NOVEL AND SUSTAINABLE TRANSFORMATION OF MARINE SHELL WASTE INTO THERAPEUTIC-GRADE CHITOSAN-CALCIUM CARBONATE HYDROGELS FOR REGENERATIVE AND WOUND-HEALING INNOVATIONS

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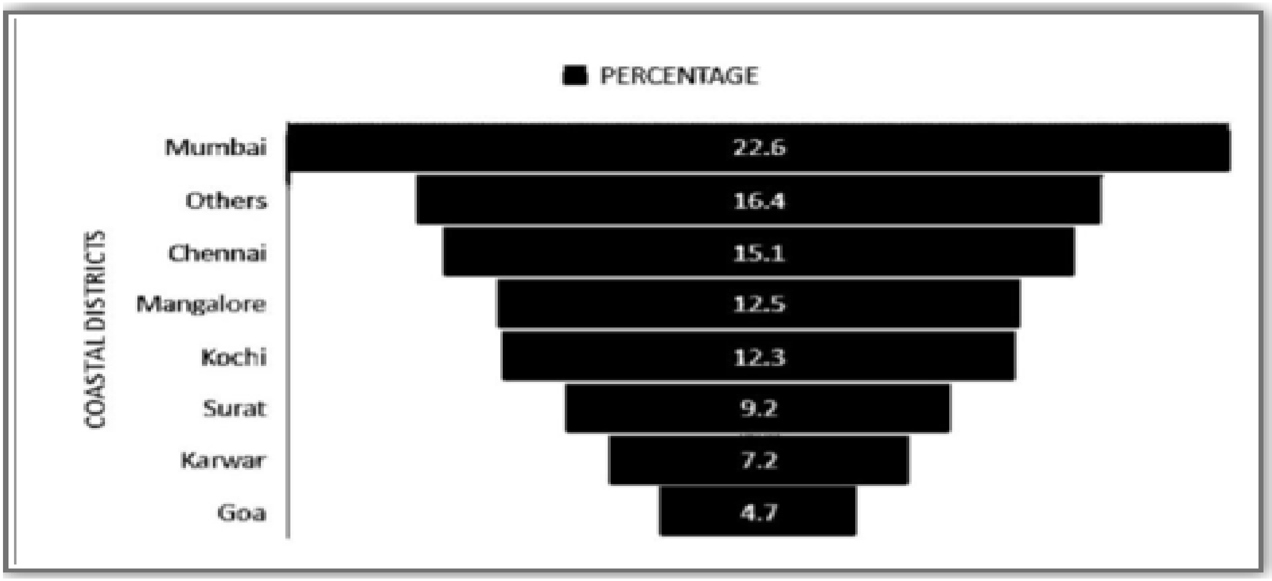
Keywords:

Chitosan, Shrimp shell wastes, Calcium Carbonate, Clam Shells, PVA Hydrogel biofilm, Hydrogel beads

Introduction:

India's rapidly expanding seafood industry generates significant amounts of marine biowaste, with nearly 50–60% of shrimp and shellfish biomass discarded as exoskeletal residues rich in chitin and calcium-based minerals. Improper disposal of this waste leads to serious environmental concerns, including the release of nitrogenous compounds, increased biological oxygen demand (BOD), and contamination of soil and water, ultimately disrupting aquatic ecosystems and threatening marine biodiversity. Despite these challenges, marine waste serves as a valuable renewable resource, as chitin from shrimp shells can be converted into chitosan, a biodegradable and biocompatible polymer widely used in wound healing, drug delivery, and tissue engineering applications. Additionally, shell waste provides calcium-rich materials that can be utilized in biomaterial synthesis. However, limited waste valorization technologies and inadequate infrastructure hinder efficient utilization, resulting in both environmental burden and economic loss. This necessitates the development of sustainable strategies aligned with the principles of the circular bioeconomy. Chitosan is typically produced through deproteinization, demineralization, and deacetylation processes, while calcium-based compounds are obtained via calcination. These materials can be effectively incorporated into hydrogels, which are three-dimensional hydrophilic polymer networks characterized by high water retention, porosity, and biocompatibility, closely mimicking the extracellular matrix. Furthermore, the incorporation of polyvinyl alcohol enhances the mechanical strength and structural stability of the hydrogel system, resulting in improved performance. Therefore, the conversion of marine shell waste into chitosan–calcium hydroxide-based hydrogels represent a promising, eco-friendly approach for advanced biomedical and environmental applications.



Sea food waste producing major coastal districts in India

Objectives:

1. Extraction of **Chitosan** from shrimp shell waste and **Calcium Hydroxide $Ca(OH)_2$** from clam shell waste and perform comparative evaluation between **extracted** and **commercially available chitosan and calcium hydroxide**.
2. Formulation of **chitosan– $Ca(OH)_2$ –PVA composite hydrogel films** and **chitosan–$Ca(OH)_2$ -TPP hydrogel beads** and perform comparative evaluation and characterization between **extracted** and **commercially available chitosan and calcium hydroxide** hydrogel films and hydrogel beads

Methodology:

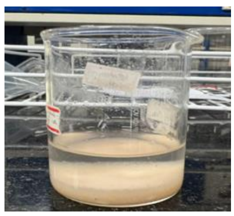
1. EXTRACTION OF CHITOSAN FROM SHRIMP SHELL WASTES

Cleaned Shrimp Shells with NaOH

Grinded shell waste Powder

Demineralization using HCl

Deproteinization using NaOH



Deacetylation using NaOH

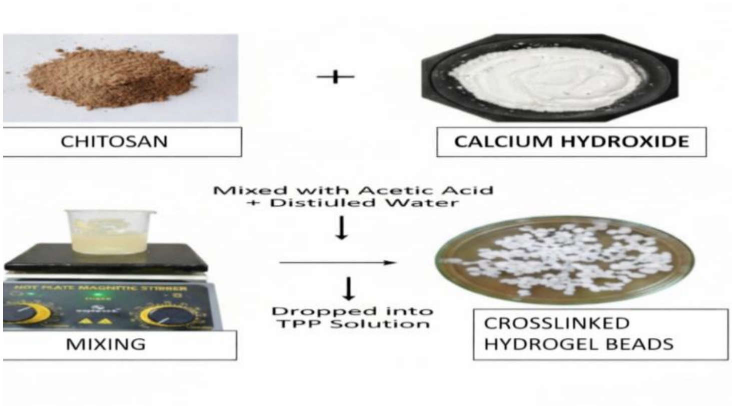
pH 7

Chitosan Powder

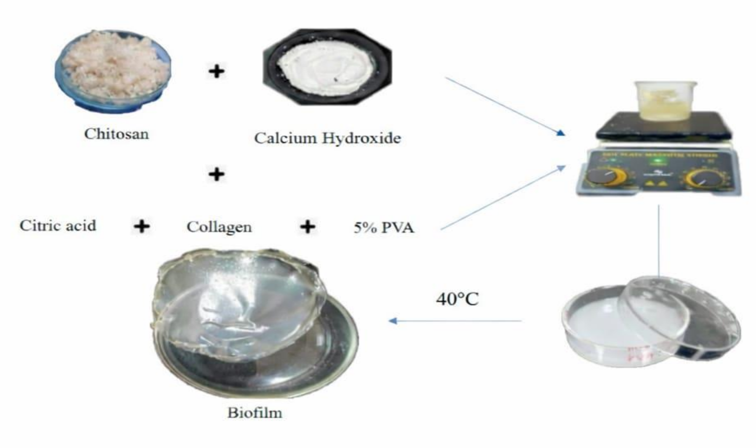
2. EXTRACTION OF CALCIUM HYDROXIDE FROM CLAM SHELL WASTES

Clam shells waste — *Sintered at higher temperatures* — *Extracted $Ca(OH)_2$*

3. FORMULATION OF HYDROGEL BEADS CROSSLINKED WITH SODIUM TRI POLYPHOSPHATE (TPP)

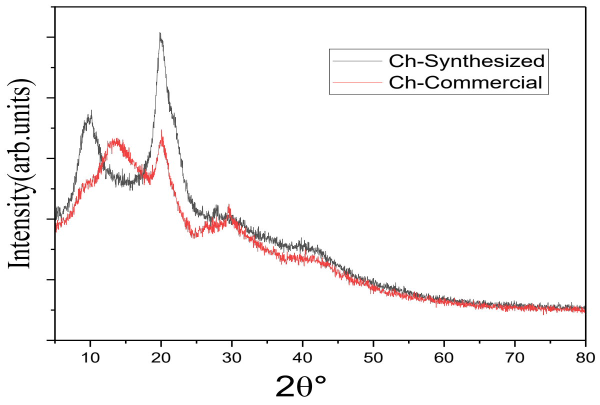


4. FORMATION OF CHITOSAN- $Ca(OH)_2$ -PVA HYDROGEL FILM

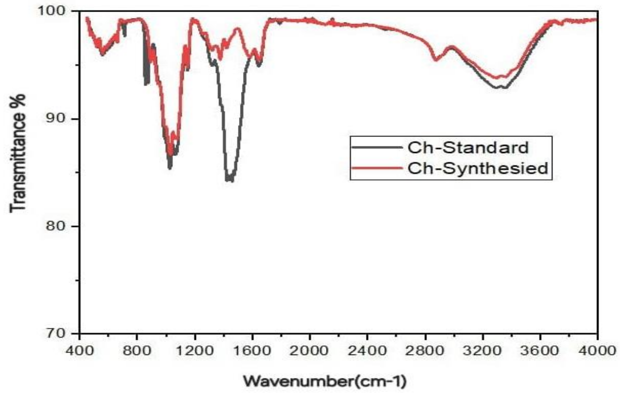


Result and Conclusion:

1. EXTRACTION OF CHITOSAN FROM SHRIMP SHELL WASTES



XRD comparison of extracted chitosan.
from shrimp shells and commercial chitosan.

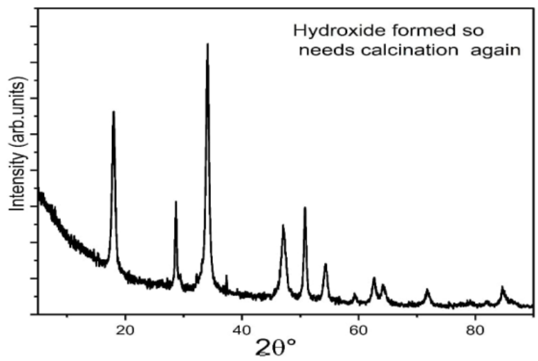


FT-IR comparison of extracted chitosan
from shrimp shells and commercial chitosan

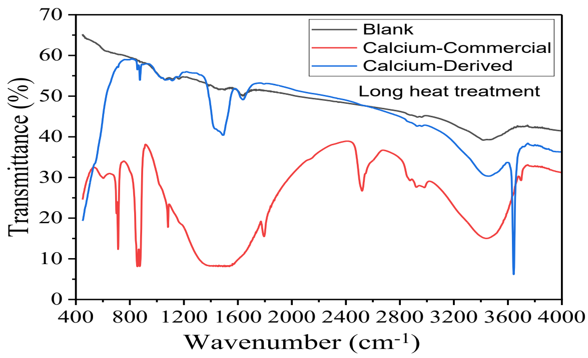
Semi-crystalline peaks at 2θ ≈ 10° and 20° in both
Synthesized chitosan: higher crystallinity & ordering, Commercial: more amorphous
No chitin peaks → successful conversion
Synthesized shows better strength, stability & biodegradation

FTIR confirms O–H/N–H, Amide I & II groups → successful chitin → chitosan conversion
DD of synthesized chitosan (65–67%) is lower than commercial (70–72%)
Lower DD indicates reduced reactivity and solubility compared to commercial

2. EXTRACTION OF CALCIUM HYDROXIDE FROM CLAM SHELL WASTES



XRD analysis of $Ca(OH)_2$ extracted
from clam shells waste

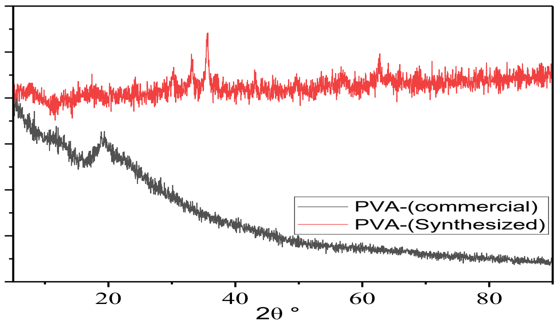


FTIR analysis of $Ca(OH)_2$ extracted and
commercial from clam shell wastes

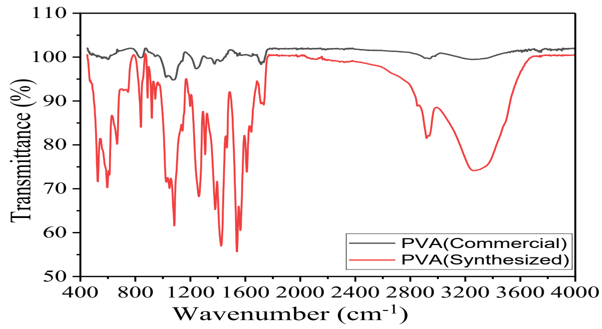
XRD confirms conversion of clam shell waste into crystalline $Ca(OH)_2$
Sharp peaks at 2θ ≈ 18° and 34° indicate ordered portlandite structure
Crystallite size ~30 nm → nanostructured material

FTIR shows sharp –OH peak at 3640 cm^{-1} → confirms $Ca(OH)_2$(high purity)
Commercial sample shows carbonate peaks (1400–1500 & 875 cm^{-1}) → residual $CaCO_3$ in commercial sample
Reduced carbonate signals in derived sample → better conversion and higher purity

3. FORMULATION OF CHITOSAN-$Ca(OH)_2$-PVA COMPOSITE HYDROGEL BIOFILM



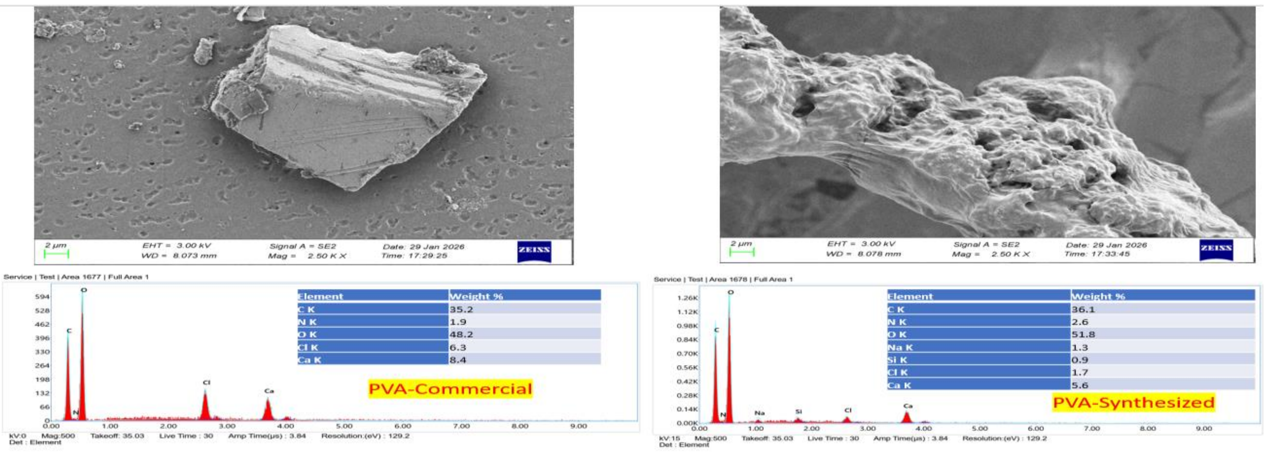
XRD analysis comparison of extracted and commercial hydrogel biofilms



FTIR analysis comparison of extracted and commercial hydrogel biofilms

Commercial hydrogel shows broad amorphous peak (~19.4°) due to PVA and chitosan
No distinct mineral peaks in commercial sample
Synthesized hydrogel shows sharp peaks at 18° and 34°
Confirms presence of crystalline $Ca(OH)_2$ in

Strong O–H/N–H bands (~3300 cm^{-1}) in synthesized blend
Distinct peak at 3640 cm^{-1} → confirms $Ca(OH)_2$
Well-defined peaks in 1000–1700 cm^{-1} region
Indicates enhanced hydrogen bonding
Shows better structural integrity than

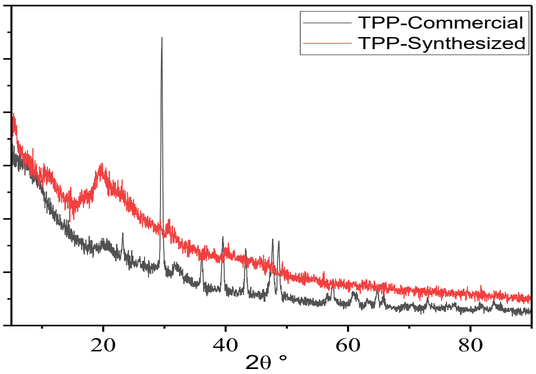


SEM and EDS analysis comparison of extracted and commercial hydrogel biofilms

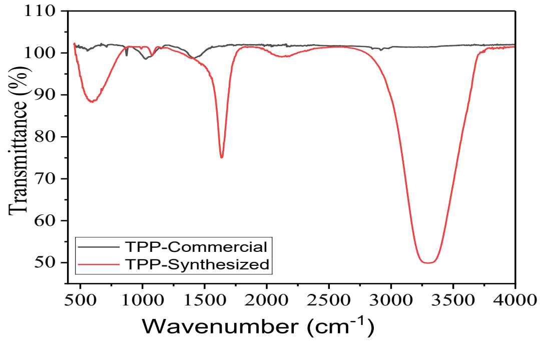
Commercial hydrogel shows large, poorly bonded $CaCO_3$ particles
Synthesized composite exhibits homogeneous, porous network
Indicates better polymer–mineral interaction
Enhances mechanical and biomedical performance

EDS shows fewer impurities in synthesized sample
Higher oxygen content → presence of hydroxyl-rich components
Confirms effective $Ca(OH)_2$ integration
Suitable for biomedical scaffold applications

4.FORMULATION OF HYDROGEL BEADS CROSSLINKED WITH SODIUM TRI POLYPHOSPHATE (TPP)



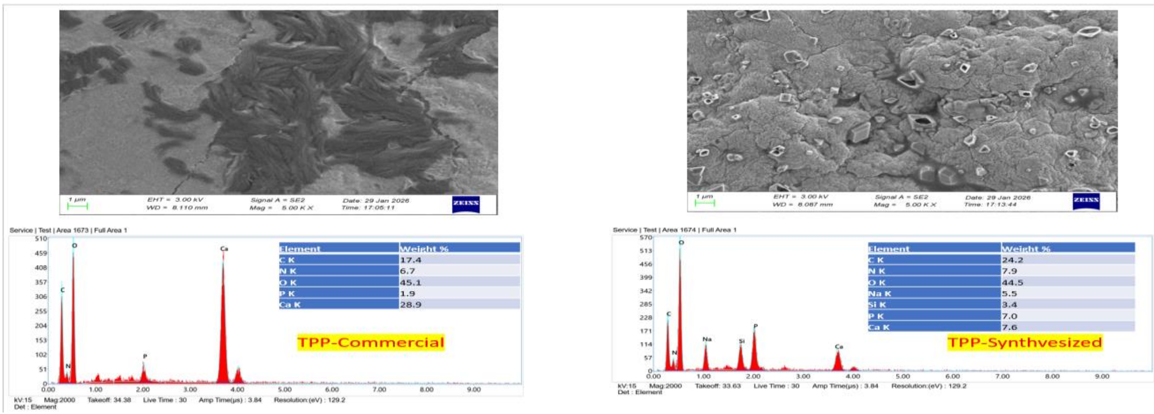
XRD analysis comparison of extracted and commercial hydrogel beads



FTIR analysis comparison of extracted and commercial hydrogel beads

Synthesized hydrogel shows broad amorphous peak at 2θ ≈ 20°
Indicates successful cross-linking
Commercial sample shows sharp crystalline peaks (e.g., 29.4° calcite)
Suggests presence of unreacted material
Suppression of crystalline peaks → better integration
Confirms nanostructured hydrogel

Broad O–H/N–H band (3200–3500 cm^{-1}) → strong hydrogen bonding
Peaks at ~1150 cm^{-1} (phosphate) and ~1645 cm^{-1} (amine)
Confirms TPP–chitosan interaction
Indicates ionic cross-linking and hydrogel formation
Shows more stable network than commercial sample



SEM and EDS analysis comparison of extracted and commercial hydrogel beads

Commercial hydrogel shows smooth structure with weak $CaCO_3$ integration
Synthesized hydrogel exhibits textured, globular morphology
Enhanced mineral incorporation and surface roughness (better for cell adhesion)
EDS shows improved elemental integration
Elevated nitrogen and trace elements (Na, Si) → stronger polymer–mineral interaction
Confirms successful incorporation of waste-derived materials
Synthesized hydrogel shows superior crosslinking, reactivity, and performance

References:

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Future Scope:

The synthesized materials, produced via a “Waste-to-Wealth” approach from shrimp and clam shells, show superior structural and chemical integration compared to commercial ones. XRD and SEM confirm high crystallinity and a porous nanostructure, ideal for stable hydrogels and PVA films. TPP-crosslinked hydrogels form a flexible 3D network through ionic interactions, stabilizing calcium minerals, while PVA films exhibit strong hydrogen bonding, enhancing mechanical strength and functionality.

The future scope of this project includes:

1. Development of antimicrobial wound patches: Fabrication of hydrogel-based film dressings exhibiting a clear zone of inhibition, ensuring effective antibacterial activity and prevention of microbial growth for improved wound healing applications.
2. In bone tissue engineering, the synthesized $Ca(OH)_2$ serves as a highly reactive precursor for hydroxyapatite formation, facilitating faster bone regeneration and improved cellular attachment compared to commercial carbonates.
3. For environmental applications, the abundance of amine and phosphate groups enables these hydrogels to act as efficient biosorbents for removing heavy metals from wastewater, demonstrating that these low-cost, sustainable materials can effectively replace expensive synthetic alternatives