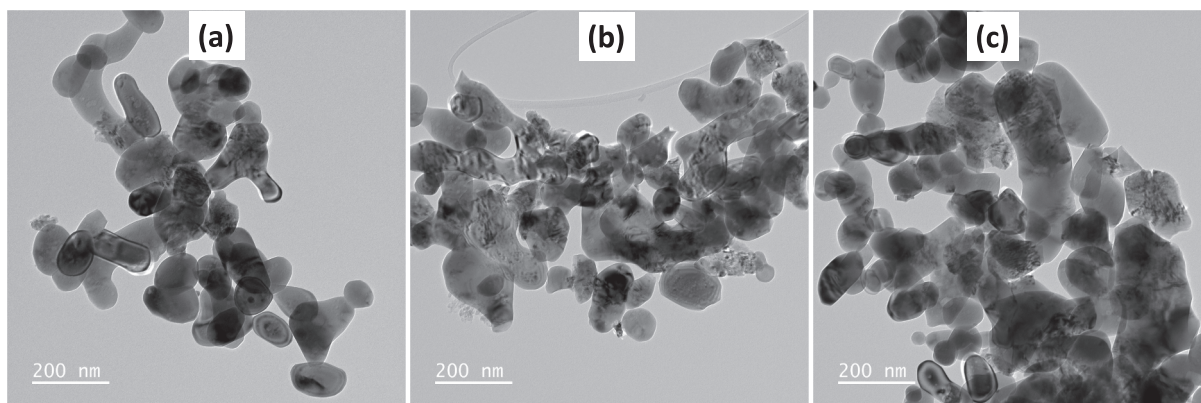


Fig. 3. TEM micrographs of Al_2O_3 NPs synthesized at different calcination temperatures of (a) 900, (b) 1000, and (c) 1100 °C.

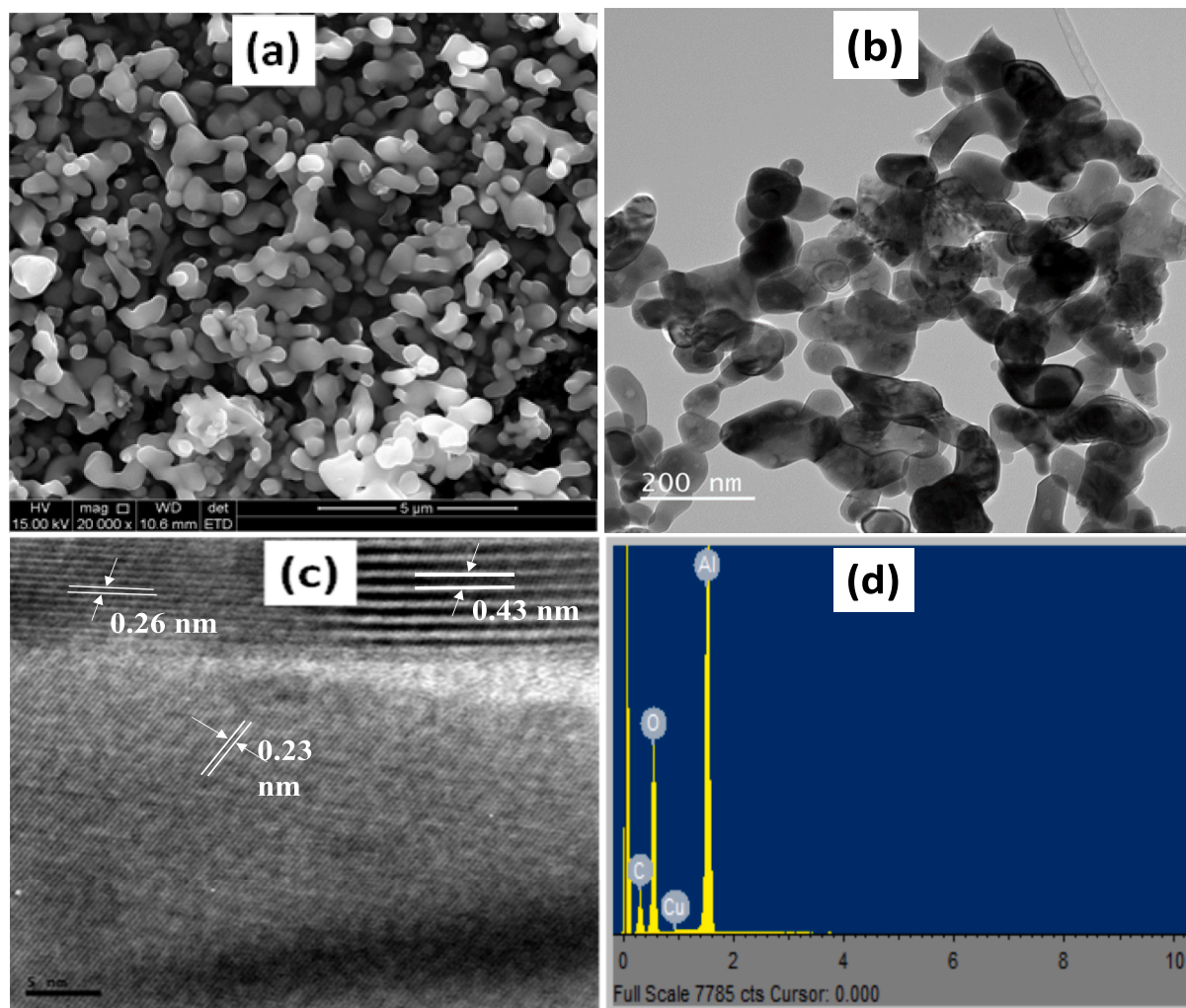


Fig. 4. (a) SEM, (b) TEM, and (c) HRTEM micrographs of $\text{CuO}/\text{Al}_2\text{O}_3$.

indicate a gradual decline in the absorption peak of MO at approximately 430 nm. Effective MO degradation (94 %) was accomplished within a 3-h reaction time utilizing a combination of 2.0 g/L $\text{CuO}/\text{Al}_2\text{O}_3$ and 20 mg/L MO concentration. Comparable outcomes have been reported in prior studies [68,69].

The performance of $\text{CuO}/\text{Al}_2\text{O}_3$ nanocomposite was compared with other studies involving Al_2O_3 composite with similar II-VI

semiconductor photocatalysts. For example, $\text{MgO}\bullet\text{Al}_2\text{O}_3\bullet\text{ZnO}$ composite, synthesized by the coprecipitation of their carbonates and evaluated for the photocatalytic degradation of methyl violet 6b exhibited a degradation efficiency of 48.7 %. Only upon the addition of H_2O_2 was the efficiency increased to 93.42 % at pH 9 [70]. The visible light activated photocatalytic performance of $\text{CdO}-\text{Al}_2\text{O}_3$ nanocomposite has been studied against metanil yellow dy. A maximum degradation

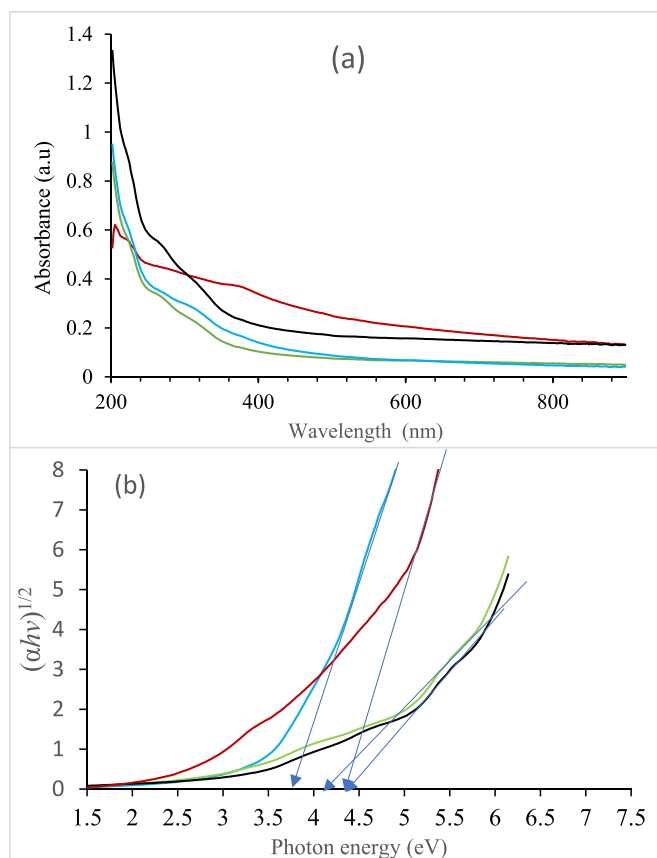


Fig. 5. (a) Absorption spectra and (b) Tauc plot of Al_2O_3 NPs synthesized at different calcination temperatures of 900, 1000, and 1100 °C. Black: $\text{Al}_2\text{O}_3(900)$; green: $\text{Al}_2\text{O}_3(1000)$; blue: $\text{Al}_2\text{O}_3(1100)$; red: $\text{CuO}/\text{Al}_2\text{O}_3$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

efficiency of 82.09 % was achieved [71]. Nanocomposites of mixed iron and aluminium oxide ($\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$) have been used for the adsorptive decolorization of Congo red dye from an aqueous system [72]. Anatase phase of TiO_2 nanoparticles were incorporated into alumina to form

$\text{TiO}_2/\text{Al}_2\text{O}_3$ composites. They were evaluated for the photocatalytic removal of methylene blue (MB) and crystal violet (CV) dyes under both UV- and visible light. The degradation efficiency was 45 and 29 % under the UV light and 84 and 81 % under visible light for MB and CV dyes respectively [73]. Yadav et al [40], reported the photocatalytic activity of $\text{ZnO}/\text{Al}_2\text{O}_3$ nano-composites using cibacron red dye. The photocatalytic efficiency of different compositional ratios were investigated and the highest recorded efficiency was 74.89 % [40].

3.5. Effect of solution pH and photocatalysts dosage

The solution pH and amount of photocatalyst used for the degradation process are some of the critical parameters in the assessment of the degradation efficiency of dyes. Therefore, the influence of the pH of the solution was assessed in the range 3–9, and the results are presented in Fig. 7a. It shows that the degradation of the dye was highest in the acidic range of the solution (pH3) compared to the alkaline range. Similarly, the effect of the photocatalyst dosage was studied by varying the concentration of $\text{CuO}/\text{Al}_2\text{O}_3$ from 0.5 to 2.5 g/L, was studied on the degradation of 20 mg/L MO concentration at pH = 3. The result presented in Fig. 7b display an insignificant increase in the degradation of MO in the absence of $\text{CuO}/\text{Al}_2\text{O}_3$, confirming that there was no much effect on the degradation of the MO without the catalyst. The efficiency of MO degradation was increased with increasing concentration of the catalyst and the highest results was achieved with the use of 2.5 g/L. This remained almost constant at this high concentration of the catalyst and could be ascribed to the effect of the increased active site on the surface of the photocatalyst as well as improved photo absorption property. Higher amount of $\text{CuO}/\text{Al}_2\text{O}_3$ implies more active sites that can absorb more photons in the solution. For example, the increase in the catalyst dosage from 0.5 g/L to 2.5 g/L increased the percentage degradation from 46.7 to 94 % after irradiating for 180 min. The

Table 1
Summary of band gap variation with temperature of calcination.

Samples	Temperature (°C)	Band gap energy (eV)
Al_2O_3 (900)	900	3.8
Al_2O_3 (1000)	1000	4.2
Al_2O_3 (1100)	1100	4.4
$\text{CuO}/\text{Al}_2\text{O}_3$ (1000)	1000	4.3

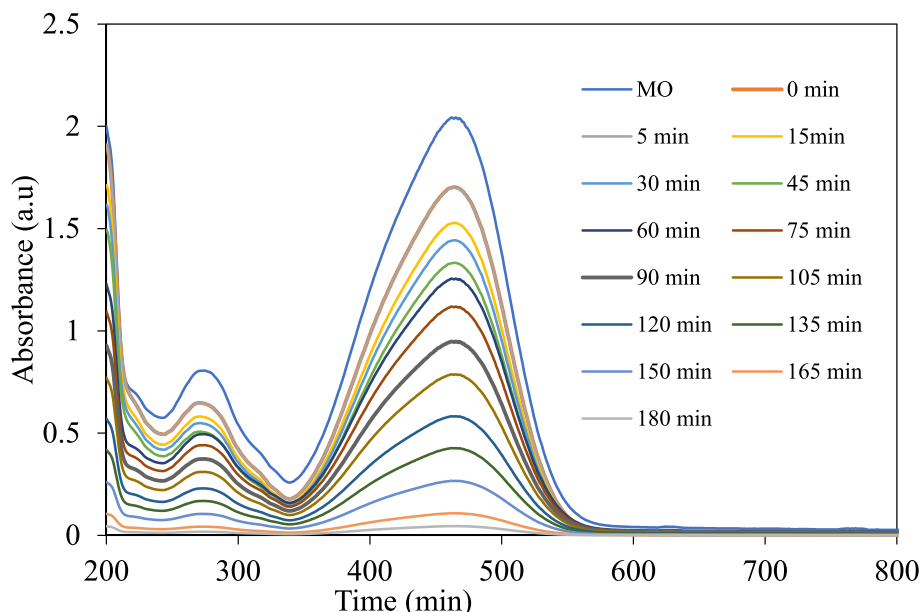


Fig. 6. UV-vis absorption spectra of photocatalytic degradation of MO using $\text{CuO}/\text{Al}_2\text{O}_3$ nanocomposite.

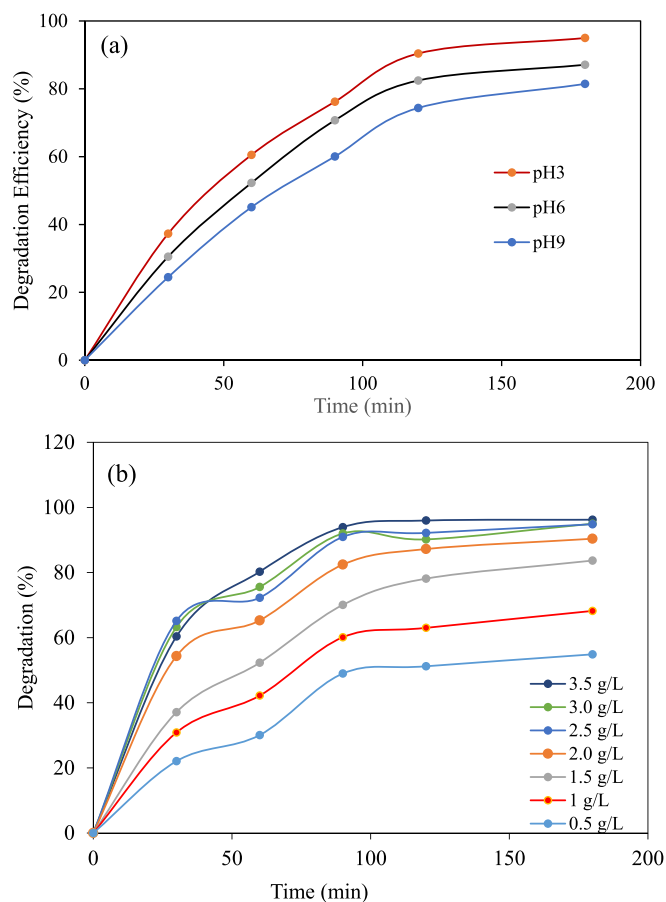


Fig. 7. Effect of CuO/Al₂O₃ nanocomposite loading on the photo enhanced degradation of 20 mg/L solution of MO at the pH: 3.0).

enhanced degradation of MO achieved with 0.25 g/L might be due to the increase in the generation of hydroxyl radicals due to the availability of surface active sites [74]. However, an excessive catalyst dose (above 2.5 g/L) does not display a distinct positive effect on the MO degradation due to the impedance in the light penetration and light scattering by the CuO/Al₂O₃. Subsequently, excess dosage has the tendency to decrease the generation of hydroxyl radicals, and facilitates the agglomeration as well as the sedimentation of the photocatalyst particles in the solution [75]. These results compare reasonably to the results reported for other similar heterojunction photocatalysts [36,76,77].

3.6. Effects of MO initial concentration

Methyl orange concentrations ranging from 20 to 110 mg/L were used to establish the effect of the initial MO concentration on the photocatalytic activity of CuO/Al₂O₃ and the result is presented in Fig. 8. The best degradation efficiency of the catalyst on MO was observed at the lowest MO concentration. After 180 min of light irradiation, about 94 % of the dye was photodegraded with the initial concentration of 20 mg/L, while 50, 80 and 110 mg/L reached 80.5, 65.1, 45.3 and 28 % efficiency, respectively. The possible reason might be the visible light screening effect of the MO and the increased formation of hydroxyl radical (\bullet OH) on lower concentration of dye compared to the higher dye concentration [65]. At high concentration of MO, a high absorption of visible light may be absorbed by the MO molecules instead of absorption by CuO/Al₂O₃. Hence, there is a shielding of the incident light by the high concentration of MO, thereby resulting in the impedance of the absorption of light by the CuO/Al₂O₃ catalyst, and this reduces the photocatalytic property of the catalyst [78,79]. Therefore, the efficiency of degradation decreased from 94 to about 28 % when the initial dye

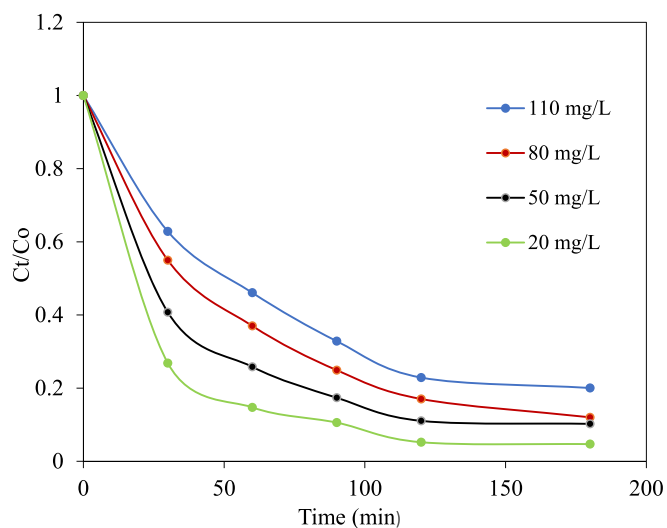


Fig. 8. Effect of initial concentration of MO on its photodegradation using CuO/Al₂O₃ (catalyst dosage: 100 mg and the solution pH: 3.0).

concentration was increased from 20 to 110 mg/L. MO degradation reaches a saturation limit at a lower concentration of the MO because the degradation efficiency increases with decreasing concentration of MO [80]. The results show that photo-enhanced reaction process is dependent on the concentration of the substrate, which is in agreement with other related studies [36,65,81].

To evaluate the recovery cycle of this photocatalyst, experiments were conducted to evaluate its reusability. Fig. 9 illustrates the results of the investigation using 2.5 g/L of the photocatalyst. Even after five consecutive cycles of recyclability assessment, the photocatalyst exhibited above 70 % in activity, suggesting they can be reused at least four times. This gradual decrease in activity with increasing reusability cycles is likely due to the loss of photocatalyst during the separation process.

4. Conclusion

The current study has described a simple approach to the synthesis of semiconductor heterojunction system of CuO/Al₂O₃. The structural properties of the nanocomposite were studied using XRD, while UV-vis spectroscopy was used for the optical characterisation, and SEM, TEM, and HRTEM analytical techniques explored the morphological

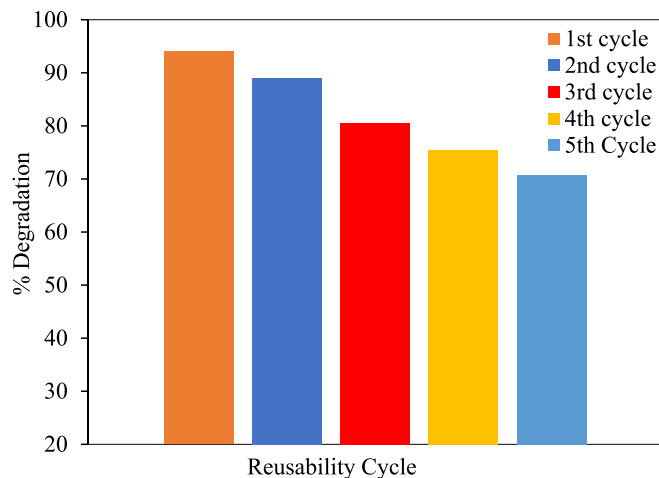


Fig. 9. Reusability cycles of mg/L CuO/Al₂O₃ nanocomposite (catalyst dosage: 2.5 g/L and the solution pH: 3.0).

properties. The absorption spectrum revealed band around 340 nm ascribable to the CuO. Both the SEM and TEM micrographs confirmed agglomerated spherical shaped nanocomposite of CuO/Al₂O₃. The diffraction patterns from the XRD measurement confirmed increased crystallinity of the Al₂O₃ as temperature increased, and subsequent formation of nanocomposite composed of hexagonal Al₂O₃ and monoclinic phase CuO. The crystallite size of the pristine Al₂O₃ was calculated to be 45.2, 48.4 and 56.8 nm. The nanocomposite showed to be effective in degrading methyl orange under visible light irradiation, with over 80 % degradation efficiency reported at the optimal conditions of 2.5 g/L catalyst dosage and 20 mg/L of MO initial concentration. Therefore, this nanocomposite has potential for the degradation of dyes in wastewater and may be further improved to address the challenges of water pollution, which unfortunately has been on the rise. Future research may involve exploring the possibility for large-scale production for application in wastewater treatment plants, the encapsulation of this heterojunction semiconductor photocatalyst into polymeric matrices to ensure the safety of nanomaterials as their usage in addressing several environmental pollution challenges continues to attract attention.

CRedit authorship contribution statement

Hanan Alhussain: Writing – original draft, Resources, Formal analysis. **Hela Ferjani:** Writing – original draft, Formal analysis. **Opeyemi A. Oyewo:** Writing – review & editing, Methodology. **Seshibe Makgato:** Resources. **Damian C. Onwudiwe:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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