Valorization of fish and mariculture waste materials

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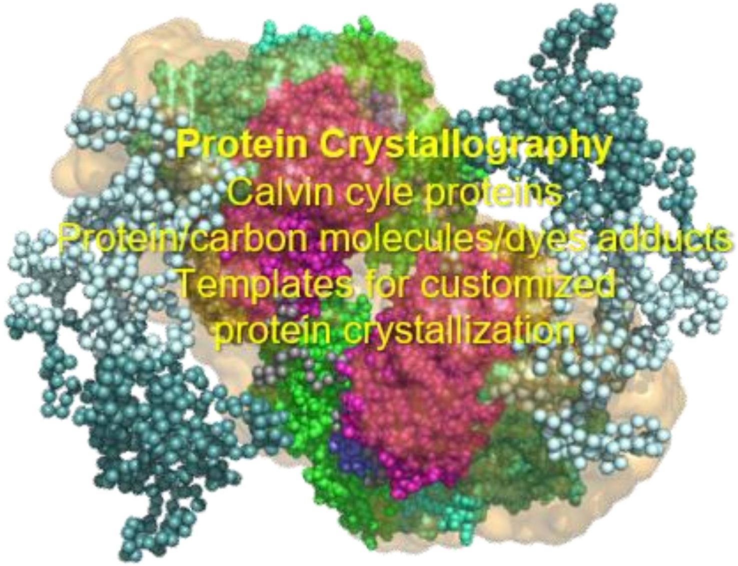
Biocrystallography and Biomineralization . . . @UniBo



- Giuseppe Falini - Simona Fermani -

Don’t waste seafood waste

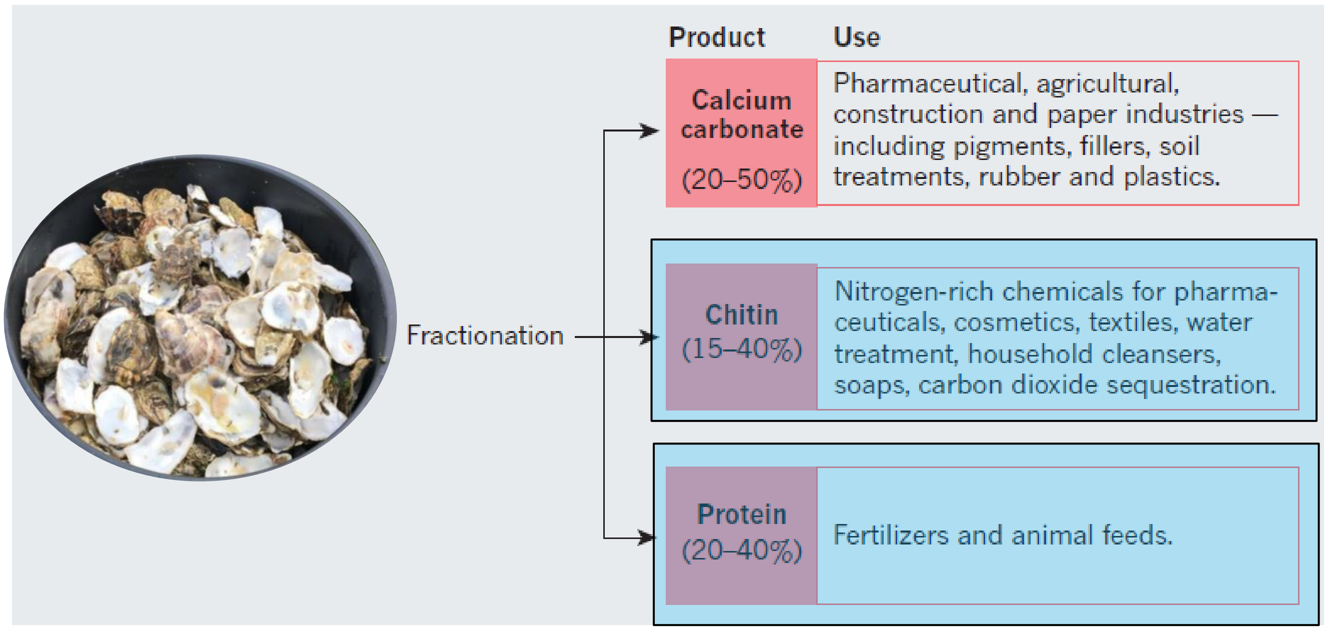
Turning cast-off shells into chemicals would benefit economies and the environment

Every year, some 6 million to 8 million tonnes of seafood waste are produced globally.

Whereas 75% of the weight of a tuna fish can be extracted as fillets, meat accounts for only around 40% of a crab’s mass and even less for mussels (about 30%).

In developing countries, waste shells are often just dumped in landfill or the sea. In developed countries, disposal can be costly — up to US$150 per tonne in Australia, for example. Yet shells harbour useful chemicals — protein, calcium carbonate and chitin.

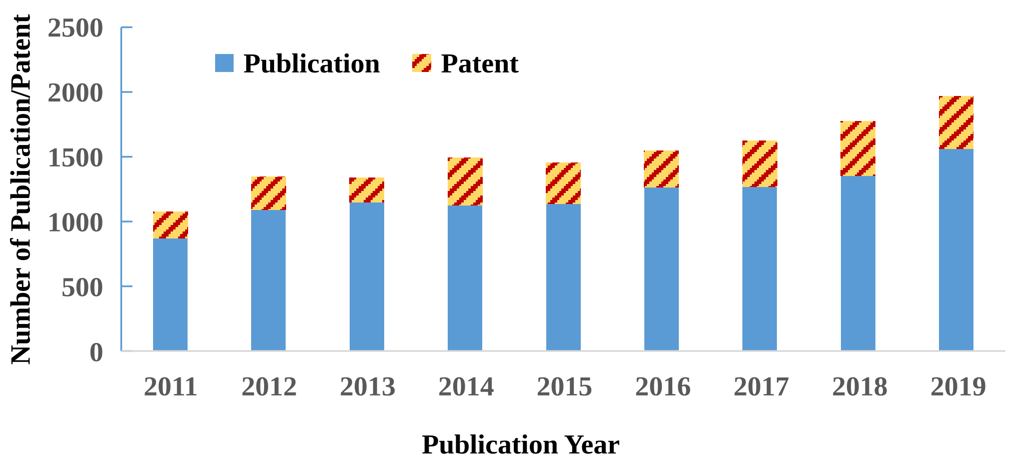
Shells contain three primary chemicals that have many industrial uses.



Developing a sustainable way to refine and give value them could add billions of dollars to the bioeconomy.

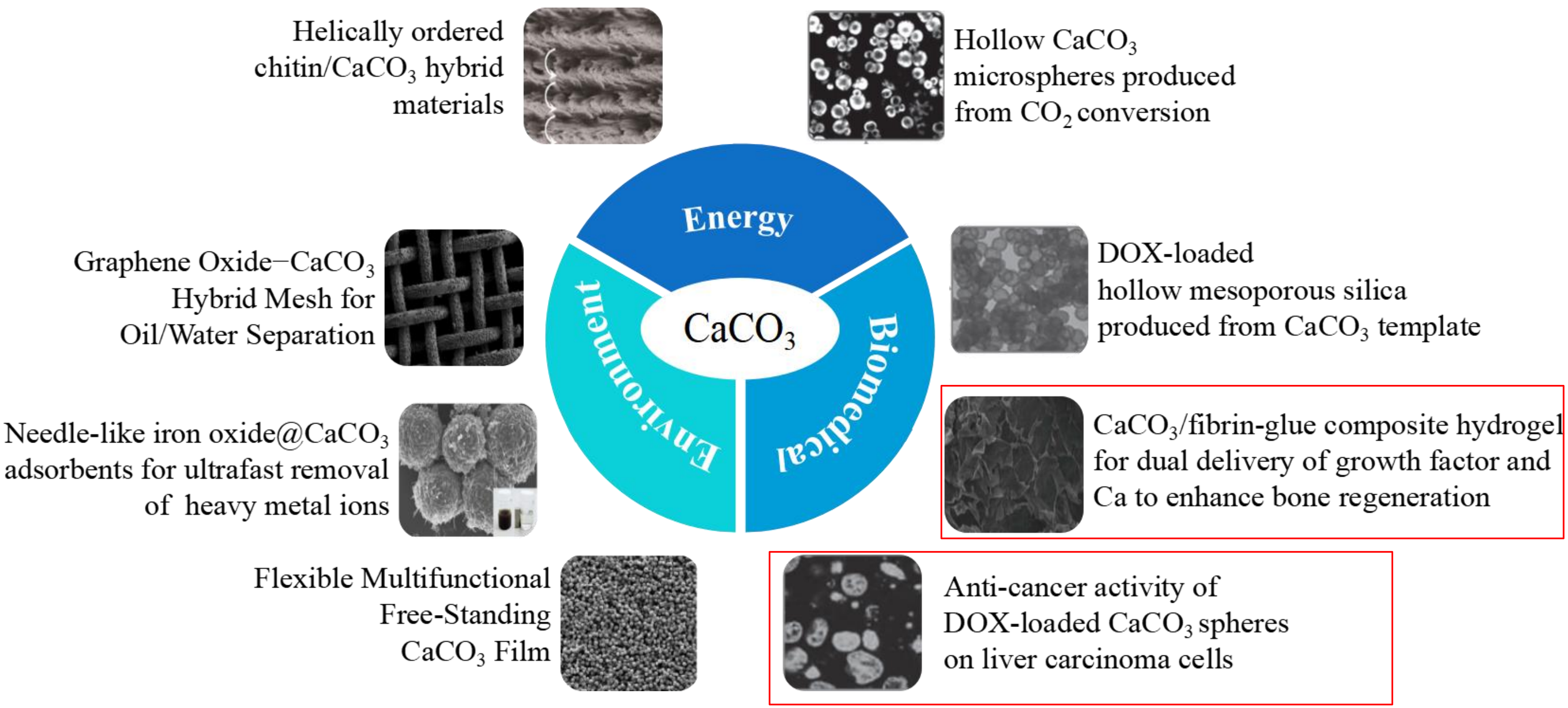
Economic and scientific interest in calcium carbonate

Global $CaCO_3$ market is expected to reach USD 28 billion by 2027 and to show compound annual growth rate (CAGR) of 6%. Source: www.transparancymarketresearch.com.



Statistics of scientific publications/patents (the data is got from Web of science/World Intellectual Property Organization (WIPO), by searching "$CaCO_3$" in theme on January 2021).

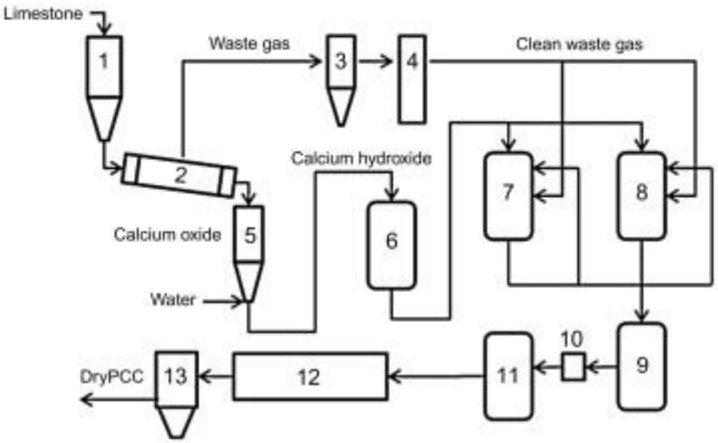
High value application of calcium carbonate



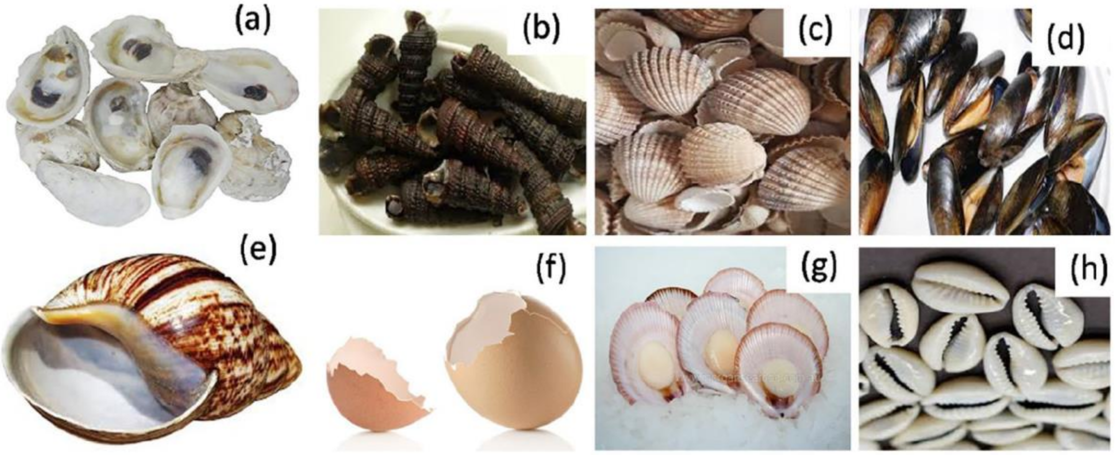
Potential applications of $CaCO_3$ in biomaterials and energy materials.

Sources of calcium carbonate

Ground calcium carbonate



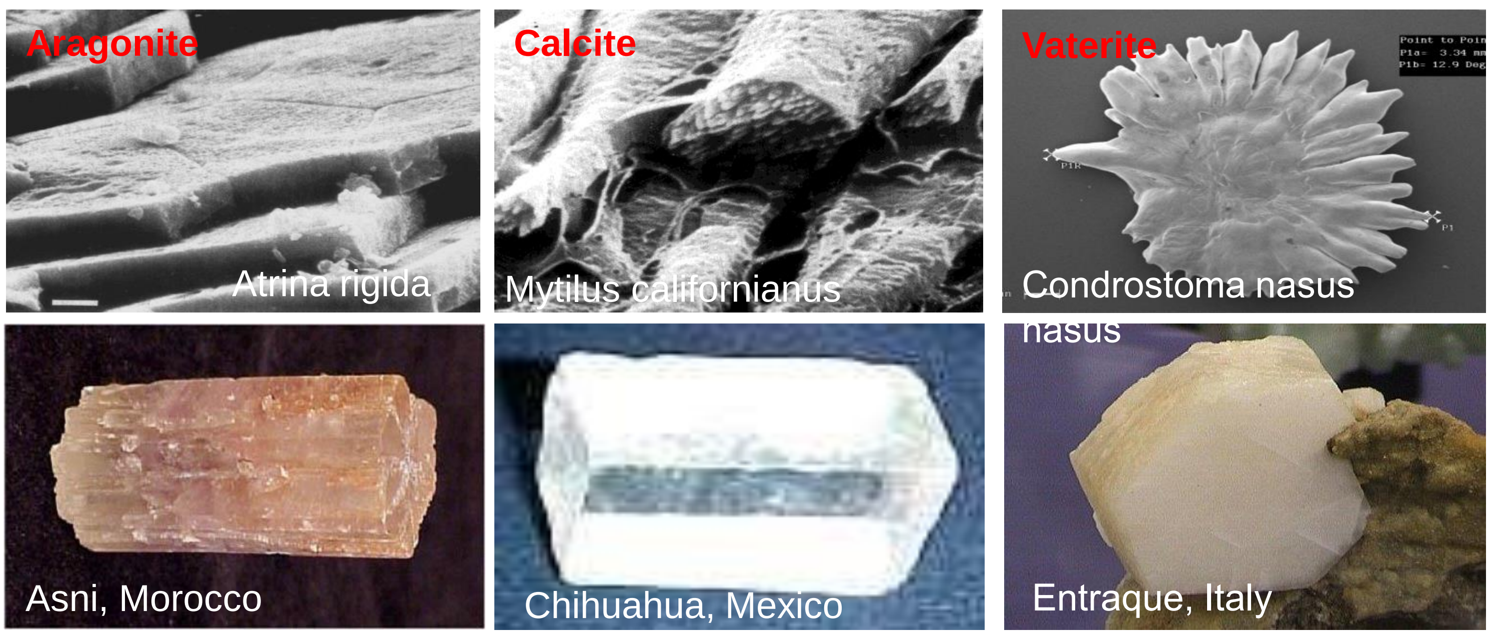
Precipitated calcium carbonate



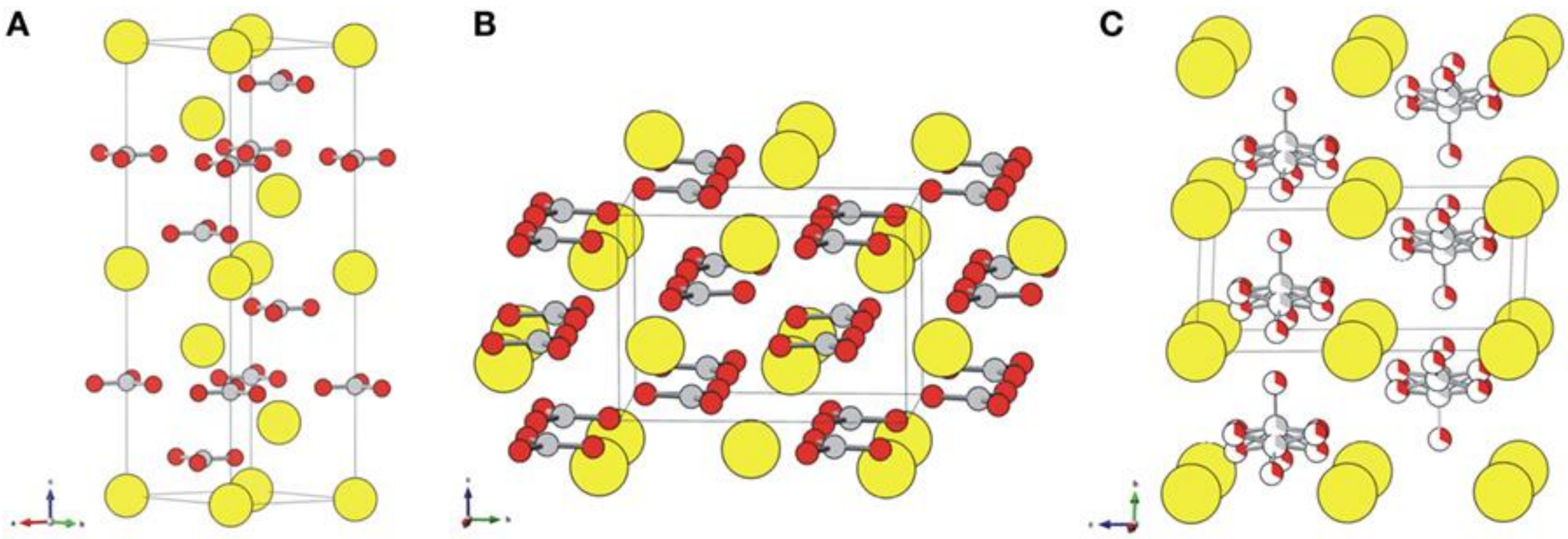
(a) oyster; (b) periwinkle; (c) cockle; (d) mussel; (e) snail; (f) eggshell; (g) scallop; and (h) cowrie.

Organisms are able to deposit uncommon minerals and have a total control over their distribution. Moreover, **they show morphologies different from their abiological counterparts**.

	Biologically	Abiologically
Calcite	Very common	Very common
Aragonite	Very common	Rare
Vaterite	Rare	Very rare
Dolomite	Very rare	Common
Amorphous $CaCO_3$	Common	Non-existent

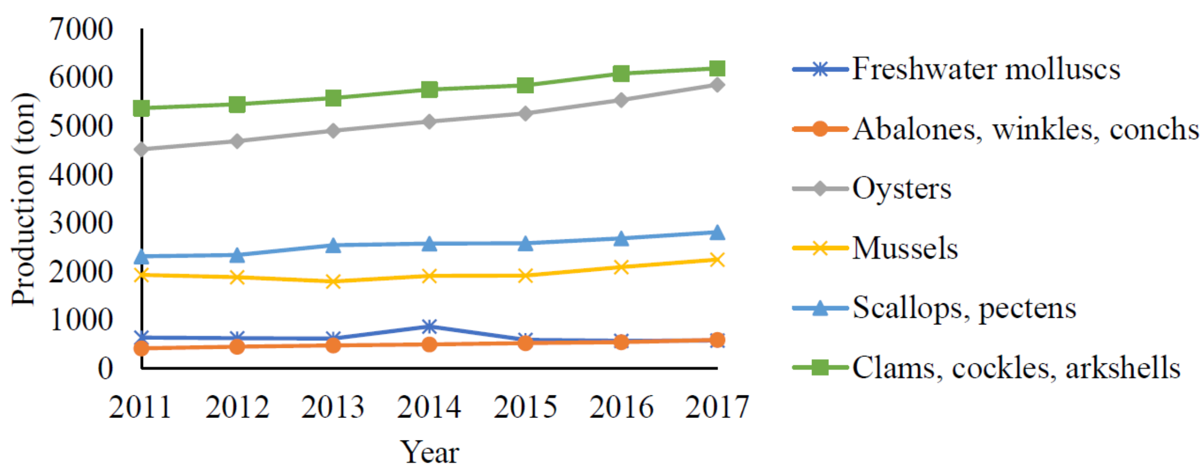


Structure of calcium carbonate polymorph



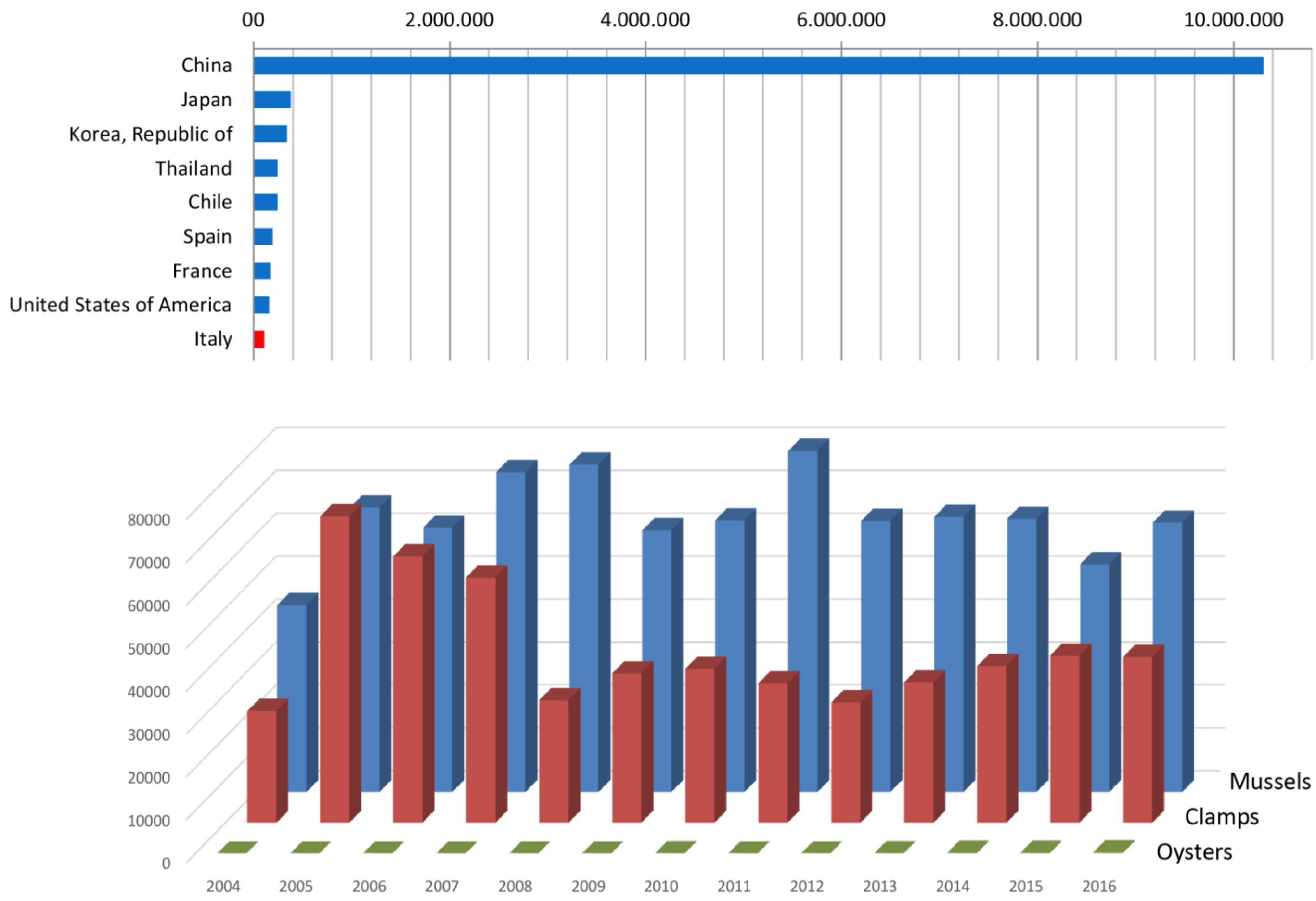
	Calcite[a]	Aragonite[b]	Vaterite[c]
Crystal structure	Hexagonal	Orthorhombic	Hexagonal
Space group	$R\bar{3}2/c$	*Pmcn*	$P6_3/mmc$
Solubility product (K_{sp}) at 25°C[d]	12.242×10^{-9}	4.623×10^{-9}	3.319×10^{-9}
Lattice parameter	a = b = 4.990 Å c = 17.061 Å	a = 4.9598 Å b = 7.9641 Å c = 5.7379 Å	a = b = 7.16 Å c = 2.547 Å
Density (mg/mL) :	2.71	2.93	2.54

Distribution of the top 10 countries in freshwater and marine mollusc aquaculture production, representing 95.7% of the total global production by live weight.



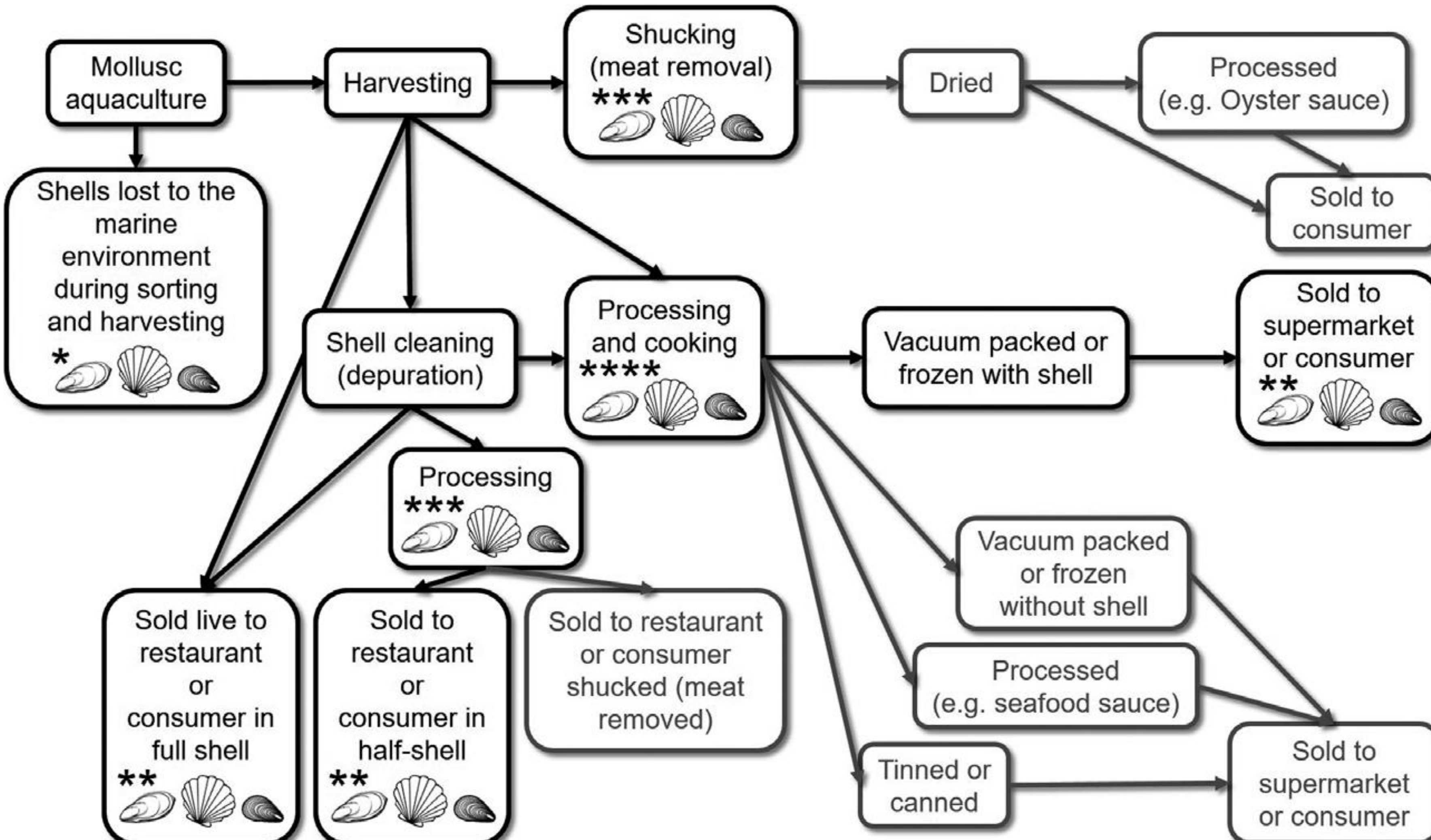
The world production of Mollusks (FAO, 2019)

shellfish from aquaculture



(top) Main countries with production of shellfish (tonnes) from aquaculture. (*bottom*) National production (tonnes) of shellfish species. Data from FishstatJ and FAO (2015).

Conceptual diagram describing some of the key processes undertaken during the delivery of commercial bivalves, such as oysters and mussels, from aquaculture to consumers, highlighting the points at which shell waste may be produced.



Galveston Bay Foundation’s Oyster Shell Recycling Program at Sweetwater Preserve in Galveston (Texas, USA)

A Program Is Turning Discarded Oyster Shells Into Treasure

Recycling Shells Actually Helps Save Restaurants Money

Curing in the sun

Why Recycled Shells Are So Important for Oysters

Putting the Recycled Shells to Work

A Monumental Task Carried Out by a Small Group of People

The future

Artificial reefs to buffer New York / Oyster-Tecture

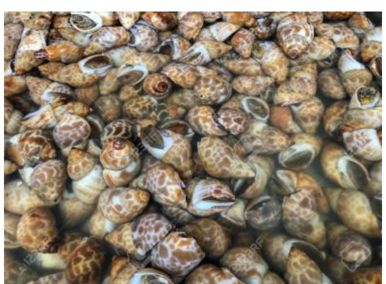
Within the next 40 years, projected sea-level rises of up to a third of a metre threaten coastal cities, including New York. By 2100, rising sea levels could inundate 21% of Lower Manhattan at high tide and warmer ocean temperatures could bring more frequent hurricanes, accompanied by storm surges 7 metres high.

Rather than relying on defensive barriers, such as levees and sea walls, the local design teams participating in *Rising Currents* suggest using wetlands, artificial islands and living reefs to absorb water and attenuate waves.

In the project Oyster-Tecture plans to seed oysters in the waters of the Bay Ridge Flats off Brooklyn to recreate a long-lost natural oyster reef.

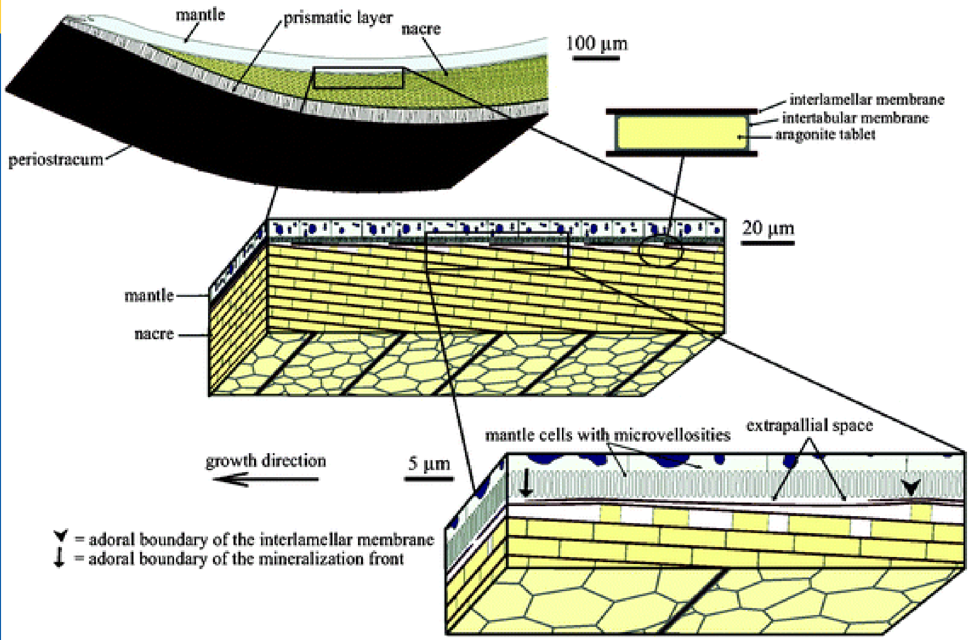
Typical inorganic composition of crushed and calcined shell-derived materials at 900 ºC

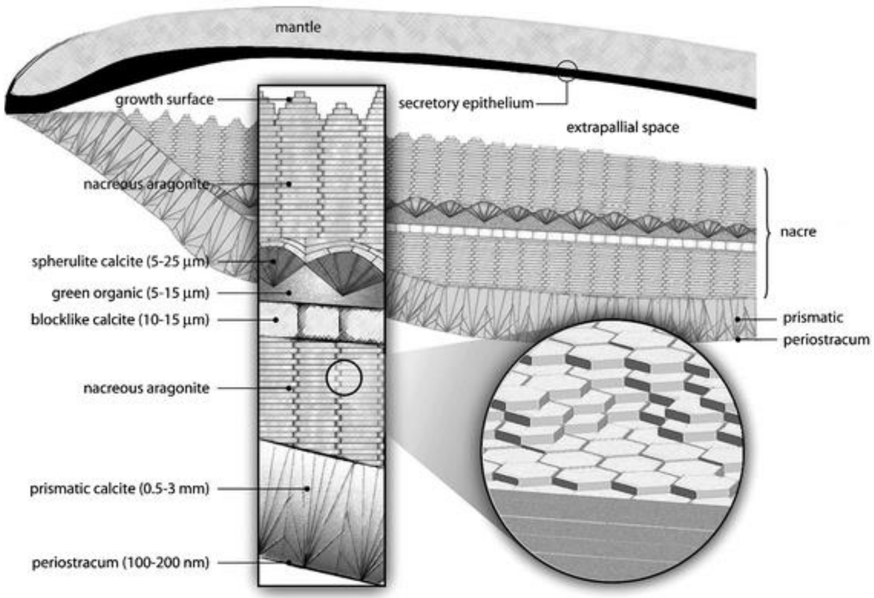
Compound	Concentration (wt.%)				
	Snail shell Laskar et al. (2018)	Cockle shell Buasri et al. (2013)	Mussel shell Buasri et al. (2013)	Oyster shell Buasri et al. (2015)	Pyramidella shell Buasri et al. (2015)
CaO	98.017	99.170	98.367	93.83	94.30
SiO_2	0.467			2.71	3.29
Fe_2O_3	0.357	0.026		0.24	0.27
MnO	0.243				
MgO	0.182			1.18	0.48
Na_2O	0.170	0.438	0.937	0.50	0.34
SrO	0.160	0.132	0.158	0.23	0.37
Al_2O_3	0.130			0.78	0.43
SO_3	0.061	0.117	0.293		
P_2O_5	0.054	0.096	0.163		
K_2O	0.074				
Cr_2O_3	0.035				
CuO	0.011				
TiO_2	0.004		–		
ZrO_2	–	–	0.046		
TeO_2	–	–	–	0.13	0.14
Loss of ignition				0.40	0.38





Shell anatomy

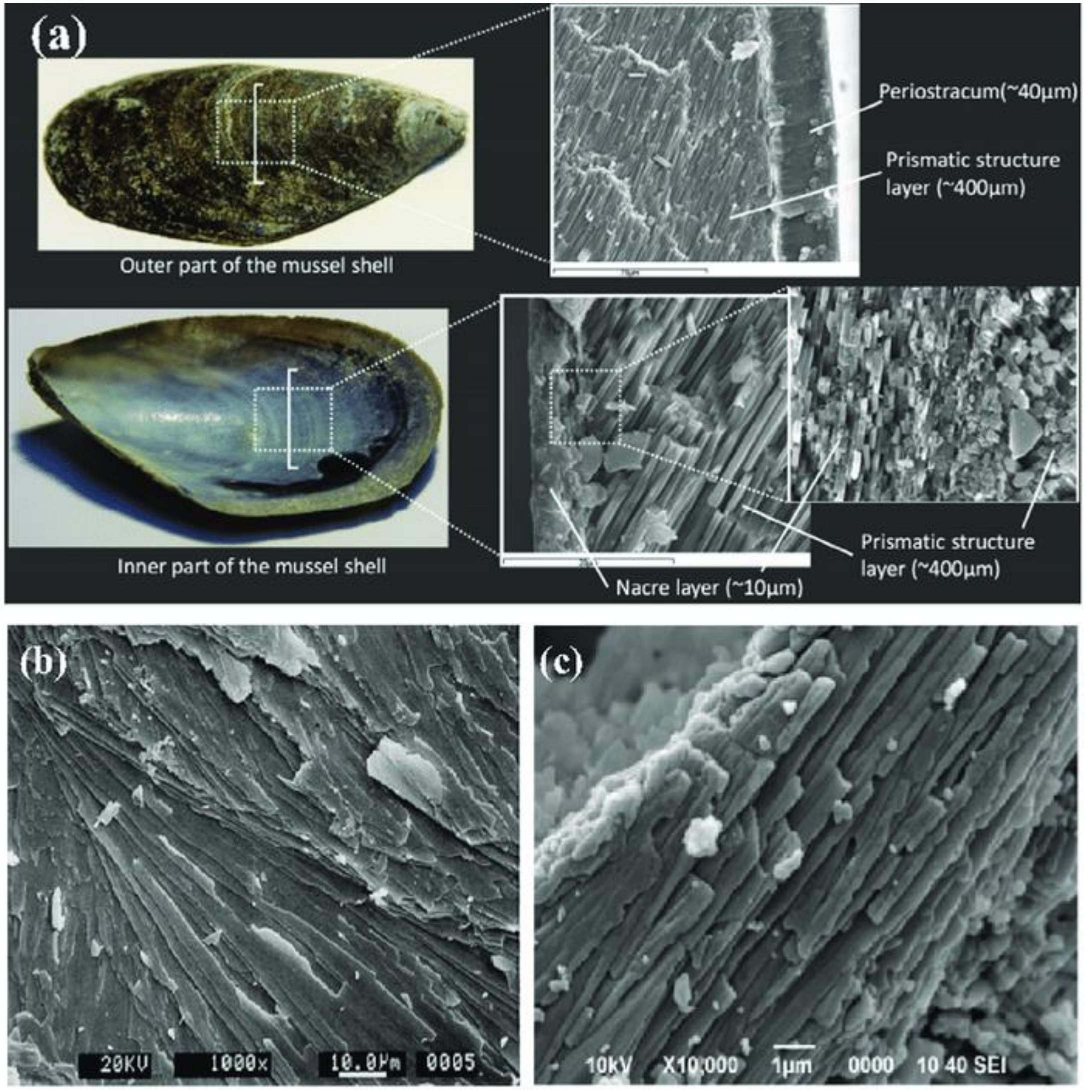




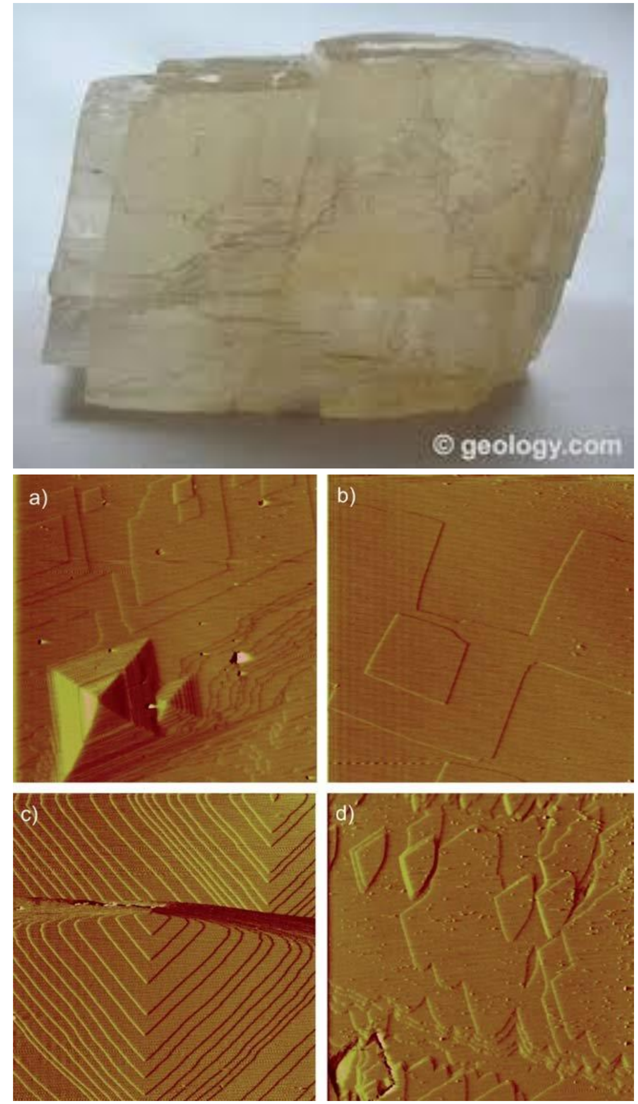
(left) Schematic of the bivalve molluscan shell anatomy. It is composed of periostracum, a prismatic layer and nacre. The liquid-filled interlamellar space exists between the mineralized shell and the mantle part of the soft body of the organism. The schematic also illustrates successive amplifications of the brick and mortar structure of nacre. The growth surface, on which the patterns are observed, is between the mantle and the shell, and extends into the page.

(right) Schematic of the red abalone (gastropod) molluscan shell anatomy, showing a vertical section of the outer edge of the shell and mantle with an enlargement indicating the thickness dimensions of the shell structures. The size of the extrapallial space is exaggerated for clarity.

The internal texture of mollusk shells vs geogenic calcium carbonate

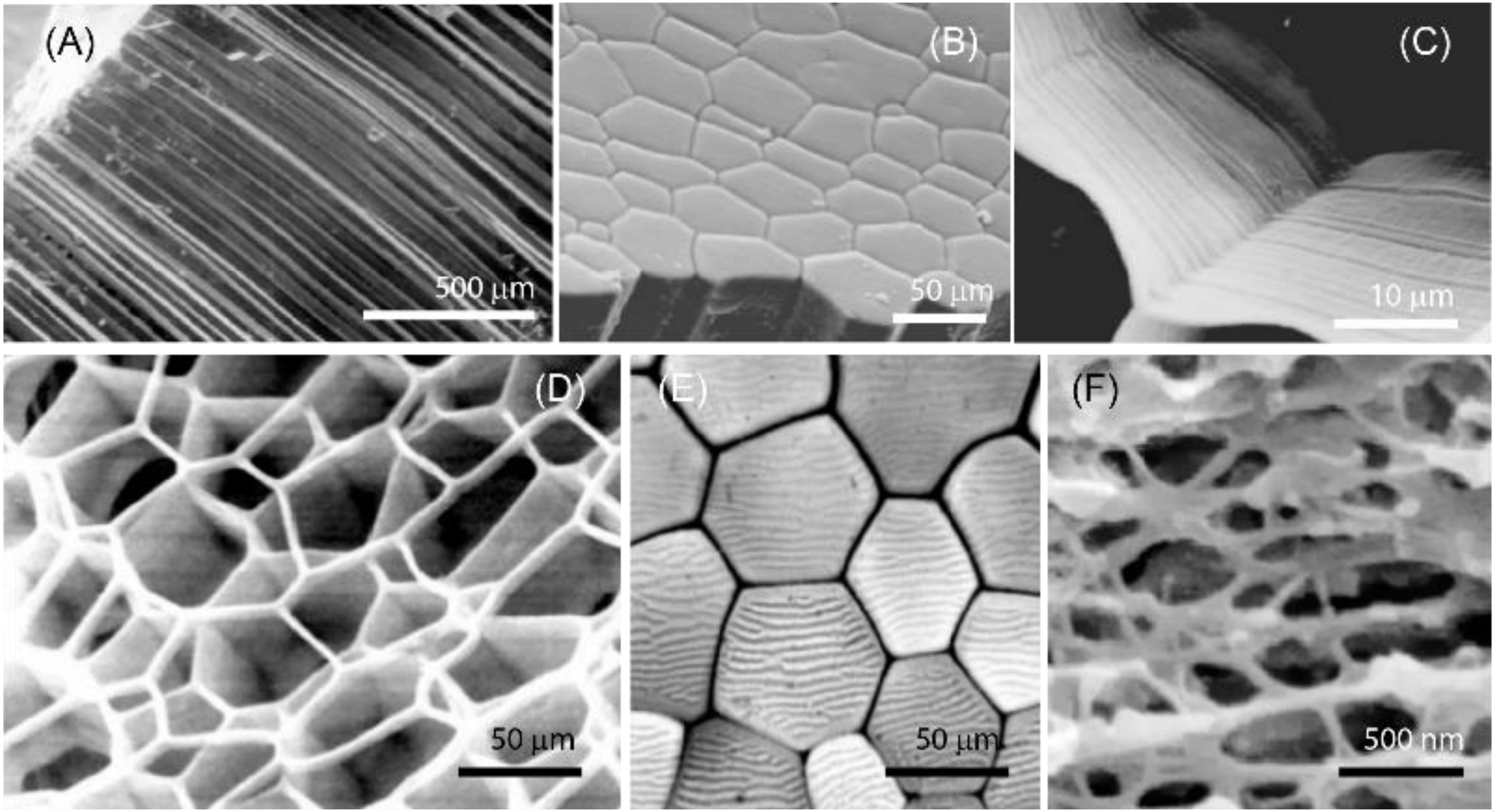


Prismatic layer of (a) mussel shell (b) oyster shell and (c) cockle shell.



(top) geogenic crystal of calcite (bottom) AFM images of growing crystals

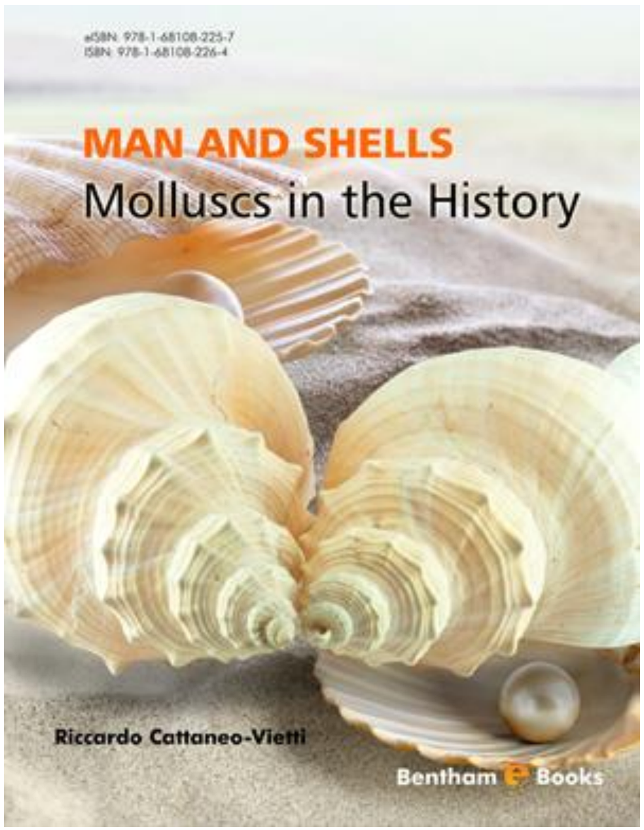
Microstructure of the prismatic layer of Pinna to illustrate the organic matrix distribution in mollusc shells.



(A) Vertical fracture showing the straight parallel prismatic units. (B) Inner surface of the shell showing the polygonal shape of the prisms. (C) Detail of the surface of inter- prismatic membranes, showing thin parallel growth layers. (D) Decalcified prismatic layer showing that the inter- prismatic organic membranes have a layered arrangement. (E) Growing surface showing crests and grooves. (F) Polished, fixed and decalcified sections showing the organic framework within a prism.

Historical value of shells

Historically, shells have been an important part of human culture: acting as a globally traded currency peaking in the mid-19th century, and as primitive tools dating as far back as 100 000 years ago, used by the Neanderthals for example.




These shells date to the middle of the Western Zhou Dynasty (947 – 858 BC)

Cowry shell money was used extensively as a mode of exchange throughout the Far East, Africa, the Middle East, India, and Oceania.

wampum

Current market for mollusc shells

There are several large-scale shell valorisation strategies that are currently exploited.

Type of application	Processing required	Quantity sold	Selling price (as of June 2017)
Poultry feed	Heat treated, crushed	1–25 kg	0.4€–3€ per kg
Pet bird nutrition	Heat treated, crushed	440 g–2.5 kg	0.6€–7€ per kg
Biofilter medium	Heat treated, crushed	600–1000 kg	0.4€–0.5€ per kg
Aquarium/pond pH buffer	Heat treated, crushed, chlorine washed	5 kg	4€ per kg
Soil liming	Heat treated, powdered	22.7 kg	0.4€–0.6€ per kg
Shell aggregates	Whole shell, dried	250–1000 kg	0.3€–0.9€ per kg
	Dried, crushed	15–1000 kg	0.3€–3€ per kg

Examples of the current online bulk mollusc shell market, quantity sold and € price per kg for each application type

Livestock feed supplement

Calcium supplementation is used to improve the health of livestock, particularly bone health, but also in laying birds as a supplement to improve the quality and strength of eggshells.

Shells are, at least, comparable to commonly used limestone as a source of calcium for livestock, with several studies suggesting shell-derived $CaCO_3$ can outperform limestone in this regard.

In 2011, there was a population of 363 million laying hens in the EU-27 group (Eurostat 2011). Of those, France was the biggest egg producer, at 924 000 tonnes in 2011 (Eurostat 2011). Laying hens require ~2.5 g of daily calcium, and with a retention rate of ~50% that would equate to 4.0–4.5 g of calcium or ~10 g of crushed shell $CaCO_3$ (taking into account a ~40% calcium content of shell-derived $CaCO_3$).

it has been shown that the addition of shells (*Venus gallina*) to a limestone supplement significantly improved the egg production performance of laying hens (S. African J. Anim. Sci. 2012, 42)

oyster shell alone performed better than snail shell, wood ash or limestone as a calcium supplement in terms of growth response (J. Animal Phys. Anim. Nutr. 2011, 95:461)

no significant difference between marine shell-derived $CaCO_3$ and mined $CaCO_3$ sources, having tested bivalve, periwinkle and oyster shells (Anim. Feed Sci. Tech.2003, 104:209)

Livestock feed supplement

Environmental Management (2014) 54:1102–1109
DOI 10.1007/s00267-014-0335-6

Making the Best of a Pest: The Potential for Using Invasive Zebra Mussel (*Dreissena Polymorpha*) Biomass as a Supplement to Commercial Chicken Feed

Claire McLaughlan · Paul Rose · David C. Aldridge

Native to the Black and Caspian Sea, zebra mussels were first introduced into North America in the ballast water of ocean-going vessels, and have continued to spread to numerous lakes by overland transport, on hulls, anchors and trailers. They are also transported by divers' wetsuits, in scientific sampling equipment and fishing gear.

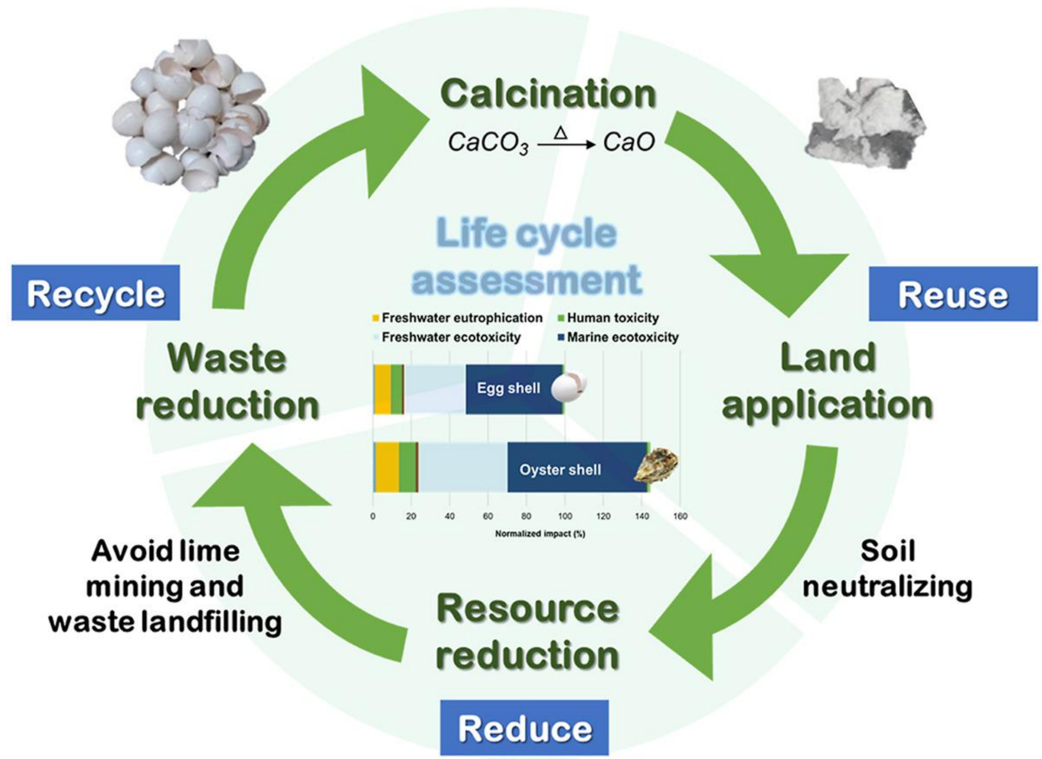
Zebra mussels cause significant harm to freshwater ecosystems by outcompeting native species for food and space and changing the whole ecology of the body of water. They can also clog water intakes and other pipes, and attach themselves to boat motors, hulls and docks.

the zebra mussel meal (meat and shell) was palatable for chickens, and despite lower than expected protein and energy levels in the feed, they concluded that zebra mussel feed could still be utilised as a calcium supplement on account of the $CaCO_3$ shells

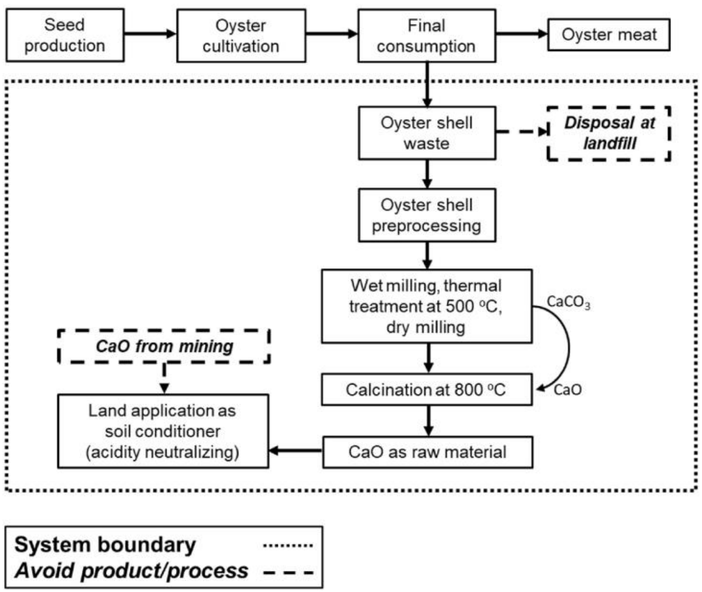
Agricultural liming agent

The second major market for shells is, in the agricultural sector, but involving the neutralisation of acidic and metal contaminated soils.

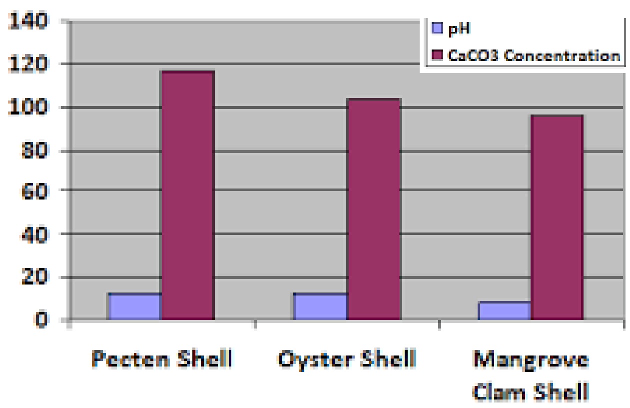
Generally referred to as liming, the practice involves treating soil or water with lime (or a similar substance) in order to reduce acidity and improve fertility and oxygen levels.



Agricultural liming agent



System boundaries of the processing and reuse of oyster shells



Correlations of $CaCO_3$ concentration of the different mollusks and their pH

Agricultural liming agent

Int. J. Environ. Sci. Technol. (2013) 10:983–994
DOI 10.1007/s13762-013-0201-8

ORIGINAL PAPER

pH-dependent copper release in acid soils treated with crushed mussel shell

B. Garrido-Rodríguez · D. Fernández-Calviño · J. C. Nóvoa Muñoz · M. Arias-Estévez · M. Díaz-Raviña · E. Álvarez-Rodríguez · M. J. Fernández-Sanjurjo · A. Núñez-Delgado

Table 1 General characteristics of the vineyard soil (soil A), the mine soil (soil B) and the crushed mussel shell (CMS)

Sample	Sand (%)	Silt (%)	Clay (%)	pH (H_2O)	pH (KCl)	C_T (%)	N (%)	eCEC (cmol kg^{-1})	Cu_T (mg kg^{-1})	Ca_T (%)	Al_T (%)
Soil A	73.4	12.0	14.6	4.5	3.5	2.6	0.17	5.30	361	0.06	2.21
Soil B	67.4	14.0	18.6	3.8	3.0	0.3	0.04	3.89	651	0.06	0.96
CMS	99.5	0.3	0.1	9.4	9.0	12.4	0.08	30.30	9	36.4	0.3

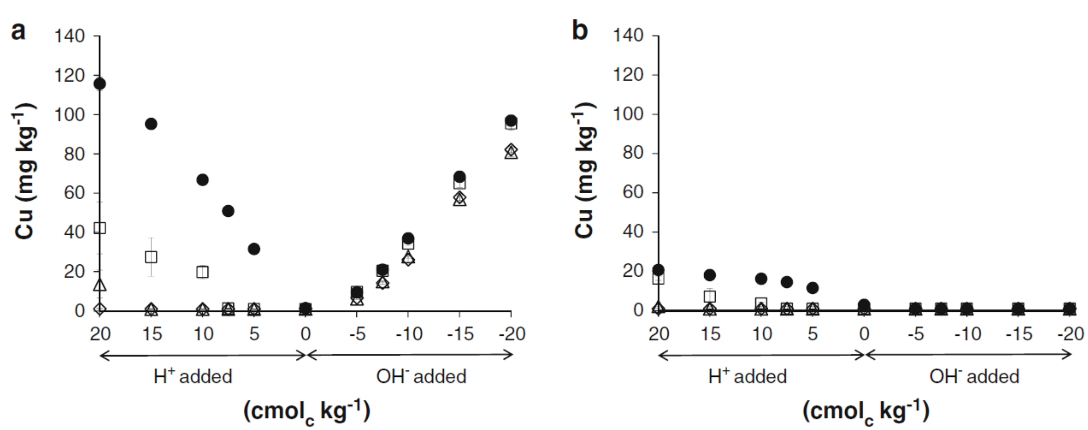


Fig. 3 Changes in Cu release as a function of the addition of HNO_3 or NaOH solutions to samples of a vineyard soil (**a**) and mine soil (**b**) non-amended (*filled circles*) and amended with 12 (*squares*), 24 (*triangles*) and 48 (*diamonds*) Mg ha^{-1} of CMS

Researcher found that mussel shell-treated soils had a higher desorption rate than untreated soils and concluded that mussel shell addition could help reduce the potential threat of copper enriched soils under acidification events.

Another study in Galicia (Spain) found that the application ground mussel shell increased the adsorption and decreased the desorption of arsenic in both forest and vineyard soils, thus reducing the risk of arsenic soil pollution in these areas

Construction material

There are many examples of shells being used as a simple material for construction or incorporated into aggregate and mortar mixes. Shell waste has many characteristics that might make it suitable for certain construction aggregates. However, care must be taken in such propositions though, as many construction materials are highly regulated for performance and safety purposes (EU Regulation No. 305/2011).

Oyster shells abounded in ancestral temples (Ming dynasties)

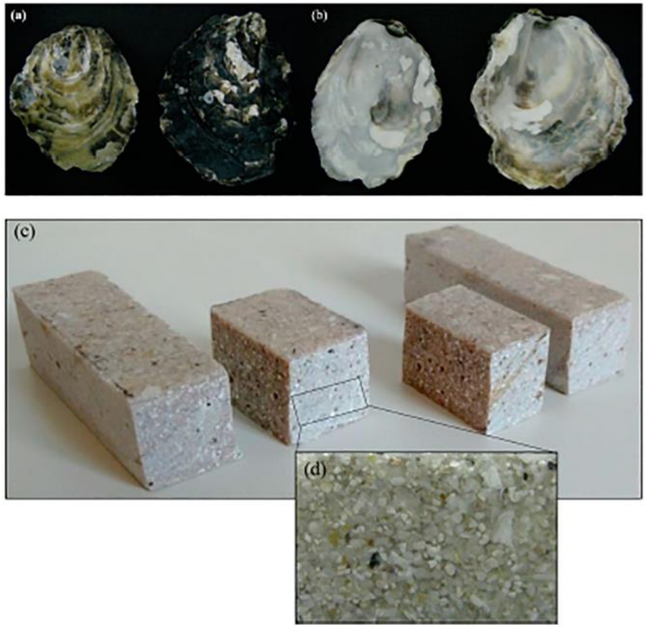
Tabby is made by burning oyster shells to create lime, then mixing it with water, sand, ash and broken oyster shells.

St Albans City Council

The concept of shell use in construction is by no means a new one: there are many historical examples of shells in construction, much of which is known as ‘Tabby’. Florida (USA) has a particularly rich history of incorporating whole oyster shells into the walls of houses, being of likeness to a modern day poured concrete structure.

Construction material

At this time, shell incorporation in aggregates and mortars is largely primitive, and there is not an established market.
This avenue of shell valorization does hold further promise for aggregates and mortars that are not tightly regulated.



Sample of synthetic stone manufacture from oyster shells: (a, b) waste oyster shells; (c) samples of synthetic stones; and (d) dispersed oyster shell powder in the resin matrix (Silva et al., 2019).

A study tested large and small particulate crushed oyster shell mixes to conventional sand mixes as a mortar. It was found that small oyster shell particles (2–0.074 mm) were a potentially viable substitute to conventional mortar sands in terms of compressive strength.

Another study, investigating the incorporation of mussel shell waste in Spain into mortars, found that differences in particle microstructure between quarried limestone (rounded particles) and mussel waste CaCO3 (elongated prismatic particles) resulted in mussel waste-derived mortars showing improved setting times and final strength.

a study investigated the incorporation of crushed limpet shells into pervious concrete mixes and concluded that shell incorporation did not have an adverse effect on the concretes mechanical strength and increased porosity allowed for better water permeability, an important characteristic of pervious concretes

Construction material

Though limited research had been carried out on the applications of waste shells as partial cement replacement in cement mortar for masonry, the use of crushed oyster, mussel, clam and mollusk shells showed that the compressive strength of the cement mortars obtained were lower than that of control sample for both 7 and 28 days' curing.
In spite of this, the observed compressive strength of the cement mortar achieved with these shells is still within the tolerable range in the construction industry

Compressive strength of crushed seashells used as partial cements replacement in concrete and cement mortar for masonry.

Type of waste shell	Use	Control sample strength (megapascal (Mpa))		Optimum replacement (%)	Compressive strength (MPa)		Reference
		7 days' curing	28 days' curing		7 days' curing	28 days' curing	
Periwinkle	Concrete	-	17.5	10	-	19	Adewuyi et al. (2015)
Snail		-	17.5	20	-	18	Adewuyi et al. (2015)
Cockle		38	45	5	34	36	Othman et al. (2013)
Clam		33.8	37	4	34	39.8	Olivia et al. (2017)
Oyster	Masonry cement mortar	31.6	43.04	5	28.59	37.59	Binag (2016)
Mussel		10.2	14.9	5	9	10.5	Lertwattanaruk et al. (2012)
Clam		10.2	14.9	5	9.9	12.6	Lertwattanaruk et al. (2012)
Mollusk		31.6	43.04	5	28.73	39.54	Binag (2016)

Separation of pollutants from wastewater and air

There is a significant body of research on the use of mollusk shells as biofiltration medium for treating wastewaters. However, a large proportion of that research does not use shells directly, but pretreats them via calcination or pyrolisation, forming CaO.

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November

Separation of Cu(II) ions from synthetic solutions and wastewater by raw and calcined seashell waste

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The use of waste mussel shells for the adsorption of dyes and heavy metals

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Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: Equilibrium, kinetic and thermodynamic studies

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Machine vision based monitoring of an industrial flotation cell in a flotation plant

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Characteristics of Waste Sea Shells for Acid Gas Cleaning Absorbent

Jong Hyeon Jung, Byung Hyun Shon*, Kyung Sun Yoo** and Kwang Joong Oh***†

the suitability of uncalcined/unpyrolysed shells as biofilter mediums has to be considered, representing both the current market for shells sold as biofilter media and also a more feasible large-scale potential valorisation strategy moving forwards.

Separation of pollutants from wastewater and air

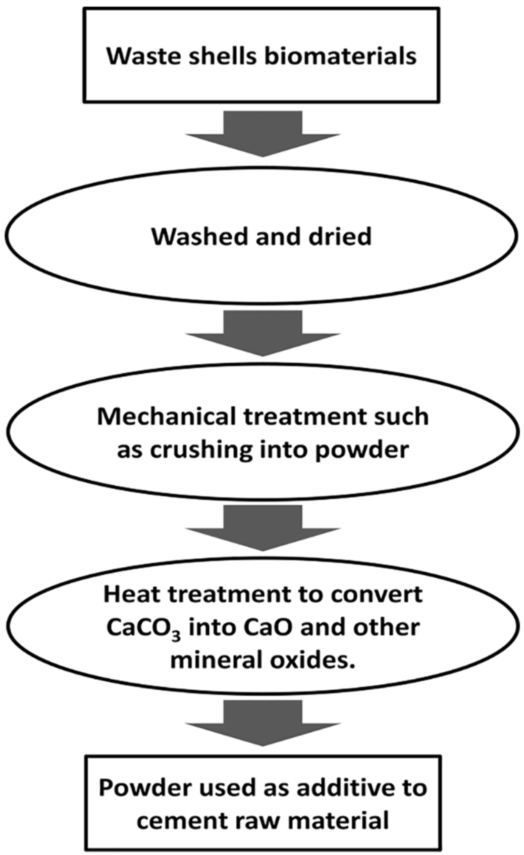
Waste shell-derived materials can serve as bio-medium or biofilter for wastewater decontamination and filtration. The heat treatment of the shaped powder from crushed shells or the original shells will create a biomaterial with a porous network due to the conversion of $CaCO_3$ to CaO.

Typical biofilter media from waste shells for wastewater treatment: (a) oyster shells; (b) mixed waste shells biomaterials; and (c) shaped waste shell powder

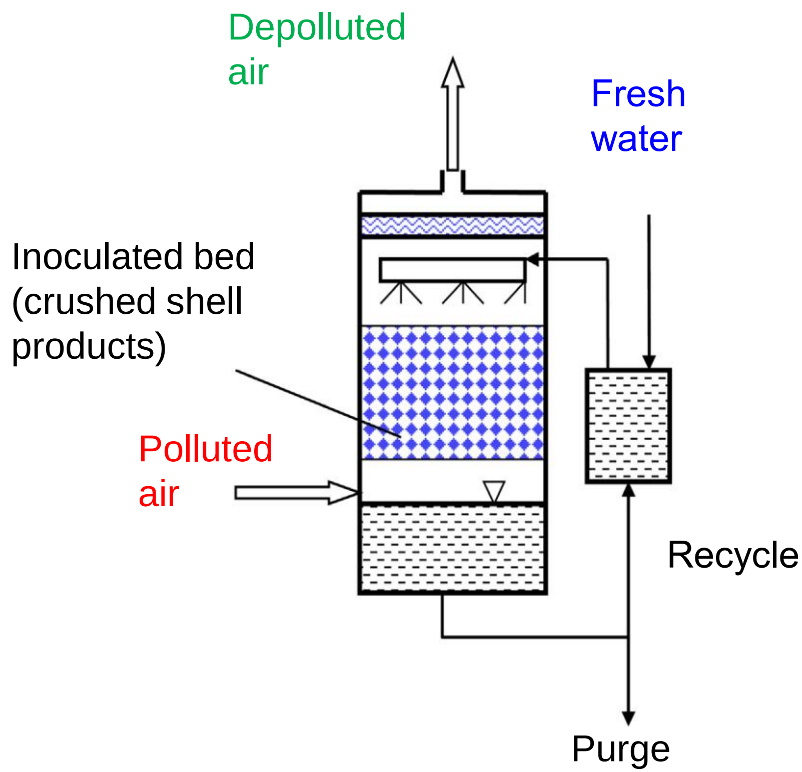
waste oyster shells as a bio-medium to purify domestic wastewater. It was observed that the purification efficiency and nitrogen removal were better with oyster shell than gravels.

Separation of pollutants from wastewater and air

Powdered waste shells can serve as an alternative to activated carbon as biofilter media to remove odour from exhaust gas from industrial activities, such as wastewater treatment plants, waste treatment or disposal facilities, paint manufacturing, oil refineries, plastics and resin manufacturing, and other agrochemical industries.



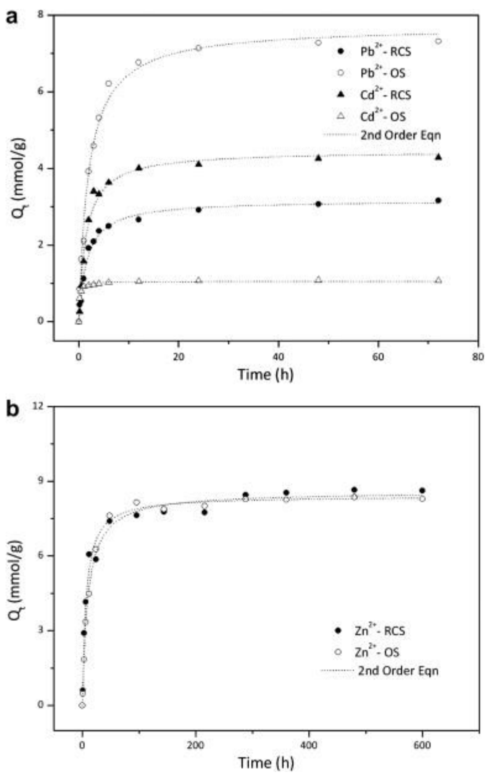
Methodology of waste shells treatment to obtain CaO

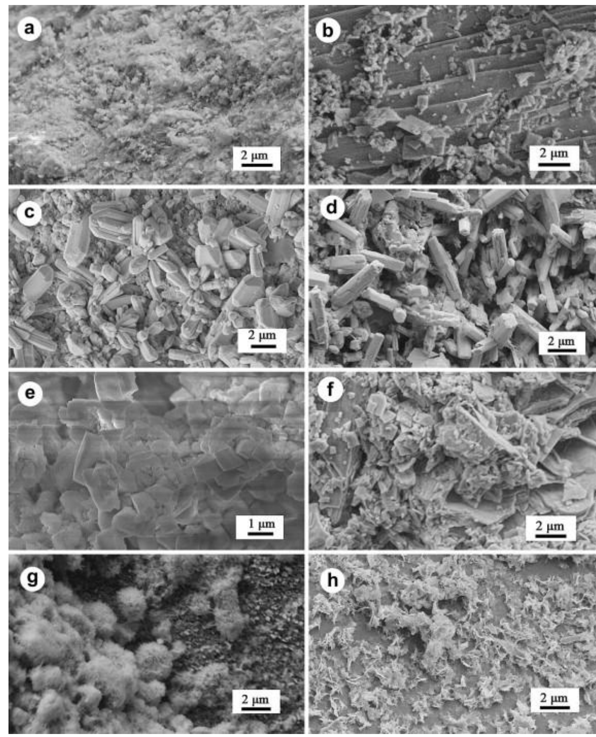


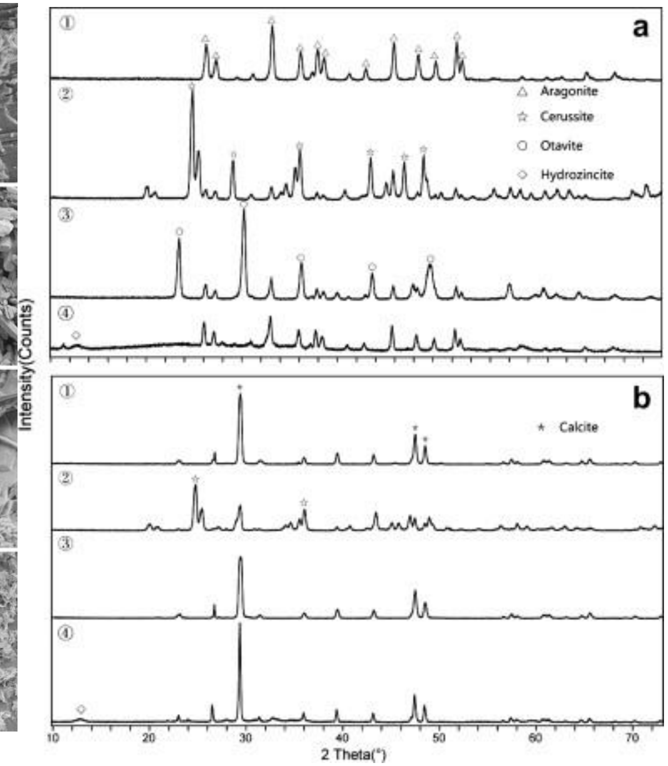
Schematics diagram of biofilter for odour removal using shell-derived materials

Separation of pollutants from wastewater and air

The potential of using mollusk shell powder in aragonite (razor clam shells, RCS) and calcite phase (oyster shells, OS) to remove Pb^{2+}, Cd^{2+} and Zn^{2+} from contaminated water was investigated. Both biogenic sorbents displayed very high sorption capacities for the three metals except for Cd on OS.







Mollusk shells display high removal efficiency to heavy metals in contaminated water.

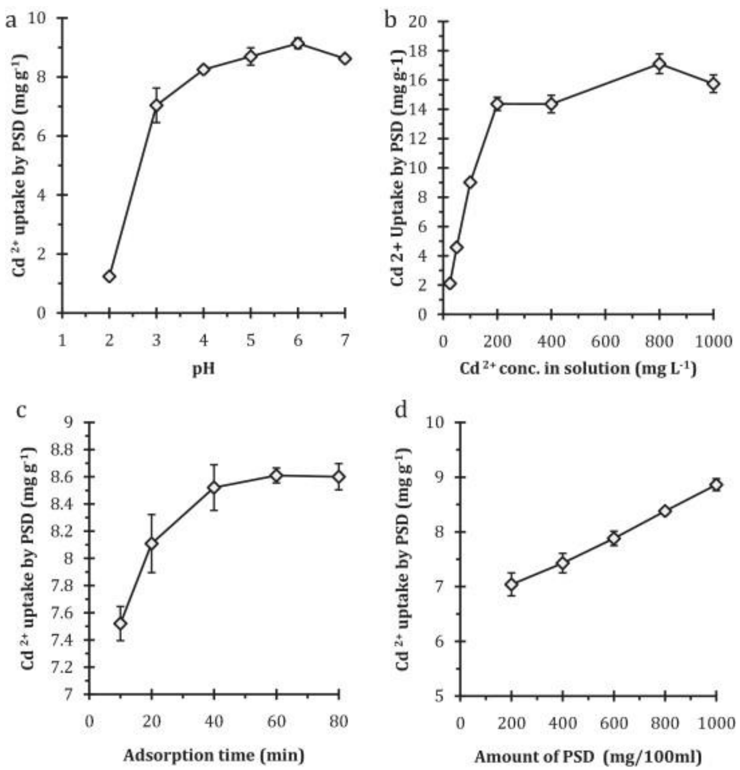
- Surface precipitation leading to crystal growth takes place during the sorption.
- pH, sorbent dosage and grain size of adsorbent affects the removal efficiency.
- Organic matter in mollusk shells affects the removal efficiency to a less extent.

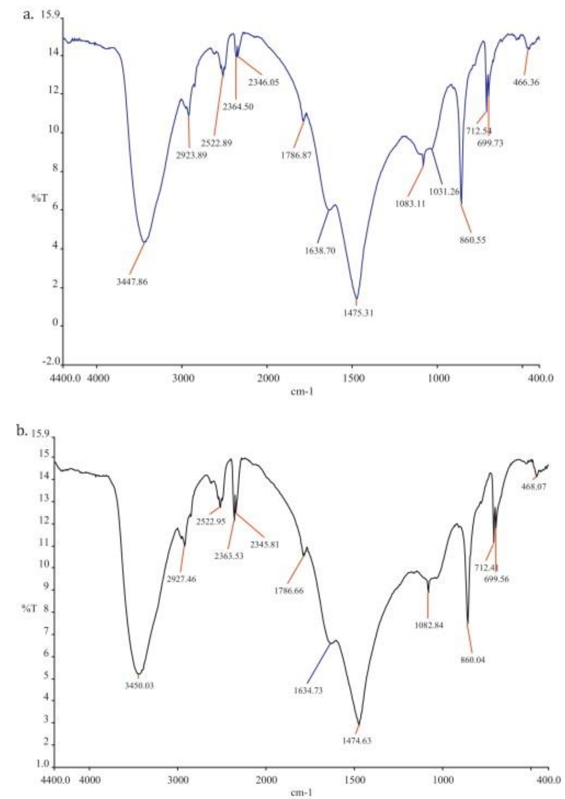
Environmental Pollution, 159, 2011, 1763-1768

Separation of pollutants from wastewater and air

Cadmium biosorption potential of shell dust of the fresh water invasive snail *Physa acuta*

The ability of shell dust of an invasive freshwater snail (*Physa acuta*) to remove cadmium from contaminated water was evaluated. The results indicate that PSD, a waste biomaterial, bear potential of cadmium removal from contaminated water with biosorption capacity of 16.66 mg g^{-1} at pH 6.



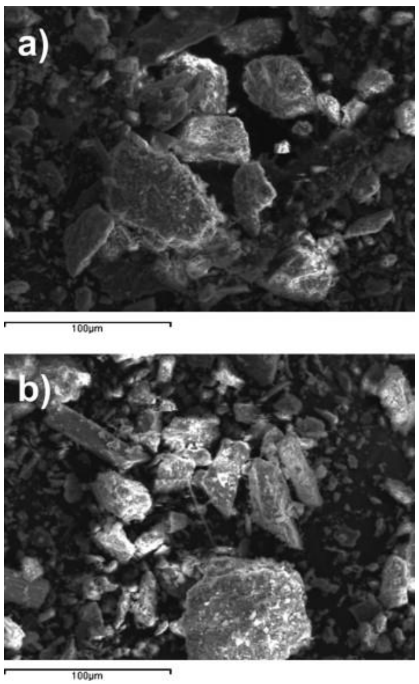


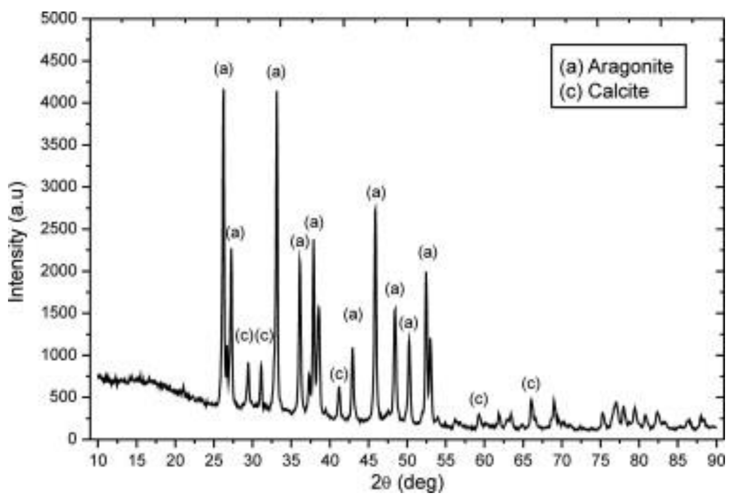
The FT-IR analyses support that the main mechanism of biosorption was cadmium chelating with different functional groups such as OH, C=, and C=C. The result obtained from the experiments show that the PSD can be used as an efficient, low cost, environmentally friendly biosorbent for cadmium from aqueous solution.

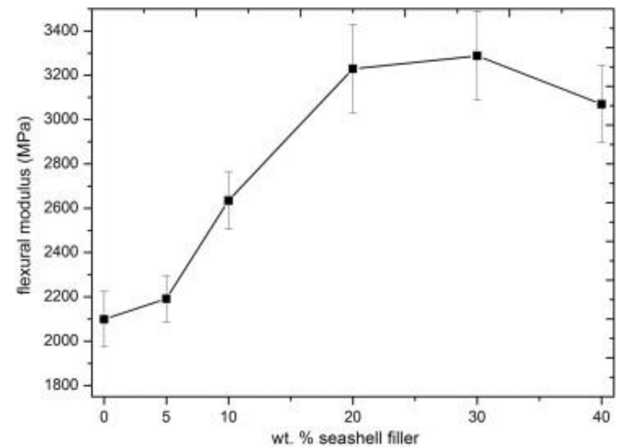
Filler

Calcium carbonate is the most widely used inorganic filler in polymers. The coarse grades are low in price and used primarily to reduce formula costs. By contrast, the finer grades are an order of magnitude higher in price and used to modify various properties of polymer composites.

Bivalve shell is a functional biomaterial and some studies have investigated its use as filler







When bio-based $CaCO_3$ was introduced, Tg presented an increase at 10 wt% filler and then decreased when the filler concentration increased to over 15 wt%. Up until a 10 wt% weight loss, though, thermal stability increased slightly, with $CaCO_3$ quantity increase. At higher temperatures, the thermal stability of the composites decreased slightly. In the presence of filler, the lifetime values of the cross-linked system rose, compared with the blank sample

De-icer grit

It is well known that chlorine-based road grits can be detrimental to both the urban environment and the natural environment: road grit is specifically not used in airports because of the corrosive effect it can have on aeroplanes. Research has shown that road grits can have negative effects on the natural environment in close proximity to its use.

The formation of an eco-friendly de-icer substance from the waste shells of shellfish aquaculture, mixed with a mild acetate waste substance from another industry such as those listed above could prove an environmentally beneficial use of shells, and with the recent localised shortfall in de-icer substances across Europe during cold periods, there is potentially a market for alternatives to road grit as de-icing agents.

Green roofing substrate

Green roofs, also known as living roofs, have seen a surge in popularity in the last decade, particularly in urban areas, as there is a growing conscience of the importance of green spaces on environmental health. Green roofs can have a number of beneficial effects: increasing habitat space for wildlife, mitigating urban heat island effects, providing building insulation, providing rainwater absorption and improved wastewater management, as well as potentially providing a stress-reducing and attention-increasing environment for those in proximity



Another potential use of waste mollusc shells is as the drainage layer in green roofing structures. The drainage layer is important in carrying away excess water from the roof. It is a 3D structure between the filter layer and the waterproof membrane. Whole shells may be ideal for such structures, as when heaped they provide a complex 3D structure to aid drainage. In addition, $CaCO_3$ shells incorporated into green roofing structures may help with the neutralisation of acid rain, and the reduction in heavy metal contamination in the resultant drainage water.

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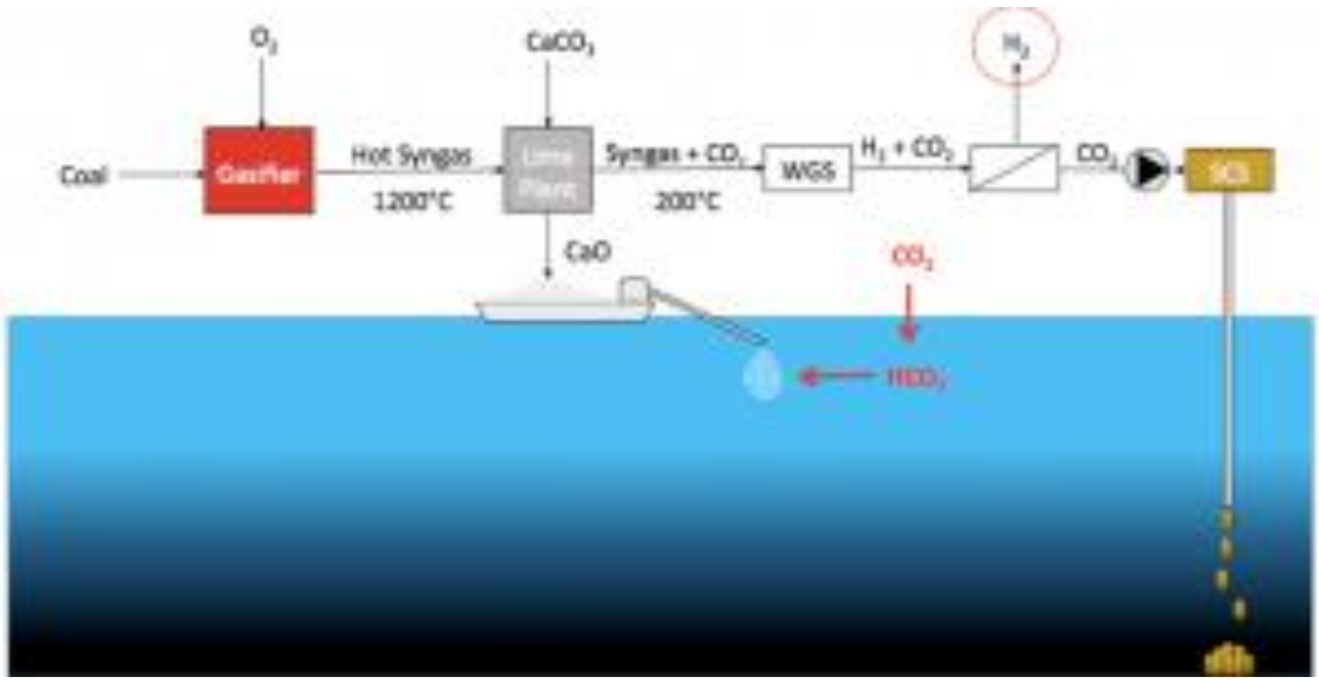
Shells returned to the marine environment

Ocean alkalinisation has been proposed as a method of limiting atmospheric CO_2 increases and ocean acidification through pH buffering.



However, there is little evidence of the use of powdered, crushed or whole waste shells as the calcium carbonate source. If significant shell waste is produced in areas where local water systems would benefit from liming practices, it could be a mutually beneficial practice, alleviating both acid water problems and the cost and environmental strain of dumping waste shells at landfill.

Shells returned to the marine environment

Waste shells can also have many positive influences from a more biological perspective. Oyster populations rely on a suitable substrate for larval settlement and attachment. In many cases, in natural systems, existing adult shells provide such a substrate, resulting in oyster reefs.

Restoration programmes and research typically use dredged shells or calcium carbonate-based structures (concrete reef balls, for instance) to create a suitable settlement site for oyster larvae, then either let the natural larval stock settle if present or seed the reef structures from hatchery stock.

These ecosystem services are not limited to reef building oyster species however. For instance, a study in Sweden has modelled the bioremediatory effects of mussel farming on the west coast of Sweden, suggesting the promotion of mussel populations for the purpose of nutrient and biotoxin assimilation, via a nutrient trading system

Some reported applications of waste shell-derived catalysts

Waste shell-derived catalyst	Reaction application	Reference
Mussel, cockle, and scallop	Transesterification reaction for biodiesel production	Buasri et al. (2013)
Ostrich and chicken eggshell	Biodiesel production through transesterification reaction	Tan et al. (2015a, 2015b)
Co–Zr eggshell supported on silica	Syngas conversion using Fischer–Tropsch process	Peluso et al. (2001)
Eggshell	Selective oxidation of methane	Karoshi et al. (2015)
Eggshell	Hydrogen production via wood gasification	Taufiq-Yap et al. (2013)
KBr-impregnated calcined snail shell and kaolin	Transesterification reaction for biodiesel production	Liu et al. (2016)
Eggshell	Lithium battery separator	Nguyen et al. (2018)
Shells of egg, oyster and clam	Biodiesel production	Risso et al. (2018)
Eggshell supported W–Mo	Biodiesel production via transesterification reaction	Mansir et al. (2017)
Oyster shell supported $CuCl_2$	Propargylamines production via coupling reaction of aldehyde–alkyne–amine	Xiong et al. (2014)
Pearl shell-powder-supported Pd catalyst	Benzene oxidation	Zuo et al. (2013)
Eggshell catalyst	Production of dimethyl carbonate from propylene carbonate and methanol	Gao and Xu (2012)
Eggshell	Coal gasification	Fan et al. (2017)
Eggshell	Oximes production from aldehydes and ketones	Taleb et al. (2017)

Biodiesel, as a potential energy substitute, has gained great attention because of potential depletion of fossil fuel resources and migrating pollutant emissions.

Among the heterogeneous catalysts, CaO shows promise, and many research studies have been conducted on CaO-catalyzed transesterification.

The utilization of calcium sources from shell waste as an economical catalyst, though, is a new trend.

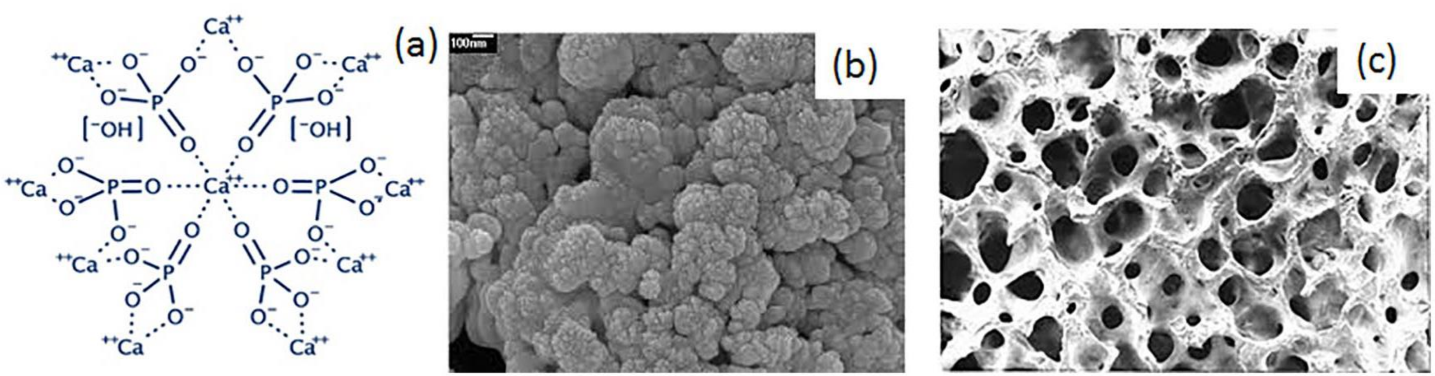
Biomedical applications

The CaO materials are commonly used in biomedical applications such as bone regeneration, dental application and drug delivery.

Waste shells are natural biomaterials and particularly seashells can be regarded as bioceramics with similarity to bones and teeth.

The method of the solid-state reactions between grounded oyster shells and calcium pyrophosphate or calcium hydrogen phosphate dihydrate was used to produce HA powder after ball milling and heat treatment in air atmosphere. The HA powder produced was pure.

Grounded seashells were used as filler to improve the mechanical properties of PMMA bio-composites material. It was found, that the PMMA bio-composite material made with nano-size seashell powder had better compressive strength.



Structure of hydroxyapatite (HA) biomaterial: (a) molecular structure [Ca_{10} $(PO_4)_6(OH)_2$]; (b) scanning electron microscope image of HA powder; and (c) porous microstructure of HA .

Shell valorisation @UNIBO

ERA-NET COFUND
BLUE BIOECONOMY

PROJECT TITLE

ADVANCED MATERIALS USING BIOGENIC CALCIUM CARBONATE FROM SEASHELL WASTES (CASEAWA)

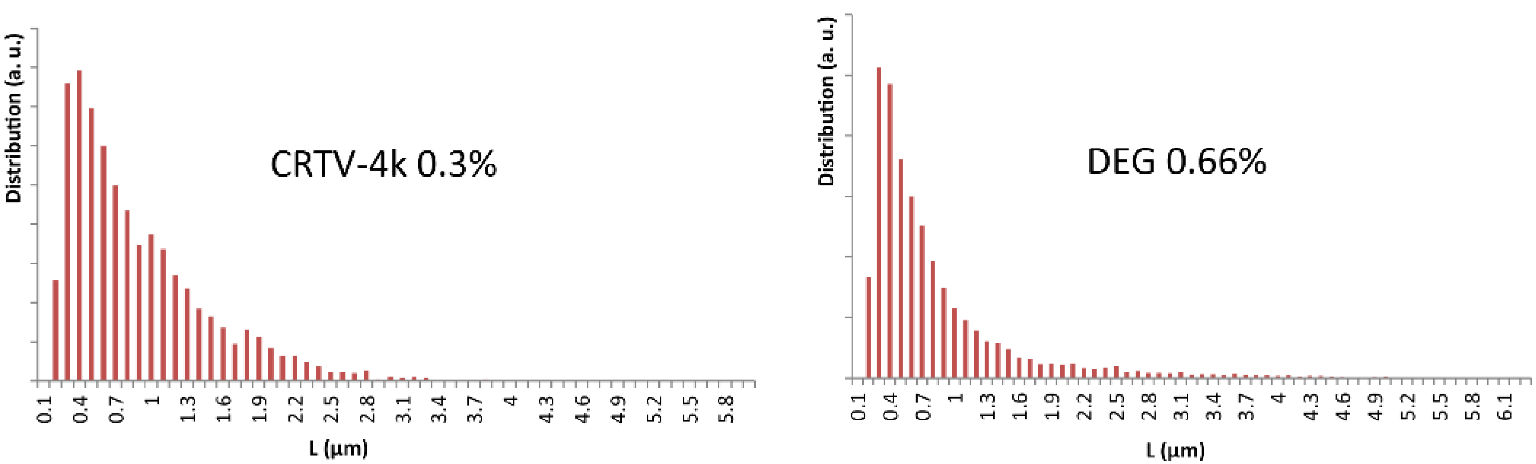
PRIORITY AREA

Exploring new bioresources

https://bluebioeconomy.eu/calls/

Shell valorisation

Milling system. (A) Crashing mill. (B) Planetary ball mill. (C) Analytical sieve.



Particle size distribution of bCC after planetary ball milling grinding in the presence of different grinding aids, poly-acrylic super-fluidificant CREATIVE 4K © (CRTV) and di-ethylene glycol (DEG).

Shell valorisation

A) Reaction of functionalization of the oyster shell particle (BP) with the rhodamine B (Rho-B) piperazine molecule. B) SEM image of bleached oyster powder (shown in the vial) after chemical functionalization with Rho-B. C) SEM image of the pristine oyster powder (shown in the vial) after chemical functionalization with Rho-B. Scale bar is 1 µm.

Conclusions

In mollusc aquaculture, shell waste remains a barrier to sustainable growth. Shells are majority calcium carbonate, with a small amount of organic matrix.

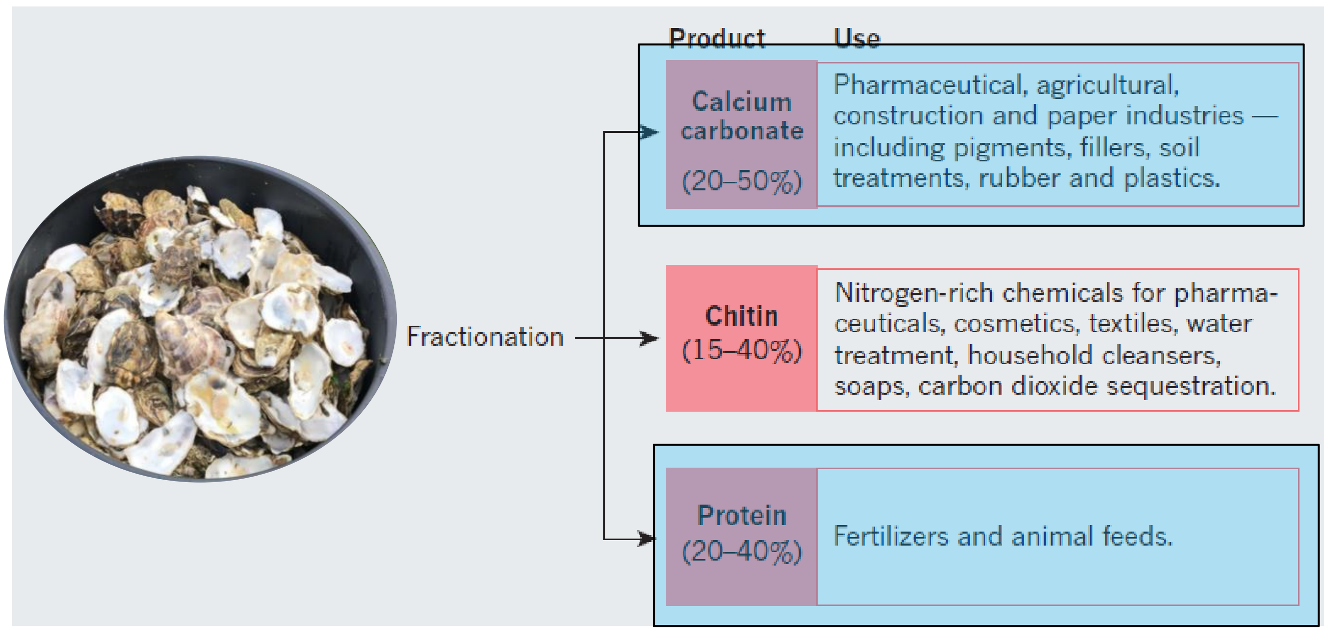
The use of shells in eco-friendly road deicer substances, to their use in green roofing structures as a functional drainage layer, it is clear that there are many potential waste shell uses that do not require high-energy processing such as pyrolysis.

Where shells are produced in a significant volume, it should be possible to find an appropriate valorization strategy for them within a close-enough proximity to make it both sustainably and economically viable.

The significant cost of proper landfill disposal in many parts of the world, cleaned shells which cannot be used for any applications could be returned to the marine environment in a directed manner, where they can have a myriad of positive effects on the environment.

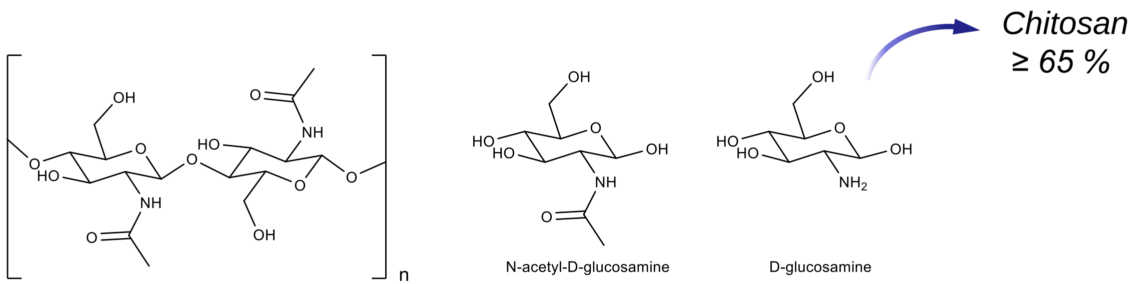
It is important that the way we view shells changes from a nuisance waste product, to a valuable commodity that could provide economic and environmental benefits if utilised correctly.

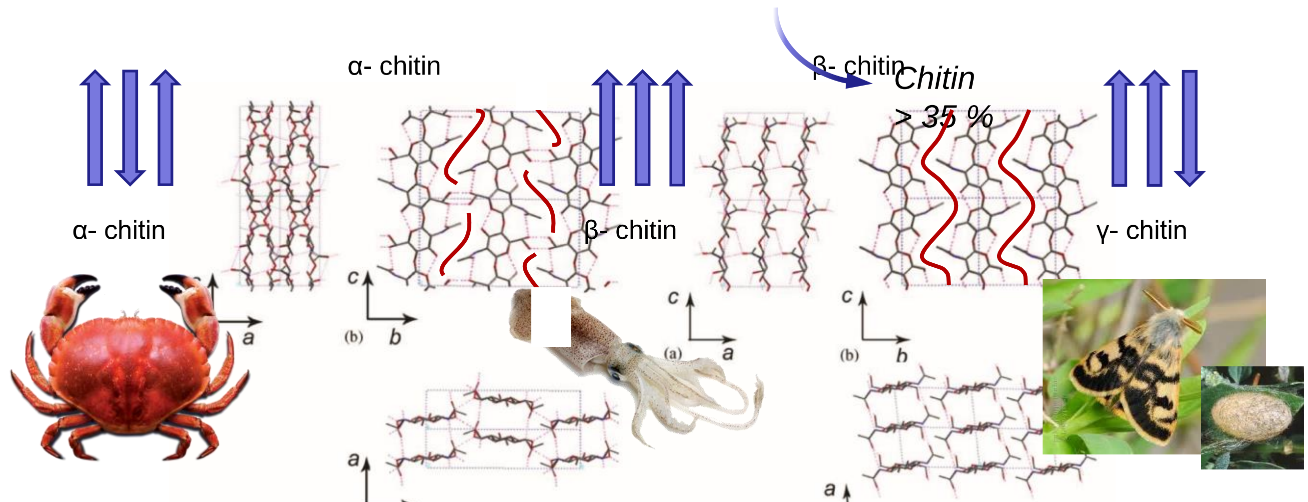
Shells contain three primary chemicals that have many industrial uses.



Developing a sustainable way to refine and give value them could add billions of dollars to the bioeconomy.

Chitin





Arthropod's exoskeleton (ex. *Potamon ibericum)*

Squid pen (ex. *Loligo vulgaris)*

Cocoon of *Orgyia dubia*

Chitin's abundance in nature

Annual production

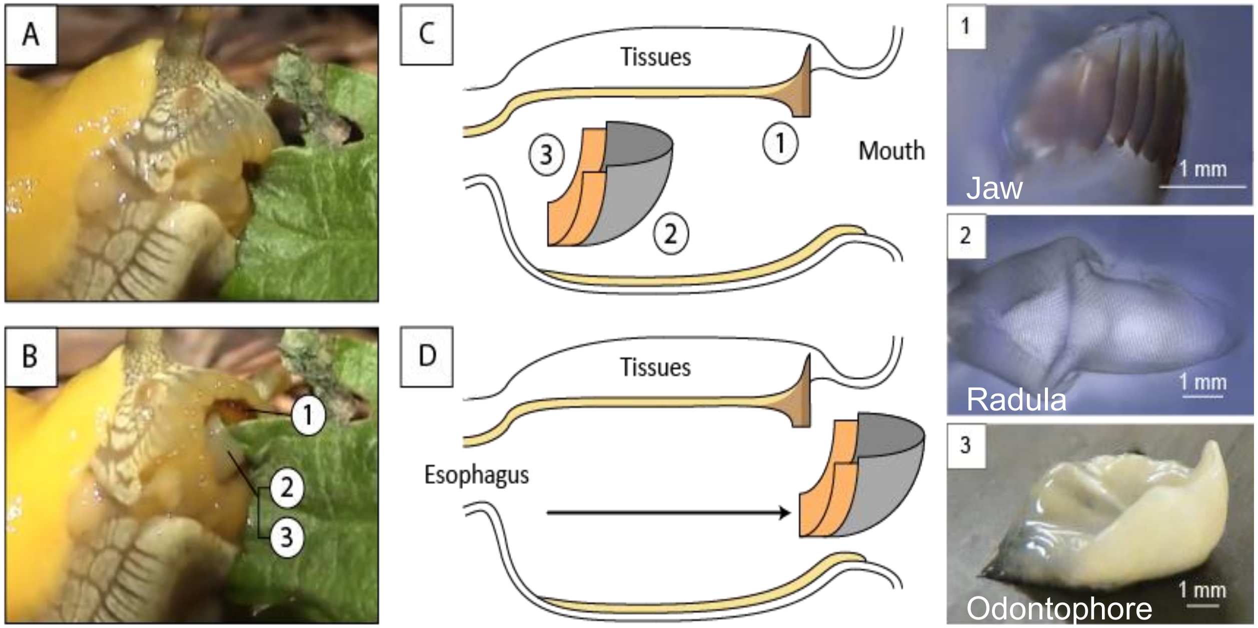
Chitin 10^6 - 10^{10} tons
Cellulose ~ 10^{12} tons

Known species

Chitin > 70%
Cellulose ~15%

The buccal mass of *Ariolimax californicus*

The buccal mass of *Ariolimax californicus*



Chitin in nature's architecture


Ferrea occa

Mineralized structure


Morpho didius

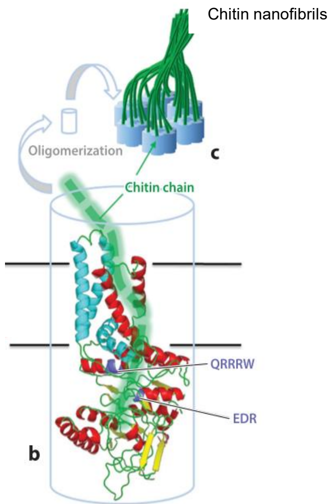
Photonic materials


Mantis shrimp

Enhance mechanical properties


Chrysina resplendens

Biogenesis of chitin-based matrices



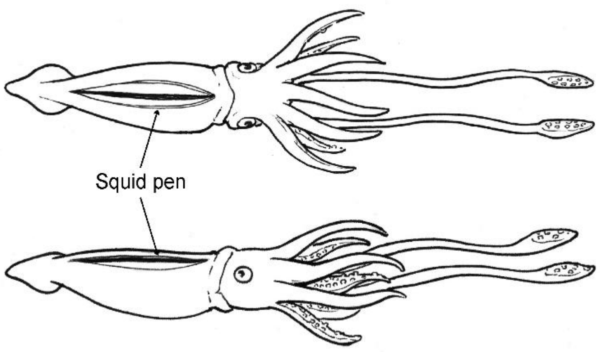
?

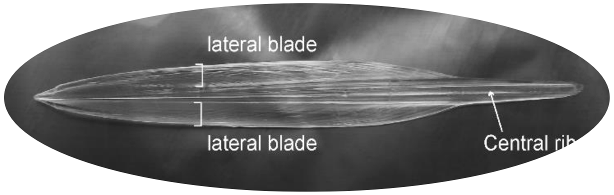
Self-assemble

image from K. Y. Zhu et al., *Annu. Rev. Entomol.* **2016**, *61*, 177.

- Mechanism of self-assembling?
- Role of proteins?
- Chemical synthesis on natural highly organized fibrous materials

Influence of Proteins on Mechanical Properties of the Squid Pen





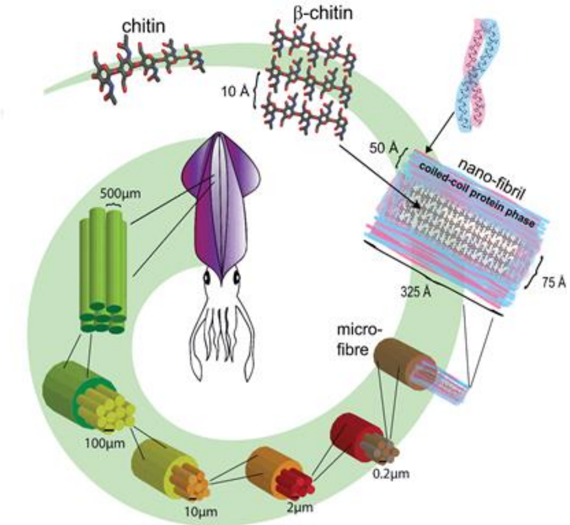
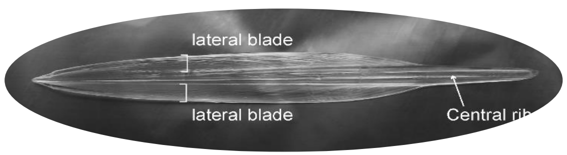


image from Fei-Chi Yang et al., *Soft Matter*, 2014, **10**, 5541-5549.
Sepioteuthis lessoniana

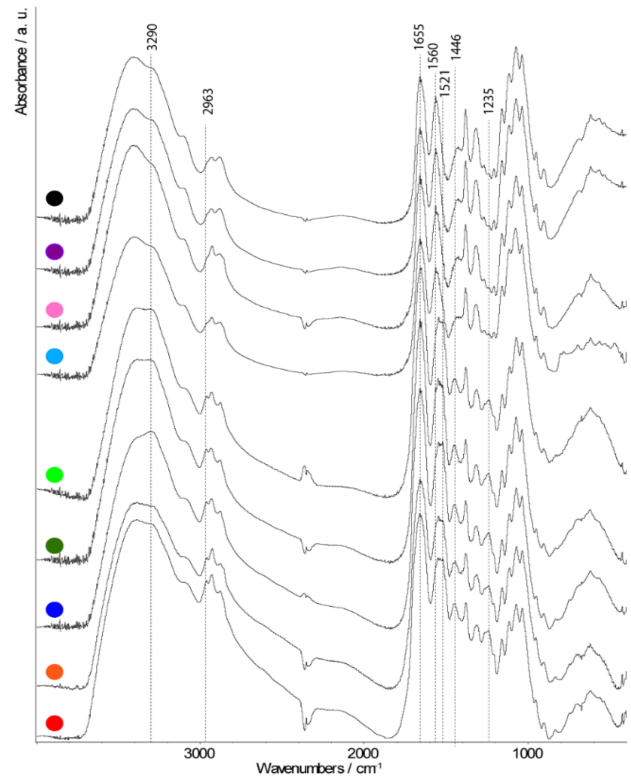
This composite material is an internal vestigial not calcified shell that acts as a support for the animal, and thus has an important mechanical role

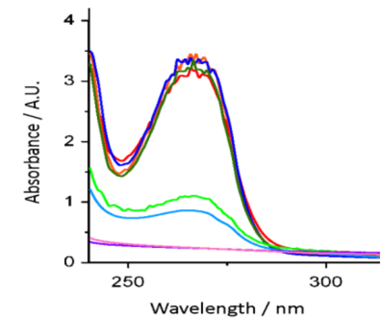
Montroni et al. Acta Biomaterialia (2020) in press

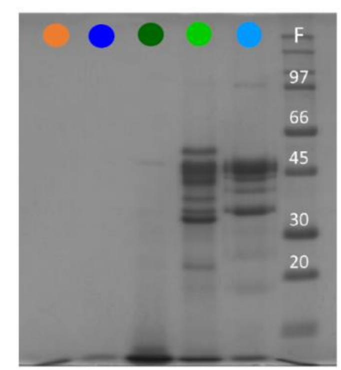
Influence of Proteins on Mechanical Properties of the Squid Pen



		weight loss / %	swelling / %
Squid pen		0*	199 ± 2
EDTA		0 ± 3	212 ± 21
Merc		0 ± 2	260 ± 20
Urea		6.3 ± 0.4	220 ± 20
Mix. 24h		40 ± 9	800 ± 100
Mix. 48h		52 ± 3	800 ± 100
Enzymes		41 ± 9	760 ± 50
NaOH		60.1 ± 0.9	450 ± 20
NaOH-dried		60.1 ± 0.9	340 ± 10







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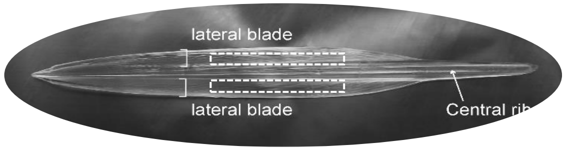
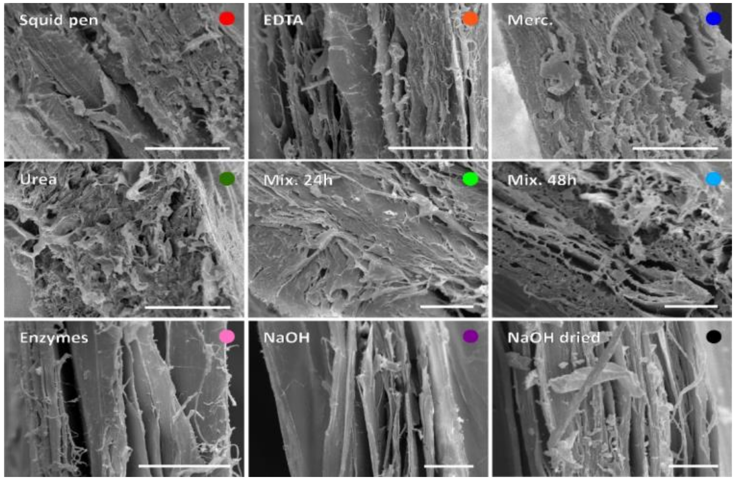
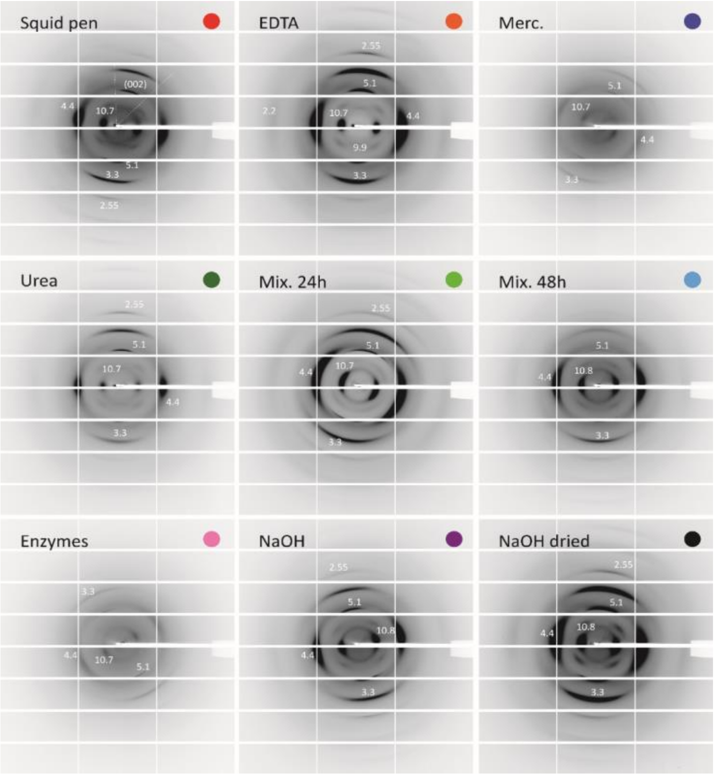
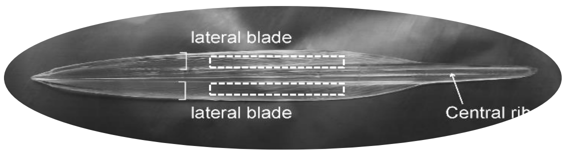
Influence of Proteins on Mechanical Properties of the Squid Pen



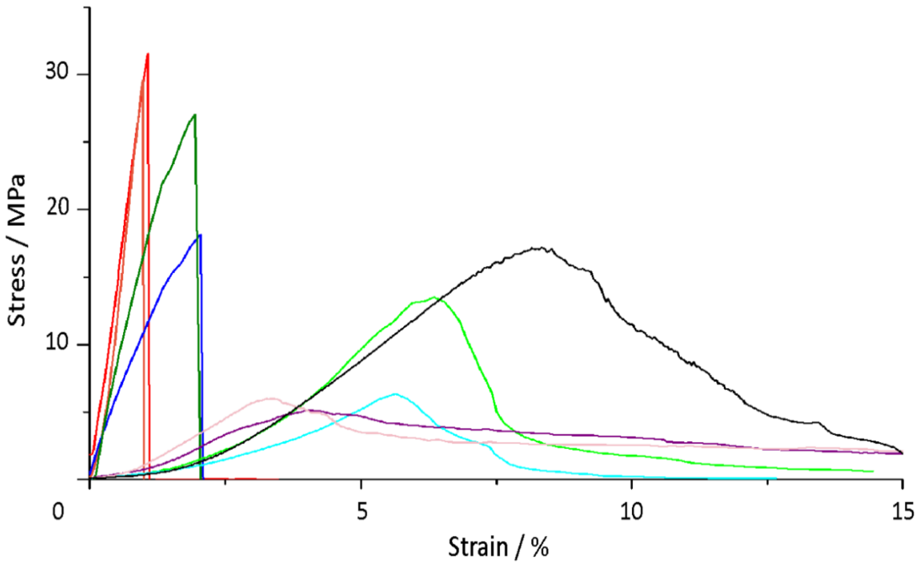




Influence of Proteins on Mechanical Properties of the Squid Pen



		σ_{max} / MPa	ε_{max} / %	E / MPa
Squid pen	red	40 ± 9	1.2 ± 0.4	4000 ± 1000
EDTA	orange	30 ± 10	0.99 ± 0.06	4000 ± 1000
Merc	blue	17 ± 8	1.8 ± 0.5	900 ± 300
Urea	dark green	30 ± 10	1.6 ± 0.6	2400 ± 400
Mix. 24h	green	11 ± 3	5 ± 2	380 ± 80
Mix. 48h	light blue	6 ± 2	4 ± 2	300 ± 100
Enzymes	pink	5 ± 1	3.9 ± 0.6	190 ± 50
NaOH	purple	7 ± 2	4.3 ± 0.5	330 ± 90
NaOH-dried	black	16 ± 2	11 ± 4	250 ± 40



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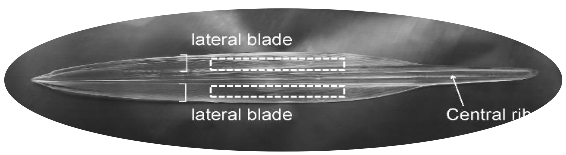

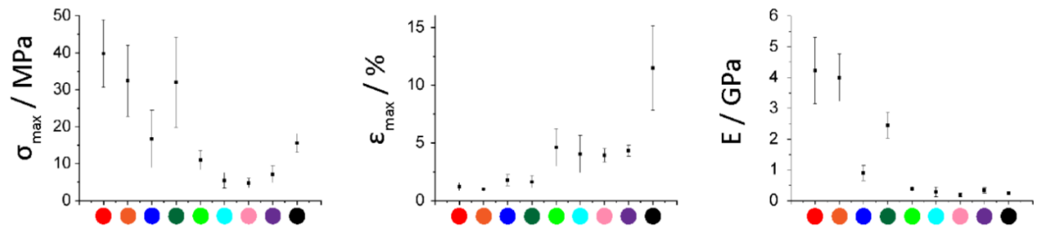

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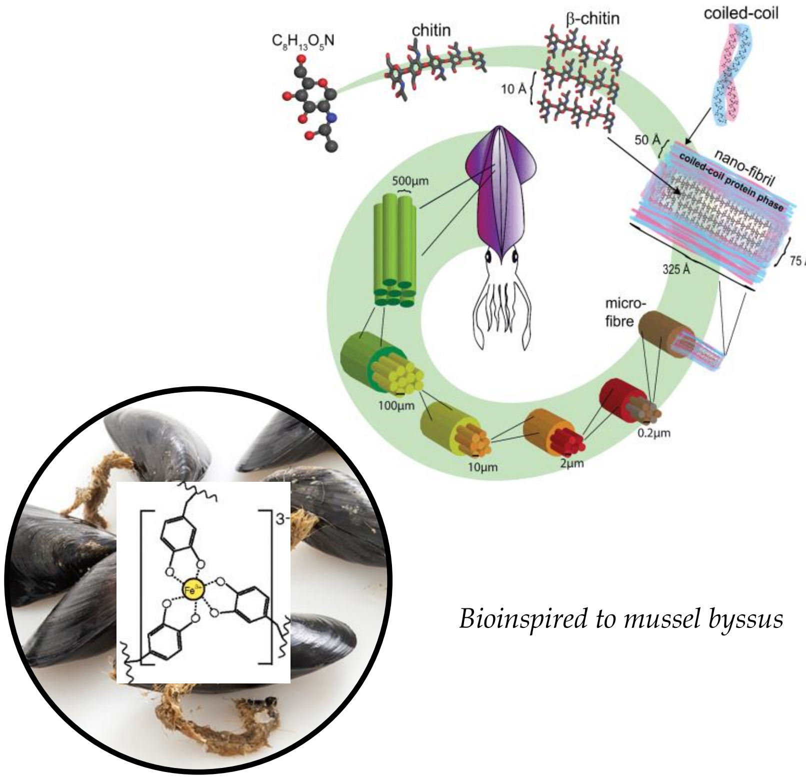
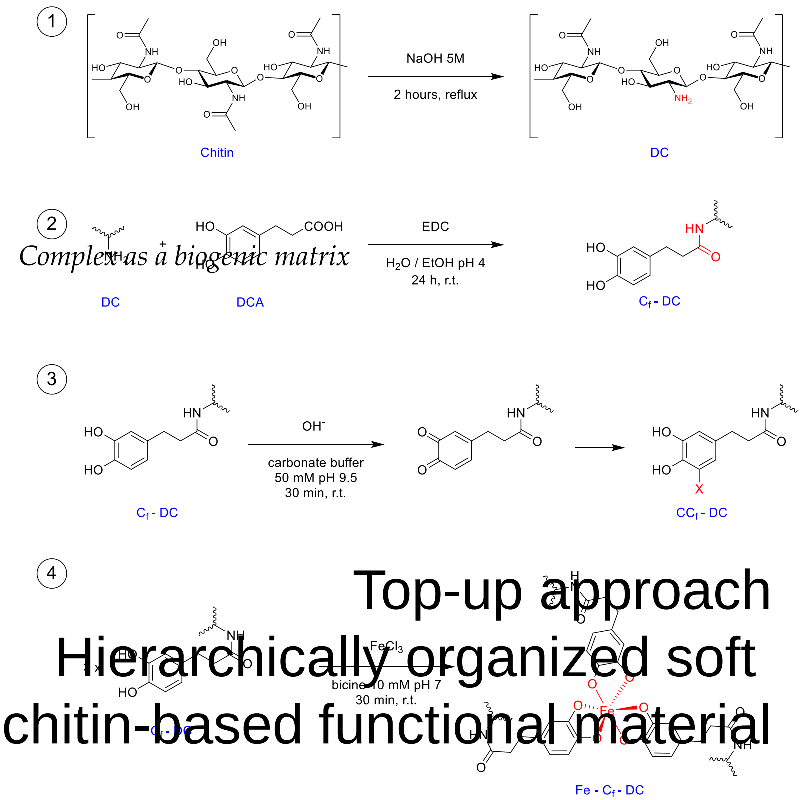
Functional chitin-based matrices



Bioinspired to mussel byssus



Complex as a biogenic matrix

Top-up approach

Hierarchically organized soft chitin-based functional material

Montroni et al. Carbohydrate Polymers (2021) 251,11698.

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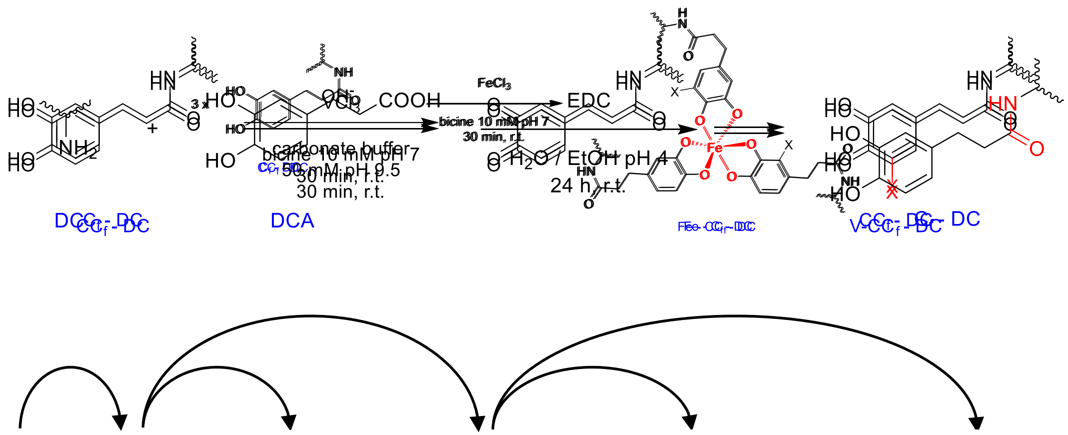
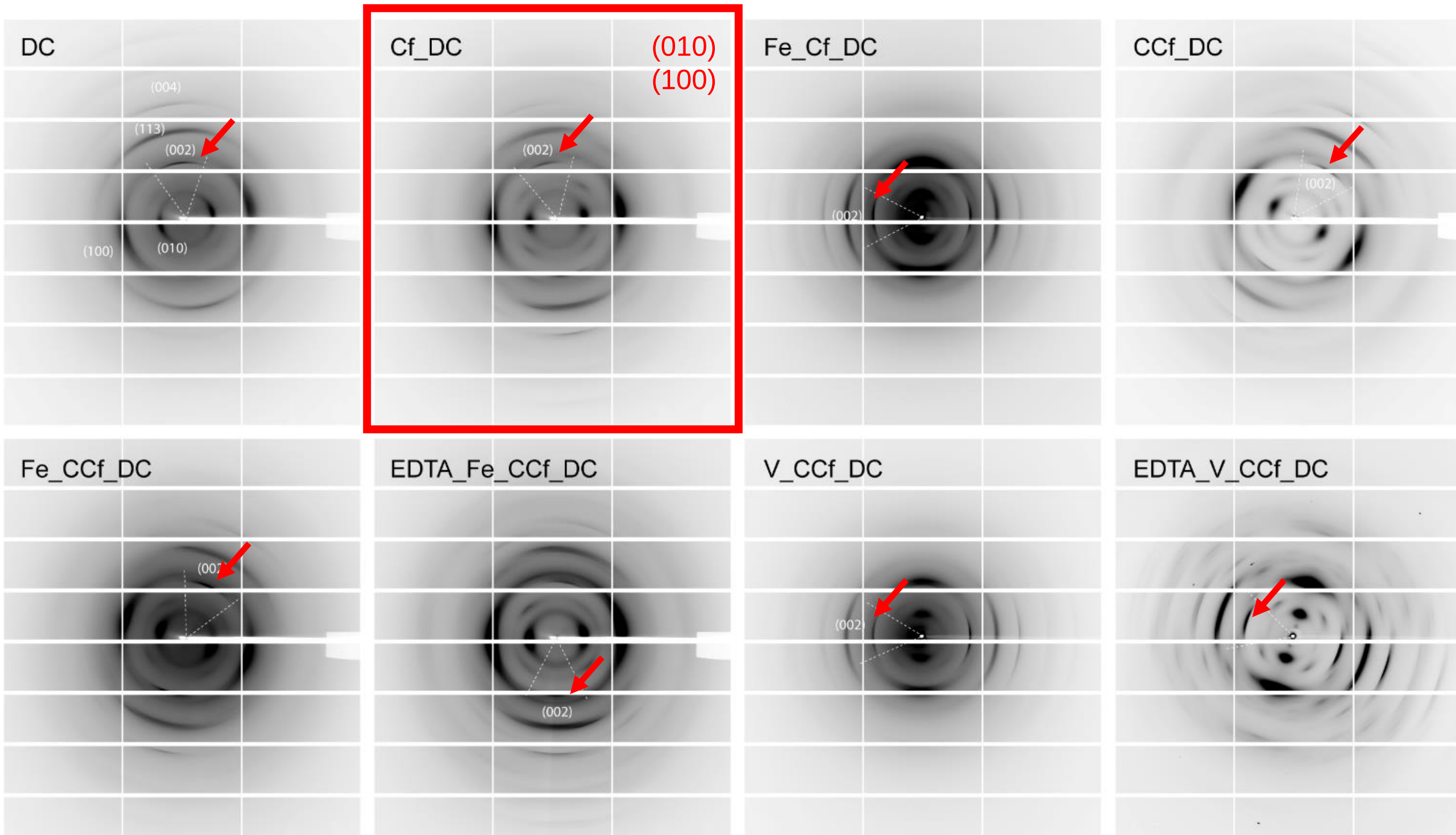
Functional chitin-based matrices

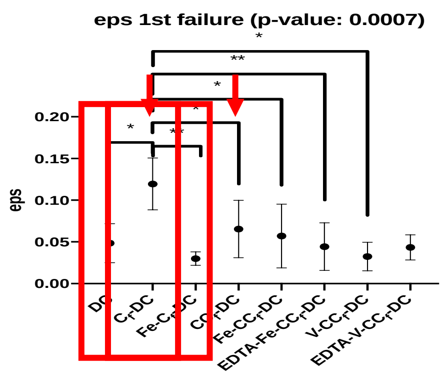


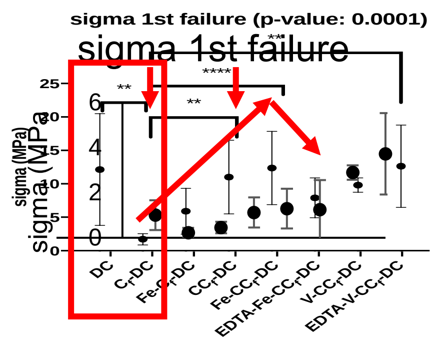
DC

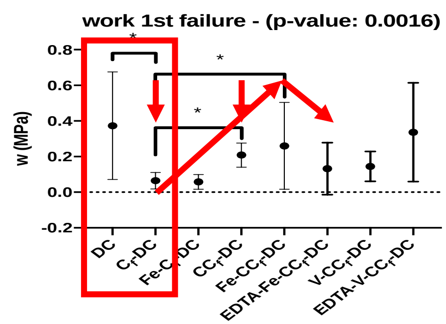
Synchrotron X-ray diffraction

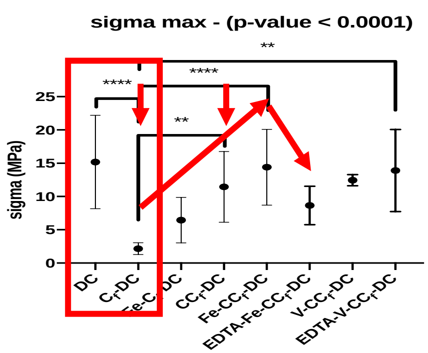


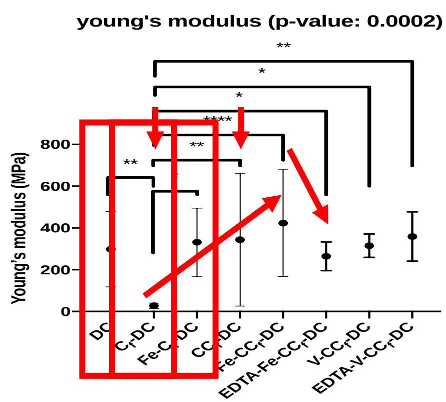
Uniaxial tensile tests











Normalizad on DC

V-CC_f-DC vs. DC

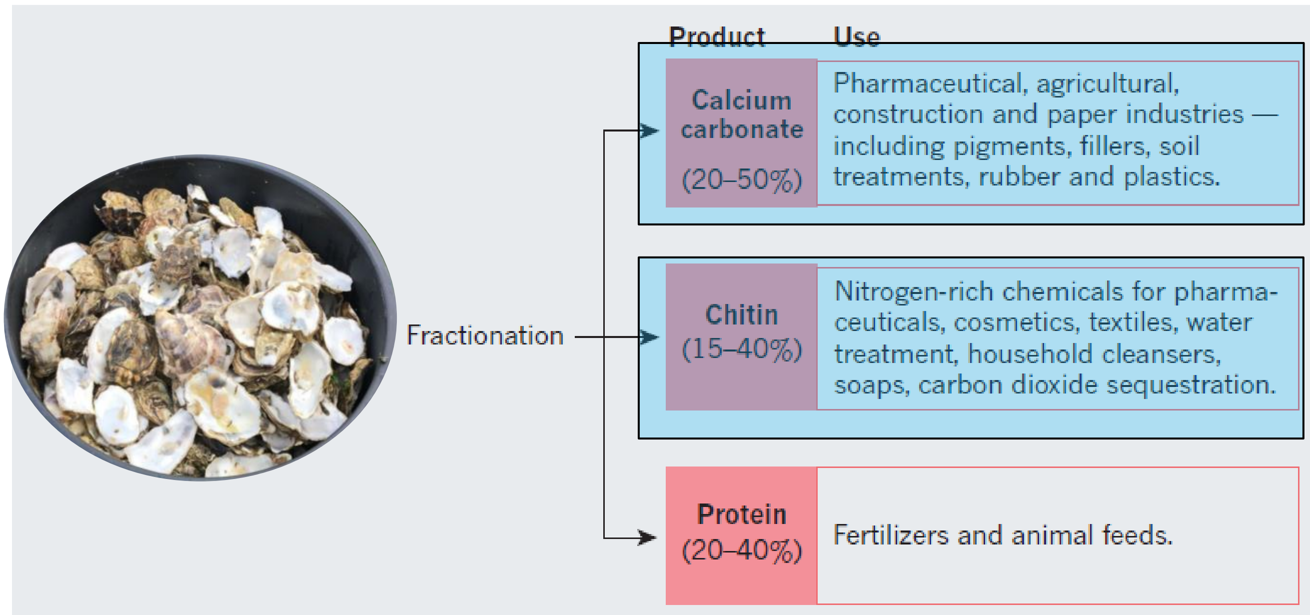
3 x Young's modulus & $\sigma_{1st\ failure}$

1/5 x σ_{max}

2 x Work $_{1st\ Failure}$

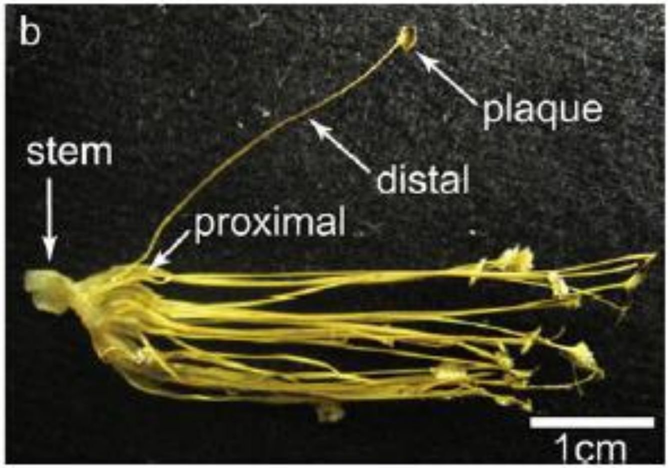
1/3 $\varepsilon_{1st\ Failure}$

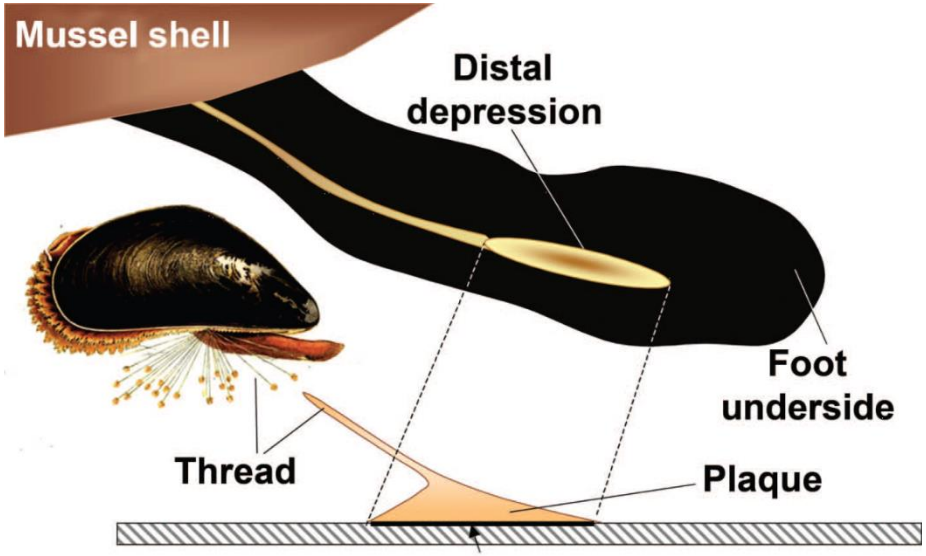
Shells contain three primary chemicals that have many industrial uses.



Developing a sustainable way to refine and give value them could add billions of dollars to the bioeconomy.

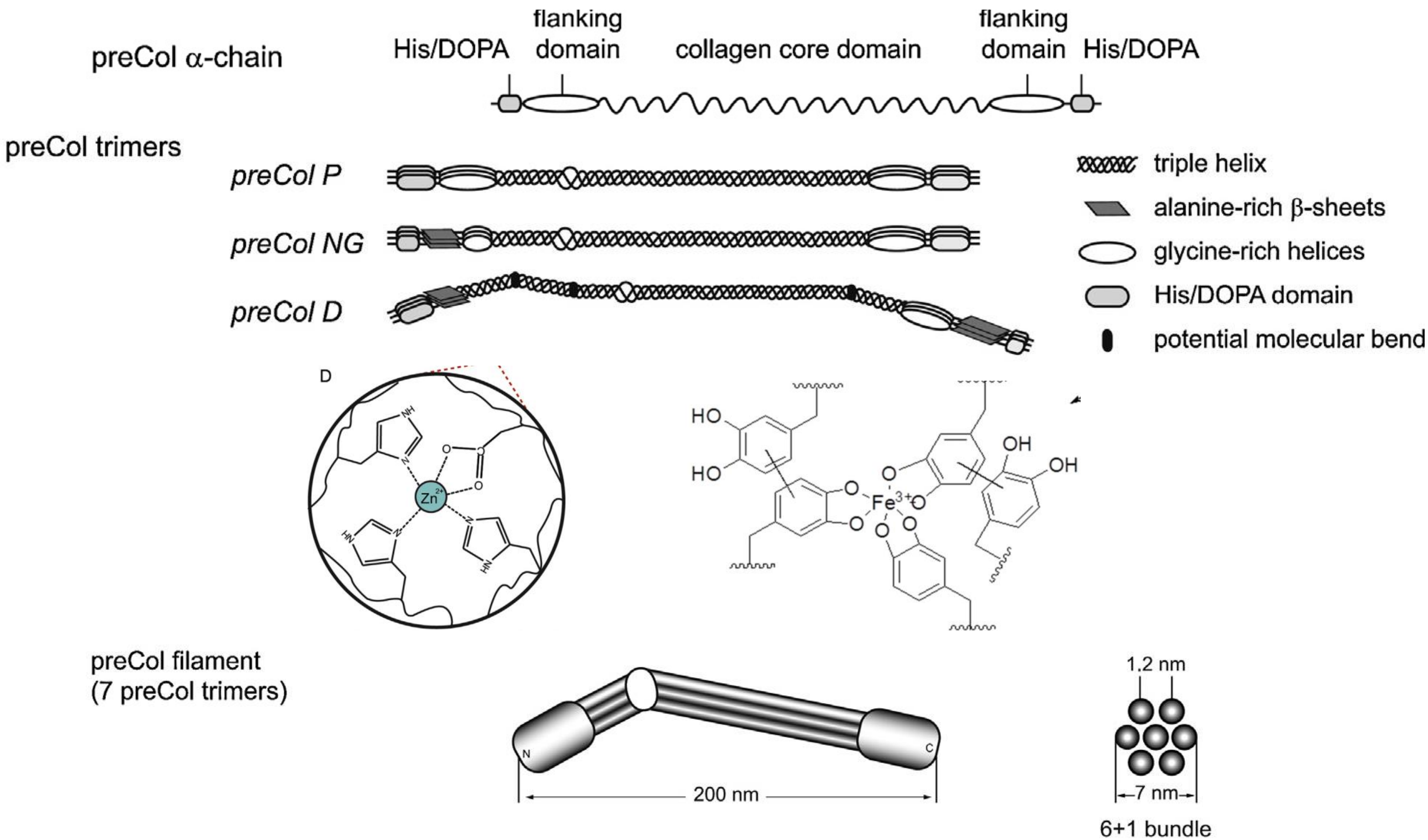
What is the byssus?





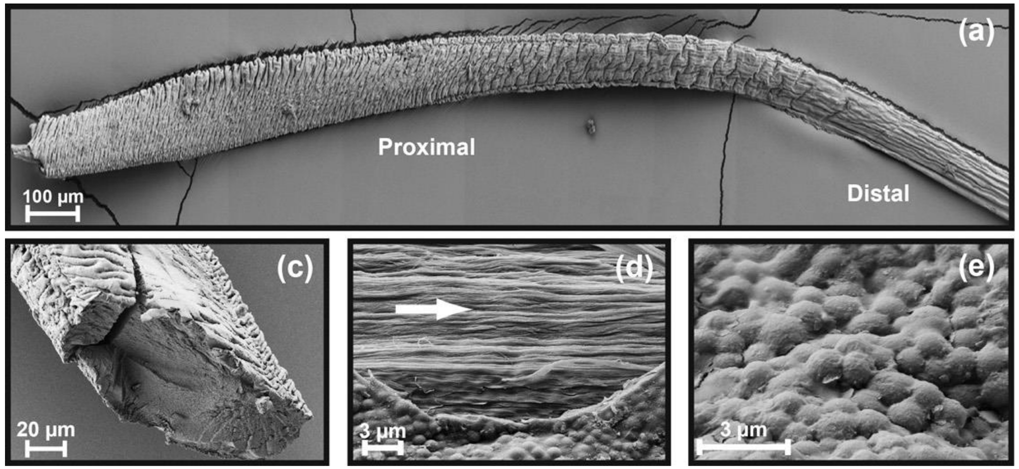
In 2 to 5 minutes proteins are deposited into the ventral groove as a liquid-crystalline protein mixture. These soluble precursors are stable in the acid pH (≈ 5) of the mussel's foot but solidify instantaneously when they are secreted outside at the basic pH (≈ 8) of the sea.

Byssus thread composition

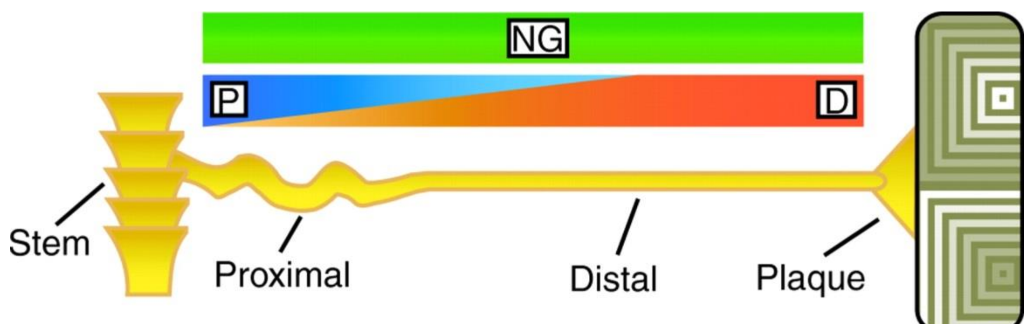


Model of the molecular structure of preCol-D, -P and -NG trimers

Byssus thread preCols distribution



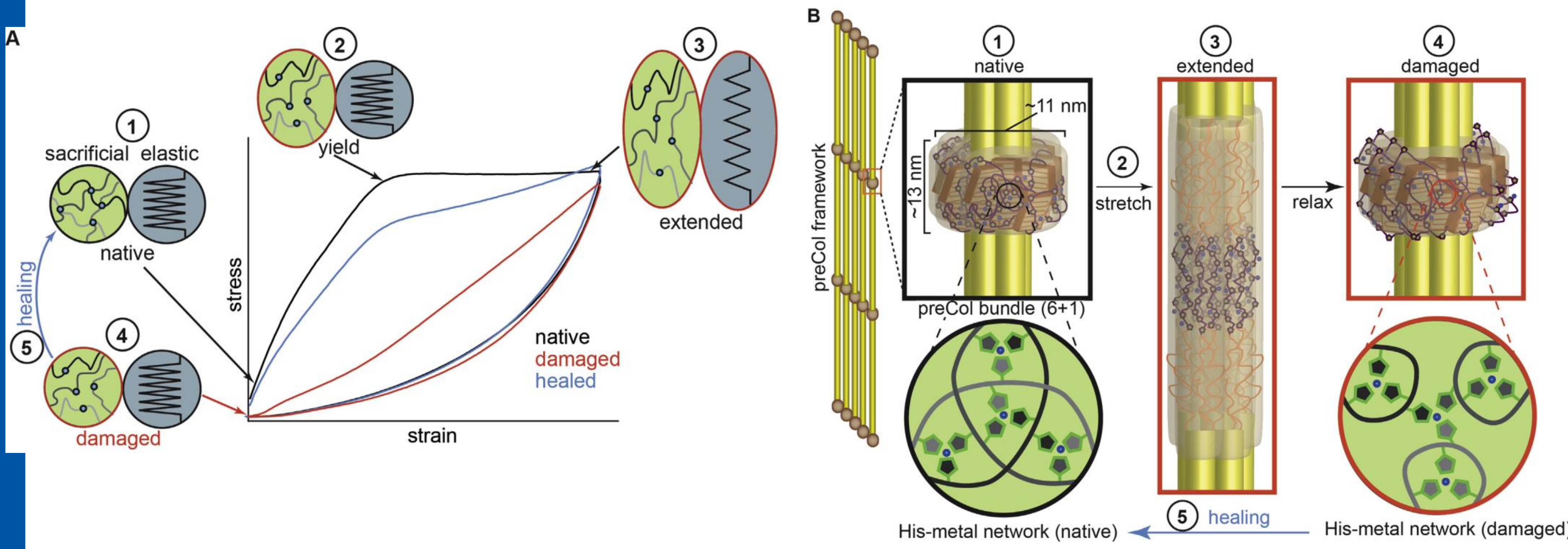
SEM images of mussel byssus of *Mytilus galloprovincialis*. (a) transition from proximal portion to the distal one; (c) cross section; (d) thread core; (e) surface structure of the byssal thread exhibiting a granular morphology;



Schematic of an isolated byssal thread showing a gradient in the relative composition of preCol variants D, NG and P.

Byssus mechanical properties

(2) sacrificial network begins to rupture. (3) unfolding of the elastic framework. (4) Unloading leads to refolding. (5) the sacrificial metal coordination network recovers.



(A) Schematic illustrating changes in the preCol sacrificial network and elastic framework at specific stages of mechanical testing. (B) Schematic model at the protein level indicating changes in protein cross-linking and secondary structure at the same stages 1–5 indicated in part (A).

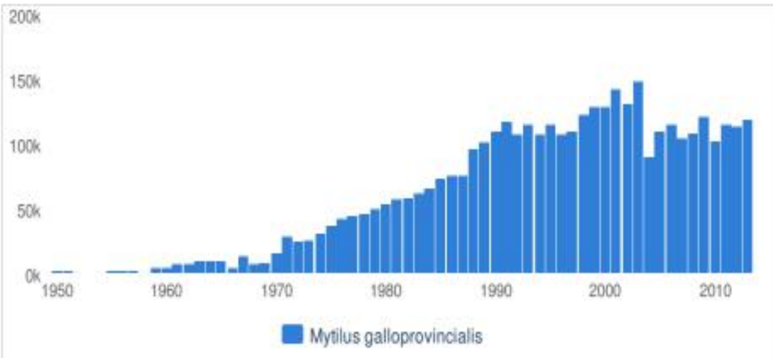
How it can be used?

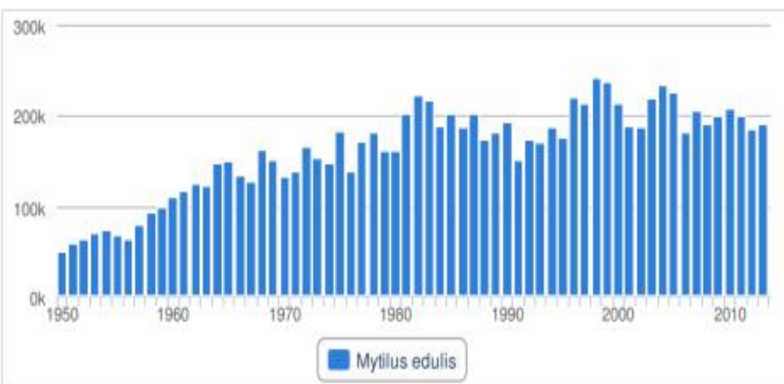
The sea silk – Threads from *Pinna nobilis*

The fiber was mentioned in various Greek, Egyptian, and Roman) Sea silk is finer than the true silk produced from silkworm cocoons.

The chasuble of St. Yves in Louannec (woven of byssus/sea silk)

Byssus from mussel. Is it a waste material?

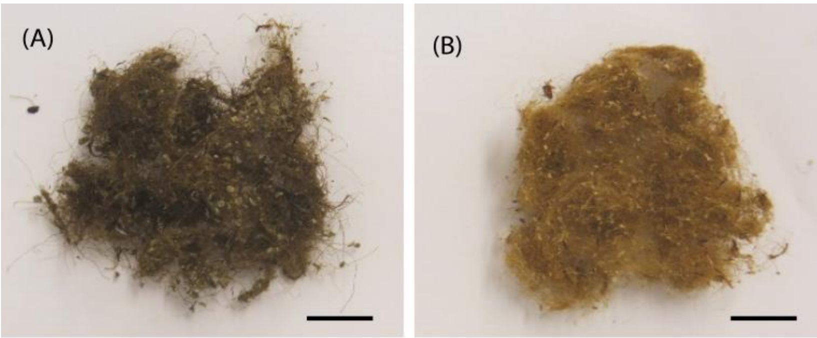


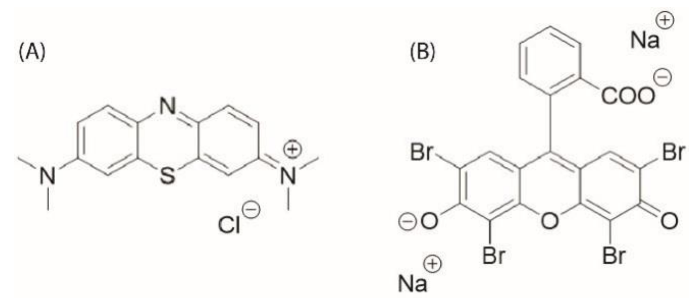


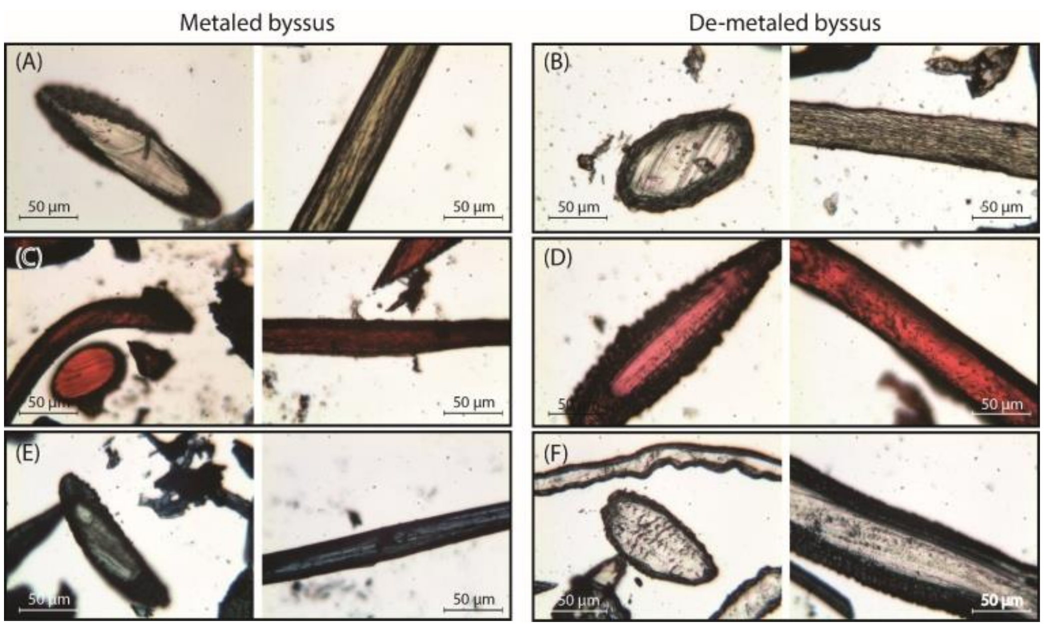
(*left*) Global aquiculture production of mussels (tonnes per year) and distribution production in Europe. Source: FAO FishStat. (*right*) Camera pictures of farming of mussels.

How mussel byssus can be used?

Water remediation







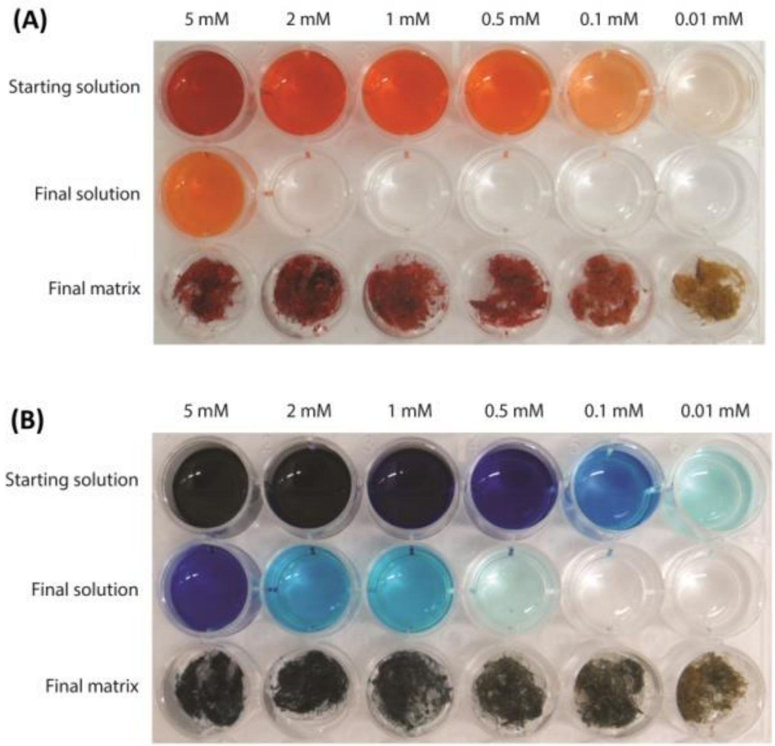
Optical microscopy images of byssus thread section of 40 mm.

On the left, metaled byssus threads, on the right, de-metaled byssus threads. (A) and (B) were control samples, (C) and (D) were treated with EosY 1 mM and (E) and (F) were treated with MB 1 mM.

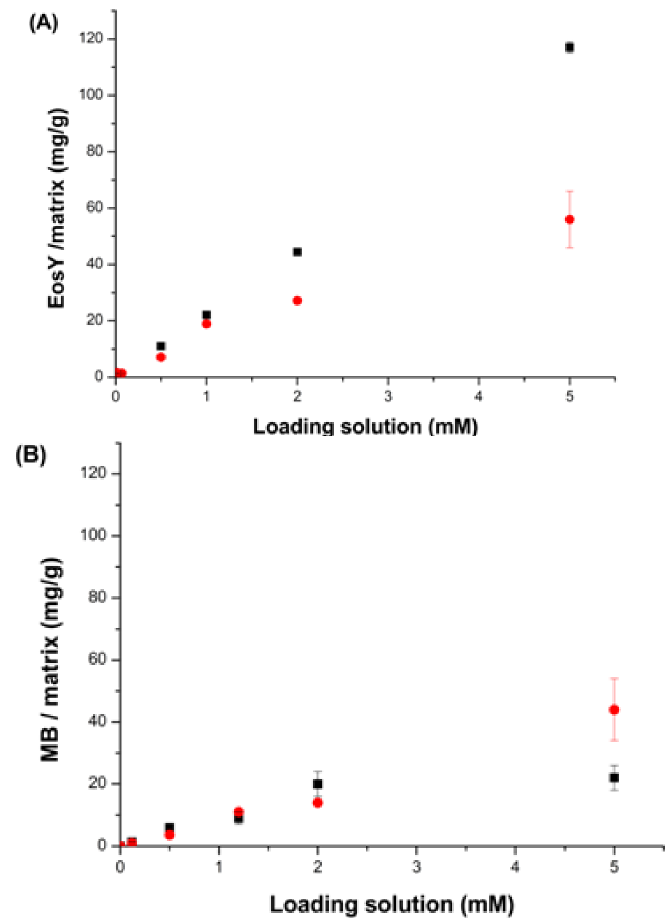
For each condition is present a longitudinal section of the thread and a transversal one.

How mussel byssus can be used?

Water remediation



Camera photographs illustrating the dye removal experiments using (A) de-metaled byssus on EosY solutions, and (B) native byssus on MB solutions.



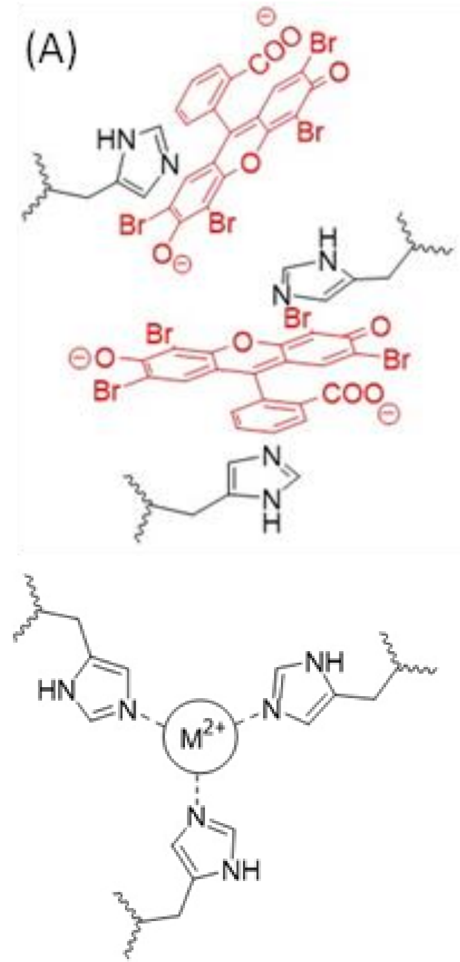
Dye removal of (A) EosY and (B) MB. In red are reported the data collected using native byssus and in black those using de-metaled byssus.

How mussel byssus can be used?

Water remediation

Langmuir, Freundlich and Dubinin Radushkevich D-R) isotherm parameters for the adsorption of MB and EosY on byssus threads

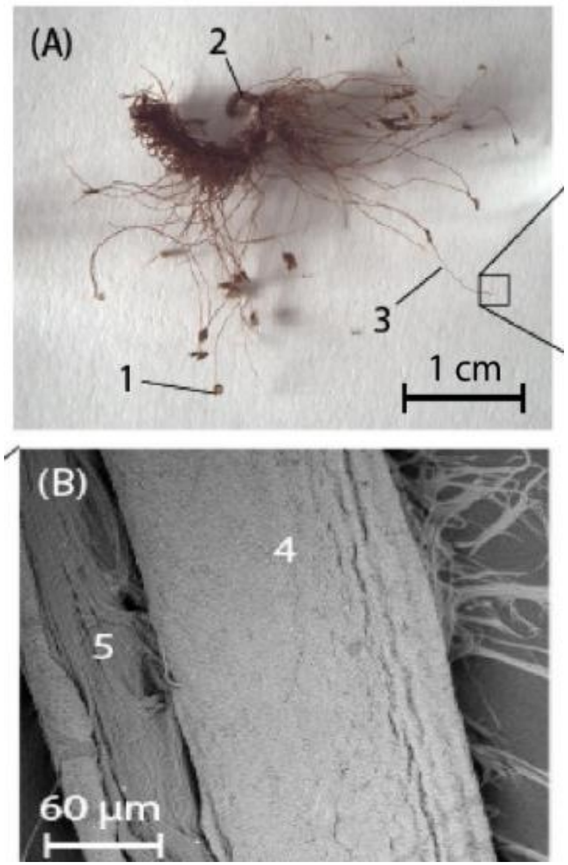
	EosY		MB	
	native byssus	de-metal. byssus*	native byssus	de-metal. byssus
Langmiur isotherm model				
q_m / mg g^{-1}	46.7	85.5	22.6	16.3
b / L g^{-1}	0.005	0.0009	0.011	0.003
R_L	0.99	0.98	0.99	0.98
R^2	0.79	0.84	0.66	0.84
Freundlich isotherm model				
K_F / mg g^{-1}	52.3	196	35.0	21.7
n	5.7	3.9	3.8	4.8
R^2	0.88	0.95	0.95	0.98
D-R isotherm model				
q_D / mg g^{-1}	52.2	133	30.9	19.8
K_D / kJ^2 mol^{-2}	0.0053	0.0044	0.0087	0.0051
E / kJ mol^{-1}	9.7	10.7	7.6	9.9
R^2	0.79	0.97	0.83	0.87



The adsorption isotherm model show that the best experimental data fitting occurs using the Freundlich isotherm model.

How mussel byssus can be used?

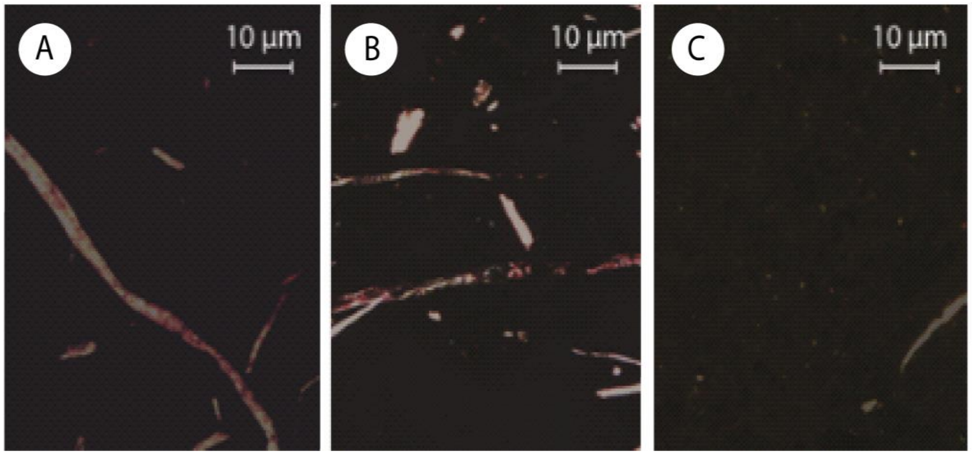
Functional porous matrices



DISSOLUTION

Forty-four denaturating conditions were tested

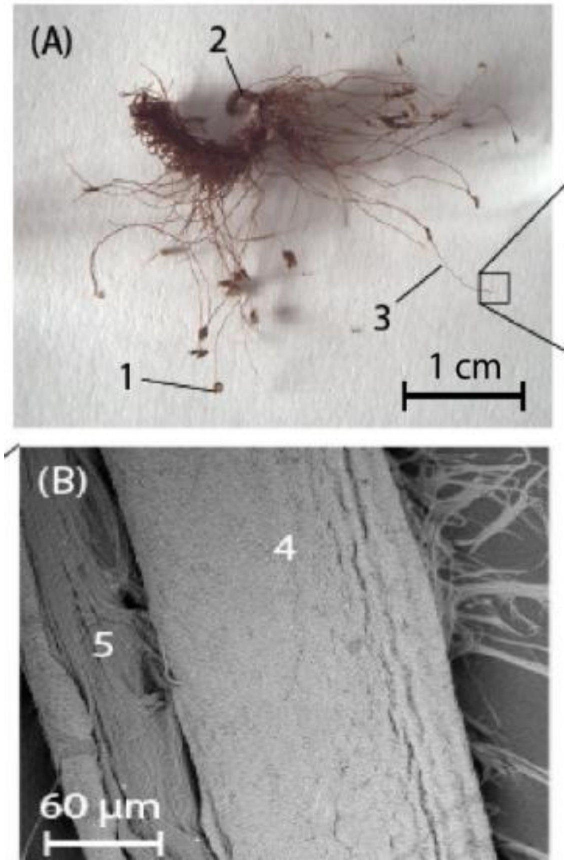
fibrous material



Polarized light microscopy images of the suspension obtained from the reaction at different times: 3 h (A), 6 h (B) and 18 h (C). The samples where stained with Picrosirius Red stain to enhance the birefringence of the fibers.

How mussel byssus can be used?

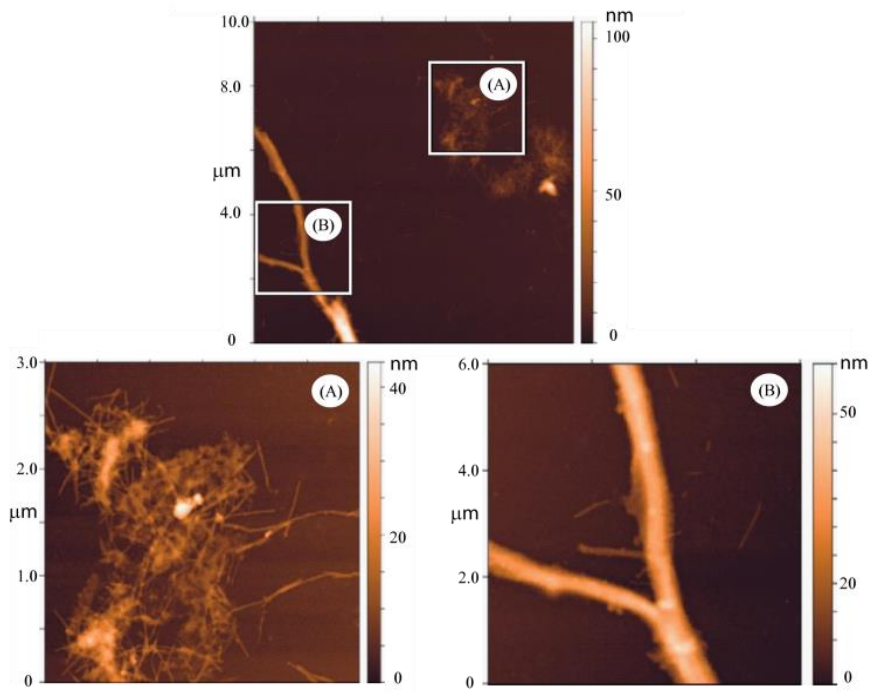
Functional porous matrices



Forty-four denaturating conditions were tested

DISSOLUTION

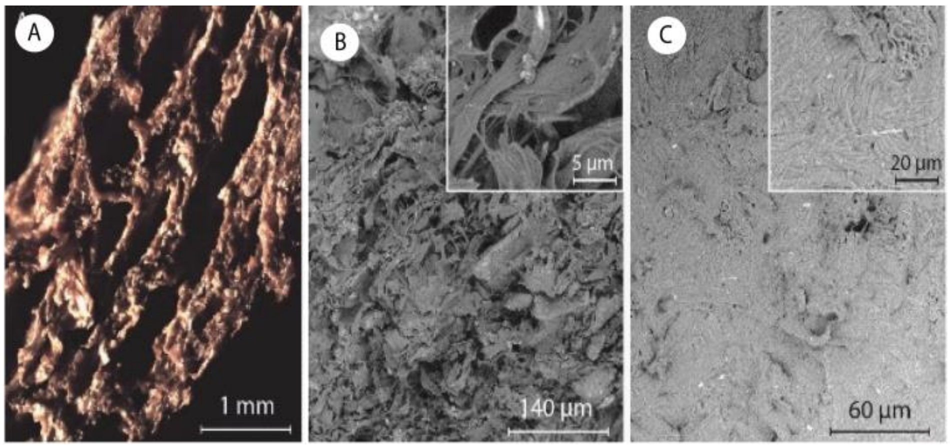
fibrous material



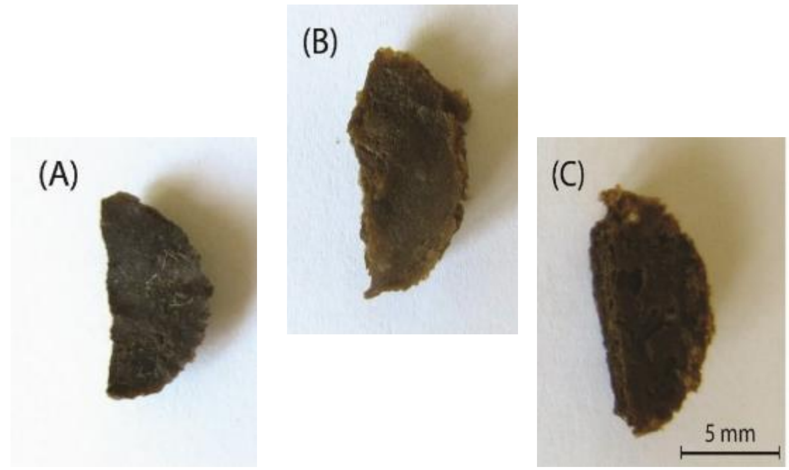
AFM images of precipitate obtained from degraded byssal threads.

How mussel byssus can be used?

Functional porous matrices



(A) Optical image of a byssus matrix transversal section. (B) SEM image of the byssus matrix section. (C) SEM image top view.



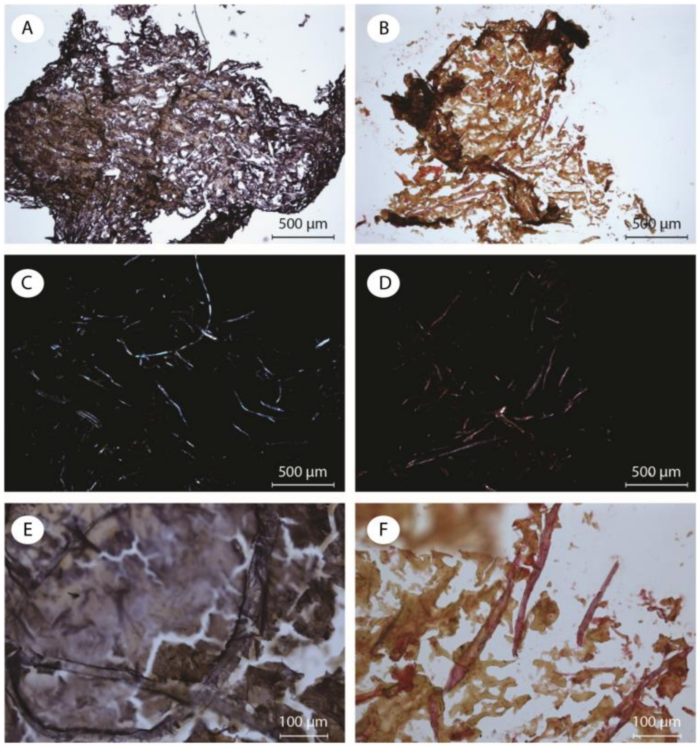
(A) the metal-treated matrix, (B) the matrix after the synthesis and (C) the EDTA-treated matrix.

	Fe	Zn	Cu
EDTA-treated matrix[1]	0.830 ± 0.004	0.070 ± 0.004	0.039 ± 0.002
Native matrix[2]	1.270 ± 0.005	0.064 ± 0.005	0.059 ± 0.002
Metal-treated matrix[3]	0.666 ± 0.007	5. 699 ± 0.007	6.299 ± 0.003

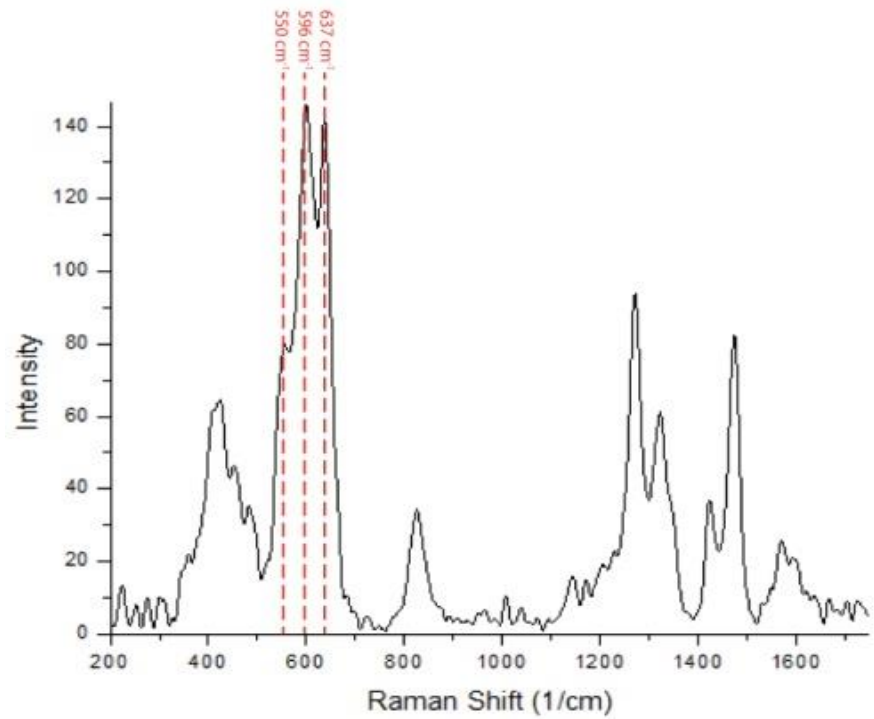
Metal content in the different matrices (mg/g).

How mussel byssus can be used?

Functional porous matrices



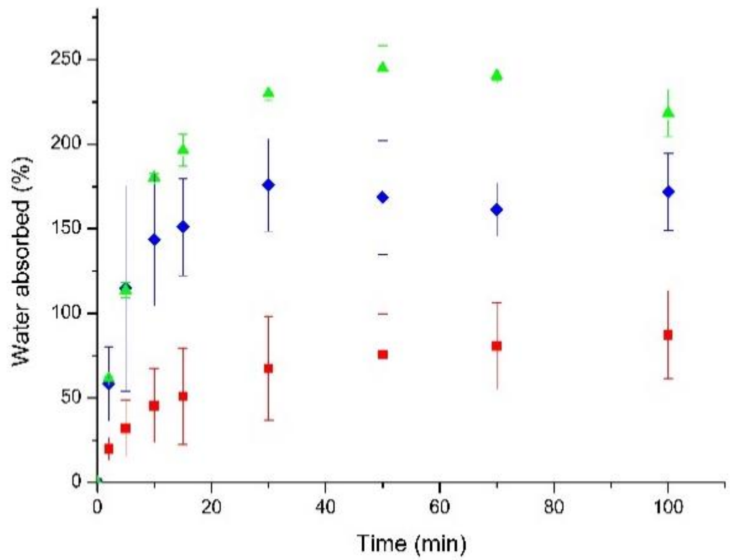
Matrix sections stained with NBT (on the left) and Sirius (on the right). A and B stained sections of the matrix. C and D are the same image observed using polarized light, to enhance the birefringent fibers. E and F are higher magnificence on the fibers



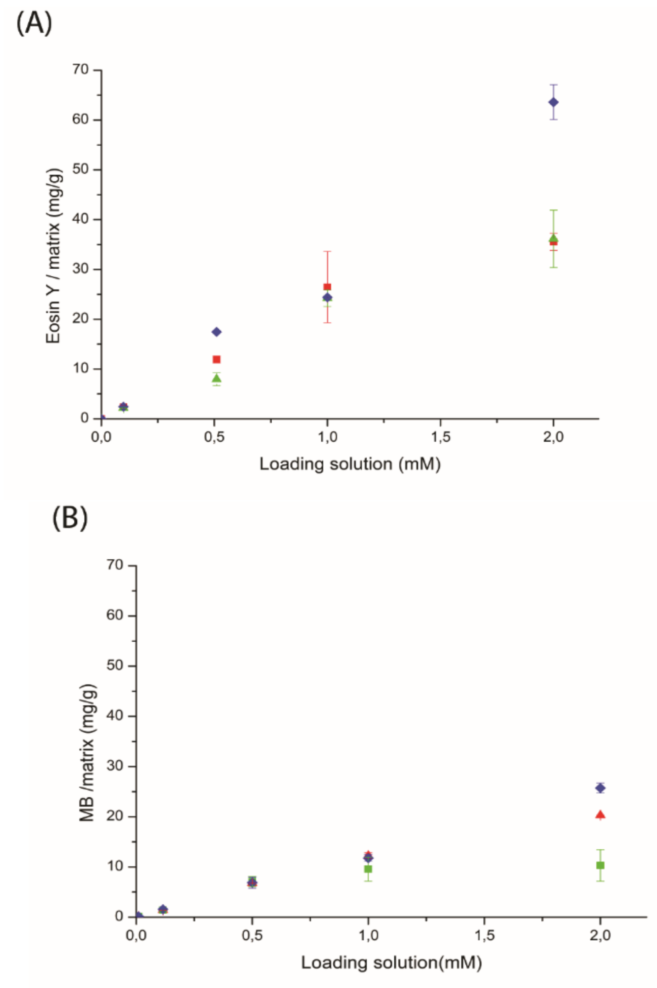
Raman spectra of a byssus matrix VCl_3 treated. In red are assigned the signals of the bi-dentate chelation of the metal ion by the phenolic oxygens of DOPA.

How mussel byssus can be used?

Functional porous matrices



Hydration kinetics.

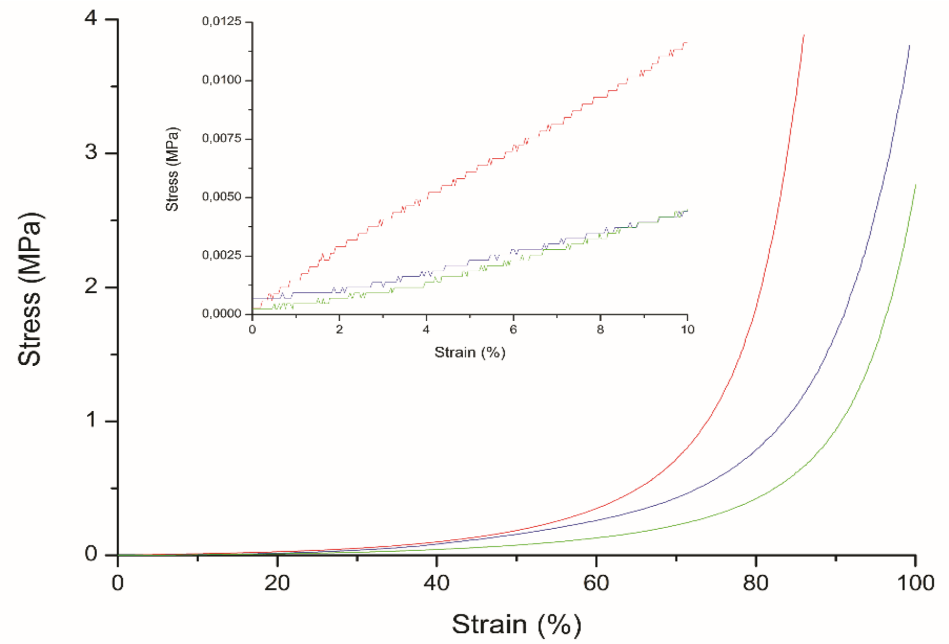


Dye loading of the three matrices at different dye concentrations. (A) EosY solutions, (B) MB solutions.

(red) metal-treated matrix- (green) native matrix – (blue) EDTA-treated matrix.

How mussel byssus can be used?

Functional porous matrices

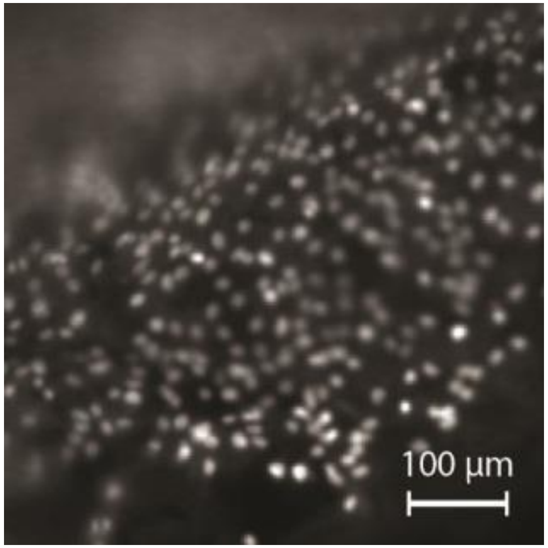


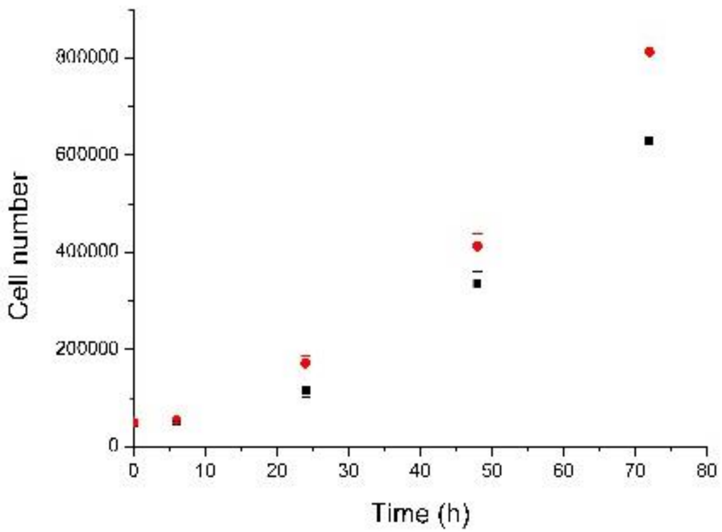
Uniaxial compression tests on the three different matrices: in red the metal-treated matrix, in green the native matrix and in blue the EDTA-treated matrix. Inset: A zoom in the 0-10% strain region.

	Stress-strain slope (kPa/%)	Strain (dens.) (%)
Metal-treated matrix[3]	1.3 ± 0.4	72 ± 8
Native matrix[2]	0.5 ± 0.1	97 ± 2
EDTA-treated matrix[1]	0.3 ± 0.1	92 ± 6

How mussel byssus can be used?

Functional porous matrices





On the left, cells grown on a byssus matrix, tagged with 4',6-diamidino-2-phenylindole and observed in fluorescence microscopy. On the right, the cells growth curve with (in red) and without (in black) the byssus matrix.

Conclusions

The chemical and physical properties of the byssus, threads or matrices, are metal ion concentration dependent

The color of byssus threads and matrices are dependent on metal ion species content.

Byssus threads can be used for diverse applications, water remediation is one of these

Byssus matrices show biocompatibility and can be prepared in blend with other biopolymers

Reusing byssus waste is a perfect example of a circular economy, particularly as byssus is a valuable biomaterial, not only does it improve the sustainability of the aquaculture industry, but it can also provide secondary economic benefits to shellfish growers and processors as well.