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Kinetic Study of 4-Nitrophenol Sonocatalytic Degradation

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Abstract

A heterogeneous CuO/Al_2O_3 (9CuA) catalyst was synthesized by the impregnation method and used in the heterogeneously catalyzed, ultrasonically enhanced degradation of 4-nitrophenol (4-NP). The produced catalyst was characterized using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Brunauer-Emmett-Teller (BET) analysis. The effects of operating variables such as catalyst dosage (0 -1.4 g/L), hydrogen peroxide dosage (0 - 40 mM), initial pH (3.0 - 6.0), degradation system temperature (50 - 70 °C), and initial concentration of 4-NP (25-300mg/L) on the degradation of 4-NP were investigated at constant ultrasonic power and frequency of 240 W and 40 kHz respectively. The rate of degradation was found to increase with increases in system temperature from 50-70 °C, in the initial solution pH from 3.0-6.0, and in the initial concentration of 4-NP from 300–25 mg/L. The results also showed that the 4-NP initial concentration of 25 mg/L was degraded to 0.03 mg/L, which is below the United States Environmental Protection Agency (USEPA) acceptable limit of 0.06 mg/L in potable water. Furthermore, the degradation of 4-NP in the system followed pseudo-second-order kinetics with respect to 4-NP, with a rate constant of 0.062 $ppm^{-1}min^{-1}$ at 70 °C. Catalyst stability, assessed by reusability, was good, as 4-NP degradation slightly declined from 99% to 94% after five consecutive experimental runs. The results demonstrate that the ultrasonic-enhanced CuO/Al_2O_3 system is an efficient and reusable treatment method for reducing 4-nitrophenol in water to environmentally acceptable levels.

Keywords: *Ultrasonic-enhanced, Catalytic, Cavitation, Fenton-like, Hydroxyl, Synergistic, Degradation, Kinetics.*

1.0 Introduction

One of the major environmental problems today is water pollution with varying concentrations of organic compounds, notably nitrophenols. Nitrophenols are widely used as raw materials and intermediates in the production of explosives, pharmaceuticals, pesticides, dyes, and other products [1]. Unfortunately, they are inadvertently discharged into water bodies via industrial effluents, constituting pollutants. Among these, 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), and 2, 4-dinitrophenol (DNP) are listed in the "Priority Pollutants List" by USEPA because their discharge into the environment poses significant health risks to both humans and aquatic fauna due to their high carcinogenicity [2]. As such, it is necessary to reduce them to a harmless concentration at least before the industrial wastewater is discharged into the environment.

Various advanced oxidation processes (AOPs) have been studied to achieve this reduction. These include ultrasonication (US)/Fenton's reagent [3], ultraviolet (UV)/ozone [4], US/ozone [5], microwave/CuO-Al_2O_3 [6] and US/(CuO, TiO_2, CCl_4) [7]. Ultrasonication can generate $HO^{\bullet}$ through the transient collapse of cavitation bubbles driven by ultrasound waves or by direct pyrolysis occurring around the collapsing bubble [8].

In ultrasound-enhanced catalytic degradation of 4-NP, Mishra *et al.* (2011) investigated the ultrasonic degradation of 4- NP in the presence of CCl_4, TiO_2, O_3, and CuO additives [9]. They found that degradation was enhanced when the US was combined with CuO (30.5%) compared with the US alone (23.2%). They deduced that the observed increase could be attributed to CuO particles serving as nuclei for additional cavitation. Furthermore, the low degradation (30.5%) was attributed to the lack of catalyst support.

US/(CuO/Al_2O_3) is a heterogeneous Fenton-like AOP that can effectively catalyze the oxidation of organic pollutants at neutral or nearly neutral pH conditions, which is beneficial for the in-situ remediation of wastewater. The porous Al_2O_3 support plays a vital role in the dispersion of the CuO particles [10].

In microwave-enhanced catalytic degradation (MECD) of nitrophenol, Pan *et al.* (2015) used CuO/Al_2O_3 as a Fenton-like catalyst under microwave irradiation to degrade 4-NP [6]. They measured 93 % 4-NP degradation within 6min under optimized conditions. Atta *et al.* (2012) studied microwave-enhanced catalytic degradation of 2-NP on alumina-supported copper oxides. 95% degradation was recorded at pH 4; 69% at pH 10 at 60 °C in the presence of 6-30 mM H_2O_2; only 3% degradation was observed in the absence of H_2O_2.

Although the use of microwave irradiation in MECD of nitrophenols was found to be very effective, deactivation of catalyst active sites due to the formation of organic intermediates, which limits the practical

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application of the process, was reported during the catalyst reusability test [6][11]. This limitation could be overcome by ultrasonication of liquid media, which creates microstreaming, microturbulence, and shockwaves that can, in turn, accelerate mass transfer rate, break up the catalyst into smaller particles with higher surface area, and also maintain the activity of the catalyst due to the resultant continuous cleaning of its surface [12]Although degradation of many organic pollutants has been reported in the open literature by combining ultrasonic cavitation with one or more AOPs and other additives [13], there is a scarcity of records in the extant literature on the ultrasonic catalytic degradation of nitrophenols in the presence of H_2O_2 over copper/alumina. Thus, the present study focused on ultrasonic catalytic degradation of 4-NP over copper/alumina catalysts. The effects of various parameters, such as initial pH, reaction time, temperature, hydrogen peroxide, and catalyst dosage, have been well reported.

2.0 Materials and Methods

2.1 Materials and apparatus

Analytical grade British Drug Houses (BDH) of 4-nitrophenol (99 % purity) and $Cu(NO_3)_2.3H_2O$ (99 % purity), H_2O_2 (30 %w/v), Al_2O_3, NaOH, and HCl were obtained from Koch-Light Laboratories Ltd, Colnbrook, Bucks, England. All the solutions used in the experiment were prepared with distilled water.

2.2 Catalyst preparations and characterization

The catalyst was prepared using an impregnation method. Typically, Cu $(NO_3)_2.3H_2O$ and Al_2O_3 were used as precursors of the CuO catalyst and the Al_2O_3 support—a measured amount of the precursor to give 9 wt. % copper on alumina was dissolved in distilled water. The alumina was then gradually added to the copper solution while it was stirred continuously at 300 rpm and ambient temperature using a magnetic stirrer. The resulting mixture was evaporated to dryness by heating at 70 ^oC. The evaporated solids were further oven-dried at 110 °C for 8 h, then calcined at 550 °C for 4 h to form the catalyst.

XRD patterns of the catalysts were then determined using a PAN Analytical/ Empyrean diffractometer with $Cu - K\alpha$ as the radiation source ($\boldsymbol{\lambda}$ =1.540598 nm), operating under a voltage of 45 kV and a current of 45 mA. The diffraction angle (2θ) was varied from $10 - 80°$.

The BET technique under liquid nitrogen characterized the catalysts' specific surface area, pore-volume, and pore diameter after pretreatment at $1 \times 10^{-4}\ Pa$ and 120 ^oC. The surface morphology of 9CuA catalysts was determined using a Phenom Pro-X Scanning Electron Microscope (SEM) at an accelerating voltage of 15 kV, a working distance of 12 mm, and a magnification of 28,000×.

2.3 Degradation procedure

The degradation experiments were performed in an ultrasonic cleaner (Model PS-40A, Ningbo Xianzhi-Technology Co., China), with a fixed frequency of 40 kHz and fixed ultrasonic power of 240W. Typically, 50 ml of simulated 4-NP solution was poured into a 100 ml conical flask. Before sonication, the pH of the solution was adjusted to the desired level using a dilute solution of HCl or NaOH. After sonication, the solution pH was adjusted to the desired level using a dilute HCl or NaOH solution, and an appropriate amount of H_2O_2 was then added. The resulting mixture was sonicated, and an aliquot was withdrawn and centrifuged to measure the residual 4-NP.

2.4 Analytical methods

A UV–vis spectrophotometer (YUCHENGTECH-752N) was used at 316 nm to measure the absorbance of 4-NP. These absorptions were then converted to concentrations using an absorption-concentration calibration curve prepared by measuring the absorptions of standard 4-NP solutions at known concentrations. The percentage degradation of the 4-NP was then calculated as follows:

$$R(\%) = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

where R % is the percentage degradation of 4-NP; C_o and C_t are concentrations of 4-NP before and after degradation, respectively.

3.0 Results and Discussion

3.1 Catalyst characterizations

Figure 1 illustrates the XRD patterns of the alumina support (A) and that of the synthesized (9CuA) catalyst. The diffraction peaks at 2θ of 25.54, 35.17, 37.80, 43.37, 57.55, and 66.45 ° observed for the support (A) are characteristic of alumina [14]. New peaks (asterisks in the upper diffractogram of Figure1) were observed after loading the active metal on the support. They are also proportionally smaller due to the lower CuO (9 wt. %). For CuO, the prominent diffraction peaks are located at 35.4^o, 38.7^o, and 48.8^o [11].

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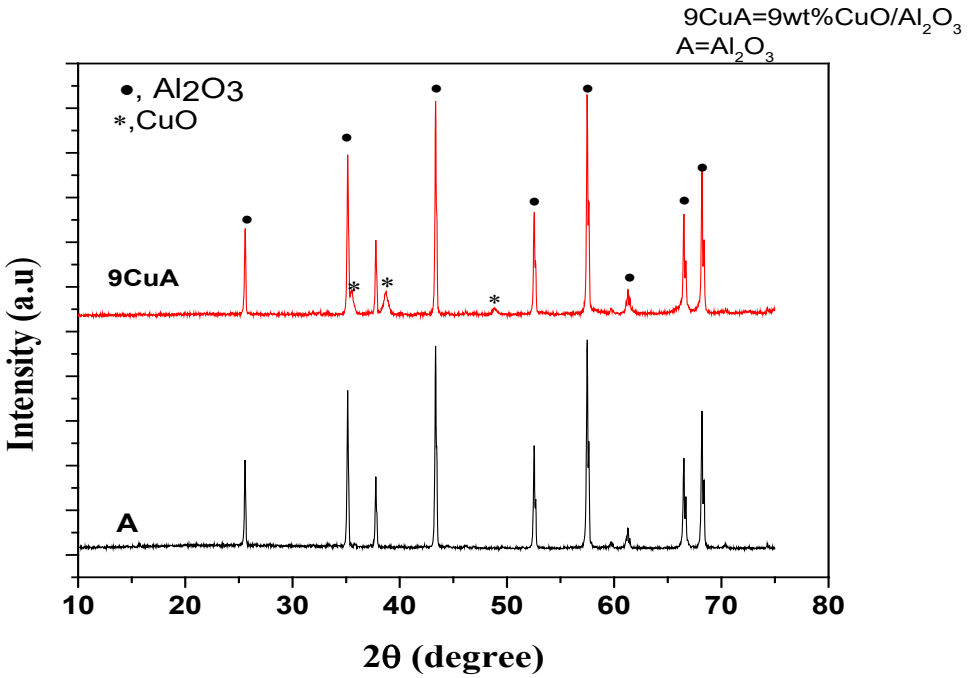

Figure 1: XRD patterns of the synthesized catalyst and support.

Table 1 presents the BET surface areas, average pore diameters, and pore volumes of thealumina support and the catalysts. When the catalyst carrier was impregnated with the active copper oxide, the pore volume raised by less than 1%, and the surface area increased by only 1.4%, and the pore volume by less than 1%. In comparison, the pore diameter decreased by about 4%, meaning these properties were comparable. This suggests that there was no agglomeration of CuO, so it was well dispersed on the Al_2O_3 support as desired, and that there was minimal pore blockage.

Table 1: BET measurements for the Al_2O_3 support and the synthesized CuO/Al_2O_3 catalyst

Sample	S_{BET}	Pore Volume (cm^3g^{-1})	Average Pore Diameter (nm)
A	464.948	0.422	2.920
9CuA	471.270	0.425	2.800

The SEM images of the alumina catalyst carrier (A) and that of the synthesized 9CuA catalysts (B) are shown in Figure 2. It can be observed that the surface morphology of A appears to be sheet-shaped, with closely packed particles of irregular sizes. The SEM image of the synthesized catalyst B shows small, dispersed, whitish flakes, consistent with copper oxide impregnated on the alumina support.

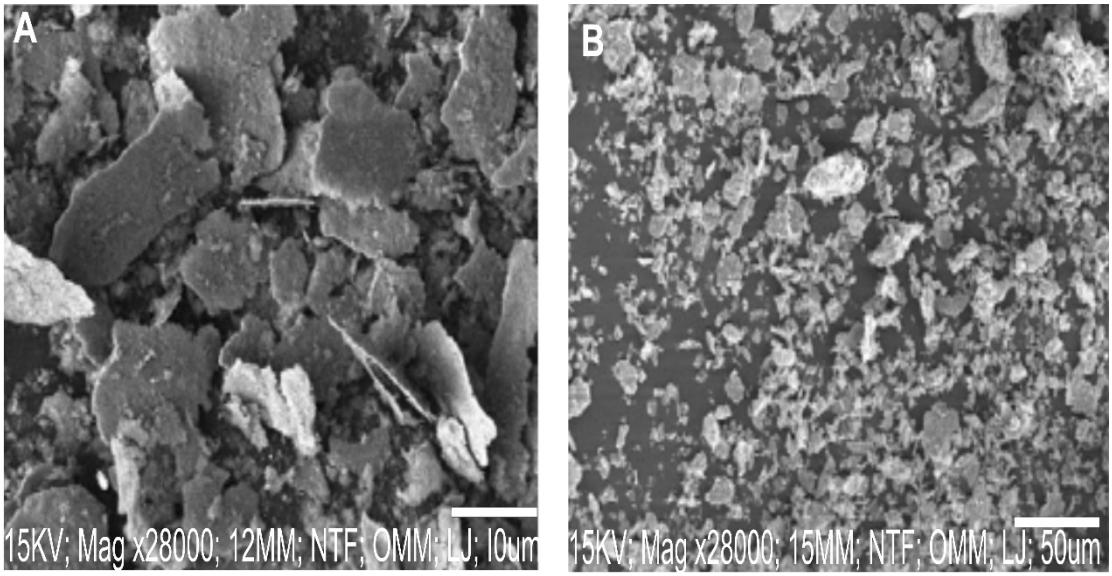

Figure 2: SEM images of the Al_2O_3 support (A) and the synthesized CuO/Al_2O_3 catalyst (B)

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This agrees with both the diffractogram and the BET measurements for the synthesized catalyst, as the surface area of the catalyst increased when the support was impregnated with the active metal and new peaks appeared in the XRD. Therefore, it can be deduced that the impregnation method employed did not block the pores of the support. Similar results were reported by [15]. According to [16];[11] blockage only occurs when there is sufficient contact time between the support and the solution used for impregnation. This finding is further supported by the BET measurement (Table 1), which shows a minimal decrease in pore diameter upon impregnation of the support with copper oxide.

3.2 Initial degradation results for 4-NP with various configurations

The initial degradation of 4-NP with various configurations was investigated at 25 mg/L 4-NP. Results, a sonic power of 240 W, pH 6, and a 100-min reaction time, and the results are shown in Figure 3. It can be seen that when 20 mM H_2O_2 was added, no measurable degradation was observed. This is because the heat energy at room temperature was not enough to activate the thermal dissociation of H_2O_2 to produce hydroxyl radicals.

Furthermore, no degradation was measured when 1g of the catalyst was introduced into the aqueous solution of 4-NP without H_2O_2. This is because there were no H_2O_2 to be dissociated by the catalyst to form hydroxyl radicals to react with the 4-NP to form degradation products. However, a combination of 20 mM H_2O_2 and 1g of the catalyst in 25 mg/L of 4-NP without ultrasound, with the other conditions remaining constant, gave 19 % degradation. This implies that the presence of the catalyst can activate the dissociation of H_2O_2 to produce hydroxyl radicals to a small extent. In another control experiment, sonication of 25 mg/L of 4-NP at sonic power of 240 W, pH 6, and 50 ^oC for 100 min without H_2O_2 or catalyst, only 4.3 % degradation was measured.

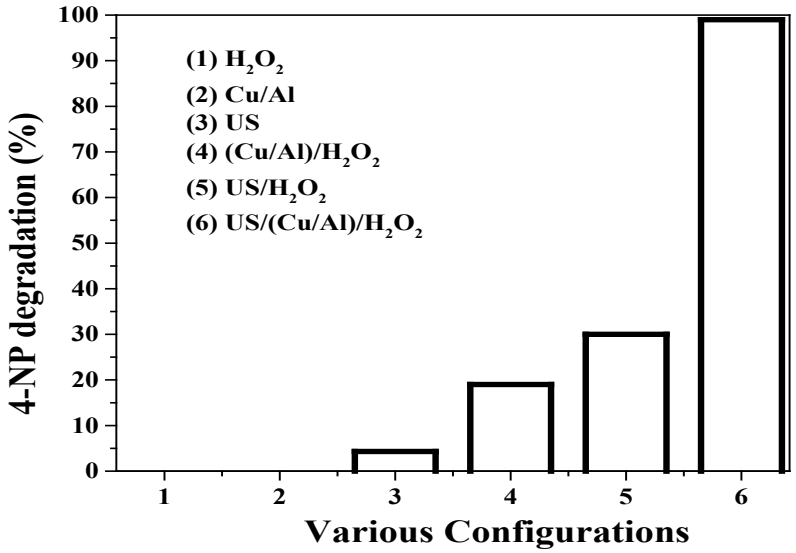

Figure 3: Degradation of 4-NP with various configurations

This shows that ultrasonication alone without a significant source of hydroxyl radicals is incapable of substantial degradation of 4-NP. Therefore, ultrasound combined with oxidant (H_2O_2) was applied to achieve higher degradation efficiency. When 20 mM H_2O_2 was added with no catalyst at 240 W sonic power with other conditions remaining the same, 30 % degradation was measured. This increase in degradation efficiency is attributable to the ultrasonic dissociation of H_2O_2 to produce hydroxyl radicals [17]. This result also implies that 240 W power dissociates H_2O_2 better than 1 g of catalyst. A higher catalyst dosage and the synergistic effect of catalyst and ultrasound in the presence of H_2O_2 may boost degradation. When 20 mM H_2O_2 was added with 1g catalyst at 240 W sonic power with other conditions remaining the same, 99 % degradation was measured. This increase in degradation efficiency is attributable to the fact that in addition to dissociating H_2O_2 to produce hydroxyl radicals, the catalyst provides additional sites for cavitation.

3.3 Effect of initial concentration of 4-nitrophenol on its degradation

Table 2 displays the effect of the initial 4-NP concentration on its ultrasonic catalytic degradation under conditions of pH 4, 1 g catalyst/0.05 L mixture, 20 mM H_2O_2, 70 °C, 240 W, and 100 min. It can be seen that increasing the initial concentration of 4-NP from 25 - 300 mg/L does not significantly decrease the percentage degradation. The percentage degradation was about 99% for 25, 50, and 100 mg/L initial concentrations, and 98% and 97% for 100 and 300 mg/L initial concentrations, respectively.

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The decrease in percentage degradation as the initial concentration increases is due to a constant amount of HO•, since the concentration and amount of H_2O_2 remain the same (fixed volume of the reaction mixture). However, as the concentration of 4-NP increases, its amount in the aqueous solution increases since the volume of the reaction mixture is fixed. Therefore, the percentage degradation must decrease.

Table 2: Effect of Initial Concentration on the Degradation of 4-NP

4-NP Initial Concentration(mg/L)	Degradation (%)	Residual 4-NP after Degradation (mg/L)
25	99.890	0.030
50	99.890	0.030
100	99.720	0.060
200	98.249	3.500
300	97.486	7.540

3.4 Effect of catalyst dosage

The effect of catalyst dosage on the degradation of 4-NP using 25 mM H_2O_2 at a pH 6, 60 ^oC reaction temperature, 60 min reaction time, and sonication power of 240 W in 50 ml reaction mixture, is presented in Figure 4. It can be seen from Figure 4 that when no catalyst was used in the 4-NP solution, the extent of degradation reached 19 %. This shows that energy produced due to ultrasonic irradiation can activate the thermal dissociation of H_2O_2 to a certain extent to produce hydroxyl radicals [18].

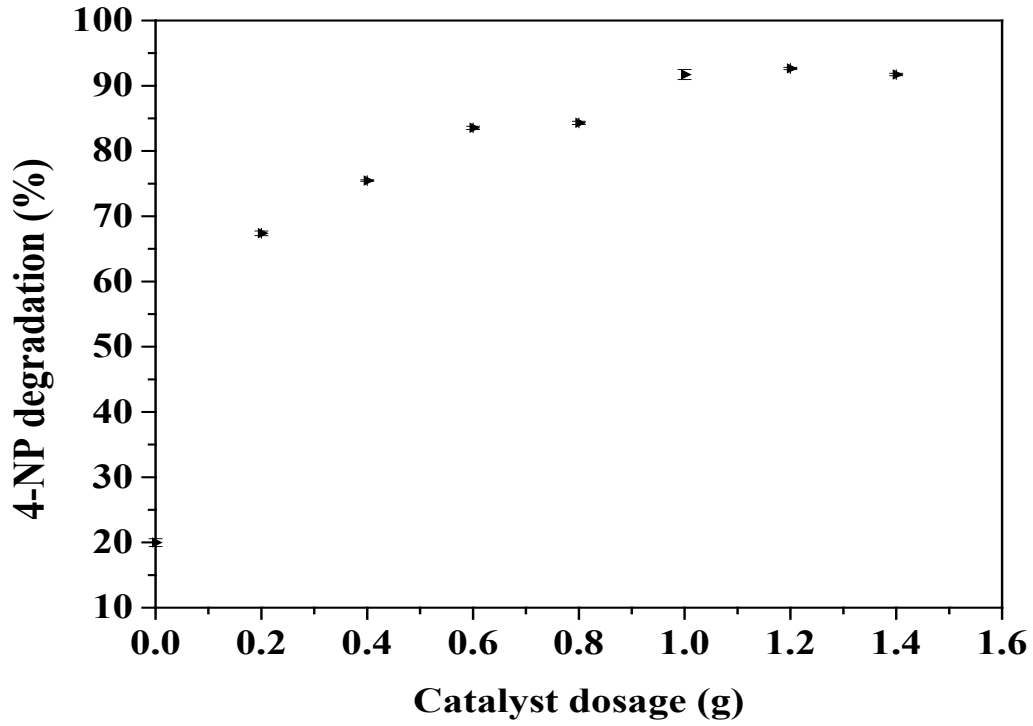

Figure 4: Effect of catalyst dosage on 4-NP degradation using 9CuA catalyst at 60 min reaction time, pH 6, 60 ^oC, 240 W sonication power, 25 mM H_2O_2

As the catalyst dosage was increased, degradation increased until a dosage of 1.0 g/0.05 L of the reaction mixture, peaking at 91 %. Further increases in the catalyst dosage did not increase the extent of degradation beyond this value. This flattening of the degradation curve is attributable to the concentration and amount (fixed amount of reaction mixture) of H_2O_2 remaining constant as the catalyst dosage increases, and no more H_2O_2 is to be decomposed by the catalyst above 1.0 g/ 0.05 L of the reaction mixture.

3.5 Effect of H_2O_2 concentration on 4-nitrophenol degradation

Figure 5 illustrates the effect of H_2O_2 concentration on the 4-NP degradation in the range of 0 - 60 mM of H_2O_2 oxidant, 1 g/0.05 L reaction mixture catalyst dosage, 60 min reaction time, pH of 6, the temperature of 60 ^oC, and sonic power and frequency of 240 W and 40 Hz, respectively.

The effect of H_2O_2 concentration on the 4-NP degradation in the range of 0 - 60 mM of H_2O_2 oxidant, 1 g/0.05 L reaction mixture catalyst dosage, 60 min reaction time,pH of 6, the temperature of 60 ^oC, and sonic power and

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frequency of 240 W and 40 Hz, was investigated as illustrated in Figure 6. In the absence of hydrogen peroxide, the percentage degradation was 23 %. The increase in percentage degradation relative to ultrasonication alone, as shown in Figure 3, can be attributed to the presence of solid catalyst particles, which introduce discontinuities in the liquid medium and facilitate the formation of cavitation nuclei. [9]; [19]. The percentage degradation of 4-NP increases steeply from 55%–89% as the H_2O_2 concentration is increased from 10 mM to 20 mM, then gradually declines beyond. This suggests the optimum for hydroxyl radical dosage is 20 mM H_2O_2.

The decline beyond 40 mM and low degradation below 20 mM is attributable to the following reasons: (i) At concentrations below 20 mM, there was not enough H_2O_2 to generate enough HO• radicals. (ii) However, above 40mM, H_2O_2 can act as a scavenger of HO (Eqs. 2 and 3) [15];[20].

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (2)$$

$$OH^{\bullet} + HO_2^{\bullet} \rightarrow O_2 + H_2O \quad (3)$$

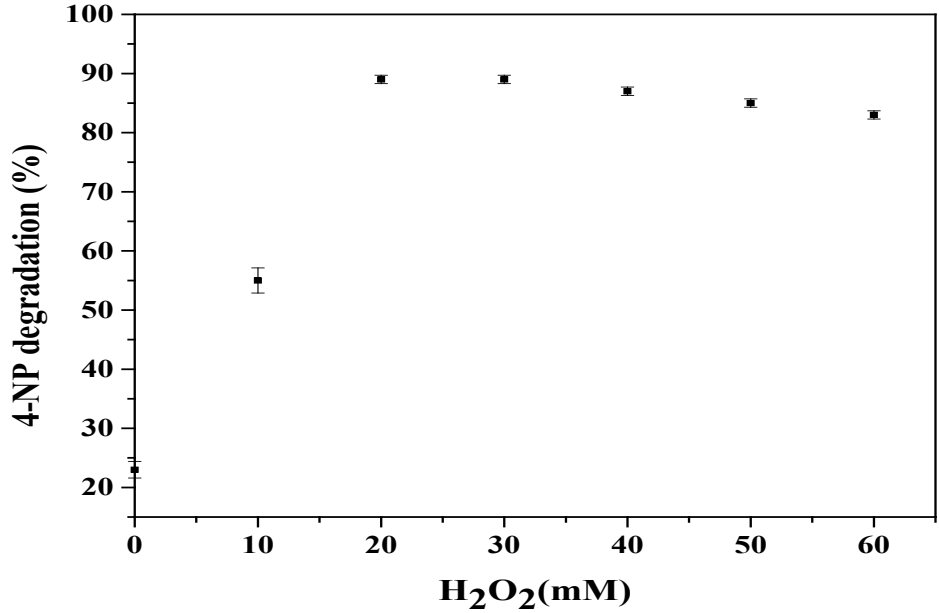

Figure 5: Effect of H_2O_2 concentration on 4-NP removal using 9CuA catalyst at 60min reaction time, pH of 6, the temperature of 60 °C, and catalyst dosage of 1 g/0.05 L

3.6 Effect of pH on 4-NP removal

The pH of the solution is an essential factor the physical and chemical properties of phenolic compounds. The effect of pH on 4-NP degradation at a temperature of 60 °C, 240 W ultrasonic power, 1g/0.05 L catalyst dosage, 20 mM of H_2O_2, and 5-100 min was investigated, and the results are shown in Figure 6.

The degradation of 4-NP increases as the pH of the reaction medium decreases. Furthermore, 4-NP was almost completely degraded (98 %) after 20 min of irradiation at pH 3.0. Also, degradation declined slightly when the initial pH was increased from 3.0 to 4.0, but remained above 94% beyond 60 min. Further increasing the pH resulted in a sharp decrease in degradation. At pH 5.0, the percentage degradation dropped to 66%, and at 6.0, it dropped to 62% after 20 min. This phenomenon is similar to that reported by some studies [21] and is attributable to several reasons. One reason is that - lower pH promotes H_2O_2 decomposition to HO• while it retards recombination of the free radicals [10]. Another reason could be the preponderance of the undissociated form of 4-NP as the solution pH decreases [21]. This undissociated form of 4-NP, which is volatile and hydrophobic, makes it possible to evaporate into the core cavity (gas-liquid film region) [22]. The higher hydrophobicity of the undissociated form than the dissociated form allows it to accumulate at the bubble water interface [23]. Therefore, the overall degradation of 4-NP at low pH is considered to occur in both the gaseous and interfacial film regions by pyrolysis and free radical attack [24]; [25]. An additional reason may be that the oxidation potentials of HO• increase as the medium becomes more acidic [26]. The HO• oxidation potential in acidic solutions is 2.78 V, while in neutral and basic solutions it is ≤ 1.80 V [27].

On the other hand, under less acidic conditions (i.e., when the pH approaches 7), the dissociated (ionic) form predominates and is hydrophilic (non-evaporative). Therefore, in this pH region, degradation is presumed to occur only in the film and bulk solution, leading to reduced degradation. Also, at higher pH values, HO• radicals

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recombine to form H_2O_2, reducing radical generation and further inhibiting the degradation process [27]. A further examination of Figure 6 shows that the degradation values for the four different pH investigated appear identical at 80 min.

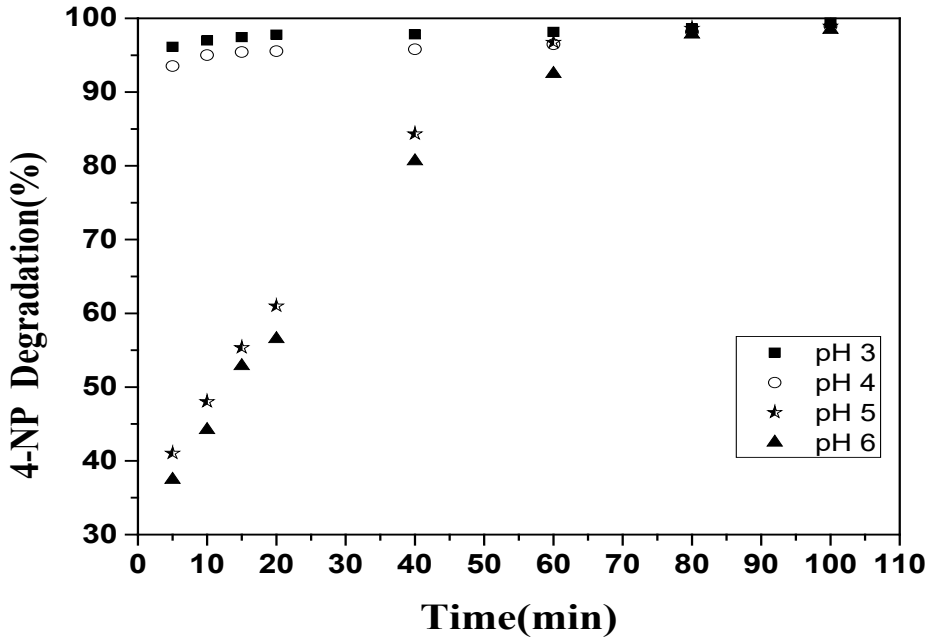

Figure 6: Effect of pH on 4-NP degradation using 9CuA catalyst up to 100 min reaction time, at 60 ^oC, 1g/0.05 L of catalyst, 240 W ultrasonic power, and 20 mM H_2O_2

3.7 Effect of Temperature on 4-NP degradation

Figure 7 shows the effect of solution temperature on the degradation of 4-NP at an initial concentration of 25 mg/L, pH 4, and 20 mM H_2O_2, with 240 W sonic power for different times up to 100 min. Previous work reported a link between sonochemical degradation of organic pollutants and bulk solution temperature [20].

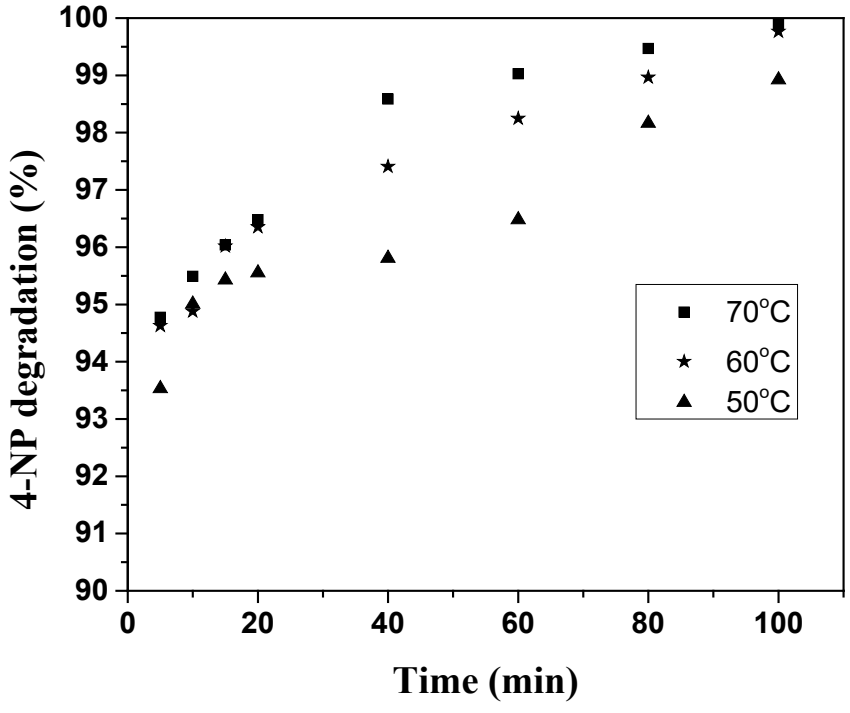

Figure 7: Effect of Temperature on 4-NP degradation using 9CuA catalyst at different reaction times, pH 4, 1 g/0.05 L of catalyst, and 20 mM of H_2O_2

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In the first 5 min. Under ultrasonic irradiation at 50 °C, degradation was 92 %, while at 60 °C and 70 °C, degradations were 93 and 96 %, respectively, within experimental error. In contrast, at 60 °C and 70 °C, degradations were 93% and 96%, respectively, within experimental error. Further sonication for 100 min increased the degradation to 98.9, 99.8, and 99.9% at 50, 60, and 70 °C, respectively. These results show a slight increase in degradation with increased temperature, with the highest degradation measured at 70 °C. A similar result was obtained in to 90 °C, with 70 °C reported as the optimum temperature [28]. This is because an increase in temperature favorably affects the kinetics of the reaction by increasing the reaction rate constant according to the Arrhenius equation. Another reason is that more HO• radicals are generated at higher temperatures [26]. Furthermore, increasing the temperature leads to a simultaneous increase in the vapor pressure of water in the bulk solution and that of the steam inside the bubble, thus increasing the gaseous region, which leads to increased degradation.

3.8 Catalysts Reusability

To investigate the reusability of the catalyst, the 4-NP degradation efficiencies over 9CuA and under ultrasonic irradiation for different cycles were assessed, and the results are shown in Figure 8. The 4-NP removal efficiency remained steady after four cycles at over 97 % degradation with only a slight decrease of about 5 % in the fifth cycle. This implies that the catalyst can still work effectively even in the fifth run under ultrasonic irradiation.

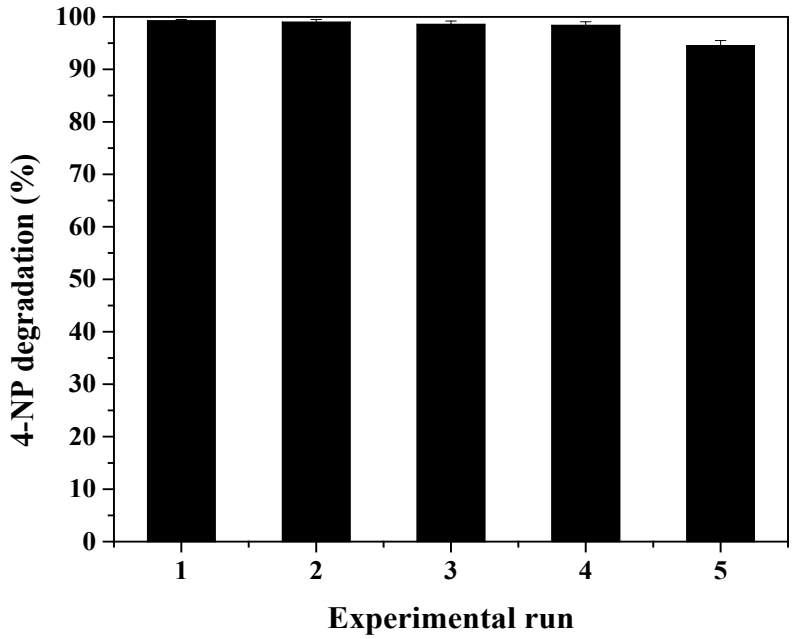

Figure 8: Stability of the Catalyst 9CuA at 60 °C, pH of 4, 20 mM H_2O_2, and reaction time of 100 min

3.9 Degradation Kinetics of 4-NP

In the degradation of 4-NP by the ultrasonic Fenton-like mechanism, the resulting H_2O_2 and HO• were strong oxidants. By cleavage of the C-NO2 and C-C bonds during ultrasonication via radical attack, 4-NP was degraded and mineralized [9]. Therefore, the kinetics of the reaction were investigated by testing both pseudo-first-order and pseudo-second-order kinetics models, taking the following assumptions: (i) the Hydroxyl radicals (HO•) produced are not used up as 4-NP is being degraded. (ii) the reactions occur within the cavity interior, gas-liquid interface, and in the bulk solution by hydroxyl radicals (HO•) attack. The experimental data were found to fit a pseudo-second-order kinetic model best at 70 °C. The rate of disappearance of 4-NP using a homogeneous non-catalytic model is described as follows:

$$4-NP + [\mathrm{HO}\bullet] \rightarrow intermediates \rightarrow Products \quad (4)$$

$$-r_{4-NP} = \frac{\mathrm{d}[4-\mathrm{NP}]}{\mathrm{dt}} = K_{app}\,[4-NP]^2 \quad (5)$$

$$\frac{\mathrm{d}[4-\mathrm{NP}]}{\mathrm{dt}} = K_{app}\,[4-NP]^2 \quad (6)$$

$$\frac{\mathrm{d}[4-\mathrm{NP}]}{\mathrm{dt}} = K_{app}[4-NP] \quad (7)$$

where K_{app}=$K[\mathrm{HO}\bullet]$

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The rate constant (K) and the excess $[HO\bullet]$ are lumped together as the apparent rate constant (K_{app}) in (Eq. 2)

$$\frac{dC}{C^2} = K_{app}dt \quad (8)$$

Integrating the equation between an initial concentration at time zero and a final concentration at time t gives

$$\frac{1}{C_t} = K_{app}\ t + \frac{1}{C_o} \quad (9)$$

A plot of $\frac{1}{C_t}$ against t gives a straight line with slope K_{app} and intercept $\frac{1}{C_o}$

To explore the feasibility of this proposed model, the experimental results are shown in Figure 9 for the degradation of 4-NP at 70 °C. The degradation followed pseudo-second-order kinetics with respect to the concentration of 4-NP.

The model-calculated apparent rate constant and correlation coefficient were 0.062 $ppm^{-1}m^{-1}$ and 0.997, respectively.

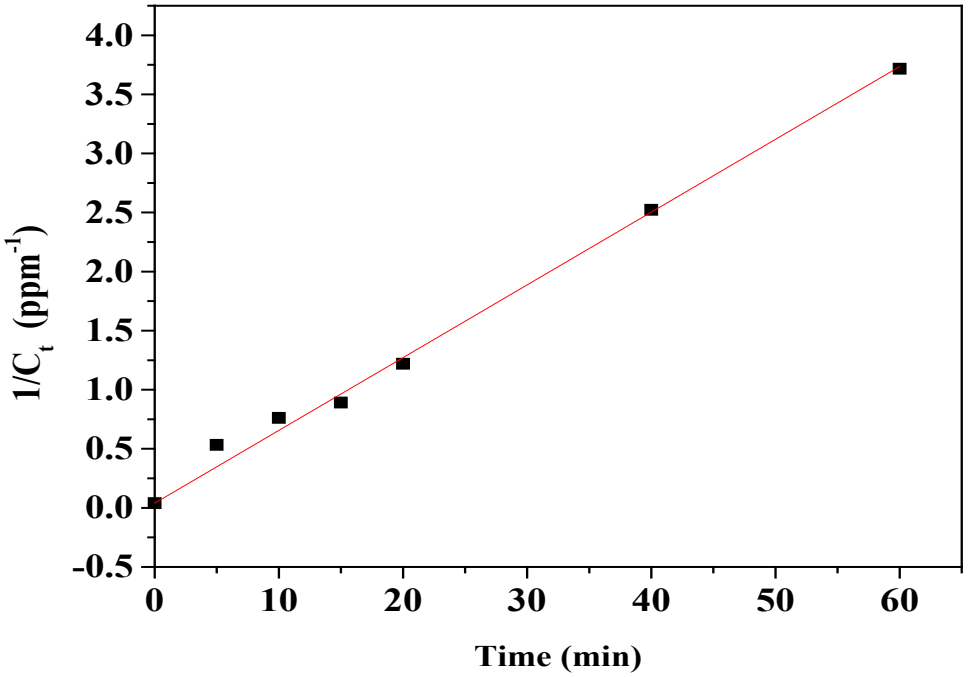

Figure 9: Pseudo- second order plot of 4-NP degradation at 70 °C

4.0 Conclusion

The study demonstrated that ultrasonic irradiation effectively enhanced the catalytic degradation of 4-nitrophenol (4-NP) in aqueous solution using alumina-supported copper oxide. Characterization results from XRD, BET, and SEM confirmed the successful formation of the CuO/Al_2O_3 catalyst and provided evidence of its structural, surface, and morphological properties, which supported its catalytic performance. The effects of catalyst dosage, hydrogen peroxide, pH, and temperature on the degradation were studied. It was found that ultrasonic irradiation enhanced the catalytic degradation of 4-NP. Also, a significant oxidizing effect of H_2O_2 on 4-NP degradation was measured. In its absence, only about 30 % degradation was achieved. The catalyst achieved over 90% 4-NP degradation at an H_2O_2 dosage of 20–40 mM after 60 min of reaction. The percent degradation of 4-nitrophenol increased as the solution pH decreased (more acidic), reaching 96 % (at pH 3), 93 % (at pH 4), 41 % (at pH 5), and 37 % (at pH 6) after 5 min of ultrasonic irradiation.

Interestingly, after 100 min of ultrasonic irradiation, more than 98% degradation was observed across all pH values, indicating that the pH difference is insignificant at longer times. Increasing the system temperature from 50 to 70 °C had minimal influence on the degradation of 4-NP. The results also show that the 9CuA catalyst exhibited good stability under ultrasonic irradiation even after five experimental runs in an acidic medium.

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