SYNTHESIS, CHARACTERIZATION AND APPLICATION OF CALCIUM ALUMINATE NANOPARTICLES

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Abstract

In recent years, scientists have recently turned to the green synthesis of nanoparticles from solid wastes and used these in many applications. The calcium aluminate phase has been made by fusing or sintering together an appropriate mixture of CaO and Al_2O_3. These two metal oxides were investigated by using waste powder as raw materials. The key distinction in this research lies in the synthesis of calcium aluminate nanoparticles from waste quail eggshells and discarded aluminum cans (specifically, Coca-Cola cans) using the sonochemical method. The synthesis of calcium aluminate with two different weight ratios of CaO: Al_2O_3 (1:1 and 1:2), as well as different calcination periods and temperatures. The calcium aluminate ($Ca_{12}Al_{14}O_{33}$) was synthesized at a calcination temperature of 1200°C, a calcination period of 1 h, and a 1:2 weight ratio of CaO to Al_2O_3. The average crystallized size of synthesized calcium aluminate nanoparticles was 43.82 nm. The antimicrobial investigation of synthesized calcium aluminate nanoparticles revealed significant antimicrobial activity against eight tested microorganisms. The inhibition zone diameters ranged from 20 to 29 mm. These results demonstrated that synthesized calcium aluminate nanoparticles hold potential as antimicrobial substances for other application fields.

Keywords: green synthesis, nanoparticles, calcium aluminate, quail eggshell, Coca-Cola cans, sonochemical method, antimicrobial activity

Introduction

The binary oxide system CaO-Al_2O_3 has been extensively researched due to the unique properties developed by the calcium aluminate phases. Calcium aluminates compounds consist of a wide range of combinations of calcium oxide and aluminum oxide, and many of these powders are found in cement technology as hydraulic powder. The calcium aluminates are described in the CaO-Al_2O_3 binary phase diagram. Within this system, five binary compounds can be distinguished that generically go by the name of calcium aluminate: $CaAl_2O_4$, $CaAl_4O_7$, $Ca_{12}Al_{l4}O_3$, Ca_3AlO_6, and $CaAl_{12}O_{19}$**.** This system is also attractive as ceramic powder for high-temperature refractory applications. These compounds play important roles in the steel industry as metallurgical slag. Calcium aluminates have a wide range of potential technological applications due to their unusual optical, electrical, thermal, and mechanical properties. The calcium aluminate phase diagram shows a low melting point, the eutectic point, located at 1400 and 1395ºC, where $C1_2A_7$ (mayenite), and C_3A (celite) are the main coexisting phases. That eutectic point composition of 50% calcium oxide and 50% aluminium oxide shows the existence of two main phases that emerge simultaneously: celite and mayenite; these two phases coexist, and thus different heat treatments and synthesis procedures can modify the proportion of each phase in the final material (Gaki, 2007).

The name mayenite was originally given to an isostructural mineral with a composition close to $Ca_{12}Al_{14}O_{33}$ (dodacacalcium hepta aluminate) discovered at the Bellerberg volcano near Mayen, Eifel, Germany (Galuskin *et al*., 2015). Mayenite compounds can be applied as an ion or electron conductor, catalyst in fuel processing, or hydraulic active phase in cement due to their chemical and physical properties such as conductivity, or the potential for water accumulation (Amer *et al*., 2022).

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In the present research, calcium aluminate nanoparticles were synthesized by sonochemical method. The obtained calcium aluminate nanoparticles were characterized by X-ray Diffraction (XRD), Fourier Transformed Infrared (FT IR) Spectrometers, Raman and Scanning Electron Microscope (SEM). And then, the synthesized calcium aluminate was tested in antimicrobial activity.

Materials and Methods

Synthesis of Calcium Aluminate Nanoparticles

The synthesized calcium oxide and aluminum oxide powders were mixed stoichiometrically according to the calcium aluminate powder desired predominantly, *i.e*., in weight-by-weight proportions of 1:1 and 1:2. An aqueous suspension was synthesized by hand mixing powders with distilled water. This suspension was subjected to an ultrasonic bath for 1 h at room temperature. The suspension was shaken periodically during the process to enhance the sonochemical effect. Finally, the suspension was filtered and oven-dried at 110 °C for 24 h on each composition. The resulting solid material was calcined at 1100 and 1200 °C for 1 and 2 h. And then, the synthesized samples were ground with a motor and pastel. Finally, calcium aluminate powder was obtained.

Characterization of Synthesized Calcium Aluminate Nanoparticles

The synthesized calcium aluminate was identified and characterized by X-Ray Diffraction Spectrometer (XRD-2000 Diffractometer, Enraf Nonius Co., Bohemin NY) in accordance with the recommended standard as reported in the catalogue. The functional groups of synthesized calcium aluminate were evaluated by FT IR spectrometer (Perkin Elmer Spectrum GX, USA). The synthesized calcium aluminate was identified by Raman Spectrometer ((LABRAM HR Evolution, HORIBA France SAS) in accordance with the recommended standard procedure reported in the Raman spectrometer catalogue. The surface morphology of the synthesized sample was studied with a Scanning Electron Microscope (JSM-5610, JEOL Ltd., Japan). And then, calcium aluminate nanoparticles were tested with *Agrobacterium tumefaciens, Bacillus pumilus, Bacillus subtilis, Candida albicans, Escherichia coli, Micrococcus luteus, Pseudomonas fluorescens, and Staphylococcus aureus* to investigate the nature of antimicrobial activity.

After preparing the bacterial media, the sample calcium aluminate was placed on the agar well with flamed forceps and gently pressed down to ensure proper contact. The plates were incubated immediately or within 30 min after incubation. After overnight incubation at 37 ºC.

Results and Discussions

Characterization of Calcium Aluminate Nanoparticles

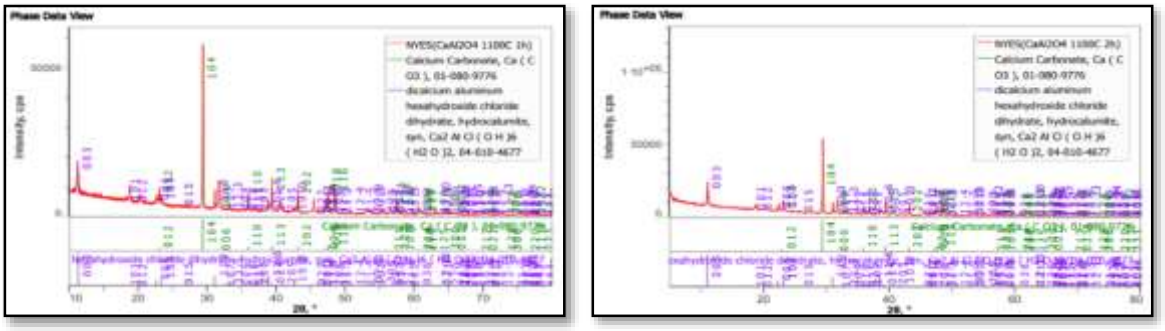
XRD Analysis

The synthesized calcium aluminate was characterized by an XRD spectrometer, and the recorded diffractograms are shown in Figures 1(a)(b) - 4(a)(b), and the results data are described in Table 1. Figures 1(a)(b) to 2(a)(b) showed X-ray diffraction patterns of synthesized calcium aluminate by a 1: 1 weight ratio of synthesized CaO and Al_2O_3 at different temperatures of 1100 °C and 1200 °C for 1 h and 2 h. It appeared that calcium carbonate and one of the calcium aluminate phases as hydrocalumite [di-calcium aluminum hexa-hydroxide chloride di-hydrate: $Ca_2AlCl(OH)_6(H_2O)_2$]. The peaks of $CaCO_3$ were shown at 2θ values around 23°, 29°, 36°, 39°, 43°, and 47° (Chengli *et al*., 2013). Obviously, the peaks of Hydrocalumite: $Ca_2AlCl(OH)_6(H_2O)_2$ at 2θ values of 11°, 22°, 23° and 31° **(**Xinhong *et al*., 2015). The Hydrocalumite calcium aluminates phase pattern showed no significant effect of calcination temperature and calcination period. The increasing amount of Al_2O_3 using 1: 2 (w/w) of synthesized CaO: Al_2O_3 at calcination temperatures of 1100 °C and 1200 °C for 1 h and 2 h was also performed. Figures

3(a)(b)-4(a)(b). Figure 3 (a) showed the XRD pattern of calcite at calcination temperature 1100 °C and a calcination time for 1 h. Figures 3 (b) to 4 (a) (b) clearly showed that the sharp peaks and pure calcium aluminate (calcium aluminium oxide): $Ca_{12}Al_{14}O_{33}$, peaks at 2θ values of 10.0°-80.0° corresponded to (211), (220), (310), (321), (420), (332), (422), (521), (611), (532), (631), (640) and (642) planes as indexing the $Ca_{12}Al_{14}O_{33}$ phase of cubic structure with space group of *I*-43*d* in the standard data (Guoqing et al., 2018). Therefore, XRD data proved that the molecular formula of synthesized calcium alulminate was $Ca_{12}Al_{14}O_{33}$ ($12CaO•7Al_2O_3$), it is also called dodecacalcium hepta aluminate. The smallest crystallite size was found at 1200 °C for 1 h, and its value is 43.82 nm. According to the XRD results, the synthesized calcium aluminate was affected by the composition of metal oxides, calcination temperatures, and calcination times. The transformation process at 1200 °C, a calcination period of 1 h, and a composition of a 1:2 ratio of CaO and Al_2O_3 was better than that of others. The lattice parameters for the synthesized dodecacalcium hepta aluminate was 11.99856 Å, which proved to be slightly larger than the value reported in the literature for pure synthetic mayenite (11.989 Å), implying the presence of the dodecacalcium hepta aluminate phase.

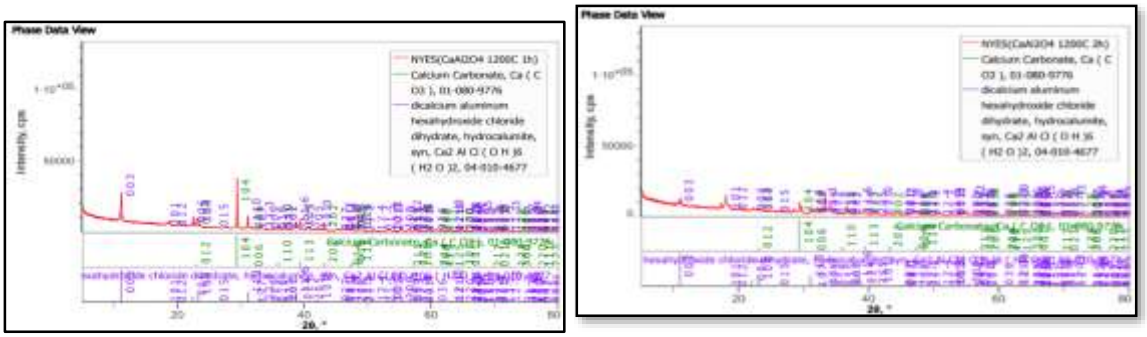
The reported literatures revealed that Mayenite ($12CaO·7Al_2O_3$) have drawn intensive attention because of a variety of promising applications, including display devices, catalysis, and transistors. This material possesses a porous cubic structure (*I*43*d*) made up of twelve Ca-Al-O nanocages, two of which are randomly occupied by the free oxygen ions inside. Such unique geometry leads to appealing characteristics including exceptional ionic conductivity, electronic conductivity, and optical transparency (Parinya Tangpakonsab *et al*., 2021).

Thus, XRD data demonstrated that utilizing synthesized CaO and Al_2O_3 nanoparticles as starting materials resulted in the formation of calcium aluminate phases at 1100 °C / 1 h**,** 1200 °C/ 1 h, and 1200 °C / 2 h**,** respectively.



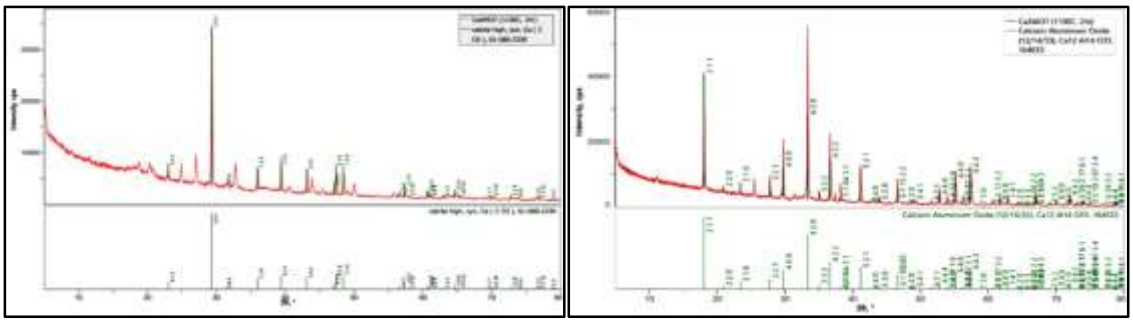
(a) **(b)**

Figure 1 X-ray diffraction pattern of synthesized calcium aluminate calcined at 1100 °C for (a) 1 h and (b) 2 h using 1:1 w/w ratio of $CaO:Al_2O_3$



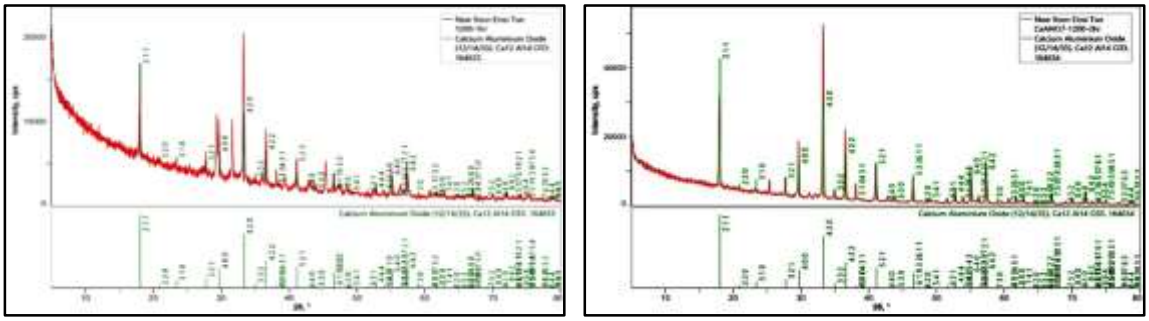
(a) **(b)**

Figure 2 X-ray diffraction pattern of synthesized calcium aluminate calcined at 1200 °C for (a) 1 h and (a) 2 h using 1:1 w/w ratio of $CaO:Al_2O_3$



(a) **(b)**

Figure 3 X-ray diffraction pattern of synthesized calcium aluminate calcined at 1100 °C for (a) 1 h and (b) 2 h using 1: 2 w/w ratio of CaO : Al_2O_3



(a) **(b)**

Figure 4 X-ray diffraction pattern of synthesized calcium aluminate calcined at 1200 °C for (a) 1 h and (b) 2 h using 1: 2 w/w ratio of CaO : Al_2O_3

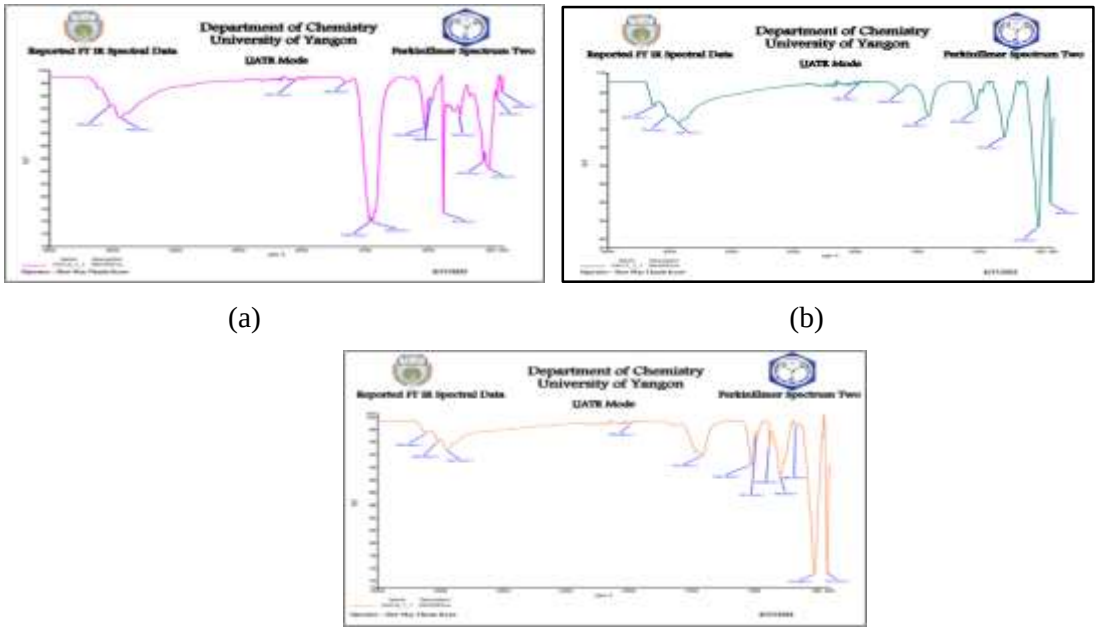
Table 1 XRD Analysis of Synthesized Calcium Aluminate

Sample	$CaO:Al_2O_3$	Calcined temperature (°C)	Calcined period (h)	Compound	Average crystallite size (nm)
CAP-1	1:1	1100	1	$CaCO_3$ $Ca_2AlCl(OH)_6(H_2O)_2$	59.21
CAP-2	1:1	1100	2	$CaCO_3$ $Ca_2AlCl(OH)_6(H_2O)_2$	62.36
CAP-3	1:1	1200	1	$CaCO_3$ $Ca_2AlCl(OH)_6(H_2O)_2$	38.72
CAP-4	1:1	1200	2	$CaCO_3$ $Ca_2AlCl(OH)_6(H_2O)_2$	25.05
CAP-5	1:2	1100	1	$CaCO_3$	50.61
CAP-6	1:2	1100	2	$Ca_{12}Al_{14}O_{33}$	80.35
CAP-7	1:2	1200	1	$Ca_{12}Al_{14}O_{33}$	43.82
CAP-8	1:2	1200	2	$Ca_{12}Al_{14}O_{33}$	76.65

FT IR analysis

The FT IR spectra of synthesized calcium aluminate (CAP-6, CAP-7 and CAP-8) are shown in Figure 5 (a) to (c) and Table 2. It was found that the formation peaks of water at 4000-

3000 cm^{-1}, corresponding to the presence of O-H stretching of hydroxyl. The peak at 1650-1400 cm^{-1}, due to -C=O stretching of carbonyl/carboxyl. The band at ~1030 cm^{-1} was assigned to C-O-C- stretching of epoxy groups. The peaks at about 900 cm^{-1} were assigned to stretching vibrations of a lattice of interlinked AlO_4 tetrahedral lattice. The band at about 890-750 cm^{-1} can be associated with the stretching mode of the free oxygen ions (O^{2-}) in the extra framework of the CaO structure. The vibration peaks at approximately 500 and 410 cm^{-1} are attributed to the stretching mode of Ca, Al and O atoms, which are characteristic of insulating $Ca_{12}Al_{14}O_{33}$ (David Torrens-Martin *et al.*, 2013).



(a) (b)

(c)

Figure 5 FT IR spectrum of calcium aluminate nanoparticles (a) CAP-6, (b) CAP-7 (c)CAP-8

Table 2 FT IR Spectral Data of Calcium Aluminate Nanoparticles (CAP-6, CAP-7 and CAP-8)

Wavenumber (cm^{-1})				Band assignment
CAP-6	**CAP-7**	**CAP-8**	***Literature**	
3436	3427	3447	4000-3000	O-H stretching of hydroxyl
1640	1628	-	1650-1400	C=O stretching of carbonyl/carboxyl
1459	1406	1413		
-	1023	1022	~1030	C-O-C stretching of epoxy groups
969	-	971	900	stretching vibrations of a lattice of interlinked AlO_4 tetrahedral
874	-	875	890-750	stretching mode of the free oxygen ions (O^{2-}) in extra framework of the CAO structure
744	786	789		
558	519	518	500-410	stretching mode of Ca, Al and O atoms as the characterization of insulating $Ca_{12}Al_{14}O_{33}$
520	420	419		

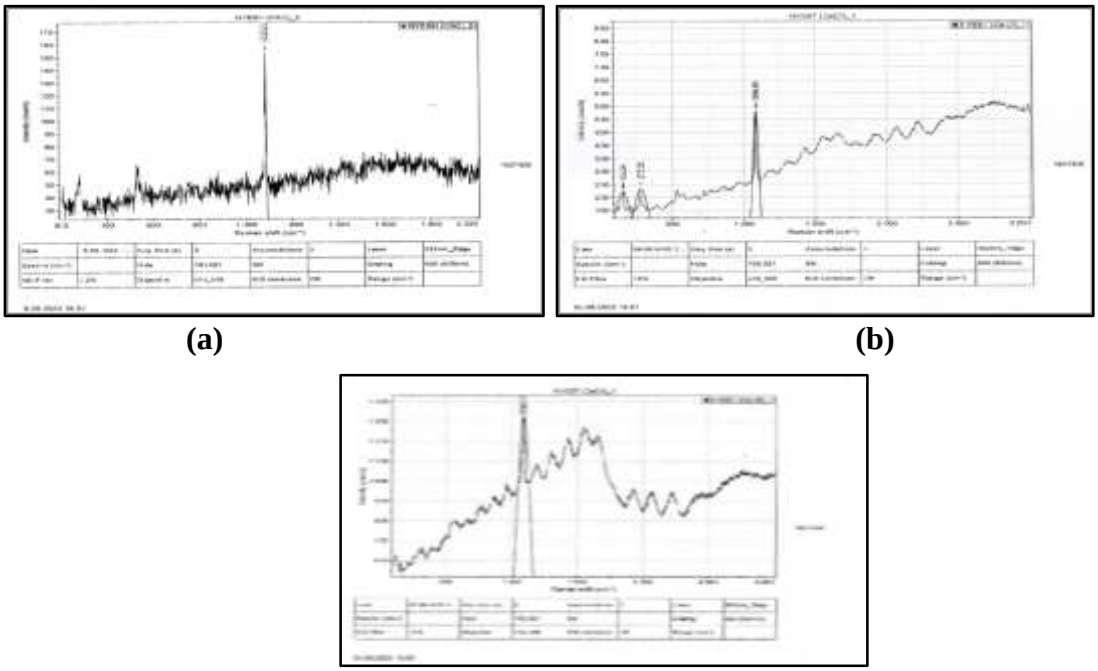
***Literature** - (David Torrens-Martin *et al.*, 2013)

Raman analysis

The Raman spectra of synthesized calcium aluminate nanoparticles (CAP-6, CAP-7 and CAP-8) are presented in Figures 6 (a) to (c). In CAP-6 and CAP-7, the strong Raman band was observed at 1084 cm^{-1} corresponding to the calcite bond. The band at 521 cm^{-1} may be associated with symmetric stretching vibration of Al-O groups and Al-O-Al linkage bonds. The remaining signals at 270 and 153 cm^{-1}, can be assigned to Ca-O bonds. In CAP-8, the Raman peak at 1088 cm^{-1} is also associated with the calcite band. The band at below 300 cm^{-1} is assigned to the Ca-O vibrations. It is shown in Table 3 (David Torrens-Martin *et al.,* 2013).

SEM analysis

The surface morphology of synthesized calcium aluminate (CAP-6, CAP-7 and CAP-8) was observed by scanning electron microscope. From Figures 7 (a) to (c), this can be seen in the presence of rigid agglomerates of flake-shaped nanoparticles. The SEM images clearly showed that synthesized calcium aluminate exhibited leaves-platelet like structure.



(a) **(b)**

(c)

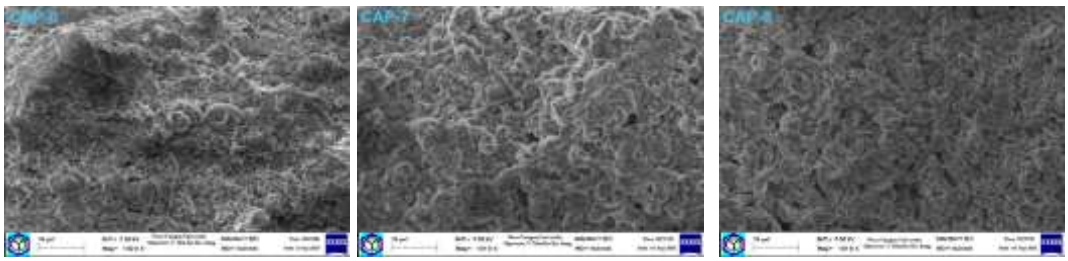
Figure 6 Raman spectrum of calcium aluminate nanoparticles (a) CAP-6, (b) CAP-7 and (c) CAP-8

***CAP= Calcium Aluminate Nanoparticles**

Table 3 Raman Spectral Data of Calcium Aluminate Nanoparticles (a) CAP-6, (b) CAP-7 and (c) CAP-8)

Wavenumber (cm^{-1})				Band assignment
CAP-6	**CAP-7**	**CAP-8**	***Literature**	
1085	1084	1088	1000	calcite band
520	521		518	symmetric stretching vibration of Al-O groups and Al-O-Al linkage bonds (υ_1 Al_4^{5-}).
280	270 153	145	<300	vibration of oxygen (O^{2-}) framework in Ca (AlO_4) crystalline and Ca-O bonding

***Literature-** David Torrens-Martin *et al.*, 2013



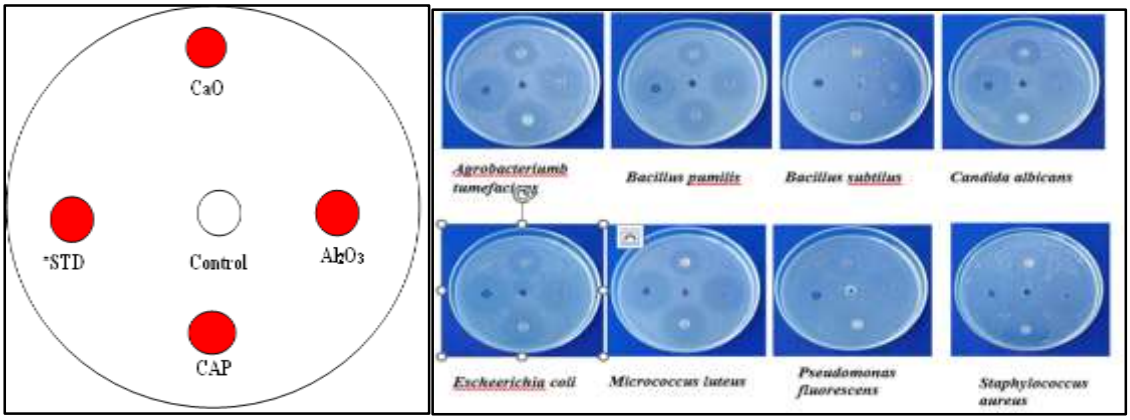
(a) (b) (c)

Figure 7 SEM image of calcium aluminate nanoparticles (a) CAP-6, (b) CAP-7 and (c)CAP-8

Antimicrobial Activity of Synthesized Calcium Aluminate Nanoparticles

In the environment, organisms can be exposed to nanoparticles *via* ingestion, inhalation, and penetration through the skin surface. Several investigations have reported the use of metal nanoparticles as an antimicrobial agent. Antimicrobial applications of nanoparticles cover not only bactericidal and bacteriostatic activities but also the possibility to detect potentially pathogenic microorganisms in medicine and food. They can be applied as components of coatings for medical devices, modification agents and impregnates for textiles, and "construction" elements for implants, cements, and resins.

Consequently, the antimicrobial activity of synthesized calcium oxide, aluminium oxide, and calcium aluminate nanoparticles against eight microbial strains (*Escherichia coli*, *Candida albicans*, *Bacillus subtilis*, *Staphylococcus aureus*, *Pseudomonas fluorescens*, *Agrobacterium tumefaciens*, *Bacillus pumilis*, and *Micrococcus luteus*) was assessed using the agar well diffusion method. The results of the antimicrobial investigation are presented in Table 4 and Figure 8. According to the results, a larger inhibition zone diameter indicates that the bacteria and fungus were more susceptible to the antibiotic and that the antibiotic has a higher antibacterial and antifungal activity. The agar diffusion antimicrobial assay proved that the synthesized calcium oxide, aluminium oxide, and calcium aluminate had good inhibitory responses against eight tested microorganisms. Thus, in the search for new applications for nanocomposites, it will be essential to evaluate their antimicrobial response in the coating of food containers, medical devices, packaging, and other fields of applications.



*Std = Standard, *CAP = Calcium aluminate nanoparticles

Figure 8 Antimicrobial activity of synthesized calcium oxide, aluminium oxide, and calcium aluminate nanoparticles

Table 4 Antimicrobial Activity of Synthesized Calcium Oxide, Aluminium Oxide, and Calcium Aluminate Nanoparticles Using Agar Well Diffusion Method

No.	Sample	Inhibition zone diameter (mm)							
		E.coli	***C.albicans***	***B.subtilis***	***S.aureus***	***P.fluorescens***	***A.tumefaciens***	***B.pumilus***	***M.luteus***
1.	**CaO**	20.8	22.2	20.0	21.4	23.4	22.0	23.0	22.9
2.	**Al_2O_3**	28.1	26.1	25.1	27.0	28.0	28.1	27.2	27.7
3.	**CAP**	27.0	24.5	25.0	26.4	27.7	29.0	27.0	27.6
4.	**STD**	33.4	30.2	28.8	31.6	33.1	33.4	33.1	32.9

Agar well diameter = 8 mm
10 mm – 14 mm = + (low activity)
15 mm – 19 mm = ++ (medium activity)
20 mm and above = +++ (very high activity)

Conclusion

In this study, calcium aluminate nanoparticles were successfully synthesized using different weight ratios of CaO and Al_2O_3 powders through a controlled calcination process. The optimal synthesis conditions, including a calcination temperature of 1200 °C, a duration of 1 hour, and a CaO-to-Al_2O_3 ratio of 1:2, led to the formation of pure dodecacalcium heptaaluminate ($Ca_{12}Al_{14}O_{33}$) with a well-defined cubic structure. XRD analysis confirmed the crystallographic planes characteristic of the $Ca_{12}Al_{14}O_{33}$ phase, with an average crystallite size of 43.82 nm. Structural characterization through Raman and FT-IR spectroscopy validated the presence of key functional groups, while SEM imaging revealed a leaf-platelet-like morphology.

Furthermore, the antimicrobial properties of the synthesized nanoparticles, assessed using the agar diffusion assay, demonstrated their potential for biomedical and environmental applications. Notably, the synthesis process employed waste quail eggshells and aluminum cans from Coca-Cola, offering an eco-friendly and sustainable approach to material development. This green synthesis method not only contributes to waste reduction and environmental sustainability but also highlights the potential of calcium aluminate nanoparticles for use in diverse technological and medical applications.

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Here are some suggested questions based on the study:

Synthesis and Characterization

1. What was the rationale behind selecting CaO and Al_2O_3 powders in different weight ratios for the synthesis of calcium aluminate nanoparticles?
2. How does the calcination temperature and duration influence the phase formation and crystallinity of the synthesized nanoparticles?
3. What structural or morphological advantages does the dodecacalcium heptaaluminate ($Ca_{12}Al_{14}O_{33}$) phase offer compared to other calcium aluminate phases?
4. How did the XRD analysis confirm the formation of pure $Ca_{12}Al_{14}O_{33}$, and what were the key crystallographic planes identified?
5. How do Raman and FT-IR spectroscopy validate the structural integrity and functional groups of the synthesized nanoparticles?
6. What does the SEM imaging reveal about the morphology of the nanoparticles, and how does it impact their functionality?

Antimicrobial and Practical Applications

7. What were the results of the antimicrobial activity tests, and how do they compare with existing antimicrobial materials?
8. What specific microbial strains were tested in the agar diffusion assay, and how effective were the nanoparticles against them?
9. What potential biomedical and environmental applications can benefit from these calcium aluminate nanoparticles?
10. How does the morphology of the synthesized nanoparticles influence their antimicrobial properties?

Sustainability and Green Synthesis

11. What are the advantages of using waste quail eggshells and aluminum cans from Coca-Cola as raw materials for nanoparticle synthesis?
12. How does this green synthesis approach contribute to environmental sustainability and waste reduction?
13. Are there any limitations or challenges associated with using waste-derived precursors in the synthesis of calcium aluminate nanoparticles?
14. How does this method compare with conventional calcium aluminate synthesis techniques in terms of cost, efficiency, and environmental impact?

Future Perspectives

15. What further modifications or improvements can be made to enhance the synthesis process and properties of the nanoparticles?
16. Are there any potential industrial applications where these nanoparticles can be commercially utilized?
17. How could the synthesis parameters (e.g., temperature, time, precursor ratios) be optimized further for better performance?
18. What are the next steps in exploring the full potential of calcium aluminate nanoparticles in medical or technological applications?

Would you like me to refine or add more questions based on a specific focus area?