Journal of Advanced Research in Applied Sciences and Engineering Technology

Journal homepage:
https://semarakilmu.com.my/journals/index.php/applied_sciences_eng_tech/index
ISSN: 2462-1943

Calcium Oxide Nanoparticle Production and its Application as Photocatalyst

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ARTICLE INFO

Article history:
Received 15 December 2022
Received in revised form 14 April 2023
Accepted 21 April 2023
Available online 10 May 2023

Keywords:
CaO; nanoparticle; degradation; photocatalyst; indigo carmine

ABSTRACT

This study aimed to synthesize and characterize calcium oxide (CaO) nanoparticles as a photocatalyst in the degradation process of indigo carmine (IC) dyes. Several steps were carried out to produce CaO nanoparticles by mixing 0.5 M of $CaCl_2$ solution with various NaOH solutions (0.5; 0.8; and 1.0 M). Experimental results showed the prospective control of CaO particle sizes. The experiments also confirmed that the greater concentration of NaOH correlates with the greater yield of nanoparticles produced. The best condition to produce CaO nanoparticles was obtained when using the ratio of CaCl2: NaOH of 1:2. Additional results showed the difficulties in the production of CaO particles in the nanometer size, which is due to the existence of solid agglomeration, giving ideas to the need in putting some additional experimental steps. The photocatalytic degradation studies showed several factors affecting the photoreaction rate, including processing time, catalyst dosage, and dye concentration. CaO nanoparticles had the best performance in catalyzing indigo carmine in 50 minutes, which was shown by the combination of 10 mg of CaO nanoparticles and 80 ppm of dye concentration.

1. Introduction

The waste generated by the textile industry has considered harmful to living organisms. Some unwanted substances can be the primary cause of environmental pollutants such as water, soil, and air [1]. The release of colored waste in aquatic environments can cause dangerous pollution and eutrophication with by-products such as oxidation reactions, hydrolysis, or other chemical reactions [2].

There is a very rapid increase in the textile industry in Indonesia by 13.74%, which is increasing the production of colored waste in water, which is also increasing rapidly [3]. Most of these industries use synthetic dyes because they are cheap, durable, easy to obtain, and easy to use. However, the use of synthetic textile dyes raises a problem, namely that the waste is difficult to degrade naturally.

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https://doi.org/10.37934/araset.30.3.168181

The waste of textile dye must be treated before being discharged into waterways because around 10-15% of dyes that have been used cannot be reused [4,5].

Indigotin or indigo carmine (IC) is one of the most used synthetic dyes. Although it is previously extracted from a plant of the genus Indigofera, it creates issues for the environment. This dye is used in conjunction with Patent Blue V to give a blue color to foodstuffs. These two blue colors are colors used in coatings, ice cream, and confectionery [6]. Although indigo carmine can be produced by the natural indigo sulfonation process, usually indigo is also made synthetically by the fusion method of the N-phenyl glycine compound in a mixture of sodamide, sodium hydroxide, and potassium hydroxide under the pressure of ammonia. Therefore, indigo carmine should be considered a synthetic food coloring [7].

According to current information, dyes have molecules that are a combination of unsaturated organic substances with chromophores as color carriers and auxochromes as color binders with fibers [8]. This chromophore group causes a molecule to produce a color. In the formation of dyes in a molecule, there are unsaturated organic substances such as aromatic hydrocarbon compounds and their derivatives, phenolic compounds, and their derivatives, as well as nitrogen-containing hydrocarbon compounds.

Indigo carmine can act as a pollutant in the aquatic environment because of its toxicity to rats, pigs, and humans. Due to its toxicity to nature, waste containing this compound must be treated to minimize or eliminate its toxic effects on biota [9].

As for several conventional ways of dealing with aquatic waste, several methods have been reported through glass, chemical and biological processes, membrane purification, chemical precipitation, adsorption, electrochemical degradation, advanced oxidation processes, and others which can be useful for treating and removing color from textile waste [10]. However, because these techniques use a lot of energy and chemicals, most of these technologies are expensive, requiring long-processing times and are often ineffective in practice [11]. Some reports showed a growing trend for diverse use of pollutant removal, based on catalytic agent and functionality [12–17]. Therefore, effective water waste management is needed to reduce water pollution [18]. One way that can be used is the use of a catalyst as an agent that speeds up the degradation process of dye waste [19,20]. One of the catalytic agents that is considered to be promising is when using catalyst in the size of nanoparticles [21,22]. In recent decades, nanoparticles have been studied for various applications. Nanoparticles have unique physicochemical characteristics, such as a large surface area, efficient catalyst dosage, and high reactivity [23,24].

In addition to their unique properties, nanoparticles also have a wealth of applications such as mobilization and activity as a water treatment catalyst, biodiesel heterogeneous catalyst, therapeutic agents in the pharmaceutical field, vaccine content, drug delivery systems, antimicrobial agents, fertilizers, sensors, cancer treatment, nanofluid content [7,25-32]. Furthermore, nanoparticles also have advantages in their applications such as more environmentally-friendly, more pollution-free, less non-toxic condition, and low cost for wastewater treatment applications due to large surface are, making them very cost-effective [33].

In addition, photocatalytic reactions are reactions that occur under the aid of light or without light with a photocatalyst [34]. This reaction has advantages, including being able to protect the environment from contaminants, being able to completely degrade a pollutant, and not producing secondary pollutants in the reaction.

One of the nanoparticles that can be used as a photocatalyst for pollutant degradation is calcium oxide (CaO) nanoparticles [35]. CaO nanoparticles are a white solid belonging to the metal oxide group [36]. This substance will first exist as a particle, $Ca(OH)_2$, which can be synthesized using various

methods, including sonochemistry, plasma-metal hydrogen reactions, the sol-gel method, water-in-oil microemulsions (W/O), and precipitation [37-40].

The emergence of variations in the CaO nanoparticle synthesis method will lead to different properties of CaO nanoparticles, such as morphology, specific surface area, and adsorption efficiency [41]. However, it is considered that the precipitation method is a relatively easy and low-cost synthesis [25,26]. The main advantage of the precipitation process is the possibility of creating pure and homogenous material [42]. Chemically, CaO nanoparticles can be used as a photocatalyst in the degradation process of organic dyes such as methylene blue, congo red, malachite green, indigo carmine, violet GL2B and crystal violet [43-48].

CaO can act as a photocatalyst in the degradation process of indigo carmine dye [35]. The photocatalytic membrane on CaO nanoparticles can accumulate pollutants near the surface of the catalyst and further degradation processes will occur [49]. In addition, fouling on the catalyst membrane can be mitigated because the addition of a photocatalyst will increase the wetting properties of the membrane [50]. Meanwhile, the semiconducting properties of CaO can be excited by higher energy light such as UV-Vis light, inducing the formation of electron-rich pairs that can involve redox reactions [28,34].

The degradation of various reactive dyes has been extensively studied (using a variety of photocatalysts, including perovskites, titanates, zinc oxide, niobates, calcium oxide, nanoparticle-nickel oxide composite, and semiconductors [51-55]. However, no research has been conducted to date that investigates the effects of varying the catalyst concentration. Even though it is known that the concentration of a solution is quite influential in determining the rate of a compound reaction. The frequency of collisions between the two reactants will increase as the reactant concentration rises. There are times when crashes don't cause a reaction (atoms misaligned or insufficient energy, etc.). More collisions and more opportunities for response result from higher concentrations [56].

Therefore, the innovative aspect of this study is the variable in concentration, which is anticipated to have a significant impact on its effectiveness as a catalyst for the degradation process. Whereas the purpose of this study was to identify the efficiency of calcium oxide (CaO) nanoparticles as a photocatalyst in the degradation process of IC dye which is expected to have better efficiency than previous studies by varying the concentration of calcium oxide.

2. Methodology

Some materials used in this study were anhydrous calcium chloride (95%), sodium hydroxide, distilled water, and indigo carmine dye.

2.1 Synthesis of CaO Nanoparticles

100 mL $CaCl_2$ at 0.5 M and 100 mL NaOH with various concentrations (0.5; 0.8; and 1 M) were used as starting reagents for the synthesis of CaO nanoparticles. Initially, both CaCl and NaOH solutions were heated in a closed Erlenmeyer flask to a temperature of 80°C. At that temperature, $CaCl_2$ was added dropwise into the NaOH solution under stirring using a magnetic stirrer (1000 rpm) for 30 minutes.

The suspension was then centrifuged at 11,000 rpm and washed twice using distilled water. We then collected the wet solids into a crucible cup with a lid, and baked them in the oven at 100°C until the solids dried (± 3 hours). After the solids were dried, they were transferred to the boat furnace and heated using a furnace at 400°C for 2 hours. Solids were weighed before and after the furnace.

CaO particles that have been weighed are marked with the name CAN 10; CAN 08; CAN 05 corresponding to the addition of NaOH concentration of 1.0; 0.8; and 0.5 M, respectively.

2.2 Photocatalytic Applications
2.2.1 Effect of dye concentration

As much as 10 mg of IC dye was dissolved in 100 mL of distilled water to produce an indigo carmine stock solution (100 ppm). In this experiment, 30 mg CaO nanoparticles (CAN 10) were added to 20 mL of IC at different concentrations (i.e., 10; 30; 50; and 80 ppm). The mixing of the two was carried out in a dark glass bottle under vigorous stirring (1000 rpm) for 60 minutes using a magnetic stirrer. The suspension was centrifuged (11,000 rpm) and analyzed using UV-Vis.

2.2.2 Effect of catalyst concentration

Solid CaO (CAN 10) nanoparticles with various amounts (i.e., 10, 20, 30, and 40 mg) were added to 20 mL of IC solution with a concentration of 10 ppm. The mixture was stirred at 1,000 rpm for 60 minutes in a dark glass bottle. The resulting suspension was centrifuged (11,000 rpm) and analyzed using UV-Vis.

2.2.3 Effect of photocatalytic processing time

IC solution (30 ppm) was put into a 20 mL dark glass bottle and 30 mg of CaO CAN 10 solid nanoparticles were added to it. We stirred with a magnetic stirrer at various times: 10, 20, 30, 40, and 50 minutes. The time interval used was 10 minutes. Then, we centrifuged and took UV-Vis analysis.

IC dye was used as a monitor for the photocatalytic activity of CaO. The percentage (%) of the pure IC solution were checked by calculating the amount of absorbance (A) of the filtrate solution treated at a wavelength in the range of 200-500 nm using a UV-Vis spectrophotometer and calculated using the Eq. (1)

$$Photocatalyst\ Efficiency\ (\%) = \frac{A_0 - A_t}{A_0}\ x\ 100 \quad (1)$$

where A_0 is the initial absorbance of the IC dye and A_t is the absorbance of the IC dye which has been treated with a variety of different variables. A_t was calculated based on the correlation (obtained from the calibration curve) presented in Eq. (2)

$$y = 0.0019x - 0.0029, R^2 = 0.9954 \quad (2)$$

where *y* was the absorbance value measured at 280 nm and *x* was the concentration of IC dye (mg/L).

3. Result
3.1 The Effect of NaOH Concentration

The CaO nanoparticles obtained were white solids with a powdery texture. The results show that the greater the concentration of NaOH, the yield produced will be even greater. This is because it takes two species of NaOH to react with one species of CaCl2 to produce $Ca(OH)_2$ particles. In addition, Na+ ions are more reactive than Ca2+ ions due to the electron configuration of the outer

cell. As a result, Na+ ions in water can attract Cl- ions to produce precipitated NaCl and $Ca(OH)_2$ that are shown in reaction scheme (3).

$$CaCl_2 + 2NaOH \rightarrow Ca(OH)_2 + 2NaCl \quad (3)$$

In this study, three concentrations of NaOH were used (i.e., 0.5; 0.8; and 1 M). These three types of NaOH concentrations produced different final masses of CaO, as shown in Table 1. The mass of CaO particles at a concentration of 1 M produced the largest mass yield of up to 2.99 g while lowering the concentration of NaOH to 0.8 and 0. 5 M produced a mass yield of CaO of 2.35 and 1.85 g. respectively. The concentration ratio of $CaCl_2$:NaOH of 1:2 produced the best mass yield. This could be because water contains more Na^+ ion species at 1 M of NaOH concentration compared to that using 0.5 and 0.8 M.

Table 1
Comparison of CaO particle mass before and after heating furnace (400)

NaOH Concentrations	CaO Mass Before Furnace (gr)	CaO Mass After Furnace (gr)
0,5M	2,71	1,85
0,8M	3,03	2,35
1 M	4,01	2,99

3.2 Characterization of CaO Nanoparticles
3.2.1 SEM analysis of CaO nanoparticles

The morphological and texture analysis of CaO nanoparticles using scanning electron microscopy (SEM) is shown in Figure 1 [57]. It was revealed that CaO has a sponge-like morphology with big and small lumps. The bright part is the surface of the CaO nanoparticles, which reveals a high electron emission when exposed to an electron beam from the SEM instrument.

Some CaO particles have reached nanometer size. The results showed that the size of the smallest nanoparticles was 65.13 nm while the largest particles were 194.245 nm (Figure 1(a)). Thus, the average particle size of CaO is 123.97 nm. These particles can be classified as nanoparticles since the sizes are in the range of between 1 and 100 nanometers. The large particle size can be caused by agglomeration events in the CaO particle spheres resulting in a larger particle size. The factor that causes this agglomeration may be the absence of surfactants in the nanoparticle manufacturing process. Thus, there are no substance that can prevent agglomeration between the formed particles [58]. However, this agglomeration revealed the polycrystalline characteristics of the CaO nanoparticles in giving spherical shape [59].

In the comparison of the results of the SEM analysis in Figure 1, different morphologies were obtained. Figure 1(a) shows less agglomeration of CaO particles compared to that shown in Figure 1(b) and Figure 1(c), informing the concentration of NaOH can affect the agglomeration properties of CaO.

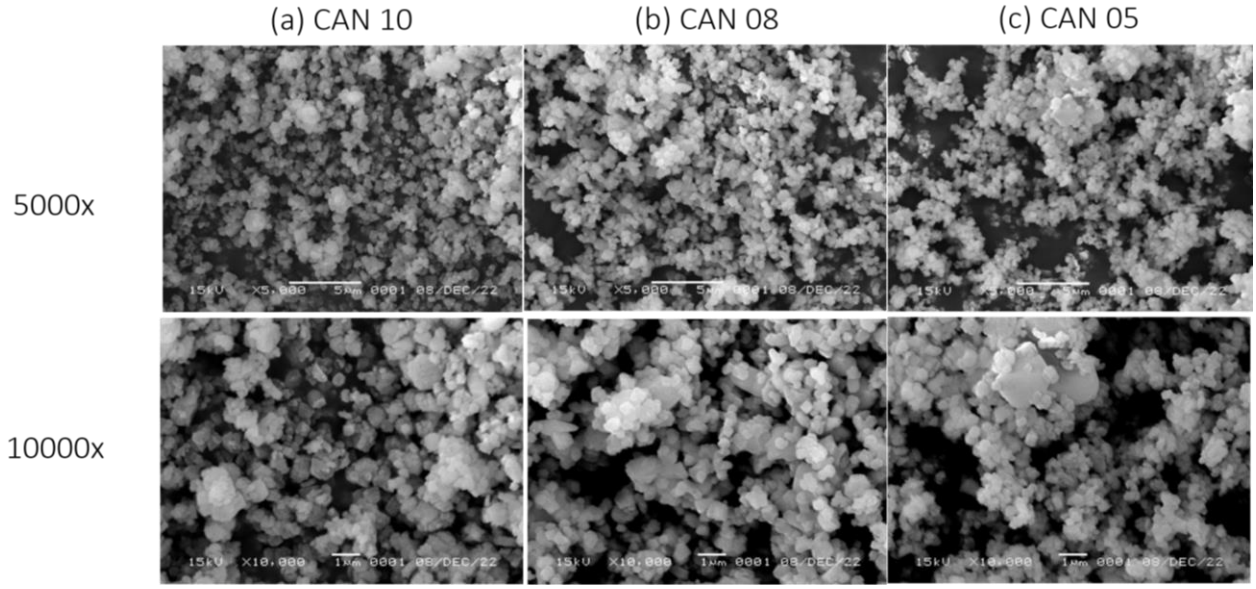

Fig. 1. SEM analysis results of CaO nanoparticles with various concentrations of NaOH

3.2.2 FTIR analysis of CaO nanoparticles

In Figure 2, the results of the analysis using infrared spectroscopy are shown, showing the functional groups possessed by CaO nanoparticles. This spectroscopy relies on electromagnetic radiation interference, providing functional groups that are on the surface of the nanoparticles. The FTIR spectrum was obtained in the range of 4000 to 500 cm^{-1}. Sharp peaks with high intensities are shown at 704, 844, 875, 1645, 2177, 2603, and 3761 cm^{-1}. These peaks indicate the presence of N-H, O-H (carboxylate), -CN, C=O, C=N, C=C, C-O, Ca-O, and other bonds in the calcium oxide nanoparticle powder.

The difference between the spectra produced by CaO nanoparticles at CAN 10, CAN 08, and CAN 05 is the difference in the intensity of the resulting sharp peaks. CAN 10 produces the highest intensity at the peak of 709 cm^{-1}, showing the Ca-O bond, while CAN 05 produces the lowest intensity at that peak. Detailed information for the FTIR interpretation is in elsewhere [60-62].

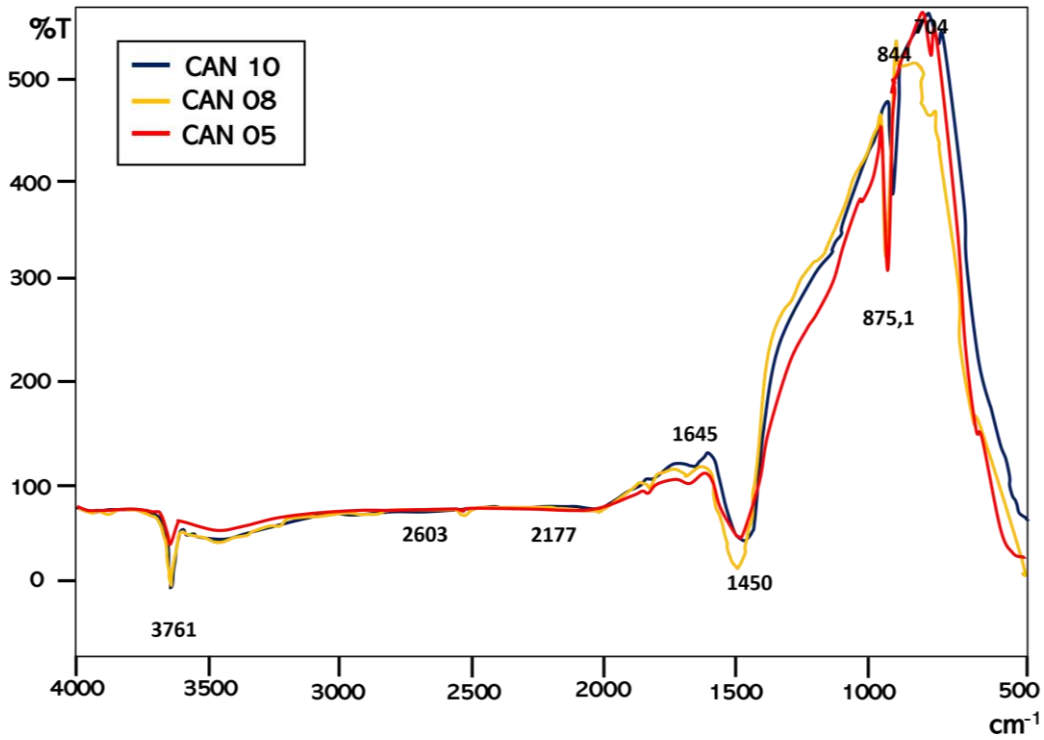

Fig. 2. FTIR analysis of CaO nanoparticles

3.2.3 XRD analysis of CaO nanoparticles

XRD instrumentation is very important as a tool to analyze the crystallinity of the sample [63,64]. Figure 3 depicts a CaO nanoparticle XRD diffraction pattern with peaks at angles of 2 29.27, 33.9, 54.18, and 64.24, which are suitable for diffraction fields (111), (200), (220), and (311). These peaks have been approved with commercial solid CaO (JCPDS-01-077-2376). The diffraction pattern for the $Ca(OH)_2$ compound approved by JCPDS-00-004-0733 is at the peak at the angle of 17.8; 28.6; 48.4; and 62.5. Based on the XRD diffraction pattern, it is confirmed the presence of CaO particles. The $Ca(OH)_2$ peak in the diffraction pattern can be attributed to water absorption when the CaO nanoparticles are handled.

In addition, the three types of CaO nanoparticles, namely CAN 10, CAN 08, and CAN 05, produced almost the same X-Ray diffraction patterns, showing no significant differences in the peak patterns. Then, the crystal size of the three types of CaO can be calculated through the Debye Scherrer equation in Eq. (4) [63]

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{4}$$

where D is the average particle size, λ is the wavelength of the K-Alpha Copper radiation, β is the width of the entire diffraction peak (FWHM), k is the sensitive coefficient (0.9), Cu Kα radiation (λ = 1.54060) and ϑ refers to the Bragg angle corresponding to the maximum intensity peak. Based on the calculations, the average size of CaO nanoparticle crystals is 27.26 nm.

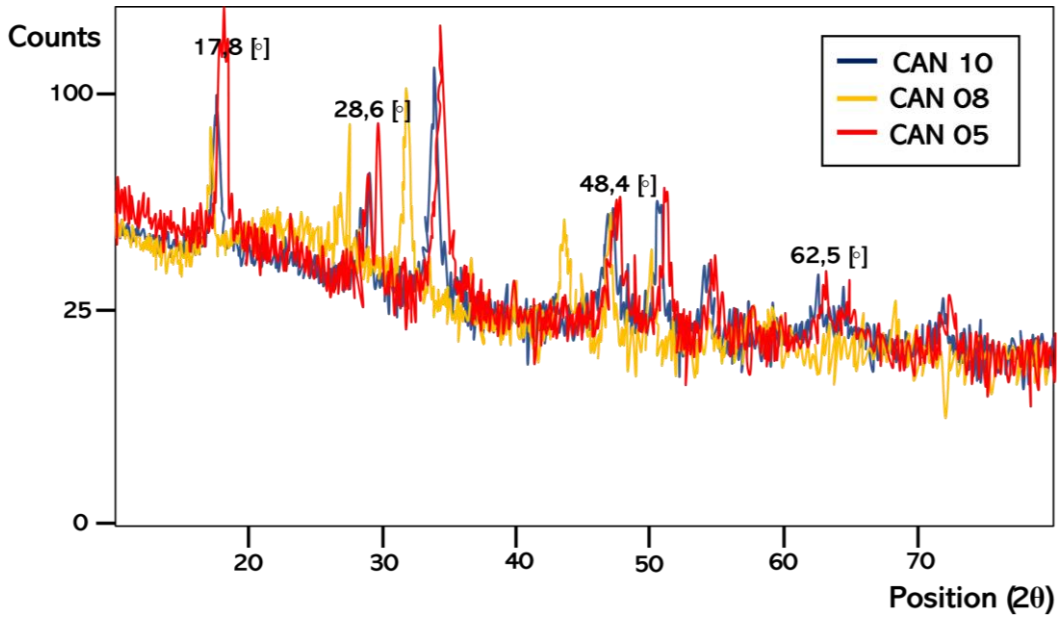

Fig. 3. XRD analysis of CaO nanoparticles

3.3 Study of Indigo Carmine Photocatalytic Degradation Efficiency

3.3.1 Effect of calcium oxide catalyst dosage

The dosage of CaO nanoparticles has an important role in the photocatalytic degradation process. This difference in catalyst dosage was carried out to determine the optimal amount of catalyst in the degradation process. Catalyst dosages of 10, 20, 30, and 40 mg were carried out at a dye concentration of 10 ppm for 60 minutes. Figure 4 shows the relationship between CaO catalyst dosage and the effectiveness of photocatalytic degradation. A catalyst dose of 10 mg showed the best results, while more catalysts for photocatalytic degradation did not occur. This could be due to the large number of active sites that are suitable for absorbing OH from dye molecules [65].

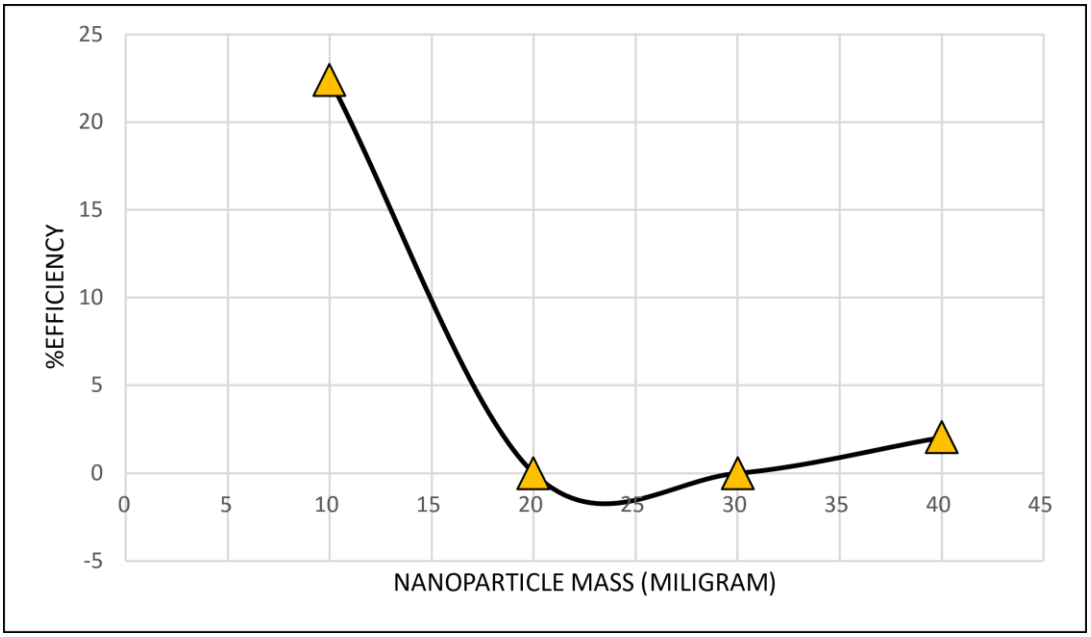

Fig. 4. Effect of dosage of CaO catalyst on the efficiency of photocatalytic degradation of IC dyes

3.3.2 Effect of dye concentration

The efficiency of photocatalytic degradation can also be affected by dye concentrations in the range of 10, 30, 50, and 80 ppm. As shown in Figure 5, the effectiveness of degradation increased as dye concentration increased. At a dye concentration of 10 ppm, it was shown that no degradation process occurred using a CaO catalyst, this could be because there were too few dye molecules. Thus, the ability of the catalyst was reduced in its degradation rate. The high dye concentration will cause the color intensity to increase, and light penetration can reduce the number of photons that enter the catalyst surface [1].

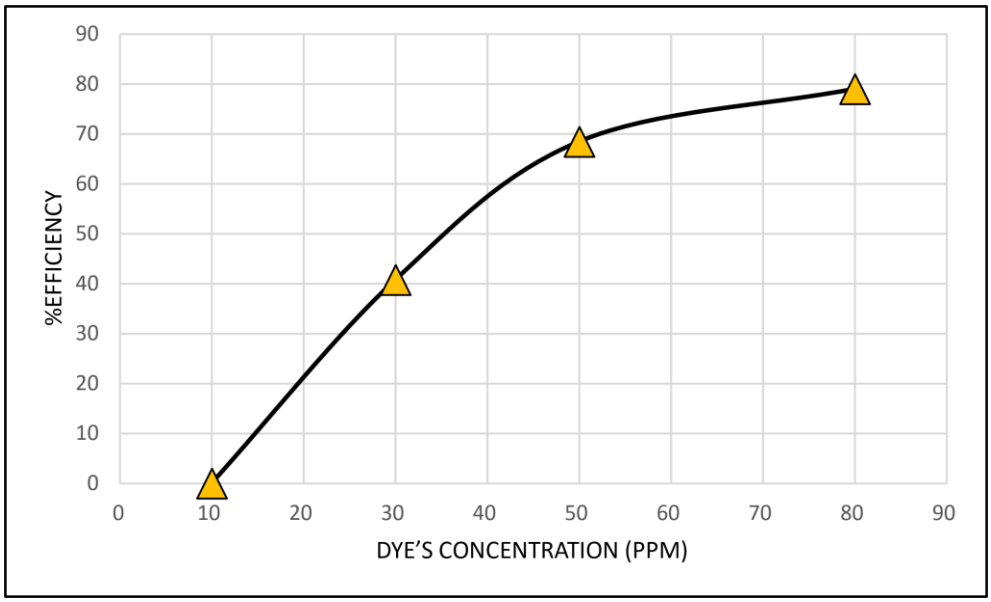

Fig. 5. Effect of IC dye concentration on the photocatalytic degradation efficiency of IC dyes

3.3.3 Effect of degradation time

Photocatalytic degradation can also depend on the timing of the process. Maximum degradation can occur if the interaction between the catalyst and dye can also occur optimally [46]. Figure 6 shows that the longer the contact time between the catalyst and the dye, the greater the absorbance efficiency produced. If the degradation time is too short, the catalyst and dye cannot encounter each other. Thus, water and pollutant have not reached the stage of passing through the catalyst membrane assisted by UV light [66].

Finally, above results showed additional information for the use of photocatalyst for being used as an alternative way for solving waste water. This is in line with current research [67-69].

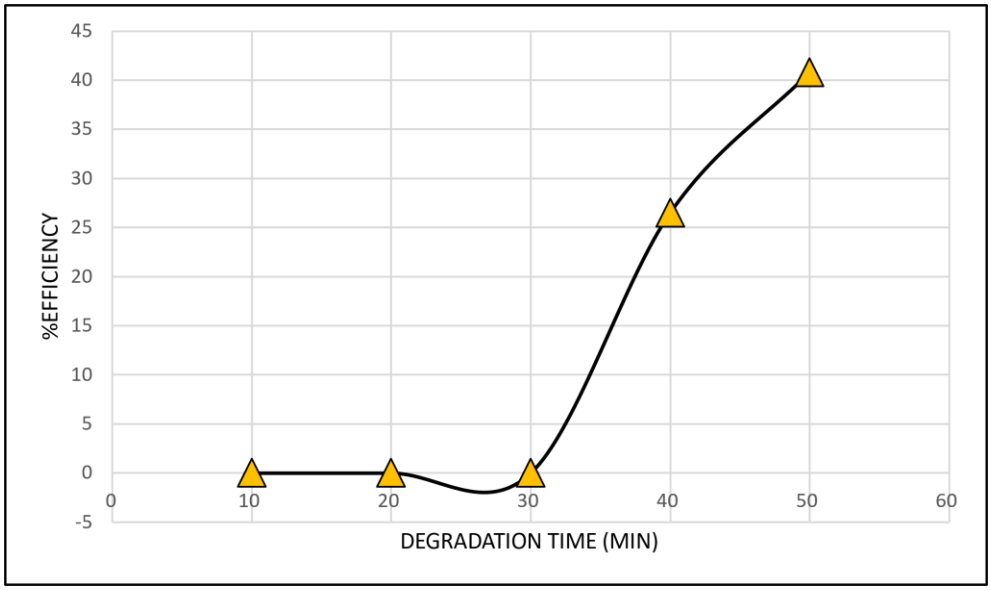

Fig. 6. Effect of degradation process time differences on IC dye photocatalytic degradation efficiency

4. Conclusion

Synthesis of CaO nanoparticles has successfully carried out with CaCl2 and NaOH ratios of 1:1, 1:2, and 4:5. The nanoparticles with a $CaCl_2$:NaOH ratio of 1:2 produced the best CaO particles. Of the three types of CaO particles, some of them still cannot reach nano size due to the agglomeration of solids. Based on the result of SEM and FTIR analysis, nanoparticles with a $CaCl_2$:NaOH ratio of 1:2 also produced the best results. In the XRD results, all three samples produced the same crystallinity properties of CaO nanoparticles. In the study of photocatalytic degradation, the results showed that time, catalyst dose, and dye concentration can affect the photocatalytic degradation process. The lower catalyst dose resulted in the better photocatalytic degradation process, while the more dye concentration and time used correlated to the better photocatalytic degradation process.

Acknowledgment

This research was supported by RISTEK BRIN (Grant: Penelitian Terapan Unggulan Perguruan Tinggi) and Universitas Pendidikan Indonesia (Grant: Bangdos).

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