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Biogenic Blend of Calcium Covered Zinc Oxide Nanoparticles from Beetroot Concentrate for Decolorization of Wastewater

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Abstract - *The development of nano-technology has directed to significant advancements in science and technology, including solutions for water contamination caused by industrial dyes, which pose serious ecological challenges. Zinc oxide nanoparticles (ZnO NPs), known for their unique photocatalytic properties at the nano-scale, offer a potential remedy for these issues. In this study, calcium-coated zinc oxide nano-particles were produced using beetroot extract as a reducing agent. The effects of these nanoparticles on various dyes were examined, and their properties were categorized through methods such as FT-IR, XRD, TEM, and UV spectrophotometry. The synthesized ZnO nanoparticles were bean or spherical-shaped, with sizes ranging from 29 to 49 nm. The calcium coating reduced the particle size further to 20–100 nm. The photocatalytic efficiency of these nanoparticles was evaluated by their ability to degrade dyes such as Rhodamine B, Methylene Blue, Congo Red, and Acid Blue 92 (AB92) under natural sunlight, with UV-Vis spectrophotometer monitoring the degradation process. Both the uncoated and calcium-coated ZnO nanoparticles demonstrated promising results in breaking down these dyes.*

Key Words: Zinc Oxide nanoparticles, FT-IR, XRD, TEM and UV Spectro-photometer, Rhodamine B, Methylene Blue, Congo Red and Acid Blue 92(AB92)

1.INTRODUCTION

In recent decades, nanotechnology has emerged is one of the significant dynamic fields in customizable materials science, with broad applications in clinical settings. This growth is largely attributed to the unique size-dependent properties of nanomaterials, which result from precise control during the synthesis process. This interaction at the nanoscale enables metal-oxide nano-particles (MONPs) to enters through biological barriers, like the blood brain barrier (BBB), which was previously a significant obstacle in drug supply. MONPs, such as zinc oxide (ZnO), titanium dioxide (TiO2), and iron oxide (Fe3O4), have demonstrated potent applications in cancer therapy, antimicrobial treatments, and imaging methods like magnetic resonance-imaging (MRI). For instance, iron-oxide nano-particles are widely applied as contrast agents in MRI due to their magnetic properties, allowing for enhanced visualization of tissues. Additionally, MONPs' ability to act as carriers for drugs or therapeutic agents opens novel targeted and controlled drug release. Their surface is to be modified with ligands, antibodies, or peptides to specifically bind to cancer cells or pathogens, minimizing side effects and improving therapeutic efficiency. However, the use of MONPs in clinical applications is not without challenges. Concerns about toxicity, environmental-impact, and potential long-term effects on human-health have prompted ongoing research to better understand the biocompatibility and safety of these materials. Researchers are focused on optimizing the synthesis, surface functionalization, and degradation profiles of MONPs to ensure their safe and effective use in medical treatments. In summary, MONPs represent a promising tool in nanomedicine, offering unique opportunities for disease identification, targeted drug delivery, and medical imaging. Continued advancements in their design and application will likely lead to further breakthroughs in healthcare. The extensive research on these metal-oxide nano-particles (MONPs) highlights their potential in revolutionizing bio-medical applications due to their diverse therapeutic and diagnostic capabilities. Each of MONPs offers unique appearances that create them suitable for different clinical uses, primarily attributed to their size, surface area, and functionalization potential, which enable targeted interaction with cells and tissues.

- **Zinc oxide nanoparticles (ZnO NPs)**: Known for their **antimicrobial and wound-healing properties**, ZnO NPs are commonly integrated into wound dressings to prevent bacterial infections and facilitate tissue repair. They also exhibit potential in **anticancer therapies** due to their capability to induce oxidative stress selectively in tumor cells.

- **Cerium oxide nanoparticles (CeO2 NPs)**: CeO2 NPs stand out due to their **antioxidant properties**, allowing them to scavenge free radicals and reduce oxidative stress, making them valuable for treating conditions related with oxidative damage, including neurodegenerative diseases. Their regenerative redox cycling also positions them as promising agents in **anti-inflammatory** treatments.

- **Iron oxide nanoparticles (Fe2O3 NPs)**: The **magnetic properties** of Fe2O3 NPs make them highly useful as **MRI contrast agents** and in **magnetic hyperthermia therapy** for cancer treatment. Their ability to be functionalized for directed drug delivery is also a major focus in precision medicine.
- **Silver oxide nanoparticles (AgO NPs)**: AgO NPs are well-known for their **broad-spectrum antimicrobial activity**, making them effective against antibiotic-resistant strains. Their inclusion in medical devices and coatings helps prevent infections, and they are frequently used in **antimicrobial wound dressings**.
- **Magnesium oxide nanoparticles (MgO NPs)**: MgO NPs exhibit **antibacterial properties** and are gaining kindness for their potential in **bone regeneration**, owing to magnesium's role in bone metabolism and its ability to promote osteoblast activity.
- **Titanium oxide nanoparticles (TiO2 NPs)**: Widely used in **photocatalytic applications**, TiO2 NPs are explored in **photodynamic therapy (PDT)** for cancer treatment. Their ability to produce reactive oxygen species (ROS) under light exposure is used to target and destroy cancer cells.
- **Nickel oxide nanoparticles (NiO NPs)**: NiO NPs are being discovered for **biosensor applications** due to their excellent electrical properties. However, further research work is required to fully understand their biocompatibility and toxicity profiles.
- **Zirconium oxide nanoparticles (ZrO NPs)**: ZrO NPs are highly **biocompatible** and are being explored in **orthopedic and dental implants** due to their hardness and resistance to wear. Their stability also creates them suitable for biosensors and drug delivery systems.
- **Cadmium oxide nanoparticles (CdO NPs)**: CdO NPs have indicates promising results in **anticancer therapy** and **biosensing applications**, but their potential **toxicity** remains a significant concern. Cadmium's known toxic effects require careful regulation and further research to mitigate risks in clinical applications.

1.1 Synthesis Methods and Key Characteristics of Metal Oxide Nanoparticles

Nano-particles can be synthesized using either a "top-down" or "bottom-up" approach. The top-down technique involves breaking down bulk substances into nanoparticles through size reduction techniques such as lithography, milling, grinding, laser ablation, or sputtering. In contrast, the bottom-up approach involves assembling nanoparticles from smaller units using chemical, physical, or biological methods, along with plant materials, microbes, or biological products.

For the blending of metal-oxide nanoparticles (MONPs), chemical and physical bottom-up approaches are commonly used, as they efficiently produce large quantities of nanoparticles. However, these method exists with certain drawbacks, such as higher costs, the application of toxic chemicals that may remain on the nanoparticle surface and cause harmful effects in biomedical applications, and the need for stabilizers to ensure nanoparticle stability. Some of the main synthesis techniques include:

- Chemical precipitation,
- Wet chemical synthesis,
- Hydrothermal methods,
- Solvothermal methods,
- Sol-gel processes,
- Solid-state pyrolytic techniques,
- Thermal decomposition, and
- Microwave-assisted synthesis.

Reaction

$$Zn(CH_3COOH)_2 + C_{24}H_{27}N_2O_{13} \rightarrow Zn + C_{26}H_{29}N_2O_{17}$$

$$Zn + 2NaOH \rightarrow Zn(OH)_2$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

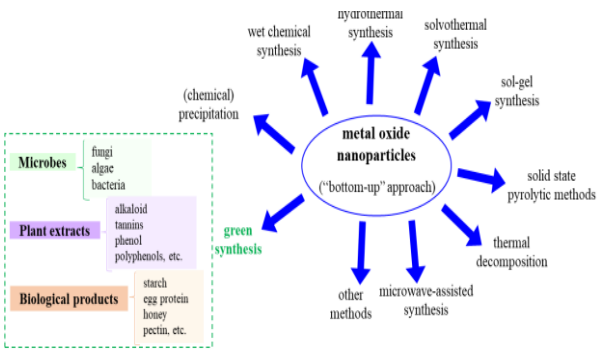

Figure 1. Potential synthesis methods for metal oxide nanoparticles (using a "bottom-up" approach)

2. METHODS AND METHODOLOGY

2.1 Preparation of beetroot extract

Beetroots were purchased from the local market and rinsed with distilled water (DW) to remove dust particles. 40 g were grinded in a beaker and boiled with distilled water (100 ml) for 15 min. Then the beaker was kept for cooling. After cooling, the solution was filtered to eliminate the insoluble part. The wine-coloured solution was then stored in glass bottles and kept in the refrigerator for further use.

2.2 Synthesis of zinc-oxide nano-particles

To synthesize ZnO nano-particles, 500 ml of beetroot extract was transferred in a 500 cm^3 beaker having a magnetic bead. The solution was heated to 60 °C followed by the mixture of 45 g of zinc acetate. The pH of the solution was maintained between 8.0.

It was stirred at this temperature and pH for 40 min. till the formation of pale yellow solution. The resulting solution was centrifuged and washed applying double distilled water at 80 °C and dried in the oven. After that, the dried powder was calcinated at 450 °C in a muffle furnace for 15 min. The synthesized samples were preserved for further experimental study.

2.3 Synthesis of Calcium coated Zinc Oxide nanoparticles

Ca-coated ZnO nano-particles were synthesized by the co-precipitation method. Zn $(CH_3COO)_2$. 2 H_2O and calcium chloride were taken in 1:1 wt. ratio. To synthesize Ca-ZnO nanoparticles, weighed Zn $(CH_3COO)_2$. 2 H_2O was dissolved in 40ml of Beetroot extract at 60 °C temperature and pH 8, followed by adding a weight amount of calcium chloride. It was agitated for 1 h and then centrifuged to separate the Nano composite. It was rinsed with Double DW to remove impurities and dried. It was calcinated at 450 °C in a muffle furnace for 15 min. The Ca-ZnO nanoparticles prepared in 1:1 ratio, The samples were retained for further experimental study.

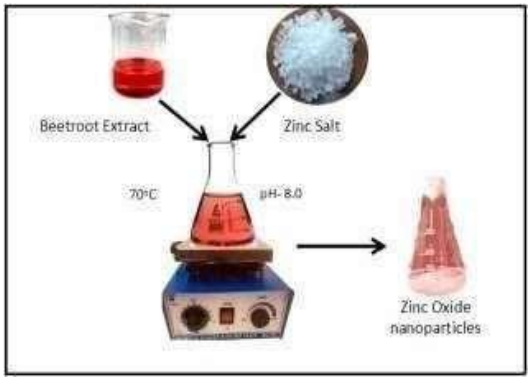

Figure 2. Schematic Representation of formation of Zinc-oxide Nano-particles

2.4 Preparation of Stock Solution

1gm of dye was dissolved in 1L of distilled water. 100mL of stock solution was taken and 1gm of nanoparticles & 10mL of this solution was placed in UV spectrometer every 10min to determine the photo catalytic degradation of the dyes.

Element	Weight %	Atomic %
O	39.80	73.06
Zn	80.11	26.46

3. RESULTS AND DISCUSSION

A. X-RAY DIFFRACTIONS STUDIES(XRD):

XRD spectra of beetroot extract mediated Zinc-oxide nano-particle was shown in figure 3. Beetroot extract refereed Zinc-oxide nano-particles have characteristic peaks at 32.08^0-100, 36.28^0 - 002, 36.57^0 - 101, 47.89° - 102, 56.79^0 - 110, 63.04^0 - 103, 68.19^0 - 201 that represents hexagonal structure. Intensity of Zine Oxide peak at 47.89°(102) was higher than the intensities of other peaks, indicating that there is growth in nanoparticles. In calcium coated Zine Oxide nanoparticles, growth mainly took place in the (102) plane. We should note that Calcium coated did not affect the crystallinity of Zinc-oxide nano-particles

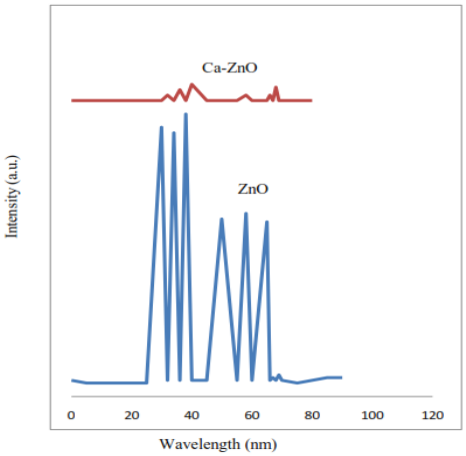

Figure 3. Beetroot extract refereed Zin-oxide nano-particles characteristics at XRD.

$$Zn(CH_3COOH)_2 + C_{24}H_{27}N_2O_{13} \rightarrow Zn + C_{26}H_{29}N_2O_{17}$$

$$Zn + CaCl_2 + NaOH \rightarrow Ca - Zn(OH)_2 + NaCl$$

$$Ca - Zn(OH)_2 \rightarrow Ca - ZnO$$

B. FTIR STUDIES:

The FTIR of Zinc-oxide nano-particles & its calcium Nano composites is indicated in figure 4. The spectra shows association of OH stretching at 3437cm^{-1}, Co group stretching at 1614cm^{-1} & Zinc Oxide stretching at 459cm^{-1} respectively.

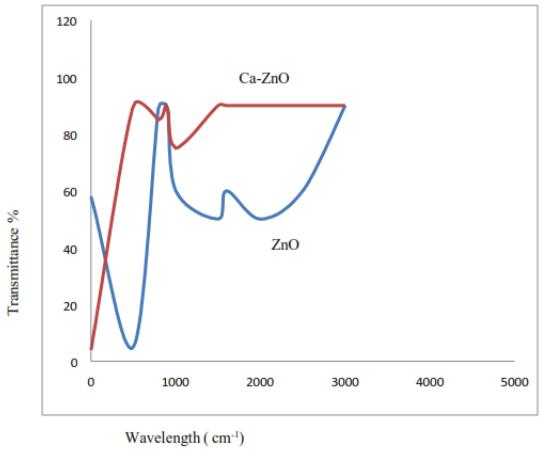

Figure 4. FTIR of Zinc-oxide nano-particles & its calcium Nano composites

C. SEM STUDIES:

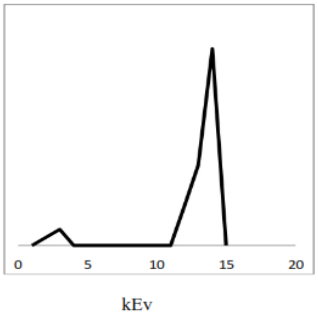

Figure 5. SEM studies of Zno nanoparticles

Table 1. SEM Zno nanoparticles

Element	Weight %	Atomic %
O	39.80	73.06
Zn	80.11	26.46

Element wise Weight% and Atomic% distribution of Zno nanoparticles and Ca-Zno nanoparticles are indicated in table 1 and table 2 respectively.

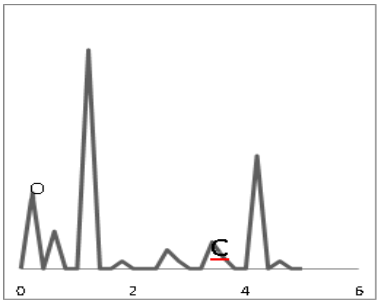

Figure 6. SEM studies of Ca-Zno nanoparticles

Table 2. SEM Ca-Zno nanoparticles

Element	Weight %	Atomic %
O	32.29	64.00
Cl	1.98	1.77
Ca	7.69	6.08
Zn	53.04	28.15

The External morphology of dried Zinc-oxide nano-particles with or without were determined using SEM. Shape and Surface morphology are displayed in figure 5 & 6. This shows that the nano-particles are likely to be hexagonal in shape. The particle size ranges from 29-49 nm for Zinc Oxide & from 72-89 nm for calcium coated Zinc Oxide nanoparticles. Figure 7 shows the variations in chemical compositions.

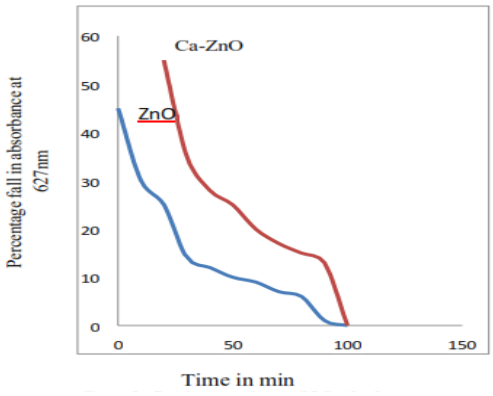

Figure 7. a,c-ZnO Nanoparticles, b,d- Calcium coated ZnO Nanoparticles shape and size

D. UV ABSORPTION:

i) Methylene Blue:

Figure 8 shows that there is 80% degradation in 100 min with blank ZnO nanoparticles at wavelength of 627nm & 100% degradation after 60min with calcium coating at 627 nm. This shows that calcium coating increases the percentage of degradation in case of Methylene Blue.

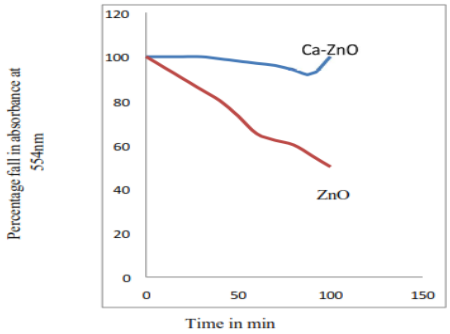

Figure 8. Absorption of Methylene Bule

i. Rhodamine B:

Figure 9 shows that there is 60% degradation after 100 mins with blank ZnO nanoparticles at wavelength of 554nm and almost no degradation with calcium coating at any wavelength. This shows that calcium coating doesn't affect the photo catalytic property of Zinc-oxide Nano-particles for Rhodamine B.

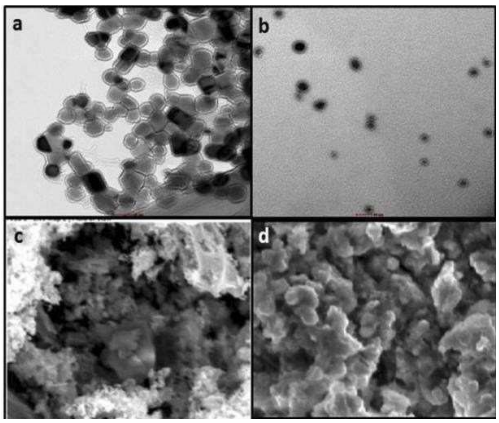

Figure 9. Absorption of Rhodamine B.

ii.Congo Red:

Figure 10 represents that for Congo red the adsorption is the maximum at 45 min and 100 min with 52% and 50% respectively for blank Zinc Oxide Nanoparticles. 54% and 52% respectively for calcium coating. This indicates that there is no much difference in degradation with or without coating. The increase and decrease in adsorption is owing to the loss of photo catalysis due to blockage created by the dye.

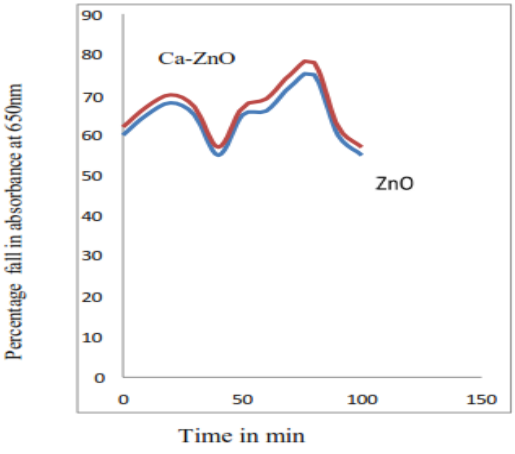

Figure 10. Adsorption of Congo Red

iii. Acid Blue:

There is no release with both blank and coated nanoparticles for acid blue dye. This shows that there is no effect of ZnO Nano-particles and Calcium coated ZnO Nano-particles on Acid blue.

3. CONCLUSIONS

The present work shows that the synthesized Zinc-oxide nano-particles and Calcium coated Zinc-oxide nano-particles (1:1) act as a good photo catalyst. Degradation efficiency of Zine oxide nanoparticles for Methylene Blue is 80% after 100 min, for Rhodamine B is 60% after 100 minutes, for Congo Red is 52% after 45 minutes.

Degradation efficiency of Calcium coated Zinc oxide nanoparticles for Methylene Blue is 100% after 60 min, for Rhodamine B there is no release, for Congo Red is 54% after 45 minutes.

These results indicate the potential application of Zinc-oxide nano-particles with or without the Calcium coating in degrading toxic organic compounds from wastewater.

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