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Synthesis and Applications of CaO Nanoparticles

Harendra Singh Bohara
Birla Institute of Applied Sciences,
Bhimtal, 263136, Uttarakhand, India.
Corresponding author: hsbohara@rediffmail.com

Riya Gola
Department of Physics,
R. H. Government P. G. College, Kashipur,
Kumaun University, Nainital, 263001, Uttarakhand, India.
E-mail: riyagolaksp@gmail.com

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Abstract
Due to the remarkable chemical, electrical, and optical properties, calcium oxide (CaO) is an incredibly significant industrial substance that is utilized as a paint additive, catalyst, toxic-waste treatment agent, and for other basic uses. CaO exhibit cubic structure and can be grown using various chemical and physical methods. The different ways to create CaO nanoparticles from biological materials, such as papaya, green tea, red dragon fruit, and Moringa oleifera plant leaves, are highlighted in this review along with some additional techniques such as sol-gel, solution combustion, precipitation, and microwave irradiation methods. CaO nanoparticles are an excellent alternative in polymer nanocomposites as antimicrobial filler to be applied for food packaging or medical devices. Also, they show their effective utilization in various disciplines such as agriculture, biomedical and environment. Application of CaO nanoparticles in these fields are also included in concise and concrete way.

Keywords- CaO nanoparticles, Green synthesis, Applications.

1. Introduction

Nanotechnology is gaining considerable attention from researchers working in different areas such as physical sciences, chemical sciences, biomedical sciences, electronics, aeronautical engineering, etc. (Porter and Youtie, 2009; Omran 2020). It is the study of fundamental and application aspects of structures having at least one dimension less than 100 nm (Jeevanandam et al., 2018). These structures are referred to as nanostructures and have different types depending upon their shape. Some categories of these nanostructures are nanoparticles, nanowires, nanotubes, nanopillars, nanofilms, etc. (Thangadurai et al., 2020; Singh et al., 2020). Nanostructures are used in various fields because of their specific physical, chemical, and optical properties (Ijaz et al., 2020; Shoukat et al., 2021; Joudeh and Linke, 2022). These properties arise due to their large surface area, unique surface properties and enormous surface potential as compared to their bulk counterparts (Shaji and Zachariah, 2017; Khan et al., 2019; Oake et al., 2019).

These nanostructures are also categorized based on the composition and type of element. Some examples are metallic nanostructures (Sun et al., 2020; Zare et al., 2022), carbon-based nanostructures (Maduraiveeran and Jin, 2021; Bagheri et al., 2022), ferrite nanostructures (Bhaduri et al., 2022; Dhyani et al., 2024) and oxide nanostructures (Guo et al., 2015; Sun et al., 2019). Due to wide use of oxides, many researchers grow nanostructures of different oxides. ZnO (Djurišić et al., 2012; Raha and Ahmaruzzaman, 2022), MgO (Prado et al., 2020; Kumari et al., 2023a), WO_3 (Huo et al., 2013; Novak et al., 2021), TiO_2 (Kamat et al., 2012; Reghunath et al., 2021), Ga_2O_3 (Jubu et al., 2020; Yadav et al., 2022) and CaO (Alavi and Morsali, 2010; Naik et al., 2023) are some examples of oxide nano structure. Ca^{2+}

being part of bones, calcium oxide (CaO) is considered as a very safe material to human beings and animals, which makes this oxide more appropriate for such applications (Kumari et al., 2023b; Wu et al., 2024). Thus, this oxide provides an ample scope to the researchers for investigating various applications owing to its particular nanostructure form and this review article is focused on this material.

2. Calcium Oxide (CaO)

Calcium oxide (CaO) is an important naturally occurring earth metal oxides. It is sometimes referred to as quicklime or burned lime. CaO nanoparticles are particles with a large surface area that can be spherical or faceted. CaO., is an alkaline earth metal oxide. Oxygen is a Block P, Period 2 element whereas calcium is a Block S, Group 2, Period 4 element. CaO is halite; rock salt structured and crystallizes in the cubic $Fm\overline{m}3m$ space group (Nguyenet al., 2021).

Ca^{2+} is bonded to six equivalent O^{2-} atoms to form a mixture of corner and edge-sharing CaO_6 octahedral. The corner-sharing octahedral 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 O-Ca_6 octahedral (Momma and Izumi, 2011; Friedrich et al., 2019). The corner-sharing octahedral are not tilted. **Figure 1** represents the crystal structure of CaO.

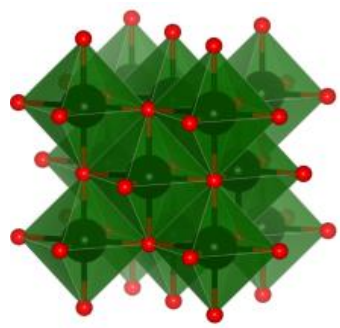


Figure 1. Crystal structures of CaO, the coordination polyhedra of Ca and Ti are shown in green and blue, respectively. Note: Ca is six-fold (octahedrally) coordinated with oxygen in CaO. Colors: Ca black, and O red (Friedrich et al., 2019, open access).

The lattice constant of CaO is 4.811 Å (Albuquerque and Vasconcelos, 2008). This is an insulating material with a band-gap value of 6.25 eV (Nguyen et al., 2021), however, nanoparticles of this material exhibit band-gap in the range of 3-4 eV (Kumar et al., 2021). Presence of no unpaired electron makes this material a non-magnetic material (Nguyen et al., 2021) but reports are available showing vacancy/defect induced magnetism in the nanoparticles of CaO (Osorio-Guillén et al., 2006; Gao et al., 2010).

3. Methods of Synthesizing CaO Nanoparticles

The properties and applications of nanoparticles depend on their size and morphology. The effects on the size, shape, uniformity, and properties of the nanoparticles are due to high temperature and nature of solvent (Balaganesh et al., 2018). Calcium oxide (CaO) nanoparticles can be synthesized by several methods. Some of the methods are discussed in the given section:

3.1 Green Synthesis

Green synthesis process of synthesizing nanoparticles is getting more popular because of its eco- friendly nature and room temperature synthesis (Shreyash et al., 2021; Hosseingholian et al., 2023). This process is cost effective in comparison to other methods because plant extracts are used and it also provides a wide range of non-toxic nanoparticle synthesis. This method encourages the use of eco-friendly chemicals, plant extracts and non-toxic solvents (Jogi et al., 2022; Guliani et al., 2024). But the manufacturing of oxide nanoparticles using biological extracts like enzymes, plant extracts remain a significant problem because of their complexity. Synthesis of calcium oxide (CaO) nanoparticles can be done by using plant extracts like peels of red dragon fruit (Ramli et al., 2019), couroupita guianensis plant (Lalithamba et al., 2023) papaya & green leaves (Anantharaman et al., 2016), peels of orange fruit, moringa oleifera plant leaves (Jadhav et al., 2022), piper betel leaf (Yoonus et al., 2021), mint leaves (mentha arvensis) (Shanmuganathan et al., 2023) etc.

Some of methodologies to synthesize these nanoparticles from various sources are given below:

3.1.1 Peels of Red Dragon Fruit

Maceration method was used to extract secondary metabolite compounds from H. Polyrhizus peels i.e., red dragon fruit peels in aqueous solution. After phytochemical identification of metabolite compounds the extracted solution was used as biological agent for the bio synthesis of calcium oxide (CaO) nanoparticles from $CaCl_2.2H_2O$ (Ramli et al., 2019).

3.1.2 Papaya Leaves and Green Tea Leaves

Washed papaya leaves are used to make papaya extract. Having been cooked for thirty minutes in distilled water and filtered through filter paper, the extract is allowed to cool before being used for the synthesis of metal oxide nanoparticles. For the preparation of green tea extract solution green tea leaves are boiled in distilled water for 30 minutes and filtered with what mann no. 1 filter paper. After cooling this, resulting extract is ready for synthesizing the Calcium oxide (CaO) nanoparticles from calcium nitrate (Anantharaman et al., 2016).

3.1.3 Moringa Oleifera Plant Leaves

Firstly, the Moringa oleifera plant leaves are washed with distilled water and then dried in oven at 80^oC for 2 hours. The powder of the dried leaves can be made by using mortar and pestle and now the MO leaves powder is taken for the synthesis of Calcium oxide (CaO) Nanoparticles from calcium nitrate (Jadhav et al., 2022).

3.1.4 Sol-Gel Method

Sol-gel method having low cost and being simple has become one of the most popular methods to grow oxide nanoparticles (Eddy et al., 2023; Hassan et al., 2023; Naik et al., 2023) as it requires low pressure and temperature. (Habte et al., 2011) synthesized the Calcium oxide (CaO) nanoparticles through sol-gel method from egg-shell. Chicken egg shell i.e. $CaCO_3$ was dissolved in the dilute solution of HCl and then NaOH is added slowly dropwise to agitate calcium hydroxide [$Ca(OH)_2$] gel. Now on drying the gel at 60^oC for 24 hours, the obtained powder is calcinated at 900^oC for 1 hour. The chemical reactions followed by the sol-gel method are as follows:

$$\mathbf{CaCO_3\ (\mathit{s}) + 2HCl\ (\mathit{aq}) \rightarrow CaCl_2\ (\mathit{aq}) + H_2O\ (\mathit{l}) + CO_2\ (\mathit{g})}$$

$$\mathbf{CaCl_2\ (\mathit{aq}) + 2NaOH\ (\mathit{aq}) \rightarrow Ca(OH)_2\ (\mathit{s}) + 2NaCl\ (\mathit{aq})}$$

$$\mathbf{Ca(OH)_2\ (\mathit{s}) + \mathit{Heat} \rightarrow CaO\ (\mathit{s}) + H_2O\ (\mathit{l}).}$$

Singh et al. (2018) reported synthesis of CaO from calcium nitrate using this method. This results the formation of CaO at $1200^{o}C$ (Singh et al., 2018). Yossaf and Tomah (2023) also utilized this method for synthesizing these particles. This method was also used to produce CaO nanoparticles from cam sea shell waste (Singh et al., 2022; Naik et al., 2023).

3.2 Solution Combustion Method

Solution combustion method is well known for growing nanoparticles (Varma et al., 2016; Parauha et al., 2021) and considered suitable for controlled growth (Wen and Wu, 2014). In this method Ca $(NO_3)_2.4H_2O$ (14.16g) and NH_2CONH_2 (6.0g) were dissolved in $100cm^3$ silica crucible using distilled water. Then obtained solution was treated at 500°C for calcinations (Bhavya et al., 2016).

3.3 Precipitation Method

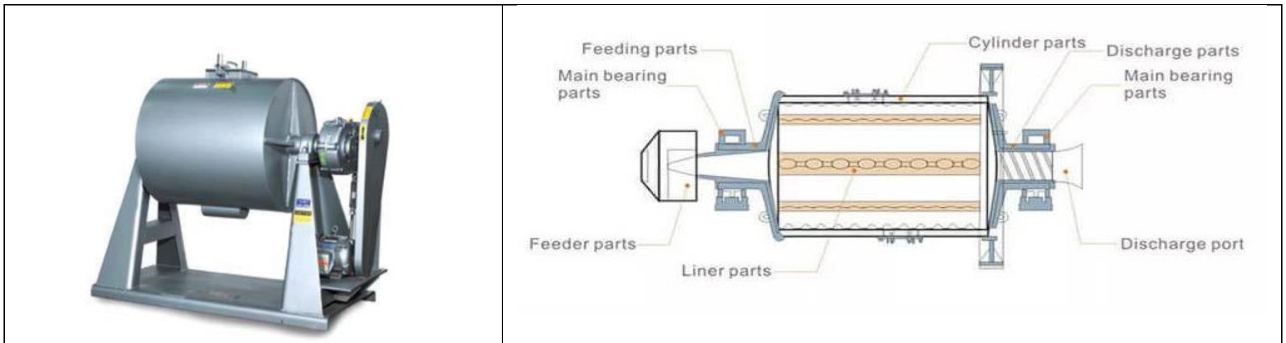
This method is cost effective as well as convenient way for the large-scale production of nanoparticles (LaGrow et al., 2019; Patil and Jagadale, 2023). Calcium oxide (CaO) nanoparticles can be produced via precipitation method i.e. via thermal treatment of calcium hydroxide [$Ca(OH)_2$] or calcium carbonate ($CaCO_3$) (Khine et al., 2020; Khine et al., 2022). Initially, the aqueous solutions of $Ca(OH)_2$ and NaOH were heated up to $80^{o}C$ and then at this temperature solution of NaOH was added drop wise into the solution of $CaCl_2$ and stirring done continuously during this process by using magnetic stirrer. Now to remove the NaCl from the suspension it was washed repeatedly for 5 times with distilled water or deionized water. Now the wet white precipitate of $Ca(OH)_2$ is formed and dried at room temperature in open air. Finally, the semi-dry precipitate was calcinated at $650^{o}C$. As a result, calcium oxide (CaO) nanoparticles of different sizes were formed. The chemical reaction scan be written as follows:

$$\mathbf{CaCl_2(\mathit{aq}) + 2NaOH(\mathit{aq}) \rightarrow Ca(OH)_2(\mathit{s}) + 2NaCl(\mathit{aq})}$$

$$\mathbf{Ca(OH)_2(\mathit{s,wet}) \rightarrow CaO(s) + H2O(\mathit{g}) \uparrow}$$

3.4 Physical Method

This method is eco-friendly and cost effective for the massive scale production and generally used for synthesis of CaO nanoparticles from egg-shell (Hsieh et al., 2021; Nagalakshmi et al., 2022; Ali et al., 2023; Vijyakumar et al., 2023). Synthesis of calcium oxide (CaO) nanoparticles can be done by chicken egg shell. Firstly, the chicken eggs were washed with distill water and then dried for 48 hours in open air. Now the egg shells were crushed with the help of mortar and pestle by using physical method for½ hour. After this the crushing powder is heated above 700°C for 7 hours to get pure calcium oxide (CaO) nanoparticles (Ashok et al., 2014). Calcium oxide (CaO) nanoparticles can be synthesized by using ball-milling method from duck egg shell powder. In this process duck egg shell powder is formed in ball-milling reactor. The duck shell powder is then calcinated for 7 hours at $700^{o}C$ to get calcium oxide (CaO) nanoparticles (Nuryantini et al., 2019). **Figure 2** represents the ball milling reactor.



(a)	(b)

Figure 2. (a) Schematic diagram of the ball milling reactor for the fabrication of duck eggshell powders (Nuryantini et al., 2019; open access).**(b)** Internal structure of ball milling reactor (https://www.jxscmachine.com/rock-crusher/batch-small-ball-mill/, Available in public domain).

3.5 Microwave Irradiation Method

Microwave irradiation method is yet another cost effective, fast, generally simple, and less time-consuming method (Gawande et al., 2014; Gao et al., 2023). In this method, domestic oven can be used for the preparation of metal oxides at laboratory scale. Roy and Bhattacharya (2011) performed this method to synthesize the calcium oxide (CaO) nanoparticles shown in the **Figure 3** below.

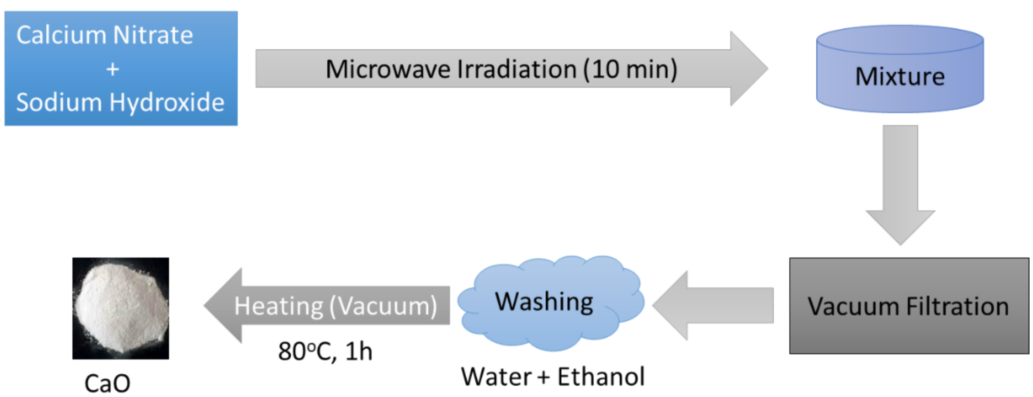


Figure 3. Experimental procedure for synthesis of Calcium oxide (CaO) nanocrystals. Schematic is drawn based on the description provided by Roy and Bhattacharya (2011).

Again, Roy et al. (2013) has reported the synthesis of calcium oxide (CaO) nanoparticles by using microwave irradiation method with minor modifications. They have used $Ca(NO_3)_2.4H_2O$ and NaOH as precursors and mixed with distilled water. On stirring the solution at room temperature for 10 minutes it turned into a white gel. After micro wave processing resulting precipitate was washed with distilled water and the absolute ethanol and dried it in vacuum at 80^oC for 1 hour. And hence the calcium oxide (CaO) nanoparticles get prepared.

4. Applications of Calcium Oxide (CaO) Nanoparticles

Calcium oxide can be used as a catalyst (Ling et al., 2019), toxic-waste remediation agent (Farah et al., 2019), adsorbent (Lee et al., 2015; Geng et al., 2021), and an antibacterial agent (Kumar et al., 2021;

Liang et al., 2022) as well Calcium oxide nanoparticles have gotten much attention due to biosensing (Hyun and Cho, 2023), biomedicines (Kumari et al., 2023b) and photolytic activities. Calcium oxide also plays significant role in the development and growth of the plant (Anand et al., 2021) like it activates the various types of enzymes, participates in metabolism, photosynthesis rate etc. Some applications of calcium oxide nanoparticles (CaO-NPs) are depicted as follows.

4.1 Agriculture

The biggest threat now a day is the arsenic (As) contamination in agricultural soils. It is becoming a barrier in the sustainable development of agriculture and food safety (Gandhi et al., 2021). To reduce this arsenic contamination from the agricultural soils and to maintain food safety there are many ways but due to their operational complexities, time-consuming and high-cost generally they are not practically possible in crop production. To alleviate arsenic toxicity calcium oxide (CaO) nanoparticles (NPs) are the most cost effective and practically easy to reduce arsenic (As) intake. Nazir et al. (2022) studied the role of calcium oxide (CaO) nanoparticles in alleviating the Arsenic toxicity of barley. Farooq et al. (2023) investigated the yield attributed of Tomato (Solanum lycopersicum L. Syn Lycopersicon esculentum Mill.) treated by CaO and its composition with ZnO (Farooq et al. 2023). Results showed the increasing phenolic content order of tomato plants under the effect of NP streatment was ZnO + CaO<CaO NPs <$ZnSO_4$< Control <$CaSO_4$<ZnO NPs as shown in **Figure 4**.

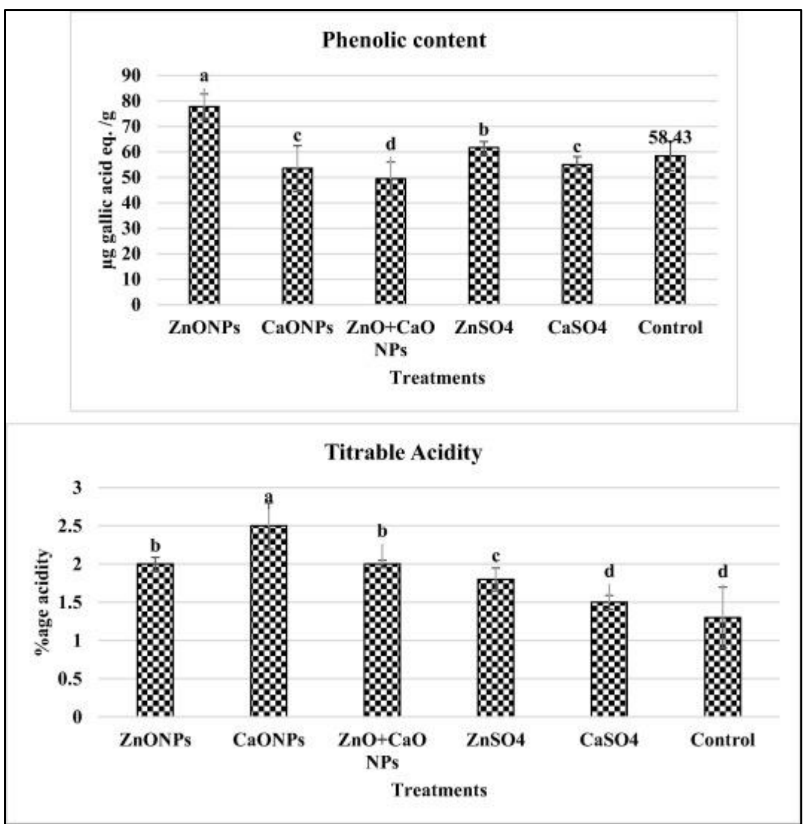


Figure 4. (a) Effect of different NPs treatments on total phenolics of S. lycopersicum, (b) Effect of different NPs treatments on percentage acidity of S. lycopersicum (Farooq et al., 2023, open access).

Deepa et al. (2015) reported that germination and growth of groundnut significantly increased with the foliar application of nanoscale calcium oxide particles (average particle size 30 nm). This is due to the phloem transport of nanoscale calcium oxide particles due to low dimension. Mazhar et al. (2023) reported improvement in the physiochemical parameter and yield growth by the use of CaO nanoparticle.

4.2 Biomedical Applications
CaO nanoparticles are one of the safest metal oxides which can be used as potential drug delivery agent because of its unique optical and structural properties. Because of their capacity to produce reactive oxygen species (ROS), which eventually cause the bacteria to die, calcium oxide nanoparticles, or CaO-NPs, may develop into a viable pharmaceutical substitute for managing microbial populations (Kumari et al. (2023b). In biomedical applications conformational changes play significant role. CaO nanoparticles are used in different therapies like Photo-thermal therapy, chemotherapy etc.

4.3 In Biodiesel Production
Biodiesel is becoming the best alternative of harmful fossil fuels. As the population is increasing, the fuel resources exhausting very fast and that why to complete the demand, researchers are finding renewable energy which is cost effective and as well as causes less damage to our environment. Calcium oxide (CaO) nanoparticles are used in bio diesel production as a catalyst in the process of alcholysis (Basumatary et al., 2023; eMelo et al., 2024). Hebbar et al. (2018) tried to optimize the biodiesel production from bombax ceiba oil (BCO) through calcium oxide nanoparticles.

4.4 Waste Water Treatment
Advancements in nanotechnology is providing various new, less time consuming, cost- effective and most importantly the environmental friendly approaches to clean waste water which is essential to human health. Treatment of waste water with calcium oxide (CaO) nanoparticles is one of those approaches. Calcium oxide nanoparticles (CaO NPs) can be used as an adsorbent to purify waste water and for the removal of heavy metals like chromium (Cr) II and mercury (Hg) II from the aqueous solutions (Toamah et al., 2019).

Industrially, it finds applications as a dehydrating agent in the creation of steel, an absorbent, as a water softener, as a potential hydrogen regulator for wastewater and in fertilizers industry. According to the world health organization (WHO), by 2025, half of the world's population would be living in water-stressed regions. In the least developed nations, percent of healthcare institutions do not have access to water, 21 percent do not have access to sanitation, and 22 percent do not have access to waste management. Contamination of different sources of water has taken different dimensions and the final consequence is in the form of polluted water (Eddy and Garg, 2022). Aquatic life affects significantly due to the presence of these unwanted particles. Due to the presence of these unwanted and harmful particles quality of water also decreased. Hence, removal of unwanted and harmful contaminants is a must before its use for different purposes like domestic, agricultural, and industrial use. There are number of techniques are available for the treatment of contaminated materials e.g., reverse osmosis, filtration, oxidation, adsorption, and biological treatment. Among these different techniques adsorption process is very important and has been very popular among the science community due to its cost-effectiveness and can remove contaminants from polluted water when implemented with biodegradable materials. Adsorption is the sticking of particles on the surface of materials and there are numerous factors that affect the adsorption process like temperature, pressure, PH value of solution nature of adsorbent etc. Nano sized material particles or nano-adsorbents are very useful for the removal of contaminants like heavy metal ions or other types of impurities like harmful micro-organism etc. Therefore, the applications of nano-adsorbents like calcium oxides (CaO) are very useful for the removal of harmful particles or impurities in water. Hence Calcium Oxide (CaO) nanoparticles have found several applications in area such as adsorption, water purification and anti-bacterial agents and is regarded safe material for human beings and animals. Calcium oxide nanoparticles also find applications in industry where industrial effluents containing heavy toxic metals or ions such as lead are a matter of great concern due to its non-biodegradable nature. These heavy metal ions find mostly in industry such as textile acid battery manufacturing, glass industry, and ceramics etc. and these heavy metal ions when released into water bodies affect many parameters like pH make the water bodies contaminated. Lead when released in the water bodies make it contaminated and when someone consume this contaminated water can lead to several disease like hepatitis, kidney damage, blood pressure, abortion, improper function in the brain etc. these heavy metal ions also affect environment because they remain in water and soil for very longtime .calcium oxide (CaO) nano particles is widely used adsorbent for the removal for these types of industrial effluents because it is environment friendly and cost effective compare toother techniques.

4.5 Carbon Capture

Calcium oxide has been regarded as one of the most promising candidates for carbon capture due to its good kinetics and high capture capacity, low running cost and even under low CO_2 partial pressures. Calcium oxide finds applications in the carbon capture process. Utilizing carbon capture and utilization (CCU) is a viable approach to lower greenhouse gas emissions and advance a sustainable economy. Sun et al. (2021) presented an integrated CCU (ICCU) approach that combines the reverse water gas shift reaction with CO_2 collection, using inexpensive, readily available CaO as both a catalyst and sorbent. Carbon neutrality, an essential goal for sustainable future development, was achieved by effectively adsorbing CO_2 and converting it in situ into useful syngas with a CO_2 conversion rate of more than 75% using the widely available, inexpensive material CaO.

Using a traditional thermal heating method, vermiculite samples were impregnated with varying concentrations of calcium oxide. The samples were then exposed to CO_2 capture tests using thermal analysis apparatus. Using a combination of 75% CaO and 25% vermiculite, Pereira et al. (2022) have noticed that the use of vermiculite impregnated with CaO increased the conversion of this oxide into $CaCO_3$ from ≈ 0.3 to ≈ 0.7. Furthermore, the highest conversion was seen for particle sizes between 106 μm and 300 μm. The findings indicate that when particles with granulometry smaller than 106 μm are used in the studies, the lamellar structure of vermiculite seems to collapse, decreasing the material's capacity to absorb CO_2.

Apart from the above applications, CaO nanoparticles are also efficient for Pb removal (Jalu et al., 2021; Kasirajan et al., 2022), Cr removal (Oladoja et al., 2012). These examples exhibit its sensitivity for removal of toxic elements.

5. Conclusion

Synthesis approaches and applications of CaO nanoparticles are reviewed in this work. Since calcium oxide (CaO) nanoparticles possess superior properties and more uses compared to bulk CaO, their synthesis and application mark a substantial breakthrough in materials science. As Ca^{2+} ions having no toxic effects, CaO is preferred for biomedical applications. Nanoparticles of these materials are utilized for agriculture applications. They also find applications for environment related issues such as carbon capture and removal of toxic elements.

Conflict of Interest
The authors declare no conflicts of interest exist.

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