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Surface protection of recycled concrete from different biogenic silica bio-deposition techniques: A sustainable approach

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ABSTRACT

The increasing generation of construction and demolition waste poses an environmental challenge. In this study, the use of recycled concretes is proposed as a possible solution, reducing the extraction of natural resources and minimising the accumulation of waste in landfills. To ensure the durability and strength of this type of recycled concrete, two diatom culture techniques were developed in controlled environments to promote the bio-deposition of biogenic silica on the surface concrete. Through the resulting protective biofilm, diatoms decreased the capillary absorption and improved the impermeability of concrete to water and gases, such as CO_2. Furthermore, these contributed to an increased mechanical strength of the concrete and a positive morphological modification of its surface by densifying and sealing surface pores. These results support the potential of diatoms as an effective solution to improve the properties and durability of recycled concrete.

1. Introduction

The construction sector has significantly developed in recent decades, driven by the creation and demolition of infrastructure around the world. This has caused a significant increase in the generation of construction and demolition waste (C&DW), whose environmental impact gives reason for concern. The proper management of C&DW has become a critical issue in the construction industry, as its storage in landfills has proven to be a major cause of ecosystem degradation and environmental problems [1].

Several studies have investigated the use of recycled aggregates from concrete elements (RCA) for the production of recycled concretes, with promising results that have generated great expectations in the construction industry [2–6]. These studies have shown that it is possible to use RCA in percentages of substitution of natural aggregates (NA) higher than 50 %, which represents a valuable opportunity to promote more sustainable and environmentally friendly practices in the field of construction.

However, despite advances in RCA research and the possibilities offered by their use, approximately 95 % of these materials are used in low-quality construction (paving, road foundations, ditch construction, etc. …) [7]. This use is mainly attributed to the loss of physical and mechanical properties of the resulting concrete when using recycled aggregates, which exhibit inferior performance compared to conventional concrete [8,9]. It should be noted that RAs have some disadvantages, mainly associated with the content of mortar attached to the aggregate [10], which contributes significantly to a decrease in the workability of the mix after the

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incorporation of RA, leading to a significant loss of flowability of the mix [11] compared to NAs. This causes the civil construction industry to be reluctant to use them in commercial concrete production, especially for structural applications [12,13].

For this reason, recycled concretes present distinctive characteristics, such as lower density and higher water absorption, mainly attributed to the characteristics of the RA [14–16]. These factors impact directly on the durability of concrete, as its strength and longevity are closely related to the structure of its pores, including their size, shape and distribution [17,18]. Therefore, it is essential to ensure an adequate porous structure and effective management of the ingress of harmful agents to significantly improve the durability of the concrete.

Different techniques based on surface treatments have been developed to extend service life and improve concrete structures. These include the use of water-repellent and pore-sealing treatments based on silica nano-materials, such as nano-silica (NS) [19–25] or the development of $CaCO_3$ bio-depositions from bacteria [26–31]. These surface treatments have been proved to increase impermeability and improve the durability of concrete and its ability to resist the action of aggressive agents.

In this context, the cultivation of diatoms is presented as an innovative and promising option to improve the durability of concrete, combining the use of nano-materials in the form of biological NS with diatom bio-depositions. These unicellular microorganisms are found naturally in aquatic environments and present an external cellular structure composed of up to 98 % silica (SiO_2), which gives them the interesting capacity to be used as microscopic silica nano-fabrication factories [32].

In the present study, the cultivation of diatoms in two artificial media is proposed, controlling various factors that influence the development of these microorganisms to produce their bio-deposition on the surface of the recycled concrete as a biological treatment. This bio-deposition involves the adhesion of diatoms in the form of biogenic silica [33], creating a biofilm on the surface of the concrete composed of diatoms and their adhesive secretions, which contain extracellular polymeric substances (EPS) [34].

The possibility of using diatoms in artificial culture environments to promote controlled silica bio-deposition on the surface of concrete represents a unique opportunity to improve its properties and durability. The silica deposited by diatoms could contribute to densifying the pores and reducing the permeability of concrete. This could encourage the use of recycled concretes with high RA substitutions (50 %), contributing to a more circular and green economy through biological treatments.

Previous studies on the growth of diatoms on the surface of concrete have yielded encouraging results [35]. This treatment has been shown to be highly effective in improving the durability and properties of hardened concrete. The controlled bio-deposition of silica by diatoms has been shown to seal pores and microcracks, which can significantly increase the impermeability of the material.

In this context, the main contribution of the present research is the optimisation of the development of diatom populations and thus the bio-deposition of biogenic silica. This progress has been achieved by controlled cultivation of diatoms in artificial environments with strictly controlled environmental and feeding conditions. Unlike previous research, the methodology adopted in this study does not limit diatom development to specific periods with more favourable environmental conditions or positive photoperiods. In addition, the ability to grow diatoms allows for flexible timeframes for prolonged colony development, resulting in increased deposition of biogenic silica over time. These improvements ensure a more efficient and controlled approach to harnessing the benefits of diatom bio-deposition more effectively.

Therefore, the aim of this study is to provide a solid basis for future research in this area, which could have major implications in the construction industry and contribute to the search for sustainable solutions to improve the construction materials and prolong the useful life of concrete structures in an increasingly demanding and environmentally conscious setting.

2. Materials and methods

2.1. Materials

2.1.1. Concrete

For the concrete mix, cement type CEM III/A 42.5 N/SR was used, which contains blast furnace slag and meets the requirements of EN 197-1 [36]. The aggregates used consist of a proportional mix (50:50) of natural siliceous gravel (NA) 4/12.5 mm large and same size RCA, together with 0/4 mm siliceous sand as fine aggregate. The particle size distribution of these materials is shown in Fig. 1, according to EN 933-1 [37].

The aggregates used comply with the specifications set out in EN 12620:2003+A1 [38] and EN 1992-1 [39], and are therefore suitable for the manufacture of concrete. Aggregate characterisation tests were performed according to EN 933-1 [37] and EN 1097-6 [40], which include the measurement of density, grain-size modulus (ratio between maximum particle size “D” and minimum particle

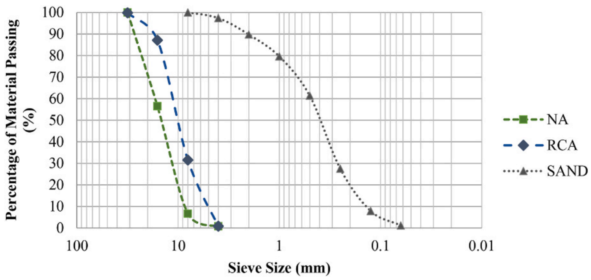

Fig. 1. Particle size distribution of aggregates.

size “d”, according to EN 12620:2003+A1 [38], this ratio must not be less than 1.4) and water absorption (wt%-24 h), as presented in Table 1.

RCA, they were analysed according to EN 933-11 [41], due to the high heterogeneity in their composition, as shown presented in Table 2. These can be classified as type A aggregates (RC90, RCU95, Rb10-, Ra1, FL2-, XRg1-), according to EN 206 [42], because the concrete components (Rc) combined with natural stone (Ru) are higher than 95 % and the ceramic content is less than 10 %.

The proportion of the recycled concrete components used is presented in Table 3, with a 50 % substitution of RCA. The mixture was produced according to the protocol described in EN 12390-2 [43], aiming for a water-cement ratio of 0.59 to obtain concrete with plastic consistency.

2.1.2. Bio-deposition of diatoms

To grow the biofilm, the concrete specimens were immersed in water for a specific period of time in two different aquatic environments: one under controlled laboratory conditions (Diatom Indoor) and the other under natural outdoor environmental conditions (Diatom Outdoor). At the end of this period, the prepared samples were removed from the water, and the biofilm was analysed and characterised. A count of diatoms per square centimetre was performed for each culture environment; the results are presented in Table 4. The samples in controlled conditions present a higher number of diatoms per square centimetre, due to the control of the factors that favour the growth and development of diatom colonies, temperature and lighting being the main factors in their formation [44].

In the present work, a complete characterisation of the biofilm formed by the bio-deposited diatoms was performed, with the identification of the main guilds (Fig. 2) and the analysis of the main families present Fig. 3. The characterisation revealed similar percentages in terms of the distribution of the different guilds (Fig. 2) in both the controlled laboratory environment (Inside or I) and the controlled outdoor environment (Outside or O). A wide diversity of species was found in the biofilm analysed; however, the group with the greatest predominance corresponded to the benthic guild. These species are deposited directly on the substrate, which makes them an essential component of the biofilm formed by the diatoms.

A similar trend was demonstrated in terms of percentages in both environments regarding taxonomic groups of the main diatoms characterised in the biofilm, as shown in Fig. 3. The predominant group was Monoraphidees, followed by the Naviculacees and Nitzschiaces in smaller proportions.

Note that the small variations in diatom diversity between the two culture environments can be attributed to the fact that both received an initial inoculum from the same source (as explained in section 2.2.1.), leading to the development of similar communities in both culture types.

2.2. Methods and tests

2.2.1. Growing diatoms

In the present study, the cultivation of diatoms in two artificial environments was analysed, considering that these microalgae grow naturally in aquatic environments. For this purpose, two similar forms of cultivation were performed: one in a controlled environment inside the laboratory and the other in a controlled environment with environmental conditions similar to those outside. These two experimental conditions facilitated the evaluation of the diatoms development and behaviour in each simulated environment.

2.2.1.1. Indoor growing of diatoms. The dimensions of the pond used for the cultivation of diatoms in a controlled laboratory environment were 3×1 m and a depth of 0.60 m, with a total capacity of 1.8 m^3. The water used to fill the pond came from the Torio river in León (Spain). The culture was started by adding to the water 100 ml of diatom inoculum, collected by brushing stones submerged in the same river to obtain the periphyton.

Diatoms were cultured for a period of 3 months (June to September) maintaining all the optimal conditions for their growth [45], which are detailed in Table 5. To achieve adequate oxygenation and continuous water circulation, two air bubble oxygenators were used, with a flow rate of 100 l/h and a recirculation pump with a flow rate of 1000 l/h. Water temperature was kept under control using a heater equipped with a thermostat; lighting was provided by an LED lamp with a timer to regulate the photoperiod.

Sodium metasilicate was added every 15 days at a concentration of 40 ppm to ensure adequate food supply for the diatoms. These conditions were established to create an ideal environment for the optimal development and growth of the diatoms in the controlled pond.

2.2.1.2. Outdoor growing of diatoms. A pond located in León (Spain) at an altitude of 835 m above sea level facing south (optimal lighting conditions) was used, for the cultivation of diatoms in the outdoor environment. The dimensions of the pond were 3×3 m with a height of 0.60 m, representing a total volume of 5.4 m^3. The water used to fill the pond was from the same source as in the indoor cultivation method (Torio river).

Once the outer pond was filled, a 300 ml inoculum of diatoms was added, following the same procedure used in the laboratory controlled environment (Section 2.2.1.1). To maintain oxygenation and water circulation, three cascade pumps with a flow rate of

Table 1
Aggregate characterisation.

Property	RCA	NA	Sand
Density ρ_p (Mg/m^3)	2.5	2.6	2.5
D/d Ratio	3.3	2.6	6.6
Wt%-24h	4.8	4.3	1.7

Table 2
Composition of recycled aggregates.

Type	Code	RCA
Concrete, mortar	Rc	47.2 %
Unbound mortar and natural stone	Ru	51.6 %
Bricks and tiles	Rb	0.2 %
Asphalt	Ra	0 %
Glass	Rg	0 %
Impurities and other	X	1 %
Floating particles	Fl	0 %

Table 3
Recycled concrete composition.

Materials	Composition (quantity/m^3)
4/12.5 mm NA (kg)	585.5
4/12.5 mm RA (kg)	585.5
0/4 mm Sand (kg)	642
Cement type CEM III 42.5 N/SR (kg)	354
Water (l)	210

After mixing, the concrete mix was poured into steel moulds to form the specimens, which were cured at a temperature of 20 ± 2 °C and a relative humidity of 100 % for 28 days.

Table 4
Concentration of diatoms on the concrete surface.

Growing environment	Diatoms/cm^2
Diatom Indoor	5.9×10^5
Diatom Outdoor	4.1×10^5

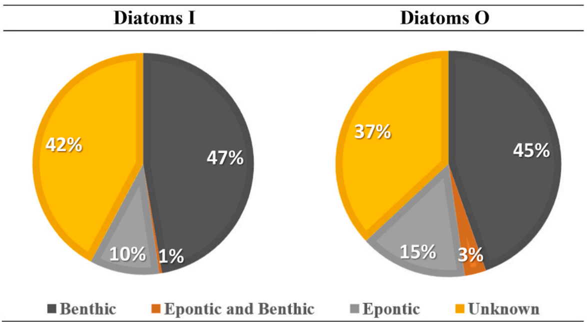

Fig. 2. Distribution of the different guilds of diatoms on the surface of the concrete in both growing environments.

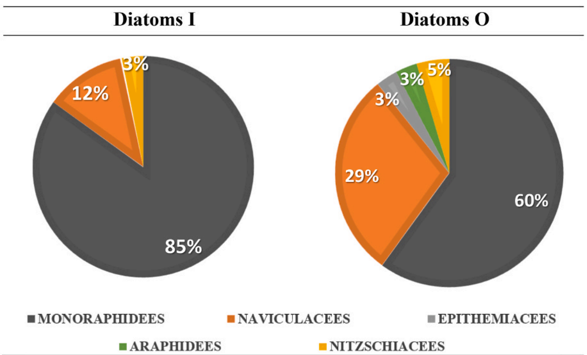

Fig. 3. Distribution of the different taxonomic groups of diatoms on the surface of the concrete in both growing environments.

Table 5
Optimal conditions for diatom growth.

Controlled factor	Value
Temperature (°C)	25 ± 1
Nutrients (Sodium metasilicate Na_2SiO_3)	40 ppm
Light (lux)	2000
Photoperiod (h)	16:8

1350 l/h were used.

The cultivation period covered 3 months (June to September), coinciding with the summer equinox in the northern hemisphere. During this period, positive photoperiods and more optimal temperatures occur [46], favouring the growth of diatoms. The environmental conditions of temperature and solar radiation during this period, which contributed to the adequate development of diatoms during the study, are shown in Fig. 4.

Furthermore, sodium metasilicate (40 ppm) was added as a nutrient for the diatoms every 15 days, following the above mentioned procedure, to provide an ideal environment for the healthy development and growth of the diatoms in the outdoor pond.

2.2.2. *Biofilm growth on the surface of concrete*

Five different tests were conducted to evaluate the effect of biofilm on the mechanical properties and durability of recycled concrete. Each test was performed using different geometries and test surfaces, in accordance with the relevant standards. The study surface, which is the flush face that is not in contact with the mould walls, was used as the substrate for biofilm development.

Diatom colonies have been shown to be able to grow on artificial substrates in as little time as 4 weeks [44], albeit with a low density of diatoms per square centimetre. Therefore, samples from each test in both environments (Indoor and Outdoor) were introduced for an optimal period of 3 months for the development of the protective biofilm. The samples were evenly distributed on the surface of both ponds, to minimise variations between them. Specimens were submerged to a depth of 20 ± 5 cm below the water surface, with the study face oriented parallel to promote diatom bio-deposition.

After the end of the biofilm growth period, specimens were removed from both ponds and dried in a controlled environment at a constant temperature of 20 ± 2 °C and a relative humidity of 45 % ± 10 % for 7 days.

Untreated control samples were prepared simultaneously for comparison. These control samples were immersed in a covered water tank (without exposure to light to prevent the growth of any biological material) for a period of 3 months. These were then removed from the water and dried under similar conditions to those of the bio-treated samples.

2.2.3. *Biofilm characterisation*

The procedures established in EN 14407 [47] were followed to characterise the biofilm, which allowed the identification and quantification of the diatoms present. First, periphyton extraction was performed from known concrete surfaces submerged in water for a period of 3 months, following the standard adapted to lentic systems EN 13946 [48]. The extraction of epilithon from the sample was collected by brushing the surfaces of the study substrates as free as possible from microalgae and sediments. The extracted samples were preserved in a 4 % (v/v) formaldehyde solution in a 50 ml vial.

Subsequently, the samples were treated with hydrogen peroxide (120 vol) at a temperature of 90 °C over a period of 3 h. Afterwards, the samples were centrifuged and decanted several times to obtain a clean suspension free of organic matter. Finally, the sample suspension was examined on a slide with Naphrax synthetic resin of high refractive index (RI = 1.74).

Diatom valves were recognised to species or subspecific level and counted under light microscopy (1000 ×, Olympus BX 60). For the identification of diatoms, the references of Hofmann [49] and other relevant sources were followed, with the aim of identifying a minimum of 400 individuals to the most detailed taxonomic level possible. The numerical data obtained were processed using OMNIDIA v. 4.2 [50] to determine the trophic indices of diatoms in each sample. Finally, from the values obtained, relative abundances of the diatom species were calculated and expressed as individuals per cm^2 of substrate. This calculation was done by extrapolating the count to cm^2, considering that the extraction surface of the samples is known.

In addition, a Hitachi S-4800 scanning electron microscope (SEM) equipped with an X-ray emitter was used for the microstructural

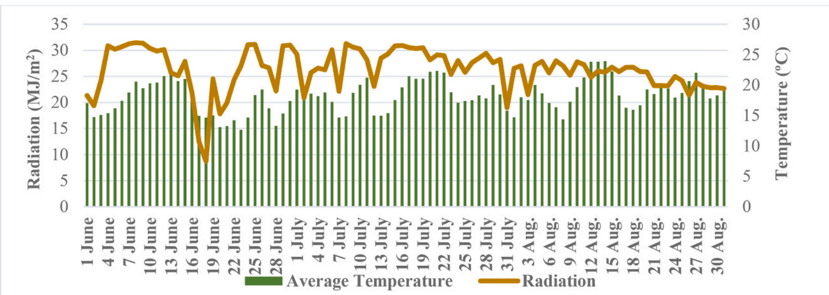

Fig. 4. External environmental factors.

analysis of the samples, which were previously metallised with a 10-nm carbon layer using QUORUM Q150T ES equipment to ensure conductivity and avoid signal masking.

2.2.4. Hardened concrete tests

2.2.4.1. Compressive strength. The compressive strength of recycled concrete samples was evaluated according to EN 12390-3 [51] after the bio-deposition period in a laboratory hydraulic press. A total of nine cylindrical specimens (∅100 × 200 mm) were used. These were divided into three groups: three samples corresponding to the indoor environment (I-Diatom), three samples corresponding to the outdoor environment (O-Diatom) and three untreated control samples (C-Sample) for comparison.

2.2.4.2. Capillary absorption. The capillary water absorption was determined following the EN 83982 [52] standard, which is used to evaluate the capillary absorption in hardened concrete. In this test, cubic specimens of dimensions 100 × 100 × 100 mm^3 were used. These specimens were conditioned according to EN 83966 [53] and waterproofed using paraffin on the lateral faces up to a height of 1 cm, so that capillary absorption occurred only on the test surface.

After conditioning, all specimens were weighed, placed on a grid with 10 × 10 mm openings and immersed in water, ensuring the immersion did not exceed 5 ± 1 mm. At time intervals established in the reference standard, the samples were weighed until a constant mass was reached, with differences between weighings less than 0.1 %. This test established the relationship between water absorption and time, which allowed the calculation of the capillary coefficient K of the concrete samples.

2.2.4.3. Water under pressure. Cylindrical recycled concrete specimens (Ø150 × 300 mm^3) were tested using a compressed air driven water-penetration tester (Reference 270200: Mecánica Científica S.A) following the EN 12390-8 [54] standards. The specimens were subjected to a hydrostatic pressure of 0.5 MPa (5 bar) for a period of 72 ± 2 h and split perpendicular to the treated surface according to EN 12390-6 [55].

The maximum depth of penetration (P_{max}) and the average depth of penetration along the entire surface (P_m) were determined to analyse the penetration front. To obtain the P_m value, the area of the penetration front in mm^2 was calculated using ImageJ software [56] and divided by the sample diameter.

2.2.4.4. Water absorption at low pressures: Karsten tubes. The low-pressure water absorption test was performed according to EN 16302 [57], using the Karsten tube method. Six Karsten tubes were distributed on the test surface of recycled concrete specimens (400 × 100 × 100 mm^3), maintaining a minimum spacing of 40 mm to avoid any interaction among them. These tubes were firmly adhered with butyl adhesive and filled with distilled water up to the 0 marker.

During the test, water uptake times were recorded at 0.1 ml intervals until 1 ml of water uptake was reached. This decision responds to the time required for complete absorption of the Karsten tube being considerably long.

2.2.4.5. Carbonation resistance. The carbonation resistance of recycled concrete was evaluated using the natural method at atmospheric CO_2 levels, following EN12390-10 [58]. Three cubic specimens (100 × 100 × 100 mm^3) were analysed for each period and treatment. These samples were placed in an outdoor enclosure in León (Spain) exposed to natural environmental conditions but protected from rainwater. Relative humidity and temperature were recorded throughout the test.

Three periods (3, 6 and 12 months) were analysed, to determine the depth of carbonation (d_k). Each tensile specimen was divided into two half-sections, and a hydroalcoholic phenolphthalein solution was applied by spraying. Carbonation front data were extracted from the tested surface only, taking measurements at five points (25, 37.5, 50, 62.5 and 75 mm) out of the total 100 mm, using a 0.01 mm precision caliper.

The carbonation rate was calculated using two methods described in EN 112390-10 [58]. The first method used formula (1) to calculate the carbonation rate in each study period, where the values of k_c (carbonation rate in $mm/a^{0.5}$), d_k (depth of penetration in mm) and t (effective time in years) were considered. The second method allowed the determination of the overall carbonation rate of the complete test cycle, from the slope analysis, which related the penetration depth (y-axis) to the square root of the time in years (x-axis).

$$d_k = k_c \cdot \sqrt{t} \tag{1}$$

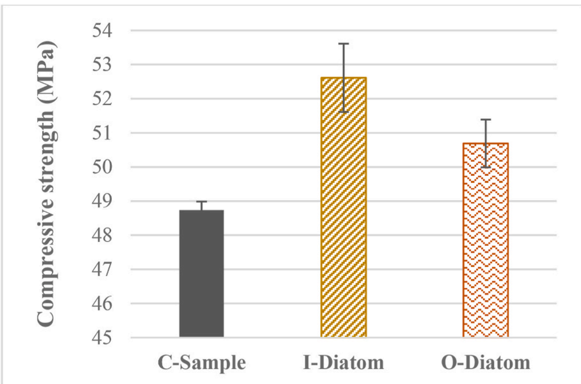

Fig. 5. Compressive test results.

3. Results and discussion

3.1. Compressive strength

The results from the mechanical compressive test of the specimens after bio-treatment are shown in Fig. 5. These results reveal that the exposure of the specimens to bio-deposition in different culture environments does not affect the mechanical properties of the samples. Moreover, an increase in compressive strength of about 4 % for the O-Diatom specimens and 8 % for the I-Diatom specimens is observed compared with that of the reference specimens. This could be attributed to an increased densification and strengthening of the surface microstructure of the specimens, as observed in previous studies with NS surface treatments [19,21]. These works have shown similar improvements in the compressive strength of concrete with diatom bio-deposition. Hou et al. [19] demonstrated an improvement of about 3 % when applying NS (30 %), while Shirzadi Javid et al. [21] achieved about a 5 % increase in strength using NS at 20 %. These results agree well with the work of Parashar & Nagar [30], where $CaCO_3$ bio-deposition through bacteria of the *Bacillus* family was also observed to lead to pore sealing and further densification of the surface matrix, increasing the compressive strength of the concrete.

This results indicate that the recycled concrete with 50 % aggregate substitution used in the present study shows mechanical strength within the range of those from previous studies that used RCA with 50 % substitutions [6]. This suggests that the use of recycled concrete with these characteristics meets the established strength standards for this type of material.

3.2. Capillary absorption

Fig. 6 shows a graph representing the mass gain by capillary absorption as a function of square root time. This graph shows a higher mass gain in the C-sample due to a more accentuated capillary water absorption, especially in the early stages of the test. This trend is maintained throughout the test. However, the bio-treated samples (I-Diatom and O-Diatom) show a less pronounced slope due to their lower capillary absorption.

When comparing exclusively the results of the diatom-cultured samples, the I-Diatom ones, with a higher concentration of diatoms, show a slightly lower mass gain, especially during the first 48 h (53.66 $min^{0.5}$), compared with that of the O-Diatom samples. However, as more time elapses, the absorption curves between the two culture media become almost similar. This suggests that, in the initial phase of capillary absorption, the surface capillary pores are filled [59] and the higher concentration of diatoms creates a more evident pore-lining effect in the concrete.

The values of the capillary water absorption coefficient (K) presented in Table 6 support the effectiveness of diatom bio-deposition as a waterproofing agent used in the surface protection of concrete: a capillary absorption coefficient of 25 % lower for the O-Diatom external culture samples and up to 31 % lower for the I-Diatom samples are observed. These results suggest that the surface pore microstructure of the concrete becomes more compact, which contributes to a better performance in terms of water absorption, decreasing the capillary absorption.

Relevant studies in the field of biological waterproofing treatments include the research of Muynck et al. [26], in which bio-deposited $CaCO_3$ coatings obtained from the culture of *Bacillus sphaericus* LMG bacteria (10^7 cells/ml) were compared with other silicon-based treatments, such as silane. Their results showed these biological coatings to be able to reduce the capillary absorption of the concrete by 47 % compared with that of the control sample, and up to 79 % in the case of the silane treatment.

Following the research line of silica-based surface treatments, given its similarity in chemical composition with diatoms, Geng et al. [22] evaluated the effect of different combinations of silane emulsion and NS prepared by the sol-gel process on the surface of concrete. The results obtained in their study showed reductions of up to 70 % in water absorption with the exclusive use of silane emulsion (600 g/m^2). However, the most effective treatments were those that combined both materials: the mixture of silane emulsion (300 g/m^2) with NS (300 g/m^2) achieved a decrease of more than 75 % in the amount of water absorption compared with that of the control sample. This waterproofing effect was also observed by Shirzadi Javid et al. [21], who achieved reductions of up to 40 % in water absorption through the exclusive use of NS at a concentration of 20 % nano-particles, evidencing the surface pore blocking effect of concrete, as shown in the present study.

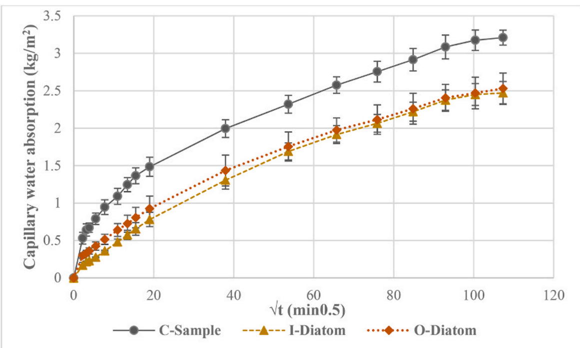

Fig. 6. Curve of capillary water absorption in hardened concrete samples.

Table 6
Capillary absorption coefficient "K".

	C-Sample	I-Diatom	O-Diatom
Capillary absorption coefficient "K" ($kg/m^{-2}min^{-0.5}$)	5.1×10^{-3}	3.5×10^{-3}	3.8×10^{-3}
Standard deviation	2.4×10^{-4}	1.4×10^{-4}	2.1×10^{-4}

3.3. Water under pressure

Fig. 7 shows the maximum height rate of water penetration at a pressure of 0.5 MPa. The bio-treated specimens show a lower water ingress into the concrete, while the untreated specimens reached maximum penetration heights of up to 29.6 mm and the I-Diatom and O-Diatom specimens experienced reductions of more than 50 % (O-Diatom: 58 %; I-Diatom: 54 %).

These results are supported by the calculation of the average penetration depth; due to the high heterogeneity in terms of concentrations across the treated surface, this parameter provides more representative values of the effect of diatom bio-deposition. These findings, presented in Fig. 8, reveal that the diatom samples reduced the penetration front by 57 % for I-Diatom and 64 % for O-Diatom samples compared with those of the C-sample. This demonstrates the waterproofing effect of the presence of diatoms in reducing water penetration into the concrete.

Note that the outdoor cultured samples showed a slight improvement compared with the indoor samples, even though the samples tested for diatom concentration presented a lower concentration of diatoms. This observation can be attributed to variations in environmental factors, specific conditions and distribution of diatoms in each sample [35]. It is important to note that the biological treatment was not evenly distributed in all samples during the test, which can influence the results obtained in each case.

The results obtained in the present study agree well with those from other bio-deposition studies; for example, Xu et al. [27] used *S. Pasteurii* DSM 33 bacteria culture in liquid and semi-solid medium with a concentration of 10^7 cells/ml, achieving a protective film and pore sealing of $CaCO_3$. This reduced permeability by 63–81 % compared with that of the control samples, depending on the culture medium used.

In addition, other studies using nano-composites of a siliceous nature, similar to diatoms, have also demonstrated waterproofing effects; for example, Li et al. [24] used 12.5 % NS with a particle size of 10 nm, and were able to reduce the penetration front by up to 42 %. Similarly, Shirzadi Javid et al. sprayed a deionised water solution with a higher concentration (20 %) of NS at the end of concrete curing, and achieved a 48 % reduction in the penetration front by the pore sealing effect conferred by the nano-material.

3.4. Water absorption at low pressures: Karsten tubes

Fig. 9 shows the results of the test using Karsten tubes and the results of the total time required for the absorption of 1 ml of water. In the graph, concrete samples treated with the diatom culture (I-Diatom and O-Diatom) require more time to absorb 1 ml of water compared with the samples without biological treatment (C-sample). The absorption curve of the untreated samples shows a less steep and constant slope as more water is absorbed. However, in the treated samples (I-Diatom and O-Diatom), starting at 0.2 ml, the absorption time increases exponentially in 0.1 ml increments, clearly distancing itself from the results of the C-samples.

In the comparative analysis shown in Fig. 10, a significant difference is observed in the time required for the diatom-treated samples (I-Diatom and O-Diatom) to absorb 1 ml of water compared with that required in the reference samples (C-sample). The absorption time for the treated samples was 650 times longer for I-Diatom and 528 times longer for O-Diatom. These results conclusively demonstrate that the biofilm present in the treated samples acts as an effective mechanical barrier to seal surface pores, reducing permeability and providing additional protection to the concrete. This effect is especially evident in a test designed to simulate the effects of rain on the surface of these materials [60].

These results demonstrate that diatom silica treatment is highly effective in waterproofing concrete, achieving hydrophobicity similar to that observed in NS coatings [61]. This is evidenced in the study by Sakr et al. [23], who used 50 nm colloidal NS as a surface treatment at various concentrations (5 %, 10 %, 15 %, 25 % and 50 % by mass). Their results indicate that samples treated with NS at the highest concentration (50 %) showed a reduction of up to 79 % in water absorption compared with that of the untreated samples.

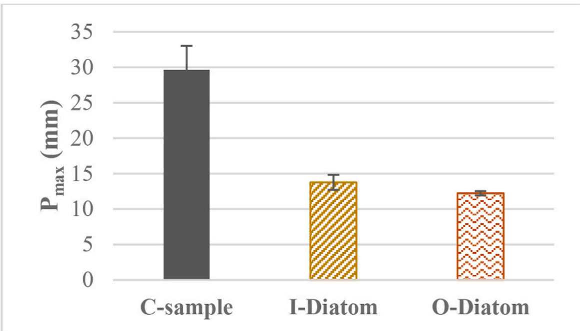

Fig. 7. Results of maximum penetration depth.

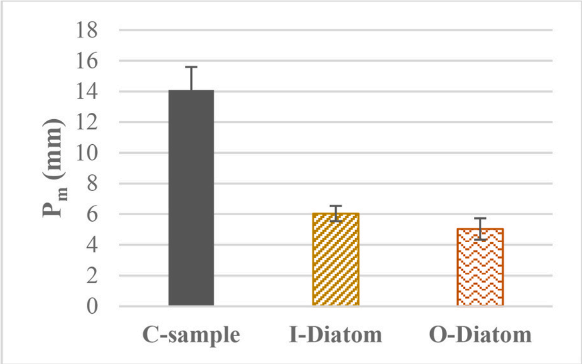

Fig. 8. Results depth of average penetration.

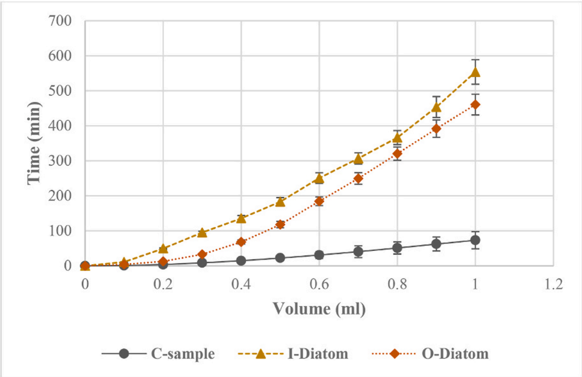

Fig. 9. Result of Karsten tube water absorption test.

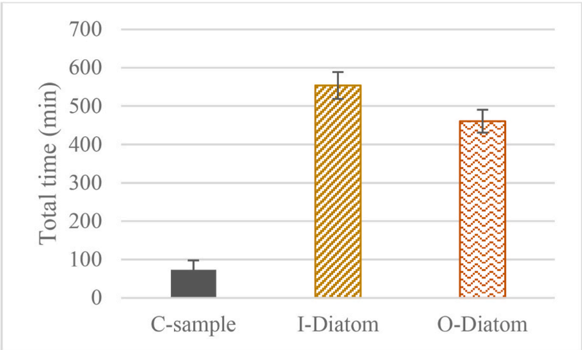

Fig. 10. Total absorption time 1 ml.

This clearly shows that NS can reduce the porosity of concrete by creating an impermeable protective coating.

Regarding to other biological treatments, Liu et al. [28] investigated the effectiveness of bacterial bio-deposition of $CaCO_3$ produced by the bacterium *Bacillus pasteurii* DSM 33 as a waterproofing coating. At higher concentrations of bacterial cells (10^9 cells/ml), these were able to improve water resistance by up to 90 % compared with that of untreated samples.

3.5. Carbonation resistance

Fig. 11 shows the results of the natural carbonation penetration fronts for the three measurement periods. C-sample samples show approximately 50 % higher penetration fronts compared with those of the diatom-cultured samples over the 12-month period. Specifically, the penetration front in the C-sample samples is 49 % higher than that in the I-Diatom samples and 45 % higher than that in the O-Diatom samples. These differences are more pronounced in the first periods (3 and 6 months), when the penetration fronts in the diatom samples are negligible, while reaching 3.5 mm penetration front in the control samples.

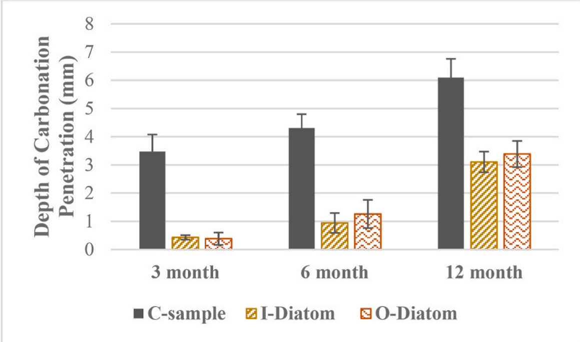

Fig. 11. Depth of carbonation penetration measured in different intervals over 1 year.

The effect of diatom bio-deposition on carbonation resistance was assessed by the carbonation rate (K_c) in mm/year$^{0.5}$. Fig. 12 shows the results of the carbonation rate in each study period, revealing the trend of protection provided by diatoms in both growing environments over time. A significant reduction in the carbonation rate is observed during the first two periods, with decreases of 87-78 % for the I-Diatom samples and 88-70 % for the O-Diatom samples. These reductions are maintained in the last period, although slightly lower, with 49 % and 44 % lower carbonation rates for the I-Diatom and O-Diatom samples, respectively, compared with those for the untreated samples.

Fig. 13 shows the global value of K_c for the whole study period to representatively analyse the effect of diatoms on the concrete surface. The carbonation rate was reduced by 47 % in the I-Diatom treated samples and by 52 % in the O-Diatom samples, compared with that in the C-sample samples. These results provide insight into the effect of diatom bio-coating at different times of the year and its interaction with environmental factors that favour carbonation, such as temperature and, in particular, high humidity [62]. These conditions favour the reaction between the calcium phases of cement and the carbon dioxide present in the air, which allows them to penetrate the concrete through its porous network, promoting the reduction of pH and ultimately its deterioration [63]. This demonstrates how diatoms contribute to the sealing of the surface porous network of concrete and their ability to increase its resistance to carbonation, as observed in similar studies with the use of NS [20,64]. Fajardo et al. [20] observed a decrease of 67–92 % in the carbonation depth after application of NS obtained by the sol–gel method and with a particle size less than 30 nm in hardened cement-based materials, due to the blocking of the surface pores. Similarly, Xia et al. [64] obtained promising results in their study on Portland cement treated with 20-nm colloidal NS at a concentration of 30 %, achieving 94–97 % reductions in carbonation.

This effect is also comparable to that of other biological treatment in previous studies, such as that of Muynck et al. [26], where $CaCO_3$ bio-deposition from the bacterium *Bacillus sphaericus* LMG (10^7 cells/ml) reduced the rate of carbonation by 35 % in concrete. Corroborating this effect, Salmasi & Mostofinejad [29], using the bacterium *Bacillus subtilis* (PTCC 1254; NCIM 2479; NCIB 8646; ATCC12711) at the same concentration as that in the Muynck et al. [26] study and for concrete samples cured in water and without steel fibre reinforcement, obtained a 36 % reduction of the penetration front at 28 days and 27 % lower at 56 days, thanks to the waterproofing effect conferred by bio-deposition.

3.6. *Microtopography*

Surface microstructure is an important parameter to visualise the effects of bio-deposition on concrete. Fig. 14 shows SEM images to analyse the changes in the surface morphology of the treated concrete samples in the indoor and outdoor environments compared with the control samples.

In *column A* Fig. 14 (× 30 magnification), the I-Diatom and O-Diatom samples present a bio-coating of diatoms covering the surface, while the C-sample shows a clean surface accessible to the penetration of water and substances harmful to the durability of the concrete. In *column B* Fig. 14 (× 1.00 k magnification), the diatom treatment presents a greater micro- and nano-roughness on the surface of the concrete, covering the surface pores, while the C-sample shows a typical concrete surface with its micro-cracks and a network of surface pores of various sizes.

The fact that the waterproofing effects of diatoms can be explained by the presence of this microroughness, has been suggested by Grumbein et al. [65], who achieved a hydrophobic effect in a cement-based material with the formation of a bacterial biofilm of *Bacillus subtilis* 3610, by increasing this microroughness, conferring a greater contact angle which increased water repellency. In addition, Li et al. [24] observed a more compact structure after the effect of the NS, which blocked pores, as occurred with the bio-deposition of diatoms.

Analysing in detail the difference between the I-Diatom and O-Diatom samples in *column B* Fig. 14, the variation in the structural morphology of diatom frustules and their sizes can be observed (yellow arrows). A higher number of smaller diatom species is found in the I-Diatom samples compared with in the O-Diatom ones. This could explain their better waterproofing behaviour, as smaller diatoms adapt to a smaller pore network through the gliding process [34]. Upon contact and adhesion to the surface, the diatoms migrate into these pores, providing them with a positive symbiosis in terms of environmental conditions and mutual protection. As a result, the concrete increases its impermeability as it reaches a network of smaller pores. M. Sanchez [66] achieved this increased waterproofing phenomenon with smaller NS particles, compared with samples treated with larger particles, achieving a higher densification of the

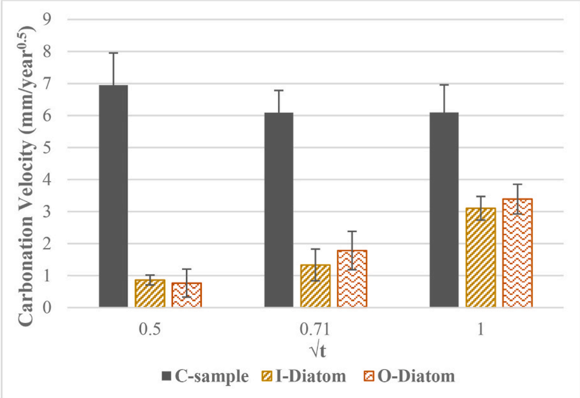

Fig. 12. Carbonation velocity (Kc) in different periods over 1 year.

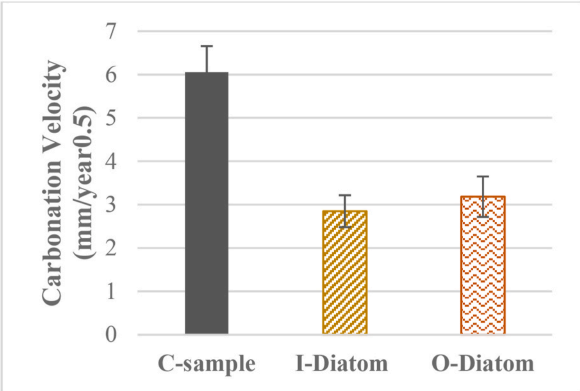

Fig. 13. Total Carbonation velocity (Kc) of the samples.

surface matrix in cement-based materials.

4. Conclusions

In the present study, the cultivation of diatoms on the surface of concrete has proven to be a highly effective treatment to improve its properties and increase its durability. The analyses performed in both controlled laboratory and outdoor environments provided the following conclusions:

Artificial cultivation of diatoms as a surface treatment for hardened concrete was successfully achieved. Furthermore, the diatom communities developed better in the controlled laboratory environments, thanks to the precise control of factors such as temperature, photoperiod and food supply. This allows for the bio-treatment to be performed at any time of the year, irrespective of outdoor climatic conditions.

In terms of mechanical strength, the diatom culture did not affect negatively the concrete; on the contrary, a significant increase of up to 4–8 % in compressive strength was observed. This improvement is due to the bio-deposition of the biogenic silica contributing to a higher surface densification of the concrete pores.

Tests in indoor and outdoor growing environments demonstrated the waterproofing effect of the protective biofilm formed by the diatoms. The capillary absorption of the concrete was significantly reduced in the treated samples, between 25 % and 31 %. Likewise, the results of the water penetration test under pressure revealed a decrease of the penetration front of 57–64 % compared with that of the untreated samples. This waterproofing phenomenon was maintained in both growing environments, although variations were observed between the different biological treatments.

Another notable finding is that the diatoms conferred an exceptional waterproofing effect on the concrete, with water absorption at low pressures between 528 and 650 times lower than that in untreated samples.

In addition, the diatoms proved to be effective in reducing the carbonation of concrete, reducing the penetration of carbonation by 49-45 %, providing a sealing effect against the ingress of gases and harmful substances such as carbon dioxide. This is essential for maintaining the long-term durability and integrity of concrete.

SEM images revealed how the diatom treatment modified the surface morphology of the concrete, forming a coating layer that covered pores and micro-cracks. Smaller diatoms were found to have a more positive impact on improving waterproofing, as these

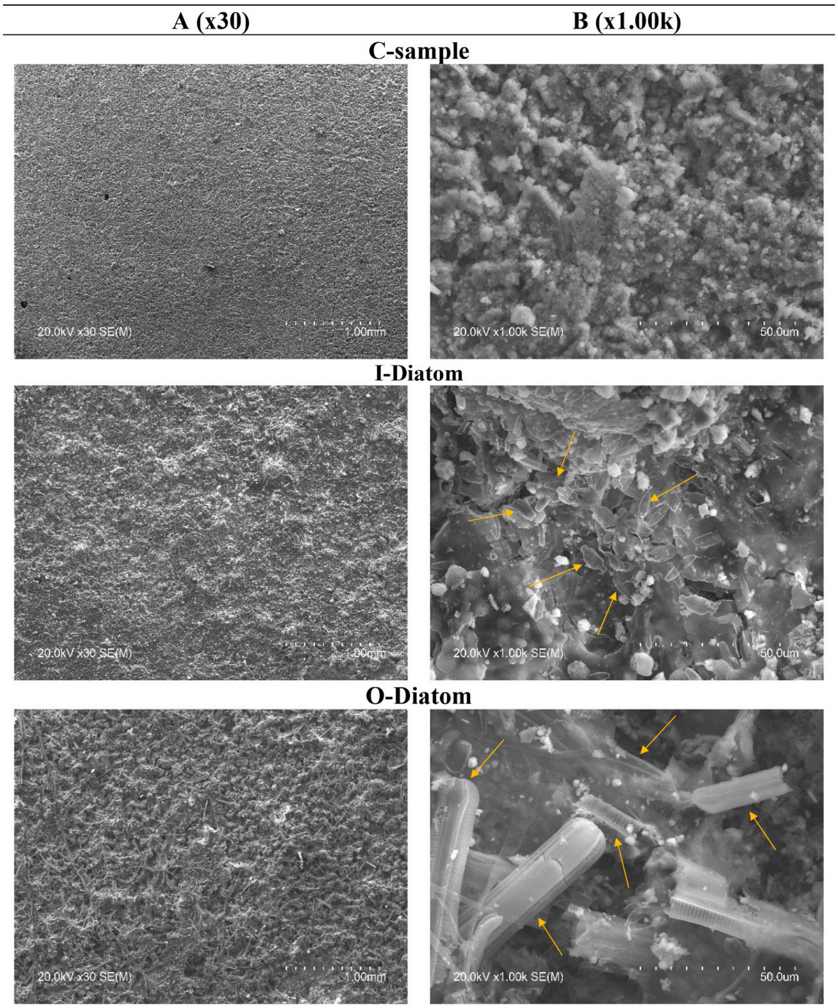

Fig. 14. Comparative surface microstructure: Column A ×30 magnification and Column B ×1.00K magnification.

were better adapted to smaller pores and provided greater protection to the concrete.

Finally, the cultivation of diatoms in concrete offers significant benefits, such as a reduction in capillary absorption, waterproofing against carbonation and water, increased mechanical strength and modification of surface morphology. In addition, the use of biological NS produced by these microorganisms has compared favourably with other types of existing biological and synthetic treatments, which have also been used to protect the surface of concrete. These comparisons contextualised the results of this study and reinforced the innovation that diatom bio-deposition contributes to the improvement of the properties of recycled concrete. Thus, the present study focused especially on comparing the bio-deposition of diatoms with a biological treatment of $CaCO_3$ deposition by bacteria, highlighting its effectiveness and simplicity in the formation of the protective biofilm offered by diatoms. Furthermore, it was contrasted with a synthetic NS treatment, given the proximity in chemical composition between the biogenic silica, making diatom culture even more attractive as a sustainable and effective option to improve the durability of concrete. It is important to note that, unlike synthetic NS, the diatomaceous biofilm is not homogeneously distributed over the surface. Despite this variability, the feasibility of diatom biofilm as an eco-friendly alternative to synthetic treatments is emphasised, thus underlining its potential as a sustainable solution for improving the properties of concrete.

These results support the potential of diatoms as an effective treatment to improve the properties and durability of concrete in various construction and civil engineering applications, opening up new possibilities for more durable and resistant structures over time.

CRediT authorship contribution statement

Daniel Merino-Maldonado: Data curation, Formal analysis, Investigation, Methodology, Software, Writing – original draft, Writing – review & editing. **Andrea Antolín-Rodríguez:** Data curation, Investigation, Methodology. **Saúl Blanco:** Conceptualization, Data curation, Investigation, Methodology, Supervision. **Julia Mª Morán-del Pozo:** Formal analysis, Resources, Writing – review &

editing. **Julia García-González:** Formal analysis, Resources, Writing – review & editing. **Andrés Juan-Valdés:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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