WWW.IJRPR.COM

International Journal of Research Publication and Reviews

Journal homepage: www.ijrpr.com ISSN 2582-7421

Sustainable Hydroxyapatite Production from Cuttlebone for Calcium Fortification in Goats – A Review

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ABSTRACT :

Marine biowaste valorisation offers sustainable solutions for converting seafood processing residues into valuable biomaterials. Cuttlebone derived from *Sepia officinalis* is a calcium-rich marine by-product primarily composed of aragonite ($CaCO_3$) with a highly porous microstructure. This study investigates the synthesis of hydroxyapatite (HAp) from cuttlebone and evaluates its potential as a dietary calcium fortifier for goats. The synthesized material was characterized for structural and physicochemical properties to determine its suitability as a feed-grade supplement. Given the essential role of calcium in skeletal development, neuromuscular function, lactation, and prevention of hypocalcaemia in ruminants, the bioavailability and nutritional relevance of cuttlebone-derived calcium were assessed. The findings highlight the feasibility of transforming discarded marine biominerals into value-added hydroxyapatite for livestock nutrition, supporting circular bioeconomy principles as a low-cost, ecologically-friendly alternative to conventional mineral supplements for smallholder and coastal farming systems.

Keywords: **Marine biowaste valorisation, Cuttlebone, Hydroxyapatite, Calcium fortification, Goat nutrition.**

Marine waste utilization for responsible consumption:

The growing volume of marine waste is now recognized as a critical issue for society, the economy, and the environment. Because landfilling, incineration, and composting cannot keep pace with the scale of marine biowaste generated, valorisation — converting these residues into value-added products — has become essential [1]. Fishing and aquaculture industries discard huge quantities of fish heads, bones, skins, scales, viscera, shellfish, and crustacean exoskeletons every year. Once treated simply as waste, these by-products are now recognized as candidates for value-added biogenic products owing to their protein, lipid, mineral, and polysaccharide content. The Food and Agriculture Organization notes that valorising fishery by-products reduces environmental pollution while improving economic returns for the seafood industry.

The main components of marine mineral waste — fish bones and mollusk shells — are calcium carbonate and calcium phosphate, which can be converted into hydroxyapatite and other calcium compounds for biomedical use, including bone grafts and dental materials [2]. Research by the International Energy Agency (IEA) and other sustainability-focused organizations has shown that marine-derived biominerals can replace synthetic materials, reducing the environmental footprint of mining natural resources.

Cuttlefish:

Cuttlefish (*Sepia officinalis*) is among the most valuable marine resources found in the Mediterranean and extending to the Red Sea [3]. In coastal areas such as the Gulf of Suez in Egypt, seafood processing industries depend heavily on cuttlefish as an export product, and the internal shell (cuttlebone) is usually discarded back into the sea as biological waste [4]. Strong currents and winds in the Gulf of Suez also wash large numbers of dead cuttlefish ashore, so that nearly 6000–8000 tons of unused cuttlebone accumulate along the coast each year.



Fig 1: **Images of a Cuttlefish**

Cuttlefish Bone:

Cuttlebone — also called the cuttlefish bone — is a rigid yet fragile internal structure found throughout the Sepiidae family; a comparable structure in other cephalopods is called a gladius. It is composed mainly of aragonite, a crystalline form of calcium carbonate, with a small organic fraction (about 3–4.5% by weight) of β-chitin and proteins. Structurally, it consists of a rigid outer dorsal layer and a fragile, chambered inner ventral section connected by a highly modified siphuncle, which the cuttlefish fills with gas or liquid to regulate buoyancy [5]. This lightweight, chambered architecture lets the animal alter its density and move up or down in the water column [6] — unlike squid, whose internal support is a flexible, feather-shaped gladius rather than a rigid, foam-like cuttlebone. Cuttlebone can withstand implosion to depths of 200–600 m (660–1,970 ft) [7], which is why cuttlefish are typically found on shallow continental shelves; after death, the buoyant cuttlebone washes ashore.



Fig 2: **Image of Cuttlefish Bones**

Beyond its natural role, cuttlebone has a long history of practical use: goldsmiths and jewelers have used its brittle, carvable, heat-resistant structure to mold gold and silver ornaments, and powdered cuttlebone has served as a jewelry polish, a toothpaste ingredient, and an antacid or absorbent, as well as an artistic medium in the 19th and 20th centuries. Today it is most widely used as a calcium supplement for caged birds, chinchillas, hermit crabs, reptiles, shrimp, and snails, though it is not regarded as a nutrient source for humans [8].

Under compressive stress, cuttlebone fails in three stages — crack formation along the wavy, corrugated vertical walls, crack propagation, and densification as the walls compact — with the wall waviness balancing stiffness against brittleness and raising the energy needed for failure [5, 9]. Because the septum connecting chambers is stronger than the vertical walls (a “plywood” structure), horizontal chamber layers fail one at a time rather than all at once, further increasing the structure's overall energy absorption [5, 10].

Calcium Fortification from Cuttlefish Bone:

Calcium is the most abundant mineral in humans and animals, with about 99% stored in bones and teeth for structural strength; it also supports muscle contraction, nerve signaling, blood clotting, and enzymatic reactions, and imbalance is linked to osteoporosis and neuromuscular disorders [11]. Because common dietary calcium sources such as milk, cereal, and tofu contain phytic and oxalic acids that interfere with absorption, supplements are instead drawn from calcium carbonate ore, animal bone, and marine or crustacean shells — among which cuttlebone stands out as a valuable calcium-rich resource [12].

Cuttlebone's aragonite structure and organic matrix of β-chitin and proteins are accompanied by trace minerals — phosphorus, magnesium, sodium, potassium, iron, zinc, silicon, and copper — that support enzyme activity in bone metabolism, although only limited in vivo and in vitro work has explored its full potential [13, 14]. The crushed cuttlebone fragments can act as xenogeneic graft material that accelerates bone-defect healing by stimulating osteogenesis, and cuttlebone-derived hydroxyapatite has shown strong in vitro bioactivity and biocompatibility in osteoblast studies [13, 15]. However, converting cuttlebone calcium into a water-soluble form remains under-studied despite its potential value for food and pharmaceutical applications and for raising the economic value of seafood by-products.

Calcium carbonate, cuttlebone's primary constituent, is a widely used supplement, but its high lattice energy limits solubility and dispersion in water, restricting its use in food and beverage fortification [16, 17]. Modifying its structure could broaden its industrial applications, which is why the present study explores converting cuttlebone-derived calcium carbonate into water-soluble calcium using weak acids [18].

Hydroxyapatite as a Source of Calcium and Phosphorus:

Cuttlefish bone is an alternative source for producing hydroxyapatite (HAp), used in bone grafts and tissue engineering owing to its non-toxicity and

structural similarity to human bone. The synthesis reacts the calcium carbonate in cuttlefish bone with a phosphate source; the bone's natural porous structure is retained in the resulting HAp, which is applied in bone grafting and dental procedures [9, 19, 20]. Stoichiometric hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is one specific composition among a broader family of calcium phosphate salts with significant medicinal value [21].

HAp is typically synthesized by a wet chemical route: mixing precursor solutions, aging the resulting residue at room temperature, filtering and drying, and calcining at high temperature. This long-established method yields nano- or micro-scale plate-like or spherical HAp particles with high yield and low aspect ratio, among several other synthesis routes developed since [22].

Calcium fortification in goat diets is delivered through gels, powders, and a balanced calcium-phosphorus supply in feed and water, often combined with Vitamin D3 to improve absorption. Calcium supports bone and joint development, muscle contraction, nerve impulses, milk production, pregnancy, blood clotting, cardiac regulation, and enzyme activation — and adequate supply helps prevent hypocalcaemia (milk fever) in lactating and pregnant does [23].

Calcium Requirements in Goats:

Oral gels*:* fast-acting, bioavailable calcium often fortified with Vitamin D3, phosphorus, and magnesium, useful around parturition and early lactation. *Powders:* added directly to feed. *Injections:* calcium borogluconate, administered by a veterinarian for severe hypocalcaemia.

Calcium is a critical macromineral for small ruminants, essential for skeletal development, nerve conduction, muscle contraction, blood coagulation, and milk production. Goat diets should maintain a Ca:P ratio near 2:1 and supply adequate calcium across growth, pregnancy, and lactation; deficiencies can reduce bone strength and productivity and cause metabolic disorders such as milk fever. While regional feedstuffs and mineral mixes (limestone, dicalcium phosphate) are common, low-cost, sustainable alternatives remain desirable for smallholder and coastal communities [22].

Cuttlebone is an underused, calcium-rich marine by-product already applied as a calcium source in food processing and for captive animals such as birds and turtles [9, 17, 24]. Beyond raw $CaCO_3$, it can be converted into hydroxyapatite or other calcium salts through calcination, precipitation, hydrothermal, or wet-chemical routes, which can improve stability, reduce dust, and alter solubility and bioavailability relative to raw powdered $CaCO_3$ [22]. This project therefore explores (a) preparing feed-grade cuttlebone calcium (powdered cuttlebone converted to a stabilized calcium salt/HA), (b) analytical characterization (Ca, P, trace elements, particle size, solubility), and (c) a small-scale feeding trial or in vitro digestibility assay in goats, to determine whether cuttlebone-based fortification meets nutritional targets without adverse effects — potentially yielding a low-cost, circular feed supplement for coastal and fisheries-adjacent communities.

Conventional drug delivery (oral, inhaled, or transdermal) is difficult to dose precisely and carries a higher risk of overdose since medication is often self-administered — acetaminophen overdose, for example, is a leading cause of liver transplantation in the United States. This has driven demand for controlled delivery systems that release drugs in a regulated manner at the intended target site. Hydroxyapatite is well suited to this role: it is a naturally occurring, low-solubility, highly porous calcium phosphate mineral that can adsorb large amounts of drug through electrostatic and hydrophobic interactions, and increasing its proportion in a delivery system prolongs drug release by providing more active sites. Alginate, a biodegradable, biocompatible seaweed-derived biopolymer with strong mucoadhesive properties, extends contact time with the intestinal lining and further slows release [25]. In this study, an alginate–hydroxyapatite composite was used as a carrier to improve feed conversion and nutrient intake in goats [9].

Ruminant Nutrition:

Goats belong to the ruminants — along with cattle, sheep, and deer — whose four-chambered stomach (rumen, reticulum, omasum, and abomasum) contrasts with the single-chambered stomach of monogastric animals such as humans, dogs, and cats. In ruminants, microbial fermentation in the rumen and reticulum precedes acid and enzymatic digestion, enabling efficient use of fibrous plant material — grass, hay, leaves, browse — that monogastric animals cannot easily digest [26].

Products of microbial breakdown are absorbed directly through the rumen wall, supplying much of the animal's energy; remaining material moves to the omasum, where larger particles are retained and water is absorbed, before passing to the abomasum and small intestine for further digestion. Rumen microorganisms also synthesize essential vitamins and convert recycled nitrogen into microbial protein — valuable on low-protein diets — and neutralize anti-nutritional compounds such as tannins, allowing goats to browse tannin-rich plants. Adequate dietary fibre is needed to sustain this activity; excessive grain intake can instead cause rumen acidosis, a sharp drop in rumen pH that impairs feed intake and digestion [27].

Calcium Homeostasis and Milk Fever:

When blood calcium falls, the body responds by increasing intestinal absorption, reducing gastrointestinal and renal calcium loss, and mobilizing calcium from bone. This regulation — calcium homeostasis — differs by species: sheep rely mainly on mobilizing skeletal calcium, while goats favor improving

intestinal absorption efficiency [23, 28].

Because milk carries substantial calcium to offspring, high-producing dairy ruminants face sharply increased calcium demand at the onset of lactation, making the final weeks before parturition critical for the animal to prepare [29]. When the body cannot mobilize enough bone calcium to offset dietary shortfalls — often worsened by reduced feed intake around calving — the result is milk fever (hypocalcaemia), frequently accompanied by hypophosphatemia and hypomagnesemia. Clinical signs (weakness, reduced alertness, coma, sternal recumbency) typically appear within 48 hours of birth. The condition is uncommon in meat-producing sheep but can affect ewes carrying twins or triplets before parturition, when fetal skeletal mineralization peaks; in high-producing dairy sheep and goats, it resembles cattle milk fever but usually appears one to three weeks postpartum, with any pre-parturition symptoms typically milder [23].

Calcium as a Nutritional Reserve:

Calcium is the chief structural component of the skeleton and teeth, accounting for 98–99% of total body calcium and serving as a reserve that is mobilized from bone to keep blood calcium constant during dietary shortfalls [12, 23]. It also acts as an intracellular messenger for nerve transmission, muscle contraction, vascular tone, and hormone release, and is closely linked to vitamin K. Of dietary calcium, 30–80% is absorbed — about 90% of it in the small intestine — through both a non-saturable diffusion process and a saturable, demand-driven active process [23, 29]. Calcium is lost mainly through faeces (85–89%) and urine (2–5%), with requirements rising sharply during pregnancy and lactation as it is excreted in milk [29]; deficiency causes rickets in young animals, osteomalacia in adults, and milk fever in lactating ruminants shortly after calving.

Young female goats bred too early may develop lameness or bowed legs, and a related hypercalcemic disorder has occasionally been reported in goats as in dairy cattle, though far less commonly [30, 31]. This study accordingly examines hydroxyapatite synthesized from cuttlefish bone as a sustainable calcium source for livestock nutrition.

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