sustainability

Review

Cleaner production of cementitious materials containing bioaggregates based on mussel shells: a review.

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Abstract: This text proposes a bibliographic review on bioaggregates obtained from mussel shells and similar materials, evaluating the main properties altered with the use of this type of recycled aggregate in cementitious materials. The bibliographic analysis highlights the main problems and challenges of using bioaggregates, related to the presence of organic impurities and chlorides and due to the lamellar and flat shape of the grains, which impair adhesion in the transition zone. The advantages of mussel shell bioaggregates include the limestone-based chemical composition, inert and compatible with the application, and the specific mass close to conventional aggregates. Regarding the use in cementitious materials, in general, there is a reduction in workability, an increase in incorporated air, porosity and water absorption, resulting in a reduction in compressive strength. Even so, it is observed that lower replacement levels, especially in fine aggregates, make it possible to use bioaggregates in cementitious materials in different applications, such as: structural concrete, coating mortar and sealing systems. The positive points are related to the thermal insulation promoted and the reduction in density, which allows for various uses for cementitious materials with bioaggregates, such as: lightweight concrete, permeable concrete, and thermal and acoustic insulation mortars. It is concluded that the use of bioaggregates in concrete and mortars is viable, but the need for more experimental work to solve the main problems encountered, such as high-water absorption and low compressive strength, is highlighted.

Keywords: mortars, bioaggregates, mussel shell, sustainability.

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1. Introduction

Aggregates are construction materials used in the production of cementitious materials, such as concrete and mortar, in paving and earthworks or in rockfill works. Their essential characteristics are the fact that they are chemically inert, adding volume to cementitious materials and helping to control shrinkage [1]. In this context, bioaggregates emerge, natural materials extracted from plant or animal sources and used as fillers for concrete and mortars. Examples include bioaggregates of plant origin, such as açaí seeds [2] and palm kernels [3] and bioaggregates of animal origin, such as mussel shells and other similar products, illustrated in Figure 1 [4]. The advantage of using this type of aggregate is the high availability of the resource and the associated low added value. The main disadvantages are the need for cleaning and impurity control treatments and the need for a grinding step or particle size adjustment. Even with this information, it is essential to highlight the need for new sources of aggregates, due to the high consumption of this material in civil construction works.

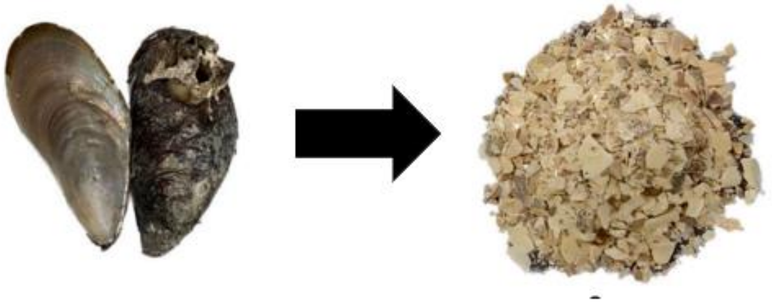


Figure 1. Bioaggregate produced from mussel shells.

It is known that aggregates are obtained from the exploitation of natural resources, which are quickly depleted and sometimes involve the removal of native vegetation, in areas of permanent preservation, generating a variety of conflicts of interests and implying the most acute atmospheric impact (AWOYERA; THOMAS; KIRGIZ, 2022). The annual global consumption of aggregates exceeds 50 billion tons every year, of which concrete production uses between 64 and 75% [6], the majority of which comes from rivers, the seabed or of the restingas. In some countries, the aggregates used in the production of mortars and concrete were obtained in quarries, producing other notable impacts, destroying natural habitats, generating airborne particulates, and transforming the environment. Inexorably, the aggregate production process carried out in quarries involves mining, crushing, grinding and sieving, inevitably leading to high energy consumption, earthquakes, generation of particulates and the most undesirable aggregation of CO_2 [7].

Currently, due to the urgency of the matter, many solid wastes are being used as alternative materials in the production of mortars and concrete, especially in countries with high rates of greenhouse gas generation [8]. Some of the waste used in previous studies includes rubber to make green and clean floors and subfloors [9], construction and demolition waste, such as aggregates for permeable concrete [10], incorporation of plastic aggregates in high strength reinforced concrete beams [11] and use of agricultural waste as pozzolanic materials and aggregates [12].

In this scenario, several clear opportunities for framing new substitute materials for aggregates can leverage regional development through sustainable routes, which add value to waste, turning them into by-products. New investment opportunities, lower-cost sustainable housing, waste reduction and job creation can be generated [13]. This is the case of bioaggregates, which appear as an alternative to conventional aggregates.

In the case of bioaggregates of animal origin, it is common to analyze shells, the resistant and inedible defensive shells of shellfish [6]. These materials stand out for their origin in natural assembly processes which, analyzed using appropriate science, reveal important lessons to be imitated in deepening the life cycle [14] and are subject to recycling. These structures can present, on average, 97% polycrystalline $CaCO_3$ (calcite, aragonite) and a small biological polymeric percentage of polysaccharides (chitin), proteins and glycoproteins [15]; generally, they are discarded inappropriately, causing significant environmental impact, generating ammonia, hydrogen sulfide and other harmful gases, due to the decomposition of residual carrion, adhered to the shells, in addition to visual pollution [16], generating problems of hygiene due to the lack of sanitary control, causing the proliferation of insects and rodents, as they are often thrown on the streets, in backyards, beaches, slopes and mangroves, as shown in Figure 2 (D et al., 2023; MELAIS et al., 2023).

Figure 2. (a) Shells on the beach of Sidi Salem, Algeria; (b) Disposal of mussel shells on Recife beach, Brazil.

Another relevant factor that justifies the use of bioaggregates from shells is the high generation of this material. In 2020, aquatic food resources reached an all-time high of 214 million tons, about US$424 billion. The production of aquatic animals was more than 60% higher than the average in the 1990s, surpassing the growth of the world population, thanks to aquaculture production [12]. The high production of aquatic resources is accompanied by the high generation of shells and other waste that can be used in construction materials, such as bioaggregates, for example.

In 2022, shellfish production was around 17.7 million tonnes, making up approximately 23% of global aquaculture industry production [12]; These molluscs are bivalves of the most common species, which represent around 89% of the entire class, including mussels (sururu), oysters, pectens, scallop abalones (scallops), whelks, clams and cockles (budigão) [6]. The Sururu, for example, has a bivalve shell and its body lives inside, formed by two equal parts, called valves, which are joined by an organic ligament. The most common genera are Perna Perna and Mytella falcata (MENEZES; MARQUES; DE SOUZA, 2022), in several coastal countries such as Brazil and Spain.

Furthermore, it should be noted that in 2023, there are records from more than 40 mussel producing countries, totaling a production of more than 15 million tons of waste, of which more than 4 million are discarded at sea, with the rest being distributed in landfills. and outdoors, as illustrated in Figure 2. Due to this fact, visual pollution and the proliferation of microorganisms, insects and rodents are common [20]. Another relevant fact is that in general 88% of the mass of sururu is made up of shells, significantly impacting the generation of this material as waste (MENEZES; MARQUES; DE SOUZA, 2022). These numbers indicate the need to develop alternative solutions, as is the case with the application of bioaggregates highlighted in this research.

Another relevant point that justifies the analysis of bioaggregates from the use of shells or other animal waste is related to the value of the oceans, which should not be understood only in an economic sense, but also due to its social value. The fishing industry employs around 200 million people in capturing, harvesting and processing fish products and provides more than 17% of animal protein worldwide [21]. It is known that, mainly in coastal areas, residents and tourists consume the mollusk, being highly appreciated as seafood and being an important source of protein. However, the high demand for these foods causes the shells to be discarded incorrectly in several coastal areas, as seen in Figure 2.

In addition to the high number of generations of this residue, another important point that justifies international scientific interest is the fact that mollusc shells present resistance properties and potential for the formation of nucleation points, improving the transition zone between matrix and aggregate [13]. Therefore, studies using this type of bioaggregates are becoming increasingly common. In this context, the objective of this research is to carry out a bibliographical review on the use of bioaggregates of animal origin in cementitious materials, proving the potential use of this material in the production of concrete and mortars. Mainly works using mussel shells or similar materials will be evaluated.

2. Bioaggregates obtained from mussel shells:

As discussed in the introduction, bioaggregates of animal origin mainly include mollusk shells, such as mussels, or similar materials. This section will discuss the main information about this type of material when applied to cementitious materials.

2.1. Bibliometric analysis:

A bibliometric analysis was carried out using the Scopus database. The key words used in the research were mussel AND shell AND mortar OR concrete OR aggregate. Through this information it was possible to find 104 documents, published until 2024, as indicated in Table 1. It is clear that the topic gained more prominence after 2011, when the number of publications on the subject grew. However, the number of works is still very low when compared to other more relevant topics, such as recycled aggregates or pozzolanic materials. It is hoped that this review will help to increase the number of works on this topic.

Table 1. Bibliometric analysis of articles on bioaggregates of animal origin.

Year	1963 – 2000	2001 – 2010	2011 – 2020	2021 – 2024
Publications	8	11	48	37

Figure 3 shows the map of correlated words. Some important information is observed, such as: the main applications of this type of bioaggregates, in cement, concrete, mortars and/or coating mortars; the main controlled properties of materials, such as: mechanical properties (compressive strength, tensile strength in flexion), thermal insulation, water absorption and particle size distribution; and the main information about the materials used, such as the fact that mussel shells are based on calcite or calcium carbonate. This information will be taken into consideration in the subsequent topics of the bibliographic review and in the discussion of the most relevant information about bioaggregates of animal origin.

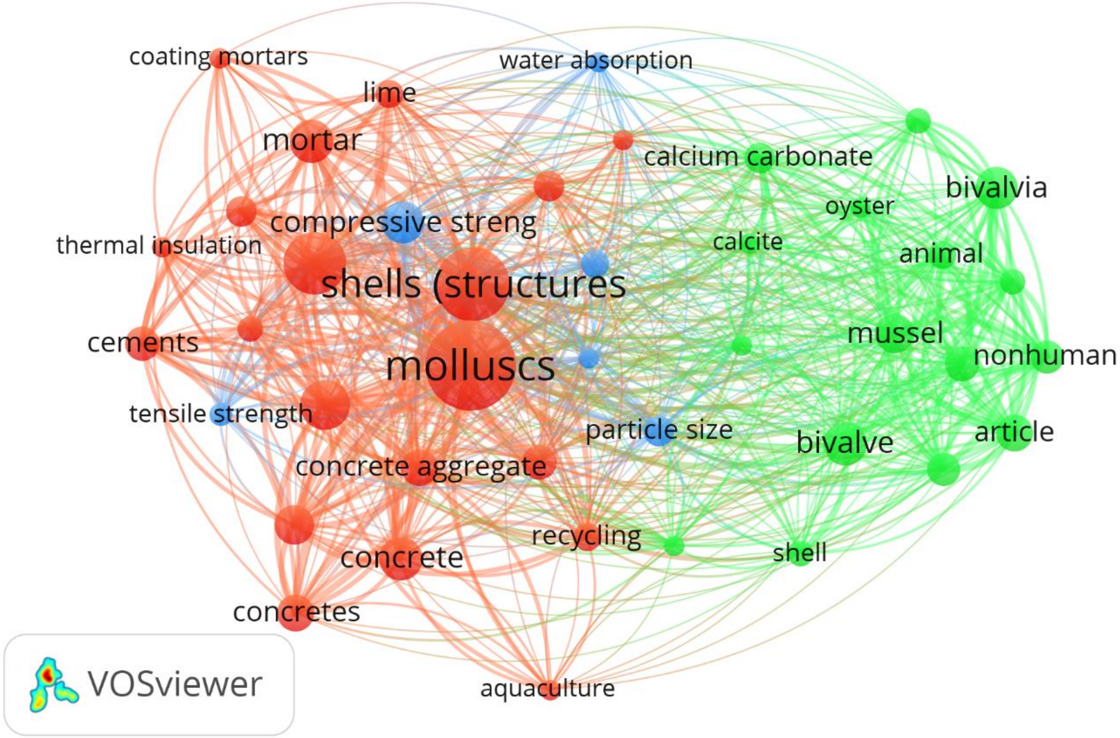


Figure 3. Bibliometric analysis of bioaggregates of animal origin.

Regarding the origin of the countries of the publications highlighted in this bibliometric analysis, the following stand out mainly: Spain, with 18 publications; Malaysia with 12 publications; China with 8 publications; and countries such as the United States of America, Italy, France, Chile and Denmark, with 4 publications in each country. It is observed that the geography of these studies is well divided, but other countries with an extensive maritime region do not stand out in this scenario. It is hoped that this literature review will help disseminate relevant information about studies on bioaggregates obtained from mollusk shells or similar materials.

2.2. *Physical and Chemical properties of mussel's shells:*

Physical properties that are important in evaluating the applications of shells as bioaggregates, due to their influence on the mechanical strength and durability of concrete and include specific mass (SM), maximum characteristic dimension (DCM), fineness modulus (FM), surface area and moisture content. Table 2 presents a summary of these properties, extracted from different bibliographic bases.

The specific mass of the bioaggregates presented in Table 2 is lower than that of conventional aggregates or that of Ordinary Portland cement (OPC), in many studies [22,23] since values for OPC vary between 3.00 – 3.10 g/cm^3. Bioaggregates, on the other hand, have a more variable specific mass, in a range between 1.85 and 2.82 g/cm^3, although there is research that presents bioaggregates with values greater than 3.00 g/cm^3. This highlights a tendency to reduce the density of cementitious materials, promoted by mussel shells and similar materials.

Regarding the specific surface area of bioaggregates, this factor is directly related to the size of the shells and the grinding process. These factors significantly affect the size of the shells. Some values found were: 1.61 µm and 13.93 µm, for wet and dry grinding, respectively [24]; 6.27 µm and 10.22 µm under the same grinding conditions [25]; and average values of approximately 23.97 µm in the dry grinding of cockle shells, a species similar to mussels [26]. These values, added to the information present in Table 2, highlight the variation in the material's properties, related to heterogeneity as it is a natural material.

It is important to highlight that, in the case of shell ash, in general, the particles are finer than ordinary Portland cement, therefore, the fineness of the mixed cement increases with the level of OPC replacement. The thinner the cementitious material, the greater the surface area, which consequently increases the rate of reactivity with other substances, creating a binder with appreciable strength and surface area [27]. In this type of situation, the material is used as a supplementary cement source. However, it should be noted that the use of shells as bioaggregates requires particle size compatible with replacement, instead of fine or coarse aggregate.

Table 2. Physical properties of shell bioaggregates

Bioaggregates	Especific mass (g/cm³)	DCM (mm)	FM	Surface area (mm)	Moisture content (%)	Researches
Cockle	3.03	-	-	13.56 – 23.97	-	[27]
Cockle	2.82	-	-	-	0.15	[28]
Cockle	2.30	4.75	2.50	-	0.50	[6]
Cockle	2.50 – 2.64	-	4,40 – 4.57	-	-	[8]
Mussel	3.01	-	-	29.87	-	[27]
Mussel	2.57	4.75	3.11	-	1.73	[4]
Mussel	2.62 – 2.73	-	1.90 – 5.38	-	-	[8]
Mussel	2.40	5.00	-	-	3.52	[16]
Mussel	2.65	4.00	4.64	-	2.56	[7]
Oyster	3.09	-	-	1.61 – 58.53	-	[27]
Oyster	-	-	-	25.1 – 46.1	-	[25]
Oyster	2.65				0.36	[28]
Oyster	1.85 – 2.48	-	2.00 – 6.50	-	-	[8]
Oyster	2.42	4.75	-	-	-	[29]
Oyster	2.48	5.00	2.80	-	2.90	[30]
Oyster	2.10	4.75	2.00	-	-	[31]

This differs from applications that propose the use of mussel shell ash as supplementary cementitious materials. In this context, it is more interesting to observe the DCM and FM values. The values shown in Table 2 are compatible with the application of fine aggregate, generally to coarse or medium sand. Furthermore, it is worth highlighting that the moisture content values identified in Table 2 are obtained after the material washing and grinding process. Before that, due to the high content of organic impurities, the associated humidity is much more excessive and should be avoided. This highlights the need for treatments to purify bioaggregates.

In the main bioaggregates used in previous studies, such as: oyster shell [32]; scallop shell [33]; mussel or sururu shells [20,34]; cockle shells and mollusk shells [13]; mainly compounds of naturally formed calcium carbonate ($CaCO_3$) were found, as shown in Table 3, and its mineral phases calcite and aragonite (Figure 4). The main chemical composition of shells is similar to that of limestone, consisting mainly of calcium oxide (CaO), post-calcination, with small fractions of other oxides. The presence of calcium carbonate in the form of calcite and aragonite is interesting for application as bioaggregates because they are stable and chemically inert phases at room temperature. Worryingly, from a chemical point of view, the presence of SO3 and SO4 appears, which can promote the formation of late ettringite as a high presence in the bioaggregate. The levels found, combined, were a maximum of 1.18% [28], a value lower than 3.00% considered problematic in cement applications. Therefore, chemically the bioaggregates are compatible with the proposed application.

According to this research, according to all types of bivalve shells, the structure of mussel shells can be divided into three parts, namely, the outer layer known as periostracum, the intermediate layer, called prismatic, and the inner nacre layer (Figure 5). A similar prismatic layer rich in $CaCO_3$ was also observed in scanning electron microscopy (SEM) values for oyster, cockle, sururu and scallop shells provided by [35,36], indicating prismatic particles in mussel shell aggregate, contrasting with the rounded particles of conventional limestone aggregate.

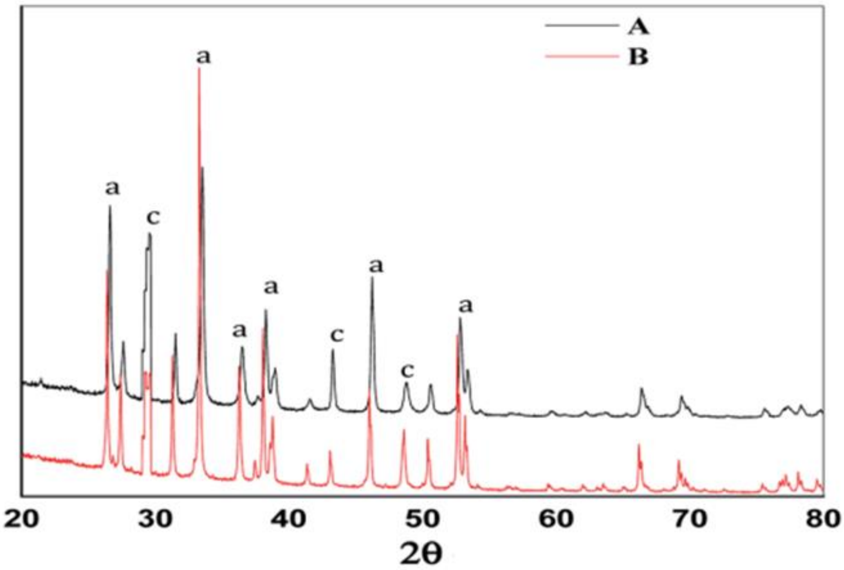


Figure 4. Diffractography of mussel shells from two species: A) C. bensoni and (B) L. marginalis. Key: a = aragonite; b = calcite.

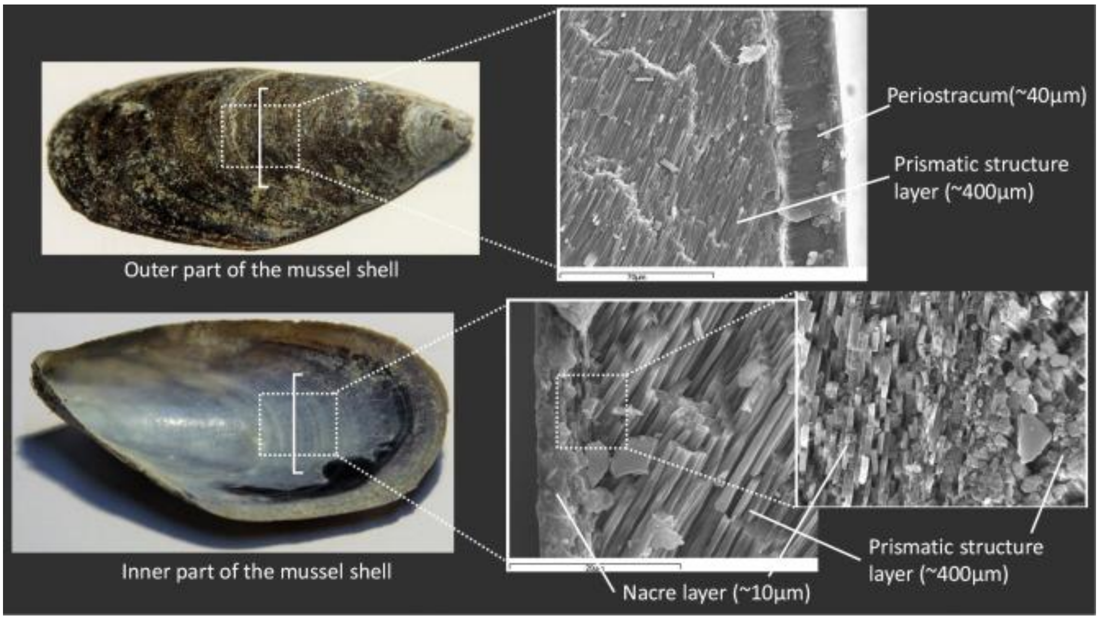


Figure 5. Scheme showing the inner faces (Nacre) – rich in prismatic aragonite and calcite crystals and the outer face of the mussel shell.

Table 3. Chemical composition of bioaggregates from mussel shells and similar materials.

Bioaggregates	$CaCO_3$	Na_2O	SO_3	$MgCO_3$	SiO_2	Al_2O_3	SO_4	Others	Researches
Cockle	96.85	0.42	0.11	0.04	0.94	0.15	0.05	1.44	[6]
Cockle	97.13	0.37	0.13	0.02	0.98	0.17	0.07	1.13	[28]
Mussel	95.09	0.35	0.18	0.21	1.12	<0.01	-	3.04	[7]
Mussel	89.46	-	0.57	-	1.26	-	-	0.07	[4]
Mussel	96.80	0.27	0.34	0.05	0.55	0.20	0.11	1.68	[37]
Mussel	95.60	0.44	0.34	0.03	0.73	0.13	0.11	2.62	[28]
Mussel	98.64	0.42	0.52	0.10	-	-	-	0.32	[38]
Oyster	95.70	0.19	0.73	0.42	1.01	0.14	0.32	1.49	[37]
Oyster	96.80	0.23	0.75	0.46	1.01	0.14	0.43	0.18	[28]
Oyster	89.56	0.98	0.72	0.65	4.04	0.42	-	3.63	[39]

A shell or seashell has a hard and protective outer layer (periostracum), which is present in a soft-bodied invertebrate marine animal composed of chitin-type proteins [7], and can be double outer (bivalve), simple external (monovalve) or even simple internal (octopus and squid).

Small amounts of impurities found in oyster shells were considered non-toxic when incorporated into concrete [40]. It was also noted that uncalcined oyster shells indicated a chloride ion content of up to 3.7%, while after calcination at 650 °C, a chloride ion content of less than 1.34% could be achieved, depending on the duration of calcination. Based on the results of leaching tests [41], it was concluded that uncrushed mussel shells can be classified as inert and non-hazardous waste regulated by the European Union (EU).

Nacre, also known as mother-of-pearl, is one of the most fascinating animal structures, one of the most solid microstructures produced by molluscs (Figure 6) and its classical mechanical studies show that its resistance to fracture is more than a thousand times greater than that of its sister. chemically precipitated inorganic, geological aragonite. As if these properties were not enough, nacre has a unique combination of optical properties that make it extremely attractive in jewelry and costume jewelry. This attractiveness is the main reason for the development of pearl culture in the Pacific and Mexico [15]. The periostracum, which remains unchanged throughout the animal's life, gives the shell its olive green glazed exterior color. Underlying the periostracum, the mineralized layer, composed of elongated crystals developed perpendicular to the surface of the shell, which define the prismatic stratum, they are made of aragonite, one of the six polymorphs of calcium carbonate, which crystallizes in the orthorhombic and represents one of the most fascinating and lacking in depth in terms of origin [42].

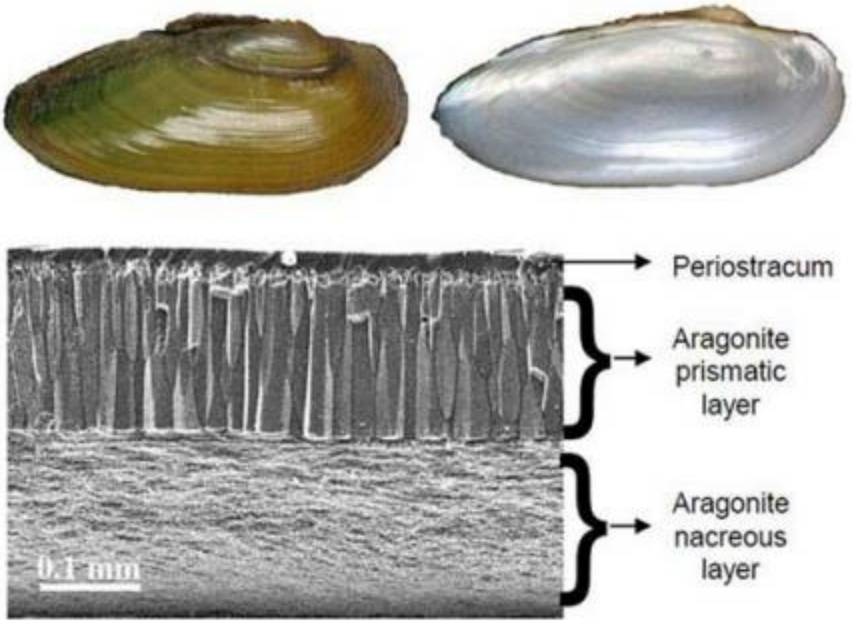


Figure 6. Section of the profile of the shell of the freshwater mussel Unio pictorum.

The presence of these crystalline forms of $CaCO_3$ is evident in Figure 4, where the two crystalline forms are explained in the diffractogram of the sururu shell powder, compared with geological limestone and in the thermal analysis, where the thermograms in Figures 7 and 8 show the resulting from thermal degradation of powdered mussel shells. In Figure 7, we can see a process that culminates at 285.5ºC, with loss of hydration and interstitial water molecules, present in the shells of bivalves, as in addition to being porous, there are components that interact with water. The most acute endothermic point, at 720.9°C, indicates the process of complete decomposition of the crystalline forms of $CaCO_3$, present in the shells of this mollusk, called calcination, where the loss of mass occurs with the abundant formation of CO_2 [20].

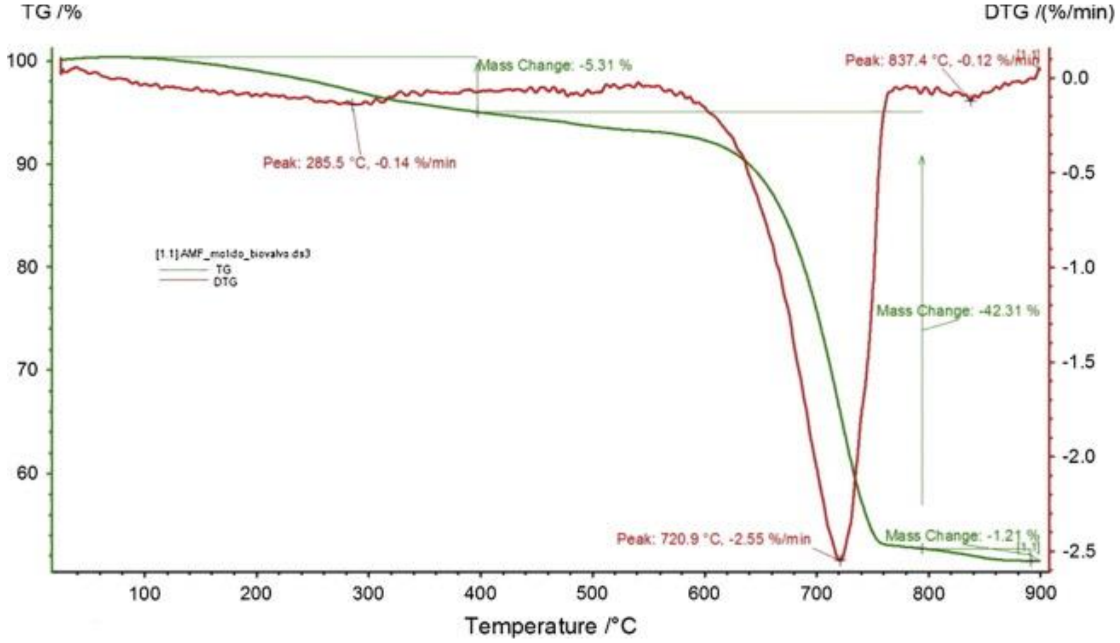


Figure 7. Thermogravimetric analysis curve for powdered mussel shells.

In Figure 8, in the first thermal stage (I), between 25°C and 150°C, there is a similar mass drop, relative to the humidity of the mussel shell, with a mass decay of 0.53%. In stage (II), mass loss between 150°C and 500°C, between 450°C and 500°C, related to the loss of organic fraction of the shell, for example polysaccharides, proteins and glycoproteins [43]. In the two cases mentioned, the mass losses are 5.31% and 3.5%, respectively, in relation to the pre-calcined specimens. In stage (III), between 500°C and 800°C, also present in the thermogram in Figure 7, it is possible to notice the decomposition of the CaCO3 crystalline structures, originating CaO and CO2, portraying the same calcination process [41].

Thermal degradation analysis was also carried out under isothermal conditions in the muffle furnace (2 h at 525 °C). These results determined mass losses close to 5.07 ± 0.12% in organic matter, similar to all studies carried out with mussels found in the literature [44]. The differences between ATG (thermogravimetric analysis) and isothermal degradation can be attributed to the different oven atmospheres adopted, with N2 (inert), controlled and more precise monitoring of mass loss, in ATG and dynamic heating in a normal atmosphere system, while in the muffle furnace, the system is open and isothermal [45].

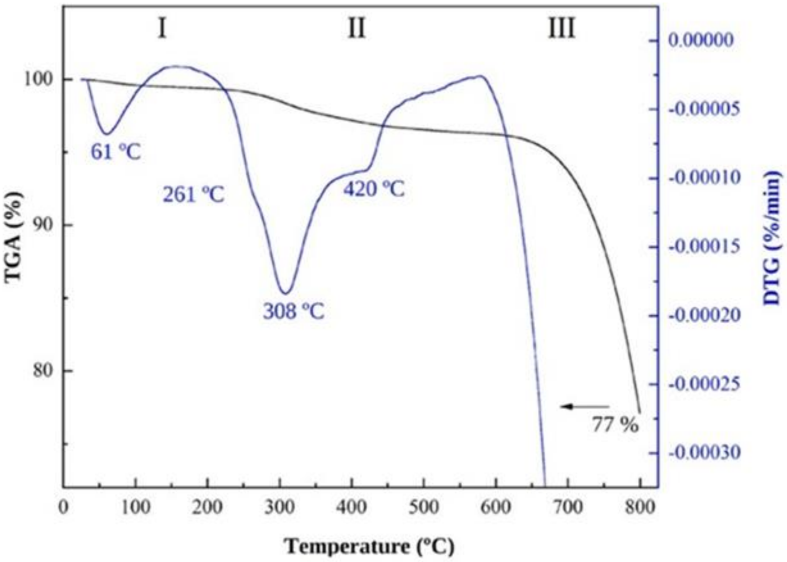


Figure 8. Monitored burning process of micronized mussel shells.

The careful analysis of the thermographic curves presented, Figures 7 and 8, allows us to affirm that there are chemical and physical peculiarities, even for shells of molluscs of the same species. Furthermore, it is important that post-calcination materials present calcium oxide levels comparable and compatible with geological limestone, as demonstrated by diffractograms and thermographic derivatives for the two materials mentioned (Figure 9), but with a more sustainable origin, given the damage caused by mining and grinding of geological limestone [46]. Other considerations not made by the authors, regarding the thermographic derivative (Figure 9), are the fact that mollusk shells exceed the CaCO content present in geologically explored limestone, as well as requiring lower temperatures and, consequently, calcination energy, which can further favor the valorization of bivalve aquaculture residue in Brazil, adding value to this productive aspect of food protein.

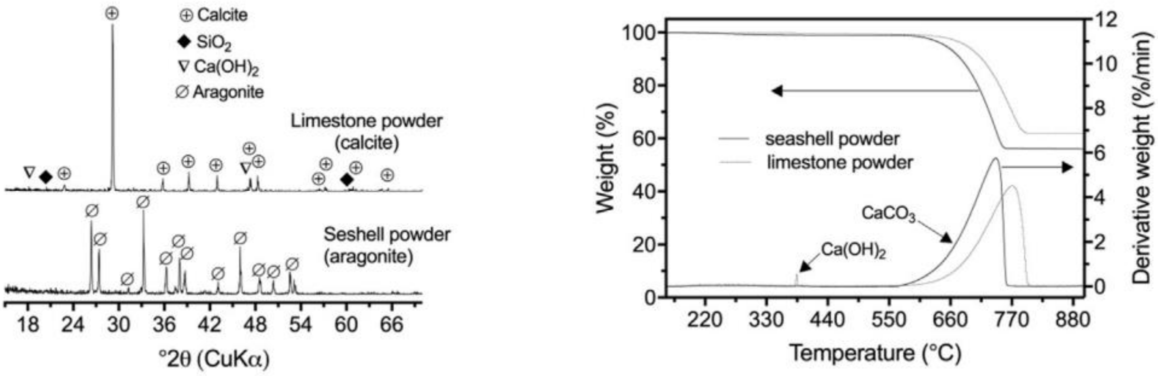


Figure 9. Comparative analysis between diffractogram and thermographic derivatives.

2.3. *Applications of Mussels shells: Life Cycle Analysis (LCA)*

Recently, several studies in the area of agro-industrial waste highlight the use of tools such as life cycle analysis (LCA). This is a necessary and accounting standard, developed by the International Organization for Standardization (ISO), applied to the sustainable development (production chain) of a given product, from cradle to grave, thinking about potential environmental impacts arising from the use of energy, water and other environmental inputs demanded, also listing the need for recycling [47]. Although LCA in the agricultural sector is relatively well established, this analysis for aquaculture production is not well established. When it is carried out, it refers almost exclusively to qualitative aspects.

In view of the significant and growing quantitative aspects of aquaculture, some authors suggest that LCA is a very important tool for evaluating the ecological compatibility and impacts of seafood products [48]. After all, without reliable data it is not possible to promote the application of a certain waste, without reliable data and consolidated scientific bases [49].

In search of the use and sustainability of shellfish shells (sururu) and aiming to reduce the environmental problems caused, research carried out in Brazil studied the feasibility of incorporating powder from these shells into porcelain tile mass. The ceramic compositions were formulated from a reference industrial porcelain tile mass and sururu shell powder or commercial $CaCO_3$ varying between 0 and 7% by mass. Specimens prepared by uniaxial pressing were technologically evaluated depending on the sintering temperature. The incorporation of up to 7%, by mass, of micronized shells, maintained the technological properties appropriate to the Brazilian Association of Technical Standards, ABNT, for the regulation of ceramic coverings from the BI group - porcelain tiles [50].

In Spain there are already initiatives aimed at valuing mussel shells from the canning industry, the second largest in production in the world, with a quantity of more than 80,000 tons of shells per year, since 2009. There, they are managed in order to study, treat and provide sustainable destination, adding value to what was previously discarded, promoting treatment of the shells (cleaning and drying), to convert them into the majority component of high purity, $CaCO_3$, eliminating water, salt, mud and meat residues, inherent to the shell from mussels, which previously caused effects related to the decomposition of organic matter and generation of leachate [22].

Also in Spain, mussel shells have been applied as an additive to animal feed (source of mineral salts and bulking agent), liming agent and as a constituent of fertilizers, aiming to recover impoverished soils present in the country, especially in the Galicia region [15].

In other European countries, however, such as Italy and France, the reality is different. Italy has an estimated annual production of 6.3 tons [51]; In this case, the shells generated from these molluscs are discarded into the sea, certainly with unaccounted for logistics costs, showing a clear example of the absence of LCA [52].

Another example of an LCA step is the essence of studying the adsorptive capacity and the physical and/or chemical interaction between the surface of the solid adsorbent and the target pollutant. This type of study is relevant and depends on the number and type of adsorption sites, resulting from the intermolecular forces developed, linked to the surface morphology analyzed in micronized oyster shells [53]. In this case, together with cans, a source of aluminum, they proved to be effective and low cost, revealing high performance in the adsorption of phosphates (PO_4^{-3}) in retention filters (Figure 10), comparable to high purity ion exchange systems and high cost for treating industrial outfalls [54].

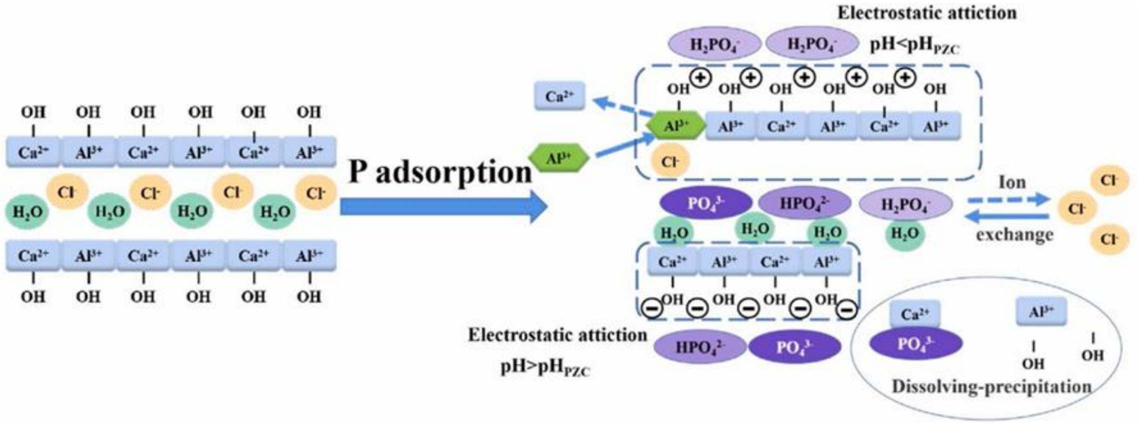


Figure 10. Schematic model of the low-cost retention filter, with high efficiency in phosphate adsorption (PO4-3).

Still following the treatment of sewage effluents, research identified a promising mixture ratio of high compressive strength (0.93 MPa), as a filtering medium, using an optimized 1:1 mixture (similar to that of Portland cement) of heavy coal ash and micronized oyster shells, for phosphate fixation, in a flow of 86 cycles, with the aid of a peristaltic pump [55]. With pozzolanic activity determined in this system, they believe they have counteracted the adverse effects of the porosity of the proposed composite, with maximum PO_4^{-3} (P) fixation of 1,403 mg/g (88.4% efficiency), attributed to synergistic precipitation effects. and adsorption. Therefore, there was effectiveness in reducing the nutrient rate in coastal sediments, revealing a relevant ecological proposal in the removal of P and silicates, highlighting the demand for more research, in order to optimize the filtering process and investigate the increase in NH_3 (N) in the sediment residual [24,56].

Recent studies have also produced valuable evidence of ACV from bivalve shells in removing Cd and other toxic metals from aqueous solutions, through a chemical interaction with calcite or aragonite, crystalline phases distinct from $CaCO_3$, present in shells. The ability to extract Cd by the aragonite phase, calcite and micronized biogenic aragonite fragments were investigated, concluding that the absorption of Cd by aragonite is fantastically more robust than the crystalline phase [57].

Through a simple heat treatment of oyster shells, another new effective adsorbent was generated, as the organic matter, composed of chitin and silk protein, is removed, generating greater porosity and increasing the surface area of the material, post-calcination; It was also found that the conversion of oyster shells into quicklime by thermochemical treatment, not only eliminates the organic residues of oyster shells, but also produces a valuable adsorbent for water and wastewater treatment, through less carbonate formation processes. soluble, cadmium (Cd), arsenic (As), lead (Pb) or mercury (Hg) [57].

Similar investigations, still related to the differences in adsorption behavior between the prismatic (CP) and nacreous (CN) layers of oyster shells, common to conchiferans (Figure 11), revealed different copper (Cu^{2+}) removal capabilities, with interactive predominance of CP of 8.9 mg/g, to the detriment of CN of 2.6 mg/g, probably related to the larger contact surface of CP. Furthermore, they demonstrated the high relationship between pH and optimal copper removal, finding that, at pH 5.5, the raw bark (CC) in powder form removed up to 99.9% of the copper, in 24 hours, in an extraction initial dose of 10 mg/L [58].

In South Korea, public finances increased after the establishment of a fertilizer factory to recycle oyster shells and solve water eutrophication problems by transforming this material into a sustainable product for efficient removal of phosphates from wastewater [55].

In the United States, the zebra mussel, an invasive lake species, led to the generation of large quantities of post-consumer shells, initially sent to landfills; in this case, after LCA, its use as a soil conditioner, liming agent and mulch for agricultural soils has been applied as an alternative [59].

Peru is another country that is carrying out experiments using scallop shells to obtain lime, as an input in various industrial sectors. In this country, there is research that evaluated levels of insertion of these pulverized shells into fresh and hardened concrete, concluding that a 5% rate of cement replacement always results in an improvement in its properties, whatever the w/c (water/cement) ratio. also inferred that in the grain size range of 1.19 to 4.75 mm, the limit incorporation content of the shell powder of this typical mollusk is 40%, without prejudice to the viscosity and mechanical properties of the concrete, showing that perhaps the species of mollusk may influence the appropriate particle size for application [33].

In the Netherlands, a model of mussel tiles was created, to use shells generated in the growing industry in the sector, as by-products, highlighting classic LCA results [49]. Other small-scale applications of shells include controlling eutrophication in ponds and water treatment systems, supplementing calcium for livestock and pets in animal feed, restoring reefs, removing atmospheric pollutants, manufacturing calcium citrate, products pharmaceuticals, paper, paints and crafts, which face preliminary energy demand as the main obstacle [40].

There is also the possibility of reusing the shells for some shellfish aquaculture applications, for example, as cultivation, where it functions as a substrate on which molluscs can form, grow and develop [60]. This would be a great tool in the fight against hunger in several coastal countries in Latin America and Africa. In addition to all the applications mentioned in this section, there is a potential for the application of mussel shells as bioaggregates in cementitious materials, which will be explored in the next topic.

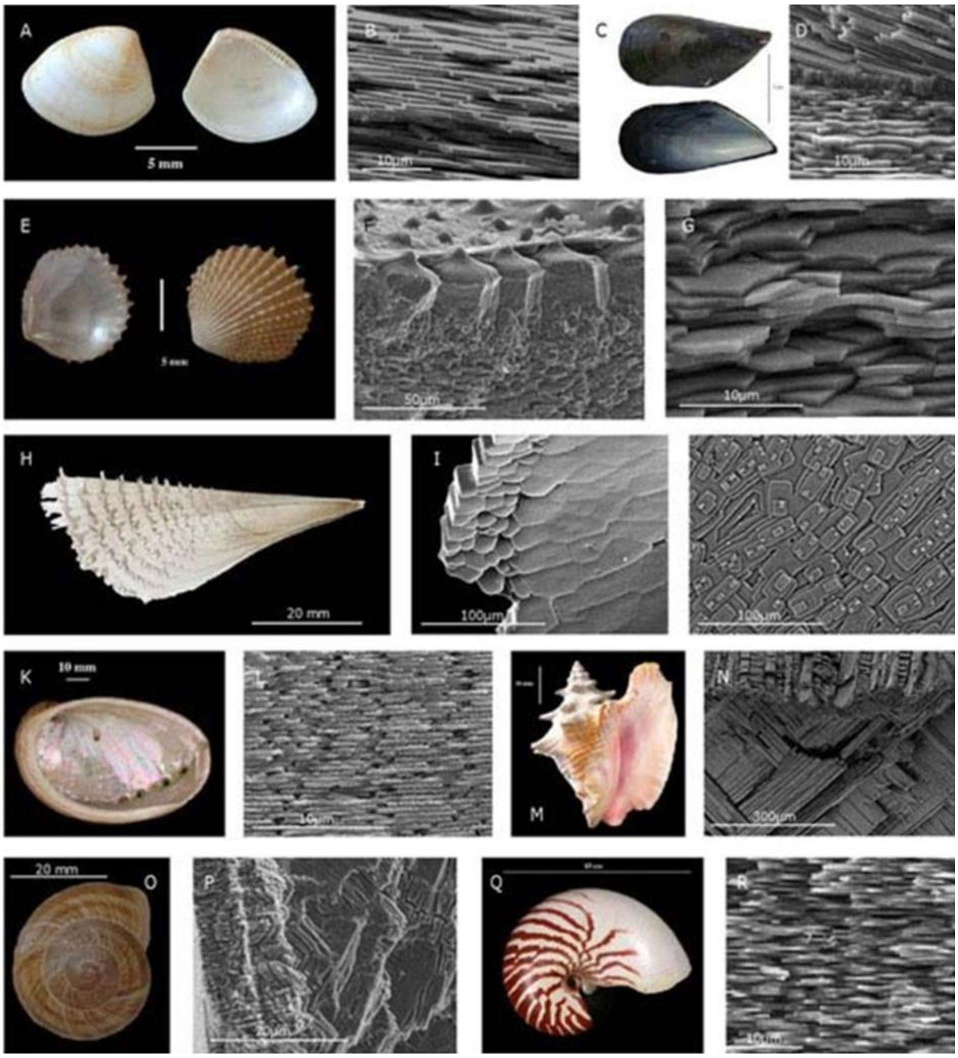


Figure 11. Examples of mollusk shells with micrographs of their associated calcified shells on 1 μm scales, side by side.

2.4. Bioaggregates applied to cementitious materials:

In this section, the main aspects related to the use of bioaggregates in mortars and concrete will be explored. It is important to make the positive and negative points of using the material clear. The main negative points are related to the material's high-water absorption, which varies between 3 and 14%, while the saturation of natural sand is between 0.3 and 4.0%. This difference results in cementitious materials with workability problems, requiring an increase in water and cement contents [60] which exactly contradicts the recycling assumption. Optimal doping generally does not exceed 25% or 30%, as reported in research on the topic [26,61]. This information must be taken into account in bioaggregate studies, since a complete replacement of conventional aggregates has been rarely reported in the literature.

Another point of concern is the rheological nature of recycled aggregates (RA), being another parameter that implies that maturity affects the behavior of cementitious materials, as well as the resistance and water absorption of the evaluated material [62]. Matured RA, when compared to natural aggregates (NA), reduces autogenous shrinkage in this type of concrete by 20%, but can increase drying shrinkage due to the hygroscopy of the material, when compared to conventional aggregates. Less rigid and earlier RA, imply even more shrinkage of cementitious materials, 10 to 20% higher; that is, the use of matured bioaggregates, which are obtained from older mussel shells, mitigates autogenous and drying shrinkage [63]. Other disadvantages will be highlighted sequentially, but they are related to an increase in total porosity and deficiencies in the paste – aggregate transition zone [61].

It is worth highlighting, on the other hand, that the presence of grains of a material similar to limestone present in bioaggregates is capable of reducing the width of the pores present in the cement matrix, due to the chemical compatibility between matrix and aggregate [26]. In other words, even if there is an increase in porosity, the use of aggregates based on calcite and aragonite, similar to limestone, in addition to the angular shape of the grains, can cause a drop in the volume of macropores, transforming them into smaller, unconnected pores. in mortars with the same particle size distribution, improving the workability of the material [64]. This indicates that the effect of porosity and workability must always be analyzed experimentally, since bioaggregates have variable physical and chemical composition. Furthermore, there may be gains in terms of reduced capillarity and reduced aggressive water absorption. Another notable point is the possibility of using bioaggregates in cementitious materials for thermal insulation [61]. It is observed that several properties are affected by the use of bioaggregates and that the variation in the physicochemical properties of this type of aggregate causes direct impacts on the behavior of mortars and concrete. In the following topics these points will be addressed.

2.4.1. Influence of bioaggregate particle size

Particle size is an essential parameter in the study of aggregates in cementitious materials, defining factors such as: packaging, paste-aggregate transition zone and mechanical resistance. In the case of bioaggregates this is no different. It is worth mentioning that in most studies of mussel shells and similar materials such as aggregates for concrete and mortars, it was observed that the material is used as fine aggregate [8]. This is due to several factors, such as: natural size of the shells and hollow shape of the material, which makes it unfeasible to be applied as coarse aggregate since the concave shape of the material hinders adhesion with the matrix; high levels of water absorption, which would be even more critical if the application was as coarse aggregate due to the particle size, and lamellar pattern of the material, which would not be compatible with application in coarse format due to regulations on the shape index [35,61].

It is known that the shape index is the relationship between length and thickness of the aggregate, which must be less than 3 for application in concrete. As the natural shape of shell bioaggregates is lamellar, if comminution were not performed, the normative parameters would not be met. Illustrating this fact, some research evaluated the size of the aggregate before the grinding process, obtaining a length and thickness of around 90 mm and 20 mm, respectively [65]. These values indicate a shape index of 4.5, much higher than the normative maximum value. Therefore, its use as fine aggregate helps to minimize this problem.

Although it has been highlighted that most studies focus on studying bioaggregates as fine aggregate, crushed shells, replacing coarse aggregate, are more suitable for the production of lightweight, low-resistance concrete, due to the excessive scaling of the particles. of shells [44]. The primary parameter that determines the maximum level of aggregate replacement and the granulometry that the material will be applied to is related to the non-significant compromise of compressive strength and workability, properties closely related to the grain size of the ground aggregate and the surface area, made available for them. This information must be taken into account when applying the material.

When studying bioaggregates replacing conventional aggregates, it is important to standardize the particle size parameters, so that the study is comparative. This can be done in two ways: (i) using information such as DCM and FM, compiled in Table 2 or; (ii) standardizing parametric granulometric curves. In the case of analysis based on DCM and FM, it is recommended to use DCM = 4.75 mm; 2.40 mm or 1.20 mm, typical values for coarse, medium and fine sand, typically used in the production of mortars and concrete [66,67]. The FM must be in the range between 2.20 and 2.90 for the optimum zone or in the ranges of 1.55 – 2.20 and 2.90 – 3.50 for the usable zones. In the case of using parametric curves, a procedure is carried out as seen in Figure 12.

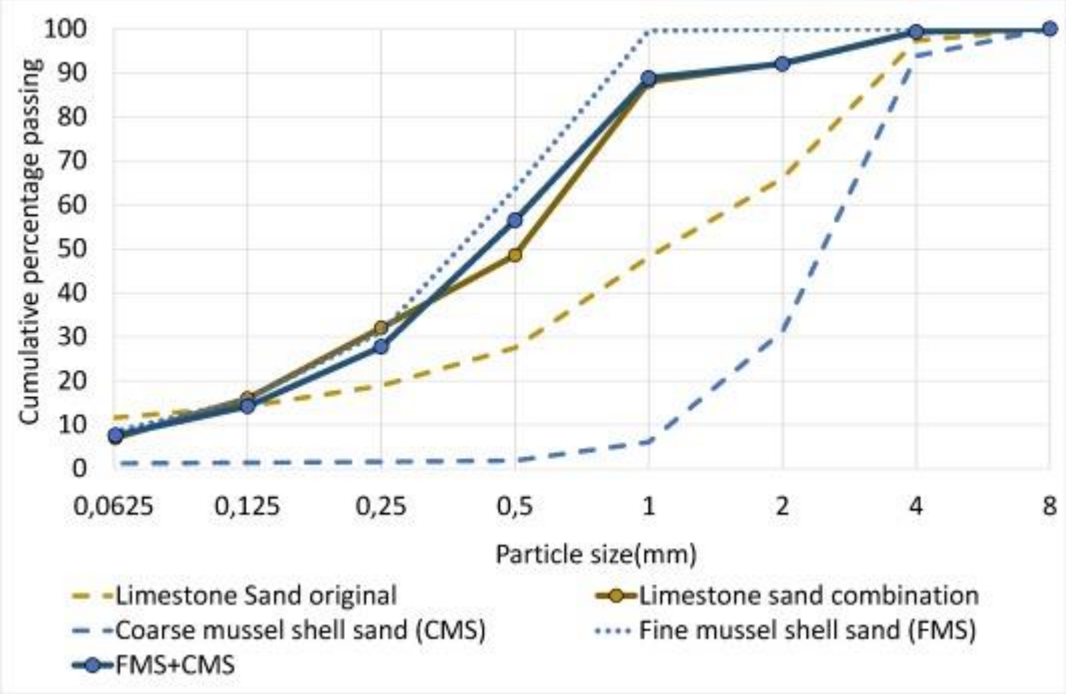


Figure 12. Particle size analysis of bioaggregates using parametric curves.

In the study, the authors grinded the mussel shell and separated it into two particle sizes: coarse sand (particles between 0 – 4 mm) and fine sand (particles between 0 – 1 mm), with MF of 1.90 and 4.64, respectively [7]. In the research, the authors carried out a comparison of the behavior with limestone sand, whose FM was 3.70. In this way, the authors combined calculated proportions of the coarse and fine fractions of the mussel shell, obtaining sand with a parametric granulometric curve of FM = 3.71, compatible with the conventional aggregate of the study. In this way, the analyzes carried out and the comparisons proposed by the authors are validated. Although this section aims to explore the particle size of bioaggregates, it is highlighted that other parameters must be considered. Some authors state that granulometry is important, but the presence of different allotropic forms of $CaCO_3$, such as calcite and aragonite, and their different reactivity and metastable characteristics have more influence on mechanical properties than physical parameters [46]. This will be discussed later in the text.

2.4.2. Influence of the specific mass of the bioaggregate.

The specific mass of bioaggregates is mainly affected by two factors: (i) shell size; and (ii) type of material from which the shell was extracted [39]. However, when compared with conventional aggregates, most bioaggregates have similar or slightly lower specific masses, as seen in Table 2. Some authors highlight typical values ranging between 2.3 – 2.9 g/cm^3 [8]. Natural aggregates, such as washed river sand, have a specific mass ranging between 2.5 – 2.7 g/cm^3 [68]. This implies that, at least in theory, drastic changes in the behavior of cementitious compounds using bioaggregates are not expected.

However, in practice the opposite is observed: the presence of mussel shell particles, for example, impairs the workability of concrete and mortars and, in the end, there are several reports that porosity increases, especially macropores. Thus, the densities of the cementitious mass, both fresh and solidified, are reduced with the use of bioaggregates, not due to the difference in specific mass, but rather due to an increase in porosity [15,27]. Its application in coatings seems suggestive, as low-density systems tend to act as thermoacoustic comfort generators [69]. There is also no doubt that the mortar generated reduces the mass load of a building, which is interesting for reducing its own weight [70]. However, for structural applications, the drop in the mechanical resistance of concrete and mortars generates serious limitations [44].

The specific mass, together with the granulometry, also affects the packaging of the final cementitious material. This can be observed through a parameter defined as packing compactness. This parameter can be obtained using a single aggregate in the analysis or using a combination of aggregates to check how the materials pack together. Some research shows that the compactness of bioaggregates with mussel shells is 0.725 when used with DCM = 4.75 mm, FM = 3.11 and SM = 2.57 g/cm^3 [4]. Comparing the values for conventional aggregates, it is observed that for a standard room sand with DCM = 4.75, SM = 2.65 g/cm^3 and unspecified FM it is possible to obtain compactness of 0.76 [71], slightly higher than mussel shell bioaggregate. In another research, it was observed that the use of 50% bioaggregate and 50% natural aggregate results in a compactness of 0.72 [16]. Values above 0.70 are considered satisfactory for application to concrete and mortars. Therefore, the values highlighted in this research demonstrate that mussel shell bioaggregates and similar materials are compatible with this type of application.

2.4.3. Influence of bioaggregate morphology.

The greater the specific surface area of the bioaggregates, the greater the contact of the material with the cement paste, improving properties such as filling and wettability, enabling the system to form appreciable resistance binders [28].

Regarding the morphology of the material, another important point is that in mussel shell particles there are many surface irregularities and microscopic holes, which is different from the surface textures of other aggregates, which are relatively more uniform. This demonstrates, as illustrated in Figure 13, how much the morphological aspects of bioaggregates can impact the rheological properties and the development of hydration and mechanical resistance of the cement present in concrete and mortars [46].

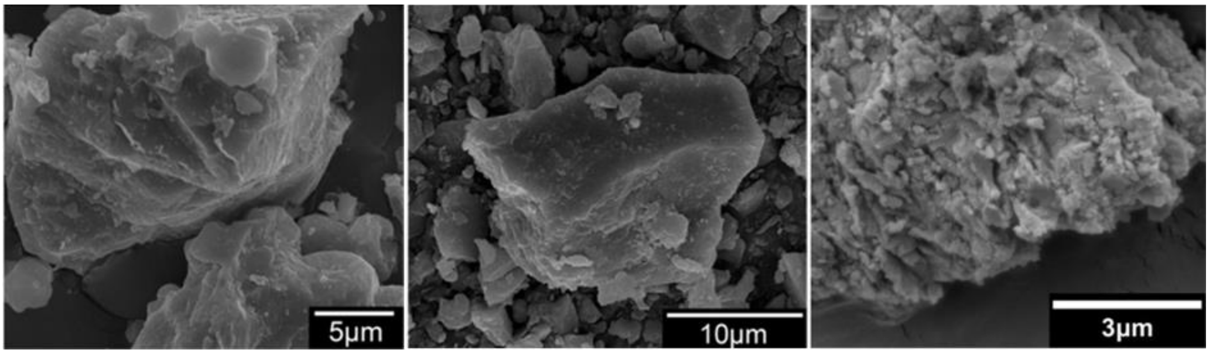


Figure 13. Surface morphology of particles of limestone, Portland cement and mussel shell.

Another important information related to the morphology of bioaggregates is linked to the transition zone between paste-aggregate, known as ITZ (paste-aggregate transition interface). The morphological characteristics of the mussel shell, for example, such as the smooth surface of the mother-of-pearl, the presence of chitin and organic contaminants and the shapes of the elongated grains, strongly damage the interfacial transition zone (Figure 13), generating micro cracks, showing a poor interaction binder-aggregate and again affecting the mechanical resistance of the generated composites [61].

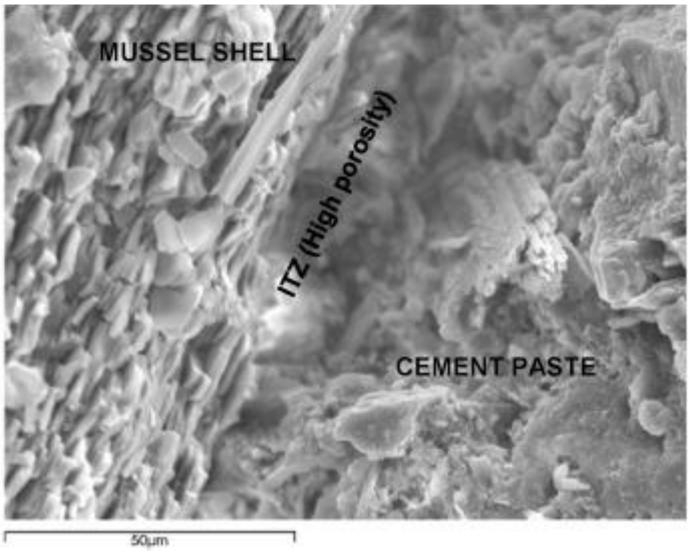
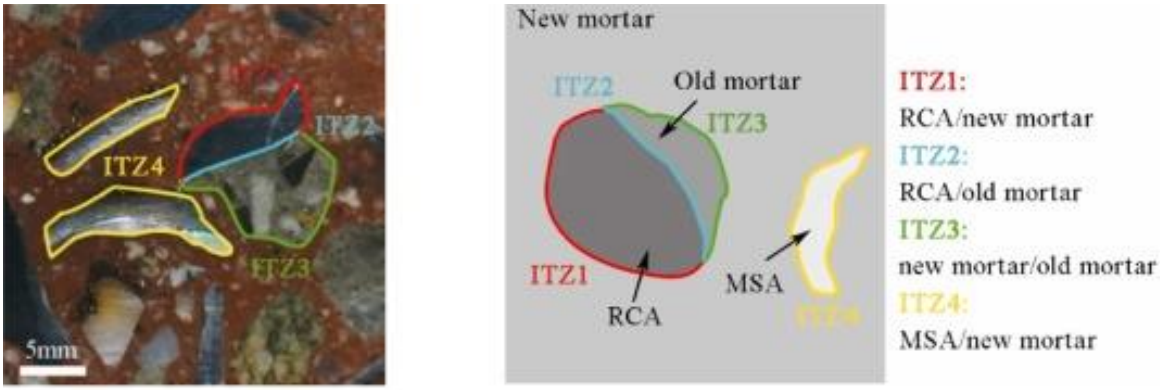


Figure 14. ITZ (paste-aggregate transition interface) for mussel shell.

Furthermore, it is interesting to compare the ITZ of mussel shell bioaggregate with other recycled aggregates, such as that obtained from construction and demolition waste (RCD). In the case of the RCD, it is possible to observe the following transition interfaces: ITZ1 – between the RCD and the new concrete paste/mortar produced; ITZ2 – between the RCD and the old paste/mortar present in the concrete that gave rise to the recycled aggregate; ITZ3 – between the old paste/mortar and the new paste/mortar of the concrete produced. Therefore, the interface between RCD recycled aggregates and concrete is multiple and complex, weakening the material. However, it is worth highlighting that there is compatibility between the transition zones, since the materials used are all cementitious.

In the case of mussel shell bioaggregates, ITZ4 is observed – between the shell and the new concrete paste/mortar produced [72]. This information is summarized in Figure 15. In this context, it is worth highlighting that the advantages of using bioaggregates, from the ITZ point of view, are related to a single transition zone. However, the main disadvantages are related to the lack of compatibility of this zone, which adds incorporated air, macropores and consequently weakens the cementitious compounds. This is one of the biggest challenges in using bioaggregates, which must be taken into account when applying the material.



(a) Concrete specimen. (b) Schematic diagram.

Figure 15. Comparison of the cement mass-particle transition interface of RCD and for mussel shell.

2.4.4. Influence of the chemical composition of the bioaggregate.

The majority chemical composition of bioaggregates obtained from shells, illustrated in Table 3, is based on calcium carbonate (> 90% $CaCO_3$), mineralologically established as calcite or aragonite. It is known that the primary function of aggregates is filling, and the use of reactive aggregates is not recommended. Therefore, the chemical composition of bioaggregates is compatible with the proposed application, since it is very similar to the composition of limestone, typically used as aggregate in concrete [73,74].

Some authors have proven that micronized mussel shells are more robust sources of $CaCO_3$ than the traditionally used mineral geological sources, including enabling carbonation points during hydration [46]. This procedure tends to reduce the pores of concrete and mortar at more advanced ages, well above 28 days, as long as the shells are free of organic matter in the composite and are rich in aragonite. In other words, the procedure delays the setting of cement in concrete and mortars, but in the long term it reduces the porosity of the material, which is favorable information for the application of bioaggregate in structural concrete or coating mortar, as it reduces the percolation of chlorides. and sulfates and improves durability. In other words, due to the different chemical composition of the lime present in the bioaggregate shells, with greater crystallinity and a more reactive contact surface, it is possible for longer hydration to occur than with the use of traditional aggregates. This occurs due to the formation of $Ca(OH)_2$ and due to the strong initial assimilation of intrastructural water of the bioaggregate particles, leading to the later formation of C_3S and C_2S [75].

Another compound present in the chemical composition of bioaggregates is $MgCO_3$. Some authors report levels higher than 0.50%, as seen in Table 3. It is worth highlighting that the Mg^{2+} ion exerts a significant influence on the precipitation of calcium carbonate and can be incorporated into the calcite crystalline network, when the Mg:Ca ratio in solution is low or induces aragonite precipitation (metastable), when the magnesium concentration is high in the biological system that gives rise to mussel shells [76]. In other words, the presence of Mg^{2+} is related to a catalysis that culminates in the precipitation of a crystalline phase of monohydrate and metastable calcium carbonate ($CaCO_3.H_2O$) together with $MgCO_3$ in the form of nesquehonite [76,77]. This is problematic because both $CaCO_3.H_2O$ and $MgCO_3$ require high enthalpy to dehydrate. Therefore, the procedures for cleaning and drying the shells are not sufficient to rid the biogregate of these undesirable compounds, which entered the hydration process late, triggering internal tensions in concrete and mortars and causing the appearance of cracks and fissures ([78]. This implies that the presence of high levels of MgCO3 must be considered problematic for the application of the bioaggregate.

Another important point observed in Table 3 is the presence of SO_3 and SO_4. It is known that the presence of sulfates in cementitious materials can be problematic as it promotes the occurrence of late formation of ettringite. The standard recommends a maximum content of 3% in relation to the mass of the cement. It is observed that the levels observed in Table 3 are lower values. Therefore, the presence of sulfate in bioaggregates is not a critical problem, as highlighted by other authors [8].

The most critical problems in the chemical composition of bioaggregates are related to the presence of chlorides and organic impurities. In Table 3 it is not possible to identify the presence of these components because the materials indicated in the table were analyzed after the shell cleaning and drying process, indicating that this treatment is sufficient to reduce problems related to chlorides and organic impurities [33]. The presence of chlorides is problematic because they can cause surface efflorescence in the concrete, reduce the pH and cause dehydration of the cement material, allowing corrosion of the reinforcement, consequently damaging the durability of the material [79].). The presence of organic impurities affects the setting of the cement, impairing the kinetics of the hydration reactions, in addition to impairing the adhesion between the aggregate and matrix. This occurs because organic impurities are present in the last layer of the shell called nacre, in the form of polysaccharides (chitin), proteins and glycoprotein [80]. In other words, the cleaning stage needs to be carried out appropriately so that the presence of unwanted compounds is minimized, making the application of bioaggregates viable.

2.4.5. Workability and rheological properties of cementitious materials containing bioaggregates.

In general, the behavior observed with the use of bioaggregates obtained from mussel shells or similar materials is a reduction in the workability of cementitious materials as the content of bioaggregate used increases. The reduction in workability is justified by the high-water absorption of the bioaggregate, which reduces the fluidity of the material and by the elongated, lamellar and flat shape of the mussel shells, increasing the dynamic viscosity and internal friction of concrete and mortars, and consequently worsening the fluidity parameters [8,72].

Exemplifying this pattern, the reduction in the consistency of mortars with an increase in the aggregate content present in the material stands out: 285 mm for 45% bioaggregate volume; 275 for 55% of the material; and 210 for 65% mussel shell volume [4]. In general, it is observed that the main tests carried out to measure the workability of cementitious materials in research with bioaggregates are consistency test in mortars or slump test in studies with concrete. Studies with other properties in the fresh state, such as entrained air or water retention, are scarce, as are rheological tests, such as dropping ball or squeeze flow. Therefore, there is a gap in these types of analysis, which are suggestions for future work.

It is known that mortar, for example, is a composite basically formed by the combination of cement, fine aggregate and water. Additives and reinforcements can be included in this system to achieve the desired physical properties of the material. When these components are homogenized, a fluid or plastic system is created (cementitious hydration phase), which must be easily moldable (workability). Over time, the cement forms a rigid matrix that binds the rest of the components together into a durable system, similar to artificial rock, with many applications. The function of the aggregate used, mainly the fine one, is to reduce the demand for cement, the most expensive component, and delay drying, without compromising the workability of the cement mix. Furthermore, as far as possible, it must be able to maintain the tenacity and durability properties of the dry structure, when compared to pure cement, which are only guaranteed when the concrete and mortar is applied without pores or concreting niches. For this, the property of workability is fundamental [81].

2.4.6 – Water absorption, porosity and capillarity of cementitious materials containing bioaggregates.

Through published research, it is observed that, in general terms, the use of mussel shell bioaggregates increases the water absorption values of concrete, due to the increase in porosity and reduction in the density of the material. The same pattern is observed in mortars. This pattern is attributed to two factors: the shape of the bioaggregate grains, which allows the formation of voids in the mortar microstructure; and the water absorption capacity of the shells, probably due to the existence of polymorphic variants of $CaCO_3$, more hygroscopic such as aragonite and due to the presence of organic impurities [19].

The mass density of cementitious materials, both in the fresh and hardened state, also presents a reduction in values, due to the high porosity that the bioaggregate promotes and due to the formation of incorporated air [61].This air forms mainly in the transition zone and increases the density reduction. As a result, bioaggregates have the potential to produce lightweight, low-strength concrete, due to the flaking of shell particles [48]. As previously highlighted, no drastic differences are observed in the specific mass of bioaggregates and conventional aggregates. Therefore, this difference in behavior is an interesting point to study.

Another possibility is to use mussel shell bioaggregates in the production of permeable concrete. In Algeria, studies on permeable concrete to evaluate the possibility of using cockle shells, replacing crushed limestone aggregate, as a form of sustainable proposition were successful. Compared to concrete with natural crushed limestone aggregates, a 20% increase in porosity was observed in concrete containing cockle shells, but with the same material dosage. Cockle shell aggregates had a considerable influence on the slump properties, reducing the density, but improving the mechanical resistance to flexural traction, for the hardened state, without, however, affecting drainage, with permeability applicable to the proposal for permeable concretes [18].

Even though there is an increase in porosity and an increase in water absorption, an interesting point highlighted in some research is that cementitious materials containing bioaggregates have lower permeability to water, both pure and aggressive. Furthermore, they also present lower capillarity values when compared to concrete and reference mortars. This information indicates an increase in the durability of cementitious materials with the use of bioaggregates [82]. The reasons for reduced capillarity and water permeability are highlighted below: presence of incorporated air, which acts as a barrier to the passage of water [75]; in the size of the pores, which, due to their large area, exert little capillary suction force; encapsulation promoted by mussel shell grains, due to their lamellar, rough and flat shape, which forms a barrier to the passage of aggressive water; and presence of hydrophobic chitin molecules in the mussel shell bioaggregate, reducing interactivity with water [15,44].

To illustrate this information, Figure 16 presents capillarity results for mortars containing 0 – 75% replacement of natural sand with bioaggregate obtained from mussel shells. The authors used two composition standards: BC, composed of mortars with a lower cement content; and SC, produced with mortars richer in Portland cement. In both cases, the effect of the mussel shell was the same, reducing water absorption by capillarity, proving that, although there is an increase in the porosity of the material, these pores are not connected and are large in size, blocking the path of water capillary, which does not have enough suction to attack the mortars [15].

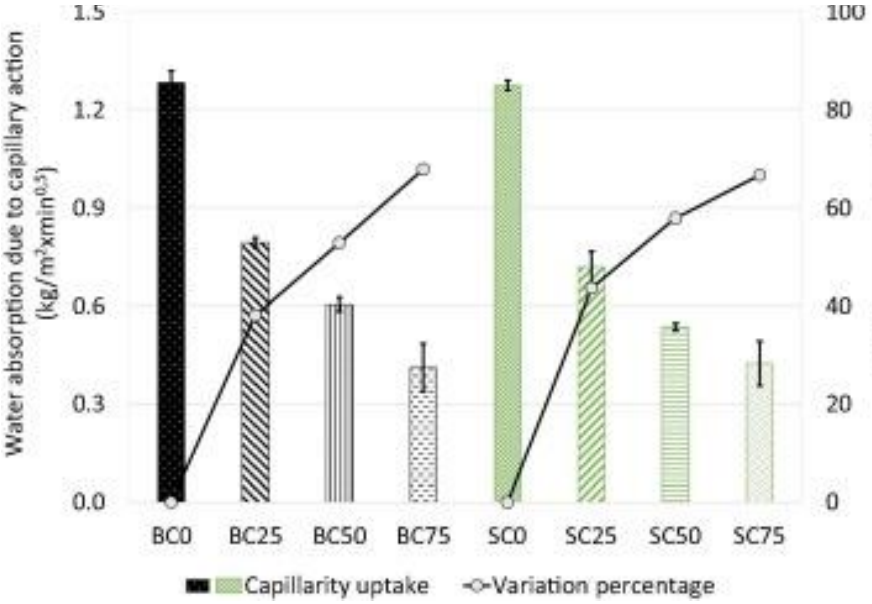


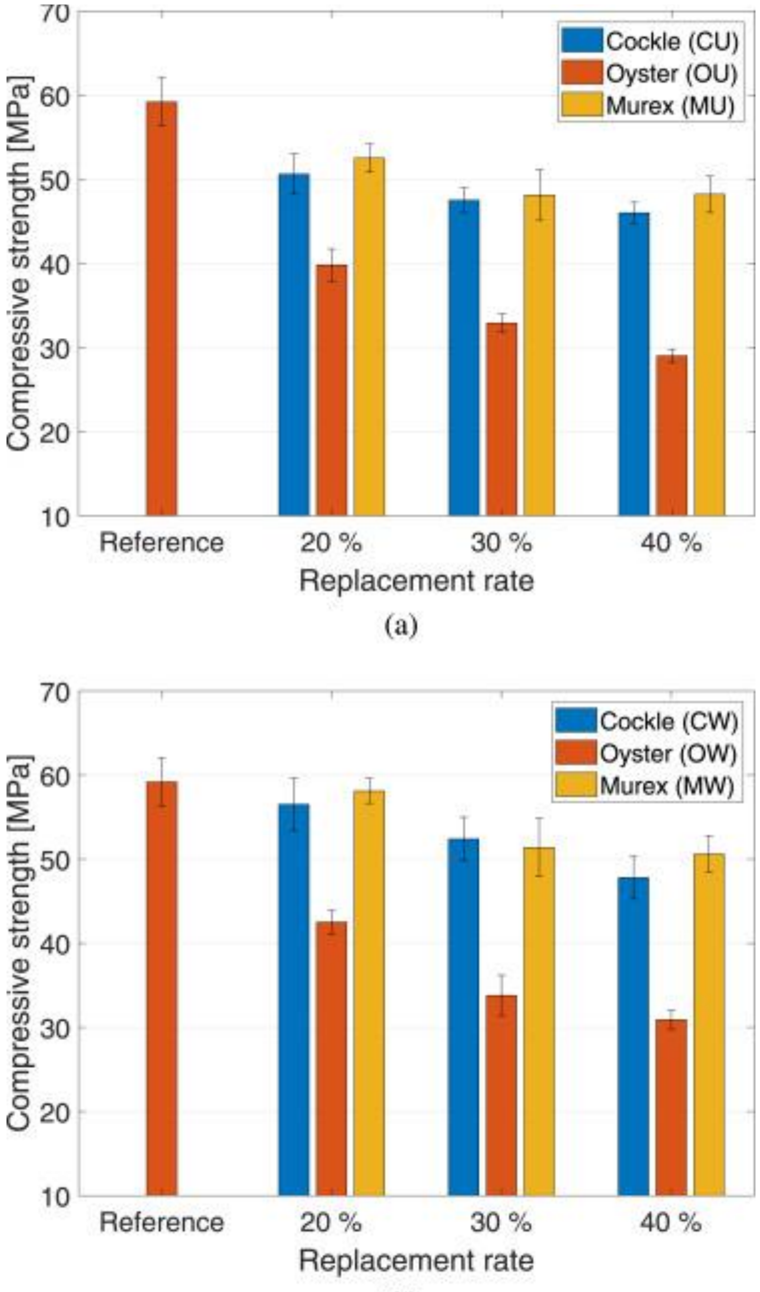
Figure 16 – Water absorption coefficient by capillary action of mortars with bioaggregates, where BC represents mortars with lower cement content and SC higher cement content.

2.4.7. Mechanical resistance of cementitious materials containing bioaggregates.

Compressive strength shows a tendency to reduce as the content of mussel shell bioaggregates in concrete and mortars increases. This effect has been reported by several authors and is attributed to the following characteristics: (i) increase in water absorption and porosity promoted by the mussel shell due to the hygroscopy of the material and due to the shape of the grains, elongated, flat and irregular, which increases the pores of the material; (ii) presence of organic impurities and chlorides that impair the cement's setting properties; (iii) increase in entrained air and consequently low adhesion in the transition zone, impairing the transfer of efforts in the cementitious materials; and (iv) problems in the production of mortars and concrete due to the lower workability of the material, containing bioaggregates [34,38,61,75].

Although this effect is highlighted by several authors, it is important to highlight that the use of mussel shells, mainly as fine aggregate, at levels of up to 25% does not cause a reduction in mechanical resistance, statistically speaking, in relation to the reference composition [61]. This evidence the viability of using mussel shell bioaggregate, generating all the economic and environmental advantages described previously [83].

Another important point is the need to carry out cleaning treatments on mussel shells and similar materials before using them as aggregates. Figure 17 presents the results of compressive strength of mortars containing 20, 30 and 40% replacement of fine aggregate with three types of bioaggregates: cockle, oyster and murex. Among these three aggregates, the one with the best mechanical parameters is the murex, due to the roughness that promotes adhesion, followed by the cockle and the oyster. A tendency for resistance to decrease with the use of bioaggregates is also observed. An important point to be highlighted is the difference in mechanical behavior when carrying out treatments on bioaggregates. In this research, ultrasonic cleaning was carried out to eliminate organic impurities and adsorbed chlorides. As a result, an increase in resistance was observed from approximately 50 MPa to 58 MPa, in the composition containing 10% oyster. The authors prove, through experimental results, the importance of cleaning the shells [70]. The presence of chlorides and organic impurities slows down the setting of cement, compromising the strength of concrete and mortars. However, even with this effect, no results of calorimetry tests or definition of the setting time of mortars and concretes containing bioaggregates were found in the bibliography. This is one of the gaps found in the bibliography, which shows a gap in these types of analysis, which are suggestions for future work.



(a)

(b)

Figure 17. (a) Compressive strength before cleaning; (b) Compressive strength after the cleaning process of different types of bioaggregates.

Information extracted from different authors is discussed below, related to compressive strength parameters: Despite the lower quality concrete, in terms of compressive strength (15 MPa), lower than the reference concrete, Portuguese authors report mussel shell concretes with applicability at ages of 28 days of curing, not compromising the minimum required by the European standard that regulates civil construction [33]. Other authors have demonstrated that even with lower resistance values, concretes containing coarse aggregate replacement with mussel shell present the possibility of developing structural concrete, lighter and at a lower cost, falling within the compressive resistance class at the established 28 days. in ASTM C330. Furthermore, there were gains in durability, resulting in longer-lasting works, which tend to reduce future demands for cement, both for renovations and reconstruction [16].

Replacing the natural aggregate with oyster shell appears to be possible. However, it negatively influences the long-term strength of concrete [40]. When crushed shell is incorporated into the concrete mix, the workability of the concrete decreases, together with the flexural strength and specific mass of the concrete [48]. Despite this, this material, transformed into sand and inserted as a partial replacement for natural aggregate (sand), in cement mortar, resulted in a cementitious mass that presented acceptable mechanical properties, when compared to the control group, made with conventional natural aggregate [18].

In an experiment carried out in Russia, the dosage of mussel shells, with an abstraction of 6% of binder, traditional cement, revealed more effectiveness, increasing resistance properties, generating increases of up to 12% in compressive strength, up to 13% in compression axial, 14% for flexural tensile strength and up to 12% for indirect tension. The deformation under compression and axial tension decreased to 9% and 12%, respectively, with an increase in the elastic modulus by 15%, relative to the reference body. This result is most impressive in terms of the reduction in the cost of construction materials, compared to traditional ones, by around 17% and in the cost of civil construction by up to 15%, thanks to the reduction in the percentage of predictable defects [75].

Other authors have proven that it is possible to reduce the cost of lightweight concrete by using regional snail shells and palm kernel shells (endemic palm), materials lighter than granite, influencing the density of the concrete. The compressive strength of the composite, as usual, decreases as substituents are added to the concrete mixtures. However, the cementitious material produced from a mixture ratio of 1:1.5:3, Portland cement, snail shells, vegetable biomass and granite fines, respectively, presented resistance comparable to the control specimen, attesting to the effectiveness of the combination in the production of lightweight concrete at an optimal level of 5% replacement of fine granite. This implies that the combination of palm kernel and periwinkle (snail) shells can reduce housing and environmental costs [13].

2.4.8. Thermal insulation of cementitious materials containing bioaggregates.

The increase in porosity promoted by the use of bioaggregates based on mussel shells promotes another interesting property: thermal and acoustic insulation. Although this information is well accepted and disseminated among authors in the field, there are few studies using mussel shells in cementitious materials for thermal insulation [8].). Figure 18 presents the thermal conductivity results as a function of the density of mortars containing mussel shell bioaggregate at levels from 0 to 20% replacement. It is easy to observe the correlation between the two properties and that the use of mussel shells reduces the thermal conductivity of mortars, mainly attributed to porosity [38]. Therefore, an interesting type of application of bioaggregates is for the production of concrete or thermally insulating mortars.

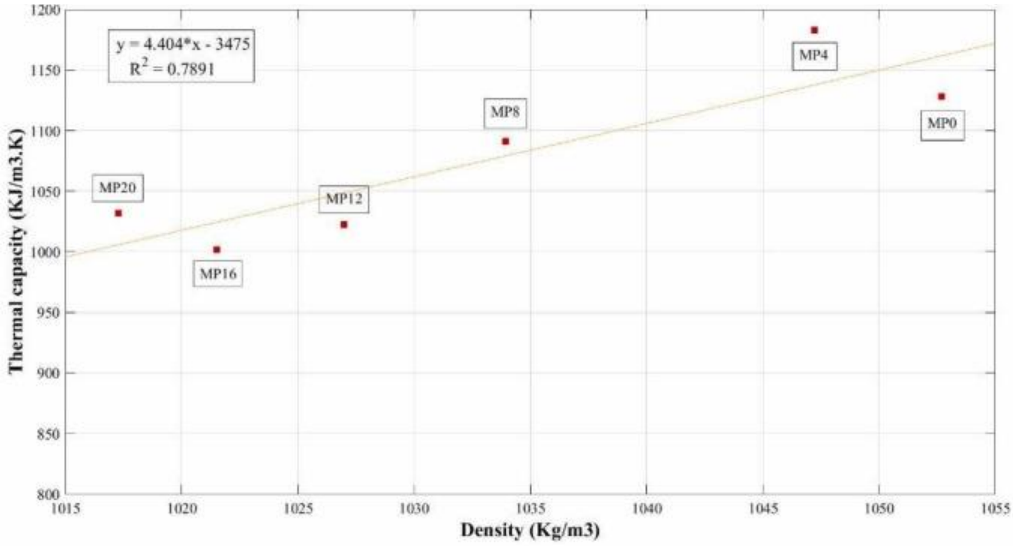


Figure 18. Relationship between density and thermal conductivity of mortars containing mussel shell bioaggregates.

3. Conclusions and Suggestions for future work:

The main conclusions of the work are:

- Bioaggregates produced from mussel shells and similar materials have potential for application in concrete and mortars due to their chemical composition, predominantly based on $CaCO_3$ in the form of calcite or aragonite, compatible with limestone aggregates and chemically inert.

- Challenges from a chemical point of view are related to the presence of organic impurities, especially in the chitin layer in the external shell, and the presence of chlorides and sulfates, which can delay the setting of the cement or impair the adhesion of the aggregate with the cement paste. Research shows that carrying out simple cleaning treatments, such as washing in running water and drying in ovens at temperatures of 100ºC are sufficient to remove impurities and enable the application of the material as a bioaggregate.

- Regarding physical properties, it is observed that bioaggregates have a specific mass similar to conventional aggregates and can be used in different particle sizes, with great variation in MF and DMC. However, there is a greater potential for application as fine aggregate, as it is less negative in the compressive strength of cementitious materials.

- The morphology of bioaggregates is complex, but the presence of lamellar, irregular, highly porous and flat particles predominate. This particle pattern harms the transition zone between paste and aggregate, promoting entrained air, porosity and a drop in strength. However, it is worth highlighting that the transition zone is less complex than using recycled construction and demolition aggregates, for example. This is an advantage when applying the material.

- From a properties point of view, it is observed that the use of bioaggregates in concrete and mortar has a tendency to worsen workability, increase water absorption and porosity, reduce density and cause damage to mechanical properties. On the other hand, there is a tendency to reduce thermal conductivity, suggesting an improvement in insulation properties. This pattern is justified by the high-water absorption of the bioaggregate, irregular, lamellar and porous particles, which impair adhesion to the cement paste, the presence of organic impurities and chlorides and other factors such as an increase in the viscosity of cementitious materials in the fresh state.

- However, several authors demonstrate that the use of lower levels of bioaggregate, generally up to 25%, does not harm the mechanical properties of concrete and mortars, emerging as an eco-friendly solution for disposing of mussel shell waste, for example.

Other possible applications are porous or permeable concrete; concrete and light mortars; material for covering, sealing or laying blocks; or even as mortars for thermal and acoustic insulation. In this way, viable solutions for the use of mussel shell bioaggregates in cementitious materials are observed.

As a suggestion for future work, the following stand out:

- Characterization of mussel shell bioaggregates, using techniques such as: Los Angeles abrasion tests, aggregate strength and tenacity tests; and/or packing compactness tests.

- Rheological tests with concrete and mortars containing mussel shell bioaggregates and similar materials, through incorporated air, water retention, rheology by dropping ball or squeeze flow; and rheology analysis using viscometers.

- Tests that evaluate the influence of bioaggregates on the reactivity of Portland cement, such as calorimetry tests and definition of setting times, together with complementary analyzes of X-ray diffraction, scanning electron microscopy or thermal analyses, aiming to explore the phases formed or altered during cement hydration.

- Additional tests on thermal, acoustic, and electrical insulation of mortars and concrete with bioaggregates, as there is potential to improve these properties with the use of mussel shells.

- Assessment of other important mechanical parameters, such as modulus of elasticity, tensile strength in flexion or diametrical compression to prove the impact of bioaggregates on other relevant properties.

- Analysis of the pore structure and porosity of concrete and mortars containing bioaggregates with mussel shells and similar materials, using tests such as mercury intrusion porosometry or micro tomography in concrete.

- Non-destructive tests on concrete and mortars containing bioaggregates using sclerometry, ultrasonic pulse and electrical resistivity tests.

- Theoretical and experimental modeling of reinforced concrete elements with bioaggregates through the analysis of beams, pillars and slabs on a reduced scale.

- Economic analysis of concrete and mortar containing mussel shell bioaggregates or similar materials.

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