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Green Chemistry Approach for the Study of Methylene Blue Degradation in Aqueous Medium by CaO Photocatalysts under LED and Halogen Irradiation

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ABSTRACT

This work presents a green chemistry approach to investigate the photocatalytic degradation of Methylene Blue in aqueous medium using calcium oxide (CaO) as a photocatalyst under LED and halogen irradiation. The study focuses on how calcination temperature and light source influence the photocatalytic activity of CaO. Structural characterization (FTIR, SEM, and EDX) confirmed that increasing the calcination temperature from 1,000 °C to 1,100 °C enhances the crystallinity and homogeneity of CaO particles. Photocatalytic experiments revealed that, in the absence of light, the degradation rate remains low (< 3%), confirming that photocatalysis is the main degradation pathway. Under halogen lighting at 1,000 °C, 60% of methylene blue (MB) degraded within 40 minutes, while LED irradiation achieved 30%. At 1,100 °C, performance improved markedly: halogen light yielded 80% degradation after 60 minutes, compared to 50% under LED. The pH of the solution significantly affected efficiency; in basic medium (pH 9), LED irradiation led to 90% degradation at 1,100 °C, surpassing halogen (50%). In acidic medium (pH 2), efficiency remained below 25% under all conditions. Complete (100%) degradation was achieved at a catalyst mass of 15 mg under halogen light at 1,100 °C. These findings highlight the importance of optimizing physicochemical parameters to improve CaO-based photocatalysis and emphasize the potential of *Green Chemistry principles* for sustainable pollutant degradation.

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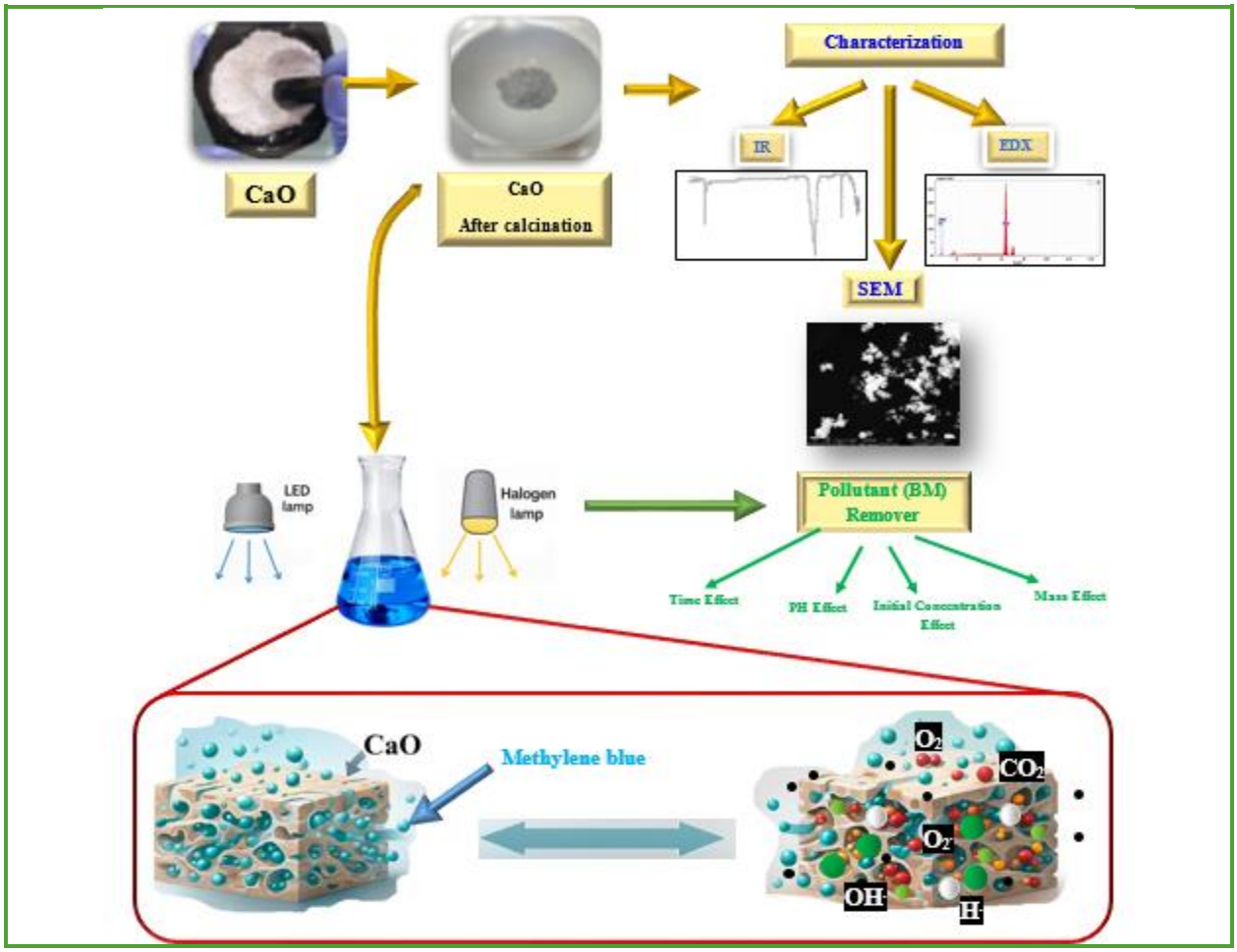
Graphical Abstract



Introduction

Water is not only necessary for survival, but also for the economic and social progress of humankind; it is the source of life [1]. It is found in many areas, particularly in industry and agriculture. However, this valuable resource remains at risk; therefore, effective measures must be implemented to protect it from pollution concerns [2]. By employing green chemistry principles, photocatalysis minimizes the use of hazardous chemicals and reduces energy consumption by utilizing solar or visible light as a clean energy source. This approach not only enhances the efficiency of contaminant removal, but also aligns to develop eco-friendly and sustainable technologies for environmental remediation [3-5]. Photocatalysis and the breakdown of pollutants in wastewater have recently drawn significant attention from scientists, as organic and inorganic impurities have an increasingly significant influence. Materials based on calcium oxide alone or in combination with other elements have shown remarkable performance in the degradation of pollutants such as organic dyes, metal ions, and other environmentally damaging compounds [6-8].

Calcium oxide, or CaO for short, is especially common in many industrial uses when it comes to pollution control. You will be shocked to learn that it rather efficiently destroys undesirable

organic dyes when exposed to light. Interestingly, combining CaO with other chemicals boosts its performance even more. This qualifies it as a serious candidate for environmentally friendly replacements for certain pollution issues. For example, there's this study by Song and others from 2009 where they mixed NiO with CaO through a process of precipitation and then heated it up to 700 °C. They found that this compound could take out 92% of the methylene blue (MB) dye in just 180 minutes when exposed to visible light, which was a great improvement compared to using NiO or CaO on their own. In fact, NiO alone managed a 65% reduction, while CaO only achieved 45%. This clearly shows how combining materials can boost their effectiveness [9]. In another piece of research by Song and Zhang, they explored Bi_2O_3/CaO composites for degrading MB. They found that after about 9.5 hours of visible light exposure, there was a 90% decrease in dye concentration, while the absence of the photocatalyst resulted in only a 10% reduction. They also tested the Bi_2O_3/CaO for reusability and discovered that it lost about 22% of its efficiency after being used five times [10]. Later that same year, Song and Zhang again created a NiO-CaO mix using a mechanical approach. This combination achieved an 80% reduction of MB in 150 minutes under visible light, which outperformed NiO alone at 60% and CaO at 40% [11]. Looking at more recent studies, Kornprobst and Plank in 2012 reported that when pure CaO was exposed to UV light, it degraded 70% of Rhodamine B after 90 minutes at a rate of 0.78% per minute. Meanwhile, the NiO-CaO combo was able to do even better, clearing out 85% of the dye under visible light after two hours [12]. Fast forward again, Gopalappa and friends compared how Acid Orange 7 dye breaks down by 99% under sunlight when $CaZnO_2$ nanoparticles are present. Without light, degradation is low, and without the catalyst, it does not occur. How well it works depends on pH, catalyst mass, light exposure time, and the initial dye amount [13]. Osuntokun's team looked into CaO nanoparticles made using a green method from broccoli extracts. It turns out that they achieved a 60.1% degradation of bromocresol green dye after 180 minutes of UV light exposure, marking a degradation rate of 0.33% per minute [14]. Coleto *et al.* discussed how CaO/$SrTiO_3$ heterojunctions could improve degradation efficiency thanks to crystal defects; although they did not specify exact degradation rates [15]. Bathla's research that same year showed that CaO taken from tap water was able to degrade malachite green dye by 95% after 90 minutes in sunlight, which was notably better than other materials used [16]. Alsohaimi experimented with an Ag@CaO composite derived from recycled eggshells. They reported a stunning 99.45% degradation of indigo carmine dye in just 25 minutes under sunlight. However, they noted that factors such as initial dye concentration and the amount of catalyst used could significantly affect its effectiveness [17]. Nassar and Alotaibi took things a step further by creating a photocatalyst from eggshells, calling it Pd@CaO. After heating it at 1,100 °C for two hours, they managed to achieve an 87.5% reduction in crystal violet dye under sunlight after an hour, with a fast degradation rate of 1.46% per minute [18]. Mohamed's team prepared CaO and a CaO/C photocatalyst from eggshells and coffee waste. They found that the CaO/C version could degrade MB dye by an impressive 99.76% after just 35 minutes of sunlight, while the pure CaO managed 88.04% [19]. Then, Ikram *et al.* found that adding cerium and cellulose nanocrystals to CaO really boosted its effectiveness against MBCF under natural light, with the blended composite showing the best degradation after 120 minutes [20]. Lastly, Eddy's research demonstrated that CaO nanoparticles derived from oyster shells were

effective in breaking down MB, achieving up to 98% degradation, as predicted by certain kinetic models in their study [21]. Ogoko's team, in recent work from 2024, examined CaO nanoparticles made from Crassostrea gigas shells for degrading bromocresol green. They reported a good 89% efficiency under sunlight and noted that the catalyst could be reused effectively. They found that the process involves some complex interactions, particularly with radicals, making it an exciting area for ongoing research [22].

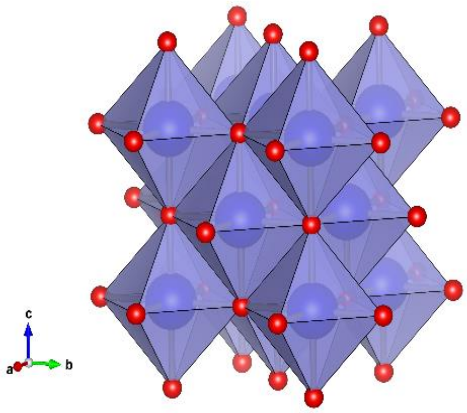


Figure 1. The structural representation of the CaO

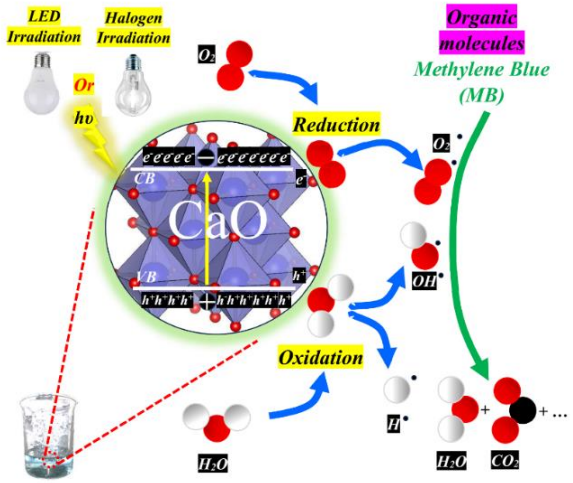


Figure 2. Mechanism of photocatalytic degradation of MB on the CaO photocatalyst

Crystal structure and properties of CaO

CaO is halite, rock salt structured and crystallizes in the cubic Fm̄3m space group (Figure 1). Ca^{2+} is bonded to six equivalent O^{2-} atoms to form a mixture of corner and edge-sharing CaO_6 octahedra [23]. The corner-sharing octahedra are not tilted. All Ca-O bond lengths are 2.40 Å. O^{2-} is bonded to six equivalent Ca^{2+} atoms to form a mixture of corner and edge-sharing OCa_6 octahedra. The corner-sharing octahedra are not tilted [24].

Mechanism for the photocatalytic degradation

Several important stages characterize the photocatalytic breakdown of MB on the CaO photocatalyst. Electrons (e^-) are excited from the valence band (VB) to the conduction band (CB) when exposed to light with energy equal to or greater than the band gap of CaO, thus creating holes (h^+) in the VB (Figure 2). These photogenerated charge carriers then move to the photocatalyst surface to engage in redox activities. Present in the valence band, the holes can oxidize hydroxide ions (OH^-) or water molecules (H_2O) to produce hydroxyl radicals (·OH), very reactive species capable of attacking organic compounds [23]. Simultaneously, the conduction band electrons reduce molecular oxygen (O_2) to superoxide radicals ($\cdot O_2^-$), which could then produce more reactive oxygen species (ROS), including hydroxyl radicals (·OH). These oxidizing agents convert MB molecules into simpler, non-toxic substances such carbon dioxide (CO_2) and water (H_2O) by means of chemical bond destruction [26]. One may summarize the entire reaction of hydroxyl radicals (·OH) destroying MB as Reaction 1:

$$\mathrm{MB} + \cdot\mathrm{OH} \rightarrow \mathrm{Intermediateproducts} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \quad (1)$$

Experimental

Materials and reagents

The materials used in this study were carefully selected to ensure accurate results. MB is a synthetic compound widely used as a dye and redox indicator. According to Sigma Aldrich (Table 1), it appears as dark green crystals with a bronze-like shine and dissolves easily in water and ethanol, creating a deep blue solution. Calcium oxide (CaO, 95%, M = 56.08 g/mol) was used as the main catalyst. Additionally, MB ($C_{16}H_{18}ClN_3S$, 319.85 g/mol, 99%), which is often used as a pollutant in experiments (Table 1), was included for testing. Also nitric acid (HNO_3, 65%, M = 63.01 g/mol) and sodium hydroxide (NaOH, 99%, M = 40.00 g/mol) were employed for pH adjustments and other reactions. All of these materials were purchased from Sigma-Aldrich and were used without further purification to maintain consistency in the experimental process.

Prepared samples

CaO (4 g) was used, and each portion was manually ground for an hour in an agate mortar. This step ensured that the powders were fine and uniform, thereby setting the stage for the next part of the process (Figure 3).

The oxide was then heated in a furnace at either 1,000 °C or 1,100 °C for six hours. This heat treatment allowed the oxide to undergo important structural and compositional changes needed for its catalytic functions. Once the calcination was completed, the sample was allowed to cool slowly to room temperature. It was then ground again for an hour to break up any clumps or agglomerates that had formed. This helped refine the powder further, ensuring its consistency and homogeneity, which would make the material more reactive and effective in its intended catalytic applications [27].

Result and Discussion

Characterization of the prepared materials

These characterizations help understand the materials' internal structures and properties, which are key to their industrial and scientific applications (Figure 4) [28].

Table 1. Physicochemical properties of MB (information extracted from the product specification sheet from the official site of Sigma Aldrich)

Property	Property value
Color	Dark green to blue crystals or powder
Trade name	MB
Scientific name	Basic blue 9
Color index (c.i.)	52030
Maximum wavelength (λ_{max}) (nm)	665
Solubility in water	Soluble in water
Molecular diffusivity (dmol) (at 25 °C)	4.7×10^{-6} (cm^2/s)
Chemical formula	$C_{16}H_{18}N_3OS{\cdot}3H_2O$
Molecular volume	390.2 (cm^3/g mol)
Molecular weight	373.5 (g/g mol)

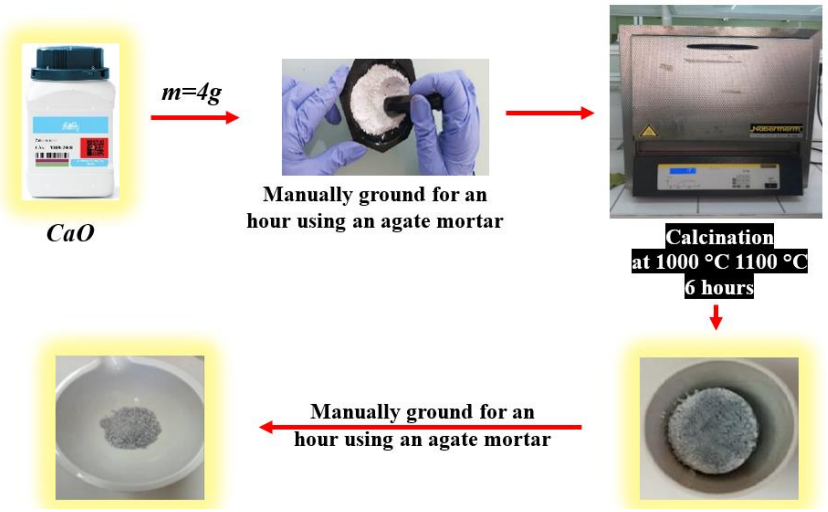


Figure 3. Descriptive flowchart for prepared samples

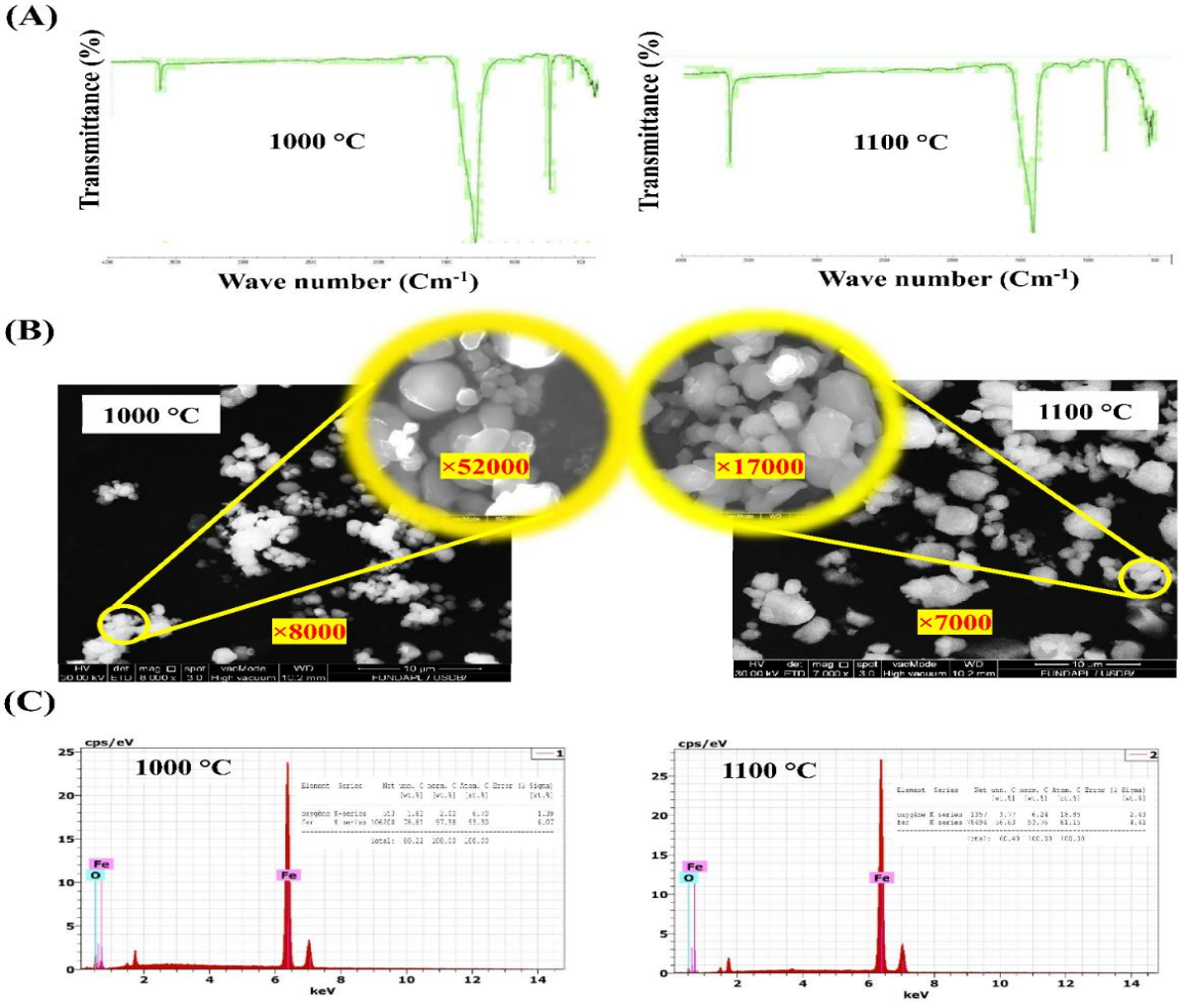


Figure 4. Characterizations of the CaO materials at 1,000 °C and 1,100 °C after 6 hours of calcination. (A) FTIR spectra, (B) SEM images, and (C) EDX spectra

The infrared spectra of CaO also provide key insights into its structures and chemical bonds (Figure 4). In CaO's spectrum, there is a band at 1,420 cm^{-1}, often linked to CO_2 vibrations, and another at 870 cm^{-1}, associated with Ca–O bonds. Check out the SEM images of CaO that were heated up to 1,000 °C and 1,100 °C. They clearly show how the shape and size of the crystals change as the heat is increased. At 1,000 °C, the crystals look pretty uneven, with sizes ranging from 2 to 16 µm. However, when the tempreture is raised to 1,100 °C, those crystals begin to appear much more uniform and better defined, reaching sizes of up to 17 µm. This uniformity seems to provide them with a boost in reactivity. Then, there is the EDX analysis, which reveals that the chemical makeup of CaO remains relatively steady, even as the temperature is changed. For instance, at 1,000 °C, the composition is about 52.88% calcium and 47.12% oxygen. At 1,100 °C, those numbers shift slightly to 51.80% calcium and 48.20% oxygen. This slight difference indicates that heating it more leads to crystals that are more consistent in structure. These findings really point out how important the calcination temperature is. Heating up to 1,100 °C not only helps make a stronger and more stable structure, but also shapes the particles in a way that enhances their reactivity. This is significant, especially for processes where catalysts or adsorption are key, as having that uniformity can greatly improve performance in those areas.

Pollutant remover

The study of parameters influencing photocatalysis offers an in-depth understanding of the factors that dictate the performance and efficiency of this light-driven process. Photocatalysis involves a delicate balance between light absorption, charge carrier separation, and interactions with target molecules, all of which are governed by specific variables. The concentration of the pollutant, MB, was measured using UV–Vis spectrophotometry at a wavelength of 665 nm (λ_{max}). The degradation efficiency (E) of MB was calculated using a specific Equation 1 [28].

$$E(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

Where, E is the efficiency (adsorbed amount %) and C_0, C_e are respectively the initial and the equilibrium concentrations of MB (mg/L).

The different degradation kinetics First and Second order curves can be classified based on the reaction mechanism and the type of degradation process [29].

In second-order degradation kinetics, the concentration drops quickly at first, and how fast it reaches half depends on the starting amount. In first-order kinetics, the concentration decreases at a steady rate that follows an exponential curve, and the half-life remains the same regardless of how much you begin with, as compared to the first and second order kinetics, mentioned in Table 2.

Table 2. Comparison of properties between first-order and second-order kinetics

Properties	First-order kinetics	Second-order kinetics
Differential equation	$\frac{dC_{(t)}}{dt} = -kC_{(t)}$	$\frac{dC_{(t)}}{dt} = -kC_{(t)}^{2}$
Solution	$C_{(t)} = C_0 e^{-kt}$	$\frac{1}{C_{(t)}} = \frac{1}{C_0} + kt$
Half-life	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k.C_0}$
Dependence of half-life on initial concentration	Independent of C_0	Dependent on C_0

Where, $C_{(t)}$ and C_0 are respectively the concentrations of MB (mg/L) of the substance at time (t) and in the initial concentration at (t = 0); k is the rate constant for degradation and $\frac{dC_{(t)}}{dt}$ shows how concentration changes over time.

Verification of the adsorption effect (without light)

The study looked into how well a photocatalyst works when there is no light available. Basically, they wanted to see how it interacts with pollutants in the dark. They carried out some experiments to examine the adsorption effect over a period of one hour, and the results can be found in Table 3.

Table 3. Results of the adsorption test (C_0=5 mg/L, m=100 mg, and V=50 mL)

Catalyst (CaO)	1,100 °C	1,000 °C
Contact time (hours)	1	1
Efficiency (%)	0.96	2.37

What they found is interesting. It turns out that the CaO material cannot just rely on grabbing onto pollutants. It really needs light to kickstart its full potential for breaking down those pollutants. Without any light, the effectiveness is low—under 3%. This means that what is really going on here is not just simple chemical reactions or adsorption; it is all about photocatalysis, which is driven by light [30]. Therefore, while the material has potential for cleaning up pollution, it really needs the right lighting conditions to work its best. Things like the type of light, how bright it is, and the specific wavelengths matter a lot.

Time effect

Now, when it comes to photocatalysis, there's this idea of how time plays a role. Basically, the longer the light shines, the better the photocatalytic reaction can be. Figure 5 in the study shows how the efficiency of degradation (that is how effective it is at breaking things down) changes as time goes on in minutes. The results show a clear improvement in how well MB breaks down when using CaO, especially when you look at the temperature and the kind of light source. When the temperature hits 1,000 °C and you use a halogen lamp, the breakdown efficiency quickly climbs, peaking at around 60% after about 40 minutes before it starts to level off and even dip a bit.

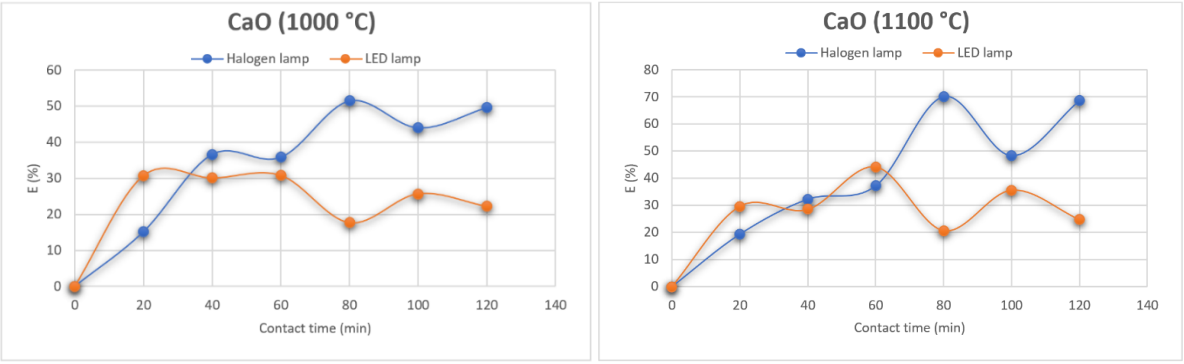


Figure 5. Degradation efficiency (%) of MB by CaO at 1,000 °C and 1,100 °C under halogen and LED lamps over time

This happens because the halogen lamp emits out a strong light that includes UV rays, which help activate the CaO quickly. When CaO is activated, it produces hydroxyl radicals (·OH) very effectively, and these are essential for breaking down MB. However, eventually, as the catalyst gets used up, the efficiency starts to decline. In contrast, when you switch to an LED lamp, the efficiency does not exceed 30%. This limited performance highlights the downsides of using LED light. Its lower intensity and narrower range of wavelengths do not effectively activate CaO, so the breakdown process really stalls – the degradation curve remains mostly flat [31]. Things get even more interesting at 1,100 °C. The halogen lamp boosts the breakdown efficiency up to nearly 80% after about 60 minutes. This increase shows that higher temperatures assist in activating the CaO better by enhancing its crystallinity and surface area. This means that there is a better interaction between the CaO and MB, which helps the breakdown process work more effectively. Conversely, even though the LED lamp does show a small increase in efficiency compared to the lower temperature, it still cannot manage to exceed 50%. That is still a lot lower than what is seen with the halogen lamp. This clearly illustrates that, even with a higher temperature, the weak light from the LED simply does not provide the necessary kick to activate the photocatalyst and generate enough free radicals for a decent breakdown. The results show a clear improvement in how well MB breaks down when using CaO, especially when considering the temperature and the type of light source. When the temperature reaches 1,000 °C and you use a halogen lamp, the breakdown efficiency quickly rises, peaking at around 60% after about 40 minutes before it starts to level off and even dip slightly. This occurs because the halogen lamp emits a strong light that includes UV rays, which help activate the CaO quickly. When CaO gets activated, it produces hydroxyl radicals (·OH) very effectively, and these are essential for breaking down MB. Hoewever, as the catalyst gets used up, the efficiency starts to decline [32].

In contrast, when you switch to an LED lamp, the efficiency does not go higher than 30%. That limited performance highlights the downsides of using LED light. Its lower intensity and narrower range of wavelengths do not do a good job of activating CaO, so the breakdown process really stalls – the degradation curve stays pretty much flat. Things get even more interesting at 1,100 °C. The halogen lamp ramps the breakdown efficiency up to nearly 80% after about 60 minutes. This increase shows that higher temperatures help activate the CaO better by boosting its crystallinity and surface area. This means that there is a better interaction between the CaO and MB, which helps the breakdown process work more effectively. Conversely, even though the LED lamp does show a small boost in efficiency compared to the lower temperature, it still cannot manage to go above 50%. That is still a lot lower than what is seen with the halogen lamp. This clearly illustrates that, even if you have a higher temperature, the weak light from the LED just does not provide the necessary kick to activate the photocatalyst and generate enough free radicals for a decent breakdown. When calcium oxide is heated to 1,000 °C, it does a good job breaking down MB, but how well it works depends a lot on the type of light that is used. If halogen light shines on it, it sees better results in the first few minutes (Figure 6). This happens because the bright halogen light activates CaO quickly. It covers a wide range of light, especially UV light, which gets the catalyst's electrons all fired up and starts making those important hydroxyl radicals (·OH) that help break down the pollutants. But as time goes on

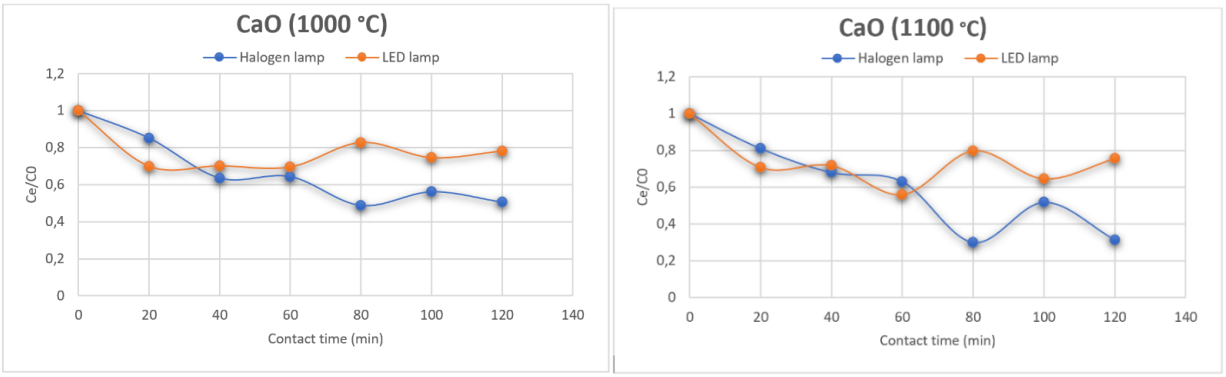


Figure 6. MB degradation by CaO at 1,000 °C and 1,100 °C: Comparison of removal rate over time under halogen and LED lamps

and the reaction continues, it is noted that the degradation slows down.

This might be because the catalyst gets saturated or because the excited electrons and holes start recombining instead of staying active. On the flip side, when an LED lamp is used, it doesn't shine as brightly and mainly emits light in the visible spectrum. Because of this, it struggles to get those CaO electrons excited. This is why a flatter curve is seen in the degradation rate with the LED, indicating that it is not as good at producing free radicals necessary for breaking down the MB. Now, when the temperature is increased to 1,100 °C, the situation improves. The CaO becomes more crystalline and has a larger surface area, which means it interacts better with the MB and gets activated more effectively when exposed to halogen light. The degradation happens much faster and remains stable under halogen settings, suggesting that this higher temperature allows CaO to produce even more hydroxyl and perhydroxyl radicals ($\bullet HO_2$). These radicals are more reactive and do an even better job of breaking down organic pollutants. Even though the LED light is still weaker at this temperature, it can still see some level of activity at 1,100 °C, but the degradation rate does not remain consistent. There are ups and downs in the curve, which suggests that the photocatalytic process is not as effective with this light source, probably because the LED simply is not capable enough to produce a significant number of free radicals.

First-order degradation kinetics

The findings show here that when it comes to breaking down MB with CaO, the temperature and the type of light make a significant difference. For starters, it appears that the process follows a first-order reaction (Figure 7). What this means there is a clear pattern in the collected data; when things are graphed out, you can see a straight line. When the temperature is raised to 1,000 °C with a halogen lamp, the process becomes much more effective. The slope of the results was 0.0067, and there was a strong correlation at R^2 = 0.9464. This indicates that there is a solid link between how long the MB is exposed and how well it breaks down. The bright light from the halogen lamp helps activate the CaO photocatalyst more efficiently than other light sources. This activation produces free radicals, especially hydroxyls (·OH), which are what actually do the heavy lifting when it comes to breaking down the pollutant. Now, when observing the results under an LED lamp, things were different.

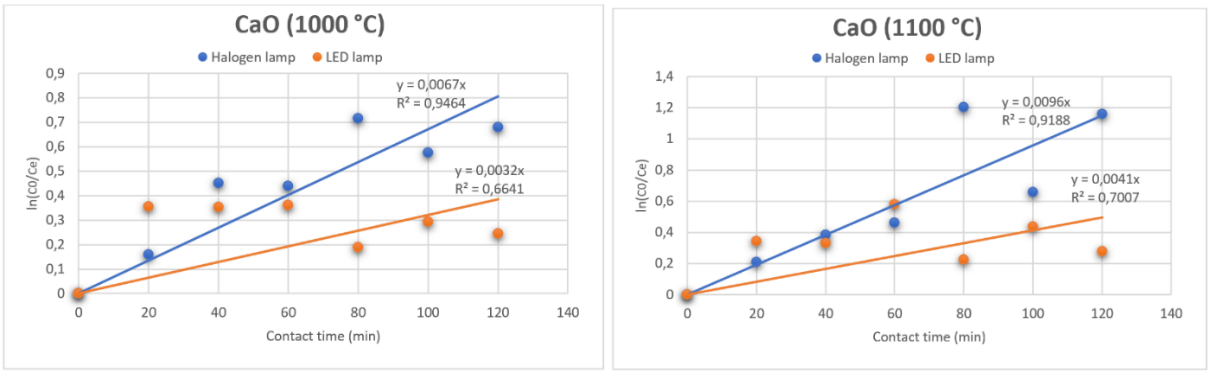


Figure 7. First-order kinetics of MB degradation by CaO at 1,000 °C and 1,100 °C under halogen and LED lamps

The slope dropped down to 0.0032, and the correlation was not as strong either, with R^2 = 0.6641. This indicates that the LED light is not as bright and it has a narrower light spectrum, which means it does not activate the CaO as well [33]. As a result, fewer free radicals are produced, which slows down the degradation process. When the temperature is increased to 1,100 °C, better performance is obtained from the photocatalyst under both light types, but the halogen lamp was still the star of the show. The slope with the halogen light rose to 0.0096 and achieved a correlation of R^2 = 0.9188, suggesting that degradation occurs even faster at this temperature. The crystal structure of CaO likely improves at a higher temperature, which gives it a larger surface area to work with. This means it can interact more effectively with MB and break it down quicker. On the flip side, the LED lamp did show some improvement compared to results at 1,000 °C, but the slope only reached 0.0041 with a correlation of R^2 = 0.7007. This indicates that although increasing the temperature helps a bit, the lower intensity of the LED light still holds the process back compared to the halogen.

Second-order degradation kinetics

An experiment heating things up to 1,000 °C and 1,100 °C was conducted to see how different lamps affected the breakdown of MB using a CaO photocatalyst, and it turned out to be pretty interesting (Figure 8).

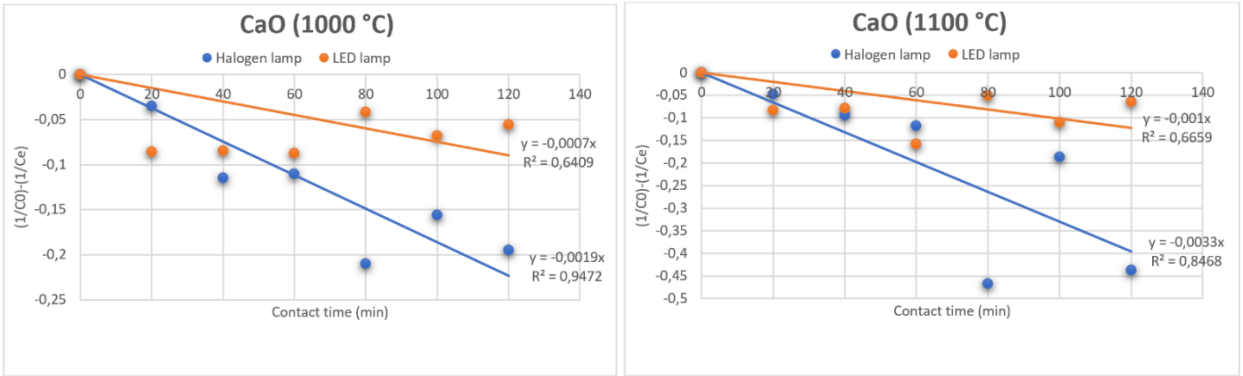


Figure 8. Second-order kinetics of MB degradation by CaO at 1,000 °C and 1,100 °C under halogen and LED lamps

At 1,000 °C, a halogen lamp is used, and the results were clear. The breakdown rate showed a nice pattern similar to a second-order reaction. A slope of -0.0019 and a correlation value (R^2) of 0.9472, tell that the whole process was pretty quick and stable. The halogen lamp emitted a lot of light, especially in the UV range, which really got those electrons in the CaO all excited. This excitement creates free radicals like ·OH, which are crucial for breaking down pollutants like MB. On the flip side, when switched to an LED lamp, things did not go as smoothly. The degradation rate plummeted to a slope of just -0.0007, and the R^2 dropped to 0.6409. This shows that LED light, which is much less intense and has a narrower spectrum, just did not activate the CaO as well as the halogen lamp did. It is clear here that the lamp type really makes a difference in how effective the photocatalytic process can be. When the temperature is cranked up to 1,100 °C, some things shifted a bit, but the halogen lamp still worked well, showing a fast degradation rate. The slope decreases slightly to -0.0033, and the R^2 slid down to 0.8468. This suggests that while it was still effective, the photocatalyst might have been reaching its limit at this hotter temperature.

It is expected that heating it up would bring better properties to the CaO, thanks to increased crystallinity and more surface area; yet, the speed of the breakdown did not boost as much as it could. Still, the halogen lamp came through as the top performer, delivering a lot of light energy for activating the CaO. Meanwhile, the LED lamp struggled on at 1,100 °C too, landing us a slope of -0.001 and an R^2 of 0.6659, showing that even with the higher temperature, it could not quite match the drying power of the halogen lamp. This meant fewer free radicals were generated to help break down MB as quickly. Therefore, to wrap it up, these results really emphasize how crucial light intensity and temperature are for how effectively CaO can work as a photocatalyst in breaking down MB. It is all about finding that the right balance to get the best performance out of the materials that work with them.

pH effect

Figure 9 reveals how effectively calcium oxide material destroys MB under photocatalytic conditions at several pH levels. The tests compared acidic (pH=2) and basic (pH=9) settings with two different lighting systems—halogen and LED lamps—using CaO calcined at two temperatures (1,000 °C and 1,100 °C). The experiments were conducted under standardized conditions: 5 mg/L initial pollutant concentration (C_0), 100 mg of CaO, and 50 mL solution volume.

The results clearly indicate that the photocatalytic efficiency is greatly affected by the pH of the solution. The LED lamp (orange bars) outperformed the halogen lamp by a large margin under a basic environment (pH=9), reaching almost 90% degradation efficiency at the higher calcination temperature (1,100 °C) and remaining high (about 80%) even at the lower temperature (1,000 °C). Conversely, under

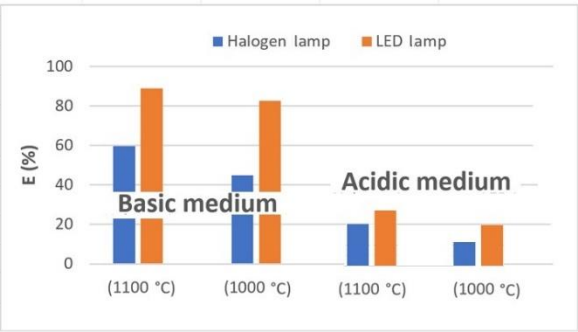


Figure 9. Variation of degradation efficacy, (E%) of CaO material as a function of pH at 1,000 °C and 1,100 °C under halogen and LED lamps (C_0=5 mg/L, m=100 mg, and V=50 mL, Acidic medium (pH=2), Basic medium (pH=9))

the same basic conditions, the halogen lamp (blue bars) exhibited modest efficiencies of around 50% at 1,100 °C and declining to about 30% at 1,000 °C, clearly indicating that LED lighting works best in strongly alkaline conditions. Under acidic conditions (pH = 2), the situation changed dramatically and general degradation efficiencies were much lower. None of the studied conditions exceeded 25% efficiency, implying very low photocatalytic activity under low pH. Particularly poor results for the halogen lamp were under 10% at 1,100 °C and just over 10% at 1,000 °C. Though still quite ineffective, the LED lamp performed somewhat better in the acidic medium (about 20% at both temperatures). These results combined indicate that, especially with CaO calcined at higher temperatures (1100 °C), maintaining a basic environment (pH=9) with LED lighting is clearly the most effective way to efficiently degrade MB with CaO as a photocatalyst. Conversely, under acidic conditions the type of lighting or calcination temperature used has little effect on photocatalytic activity. Controlling pH and choosing appropriate lighting conditions help to maximize the photocatalytic potential of CaO in water treatment activities.

Initial concentration effect

Figure 10 shows how well calcium oxide can break down MB under different conditions. The study tested a fixed amount of CaO (100 mg) at two temperatures (1,000 °C and 1,100 °C) and used two types of lights (halogen and LED). They looked at various MB concentrations, from 1 mg/L to 20 mg/L, keeping the pH at 9 and the solution volume at 50 mL. The results showed that the starting concentration of MB, the temperature of the CaO, and the type of lamp all affect the degradation process. The halogen lamp worked better with CaO heated at 1,100 °C. At the lowest concentration (1 mg/L), the degradation efficiency was about 90%, dropping to around 80% as the concentration increased to 20 mg/L. In comparison, the LED lamp was less effective, starting between 70% and 75% at lower concentrations and going down to about 60% at higher levels. This suggests that the halogen lamp is more effective with higher temperature CaO. Things changed slightly with CaO heated at the lower temperature of 1,000 °C.

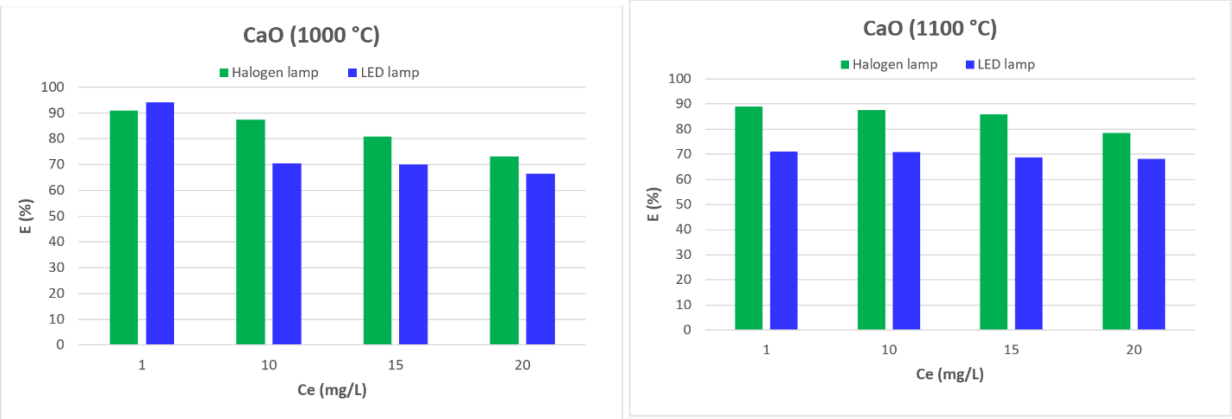


Figure 10. Variation of degradation efficacity, (E%) of CaO material as a function of initial concentration (mg/L) at 1,000 °C and 1,100 °C under halogen and LED lamps (m=100 mg, V=50 mL, and pH=9)

At the lowest concentration (1 mg/L), the LED lamp performed slightly better, around 95%, compared to the halogen lamp's 90%. But as the concentration increased, the LED lamp's performance dropped quickly; by the highest concentration (20 mg/L), it fell to about 60%. The halogen lamp, however, was more consistent, from about 90% at low levels to around 70% at higher ones.

Mass effect

Figure 11 shows how well calcium oxide helps break down MB when using light. The degradation efficiency (E%) varies based on how much CaO is used, from 10 mg to 40 mg, and considers two temperatures—1,000 °C and 1,100 °C—along with two types of lights (halogen and LED). These tests were done under controlled conditions: the starting concentration of the pollutant was set at 1 mg/L, the solution volume was 50 mL, and the pH level was kept at 9. The results clearly show that how well the degradation efficiency depends significantly on the temperature of the CaO and the type of light. At 1,100 °C, the halogen lamp is very effective, achieving nearly 100% breakdown with just 15 mg of CaO, and it still performs well (over 80%) with only 10 mg. On the other hand, using LED lights is less effective, with a peak performance of about 60% at 20-25 mg, dropping to around 20% with just 10 mg. When the CaO is calcined at 1,000 °C, it still works well with halogen lighting, achieving almost the same results as at 1,100 °C, and again reachibng near-total degradation from about 15 mg. With LED lights, however, the effectiveness drops significantly, peaking around 40% with 25 mg of CaO, much lower than at 1,100 °C. At lower amounts (10 mg), the results are not good, remaining under 20%. These tests show that using CaO at 1,100 °C with halogen lighting is the best way to break down MB effectively. This method maximizes results while requiring less catalyst to clean up low-concentration polluted solutions (1 mg/L) in mildly alkaline conditions (pH=9).

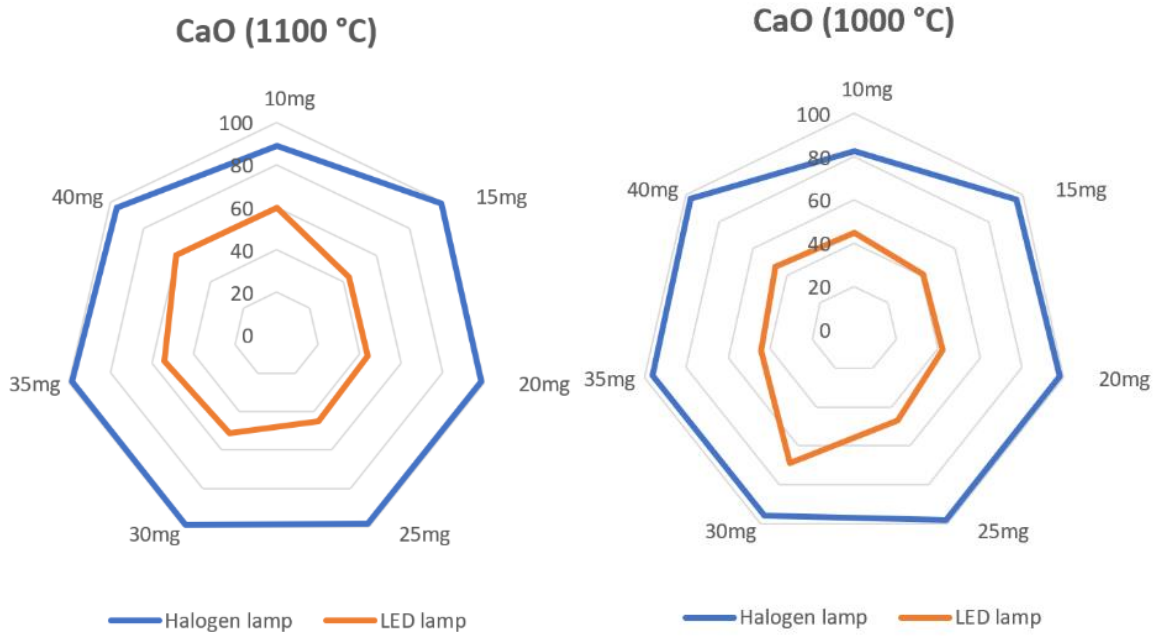


Figure 11. Variation of degradation efficacy, (E%) of CaO material as a function of mass (mg) at 1,000 °C and 1,100 °C under halogen and LED lamps (C_0=1 mg/L, V=50 mL, pH=9)

In contrast, LED lighting significantly reduces the efficiency of the process works; therefore, much more catalyst is needed for decent results.

Conclusion

This study demonstrates that the photocatalytic efficiency of calcium oxide in degrading MB is strongly governed by calcination temperature, illumination type, and reaction conditions, emphasizing a green-chemistry approach for sustainable pollutant removal. Structural characterization confirmed key material features, with FTIR showing distinct peaks at 1,420 cm^{-1} (CO_2 vibrations) and 870 cm^{-1} (Ca–O bonds), SEM revealing improved particle uniformity at 1100 °C (up to 17 μm compared to 2–16 μm at 1,000 °C), and EDX indicating consistent elemental composition. Photocatalytic tests showed that CaO had negligible activity in the absence of light (<3%), confirming photocatalysis as the main degradation mechanism. Under halogen light, CaO calcined at 1,000 °C achieved ~60% MB removal in 40 min (k = 0.0067, R^2 = 0.9464), while LED illumination remained below 30% (k = 0.0032, R^2 = 0.6641). Increasing the calcination temperature to 1,100 °C significantly improved performance, allowing halogen illumination to reach nearly 80% degradation in 60 min (k = 0.0096, R^2 = 0.9188), whereas LED efficiency remained ≤50%. Reaction order analyses supported these trends, with halogen light fitting second-order kinetics more effectively, especially at 1,000 °C. pH studies showed that degradation was highest under basic conditions (pH 9), where LED unexpectedly outperformed halogen (~90% vs. ~50% at 1,100 °C), while acidic conditions (pH 2) consistently resulted in poor removal (<25%). The halogen lamp showed stronger tolerance to increasing MB concentration at 1,100 °C, maintaining ~80–90% degradation from 1 to 20 mg/L, whereas LED efficiency declined sharply. Increasing catalyst mass further enhanced performance, with halogen light at 1,100 °C achieving complete degradation at 15 mg, compared to LED's maximum of ~60% at the same mass. Overall, the results confirm that higher calcination temperature enhances CaO crystallinity and reactivity, and halogen illumination generally provides superior photocatalytic activation, positioning thermally optimized CaO as an effective, light-driven, and environmentally friendly photocatalyst for dye degradation.

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Conflict of Interest

The authors declare that they have no competing interests.

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