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Photocatalytic treatment of coffee shop wastewater using zinc oxide (ZnO) catalyst

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Abstract: This study aims to evaluate the effectiveness of the photocatalytic process using Zinc Oxide (ZnO) as a catalyst in reducing caffeine concentration and improving water quality parameters, including Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Suspended Solids (TSS), and pH. The investigated variables include the initial pH levels (4, 7, and 9) and ZnO catalyst concentrations (1000, 2000, and 3000 ppm), both with and without the addition of 0.01 M H_2O_2. The photocatalytic process was conducted under UVA illumination for 4 hours. Results indicated that the optimal condition was at pH 7 with a ZnO concentration of 3000 ppm, achieving a caffeine degradation efficiency of 74.58%. The COD value significantly decreased from 5203 mg/L to 4470 mg/L, while BOD slightly decreased from 948 mg/L to 917 mg/L. The lowest TSS value was recorded at pH 7 with 98 mg/L, indicating good ZnO stability under neutral conditions. The addition of H_2O_2 tended to reduce the final pH and enhance degradation performance at pH 9, but reduced caffeine degradation efficiency at pH 7 due to adsorption competition between H_2O_2 and caffeine on the catalyst surface. The photocatalytic method using ZnO effectively reduced caffeine levels and major pollutant parameters in coffee shop wastewater, demonstrating its potential as an environmentally friendly alternative for wastewater treatment technology.

Keywords: *Caffeine, Photocatalysis, Coffee shop wastewater, Degradation, Wastewater treatment.*

1. Introduction

The coffee processing industry is one of the fastest-growing sectors, particularly in coffee-producing countries such as Indonesia. According to Statistics Indonesia [1], national coffee production has increased by 11.07% since 2013. Despite this growth, coffee imports have also risen sharply by 148.9% since 2013, indicating a substantial increase in domestic coffee consumption [1]. This condition has driven the rapid expansion of commercial coffee-based enterprises, particularly coffee shops. With the amenities and ambience offered by modern coffee shops, coffee consumption has evolved from a daily necessity into a lifestyle element among urban communities [2]. Consequently, the volume of waste generated from coffee brewing activities has also increased, including both solid residues, such as spent coffee grounds, and liquid effluents. Although the scale of coffee shop wastewater is smaller than that of industrial coffee processing plants, it still contains complex organic compounds that can contaminate aquatic environments if improperly managed [3].

One of the key organic compounds found in coffee shop effluents is caffeine. Although caffeine is a naturally occurring alkaloid, its persistence in the aquatic environment makes it a potential pollutant of concern. At elevated concentrations, caffeine exhibits toxic effects on aquatic microorganisms, disrupts fish metabolism, and alters behavioral and reproductive processes in aquatic organisms [4, 5]. The chemical characteristics of this wastewater are typically represented by high values of Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), and Total Suspended Solids (TSS). Previous studies have reported COD levels ranging from 127 to 1576 mg/L, BOD around 65 mg/L, and TSS

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reaching up to 1417 ppm in coffee wastewater [3, 6]. The presence of phenolic compounds and other organic constituents can also disturb aquatic ecosystem balance and inhibit the growth of aquatic biota [7, 8].

A promising approach for the treatment of such wastewater is the photocatalytic process using Zinc Oxide (ZnO). ZnO is a semiconductor known for its high photocatalytic activity. Under ultraviolet (UV) irradiation, ZnO generates highly reactive hydroxyl radicals (•OH) capable of oxidizing and decomposing caffeine into simpler, environmentally benign compounds such as carboxylic acids, CO_2, and H_2O [9, 10].

The advantages of ZnO-based photocatalysis include its high efficiency in degrading organic pollutants without producing hazardous residues and its ability to perform effectively under various environmental conditions [5, 7]. Furthermore, optimization studies using advanced techniques such as response surface methodology (RSM) have demonstrated that both the synthesis and operational parameters of ZnO can be precisely adjusted to maximize photocatalytic performance, enabling effective application in industrial wastewater treatment [11, 12].

Given the growing environmental concern associated with coffee industry wastewater, this study aims to evaluate the potential of ZnO in degrading caffeine and to determine the optimal parameters to enhance photocatalytic efficiency, as assessed through TSS, COD, BOD, and pH values. The findings of this research are expected to contribute to the development of sustainable wastewater management systems for coffee-based industries and support ongoing environmental conservation efforts [5, 7].

2. Methodology

The wastewater sample used in this study was a final effluent from coffee processing, collected in a total volume of 50 L from a coffee shop located on Jl. Kedung Halang, Ciluar, North Bogor District, Bogor City, West Java, Indonesia. The sample was stored in a refrigerator at 4°C to prevent biological degradation prior to pretreatment. The wastewater was initially filtered to remove coarse suspended solids. A coagulation–flocculation step was conducted using polyaluminum chloride (PAC) as a coagulant. Liquid PAC was added to the sample at a concentration of 500 ppm and allowed to stand for 90 minutes to promote floc formation and sedimentation.

The coagulation process began with rapid mixing for 1 minute, followed by slow mixing for 15 minutes. Afterward, the mixture was allowed to settle for 90 minutes. The resulting supernatant was collected and used for subsequent photocatalytic treatment. This pretreatment stage aimed to reduce the initial turbidity of the wastewater and improve UV light penetration during the photocatalytic process.

The photocatalytic process was conducted in a cube-shaped reactor measuring 60 × 60 cm. The inner walls of the reactor were lined with aluminum foil to improve UV light reflection. The pH of the pretreated wastewater was adjusted according to the desired experimental conditions. When necessary, NaOH or HCl solutions were added to adjust the pH to the target level.

ZnO catalyst powder was weighed according to the specified concentration and added to a beaker containing the wastewater sample. In certain experiments, 0.01 M hydrogen peroxide (H_2O_2) was added to evaluate its effect on the degradation process. The mixture was then placed on a magnetic stirrer inside the reactor box equipped with UVA lamps. The UVA lamps were operated continuously for 4 hours under constant stirring, and the reactor box was kept closed to prevent light dispersion.

After 4 hours of irradiation, the lamps were turned off, and the photocatalyzed sample was allowed to stand until the catalyst particles settled. The clear supernatant was then carefully separated, filtered through a 200 μm paper filter followed by a 0.45 μm membrane (for caffeine analysis), and stored in labeled glass bottles for further physicochemical characterization.

3. Results and Discussion

3.1. Effect of pH on the Photocatalytic Process

The results of the study in Table 1 show that initial pH variation has a significant effect on photocatalytic reaction performance and the final pH of treated waste. At an initial pH of 7, the final pH decreased to the range of 5.45–5.74 across ZnO concentrations from 1000 to 3000 ppm. At pH 9, the treated samples appeared clearer, and the final pH decreased more sharply. The lowest final pH value of 4.04 was obtained at an initial pH of 9 with a ZnO catalyst concentration of 3000 ppm. During the photocatalytic process, hydroxyl radicals (•OH) are generated through the reaction between valence band holes (h^+) and hydroxide ions (OH^-) on the ZnO surface. This reaction becomes more intense under alkaline conditions due to the higher availability of OH^- ions [13]. Consequently, at pH 9, the increased OH^- concentration enhances the formation rate of •OH radicals, leading to more efficient chromophore degradation. As the degradation proceeds, pollutants are oxidized into intermediate organic acids such as oxalic, malonic, maleic, formic, and acetic acids [14]. However, when mineralization is incomplete and these intermediates are not fully converted into CO_2 and H_2O, their accumulation leads to a substantial decrease in pH during the reaction [13].

Table 1.
Results of Photocatalytic Treatment without H_2O_2 Addition.

TSS				
pH	**Initial Value**	**ZnO Catalyst Concentration (mg/L)**		
		1000	2000	3000
4	1220	124	158	310
7	1220	98	98	352
9	1220	98	203	294
BOD				
pH	Initial Value	ZnO Catalyst Concentration (mg/L)		
		1000	2000	3000
4	948	971	968	947
7	948	929	929	917
9	948	919	946	946
COD				
pH	Initial Value	ZnO Catalyst Concentration (mg/L)		
		1000	2000	3000
4	5203	5167	5200	5670
7	5203	4470	5112	4732
9	5203	4963	4953	4607
Caffeine				
pH	Initial Value	ZnO Catalyst Concentration (mg/L)		
		1000	2000	3000
4	134.4928	87.43	111.0308	111.5362
7	134.4928	62.9442	61.2956	34.1881
9	134.4928	96.2834	89.5429	80.5472
pH				
pH	Initial Value	ZnO Catalyst Concentration (mg/L)		
		1000	2000	3000
4	4.05	5.09	5.33	5.95
7	7.02	5.74	5.45	5.63
9	9.02	4.73	4.59	4.04

However, at an initial pH of 4, the final pH increased to the range of 5.09–5.95, with the highest value (5.95) observed at a ZnO catalyst concentration of 3000 ppm. The excessively acidic environment during the photocatalytic process enhanced the dissolution rate of ZnO according to the reaction: ZnO ($ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$). This dissolution process not only elevated the pH but also reduced the number of active sites available on the catalyst surface, thereby lowering the degradation efficiency. Under such conditions, photogenerated holes (h^+) are diverted away from forming hydroxyl radicals (•OH), resulting in an insufficient amount of •OH radicals to effectively degrade pollutants. Moreover, under either strongly acidic or strongly alkaline conditions, ZnO becomes susceptible to photocorrosion, where the catalyst itself undergoes oxidative degradation following the reaction: ($ZnO + 2h^+ \rightarrow Zn^{2+} + \frac{1}{2} O_2$). The consumption of H^+ ions in these reactions accounts for the observed increase in pH [15].

From the perspective of Chemical Oxygen Demand (COD), as shown in Figure 1, the lowest COD value was recorded at pH 7 with a ZnO concentration of 1000 ppm. At pH 9, COD values were higher than those at pH 7 but still lower than those obtained under acidic conditions (pH 4). Under acidic conditions, COD values even increased compared to the initial state, indicating that photocatalysis at low pH was ineffective for the mineralization of organic compounds. One primary reason is the photocorrosion of ZnO under acidic conditions, where the catalyst surface dissolves into Zn^{2+} ions, drastically reducing the number of active catalytic sites. As a result, caffeine and other organic molecules were not completely degraded [16]; instead, aromatic intermediates or chromophoric compounds were formed, which continued to contribute to COD [17]. The increase in final pH from 4.05 to 5.95 confirms the consumption of H^+ ions during the photocatalytic reactions. Under neutral conditions, COD experienced the most significant reduction, reaching approximately 4470 mg/L at 1000 ppm ZnO. This observation indicates that near-neutral pH provides the most favorable environment for photocatalytic oxidation, facilitating partial mineralization of organic pollutants and enhanced degradation efficiency.

The Biochemical Oxygen Demand (BOD) values after photocatalysis showed only slight variations from the initial BOD of 948 mg/L. The lowest BOD value (917 mg/L) was obtained at pH 7 with 1000 mg/L ZnO, while the highest value (971 mg/L) was observed at pH 4 for the same ZnO concentration. At pH 4, the photocatalytic degradation was less efficient, and large organic molecules such as caffeine, polyphenols, phenolic compounds, and proteins from coffee residues were only partially fragmented into smaller intermediates that remained carbon-rich [17]. These partially oxidized intermediates are more readily biodegradable than their parent molecules, thus increasing the BOD value. In this case, photocatalysis did not reduce the overall biodegradability load but instead generated new, more biodegradable substrates. At pH 9, although some degradation occurred, the accumulation of organic acid intermediates contributed to the BOD value, resulting in only a modest decrease. At neutral pH (7), the degradation products were more mineralized, as evidenced by the lower COD and more stable final pH, leading to slightly lower BOD values than at other pH levels. Wei-Chin et al. [18] reported that photocatalytic processes can convert biorecalcitrant compounds into intermediates that are more amenable to microbial degradation, which aligns with the findings of Kee et al. [19].

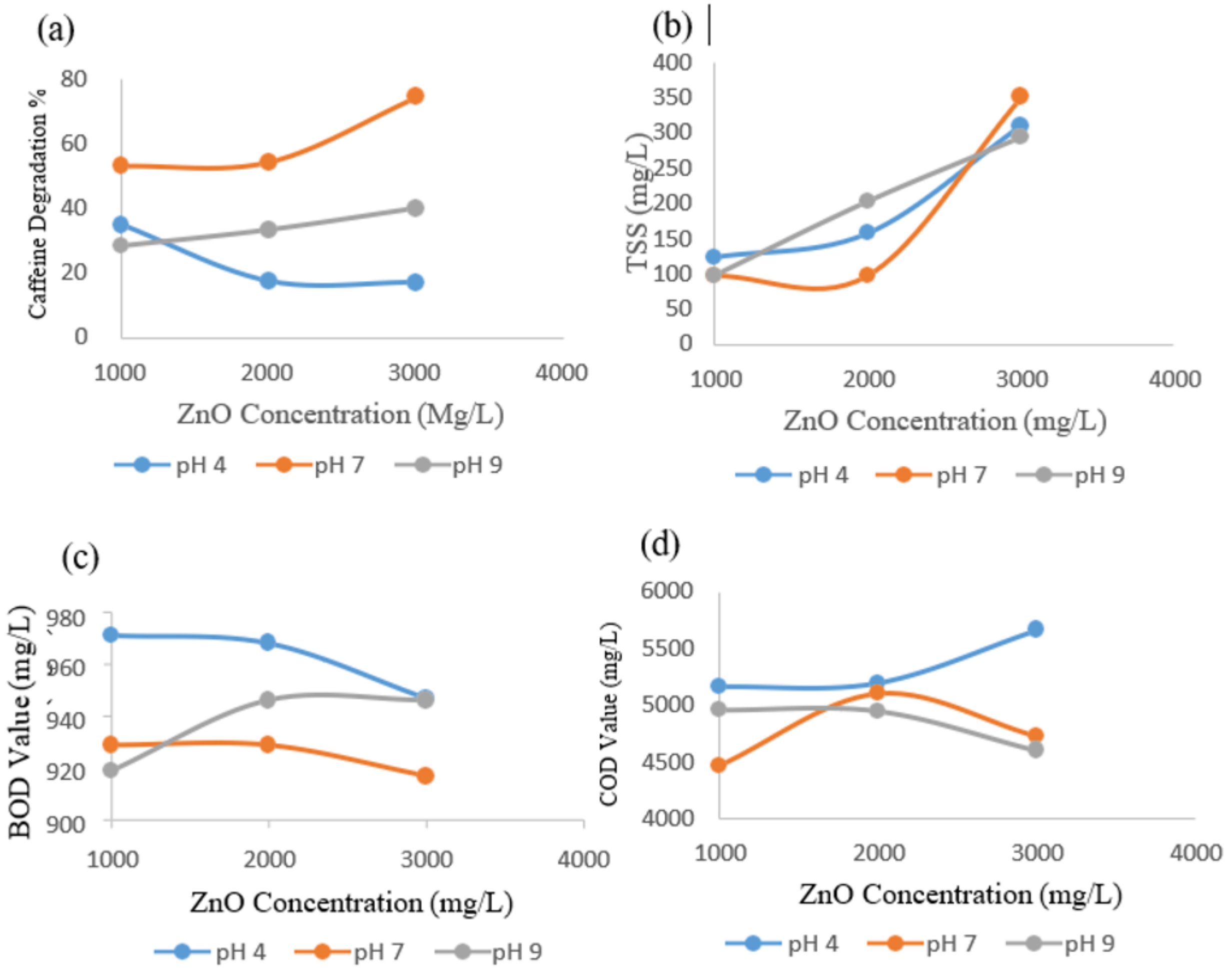

Figure 1.
Effect of ZnO Concentration on (a) Caffeine Degradation Efficiency, (b) TSS, (c) BOD, and (d) COD at Various pH Conditions.

When observed in terms of caffeine degradation efficiency, the optimum result was achieved at pH 7, reaching 74.58%. Interestingly, this trend differed slightly from that of color change. At pH 9, the highest caffeine degradation was only 40.11%, despite the treated samples appearing visually clearer. This discrepancy occurs because caffeine itself is colorless; thus, decolorization does not necessarily correspond to caffeine degradation. At pH 7, caffeine degradation was high, yet some chromophoric compounds (color-causing species) remained, making the solution appear darker than those at pH 9. As stated by Rochkind et al. [20], color change cannot reliably indicate the efficiency of molecular degradation, since the color intensity depends on the nature of intermediate products formed during photocatalysis. Caffeine is a neutral molecule and is therefore not easily ionized under aqueous conditions. According to a review by Fakioğlu and Kalpaklı [21], caffeine degradation is most efficient within a pH range of 5–8. Sotelo et al. [22] further explained that this is due to the role of hydrogen bonding interactions between caffeine molecules and the adsorbent surface, which are optimal under near-neutral conditions.

The Total Suspended Solids (TSS) were also strongly influenced by the pH condition. Under acidic conditions, ZnO underwent photo-corrosion, dissolving into Zn^{2+} ions and thereby reducing the number of active catalytic particles [23]. With fewer catalyst particles serving as coagulation nuclei, the system's ability to flocculate suspended solids decreased [24]. Consequently, although TSS decreased significantly (by up to approximately 90%), the reduction was not as pronounced as that at pH 7. At neutral pH, ZnO exhibited the highest chemical stability; it remained insoluble and well-dispersed throughout the suspension [25]. This condition promoted optimal simultaneous adsorption–coagulation mechanisms along with partial oxidation by hydroxyl radicals (•OH). Hence, the most effective TSS reduction was observed at pH 7, yielding a final TSS value of 98 mg/L at the optimal ZnO dosage. Under alkaline conditions (pH 9), TSS values were slightly higher than at neutral pH. In such conditions, the ZnO surface becomes negatively charged, as do many dissolved organic compounds (e.g., ionized phenolic and polyphenolic acids). This results in electrostatic repulsion, which reduces adsorption and coagulation efficiency [24].

3.2. Effect of ZnO Concentration on Photocatalysis

The concentration of the ZnO catalyst is a fundamental parameter that strongly influences the effectiveness of the photocatalytic process. A higher catalyst concentration provides more active sites on the ZnO surface capable of absorbing UV photons and generating electron–hole pairs. These charge carriers subsequently participate in redox reactions that produce hydroxyl radicals (•OH) and superoxide radicals (O_2^{-}•), both of which are highly reactive oxidizing species [26]. At low catalyst concentrations, the limited number of active sites results in a relatively slow degradation rate. In contrast, at moderate to high concentrations, the number of active sites increases, enhancing the degradation of complex organic compounds such as caffeine, phenols, and chromophoric substances. This behavior is consistent with the theory that increasing the catalyst loading expands the total number of active sites and accelerates hydroxyl radical (•OH) formation but only up to an optimal threshold [27]. Beyond this limit, excessive catalyst loading can reduce efficiency due to light scattering and particle agglomeration, which in turn decreases UV light penetration and the effective surface area available for photocatalytic reactions [28].

The effect of ZnO concentration is also strongly dependent on the initial pH of the reaction, as shown in Figure 2. Under alkaline conditions (pH 9), increasing the catalyst dosage from 1000 to 3000 ppm enhances reactive oxygen species (ROS) generation, especially •OH radicals, leading to efficient chromophore degradation visibly observed as a lighter or more transparent solution. Conversely, under acidic conditions (pH 4), ZnO becomes more susceptible to photocorrosion through Zn^{2+} ion release, accompanied by surface reactions that consume H^+ [24]. As the number of catalyst particles increased (1000 → 3000 ppm), the total exposed surface area under acidic conditions also increased, accelerating ZnO dissolution. The release of Zn^{2+} ions and concurrent H^+ consumption explain the observed increase in final pH (from 5.09 to 5.95), even though organic degradation was inefficient. This phenomenon was corroborated by the reduction in caffeine degradation efficiency (from 34.99% to 17.07%) and the increase in COD (from 5167 mg/L to 5670 mg/L) with increasing catalyst concentration. At neutral conditions (pH 7), the addition of ZnO catalyst from 1000 to 3000 ppm resulted in a decrease in final pH within the range of 5.73–5.45, indicating the formation of organic acid intermediates during photocatalysis. This observation confirms that the oxidative degradation of pollutants occurred effectively. Correspondingly, caffeine degradation efficiencies were relatively high, 53.2% at 1000 ppm, 54.42% at 2000 ppm, and 74.58% at 3000 ppm, showing a nearly linear improvement with increasing catalyst concentration.

Although the caffeine degradation efficiency exhibited a clear upward trend, the COD profile displayed a more complex behavior. At pH 7, the lowest COD value (4470 mg/L) was observed at 1000 ppm ZnO, suggesting that this concentration was sufficient to promote substantial degradation of organic compounds, albeit not yet optimal. At 2000 ppm, COD increased slightly, which can be attributed to the adverse effects of light scattering that reduce photocatalytic efficiency. However, at 3000 ppm, the COD value decreased again compared to 2000 ppm, indicating that although light scattering occurs at higher loadings [28], the larger number of active sites at 3000 ppm effectively

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compensates for this limitation by maintaining a high level of photocatalytic activity.

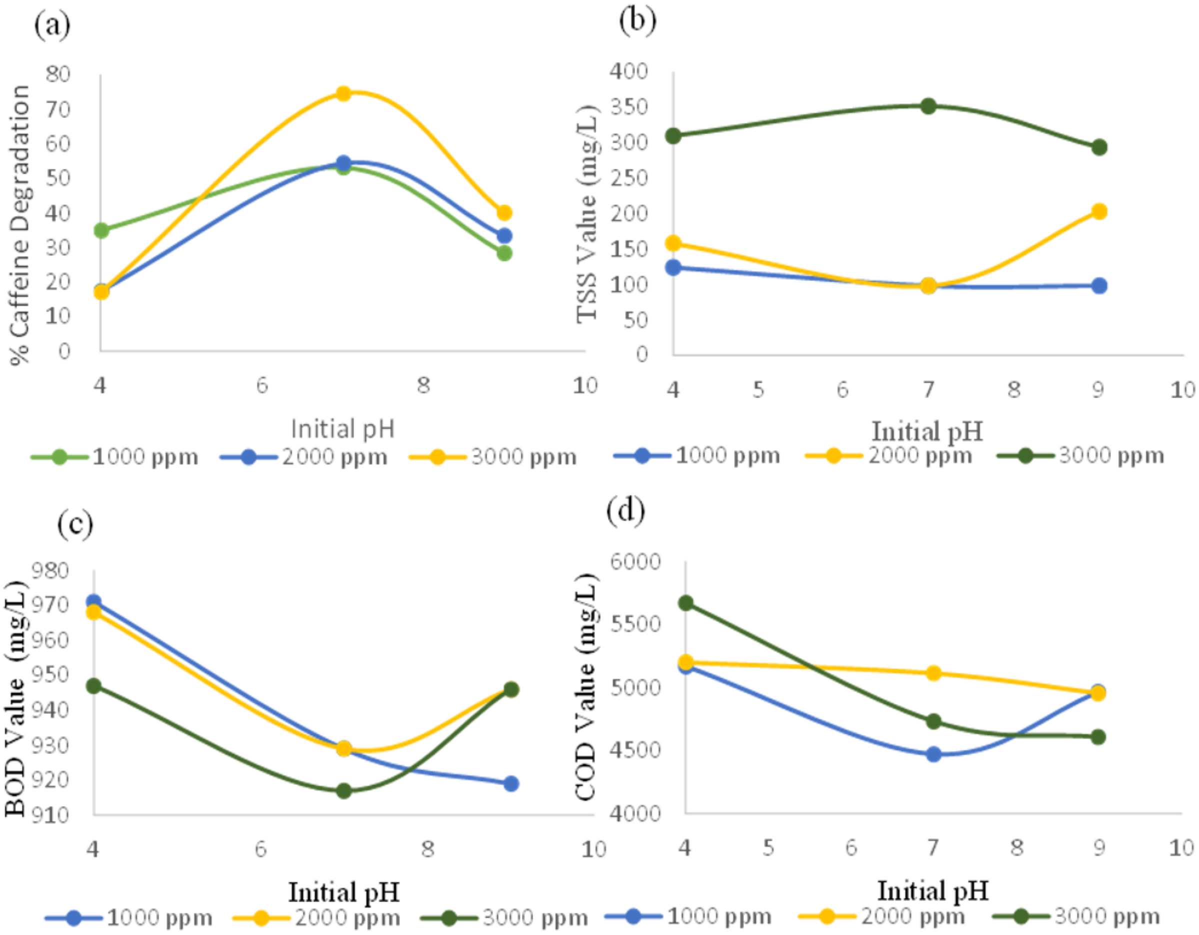

Figure 2.
Effect of Initial pH on (a) Caffeine Degradation Efficiency, (b) TSS, (c) BOD, and (d) COD at Various ZnO Concentrations

The influence of ZnO catalyst concentration on TSS was clearly evident from the experimental data. At pH 4 without H_2O_2 addition, the initial TSS of 1220 mg/L sharply decreased to 124 mg/L at a ZnO concentration of 1000 ppm, indicating that a low catalyst dosage can act effectively as a micro-flocculant. This occurs because ZnO particles interact with organic colloids in the wastewater, promoting coagulation and sedimentation [24]. However, when the ZnO concentration was increased to 2000 ppm, the TSS rose again to 158 mg/L, and at 3000 ppm, it increased further to 310 mg/L. This suggests that excessive catalyst loading contributes additional suspended solids, as ZnO particles themselves are difficult to separate from the treated effluent and may become part of the TSS fraction [29]. Such behavior not only increases the turbidity of the solution but also adds to the filtration load in the subsequent treatment stages.

In addition to TSS, the Biochemical Oxygen Demand (BOD) exhibited a more complex relationship with ZnO concentration. Generally, BOD declined with increasing catalyst dosage; however, the change was minimal (<50 mg/L). This indicates that partial degradation of complex organic compounds led to the formation of simpler, more biodegradable intermediates [30]. As a result, although large organic molecules such as caffeine were broken down, the presence of these oxygen-rich intermediates maintained or even slightly increased the BOD due to enhanced microbial

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accessibility.

3.3. *Effect of H_2O_2 Addition*

The addition of hydrogen peroxide (H_2O_2) aimed to enhance the oxidation process by generating additional hydroxyl radicals (•OH). H_2O_2 functions as an electron acceptor in the photocatalytic system, as described by Masoumi et al. [31]. The molecule captures photogenerated electrons from the ZnO conduction band, thereby reducing the probability of electron–hole recombination. The reaction mechanism can be represented as follows:

$$H_2O_2 + e^-(cb) \rightarrow \cdot OH + OH^-$$

This reaction not only increases the availability of hydroxyl radicals (•OH), which possess strong oxidative potential, but also produces hydroxide ions (OH^-) that help stabilize the pH, preventing excessive acidification during the reaction. With the higher abundance of •OH radicals, intermediate organic acids can be further oxidized into CO_2 and H_2O, resulting in a more complete degradation system. In this study, the concentration of H_2O_2 used was 10 mM (0.01 M), as adopted from the findings of Kholidah et al. [32].

Experimental results in Table 2 indicate that the ZnO catalyst concentrations tested were 1000 ppm, 2000 ppm, and 3000 ppm at pH 7, and 3000 ppm at pH 9. At pH 7, the final pH values after photocatalysis with H_2O_2 were 5.52 (1000 ppm), 5.75 (2000 ppm), and 6.18 (3000 ppm). These values demonstrate that, although degradation occurred, the accumulation of organic acids was less pronounced than in the system without H_2O_2. In the trial conducted at pH 9 and 3000 ppm ZnO, the final pH of the treated solution was 6.37, considerably higher than that of the system without H_2O_2 (4.04). The higher final pH suggests that fewer organic acid intermediates accumulated, indicating that degradation proceeded beyond the formation of organic acids toward a more complete mineralization stage [13]. The near-neutral pH may also reflect the decomposition of H_2O_2 into H_2O and O_2 [33].

Despite this improvement in pH stability, the addition of H_2O_2 generally reduced caffeine degradation efficiency. Caffeine degradation strongly depends on its ability to adsorb onto the ZnO surface via hydrogen bonding. Consequently, at pH 9, the difference in degradation efficiency between systems with and without H_2O_2 was only 3.3%. At pH 7, however, the effect was more pronounced: the photocatalytic degradation of caffeine was significantly lower in the presence of H_2O_2. This is attributed to competition between H_2O_2 molecules and caffeine for adsorption onto ZnO active sites. As a result, although the total number of radicals increased, the proportion of radicals effectively attacking caffeine decreased, leading to a decline in degradation efficiency.

Table 2.
Results of Photocatalytic Treatment with H_2O_2 Addition.

TSS				
pH	**Initial Value**	**ZnO Catalyst Concentration (mg/L)**		
		1000	2000	3000
7	1220	248	243	348
9	1220		-	64
BOD				
pH	Initial Value	ZnO Catalyst Concentration (mg/L)		
		1000	2000	3000
7	948	906	912	885
9	948			945
COD				
pH	Initial Value	ZnO Catalyst Concentration (mg/L)		
		1000	2000	3000
7	5203	5153	5183	5017
9	5203			4501
Caffeine				
pH	Initial Value	ZnO Catalyst Concentration (mg/L)		
		1000	2000	3000
7	134.4928	95.6943	95.1952	90.2483
9	134.4928			85.0055
pH				
pH	Initial Value	ZnO Catalyst Concentration (mg/L)		
		1000	2000	3000
7	7.02	4.52	6.18	5.75
9	9.02	-	-	6.37

The addition of H_2O_2 caused a slight reduction in BOD. At pH 7, the final BOD values were 906 mg L^{-1} (1000 ppm), 912 mg L^{-1} (2000 ppm), and 885 mg L^{-1} (3000 ppm), corresponding to a modest 3–6% decrease compared to the initial BOD. Although this represents an improvement over the system without peroxide, the reduction remains minor. At pH 9 (3000 ppm ZnO), the final BOD was 945 mg L^{-1}, virtually unchanged from 946 mg L^{-1} without peroxide. The BOD_5/COD ratios under all conditions ranged from 0.17 to 0.20. According to the classification of Rudaru et al. [34], a BOD_5/COD ratio below 0.2 indicates that the wastewater is poorly biodegradable, while a ratio of 0.2–0.4 still corresponds to low biodegradability. Hence, both with and without peroxide addition, the treated effluent remained difficult to process. Biological COD results with H_2O_2 addition were generally higher than those obtained without peroxide, except under one condition. At pH 7, the final COD values were 5153 mg L^{-1} (1000 ppm), 5183 mg L^{-1} (2000 ppm), and 5017 mg L^{-1} (3000 ppm), all higher than those without H_2O_2. This indicates that, at the tested dosage, H_2O_2 reduced mineralization efficiency. Mechanistically, H_2O_2 is expected to capture conduction-band electrons and generate hydroxyl radicals; however, at excessive concentrations, H_2O_2 reacts with existing •OH radicals to form less reactive species, thereby depleting the pool of effective oxidants [35].

At pH 9, data were available only for 3000 ppm ZnO. Here, the COD decreased to 4501 mg L^{-1}, which is slightly lower than the 4607 mg L^{-1} measured without H_2O_2, a 13.5% improvement, representing the most significant enhancement achieved with peroxide in this study. The combination of alkaline pH (which enhances adsorption of organic molecules onto the catalyst surface) and additional radicals from H_2O_2 may have produced a synergistic effect, promoting oxidation of organic compounds. Nevertheless, the resulting COD values remained far above the permissible discharge limits.

The effect of H_2O_2 on TSS varied with pH. At pH 7, TSS decreased from an initial 1220 mg L^{-1} to 248 mg L^{-1} (1000 ppm ZnO), 243 mg L^{-1} (2000 ppm), and 348 mg L^{-1} (3000 ppm). These values were still higher than those obtained in the system without peroxide, suggesting that H_2O_2 did not enhance

TSS removal under neutral conditions. This may be due to the fragmentation of organic matter into finer suspended particles that remained in dispersion, while ZnO particles persisted in suspension. At pH 9 (3000 ppm), however, TSS dropped drastically to 64 mg L^{-1}, a 94.8% reduction from the initial value. Under alkaline conditions, floc formation is favored, enabling solid particles to settle more easily, while H_2O_2 accelerates the breakdown of organic matter [24]. Nonetheless, a TSS level of 64 mg L^{-1} still exceeds most discharge standards.

Overall, these findings indicate that the addition of H_2O_2 does not consistently increase TSS removal, as seen in the comparison of photocatalysis results in Figure 3. Its beneficial effect is more pronounced under alkaline conditions, whereas at neutral pH, the impact is minimal or even adverse. Adeyinka and Rim-Rukeh [36] reported that hydrogen peroxide can enhance oxygen supply and oxidation rates of both dissolved and bound particles, thereby promoting TSS removal. However, in the present system, the H_2O_2 dosage was likely insufficient to maximize this effect.

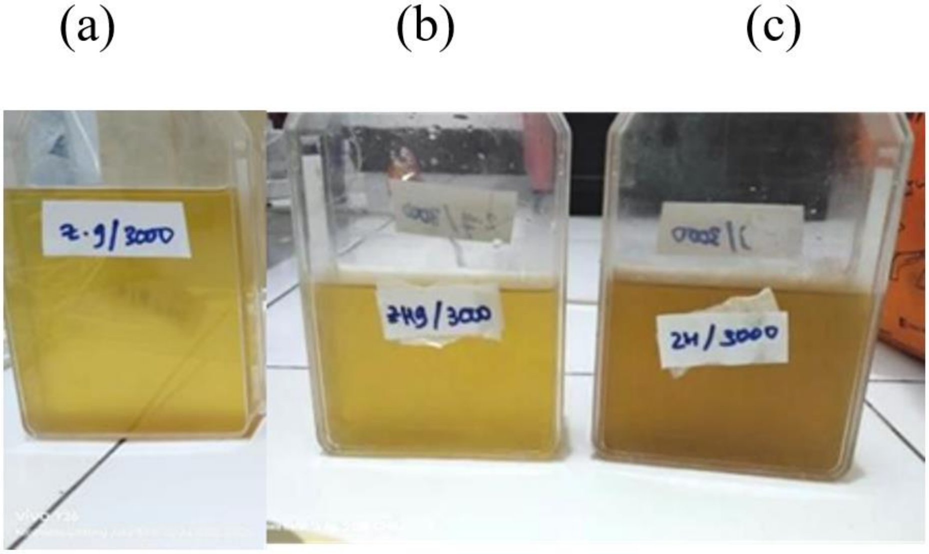

Figure 3.
Comparison of photocatalytic results at 3000 ppm ZnO under different conditions: (a) without H_2O_2 at pH 9, (b) with H_2O_2 at pH 9, and (c) with H_2O_2 at pH 7.

4. Conclusion

The photocatalytic process using Zinc Oxide (ZnO) as a catalyst proved effective in reducing caffeine concentration and several key pollutant parameters in coffee shop wastewater. The optimum condition was achieved at pH 7 with a ZnO concentration of 3000 ppm, yielding the highest caffeine degradation efficiency of 74.58%. Under this condition, ZnO exhibited the greatest chemical stability, enabling optimal particle adsorption and oxidative reactions. The most significant COD reduction occurred at pH 7 with 1000 ppm ZnO, where COD decreased from 5203 mg/L to 4470 mg/L, demonstrating the highest oxidation efficiency without light scattering interference. The final BOD values ranged from 917 to 971 mg/L, indicating that the photocatalytic process generated intermediate compounds that remain partially biodegradable. The lowest TSS value of 98 mg/L was also recorded at pH 7, confirming ZnO's dual function as an effective adsorbent and micro-coagulant under neutral conditions. Under acidic conditions (pH 4), photocatalytic activity declined due to ZnO photo-corrosion, while under alkaline conditions (pH 9), decolorization efficiency improved, but caffeine degradation decreased because of electrostatic repulsion between negatively charged species. The addition of 0.01 M H_2O_2 produced varied effects: at pH 7, it decreased caffeine degradation efficiency due to adsorption competition between H_2O_2 and caffeine, whereas at pH 9 it enhanced mineralization, resulting in COD and TSS values of 4501 mg/L and 64 mg/L, respectively.

Overall, the optimal photocatalytic performance was obtained at pH 7, ZnO concentration of 3000 ppm, without H_2O_2 addition, and a UVA irradiation time of 4 hours. These findings demonstrate that ZnO-based photocatalysis offers a promising, efficient, economical, and environmentally friendly alternative technology for treating coffee shop wastewater.

Transparency:

The authors confirm that the manuscript is an honest, accurate, and transparent account of the study; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained. This study followed all ethical practices during writing.

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