

DEGRADATION OF PESTICIDE WASTE VIA PHOTOCATALYSIS USING CAO UNDER VISIBLE LIGHT IRRADIATION

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ABSTRACT

Diazinon contamination aquatic environments is a serious problem due to its toxicity, persistence, and resistance to natural degradation. One potentially effective approach to decompose this compound is the photocatalytic process, which is capable of forming reactive oxidative radicals under light exposure. This study aims to evaluate the performance of calcium oxide (CaO) derived from eggshell waste photocatalyst in the diazinon photodegradation process using visible light source. The CaO material was prepared through calcination process and then characterized using SEM, FTIR, and UV-Vis to determine surface structure, functional groups, and band gap values that support its photocatalytic activity. The optimum conditions were achieved neutral pH, low initial concentration, and 100 watts of light power with the highest degradation efficiency 49.65%. Kinetic analysis showed the process follows pseudo-first-order model with good agreement with the experimental data. Overall, the results of this study demonstrate that CaO from eggshells has the potential to be used effective, economical, and environmentally friendly photocatalyst in the photodegradation diazinon under visible light exposure, thus providing an alternative technology for pesticide waste treatment.

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Introduction

Pesticides are toxic chemical compounds used to control agricultural plant pests, as well as to eradicate or prevent pests and unwanted plants [1]. [1][1]The use of chemicals in agriculture, such as pesticides, is necessary in large quantities to increase agricultural productivity [2]. However, the use of pesticides raises concerns regarding their potential adverse impacts on the environment, including the quality of water resources [3]. This has a big impact on water sources, where the greater the amount of pesticide use, the more toxic materials will dissolve and contaminate the water [1]. If pesticide residues accumulate in soil or water, they can impact the life of the organisms involved, including posing various

disease risks to humans. Among the many pesticides, diazinon is the organophosphate insecticide most widely used in agriculture [4].

Generally, diazinon is used in the agricultural sector to control aphids, fruit flies, and leafhoppers on apples and grapes [5]. The relatively cheap price but high efficiency in eradicating pests makes this type of pesticide popular with many agricultural actors [6]. However, the World Health Organization classifies diazinon as an insecticide with a moderate hazard risk (class II) [4]. Its toxicity has been demonstrated in several studies, where oral exposure to diazinon caused nervous system damage and histopathological changes in liver and kidney function. Therefore, this pesticide poses a serious threat to human

health due to its toxic effects [7]–[9]. Therefore, efforts are needed to remove diazinon residues from the environment.

Diazinon photodegradation has been extensively studied by researchers using various degradation methods, such as adsorption, chemical coagulation, magnetic nanoparticles, biological methods, photocatalysis processes, precipitation, and oxidation processes [10]–[12]. Among these processes, Advanced oxidation process (AOPs) is the most effective method because it can remove harmful compounds without producing byproducts such as polycyclic or aromatic. Photocatalysis is the most superior subclass of AOP, where light energy activates semiconductor materials to produce Electron/hole (e^-/h^+) pairs that form highly reactive radical species (ROS), such as hydroxyl radicals ($\bullet\text{OH}$) and superoxide ($\text{O}_2\bullet^-$), under light exposure. These radicals are responsible for the photodegradation of organic pollutants. Photocatalysis, is considered a practical AOP technique because of its ability to mineralize toxic compounds into harmless end products using light as an energy source. [13].

In the photocatalytic process, CaO material irradiated with visible light absorbs photon energy. When the energy is equal to or greater than its band gap energy of 2.8 eV, electrons in the valence band will be excited to the conduction band. This process results in the production of electron-hole pairs (e^-/h^+) which play an important role in the formation of hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\text{O}_2\bullet^-$) in redox reactions. These active radicals are strong oxidizing agents that can break C–N, P=O, and C=C bonds in complex organic molecules, such as diazinon [10].

In the photocatalytic degradation of diazinon, electrons from the metal oxide are excited and transferred to the conduction band from the valence band, generating electron-hole pairs. Then, a reaction occurs between the electrons and O_2 , while the positively charged holes react with H_2O or OH^- to release reactive $\text{OH}^\cdot$ which can oxidize diazinon and its degradation fragments. The following is the mechanism of photocatalytic degradation of diazinon [6].

The distribution of reaction fragments from diazinon photodegradation in aqueous media through advanced oxidation processes states that hydroxyl radicals ($\bullet\text{OH}$) produced through oxidation by H_2O will react quickly and selectively with diazinon organophosphate molecules. hydroxyl radicals ($\bullet\text{OH}$) break down sulfur-containing groups in the diazinon structure into sulfate ions (SO_4^{2-}). Then, other parts in the broken down diazinon organophosphate are oxidized to form phosphate ions (PO_4^{3-}), carbonate (CO_3^{2-}), and nitrate (NO_3^-) [6]. Furthermore, superoxide radicals ($\text{O}_2\bullet^-$) and hydroxyl radicals ($\bullet\text{OH}$) break down pieces of the diazinon ring structure until they are oxidized to H_2O and CO_2 [14].

Generally, photocatalysts use metal oxide semiconductors such as titanium dioxide, iron oxide, cadmium sulfide, zinc sulfide, zirconium dioxide, and zinc sulfide [13]. However, to enhance their photocatalytic activity, these semiconductor materials are often modified through various methods such as metal doping, composites, or structural engineering. These modification processes are relatively expensive [14]. Therefore, a cheaper alternative photocatalyst semiconductor is needed. Eggshells are one of the abundant waste products that can be utilized as an alternative, given their mineral content, which consists of CaCO_3 crystals (98.41%), MgCO_3 (0.84%), and $\text{Ca}_3(\text{PO}_4)_2$ (0.75%) [15]. The main component of eggshells in the form of CaCO_3 is easily synthesized into CaO which is widely used as a catalyst in many industries as a toxic waste remediation agent, bactericide, adsorbent, and binder in paint [16]. Therefore, CaO obtained from eggshells can be used as a catalyst to degrade pesticides.

Calcium carbonate (CaCO_3) in raw eggshells can be converted into CaO after calcination [17]. Furthermore, FTIR characterization showed that after calcination, vibrations appeared that could be directed at the -OH group (especially from $\text{Ca}(\text{OH})_2$) in the range of 3600 cm^{-1} [18]. Furthermore, XRD results also reported that the synthesis of CaO from eggshells through calcination had a high CaO purity of 97.93% [19].

Based on the description above, this study aims to synthesize and characterize a CaO-based photocatalyst material from eggshell waste and to test its effectiveness in degrading organophosphate pesticide compounds (diazinon) in water using visible light from a white light LED lamp. The results of this study are expected to provide a scientific contribution to the development of efficient and sustainable wastewater treatment technologies, while supporting environmental conservation efforts in the agricultural and industrial sectors.

Materials and Methods

1. Tools and materials

The materials used in this study include Aquades, eggshells, Diazinon 600 g/L, HCl 0.01 M, NaOH 0.01 M, 20% KOH. The HCl, NaOH, and KOH chemicals used were obtained from Merck. Meanwhile, Diazinon 60 EC is a commercial pesticide produced by Petrokimia Kayaku, Indonesia. The equipment used in this study includes glassware, pH meter, magnetic stirrer, digital balance, tray, FTIR (Jasco FT/IR-4600, ATR PRO ONE), SEM (Hitachi SU3500 equipped with EDAX Octane Pro), and UV-Vis spectrophotometer (Jasco V-730).

2. Method

Preparation of Calcium Oxide (CaO) from Eggshells

Eggshells were washed, dried at 110 °C for 24 hours, ground, and sieved 60 mesh. The powder was calcined at 800 °C for 4 hours to produce CaO, then impregnated with a 20% KOH solution at 60 °C for 24 hours. After drying, the CaO was recalcined at 450 °C for 4 hours before being use as a photocatalyst.

Photodegradation Test of Pesticide Waste

This stage aims to evaluate the photocatalytic activity of CaO synthesized from eggshell waste for degrading the organophosphate pesticide Diazinon under visible light irradiation. The visible light spectrum was selected based on the dominance of solar energy in the 400-700 nm wavelength range, making it more practical and energy-efficient compared to UV-based systems [20].

Several studies have used varying concentrations of KOH to impregnate CaO from eggshells [21], [22], [23]. It has been suggested that the catalytic activity of CaO can be

enhanced by incorporating varying concentrations of alkali metal KOH using a wet impregnation method accompanied by heating [22]. Thus, CaO from eggshell waste is an inexpensive, environmentally friendly, and efficient photocatalyst alternative for pollutant degradation.

All experiments were conducted using a 100 mL glass batch photocatalytic reactor equipped with a magnetic stirrer to maintain suspension homogeneity. The light source was an 80-160 W white light LED lamp positioned about the reactor at a distance of 10 cm. Prior to irradiation, the catalyst suspension and Diazinon solution were stirred for 30 minutes in the dark to achieve adsorption-desorption equilibrium.

The effect of operational variables on photodegradation efficiency was evaluated by varying the photocatalyst dosage (8-24 mg), solution pH (3-11), initial Diazinon concentration (30-130 mg/L), irradiation time (30-150 minutes), and lamp power (80-160 W). The solution pH was adjusted using 0.01 N NaOH or 0.01 HCl. Each experiment was conducted under controlled conditions to determine the optimum parameters that yielded the highest photodegradation efficiency.

3. Data analysis

Material Characterization

The characteristics of CaO were analyzed using various techniques. Scanning Electron Microscopy (SEM) analysis was performed to determine the surface morphology of CaO using a Hitachi SU3500 equipped with EDAX Octane Pro. In addition, UV-Vis spectroscopy was used to determine the band gap energy of CaO using UV-Vis spectroscopy (Jasco V-730) based on absorbance values and absorption spectrum.

Evaluation of Degradation Efficiency Based on UV-Vis Spectroscopy

Data analysis was carried out by converting the absorbance values of the UV-Vis spectrophotometry data into concentration using the equation:

$$A = \epsilon bc \quad (1)$$

According to the Beer-Lambert law, absorbance is directly proportional to the

concentration of Diazinon in the solution. The independent variables analyzed included solution pH, initial concentration, and contact time, while the dependent variable was the percentage of pesticide degradation. The data obtained were analyzed to evaluate the effect of each variable on degradation efficiency and to determine the optimal conditions yielding the highest degradation efficiency. The percentage of pesticide degradation was calculated based on spectrophotometric data using the equation:

$$\text{Degradation (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

Where C_i and C_f are the initial and final concentrations of Diazinon, respectively.

Results and Discussion

1. Characterization of CaO from Eggshells

The morphology and surface structure of the calcined CaO derived from eggshells were characterized using Scanning Electron Microscopy (SEM). SEM analysis was carried out at various magnification, 2,500x, 5,000x, and 10,000x, as shown in Figure 1 (a), (b), and (c).

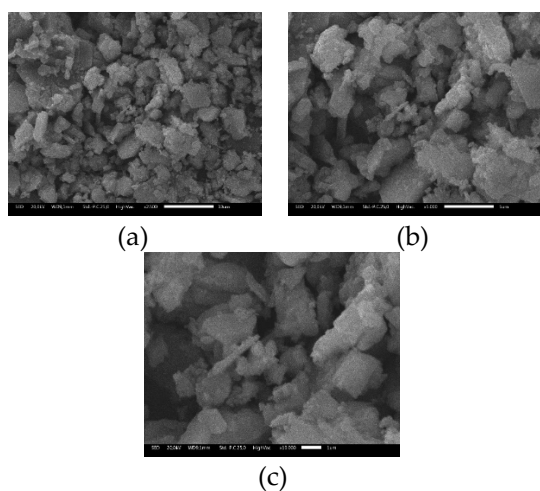


Figure 1. SEM Characteristics of CaO:
(a) 2.500x; (b) 5.000x; (c) 10.000x

The SEM micrograph in Figure 1(a) shows that the surface of the calcined CaO derived from eggshells at 2,500x magnification has an irregular structure with a rough texture and porous particles. The porosity formed in this material structure is caused by the calcination process which involves the decomposition reaction of CaCO_3 at high temperatures which

forms CaO and releases CO_2 gas, thus forming pores on the material surface [24]. In Figure 1(b), the surface morphology of the CaO at 5,000x magnification is dominated by fine particles that adhere to each other, indicating agglomeration. Furthermore, CaO exhibits polygonal crystallites that form aggregates in some areas. This finding is consistent with previous studies that explain that high calcination temperatures increase particle mobility, causing significant particle agglomeration [24]. SEM observations of CaO with various magnifications on a scale of 1–10 μm indicate that most of the CaO produced can be classified as submicron-sized particles. Figure 1(c) confirms the presence of a combination of micro and nano particles in the CaO as indicated by the surface structure of the crystallites which is dense but has a porous network on the microscale. This combination of micro and nano particles can strengthen the stability of the structure and increase the active surface area of the material [18,19].

The overall structure and morphology of CaO exhibits a rough, irregular, porous, and small-sized surfaces. This finding is validated by several previous studies which report that CaO has irregular particle shapes, porous structures with rough surfaces, and micro to nano sizes [20,21]. Porous morphology provides a diffusion pathway for water and oxygen molecules which can increase the effectiveness of organic compound degradation under visible light [16]. In addition, the irregular structure with micro-nano particle sizes can increase the distribution of active sites on the surface of the CaO material which can increase the efficiency of organic compound photodegradation [28]. Thus, the structure and morphology of CaO from eggshell waste are ideal for use as an economical and environmentally friendly photocatalyst in diazinon degradation.

The functional groups present in CaO were analyzed using Fourier Transform Infra Red (FTIR) with a wavelength of 500–4000 cm^{-1} . Functional groups in the material were identified based on the absorption bands observed in spectra. FTIR analysis was carried out on eggshells, KOH-impregnated eggshells, and commercial CaO as shown in Figure 2.

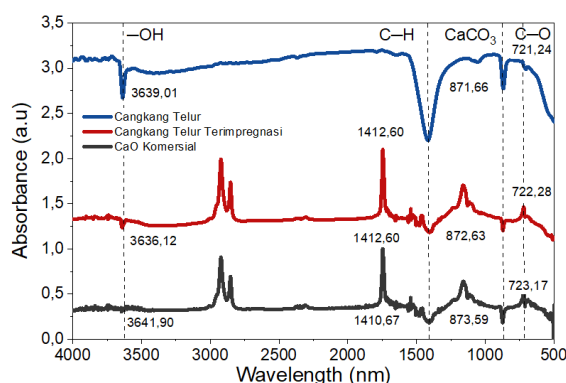


Figure 2. FTIR Characteristics

The FTIR spectrum in Figure 2 shows that the functional groups in CaO derived from impregnated eggshells has a similar pattern to commercial CaO. The absorption band of impregnated eggshells at 3636 cm^{-1} is close to the absorption band of commercial CaO at 3641 cm^{-1} and eggshells at 3639 cm^{-1} , indicating the presence of stretching of the hydroxyl group ($-\text{OH}$). The $-\text{OH}$ group indicates the presence of water adsorption on the surface of the CaO to form $\text{Ca}(\text{OH})_2$, which confirms the adsorption ability of the CaO material [29].

Furthermore, the absorption bands at 1410–1412 cm^{-1} and 871–873 cm^{-1} identified the presence of carbonate functional groups $(\text{CO}_3)^{2-}$ [30]. Absorption bands were also formed at 721–723 cm^{-1} indicating the presence of C–O bonds [31]. The presence of $(\text{CO}_3)^{2-}$ and C–O functional groups indicates the presence of CaCO_3 on the material surface caused by the formation of structural defects in the form of oxygen vacancies during the calcination process, so that CaO becomes more reactive and triggers recarbonation leading to the reformation of CaCO_3 [26,4]. The similarity of functional groups from CaO derived from impregnated eggshells and commercial CaO indicates that impregnated eggshells can be used as photocatalysts in the degradation of Diazinon.

Optical analysis was carried out to determine the band gap energy of the CaO photocatalyst, which was determined using the Tauc plot method. The optical properties of CaO derived from eggshells are shown in Figure 3.

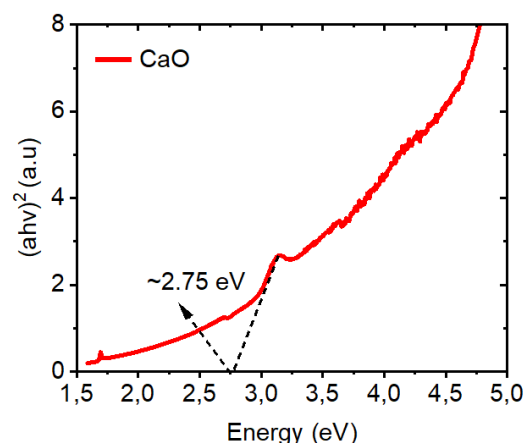


Figure 3. Band Gap

The optical analysis results in Figure 3 show that the band gap value of the CaO photocatalyst derived from eggshells is 2.75 eV. Previous studies have stated that photocatalyst materials with narrow band gaps, namely 1.9–3.2 eV, are able to absorb lower-energy, thus maximizing the use of visible light [33]. The photon energy from visible light is able to excite electrons from the valence band to the conduction band, thus producing sufficient reactive species such as hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\text{O}_2^{\bullet-}$), which play an important role in the photodegradation of organic pollutants [27]. These findings indicate that CaO derived from eggshell has the potential to act effectively as a photocatalyst in the degradation of Diazinon under solar irradiation without additional ultraviolet light sources.

However, the band gap value of CaO derived from eggshell is lower than pure CaO, which is around 3.2–3.4 eV. This indicates the presence of impurities in the eggshell that form defect states, resulting in a narrower band gap [27]. Notably, a narrower band gap energy allows for more efficient utilization of visible light and increases photocatalytic activity [34]. Conversely, a wider band gap energy limits the application of photocatalysts to only UV light [35]. Previous studies have shown that a decrease in the band gap provides a better light response, this condition supports photocatalytic activity under visible light through an efficient electron-hole pair formation mechanism [21, 28]. Thus, the calcined eggshell CaO has better

photocatalytic activity without requiring additional UV light compared to pure CaO.

2. Effect of Operational Variables on Diazinon Degradation Efficiency

Effect of Initial Diazinon Concentration

The effect of initial Diazinon concentration on the performance of CaO photocatalyst derived from eggshell in diazinon photodegradation under visible light was investigated using concentrations of 30, 70, 90, and 130 ppm as shown in Figure 4.

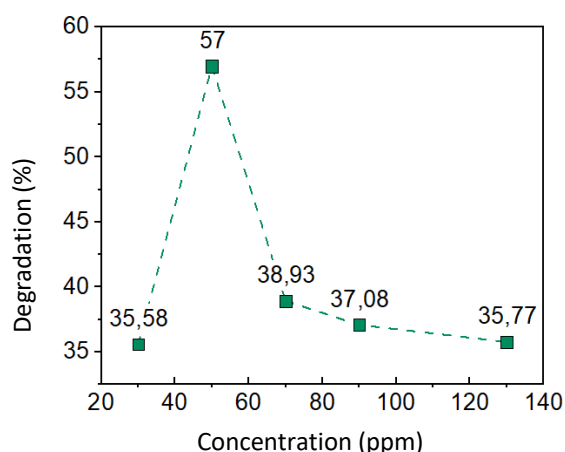


Figure 4. Effect of Concentration

Experimental results at various concentrations showed that the photocatalytic degradation efficiency under visible light increased from 35.58% at 30 ppm to 57% at 50 ppm, followed by a significant decrease at concentrations of 70-130 ppm. A similar pattern was also found in previous studies that reported a decrease in degradation efficiency at higher initial Diazinon concentrations [6, 10, 13]. The increase in degradation efficiency at lower concentrations is due to the active sites available on the catalyst surface for absorption abundant [37].

Notably, further increasing the initial concentration causes the catalyst surface to become more saturated with excess Diazinon molecules due to the limited active sites on the catalyst surface. This inhibits the formation of $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$ radicals which play an important role in the oxidative degradation process, thereby slowing down the reaction rate [33, 34, 35]. In addition, a higher initial concentration can inhibit light penetration in the

photocatalytic process, resulting in a reduced degradation rate [16]. This phenomenon is associated with an increase in solution turbidity and the screening effect, where excessive Diazinon molecules absorb or scatter incident light before reaching the catalyst surface. Consequently, fewer photons are available to excite electrons from the valence band to the conduction band, reducing the generation of electron-hole pairs and reactive radicals. Furthermore, at higher concentrations, competition among Diazinon molecules for adsorption site becomes more intense, limiting effective contact between the pollutant and the active site responsible for photocatalytic oxidation. Therefore, the optimum initial concentration of Diazinon for photodegradation using eggshell-derived CaO catalyst is 50 ppm.

Effect of Catalyst Dose

The efficiency of diazinon degradation was also evaluated based on the variation of CaO photocatalyst dosage. Various dosages ranging from 8, 12, 16, 20 and 24 mg of CaO photocatalyst were applied to the photodegradation process, the effects of which are shown in Figure 5 below.

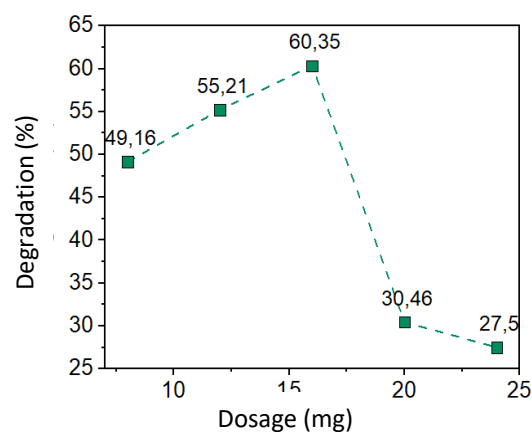


Figure 5. Dose Effect Graph

The degradation efficiency increased gradually with increasing catalyst dosage from 49.15% at 8 mg to 60.35% at 20 mg dosage. This increase was due to the large catalyst dosage being able to provide the availability of active sites and a larger surface area, which encourages the formation of electron-hole pairs to produce reactive oxidative reactions. Hydroxyl radicals ($\bullet\text{OH}$) and superoxide

radicals ($O_2^{\bullet-}$) are strong oxidants responsible for the degradation of organophosphate compounds such as diazinon into simple compounds such as CO_2 , H_2O , and other inorganic ions [39]. It is this increased formation of oxidative species that enhances photocatalytic degradation [40]. Thus, a higher catalyst dosage increases the number of active sites for diazinon degradation.

However, when the CaO photocatalyst dosage exceeds 20 mg, the observed degradation efficiency actually decreases. This significant decrease is due to catalyst agglomeration, which reduces the surface area and active sites accessible on the catalyst surface [41]. When catalyst particles aggregate, a portion of the active surface becomes buried within larger cluster, thereby decreasing the number of exposed active sites available for adsorption and photocatalytic reactions. Agglomeration also limits the contact between the catalyst surface and the Diazinon molecules, reducing the efficiency of pollutant adsorption prior to degradation. Furthermore, larger particle aggregates can hinder light penetration and promote light scattering within the suspension, resulting in a lower generation of electron-hole pairs and reactive radicals ($\bullet OH$ and $O_2^{\bullet-}$). Consequently, despite the higher catalyst dosage, the effective photocatalytically active surface area decreases, leading to a reduction in degradation efficiency.

In addition, excessive doses of CaO photocatalyst can increase the turbidity of the solution, thereby reducing the accessibility of light to the catalyst surface. Excessive doses of CaO photocatalyst can also create self-shadowing or deactivation effects through interparticle collisions [40]. These findings indicate that adding catalyst above the optimum dose no longer increases the efficiency of diazinon degradation, necessitating optimization of the catalyst dose. Therefore, the optimum dose of CaO photocatalyst in the diazinon photodegradation process is 16 mg

Effect of pH of Solution

Figure 6 shows the effect of varying solution pH on the efficiency of diazinon degradation using CaO photocatalyst from eggshells under optimum conditions. The pH values used varied from 3, 5, 7, 9, and 11.

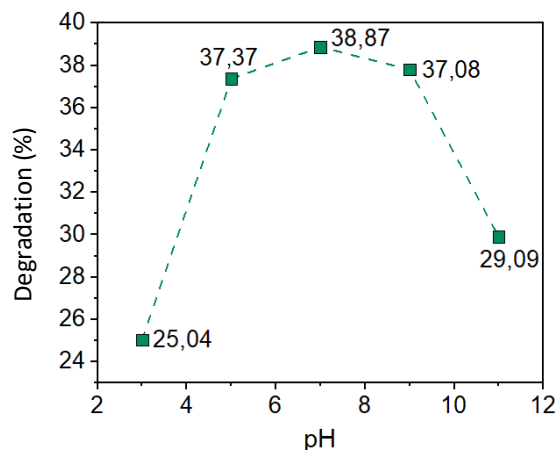


Figure 6. Graph of the Effect of pH on Solution

The degradation efficiency increased with increasing pH from 25.04% at pH 3 to 38.87% at pH 7. However, degradation efficiency decreased at pH 9-11. This finding indicates that diazinon degradation reaches its maximum efficiency at neutral pH. The increase in efficiency from acidic to neutral conditions is related to the electrostatic interaction between the CaO photocatalyst surface and diazinon molecules. Under these conditions, diazinon has a pKa of approximately 2.6, while the CaO nanoparticle catalyst has a pH_{pzc} of 6.82, which implies that the CaO surface is positively charged in acidic to neutral conditions, while the diazinon molecules are negatively charged [6, 39]. Thus, a strong electrostatic attraction occurs between diazinon and the photocatalyst surface, which increases the adsorption and degradation rates. The effect of pH on photocatalytic is closely related to changes in the surface charge of CaO. At pH values below the pH_{pzc} (6.82), the CaO surface tends to undergo protonation, forming positively charged surface hydroxyl groups ($\equiv CaOH_2^+$). These positively charged sites promote the adsorption of negatively charged Diazinon species through electrostatic attraction. As the pH approaches neutrality, the balance between pollutant adsorption and reactive radical generation becomes more favorable, resulting in enhanced photodegradation efficiency. In addition, neutral conditions facilitate the formation of hydroxyl radicals ($\bullet OH$), which

are the primary oxidizing species involved in Diazinon degradation.

Similarly, the decrease in diazinon degradation efficiency after neutral pH can be explained by electrostatic interactions. Under alkaline conditions, the solution pH is greater than the p_{Hpzc} of CaO. Consequently, the CaO photocatalyst surface becomes deprotonated and negatively charged, resulting in electrostatic repulsion between the CaO photocatalyst surface and the diazinon molecules [42]. Likewise, high pH can also inhibit photocatalytic activity. Under alkaline conditions (pH > p_{Hpzc}), the CaO surface becomes deprotonated, leading to the formation of negatively charged surface groups ($\equiv\text{CaO}^-$). As a result, electrostatic repulsion between the negatively charged catalyst surface and Diazinon molecules reduces adsorption efficiency. Furthermore, excessive OH⁻ ions in solution may compete with Diazinon molecules for active sites on the catalyst surface and alter the surface reaction pathway. These factors collectively decrease the utilization of active sites and reduce the overall photodegradation efficiency. Therefore, this study concluded that pH 7 provides optimal conditions for diazinon photodegradation.

Effect of Exposure Time

Irradiation time is an important parameter that directly affects degradation efficiency. This study analyzed the effect of irradiation time on the degradation efficiency of diazinon with time variations of 30, 60, 90, 150, and 240 minutes using visible light as shown in Figure 7.

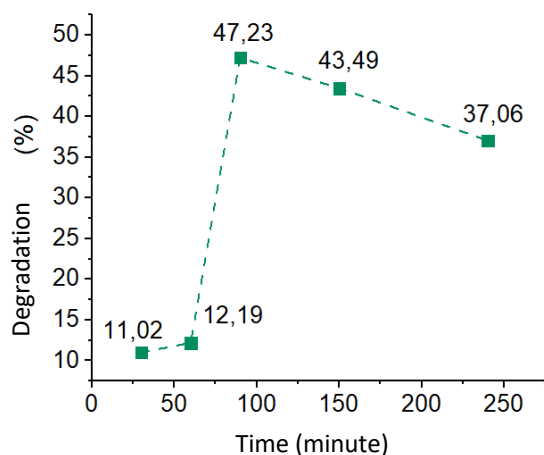


Figure 7. Effect of Exposure Time

The experimental results showed that diazinon degradation efficiency increased significantly with longer irradiation times. Initial measurements at 30 minutes showed a minimum degradation efficiency of 11.02%, then increased sharply at 90 minutes to 47.23%. Grafuj also showed a similar pattern to the previous parameters, namely a decline after reaching the optimum time. The low initial degradation efficiency after irradiation is due to the limited number of photons absorbed by the catalyst, resulting in the formation of electron-hole pairs that are not optimal. This means that prolonged interaction between photons and the CaO photocatalyst can increase the efficiency of diazinon degradation, resulting in a sharp increase in efficiency, reaching 47.23% at 90 minutes.

However, the photodegradation efficiency after 90 minutes gradually decreased with increasing irradiation time. The findings showed that the degradation efficiency continued to decline to 37.05% at 240 minutes. This is due to the CaO photocatalyst reaching its optimum point, explained by increased electron-hole recombination, saturation of active sites due to the closure of intermediate products, and the formation of more stable intermediate compounds that are more difficult to decompose [43]. In addition, prolonged irradiation may contribute to partial photocatalyst deactivation due to the accumulation of degradation intermediates on the CaO surface. These intermediates can block active sites and reduce the accessibility of reactant molecules to the catalyst surface. Extended exposure to light may also induce localized photothermal effects, which can alter surface interactions and accelerate electron-hole recombination, thereby decreasing the efficiency of reactive radical generation. Consequently, although longer irradiation provides more time for pollutant degradation, excessive irradiation does not necessarily improve photocatalytic performance and may instead reduce the overall degradation efficiency. This study concluded that the optimum irradiation time for diazinon photodegradation with CaO photocatalyst was 90 minutes.

The Effect of Light Power

This study also analyzed the effect of light power on the photodegradation efficiency of diazinon, as the photocatalytic rate depends on the light intensity. The photodegradation efficiency with power variations of 80, 100, 120, 140, and 160 Watts is shown in Figure 8.

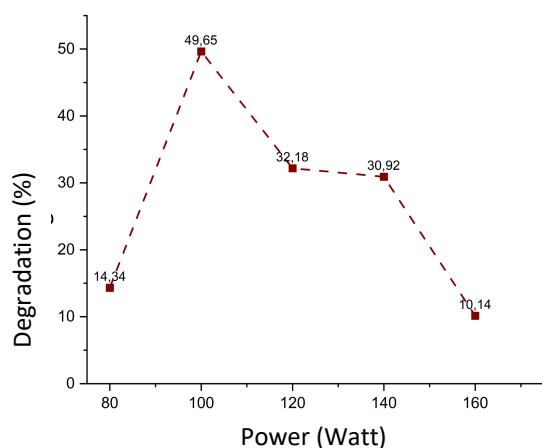


Figure 8. The Effect of Light Power

The efficiency of diazinon degradation increased with increasing lamp power. At 80 watts, the degradation efficiency was 14.34%. This value is relatively low because the photon energy generated at 80 watts is not enough to optimally activate the catalyst, resulting in limited formation of hydroxyl radicals ($\bullet\text{OH}$). Therefore, increasing the power to 100 watts was able to increase the degradation efficiency to 49.65%. This finding is consistent with previous photodegradation studies that stated that increasing radiation intensity is only effective up to a certain optimum point, after which efficiency will decrease if the light intensity exceeds the optimum limit [16].

Indirectly, these findings explain the reason for the decrease in diazinon degradation efficiency after 100 watts, which decreased to 10.14% at 160 watts. The increased electron-hole pair recombination at high light intensities decreases the number of hydroxyl radicals ($\bullet\text{OH}$) available for oxidation [15, 29]. At excessively high light intensities, the rate of electron-hole pairs generation may exceed the rate at which these charge carriers participate in surface redox reactions. As a result, electron-hole recombination becomes more dominant, reducing the quantum efficiency of the photocatalytic process. Consequently, a smaller

fraction of the absorbed photon energy is utilized for reactive oxygen species generation, leading to a decline in Diazinon photodegradation efficiency despite the increased light power.

In addition, excessive photon energy can also cause heating of the system and change the morphology of the catalyst, so that the adsorption process of diazinon molecules on the catalyst surface is hampered [44]. This phenomenon may also be associated with photothermal effects, where prolonged exposure to high-intensity irradiation increases the local temperature around the catalyst particles. Elevated temperatures can alter adsorption-desorption equilibria on the catalyst surface, reducing the residence time of Diazinon molecules on active sites. Furthermore, excessive heating may promote particle aggregation and reduce the effective surface area available for photocatalytic reactions. Therefore, increasing light power beyond the optimum level does not necessarily enhance photocatalytic performance and may instead reduce degradation efficiency. Accordingly, the optimum power for diazinon photodegradation efficiency is 100 watts without any excessive power increase.

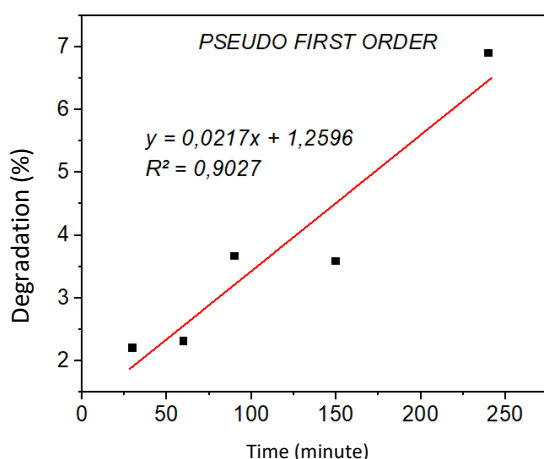
3. Kinetics of Diazinon Photodegradation Reaction

Photodegradation kinetic modeling was performed using data on a catalyst dose of 16 mg, a solution concentration of 50 ppm, pH 7, and time variations of 30, 60, 90, 150, and 240 minutes. The kinetic models tested included zero-order, first-order, pseudo-first-order, second-order, and pseudo-second-order. This reaction mechanism approach is based on the Langmuir-Hinshelwood model, which is commonly used to explain the kinetic mechanisms of heterogeneous catalytic degradation processes of organic waste by characterizing solid-state catalytic reactions.

Table 1. Reaction Kinetics

Model	K(/min)	R ²
First Order	0.0121	0.8437
Pseudo First Order	0.0217	0.9027
Second order	0.00006	0.7591
Pseudo Second Order	0.0157	0.8855
Zero Order	4.480	0.793

Table 1 shows the results of linear regression analysis on various kinetic models. The pseudo-first-order model provided the highest R² value of 0.9027, followed by the pseudo-second-order model at 0.8855 and the first-order model at 0.8437. Meanwhile, the second-order and zero-order models showed relatively lower R² values, at 0.7591 and 0.793, respectively. The comparison of these R² values indicates that diazinon photodegradation follows a pseudo-first-order kinetic model.

**Figure 9.** Reaction Kinetics

The suitability of this pseudo-first-order kinetic model is shown by the graph of the relationship of $\ln(C_0/C_t)$ against time with a linear equation $y = 0.0217x + 1.2596$ shown in Figure 9. The slope value of 0.0217 indicates the reaction rate constant (k), while the R² value of 0.9027 indicates that more than 90.27% of the data variation can be explained by the model. These results are in line with previous studies that reported that the kinetics of diazinon photodegradation follows a pseudo-first-order kinetic model [6, 38]. In heterogeneous

photocatalytic systems with low initial pollutant concentrations, the pseudo-first-order kinetic model is often found because the number of active sites available on the photocatalyst surface is relatively greater than the number of adsorbed pollutant molecules. Under these conditions, the level of surface coverage by diazinon is relatively low so that the degradation rate becomes proportional to the diazinon concentration. This behavior is in accordance with the Langmuir–Hinshelwood mechanism which assumes that the photocatalytic reaction takes place on the catalyst surface after the pollutant molecules are adsorbed. At low concentrations, the Langmuir–Hinshelwood equation can be simplified to a pseudo-first-order form, which indicates that the photodegradation rate is controlled by the adsorption process of diazinon on the catalyst surface and subsequent oxidation by reactive radicals generated on the CaO surface [16].

Under these conditions, the zero-order, first-order, second-order, and pseudo-second-order kinetic models are less suitable for the reaction mechanism of photocatalytic degradation of diazinon. Zero-order kinetics assumes that the reaction rate is independent of the reactant concentration [45], so it does not correspond to the photocatalytic degradation reaction where the decrease in concentration is influenced by the degradation rate. First and second order kinetics only assume the reaction rate is dependent on the concentration of the reactant [45], without considering the reaction on the catalyst surface, making it less suitable for heterogeneous reactions such as photocatalytic degradation. Meanwhile, pseudo-second-order kinetics describes the reaction rate as being more influenced by the chemical interaction between the substrate and the active sites on the catalyst surface [46]. Therefore, the photodegradation rate of diazinon depends on the adsorption process of molecules on the catalyst surface and the oxidative reaction by hydroxyl radicals formed during visible light irradiation.

Research Limitations

The study has several limitations, including relatively low maximum degradation

efficiency (49.65%), the absence of intermediate products identification, and the lack of catalyst stability and reusability evaluation. These aspects should be addressed in future studies to further.

Author contribution

Keisha Ekya Larissa contributed to the conceptualization of the study, implementation of the study, data collection, data processing and curation, formal analysis, interpretation of the results, and preparation of the initial draft of the manuscript. Andini Nur Aisyah contributed to the implementation of the study, data collection and processing, validation of the research data, and review and editing of the manuscript. Auliya Shofie contributed to the laboratory experimental procedures, implementation of the study, data validation, documentation of research activities, data visualization, and review and editing of the manuscript. Hilman Imadul Umam contributed to the conceptualization and design of the research methodology, research supervision, interpretation of the results, and critical review and editing of the manuscript. Teguh Pambudi contributed to the supervision, evaluation of the research results, critical review, editing, and refinement of the substance of the manuscript before publication. All authors have reviewed and approved the final version of the manuscript and declare responsibility for all the contents of the published research.

Conclusion

CaO synthesized from eggshell waste exhibits physicochemical characteristics that support its application as a photocatalyst. The efficiency of Diazinon photodegradation is significantly influenced by operational variables, including catalyst dosage, contact time, pH, initial concentration, and light intensity. Increasing these variables increases degradation until it reaches optimum conditions, but excessive addition causes a decrease in efficiency due to light penetration barriers, limited generation of reactive radicals, and increased electron-hole recombination. Kinetic analysis shows that the Diazinon photodegradation process follows the Langmuir-Hinshelwood model with pseudo-

first-order kinetics, indicating that the reaction is controlled by pollutant adsorption on the catalyst surface and oxidative reactions on the surface, confirming that eggshell waste-based CaO has the potential as an environmentally friendly and effective photocatalyst for pesticide remediation in waters.

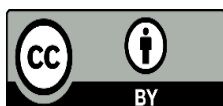
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