Key Insights, Tools, and Future Prospects on Oyster Shell End-of-Life: A Critical Analysis of Sustainable Solutions

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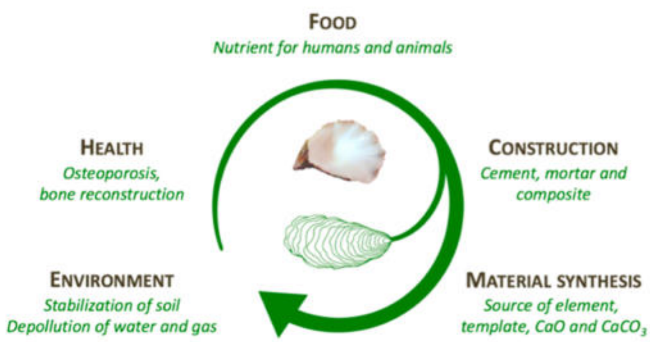
ABSTRACT: Oyster farming represents one of the most developed aquaculture activities, producing delicacies unfortunately related to a direct accumulation of waste shells. Facing what is becoming an environmental issue, chemists are currently developing solutions to add value to this wild source of raw material in line with the principles of sustainable chemistry. An argumentative overview of this question is proposed here with a focus on recent data. Starting with a presentation of the environmental impact of oyster farming, existing and promising applications are then classified according to the type of raw materials derived from the oyster shell, namely the natural oyster shell (NOS), the calcined natural oyster shell (CNOS), and biomolecules of the organic matrix extracted from the oyster shell. Their relevance is discussed in regard to their scalability, originality, and sustainability. This review constitutes the first critical compilation on oyster shell applications, with the aim to provide essential elements to better comprehend the recycling of waste oyster shells.



1. INTRODUCTION

Whether for consumption or the generation of pearls, the vast majority of oyster production comes from oyster farming. In both cases, the proportion of material that is actually valued in the form of foodstuff or pearls represents a negligible part, less than 10% of the whole oyster mass. According to the FAO, in 2015, the world oyster production totaled nearly 5.2 million metric tons live weight, representing approximately 3.9 million metric tons of shells[1] leading to a real environmental issue. For example, in South Korea the annual waste is estimated to be approximately 300 000 tons of oyster shells covering 4100 ha of coastline each year. For Taiwan, this figure is estimated at 25 000 tons.[2] Without treatment, piles of oyster shells produce sanitation problems and foul-smelling noxious odors.[3] Being nonbiodegradable, the oyster shells modify local soils, natural waters, and marine ecosystems, especially if their disposal is not controlled.[4] The answer to this ecological challenge should be strongly correlated with the value of oyster shell as raw material, especially in regions of the world where oyster farming constitutes a large part of the local economy.

Oyster shell can be used in well-known applications, especially in the fields of water treatment, CO_2 capture, building materials, reef restoration, agricultural supplements, high-tech polymer manufacturing, catalysis, and biodiesel production.[5] Unlike other reviews on the recycling of aquaculture coproducts,[6,7] this review provides a large and critical description of the different uses of the oyster shell; it also questioned the relevance of the different applications and the challenges that face up their recycling.

2. APPLICATIONS OF OYSTER SHELLS

The oyster shell is a structured biogenic composite of mainly anhydrous calcium carbonate (>95 wt %) in association with an organic matrix (up to 5 wt %). In light of the phylogeny (Figure 1), it appears that oysters arise from two distinct orders whose shell composition and structural characteristics are very different (Supporting Information (SI) Figure S1 and Table S1). In some applications, this feature is essential.

Since oysters are filter-feeders, the biochemical composition of the shell is highly reliant on the breeding environment and bioaccumulation processes, especially toward heavy metals.[8−10] This point is important to keep in mind from the perspective of health applications, such as the trending use as a source of natural calcium in nutritional supplements for adults and children.[11,12]

Natural oyster shell (NOS), calcined natural oyster shell (CNOS), and biomolecules of the organic matrix extracted from the oyster shell constitute the raw materials for any potential application. The following subsections provide a

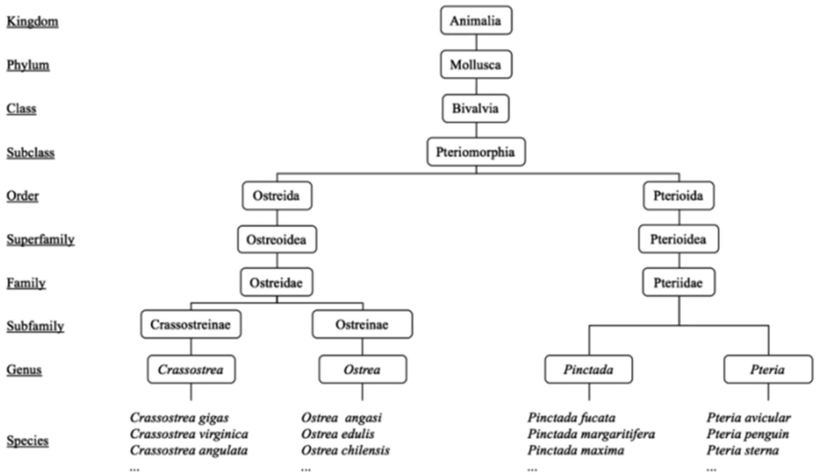


Figure 1. Phylogeny of oyster species.

critical description of valuable routes including processing methods when necessary.

2.1. Potential Applications of NOS. Before any treatment, shells are generally decontaminated of organic substances and salts by radiation, thermal treatment, brushing or oxidation with soaking solutions (NaOH, NaOCl, H_2O_2, . . .). In most cases, shells are roughly crushed to reduce storage and transport volumes. Milling gives a uniform and easy-to-use powder, allowing to increase the roughness and the available specific surface area for chemical and physical transformations.[13] The mother of pearl (the inner layer of Pteriidae shells) is highly prized especially for body art and fashion purposes. In this case, the animal is specifically farmed for its shell and pearl, it only requires a surface treatment followed by shaping.

2.1.1. Food and Cosmetic Industries. NOS powder is a relevant source of calcium, offering real value for food, nutraceutical, or cosmetic purposes. Traditional Chinese medicine praises the health benefits of what is commonly known as *Concha ostrea* in Latin (Mu-li in Mandarin). The recent edition of the Chinese Pharmacopeia lists NOS powders of different species; *C. gigas* is the major source of this material, and $CaCO_3$ the major effective constituent.[14,15] Another review summarizing cosmetics in Roman antiquity referred to oyster shell powder as an ingredient for smoothing skin due to the potential local burning effect of lime.[16]

NOS powder is a potential natural and organic alternative for synthetic phosphate in pork-based products and has attracted substantial interest.[17,18] With a clean label, this calcium source acts as a real additive for food and health products[19,20] or animal feeding.[21−24] Different oyster shell powders are commercially available for their benefit effects against bone-related deficiencies. For the development of such products, the granulometry of the oyster shell powder and its association with other elements have a direct influence on the bioavailability and solubility of calcium as was observed on ovariectomized and albino rats by oral administration.[25,26] The oral uptake of Mg-, Fe-, Cu-, and Zn-rich mollusk shell powder carries health benefits, however, the high bioaccumulation ability of oyster shell, higher than that of eggshells, suggests that traces of toxic heavy metals may often be present or can lead to adverse effect by oral or dermal route.[27] Therefore, caution and safety-oriented approaches are recommended for food, animal feeding or other human uses. To protect humans from exposure and consumption, different organizations have specified allowable levels of heavy metals. An evaluation of NOS powders of *P. margaritifera* from French Polynesia revealed that calcium constitutes 40% of the total weight of the shell. If we consider a human intake of 2.5 g per day, the levels of hazardous metals such as Cd, As, Hg, and Pb are lower than the maximum levels authorized by food committees.[28]

2.1.2. Medical Uses. Nacre produced by the *Pinctada* genus, have been considered as a prime candidate for bone tissue bioengineering applications, as this biomaterial is compatible with bone tissues and has high mechanical properties.[29] Based on in vitro and in vivo studies, nacre is described as a natural, biocompatible, and biodegradable biomaterial with osteoinductive, osteointegrative, and osteoconductive properties and is therefore extensively studied for its bone substitution capacity. One of the first historical instances of the use of nacre in bone tissue bioengineering was observed in 1931 in the lower jawbone of a Mayan individual (Figure 2).[30]

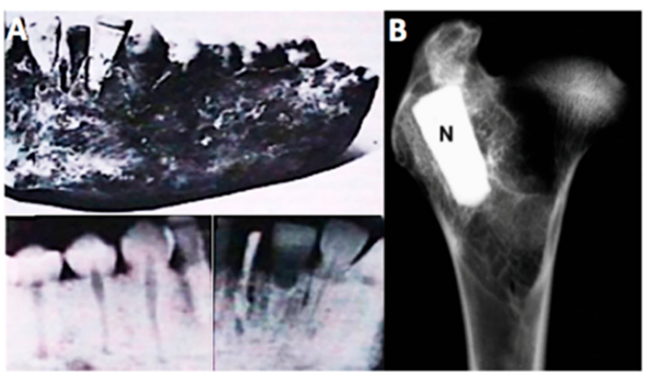


Figure 2. Examples of nacre bone substitute. (A) Incisors of the lower jawbone replaced by nacre.[30] (B) Solid nacre (N) implanted in the femur of sheep after 10 months.[31]

Later, major breakthroughs have been made by the group of Prof. Lopez in the field of bone graft substitution by nacre of *Pinctada* spp. shells, as highlighted by Westbroek and Marin.[32] This work includes in vivo and in vitro studies with various nacre preparations, such as nacre powder mixed with blood, nacre chips, and nacre prostheses;[29] alginate hydrogels including nacre powder have also been investigated.[33] In contrast, only one study has focused on the osteogenic capacity of Ostreida shells.[34] This study is attractive since it shows the potential use of NOS for bone tissue bioengineering, not only restricted to nacre from *Pinctada* shells. With the advance of material science, this field of research is in constant progress. The development of functionalized and specific composites with various shapes constitutes one of the main challenges. Promising perspectives were recently obtained with the design of hydroxyapatite nanoparticles coated on substrates of nacre from *P. maxima* shell,[35] with composite of calcium sulfate and oyster shell[36] or with scaffold composites of dried oyster shell powder and poly(L-lactide).[37] Moreover, the use of innovative technologies for the development and production of personalized bone-like implant, with controlled porosity and shape starts to be used in research laboratories. A good example is the use of fused deposition modeling technology recently applied to design scaffolds of NOS powder dispersed in a polycaprolactone matrix with a positive osteogenic activity when tested in vitro on osteoblast-like cells.[38]

By combining new technologies with material science and biology, these studies show the outstanding properties of NOS for use in bone grafting. It would be interesting to evaluate the osteogenic performances of NOS compared to others more accessible and less expensive natural composites. Other potential medical uses stay underexplored despite the presence of few preliminary studies in the literature. For example, the stimulation of skin fibroblasts by nacre powder implanted between dermis and hypodermis in rats was observed by Lopez et al. (2000),[39] as well as the anticarcinogenic potential of *C. gigas* shell powder when administered to mice with induced tongue tumors.[40]

2.1.3. Pollutant Remediation. Soil Quality Improvement. The pKb of hydrogen carbonate (6.6) has led to consider NOS as an efficient base to neutralize the acidity of soil in different environments, natural or polluted.[41] Treatment of acidic soil with pulverized NOS causes neutralization but also a beneficial increase in Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} and the stabilization of heavy metals that are less exchangeable upon lixiviation (SI Table S2). Surface adsorption is a possible explanation, in addition to the formation of poorly soluble metal hydroxides or metal carbonates. The specific sorption of metal cations by the $CaCO_3$ mineral phases distributed in oyster shells (aragonite and calcite) plays an important role in surface adsorption.[42] Such decontamination or stabilization is also dependent on the pH, aerobic conditions, ion composition, and counterion but in general, the efficiency of NOS to stabilize soil has been established. Some studies mentioned a putative role of chitin occurring in the organic matrix and the possible coordination of heavy metal cations. Although not enriched in carbon, NOS powder can be a source of carbon for plant growth; the presence of residual NaCl is apparently not injurious in most cases.[43] Combining NOS and biochar or biopolymer improves soil fertility, carbon sequestration, and worm activity.[44,45] Given the overuse of fertilizers, especially in agriculture, and the resulting deterioration in water quality, NOS powders were found to be effective in phosphorus removal and are applicable as a beneficial media in artificial wetland systems.[46,47]

Water Treatment. Living oysters are well-known for their capacity to reduce eutrophication in natural water,[48] as well as metals cations, plastic particles, and other chemicals in some cases.[49−52] Although, high efficiency is not always achieved, the list of pollutants that can be potentially removed by NOS is summarized in SI Table S3, including anions, cations, organics such as antibiotics,[53] neurotoxins,[54] and nitrogen.[55]

Two major phenomena can explain the ability of NOS to remove such pollutants: first, the ionic interaction between ions and the surface of the NOS; and second, the precipitation on the NOS surface of insoluble salts resulting from the presence of carbonate, calcium, and hydroxyl. Unfortunately, many experimental parameters are not systematically reported which limits comparability. The shell structure and its microstructures are parameters that can drive the ability of NOS to adsorb pollutants as it was shown for the different adsorption behaviors between the prismatic and nacreous layers.[56] The organic matrix may also participate in the complexation of cations and can explain why removal is more efficient with NOS than with calcined NOS.

Thanks to its porous structure and its buffering properties, NOS in collaboration with microorganisms is also relevant in eco-friendly remediation of wastewater achievable in packed-bed bioreactors.[57−65] In general oyster shells served a 3-fold purpose: as a biofilm carrier, a source of organic carbon, and as a basifying agent.[64,66,67] Research conducted in this field has also been developed at the pilot-plant scale using oyster shells mixed with inorganic minerals like zeolite for phosphorus and nitrogen removal[68] or for the growth of biofilms.[69]

NOS is efficient to remove a wide range of pollutants from wastewater at various processing scale, it would be interesting to evaluate its sorption capacity toward highly hazardous pollutants. NOS could also be a relevant fixing support in aquaculture as it is the case for the development of *C. gigas* larvae in hatchery[70] or wastewater treatment.

Dechlorination of Waste. This is certainly not the most appealing route for recycling oyster shells, but surely a useful and simple application. When mixed with polyvinyl chloride (PVC), NOS neutralizes harmful HCl resulting from PVC incineration with an efficiency similar to commercially available calcium carbonate and with $CaCl_2$ as byproducts.[71,72]

2.1.4. Material Synthesis. Composites. Recent researches demonstrate that NOS can be used as filler in polymers such as polyethylene.[73] Although performances are limited, the thermal decomposition of NOS at high temperature generates CO_2 that is relevant for retarding the thermal decomposition of the polymer. Composites made of NOS and polyethylene, polypropylene, natural rubber, or asphalt present remarkable mechanical and thermal stability.[74−78] The granulometry of NOS powder and the mediation of interfacial weak interactions revealed to be crucial points for the development of such composites. These studies show that NOS is a cheap, natural, and easy to work substitute of common fillers in polymeric industry.

Foaming Agent. Due to the production of CO_2 resulting from the decomposition of calcite at $T > 550$ °C, NOS has been used as a foaming agent for the preparation of vitrocrystalline foam. The best results were obtained with 91% glass bottles and 9 wt % oyster foams fired at 900 °C, demonstrating characteristics and properties similar to (or better than) those of analogous commercial products such as glass and alumina foams.[79]

Templates in Material Science. In this field, the general approach is the replication of natural organs leading to materials biomimicking natural structures. Since it is easily removed by acidic treatment, NOS is an interesting option as sacrificial template for such morphological mimicry. Careful attention should be paid to the shell structure selected as the template and the targeted application. For example, the design of folded SiO_2 requires a shell substrate made of chalky and foliated structures only occurring in Ostreidae shells.[80] Another example is the pyrolysis of powdered NOS with layered structure mixed with soft pitch to prepare porous carbon anodes in lithium ion batteries.[81] However, materials are not performant enough to be an attractive way of recycling.

Support for Catalysts in Organic Chemistry. The use of NOS as support of catalysts is a growing field of research with high potential. Heterogeneous catalyst was formulated with powders of CuBr and NOS with higher efficacy than a mixture of CuBr and $CaCO_3$.[82] The authors hypothesized an important chelating role of chitin and proteins constituting the organic matrix of NOS for [Cu]-active species. The good chemical stability and reusability (at least eight times) of the [NOS–CuBr] composite are among the attractive points of this approach. Among other recent attractive data, NOS powder has been found to be useful as a support for MgO, Al_2O_3, $CaCO_3$, and zeolite (ZSM-5) to catalyze gas produced by the pyrolysis of waste tires.[83] Despite the novelty of the approach, the latter is limited by the necessity to avoid any contaminant from the shell that would disturb the catalytic activity.

Relevant Original Source of Calcium, Calcium Carbonate, and Sodium. The most general way of recycling seashell waste is the use as aggregates for the formulation of concrete that could easily be established in aquaculture where concrete is used as a growing support. The important points being the granulometry of NOS and other minerals entering in the formulation.[84,85] Despite the relative simplicity for the implementation of this type of material, their long-term durability is not well-known. Such applications are not innovative but still relevant for a large-scale recycling of NOS.

The use of NOS instead of ores as source of $CaCO_3$ can also be innovative for the production of advanced materials such as aragonite needles,[86] high-purity calcite submicrometern powder[87] and $CaSO_4{:}2H_2O$ powder or whiskers.[88] In this field the hydroxyapatite is the paramount example of a high-demanded Ca^{2+}-containing material (eq 1), and NOS was found useful for its synthesis with different morphologies and specific surface areas depending on the conditions of the hydrothermal process (Figure 3).[89,90]

$$10CaCO_3 + 6(NH_4)_2HPO_4 + 2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6(NH_4)_2CO_3 + 4H_2CO_3 \quad (1)$$

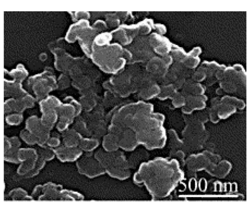


Figure 3. SEM image of hydroxyapatite produced by hydrothermal processing of NOS at 200 °C for 92 h.[89]

In an innovative approach, NOS was used for the preparation of 1D nanostructured single-crystalline $Na_2Ti_6O_{13}$ and $Na_2W_4O_{13}$ with lower processing temperature and higher yield than with chemical mixtures (Figure 4).[91]

2.2. Potential Applications of CNOS. Calcination of NOS leads to the so-called calcined natural oyster shell (CNOS), a potential multiuse raw material. This is usually performed on mixed batches of shells with unreliable traceability and poor consideration of the composition and structural differences among oyster species. This is a limit to the recycling of shells, especially when targeting specific synthesis of advanced materials. Calcination of NOS starts with water loss and decomposition of the organic matrix at temperatures of approximately 200–400 °C, leading to a weight loss of 2–4%.[92] In the case of aragonite-rich shells like *P. margaritifera*, a thermal structural phase transition from aragonite to calcite occurs between 280 and 500 °C.[93,94] At higher temperatures, the decomposition of calcite leads to the eco-valuable production of calcium oxide, which is concomitant with the release of carbon dioxide between 550 and 800 °C (weight loss of 40–45%) but calcite can still be present up to 900 °C (eq 2).[95]

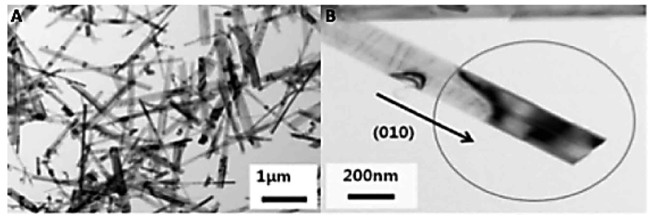


Figure 4. TEM images of $Na_2Ti_6O_{13}$ nanorods prepared with NOS.[91]

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \Delta H = 178 kJ/mol \quad (2)$$

In light of the energy required, thermal treatment of NOS should be considered only for attractive applications. An innovative microwave calcination treatment was recently applied to oyster shell powder with quasi-complete decomposition obtained at 900 W (2.45 GHz; 20 min).[96] Considering the time and energy required, microwave calcination is an attractive method. NOS powder can also be decomposed with high-voltage electric current under a reduced oxygen concentration at approximately 800 °C.[97,98] Known as active absorbable calcium (AACa) or oyster shell electrolysate (OSE), this powder is mainly composed of lamellar CaO structure.[97,99] However, the description of the preparation of AACa suffers from a lack of scientific criteria of repeatability.

2.2.1. Medical Uses. The research group of Fujita extensively studied the effect of preparations of CNOS in the prevention and treatment of calcium metabolism-related diseases. Their review on osteoporosis summarizes the contributions of AACa and active absorbable algal calcium (AAACa).[100] Compared to $CaCO_3$, AACa is described as a readily absorbable form of calcium,[98] favorable for the treatment of osteoporosis by oral route[101,102] as well as AAACa, which is a mixture of AACa with an extract of the seaweed *Cystophyllum fusiforme*.[103−105] AAACa was suggested to be the most efficient ingredient at preventing osteoporosis[106] with positive analgesic effect on joint pain.[107] More surprisingly, supplementation with AAACa has been reported to prevent light, sound, and emotional stress resulting from neuromuscular instability.[108] Among these various studies, no adverse effects have been observed.

This substantial work displays interesting effects of CNOS toward the prevention of osteoporosis. Combining CNOS with other active ingredients could be an innovative approach for the development of nutraceuticals as it was recently shown for the treatment of inflammatory bowel disease on mice by oral administration of zeolite-CNOS mixture.[109] The development of such products has to be evaluated in comparison with NOS-based products given the low sustainability of NOS calcination.

2.2.2. Pollutant Remediation. Soil Quality Improvement. Compared to NOS, CNOS is sometimes more effective for stabilization and pH neutralization of contaminated soils (SI Table S4).[41] Further comparative researches are needed to evaluate the relevance of CNOS compared to NOS.

Water Treatment. CNOS generally removes cationic pollutants more effectively than NOS as described for Cd(II) (SI Table S4).[110,111] The higher the temperature of calcination, the better is the efficiency of CNOS. This observation is directly related to the large increase in the specific surface area of the material upon calcination.[112] This phenomenon can also be explained by the formation of insoluble metal hydroxides by adsorption of the metal on the surface of CNOS. Unlike NOS, CNOS was applied to remove and recover other chemicals such as boron,[113] free fatty acids and iodine from the bleaching process of palm kernel oil,[114] and pathogen like *E. coli*.[115]

Gas Treatment. The basic character of CNOS is well-adapted to remove pollutants such as SO_2, SO_3, H_2S, and NO_x in dry or wet processes as well as CO_2 sequestration.[116−118] Obviously, this strategy is relevant only if the cyclability of the process allows higher CO_2 sequestration than CO_2 generation due to calcination.[119]

2.2.3. Material Synthesis. Standard Reagent. Different studies support that NOS-derived CaO powder can be used as a standard chemical reagent and can be classified in the reactive class R4.[120] Dissolution of CNOS leads to a $Ca(OH)_2$ solution/suspension that is useful for the preparation of hydroxyapatite,[121] unfired fly ash bricks,[122] mortar,[123] or nanomaterials like $Ca(OH)_2$ hydoxide nanoplates (Figure 5).[124] Hydroxyapatite can also be obtained by direct solvent-free ball-milling and calcination,[125,126] an interesting way to produce chemicals with higher added value than NOS.

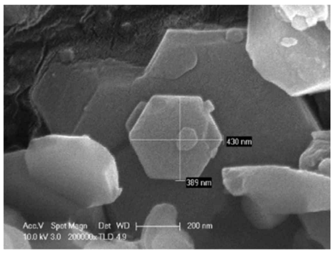


Figure 5. $Ca(OH)_2$ nanoplates prepared from CNOS according to Khan et al. (2018).[124]

In the field of nanotechnology, nanomaterials are easily accessible by reacting CNOS with $K(MnO_4)$ to form nanostructured Mn/Ca mixed-oxides decorated with Mn_3O_4 nanoparticles that have potentially high adsorption capacities for Pb(II) and Eu(III).[127]

Silicate nanofibers prepared hydrothermally with CNOS (Figure 6) are efficient porous absorbent of metal cations, such as Cu(II), Cr(VI),[128] and anion such as phosphates.[129] In the same application field, calcium silicate wollastonite and pseudowollastonite were obtained at 1100−1200 °C by mixing NOS and waste float glass from building demolition. This work represents an additional step toward the synthesis of advanced materials made from 100% waste.[130]

Catalyst and Support for Catalysts. CNOS is potentially attractive for catalysis or cocatalysis in processes that require basic media, a typical case being the transesterification of soybean oil.[131−135] Very recently, CNOS nanoparticles were employed as a catalyst for the preparation of 1,8-dioxo-octahydroxanthenes via the one-pot condensation of 5,5-dimethylcyclohexane-1,3-dione or dimedone with various aldehydes under solvent-free conditions.[136] Chemical stability and reusability of CNOS catalyst are among parameters to be investigated.

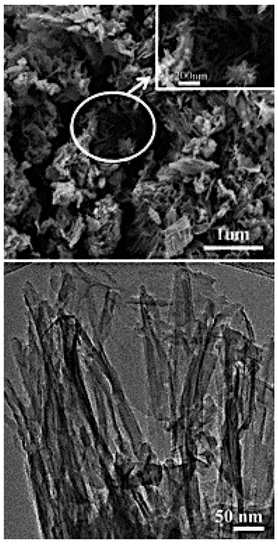


Figure 6. Calcium silicate prepared with CNOS. Reproduced with permission from Ref.128 Copyright 2015 The Physical Chemistry Chemical Physics Owner Societies.

Filler in the Synthesis of Polymer. Applications of CNOS in this area are limited, CNOS powder was reported as a filler in a polypropylene polymer.[137] Thermal and mechanical properties of this material are comparable to those obtained with commercial $CaCO_3$, thus questioning the relevance of NOS calcination.

2.2.4. Antibacterial Agent. The antibacterial activity of NOS calcined under ohmic heating was evaluated against *E. coli*, *Salmonella*, and *Listeria monocytogenes* inoculated on the surface of tomatoes.[138] CNOS had an efficient antimicrobial activity, higher than that of a preparation with 200 ppm chlorine and distilled water. The antibacterial activity is certainly attributed to the basicity of the preparation due to the hydration of CaO.[139] This emerging application shows that CNOS is a potential antibacterial agent of interest as a substitute of synthetic commercial chemicals or in the polymer industry where antibacterial polypropylene/CNOS composites were recently investigated.[140]

2.3. Potential Applications of Biomolecules Extracted from the Organic Matrix. Frequently described as a set of macro- and low-molecular-weight biomolecules, the organic matrix is actually an extremely complex material whose exact composition, assembly, and mechanism of action are not fully defined at the molecular level. The organic matrix can be classified into sets of biomolecules based on their extraction process and solubility, that is, the water-soluble matrix (WSM), ethanol-soluble matrix (ESM), acid-soluble matrix (ASM), acid-insoluble matrix (AIM), EDTA-soluble matrix (EDTASM), EDTA-insoluble matrix (EDTAIM), and fat-soluble matrix (FSM).

The nature of AIM (sometimes called conchiolin) has been shown to be proteinaceous and constitutes more than 90% of the organic matrix.[141] ASM and AIM can be obtained after dissolution with acids followed by several separation steps.[141,142] Calcium-chelating agents, such as EDTA, are also employed at neutral pH. A general protocol was proposed by the research group of Marin which was described to minimize the degradation of proteins and avoids the formation of aggregates.[143,144] In the nacre of *P. maxima* shell, the extraction yields of ASM and AIM are 1.20 and 0.17 wt %, respectively.[145] WSM extraction from nacre was originally applied and patented by the research group of Prof. Lopez. The extraction method does not allow recovery of molecules strongly bound to the mineral phase but is directly compatible with biological purposes such as in vitro and in vivo trials. The achievable extraction yield varies from approximately 0.2 to 5 wt %.[146,147] A method was recently developed to extract and fractionate ESM from the nacre of *P. margaritifera*;[148] to the best of our knowledge, the molecular characterization of ESM has not yet been investigated. In addition, extraction yield has not been reported.

Among these extracts, WSM is the most studied, but has almost exclusively been investigated for its osteogenic activity. The different potential applications of these extracts are summarized in the following subsections.

2.3.1. Water-Soluble Matrix (WSM). Bone Tissue Bioengineering. The osteogenic activity of WSM originally extracted from the powdered nacre of *P. maxima* shell (50−150 μm) was highlighted by the research group of Prof. Lopez.[149] WSM was revealed to be osteoinductive, enhancing in vitro bone cells differentiation and cellular osteogenic markers. Osteogenic activity studies of WSM were extended to *P. fucata* and *P. martensii* nacre. As an example, this academic research has been developed in the form of cosmetic and nutraceutical ingredients by the French company StanSea. To the best of our knowledge, no in vivo or in vitro studies have been published on the osteogenic activity of WSM extracted from *Pteria* and Ostreida oyster shells, whereas the presence of WSM in the shell of *C. gigas* is well-known.[150] Only a few studies have described the relationship between WSM proteins of Ostreida shells and osteogenic activity.[151,152] To confirm this assumption, in vitro trials are further required.

Other Biological Activities: Antioxidant Activity, Anti-Inflammatory Activity, and Dermal Fibroblast Regulation. The antioxidant activity of WSM extracted from the nacreous layer of *P. fucata* shell was investigated in terms of its capacity to scavenge free radicals (DPPH and ABTS tests), to inhibit lipid peroxidation and to reduce damage in human keratinocyte cells after inducing oxidative stress.[153] The authors showed that WSM can scavenge free radicals in a dose-dependent manner, reducing the effect of oxidative stress in human keratinocytes.

WSM was also tested in vitro for its anti-inflammatory and antioxidant activities on mouse macrophages.[154] WSM suppresses or decreases pro-inflammatory factors linked to pro-inflammatory cytokine inhibition and exhibits antioxidant activity. Unfortunately, information on the oyster species used in this study was not presented.

For a different purpose, Latire et al. (2017) described the fact that WSM extracted from *C. gigas* shell can favor the catabolic activities of human dermal fibroblasts in vitro.[150]

In comparison with the numerous osteo-benefits attributed to WSM, these are the only examples found in the literature highlighting other biological properties, and therefore the field is still highly open.

2.3.2. Ethanol-Soluble Matrix (ESM). Brion et al. (2015) originally described the osteogenic effect of ESM from the nacre of *P. margaritifera*.[155,156] This topic was further investigated in vitro by the stimulation of mouse preosteoblasts and human osteoarthritis osteoblasts with ionic fractions of ESM.[148] This study reveals clues about the cationic nature of the osteogenic compounds found in the nacre of oyster shells. Comparative osteogenic and scalability studies between ESM and WSM are required knowing that the process by which ESM is obtain does not require a freeze-drying step as it is the case for WSM extraction.

2.3.3. Acid-Soluble Matrix (ASM). Prevention of Cognitive Diseases. Recently, ASM extracted from the nacreous layer of *P. fucata* shells was tested in vivo against scopolamine-induced memory impairment in Wistar rats and ICR mice.[157] In both cases, ASM improved memory and cognitive impairments, suggesting that ASM can affect brain function by protecting against the dysfunction of glutamate neurotransmission. This mechanism was supported by the examination of the known genes associated with memory.

Free Radical Scavenging. A purple organic substance precipitated from a solution of ASM was capable of scavenging hydroxyl and superoxide radicals.[158] With an extraction rate of approximately 2.49 wt %, this extract could be of great commercial interest, especially for food, nutraceutical, or cosmetic products. Unfortunately, the article lacks sufficient experimental details to allow easy reproduction of the protocol.

Dermal Fibroblast Regulation. Latire et al. (2017) recently described the regulatory activities of ASM on the metabolism of dermal fibroblasts in vitro.[150] This pioneer work was performed with ASM obtained from the shell of *C. gigas*.

Material Synthesis. Adding supersaturated $CaCO_3$ solution to ASM extracted from the nacreous layer of *P. margaritifera* shell produces nanostructured $CaCO_3$ crystals whose morphology depends on the concentration of ASM.[159] A protein isolated from the ASM of the nacre from *P. fucata* shell was employed to induce the formation of aragonite and calcite crystals.[160] Such innovative results open new pathways for the synthesis of inorganic phases.

2.3.4. Acid-Insoluble Matrix (AIM). Natural Multifunctional Biopolymer. Chitin (poly 2-acetamido-2-deoxy-β-D-glucose) is a nontoxic, biodegradable, and biocompatible biopolymer of considerable interest for the pharmaceutical, cosmetic, biochemical, agricultural, and food industries. This biopolymer was identified for the first time in the AIM of the prismatic layer of *P. fucata*.[161] Recently, extraction of chitin was reported from undefined raw oyster shell species,[162] but the reported content of chitin extracted from the shell (69 wt %) is inconsistent with all other reported mass fractions of the organic matrix in the oyster shell.

Material Synthesis. In the design field of crystal growth, a promising application describes the preparation of macro-mesoporous TiO_2.[163] TiO_2 nanoparticles were grown onto AIM macrotemplate by sol−gel. The resulting anatase showed interesting photocatalytic activity, especially for samples calcined at 450 °C. However, the chemistry by which AIM and TiO_2 nanoparticles interact is not described. This study shows the prime importance of the shell structure for such material synthesis.

2.3.5. EDTA-Soluble Matrix (EDTASM). The only application found in the literature regarding the use of EDTASM concerns material synthesis. Calcite and aragonite crystals were

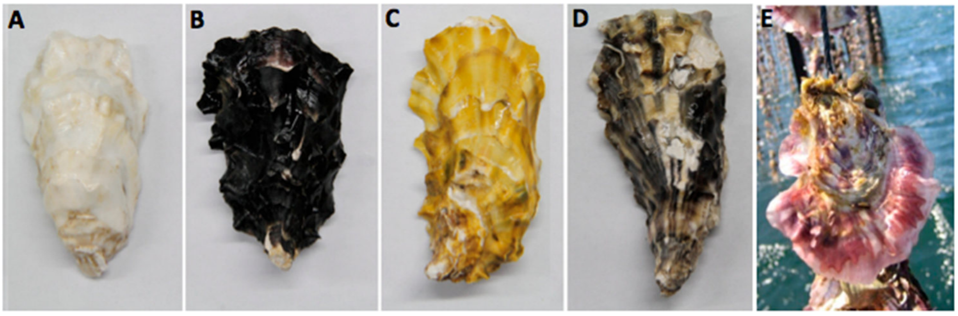


Figure 7. *C. gigas* oyster shells with six coloration types. (A) Whole white shell, (B) whole black shell, (C) whole golden shell, (D) partially colored shell.[172] (E) Pink oyster from the French oyster farming Tarbouriech (Thau, France).[173]

selectively prepared with the help of EDTASM proteins extracted from specific microstructures of *C. gigas* shells.[164,165]

2.3.6. EDTA-Insoluble Matrix (EDTAIM). A single article relates the use of the proteinaceous fraction of EDTAIM to induce aragonite crystals formation in saturated $CaCO_3$ solution with the addition of Mg^{2+}.[166] It is important to note that the aragonite crystals do not grow either without Mg^{2+} or with individual components of the fraction.

2.3.7. Fat-Soluble Matrix (FSM). Perhaps more unexpected, lipids are part of the shell organic matrix. The research group of Prof. Lopez highlighted the fact that FSM extracted by maceration of nacre with a mixture of methanol and chloroform can promote the restoration of the stratum corneum in vitro.[167]

2.3.8. Shell color related compounds. A potential application is never mentioned in reviews on the topic: the use of pigments and dyes extracted from the oyster shell. Shell color generally varies from dark-red to brown, and sometimes golden or even pink (Figure 7). In the current industrial context, synthetic pigments and dyes tend to be substituted by natural equivalents, especially in health products. One key challenge to be resolved lies in the identification of compounds at the origin of shell coloration and thus their selective extraction. The presence of melanin extracted in black *C. gigas* shell is a hypothesis but has not yet been convincingly established.[168] To date, no biomolecules have been associated with shell coloration other than black excepted for the presence of fluorescent porphyrins in the shells of *Pinctada* and *Pteria* genius.[169−171] This innovative recycling of oyster shell is still at the level of fundamental research and lacks of substantial and exhaustive works.

3. CRITICAL ANALYSIS

The economic viability of any recycling process depends on two essential parameters: the cost and the logistic to collect the shell on one hand, and the added-value of the product resulting from the recycling on the other hand. The generation of pollutants, emissions, or new waste must be minimized in an environmentally friendly philosophy; however, this might be acceptable if the added value of the final product can cover the expense of the treatment in eco-friendly conditions.

So far, oyster shells collection remains to be organized since it is actually considered as a diffuse pollution (consumers, factories, and farms). Recently, de Alvarenga et al. (2012) examined the LCA of oyster shell waste according two scenarios: (i) the direct deposit of shells in a landfill or (ii) the implementation of a simple process to produce CNOS powder (<20 μm).[174] They concluded in favor of the chalk production process. Although this option is strongly dependent on the distance between the source point and the shell-processing facility. Figure 8 gives an overview of possible application fields for the recycling of waste oyster shells.

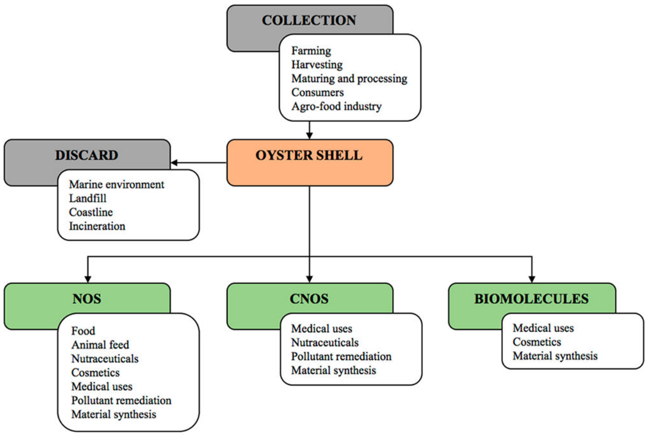


Figure 8. Application fields of waste oyster shell described in this review.

As raw material, NOS is useful for basic applications requiring simple and low-cost processing technologies at large-scale such as animal feeding (SI Table S5).

In economic terms, these applications do not bring high added-value but they allow the distribution of large quantities of NOS with adapted performances. For the other highly documented applications of water and soils depollution, the use of NOS is performant and cheap, but probably requires standardization of the manufactured product. It also raises the question of the elimination of the resulting contaminated NOS. An alternative remaining to be explored would be to consider the presence of metals at the surface of NOS as a possible catalyst. This would be similar to what has been successfully developed by the team of C. Grison using metal-hyperaccumulating plants to produce metal oxide catalyst.[175]

The use of NOS in building materials or as filler in composites represents an interesting option with more added-value but probably requires here again a standardization of materials. Besides, the durability of these materials remains limited, still relatively unknown,[84] not fully studied, and hardly documented.

Other applications with higher economic potential concern NOS and CNOS in material and health fields. NOS as a source of calcium in food requires simple treatments without altering its quality, in line with consumer's expectations. The major limit lies in human safety directly related to heavy metals and hazardous chemicals content as a consequence of the possible bioaccumulation of toxins in the shell. As an excipient or source of calcium in pharmaceutical products, NOS has to be declared and requires to be produced following GMP guidelines. Besides, the real economic advantage of NOS compared to other $CaCO_3$ sources is not always obvious. The answer may probably be driven by a significant shift in mind-sets and ways of working. This is actually the case in the cosmetic industry, where the naturalness of ingredients is highly marketed. As a cosmetic ingredient, NOS powder has a real interest, especially for its soft abrasive properties (skin soft-peeler), making it a potential substitute for plastic microbeads used in cosmetics. This expanding market meets a growing demand for natural, safe, and effective ingredients. This may be reinforced if further research demonstrates additional biological activities of NOS, especially of the organic matrix.

Among the applications with high economic value, the use of NOS in bone grafting seems to be a promising route but requires deeper knowledge about long-term biocompatibility and stability.

Concerning materials chemistry, NOS is an interesting template of advanced material or support for catalysts as evidenced by the increasing number of publications on this subject. However, the scalability and the repeatability of these applications remains linked to the collection, selection and standardization of the shell.

The unsustainability of NOS calcination in oven questions the relevance of CNOS, especially since these applications are frequently similar to those with NOS. Few applications reported better performances of CNOS compared to NOS but do not seem high enough to justify the calcination cost and the carbon dioxide emission. Thus, calcination in oven has to be considered only for applications where the required performance level is not achievable with NOS. In this instance, the development of sustainable calcination processes is needed such as fast microwave calcination,[96] or solar oven combined with carbon dioxide sequestration.

Biomolecules of the organic matrix (SI Table S6) are perhaps the best candidates for applications with high value, being entirely competitive with chemical sources of calcium carbonate. The high performance of these biomolecules compensate for the low scalability of the extraction process. WSM as a cosmetic and nutraceutical ingredient commercialized by StanSea is a good example. This research area is still highly open both for the identification of new biological activities for health applications and for the synthesis of innovative advanced materials. The future development of these applications depends on the progress made in the characterization of these extracts, in particular their composition and mechanisms of action. The difficulty relies on low yields and does not solve the problem of recycling calcium carbonate wastes, which should be handled together.

4. PERSPECTIVES AND OUTLOOK

The globalization of oyster farming generates short-term profits for local economic actors, but the massive production of shells starts to raise ecological questions. In this context, several studies disclose promising recycling applications from low to high value. The economics of recycling is dominated by the balance between the cost of collection/decontamination/processing and the added value of the product and its use. This can change due to the great consideration of environmental issues by consumers and their demand for a natural product. From depollution of soil and water to bone tissue reconstruction and production of nanomaterials, oyster shell has plenty to offer for chemists. To effectively treat the recycling and recovery of this byproduct, diverse issues need to be addressed, especially those related to the variability of composition and microstructures of the shell. Some other aspects still need to be better explored, such as parts of the shell, including pigments and the organic matrix, that still lack detailed characterization but can lead to new valuations.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b03736.

Structure of oyster shells, soil and water remediation, and comparative analysis of applications (PDF)

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Notes

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