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Engineering Portland cement and concrete with agricultural-origin functional additives: Valorization of agro-waste

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ABSTRACT

Decarbonization, energy and resource efficiency, and the durability of construction activities have become critical issues in addressing several UN Sustainable Development Goals, including Life Below Water, Life on Land, Climate Action, Responsible Consumption and Production, Sustainable Cities and Communities, and Industry, Innovation, and Infrastructure. The clinker, the primary constituent of Portland cement, is manufactured through a highly energy-intensive process that results in substantial CO_2 emissions. In this context, the agricultural-origin supplementary cementitious materials offer the possibility of a greener cement by partially replacing clinker and tuning the properties of Portland cement. Therefore, understanding the options of using different agricultural-origin supplementary cementitious materials is paramount. These agricultural-origin supplementary materials may include natural fibres, nanocellulose, lignin, plant extracts, agricultural waste ashes, and biochar. These are employed to partially replace clinker in Portland cement, as well as for reinforcement, fine aggregates, or other supplementary components in cement and concrete. This review article examines the applications of various agricultural-origin materials in cement and concrete, based on existing literature. It also reviews SWOT analyses and life cycle assessments, highlighting the promising environmental and economic benefits of these materials. However, the lack of standardization and supply chain inefficiencies remain significant barriers to their widespread adoption.

1. Introduction

Concrete is the most widely used human-made material, second only to water in global consumption due to its affordability, versatility, and durability [1,2]. With an annual production of 25–30 billion tons, the concrete industry accounts for 2–3 % of global energy consumption, 9–10 % of industrial water use, and 8–9 % of man-made greenhouse gas emissions [3,4]. Ordinary Portland cement (OPC), the primary binder in concrete, poses challenges to sustainable development due to its environmental impact, including excessive limestone extraction and high CO_2 emissions [5,6]. The clinker is the main component of ordinary Portland cement, and its production is associated with huge emissions of CO_2 gases [7]. For example, typical cement production releases approximately 0.8 tons of CO_2 per ton of cement into the atmosphere, making the cement industry one of the major industrial sources of greenhouse gases [8,9]. An illustration of carbon footprint generation during cement production is shown in Fig. 1 [10].

The problem of decarbonization of Portland cement production is becoming alarming because of its increase in consumption and hence production. The total annual cement consumption in 2016 was 4.13 Gt, and it is expected to grow to 4.68 Gt/year by 2050 [11]. There are extensive efforts to decarbonise cement and concrete production involving new strategies, technologies, policy considerations, case studies, and economic implications, but there are still considerable challenges to addressing this issue effectively [12]. While clinker remains essential to Portland cement production, its environmental impact can be reduced by exploring alternative formulations and supplementary materials. The Portland cement industry could employ a range of technological and material interventions to address this challenge, as given below:

1. Reduction of the cement-to-clinker ratio using supplementary cementitious materials (SCMs) [10,13,14].
2. Alternate formulations of cement such as lime calcined clay cement (LC^3) and calcium sulfoaluminate (CSA) cement [15,16].
3. Reducing energy consumption using grinding aid [17,18].
4. Development of new process technologies and renewable electricity [19–21].

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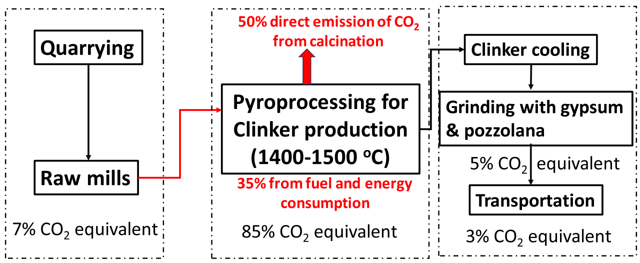

Fig. 1. Schematic illustration of CO_2 equivalent generation of carbon footprints during a typical ordinary Portland cement production.

5. CO_2 capture from the clinkering process, use and storage (CCUS) [22].

Several supplementary cementitious materials (SCMs) options are available for partially replacing clinker in ordinary Portland cement [23, 24]. Some of these promising options could be the agricultural-origin supplementary materials and the recycling of industrial by-products [25]. Agricultural waste, such as rice husk ash, sugarcane bagasse ash, wheat straw ash, and corn cob ash, contains reactive silica and alumina, making them effective supplementary cementitious materials (SCMs). These materials partially replace clinker in Ordinary Portland Cement (OPC), reducing CO_2 emissions associated with clinker production. Simultaneously, agricultural waste materials enhance the mechanical properties and durability of cementitious composites. Agricultural-origin materials are renewable and require less energy compared to conventional building materials. Since agricultural by-products such as hemp, rice husk, bagasse, shells and straw are naturally occurring and minimally processed, their production consumes fewer fossil fuels, reducing overall greenhouse gas emissions, making construction more sustainable and providing a possibility of waste valorization. Therefore, the use of agricultural-origin materials in construction offers multiple benefits, including a lower carbon footprint by reducing energy-intensive clinker production, enhanced strength and durability through optimized particle packing and pozzolanic reactions, effective waste utilization that minimizes landfill disposal, and improved water and energy efficiency. By integrating agricultural waste-derived SCMs and recycled materials, cementitious composites can achieve ultrahigh performance while significantly reducing CO_2 emissions, paving the way for a more sustainable and resilient construction industry.

2. Agricultural-origin materials in construction

Masonry construction involves using materials such as bricks, blocks, and stones, which are bonded with mortar to create strong and durable structures. Cement plays a vital role in this process, acting as a binding agent in both concrete and mortar. In addition to cement, aggregates such as coarse stones and fine particles (like sand) are essential for providing strength and improving the workability of concrete. Reinforcement is another critical component, typically involving steel bars (rebars), welded wire mesh, or fibre reinforcements that enhance the tensile strength of concrete and its resistance to cracking. Agricultural-origin materials are gaining attention as sustainable alternatives for partially replacing Portland cement, clinker, sand, and steel fibres in construction. The agricultural waste products have shown excellent potential as supplementary cementitious materials (SCMs) due to their pozzolanic and cementitious properties [26]. Several components derived from agricultural waste can be used as admixtures. For example, lignin, a natural polymer found in plant cell walls, is being explored as a substitute for gypsum in cement production. Gypsum is traditionally added to Portland cement to regulate the setting time and improve workability. Lignin, particularly in its modified forms such as lignosulfonates, has demonstrated promising results in performing similar functions to those performed by gypsum. In the case of sand replacement, materials like crushed coconut shells, groundnut shells, etc, have shown promising results. These alternatives not only reduce the demand for natural sand but also enhance the workability and reduce the overall weight of concrete. Natural fibres such as coir and jute are effective in improving crack resistance, tensile strength, and overall toughness for steel fibre replacement. In general, the agricultural-origin materials in the construction could be reinforcement, partial replacement of sand and fine aggregates, and supplementary cementitious materials [27]. A brief account of agricultural origin materials in construction is described in the following sections.

2.1. Reinforcement

2.1.1. Cellulosic natural fibres

Coir (coconut), jute, sisal, date palm, hemp, rice straw, ramie, flax and hibiscus are the most commonly used natural plant fibres for reinforcement in cementitious materials. The coir fibres had been used as the reinforcing material to prevent crack progression in concrete [28]. It has also been reported that the coir fibres improve the tensile strength and restrict the degradation of concrete in corrosive environments [29]. In addition to this, coir fibres also enhance the resistance and ductility [28–31]. It has been reported that the fibres treated with NaOH and those exposed to cement pore solution had higher densities than untreated fibres, while the tensile strength was increased significantly [32]. This suggests that the mechanical properties of coir fibres are improved with NaOH treatment and the actual environment prevailing in cementitious materials. The treatment of coir fibres with oxalic acid was found to be effective for partial removal of lignin and hemicellulose content [33]. With this treatment, the tensile strength of coir fibres increased by 23 % concerning the untreated fibres. The increase in coir fibre roughness after chemical treatments leads to better interaction with the cement paste and enhances the reinforcement of the cementitious materials. It is important to note that the addition of natural fibres to the cement may also influence its setting time and hydration behaviour. The effects of treated and pristine jute fibres were studied by Jo et al. [34]. They observed that fibre-cement compatibility was increased and the hydration delaying effect was minimized by mild alkali treatment of jute fibre employed as fibre reinforcement. Wang et al. have reviewed the literature on coir fibre and coir fibre-reinforced cement-based composite materials from 2000 to 2021 [35]. It was shown in this review that coir fibre reinforced concrete (CFRC) is a lightweight construction material with excellent thermal and acoustic insulation. The mechanical properties of CRFC, including compressive, flexural, and tensile strength, as well as fracture toughness, were found to improve depending on fibre content. However, higher coir fibre content reduces workability, increasing matrix porosity and weakening load-bearing capacity. This review also deals with the long-term performance of CFRC, i.e., showing better retention of mechanical properties compared to other plant-based fibres like sisal and jute. In essence, it can be seen from this review that the different modification methods applied to coir were found to enhance fibre-matrix bonding, reduce fibre degradation, and improve mechanical strength. Consequently, CFRC demonstrate strong potential as lightweight construction materials with superior thermal and acoustic insulation properties [35].

The cellulose nanofibers have also been employed to improve the mechanical properties of cementitious materials. Rocha et al. have systematically reviewed the literature on the use of cellulose nanofibers in cementitious materials over the last five years [36]. Cellulose nanofibers contain hydroxyl groups and carboxylate groups, which are known to strongly influence the chemistry of cement hydration and hydrogen bonding with the hydrated product of the cement, such as C-S-H gel. C-S-H gel (calcium silicate hydrate) is the primary binding phase formed during cement hydration, responsible for the strength and durability of concrete. This literature survey seems to suggest that the presence of cellulose nanofibers in cement has positive effects on rheology,

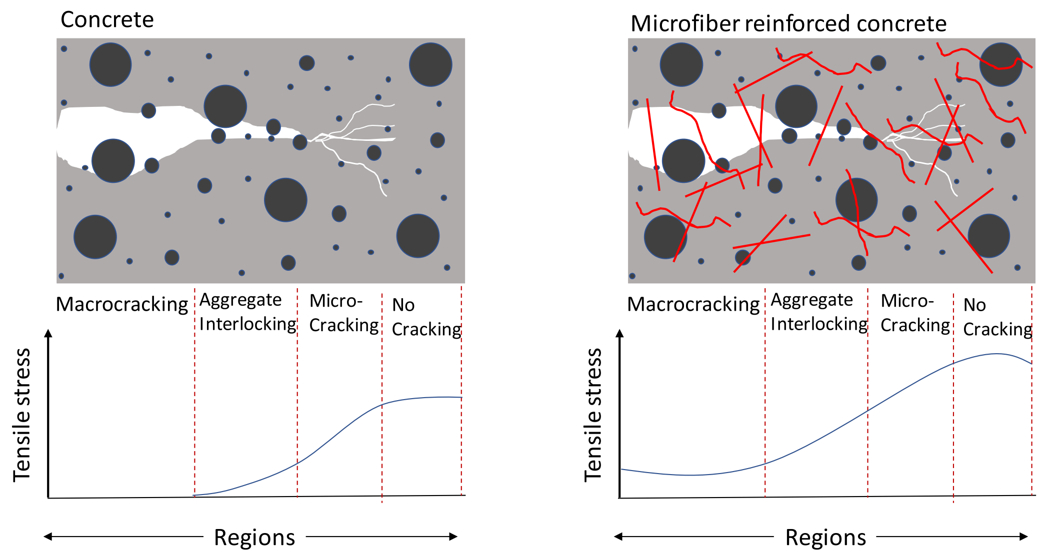

Fig. 2. Representative illustration of tensile stress in the crack along the crack length in concrete and microfibres reinforced concrete [adapted from Ref. 35].

hydration, compressive strength, flexural strength, fracture energy, and other properties. These properties are strongly influenced by the production methods and chemical treatments. For example, an addition of 0.15 % by weight of cellulose nanofibers increased to an extent of 15 % and 20 % of the flexural and compressive strengths of cement paste as compared to that without cellulose nanofibers [37]. The improved mechanical properties are due to better hydration and a denser, more uniform microstructure of the hardened cement paste when cellulose

Table 1
Comparison of mechanical properties of plant microfibers and their carbon footprints for use in concrete reinforcement [data taken from Ref. 35,40–44].

Fibres	Dimension		Mechanical properties	Carbon footprints ((kg equ. CO_2/kg)	Remark
	Length (mm)	Dia. (μm)			
Steel	25–60	300–800	Density (g/cm^3): 7.8 Tensile strength (MPa):400–2100 Young Modulus (GPa):154–200 Elongation (%): 3.0–4.0	2.0–3.1	Ductility, excellent crack control
Poly(propylene)	12–50	20–50	Density (g/cm^3):0.91 Tensile strength (MPa): 400–650 Young Modulus (GPa): 5–8 Elongation (%): 18	5.0	Alkali-resistant, low-density, reduces shrinkage
Coir C= 19.9–36.7 % HC= 11.9–15.4 % L= 32.7–53.3 % M= 0.2–0.5 %	20–50	100–300	Density (g/cm^3): 1.15–1.46 Tensile strength (MPa):131–200 Young Modulus (GPa):4–6 Elongation (%): 15–40	0.2	Degradable unless treated, good elongation, poor bonding with cement
Jute C= 59–70 % HC= 15–20 % L= 11–15 % M= 12 %	10–30	100–200	Density (g/cm^3): 1.3–1.5 Tensile strength (MPa): 610–780 Young Modulus (GPa): 15–30 Elongation (%): 1.0–19	-	Degradable unless treated, moderate bonding with cement
Sisal C= 65–76 % HC= 10–15 % L= 7–13 % M= 11 %	30–60	100–200	Density (g/cm^3): 1.3–1.6 Tensile strength (MPa): 540–720 Young Modulus (GPa): 13 Elongation (%): 2.2–3.3	-	Durable natural fibre with good bonding with cement
Flax C= 62–71 % HC= 18–20 % L= 2–5 % M= 8–12 %	10–50	50–80	Density (g/cm^3): 1.4–1.5 Tensile strength (MPa):343–2000 Young Modulus (GPa): 27–103 Elongation (%): 1.2–3.3	-	Good binding with cement
Hemp C= 68–74 % HC= 15–22 % L= 4–10 % M= 10–14 %	20–50	40–100	Density (g/cm^3): 1.2 Tensile strength (MPa): 270–900 Young Modulus (GPa): 4.8 Elongation (%): 1–3.5	0.6–1.0	Good thermal resistance, moderate bonding with cement

C= Cellulose, HC=Hemicellulose, L=Lignin and M= Moisture. Natural fibres are eco-friendly but degrade faster unless treated. The tensile strength of natural fibres is highly variable depending on source and processing.

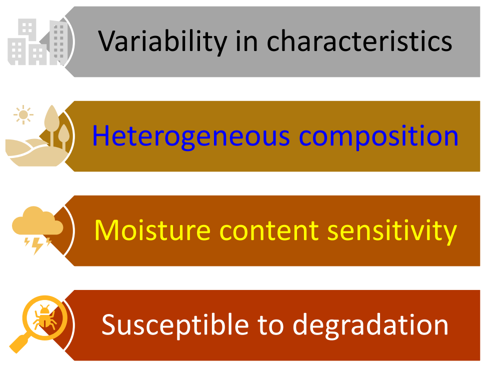

Fig. 3. Challenges associated with using natural fibres for reinforcement in cementitious materials.

nanofibers are added.

Nair et al. studied the long-term durability of ordinary Portland cement (OPC) composites with lignin-containing cellulose nanofibers and delignified cellulose nanofibers [38]. The heat of hydration and microstructural studies confirmed that these two types of cellulose nanofibers do not exhibit negative effects on early-age cement hydration. However, the addition of both fibres resulted in the densification of the matrix. When these fibres containing mortar samples were exposed to 5 % $MgSO_4$ and 5 % Na_2SO_4 for 6 months, it was observed that the cellulose nanofibres improved the resistance of mortar against sulphate attack as compared to control samples. For all the tested parameters, lignified cellulose nanofibers-containing samples showed better performance than delignified cellulose fibres-containing samples. This seems to suggest that alkali treatment of cellulose nanofibers may be more related to surface roughness and exposing more functional groups for interaction with cement particles. The rough surface of nanofibers may likely help in the nucleation and growth of C-S-H, leading to a better microstructure of the hardened cementitious matrix. Also, the exposure of functional groups such as -COOH and -OH may promote a nano-scale hydrogen-bond network between cellulose nanofibers and cement particles (C-S-H), improving the durability of cementitious materials [39].

Concrete generally possesses high compressive strength but relatively low tensile strength. Incorporating dispersed short fibres into concrete is considered an effective method to enhance its tensile strength and improve its brittle failure behaviour, transforming it into a more ductile material. The tensile strength of microfibre-reinforced concrete, which represents the maximum stress it can withstand and the fracture energy (the area under the stress-strain curve), is higher than that of plain concrete [35]. The primary function of these fibres is to control crack initiation and propagation, thereby improving the overall durability and performance of the concrete. When concrete is subjected to tensile forces, such as the load direction during a tensile test, the hoop direction in a compression test, or the tension zone at the bottom of a beam during bending, its tensile strength is reached relatively quickly, initiating crack development. As depicted in Fig. 2, the crack formation process generally involves three stages, i.e., macro-cracking, aggregate interlocking, and micro-cracking. In the macro-cracking region, the crack surfaces are fully separated, resulting in no tensile stress being transferred across the crack. In contrast, the aggregate interlocking region features narrower crack openings that allow contact between aggregates, enabling a limited amount of tensile stress to be carried. The micro-cracking region not only facilitates stress transfer through aggregate interlocking but also allows tensile stress to circumvent crack tips, enabling this region to bear higher tensile stress compared to the other two regions. When microfibres are incorporated into the concrete, they bridge the opposite crack surfaces, enhancing the transfer of tensile stress along the fibres. This fibre-bridging mechanism results in greater tensile stress being sustained along the crack path compared to plain concrete, as shown in Fig. 2. This reinforcing effect is

Table 2
The commonly used treatment methods for natural fibres [45].

Treatment method	Advantage	Limitation
Plasma method	Surface modification without bulk alteration, improved fibre-matrix adhesion, mild and reagentless treatment conditions, increases surface energy and improves wettability	Requires specialised vacuum or atmospheric plasma equipment, uniform treatment on large-scale or irregular fibre surfaces can be difficult. only surface-level treatment
Radiation treatment	Sterilization, increases surface energy, wettability, and compatibility with matrices, depending on radiation dose & fibre type, can improve or tailor mechanical behaviour by crosslinking.	High initial cost and safety concerns, excessive exposure can degrade cellulose structure, reducing tensile strength and flexibility, and use of radioactive sources (e.g., cobalt−60) involves strict regulatory compliance.
Alkali treatment	Removes lignin and hemicellulose that may contribute to certain desirable properties like biodegradability or toughness, increasing surface roughness and promoting mechanical interlocking with the matrix, increasing fibre hydrophilicity and surface energy, improving compatibility with cementitious and polymer matrices.	Over-treatment or high NaOH concentrations can damage cellulose chains, reducing tensile strength and flexibility, a large volume of water is needed for washing, and a long pretreatment residence time.
Silane treatment	Silane forms covalent bonds with both hydroxyl groups on the fibre and functional groups in the matrix, greatly enhancing interfacial bonding, leading to better load transfer at the fibre-matrix interface, improving tensile and flexural properties	Silane coupling agents are relatively expensive compared to alkali or other treatments, Requires precise control of pH, hydrolysis time, and concentration for effective silanization.
Acetylation treatment	Acetylation involves treating natural fibres with acetic anhydride (or sometimes acetic acid) to replace hydroxyl (-OH) groups in cellulose with acetyl groups ($-COCH_3$). This reduces hydrophilicity and improves dimensional and interfacial stability.	Requires multiple steps including reaction, washing, and drying, making it less suitable for large-scale, low-cost applications.
Maleic anhydride treatment	Maleic anhydride is typically grafted onto polymers (like polypropylene or polyethylene) or used as a coupling agent. When used with natural fibres, it improves compatibility with hydrophobic matrices, especially in thermoplastic composites.	Involves grafting processes or the use of maleic anhydride-grafted polymers, which adds cost and complexity.
Benzoylation Treatment	Benzoylation involves treating natural fibres with benzoyl chloride in an alkaline medium (usually NaOH). This substitutes hydroxyl groups (–OH) in the fibre with benzoyl groups ($–C_6H_5CO$), making the surface more hydrophobic and chemically compatible with non-polar matrices.	Benzoyl chloride is toxic, corrosive, and releases HCl gas, it requires careful handling and safety precautions.
Retting treatment	Retting is a biological or chemical process used to separate fibre bundles (e.g., flax, jute, hemp) from the woody core and surrounding tissues by degrading pectin, hemicellulose, and other	Dew and water retting can take several days to weeks, depending on conditions, low scalability.

(continued on next page)

Table 2 (*continued*)

Treatment method	Advantage	Limitation
	binding materials. It helps extract long, clean fibres for further processing. Compared to harsh chemical treatments, certain retting methods (dew or enzymatic) retain natural mechanical properties.	

commonly known as the "fibre-bridging effect". The plant microfibres can be used in reinforced concrete with a lower carbon footprint. The comparison of different plant microfibres given in Table 1 seems to suggest that these microfibres have good mechanical properties with very low carbon footprints [40–42]. The additional importance is the possibility of hydrogen bonding between the cement matrix and plant fibres due to the presence of a large number of carboxylate and hydroxyl groups. Table 1 compares the compositions and mechanical properties of natural fibres with those of synthetic and steel fibres, highlighting the significant variability observed in natural fibres across both parameters [43,44].

There are several issues in using natural fibres in the concrete as illustrated in Fig. 3 [43]. One of the major problems is associated with significant variations in the physical characteristics of the natural fibres. Natural plant-based fibres show inherent variability in length, diameter, orientation, and composition due to differences in species, growth conditions, harvesting, and processing, unlike uniformly produced synthetic fibres. Moreover, natural fibres have a heterogeneous structure of cellulose, hemicellulose, lignin, pectin, and extractives, with varying composition and defects like knots, voids, and impurities, leading to inconsistency. Natural fibres are hygroscopic, absorbing moisture that alters their weight, size, strength, and stiffness, affecting their bond with the cementitious matrix. Apart from these, natural fibres biodegrade under environmental factors like heat, humidity, UV, and microbes, reducing their mechanical strength and long-term reinforcement performance. The inconsistent behaviour of natural fibres significantly impacts the performance of cementitious concrete, affecting tensile strength, flexural strength, and impact resistance. This variability makes it difficult to predict and control the behaviour of fibre-reinforced concrete in practical applications. To address these challenges, a tailored approach involving fibre extraction and surface treatment techniques has been suggeted to reduce variability and enhance the performance of natural fibre-reinforced cementitious materials [45]. The commonly used treatment methods to address some of the challenges in using natural fibres are listed in Table 2.

In general, several studies suggest that the treated natural fibres, such as jute, hemp, flax, coir, sisal, and kenaf, are increasingly being used in construction due to their sustainability, low cost, and lightweight nature. These fibres are primarily used as reinforcement in cementitious composites, insulation panels, roofing, and plastering materials, as illustrated in Fig. 4.

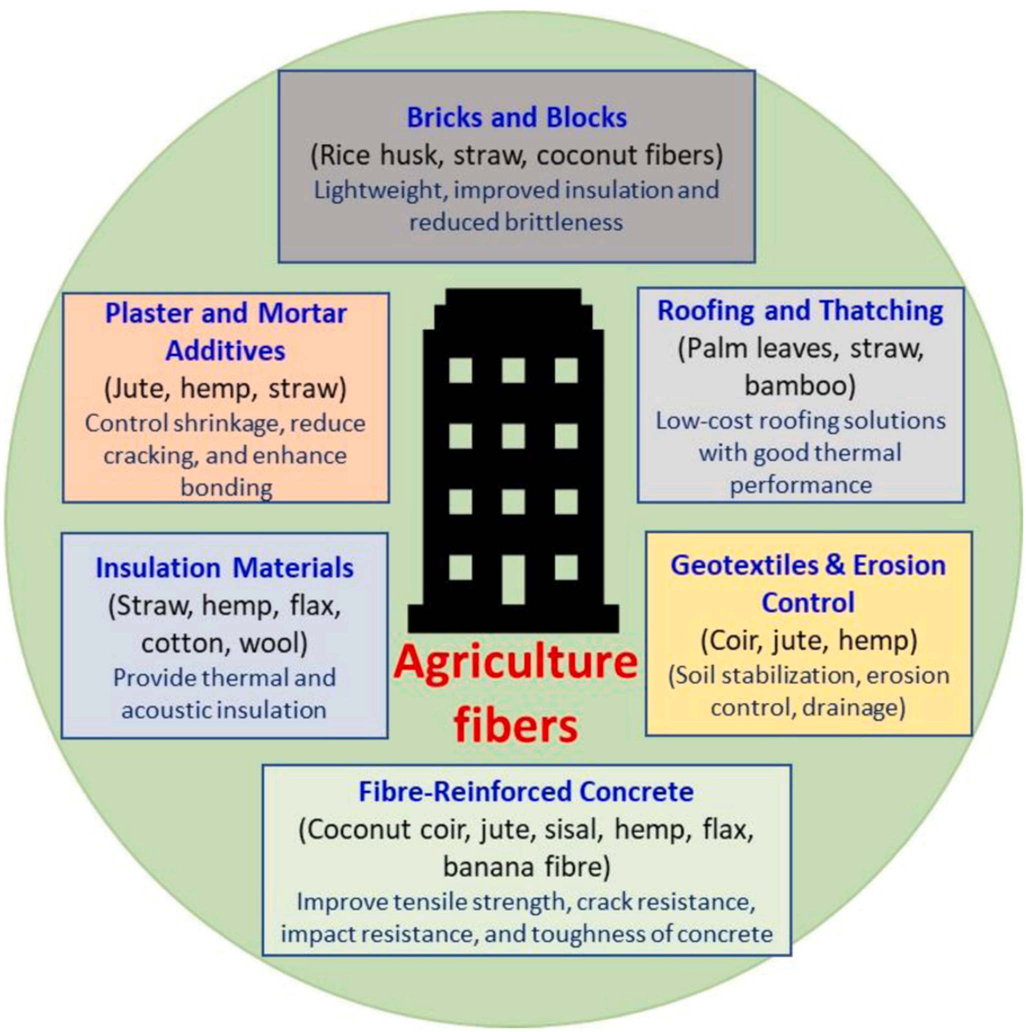

Fig. 4. Applications of natural fibres in different construction activities.

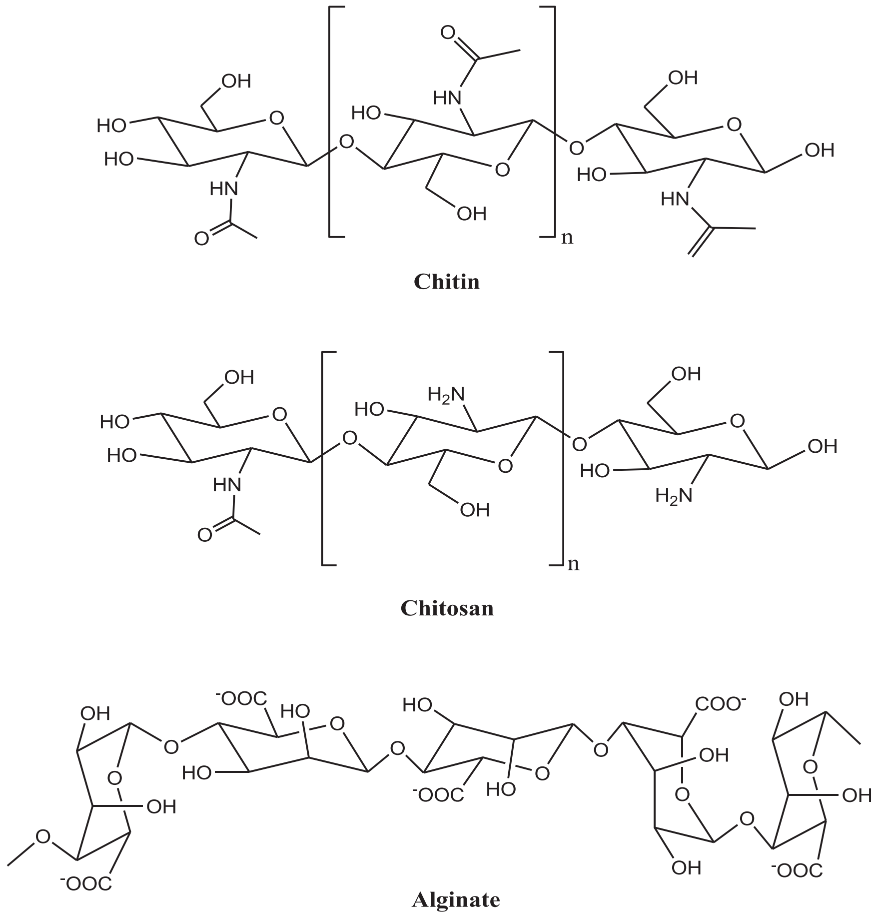

Fig. 5. Chemical structures of chitin, chitosan and alginate.

2.1.2. Non-cellulosic natural fibres

Chitin and alginic acid are other biopolymers besides cellulose, which can be used as admixtures in cement composites. Insects, certain plants and animals, and shellfish (such as lobster, crab, and prawns) all contain chitin in their exoskeletons [46]. Approximately 70 % of the 6–8 million tonnes of waste produced annually by the seafood sector consists of bark, with the remaining 20–30 % comprising chitin. Among natural biopolymers derived entirely from renewable raw materials, chitin is the second most abundant after cellulose. The by-product of chitin de-acetylation is chitosan, which is soluble in acetic acid solution. Chitin can potentially be a sustainable biomass source for cementitious systems that divert seafood waste from landfills or the ocean by producing strong structural nanofibers and nanocrystals. Alginates are naturally occurring biopolymers that are extracted from *Phaeophyceae* brown algae. The chemical structure and molecular weight of algae might differ depending on the species, growth conditions, and postharvest processing. Alginate is a great candidate for cement admixture since it possesses several free hydroxyl and carboxyl groups distributed throughout its backbone. The chemical structures of chitin, chitosan, and alginate are given in Fig. 5, and a detailed discussion of their extractions and properties can be found in the published reviews [47–49].

The effects of chitin nanofibers and nanocrystals from leftover shrimp shells on the mechanical characteristics, setting time, and late-age hydration of mortar have been investigated by Haider et al. [50]. Chitin nanofibers improved the C-S-H structure by increasing polymerization by 41 %, silicate chain length by 9 %, and hydration by 15 % at 28 days, leading to better mechanical properties of cement-based materials. Chitosan, a derivative of chitin, has also been studied for its efficacy in improving the rheological and mechanical properties of cement paste and cementitious materials with and without chemical modification [51–54]. The chemical modification of chitosan was intended to increase its solubility in aqueous solution [51]. All these studies indicate that chitin and chitosan can be employed in cement composites with positive outcomes. As can be seen from Fig. 5, the alginate chemical structure consists of functional groups that may influence the hydration of cement. Therefore, the effect of alginates on the hydration of calcium aluminate cement was examined by Engbert et al. [55]. This study showed that adding alginate to cement paste appears to shorten the dormant phase of cement hydration, thereby accelerating the start time of the hydration reaction, resulting in notably greater early strengths. Murugappan and Muthadhi have reviewed the effects of alginate on the durability and mechanical qualities of concrete, demonstrating its ability as an admixture to increase the viscosity of the cement paste [56].

2.2. Partial replacement of aggregates

Concrete, which is composed of Portland cement, fine aggregate (such as sand), and coarse aggregate (including gravel and stone), is primarily derived from natural resources. Incorporating agro-waste as a partial replacement of fine or coarse aggregates in concrete presents several significant advantages, provided that essential requirements are met for successful implementation. Environmentally, this approach valorizes agricultural by-products that might otherwise accumulate as solid waste and contribute to pollution, thereby promoting sustainable waste management practices. It also reduces dependency on natural, non-renewable aggregates, which in turn diminishes the ecological footprint associated with their extraction and processing. Furthermore, utilizing locally available residues can yield economic benefits by lowering material costs and stimulating regional economic

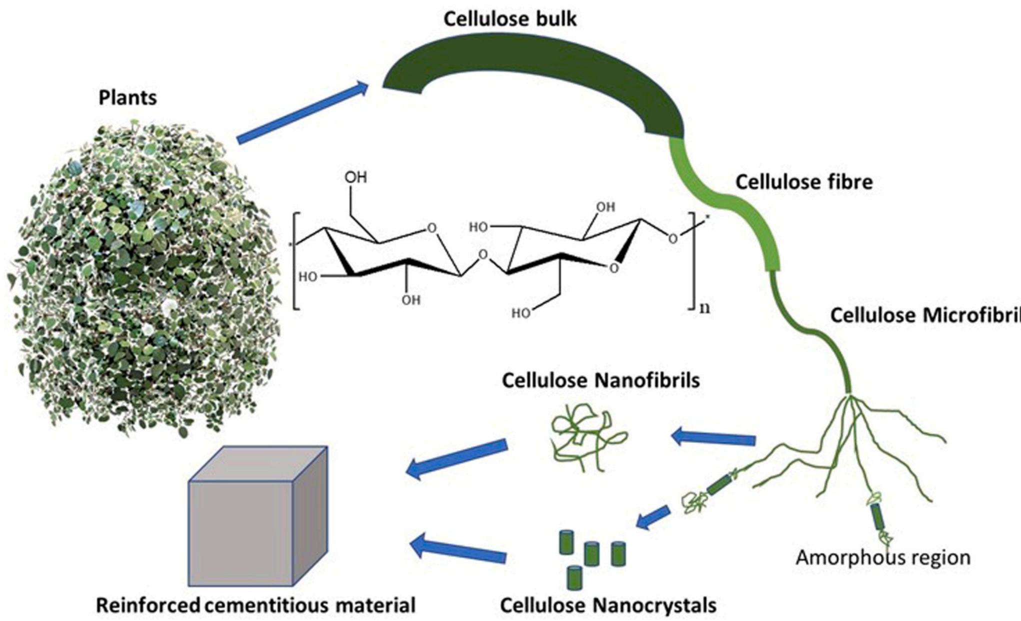

Fig. 6. Schematic illustration of obtaining cellulose nanocrystals and cellulose nanofibrils from plants, and molecular structure of cellulose.

development. Gunasekaran et al. examined concrete with coconut shells as a coarse aggregate, evaluating properties such as compressive strength, flexural and splitting tensile strengths, and impact resistance [57]. Their findings confirm that coconut shell is an effective lightweight aggregate. In another study, it was observed that the ultimate bond strength of this concrete exceeded theoretical predictions [58]. They also demonstrated that coconut shell-reinforced beams exhibit satisfactory flexural performance comparable to other lightweight concretes [59]. Similarly, Sathiparan and Zoysa assessed the use of agro-waste, including rice husk, sawdust, peanut shell, rice straw, and coconut shell, as a partial sand replacement in cement blocks [60]. Their experiments showed that these blocks meet ASTM strength requirements, with those containing coconut and peanut shells exhibiting reasonable strength and durability. Similarly, palm oil shells were also found to be effective as coarse aggregates in concrete [61].

Several agricultural wastes such as vermiculite, sugarcane bagasse, coconut husks, and nutshells (ground nuts, pistachios, walnuts, and hazelnuts) have been explored for partial replacement of sand in concrete [62–64]. In optimum amounts, these agro-waste fine aggregates were found to improve mechanical properties and durability. In most cases, concrete blocks incorporating agricultural waste demonstrated sufficient strength to meet ASTM standards. Notably, specimens containing coconut husks, pistachio shells, and similar materials maintained robust strength and durability even under dry conditions. The partial use of agro-waste fine aggregates in concrete was also found to improve thermal insulation. However, because these materials often have higher porosity and water absorption compared to natural sand, careful adjustments to the mix design are essential. Pre-treatment processes like cleaning, drying, and grinding are typically required to ensure uniformity and compatibility with the cementitious matrix. When properly processed and optimized, concrete and mortar incorporating partial agricultural waste fine aggregates can achieve mechanical and durability properties that meet structural requirements, thus contributing to both environmental sustainability and improved resource efficiency.

2.3. *Supplementary cementitious materials*

Agriculture-based supplementary cementitious materials, derived from agricultural waste such as nanocellulose, lignin, agricultural ash, and other plant-based residues, offer a sustainable alternative to conventional cementitious components. These materials serve multiple roles in ordinary Portland cement, such as superplasticizers, retarders, and pozzolanic agents. As a result, these not only enhance the performance of concrete but also help reduce the environmental impact of cement production.

2.3.1. *Nanocellulose*

Nanocellulose is derived from cellulose, a natural material found in plants. It has nano dimensions with features like being high tensile strength, light, biodegradable, and having a large surface area. Owing to its exceptional properties, nanocellulose could be a highly versatile material in a wide range of applications, particularly in cementitious systems where it enhances strength, durability, and overall performance [65–68]. The primary forms of nanocellulose are cellulose nanocrystals, cellulose nanofibrils, and bacterial nanocellulose [69]. Plant-derived cellulose is hydrolyzed in an acidic solution to produce stiff, rod-like structures known as cellulose nanocrystals (CNCs). The mechanical fibrillation of cellulose results in the formation of flexible, thread-like structures known as cellulose nanofibrils (CNFs). On the other hand, bacterial nanocellulose (BNC) is a highly pure material with superior mechanical qualities that is produced by specific bacteria such as gram-negative bacteria *Gluconacetobacter xylinus, Agrobacterium, Achromobacter, Aerobacter, Azotobacter, Pseudomonas,* and *Rhizobium* [70]. Some characteristics of these nanocelluloses, such as aspect ratio, excellent strength, low density, high surface area, etc., are comparable even if these differ from their source and isolation techniques. Nanocellulose contains many hydroxyl groups on its surface, which makes it hydrophilic, or water-attracting. This means it can absorb and hold water when mixed with cement-based materials, influencing the hydration process, improving workability, and potentially enhancing the mechanical properties of the final product. The schematic representation of cellulose nanocrystals and cellulose nanofibrils obtained from plant sources is given in Fig. 6.

The use of nanocellulose in reinforcing cementitious materials has been reviewed by Balea et al., Fu et al., and Guo et al. [71–73]. These reviews suggest that the properties of cementitious materials are significantly enhanced by nanocellulose. For example, nanocellulose improves the mechanical properties of cementitious materials, depending on the dosage used [74–76]. Higher doses of nanocellulose are detrimental to mechanical properties due to the aggregation of nanocellulose. Apart from this, nanocellulose could be employed as a viscosity-modifying agent to improve the rheological behaviour of the cement paste. Thus, nanocellulose may have several functions in cementitious materials, such as improving mechanical properties (internal bonding strength, modulus of elasticity (MOE), and modulus of rupture (MOR)), the rheology of the cement paste, and affecting the durability of the cementitious composites.

Regardless of its physical form, the reinforcement of nanocellulose in cement composites generally significantly impacts the mechanical, rheological, microstructure, hydration, durability, and shrinkage of cementitious materials. However, the degree to which these characteristics are altered depends on the physical shape of nanocellulose. The major factors that influence the mechanical properties of cementitious composites are: (i) the intrinsic mechanical properties (bending strength, stiffness, tensile strength) of the reinforcing nanofibers, (ii) the dimensions, (iii) the dispersion and orientation of the NCs, (iv) the interactions between the matrix and the reinforcing fibres, and (v) the effects of NC on cement hydration.

Cellulose nanofibrils (CNFs) are most effective in the reinforcement of cement composites [77]. It has been reported that CNF reinforcement gives rise to higher strength in cementitious materials than CNC [78]. This could be attributed to its large surface area, higher hydroxyl group density on its surface, higher mechanical strength, and higher length/width ratio [79]. The hydroxyl groups are conducive to hydrogen bonding interactions of CNFs with C-S-H and calcium hydroxide [80]. Dai et al. and Correia et al. suggested the contribution of hydroxyl groups to enhance the interaction between CNFs and the cement matrix, leading to better microstructure and mechanical properties [81,82]. Santos et al. analyzed the published literature and suggested that CNFs significantly enhance the mechanical properties of reinforced cementitious materials [77]. They summarised that the maximum enhancement of compressive strength was 43 % with the addition of 0.3 % CNFs [83], 106 % in flexural strength addition of only 0.1 % CNFs [84], 5 % in modulus of elasticity [82], 71 % in flexural modulus, 50 % in fracture energy for the reinforcement of 3 % of CNFs [85], and 192 % in toughness [86], as compared to the absence of CNFs. In these experimental works, the CNF concentrations were kept between 0.10 % and 3.00 % (by mass of cement) to produce the best mechanical quality enhancement. The dispersion techniques of CNFs, the type and concentration of dispersing agents, and the properties of the raw materials used in cement composites are critical factors in achieving optimal enhancement of mechanical properties. The mechanical properties of cementitious materials are highly correlated to the hydration of cement and the microstructure of the hardened cementitious material. Several researchers have attributed the enhancement of mechanical properties by CNFs to greater hydration of the Portland cement [81,83,84,87]. CNFs provide nucleation sites for C-S-H, leading to a faster hydration process. It has been observed that the degree of hydration and the formation of crystallites, such as portlandite, ettringite, and C-S-H, increase with the increase in CNF content up to the optimum amount to prevent agglomeration [83].

The effect of CNFs on the hydration of cement appears to play an important role apart from normal reinforcement. Several studies have shown that the hydrophilic and moisture-absorbing (hygroscopic) nature of CNFs allows them to act as internal water reservoirs within their network. This effect is enhanced when more calcium ions (Ca^{2+}) are attracted to the negatively charged surface of the nanofibrils [83,84,88,89]. In addition, water diffuses through the nanofibril network more quickly and easily compared to when water travels through the matrix [90]. These two facts accelerate the formation of C-S-H gel during hydration at the fibre-matrix interface. As a result, there is an increase in the physical connection between the fibres and the matrix and an accumulation of hydration products at the interface. Santos et al. suggested that CNFs get attached to the cement particles and remain intact in the hydration product shell, which may form a path to transport water to the unhydrated cement interior and facilitate better cement hydration [91]. Hisseine et al. observed that CNFs enhanced the degree of hydration of ultra-high-performance concretes, which could be attributed to an increase in the extent of chemically bound water [92]. Due to the higher water uptake, CNFs also provided a supplementary source of water. The water sorbed in CNFs enables a time-dependent water release and contributes to replenishing the empty matrix pores, which eventually decreases autogenous shrinkage and prevents the formation of microcracks at early ages by the release of heat of hydration [93]. The hydration is intensified due to the alkaline hydrolysis of CNFs [84,94]. In general, the CNFs enhance the matrix packing density, lower the porosity of the matrix, and improve the strength of the interfacial zone [87,95]. Another important contribution of CNFs is the bridging effect that intercepts the cracks in the matrix, preventing their propagation, enhancing the fracture energy, and resisting brittle failure [80,83,85,86]. After 20 wet-dry accelerated ageing cycles and 28 days of humidity chamber curing, Claramunt et al. evaluated the flexural modulus to assess the durability of cement reinforced with ordinary pulps, CNF, and a combination of both [96]. The findings demonstrated that fibre debonding and mineralization caused a decrease in the flexural strength and fracture energy of cement composites without CNF or with less than 4 % of CNF. However, after ageing, the presence of 4 % or more CNF content preserved the fracture energy and raised the flexural strength. This impact is attributed to the strong interactions between CNF and the matrix, as well as the densification of the interfacial zones [96].

Porosity allows water to enter the matrix and dissolve hydration products, primarily calcium hydroxide, which precipitates again during the dry stage of the cycle due to water evaporation. This issue can be effectively mitigated by incorporating CNFs, which significantly reduce porosity [82,83,90,97–100]. The microstructure of the cementitious matrix is significantly influenced by low doses of CNFs, resulting in a denser matrix with reduced porosity compared to mixes without CNFs [83]. This can be attributed to the absorption of water and then release of water by CNFs, which promotes a more uniform formation of hydration products. Barnat-Hunek et al. compared the microstructures of concrete with CNFs and CNCs and found that concrete with CNFs had smaller pores and cracks, measuring up to 951 nm [101]. Conversely, concrete containing CNCs exhibited a denser microstructure, with negligible evidence of pores or cracks. These findings indicate that CNCs outperform CNFs in mitigating the formation of micro-pores and micro-cracks. A low dosage of CNFs ($\leq$ 0.5 %) was found to reduce the free shrinkage of cement pastes with a low water-to-cement ratio (w/c = 0.35), as the CNFs functioned as internal curing agents by gradually releasing water to counteract shrinkage [102].

The workability of cement pastes in terms of pumping, spreading, moulding, and compaction largely depends on their rheology. In freshly produced cement paste, some bigger particles interact directly through friction or collisions. In comparison, smaller particles interact by colloidal forces such as Van der Waals, electrostatic repulsion, steric hindrance, and hydrogen bonding interactions. Nanocellulose notably affects these interactions due to its large active surface, which provides greater contact with particles. The rheological properties of cement govern the workability of cement paste. The use of high surface area CNF enhances the yield stress of the cement paste, as shown in several studies [83,88,103,104]. For example, merely 0.2 wt% of CNF in a fresh cement paste substantially increased the yield stress without affecting plastic viscosity significantly [103]. This could be attributed to the hydrophilicity of the CNF, which leads to the adherence of water to nanocellulose. This results in thickening the fresh cement paste. CNF in cement paste increase the yield stress and slightly raises the plastic viscosity. This combination reduces the sedimentation of solid particles and decreases the slump, resulting in a mix that is easier to handle and pump. A higher yield stress is an advantage in the construction of rigid pavements, plastering tiles, etc., where fresh paste is needed to retain its shape. Under shearing pressure, CNC/CNF releases water molecules and disperses cement particles through electrostatic and steric stabilization while lowering the yield stress [90,105,106]. The rheology of the

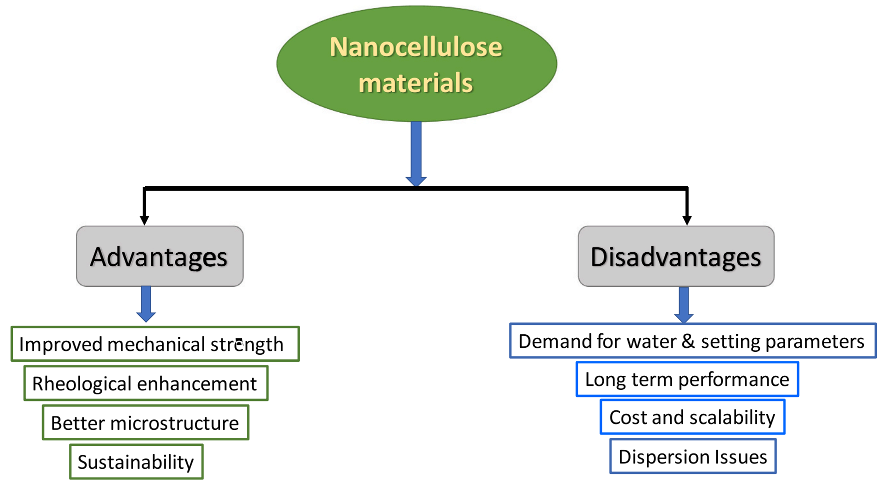

Fig. 7. Comparison of advantages and disadvantages of using nanocellulose materials in cement composites.

cement paste is improved more with CNC as compared to CNF, owing to its smaller size under similar conditions.

Bacterial nanocellulose (BNC) has also been explored extensively for reinforcing cement composites [107–109]. Haque et al. have carried out a comparative study to understand the efficacy of BNC with respect to plant-based nanocellulose for reinforcing cement composites [109]. Over 90 days of curing, Haque et al. found that both CNF and BNC enhanced the compressive strengths and flexural strengths by 10 % and 55 %, respectively [106]. However, CNF reduced the 33 % expansion of mortar samples caused by the alkali-silica interaction. It was observed that BC delayed the early-age cement hydration, whereas CNF sped it up. After long-term curing, both types of nanocellulose showed increased C-S-H contents and decreased calcium hydroxide (C-H) contents when compared to the control batch. BNC-coated polypropylene fibres exhibited improved mechanical properties of cement paste as well as the workability of poly(propylene) fibres [108]. It is interesting to note that the advantages obtained by different nanocelluloses are different. For example, the presence of CNFs in the mortar mixture resulted in an increase of up to 43 % in flexural strength values, whereas CNCs were more effective in raising compressive strength values (up to 21 %) [110]. Also, the effects of different nanocellulose in reinforcing the cement may vary depending on production methods [111]. The prospects and challenges in the development of biomass-derived nanocellulose-modified cementitious composites have been reviewed by Wang et al. [112].

Applications and research in civil engineering have focused heavily on nanofiller-reinforced cementitious materials because of their superior strength, toughness, and endurance. Various industrial nanofillers, such as graphene, carbon nanotubes, carbon nanofibers, etc., are used to construct nanofiller-reinforced cementitious materials. While the qualities of traditional cementitious materials are enhanced, adding the aforementioned nanofillers comes at a significant expense and adversely affects the environment. In contrast to carbon nanofillers that require a significant amount of energy, nanocellulose is a biomass-derived nanofiller that exhibits exceptional nanomaterial properties, biological performance, and composite effects. It has demonstrated great potential as a green filler to improve the mechanical, functional, and long-term qualities of cementitious composites while reducing their carbon footprint. Nevertheless, the application of nanocellulose is still in its infancy, and Fig. 7 summarises its many benefits and drawbacks.

2.3.2. *Lignin*

Plant cell walls include lignin, a complex organic polymer that offers protection and structural support. Only cellulose is a more prevalent

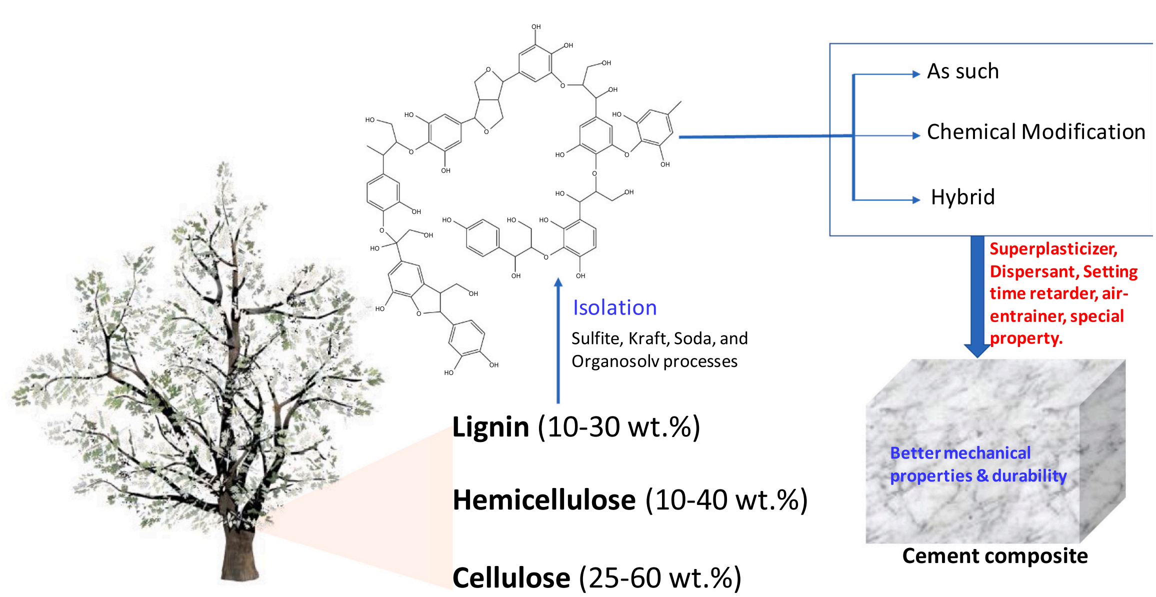

Fig. 8. Schematic illustration of the route from the lignin source to cement composite application.

naturally occurring polymer on Earth than lignin. Wood contains lignin in addition to cellulose and hemicellulose. Depending on the source, the percentage of lignin in lignocellulosic raw materials could range from 10 % to 30 %. Cellulose fibres organized in a cylindrical configuration of wood cells are covered with lignin. As illustrated in Fig. 8, aromatic alcohols such as p-coumaryl, coniferyl, and sinapyl make up the majority of lignin [113,114]. Due to the presence of a large number of hydrogen bonding groups, such as -OH, lignin decreases the water content in a concrete mix without affecting the fluidity of cement paste. Therefore, lignin is considered a water-reducing agent. Also, lignin generates electrostatic charges when adsorbed on cement particles and works as a dispersant by preventing the aggregation of the cement particles [115,116]. In cement composite studies, lignin has emerged as a valuable additive with multiple benefits [117–132]. The published reviews on using lignin as an admixture suggest its wide range of functions in the cement composite [133,134]. These functions can be categorized as the set retarders [114,121], dispersants [120,123–125], air-entraining admixtures [132], plasticizers [119,129], superplasticizers [117,118,122], and water reducers [131]. Lignin capsule-based autonomous self-healing was found to be promising, with exceptional survivability of the capsules during mixing and application [127]. Many of these functional gains using the lignin and lignin-based materials are interrelated and could be attributed to the presence of a large number of hydroxyl groups, which also act as the linkers for attaching desired functionality. When incorporated into cement, lignin improves compressive and flexural strength, in addition to those stated above. It functions as a binder, enhancing the bonding between cement particles and aggregates, resulting in stronger and more durable concrete. Additionally, lignin can improve the durability of cement composites by reducing permeability and increasing resistance to environmental degradation, such as freeze-thaw cycles and chemical attacks. The summary of lignin from source to cement composite is schematically illustrated in Fig. 8.

In hydraulic cement, the water-to-cement (w/c) ratio is an important factor. The bare minimum for full hydration is 0.3 w/c; however, in actual use, greater values are employed to lessen the yield stress of the paste [135]. Nevertheless, adding more water than required lowers the strength of cementitious composites [136]. High-performance concrete in modern construction requires a low w/c ratio, which causes several issues such as stickiness, slow flow rate, and deterioration of the desired mechanical properties. These lead to difficulties with workability and are usually resolved by adding plasticizers. The plasticizers are chemical admixtures that reduce water content and are typically long-chain polymers with anionic backbones. Plasticizers, also known as superplasticizers if water reduction exceeds 12 %, are frequently added to cement pastes to enhance the strength, flowability, and durability of concrete [137]. Superplasticizers reduce the agglomeration of the hydrating cement components [138,139] and also reduce water requirements without adversely affecting strength [140]. Superplasticizers may adhere to the cement particle surface and, in certain chemical designs, via steric and/or electrostatic effects, enhance workability of the cement paste [141–146]. The electrostatic repulsions created by the sorption of anionic superplasticizer on the hydrated particles in the cement paste increase the fluidity of the cement paste [147–149]. In essence, these admixtures enhance the dispersion of cement particles and maintain the availability of mixed water for lubricating during the early stages of mixing and setting.

Kraft lignin (KL) and lignosulfonate (LS) are the two main types of commercially extracted lignin [150]. LS and KL are distinguished by differing amounts of sulfonate groups and carboxylate groups, respectively. Because of sulfonate functional groups, LS dissolves easily in water. LS is a by-product of sulfite pulping and can be employed as an admixture (superplasticizer and dispersion) in cement composites. LS has a lower sulfonate group-based charge density, and its global production is also limited. In addition to this, early shrinkages may be caused in the sulfonate compounds as reported elsewhere [151]. Conversely, KL is more widely generated worldwide and can be recovered from black liquor by a commercial-scale Kraft method. Nonetheless, the primary application of KL is as an energy source [152,153]. Unlike LS, KL lacks sulfonate groups and is insoluble in water. Black liquor is acidified during the kraft pulping process to produce KL. It makes up almost 85 % of the world's total lignin production [154]. During the Kraft process, lignin reacts with the hydroxide and hydrosulfide anions, extensively fragmenting it into different molecular weights and making it insoluble in water at neutral pH. Kraft pulping causes widespread breaking of β-aryl ether linkages, which increases the number of phenolic hydroxyl groups in KL compared to pristine lignin [155,156]. The carboxylate group in KL is primarily anionic, and although it is produced in much larger quantities than LS, this biopolymer has not been demonstrated to be a useful superplasticizer. This is explained by the limited anionic charge density of KL, which makes it insoluble in water. The end-use applications of KL in the cement composite can be improved by making it more soluble in water by chemical modifications [156,157]. Some of the techniques used for chemical modification of lignin are sulfonation, oxidation, polymerization, and sulfomethylation [157–159].

It is interesting to note from the literature that both LS and KL have been subjected to chemical modifications for their application in cement composites. LS was quaternized with 3-chloro-2-hydroxypropyl trimethylammonium chloride to form quaternized lignosulfonate, which improved fluidity of the montmorillonite (MMT) containing cement paste due to a reduction in yield stress and rheological behaviour index [160]. The chemical modification of KL was carried out using a combination of oxidation and sulfomethylation to obtain sulfomethylated lignin [127]. The sulfomethylated lignin with a higher charge density considerably improved the fluidity of a cement paste as compared to commercial lignosulfonates. The carboxymethyl lignin from sugar cane bagasse was synthesized for application as a cement retarder additive for oil well application. This process has the potential to avoid the burning of bagasse by generating more valuable material [121]. In another route, lignin was extracted from sugarcane bagasse and coffee chaff using new emerging green solvent deep eutectic solvents, and carboxymethylated [161]. As expected, this carboxymethylated lignin was found to increase the workability of cement paste. A green cement plasticizer was produced in one-step aerobic oxidation of KL in the presence of KOH, which led to the higher carboxylic acid group density of 2.6 mmol/g [162]. This chemically modified lignin was found to be adsorbed on the cement particles more readily than a commercial plasticizer, increasing the flowability of the pastes. In addition to flowability, the compressive strength of cement was improved by oxidized lignin as compared to commercial plasticizers and lignosulfonate [162]. Apart from anchoring functional groups, the different polymers have also been anchored on the extracted lignin to enhance its properties relevant to the cement composites [163]. Hydrophilic-polyacrylamide grafted via controlled radical polymerization on kraft lignin improves the workability of Portland cement blended with two natural, finely divided mineral materials (kaolin clay and clinoptilolite zeolite), which can be potentially used to reduce the cement clinker content in cement [164]. It is reported in the literature that carboxylate functional groups lead to adsorption onto cement particle surfaces, while pendant poly(ethylene glycol) (PEG) groups reduce particle coagulation and network formation through steric interactions [165]. Therefore, these polymers have also been anchored on the lignin. KL and LS were grafted with anionic polymers such as poly(methacrylic acid) (PMAA) and poly(3-sulfopropyl methacrylate) using atom transfer radical polymerization, which exhibit significant reductions in the cement water content [166]. Similarly, a lignin-grafted polycarboxylate superplasticizer was also developed, which showed greater water reducer ability than its pure polymer analogue [167]. Poly (ethylene oxide)-grafted lignosulfonate superplasticizers also showed improved performance, which could be attributed to an increase in steric interactions [168].

Nanoparticles have the effect of speeding up the hydration of Portland cement binder by adding more active sites for the C-S-H phase to nucleate and grow [169]. This, in turn, enhances the strength of the Portland cement binder during the initial setting and densification phases by creating a denser cement matrix microstructure, which improves its resistance to physical and chemical degradation. Additionally, due to hydrogen bonding, the porous structure of lignin effectively hosts and stabilizes oxide nanoparticles. According to reports, metallic oxides can also increase the initial and final compressive strengths of the Portland cement composite significantly [170]. Blending suitable oxide nanomaterials like silica with chemically modified lignin can create hybrid materials that improve workability, reduce water demand for hydration, and enhance the strength and durability of Portland cement composites. The experiments have been conducted on alumina-lignin hybrid materials in cement composites [171–173]. The presence of lignin in cement composites boosted the mixture's plasticity, as anticipated, while the silica component enhanced the final mechanical qualities of the composites. ZnO and ZnO-SiO_2 containing lignin-based hybrid materials were found to inhibit the biodeterioration of the Portland cement composites in addition to the functional advantages discussed above [174]. Therefore, the lignin-oxide nanoparticles hybrid admixture may play a significant role in the development of a better composition of cement.

The setting time was found to be affected when different metal-cation-containing lignosulfonate-based plasticizers were examined for their effects on the characteristics of concrete mixtures made with Portland cement. It was found that cement containing an admixture of calcium-lignosulfonate salt had the maximum 28-day compressive strength [175]. Tricalcium aluminate (C_3A), a main component of cement, interacts instantly with water to generate the metastable layered phases C_4AH_{19} and C_2AH_8, in the absence of gypsum. When gypsum is present, C_3A will react with water to generate ettringite ($C_6AS_3H_{32}$) and other compounds that are part of the layered double hydroxide (LDH) group. An increase in particle surface area and more ettringite production were the results of a calcium lignosulfonate dosage [176,177]. This seems to indicate that calcium lignosulfonate functions in a manner akin to gypsum while Portland cement is hydrating. According to mechanistic studies carried out by Zou et al., the plausible mechanism of cement hardening involves four stages of the hydration process of cement paste, i.e., dissolution, crystallization, acceleration, and decline [178]. The air-entraining effect of calcium lignosulfonate keeps the cement paste in a stable suspension state during the dissolution stage. The electro-repulsion of calcium lignosulfonate slows down the hydration process and the production of hydration products during the crystallization stage. The inclusion of calcium lignosulfonate lowers the formation of bound water in the flocculation structure of the cement slurry during the acceleration stage, and the released filled water takes part more actively in the hydration reaction. During the decline stage, the water in the system is mostly in the porous medium since the cement paste has solidified.

2.3.3. Plant by-products

Several plant-derived materials, such as plant extracts, possess interesting properties as a low-cost chemical admixture in Portland cement composites. Several plant-based admixtures such as blue gum, guar gum, xanthan gum, black gram pulses, okra, cactus, palm liquor, green plant extract, beetroot molasses, etc., have been studied with positive outcomes [179–187]. Hydrophobic green plant extract of *Bambusa Arundinacea* was found to be an inhibitor for reinforced concrete and could be a better substitute for nitrite-based (calcium nitrite) corrosion-inhibiting admixtures for durable concrete structures [188]. Xanthan gum, produced by the fermentation of sugars by the *Xanthomonas campestris* bacteria, is used as a rheology modifier in Portland cement and concrete. It enhances the viscosity and stability of fresh concrete, reduces segregation and bleeding, and improves overall mixture quality. Similarly, guar gum, extracted from guar beans, acts as a thickening agent and stabilizer, increasing viscosity and workability while enhancing mechanical properties. Woldemariam et al. found that the blue gum extract functions as a shrinkage-reducing admixture for concrete [179]. The studies carried out by Otoko et al. suggested that palm liquor enhances the workability and retard the setting time of the cement mixture [184]. Black gram pulse powder has been reported by Dwivedi et al. to be a low-cost plasticizer in cement mortar and concrete applications [182]. Okra is a cheap, naturally occurring source of biopolymer. In another investigation, Karandikar et al. noted that okra extracts enhanced the mechanical qualities of cement mortars [189]. According to Hazarika et al., the inclusion of an okra aqueous extract enhanced the behaviour of cement mortars and concrete in terms of compressive strength, but this behaviour is also reliant on the okra extract concentrations in cement composites [190]. The inclusion of okra extracts also reduced the porosity mortar sample and its ability to absorb water. Polysaccharide-containing additives often improve the water retention ability of concrete, keeping the concrete mix from drying out too soon and minimizing shrinkage cracks. The viscosity of the concrete mix is improved by cactus extract, which also makes the concrete mix more workable [191]. The findings of experiments by Shanmugavel et al. also revealed that the concretes modified by adding cactus extract exhibited improved durability and mechanical qualities [191]. Specifically, proteins and fats affect the workability and durability of concrete, whereas polysaccharides affect the strength properties of additively modified concrete. Grape and mulberry extracts were tested as natural admixtures for concrete and found to enhance the enhancement of concrete compressive strength tested at 3, 7, and 28 days and the 28-day modulus of elasticity as compared to chemical admixture [192]. Wang et al. have studied coffee extract with various concentrations on the compressive strength, setting time, hydration properties and microstructure of the hardened mortars [193]. They observed hydration-promoting as well as hydration-retarding effects when the coffee extract was mixed with water for preparing cementitious materials. They attributed these effects to the polyphenols in the coffee extract, which functioned as a Ca^{2+} absorbent, and a complex of polyphenols-Ca may form the initial seeds for promoting the hydration of Portland cement in cementitious materials [193].

Most of the plant-based materials contain polysaccharides, which make them useful as admixtures in cementitious materials. Numerous studies have been conducted to better understand the role that polysaccharides play in the hydration of cement pastes [194–200]. The sodium salt of alginic acid, carrageenan, diutan gum, xanthan gum, and hydroxypropyl derivatives of guar gum and chitosan are natural viscosity-enhancing admixtures, and exhibit the set retarding ability as they are all polysaccharides origin [201]. The majority of polysaccharides affect the nucleation and development of C-S-H as well as the setting time through a variety of mechanisms that impact the hydration of Portland cement. The adsorption of polysaccharide molecules onto cement particles and freshly formed hydration products is their main effect on nucleation and growth [200]. Because of this adsorption, the surface energy is changed, which makes it less advantageous for the nucleation of compounds like calcium hydroxide and C-S-H. Furthermore, some polysaccharides can form complexes with calcium ions (Ca^{2+}) in the solution, which decreases their availability for hydration processes and prevents these phases from growing quickly [199]. By surrounding cement particles in a protective coating, polysaccharides act as retarders and prolong the setting time of Portland cement [193]. This layer serves as a physical barrier that delays the breakdown of clinker phases by preventing water from readily penetrating the cement surface. Additionally, polysaccharides can alter the supersaturation levels required for the precipitation of hydration products by reacting with ions in the solution. This alteration slows down the processes of setting and hardening by delaying the growth and creation of C-S-H and other stages. Additionally, the large size of polysaccharides can create steric hindrance, which acts as a physical barrier that slows down the formation of hydration products. Polysaccharides can significantly affect the rheological properties of Portland cement paste, improving its overall workability. By increasing the viscosity of the mixture, polysaccharides enhance its cohesiveness and reduce the risk of segregation. This makes the cement paste easier to handle and apply. Additionally, polysaccharides help retain water within the paste, minimizing bleeding and promoting a more uniform mix. This water-retention ability is especially valuable in hot or dry conditions, where rapid water loss can be problematic.

2.3.4. Agriculture waste ash

The utilization of agricultural waste ash as a pozzolanic material in cement production has gained significant attention due to its potential to decarbonise Portland cement production, reduce agro-waste disposal issues, and improve concrete performance [202,203]. Agricultural waste materials such as rice husk, sugarcane bagasse, palm oil fuel ash, and wheat straw, when incinerated, produce ash having pozzolanic activity due to the presence of higher content of amorphous silica and minor content of alumina, calcium oxide, and other reactive oxides [204,205]. Rice husk ash, for instance, may contain up to 90 % silica in an amorphous state, ideal for reacting with calcium hydroxide to form C-S-H, enhancing the strength and durability of cementitious materials. The presence of calcium oxide in agricultural waste ash further improves its ability to act as a cementitious material, accelerating early strength gain and improving bonding in the concrete matrix. Compared to fly ash, agricultural waste ash often shows improved reactivity due to higher calcium oxide content, making it advantageous in faster-setting concrete applications. Unlike fly ash, agricultural waste ash contains negligible toxic elements. However, proper grinding and processing are essential for the pozzolanic activity of the ash and ensuring better integration into the Portland cement matrix [204,205]. For example, alkali-activated rice husk ash, olive waste ash, and coconut-based waste ash are found to have greater reactivity compared to uncalcined agro-waste ashes [205]. The presence of free lime, alumina, ferric oxides, and trace minerals contributes to improved mechanical and chemical performance. Incorporating agricultural waste ash in cement offers numerous benefits. Pozzolanic reactions improve compressive strength, reduce permeability, and enhance resistance to sulfate attacks and alkali-silica reactions. Using waste ash reduces carbon emissions associated with clinker production and minimizes landfill waste. Substituting agricultural waste ash can lower raw material costs and reduce energy consumption in Portland cement production. The fine nature of pozzolanic ash improves the fresh properties of cementitious mixes. However, there are several issues in using agricultural waste ash. Achieving consistent chemical composition and particle fineness is critical for ensuring predictable pozzolanic activity. Ash requires careful proportioning to balance setting time, workability, and mechanical performance. Efficient combustion and proper grinding are necessary to achieve the desired amorphous silica phase for optimal pozzolanic reaction. Agricultural waste ash can be effectively used in blended Portland cement by replacing a portion of Portland cement in formulations.

Biochar is produced through pyrolysis of agricultural wastes in the absence or limited presence of oxygen, resulting in a stable, carbon-rich material having 70 % carbon or more by weight. Many times, biochar requires activation for the desired function [206]. Biochar has good potential for carbon capture due to its robust CO_2 adsorption capacity and its eco-friendly, cost-effective, and low-carbon production process [207]. It has been reported that biochar enhances the mechanical properties of cementitious materials [206,208,209]. As biochar is a good absorber of CO_2, biochar in cement-based composites is also expected to involve CO_2 curing [210].

Agricultural waste ashes and biochar derived from rice husk, sugarcane bagasse, palm oil waste, wheat straw, coconut shell and other agricultural wastes are increasingly being recognized as valuable supplementary cementitious materials (SCMs) in the production of blended Portland cement. There are dual advantages of using agricultural waste ashes and biochar, i.e. reduction of the amount of clinker in cement and valorisation of agricultural wastes [210]. Charitha et al. have studied fourteen agro-waste ashes as the pozzolana in cement for effective upcycling of locally available resources [211] These agro-waste ashes were: sugarcane bagasse ash, rice husk ash, palm oil fuel ash, corncob ash, coconut shell ash, wood ash, groundnut husk ash, cassava peel ash, wheat straw ash, elephant grass ash, rice straw ash, sugarcane straw ash, tobacco ash and bamboo leaf ash. They observed that agro-waste ashes mostly consist of silica content above 50 %, except for tobacco ash and groundnut husk ash. The addition of the agro-waste ashes in Portland cement was found to reduce the slump of concrete, except for palm oil fuel ash, wheat straw ash, and rice straw ash blended concretes. Significant reduction in the permeability and subsequent enhancement in the durability of agro-waste ash blended concretes were experimentally observed. The pozzolanic action of agricultural waste ash in cement enhances the properties of concrete, which involves the reaction of SiO_2 with water and calcium hydroxide ($Ca(OH)_2$) to form compounds with cementitious properties.

Rice husk is produced every year in millions of tons as a by-product of rice milling [212]. Rice husk ash (RHA) contains a significant amount of amorphous silicon oxide, which exhibits a high pozzolanic activity [213–215]. This makes RHA well-suited as a supplementary cementitious material for the partial replacement of Portland cement in concrete mixtures [216]. The pozzolanic properties of rice husk ash (RHA) are primarily attributed to its high amorphous silica content, large specific surface area, and fine particle size, which are influenced by controlled combustion and grinding processes. Due to its finer particle size compared to cement components, RHA blends well with cement concrete, enhancing fresh properties such as workability, consistency, and setting time [217]. The mechanical properties, such as compressive, tensile, and flexural strength, were found to be enhanced in RHA-containing cementitious materials with an increase in RHA content up to an optimum level (20 wt%) [218]. In addition to this, the use of fine RHA particles improved the microstructures (denser and uniform) of the cementitious materials, resulting in enhanced water absorption, chloride resistance, corrosion resistance, and sulphate resistance [219]. However, fine RHA particles in cement increased the water-cement ratio. Typically, RHA could replace clinker content in cement up to 10–20 % without any significant effects on concrete performance, similar to other pozzolanic materials. Jaya et al. found that 15 % RHA, burnt below 800 °C, exhibited a higher compressive strength in the cementitious material [220]. This could be due to the existence of an amorphous silica phase below 800 °C.

Apart from rice husk ash, sugarcane bagasse ash (SCBA) is the most promising supplementary cementitious material [221]. Sugarcane bagasse originates as a waste product from the sugar and alcohol industry. Similar to RHA, SCBA produced by calcination between 600 and 700 °C shows high pozzolanic activity due to the formation of ultrafine amorphous silica, which makes it a promising supplementary cementitious material [222–225]. Calcination temperature significantly influences the pozzolanic activity of SCBA, as the crystallinity and particle sizes of SCBA are significantly influenced by calcination temperature and duration [225]. Therefore, optimized calcination temperature and duration are requisite to obtain higher pozzolanic activity of SCBA. Ultra-fineness of amorphous silica enhances surface area, resulting in enhanced reactivity when SCBA reacts with $Ca(OH)_2$ during the hydration of cement, thus leading to nucleation and growth of C-S-H [224]. However, it has been reported that the SCBA retards the initial hydration, leading to an increase in setting time [226,227]. In addition to influencing the hydration of cement, SCBA enhances water demand [228], similar to that observed for RHA. The ideal amount of SBCA in Portland cement depends on its silica content and can range from 10–20 % by weight without noticeably affecting mechanical properties [226–229]. As observed in several studies, SCBA in Portland cement produces dense and better microstructure during hydration, which imparts enhanced physical properties, mechanical strength, microstructure, and durability [230–234]. Due to better microstructure and

Table 3
Comparison of probable chemical compositions of corncob ash (CCA), palm oil fuel ash (POFA), rice husk ash (RHA), sugarcane bagasse ash (SCBA), and groundnut shell ash (GNSA) with ordinary Portland cement (OPC) [250].

Oxides	OPC (%)	CCA (%)	POFA (%)	RHA (%)	SCBA (%)	GNSA (%)
SiO_2	17–25	60–70	50–65	80–95	50–75	27
Al_2O_3	3–8	5–7	3–5	< 2	2–5	5.8
Fe_2O_3	5–6	3–5	4–7	< 2	2–6	0.5
CaO	63–68	7–10	5–10	< 2	6–12	9.5
MgO	1–2	< 2	3–5	< 1	< 2	5.6
Na_2O	< 1	< 0.5	< 2	< 1	< 1	1
K_2O	< 1	2–6	6–8	< 1	< 2	20

compact matrix, the SCBA containing Portland cement in mortar or concrete exhibits low permeability, leading to acid resistance, carbonation resistance, resistance to chloride penetration, resistance to sulfate attack [227–229,235,236], and stability at elevated temperatures [237].

In addition to RHA and SCBA, several studies have been carried out to explore the possibility of using coconut shell ash (CSA) as an alternative supplementary cementitious material [238–242]. CSA also possess pozzolanic property. CSA is also produced by the combustion of coconut shells in open air at around 800 °C for 4–8 h. It is interesting to note that chemical constituents in the CSA are similar to Portland cement, i.e. lime (CaO), silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3) [242], indicating the potential of CSA as a supplementary cementitious material. The presence of a significant amount of amorphous silica (SiO_2) in the CSA provides pozzolanic activity by reacting with water and calcium hydroxide to enhance the formation of C-S-H gel in concrete. Therefore, the mechanical properties, durability and resistance to corrosion of the cementitious materials are enhanced by using CSA in cement [243,244]. Olive waste ash is also suggested as a cementitious material [245,246]. However, it has low pozzolanic activity due to low silica content, but is rich in carbon content [247,248]. It is interesting to note that olive oil waste can be used in lower amounts (0.35 %), increasing compressive strength [249]. The comparison of the most probable chemical compositions of different agricultural waste ashes is given in Table 3 [250]. However, the comparison of compressive strength across concretes incorporating different types of agricultural wastes reveals significant variability, with no conclusive trend regarding the optimal proportion of waste ash addition to ordinary Portland cement (OPC) without compromising strength. Nevertheless, the majority of data indicate that the incorporation of 15–20 % agricultural waste ash, such as rice husk ash (RHA) and sugarcane bagasse ash (SCBA), is feasible, with some studies even reporting improvements in compressive strength at these replacement levels [250].

Rodier et al. have studied the pozzolanic activity and hydration of cement pastes containing sugarcane bagasse (SCBA) and bamboo leaves ashes (BLA) [251]. To quantify the impact of the SCBA and BLA on the Portland cement, the energy necessary to produce the Portland cement (E_n) and the energy performance (E_p) of mortar were evaluated using the following equations [252]:

$$E_n\ (\mathrm{kWh/t}) = X_C\ (E_{prod} + E_{grind}) + X_A\ (E_{prod} + E_{grind})$$

$$Ep\ (\mathrm{kWh/t/MPa}) = E_n / \sigma_{cs}$$

Where X_C and X_A represent the weight fractions (%) of Portland cement and ashes in the matrix, respectively. E_{prod} and E_{grind} are the energy inputs (kWh/t, k = kilo, W = watt, h = hour, t = ton) in the manufacturing process and the grinding of Portland cement, respectively, and σ_{cs} is the compressive strength of the thus-formed mortar. E_n and E_p are calculated for binary (Portland cement + BLA) and ternary (Portland cement + SCBA + BLA) mortars using compressive strength at 28 days, and other data from the literature i.e. $E_{prod} + E_{grind}$ to produce cement is 112kWh/t [253], the ashes are considered as a residue (E_{prod} =0 kWh/t), and the energy input for obtaining the required particle size is about 40 % of the total energy needed to produce cement [254]. The values of E_n and E_p obtained by Rodier et al., shown in Table 4**,** suggest that producing 1 ton of Portland cement mixed with agro-waste ashes has a lower energy requirement than conventional Portland cement used as the control [251]. Consequently, these mixed binder exhibits lower energy requirements for obtaining the same compressive strength as that of conventional Portland cement mortar. They have also shown the cost benefits of using SCBA and BLA in Portland cement binder [251].

Table 4
The comparison of energy requirements to produce the cement (E_n) and the energy performance (E_p) of mortars cured for 28 days [251].

Composition	Normalized compressive strength	E_n (kWh/t)	E_p (kWh/t/MPa)
Portland cement (Control)	1	112	3.0
Portland cement + BLA 20 wt%	1.2	99	2.1
Portland cement + BLA 10 wt% + SCBA 10 wt%	1.3	99	2.2

2.3.5. *Biorefinery and fermentation-derived products*

Fermentation-derived products such as sodium gluconate and xylonate salts (e.g., calcium xylonate and sodium xylonate) are emerging as promising cement admixtures. These function as water reducers that delay setting time while enhancing compressive strength [255–258]. Microbial fermentation of xylose, especially using *Gluconobacter oxydans* (*G. oxydans*), is emerging as a more promising approach for producing xylonic acid (XA) compared to chemical or enzymatic methods [259, 260]. Zhou et al. reported the highest XA titer of 586 g/L from pure xylose using *G. oxydans* in a batch-fed, oxygen-injected stirred reactor, effectively addressing the challenges of high oxygen demand and severe foaming during whole-cell catalysis [261]. Recent research highlights the growing interest in using *G. oxydans* to convert lignocellulosic hydrolysates, such as hemicellulose, into XA. This strain not only shows superior xylose bioconversion efficiency but also demonstrates notable tolerance to lignocellulosic inhibitors, making it a strong candidate for industrial applications [262].

Han et al. investigated the direct production and application of XA-based water reducers, XA-Ca and XA-Na powders, using corncob residue as a feedstock [255]. Their study showed that XA-Ca is more cost-effective for industrial use due to its lower production cost and zero wastewater discharge. In performance tests, both XA-Ca and XA-Na significantly improved concrete strength: compressive strength increased by 33 % and 36 % at 7 days, and by 24 % and 34 % at 28 days, respectively. Flexural strength also improved, with XA-Ca-H and XA-Na-H achieving 24 % and 30 % gains at 7 days, and 7 % and 9 % at 28 days, respectively. Zhou et al. successfully synthesized crude powdered calcium xylonate from wheat straw pre-hydrolysate, showing improved water-reducing and retardation effects, along with enhanced compressive strength [256]. This study also highlights calcium xylonate as a promising, low-cost concrete admixture. These findings suggest that valorizing wheat straw pre-hydrolysate can support the cost-effective utilization of lignocellulosic biomass. Zhang et al. demonstrated that *Gluconobacter oxydans* DSM 2003 efficiently produced gluconic and xylonic acids from dry dilute acid-pretreated and biodetoxified corn stover [257]. Fermentation achieved titers of 132.46 g/L sodium gluconate and 38.86 g/L sodium xylonate, with successful scale-up. The resulting product outperformed commercial sodium gluconate as a cement retarder. Techno-economic analysis using Aspen Plus confirmed its cost and performance advantages over corn starch–based processes, highlighting the commercial potential of lignocellulosic biomass for sodium gluconate and xylonate production.

Han et al. demonstrated that the carboxyl and hydroxyl groups in xylonic acid chemisorb onto Si-O bonds on cement particle surfaces [258]. This interaction reduces water demand and delays setting by hindering Ca^{2+} ion aggregation during C-S-H gel formation. The notable

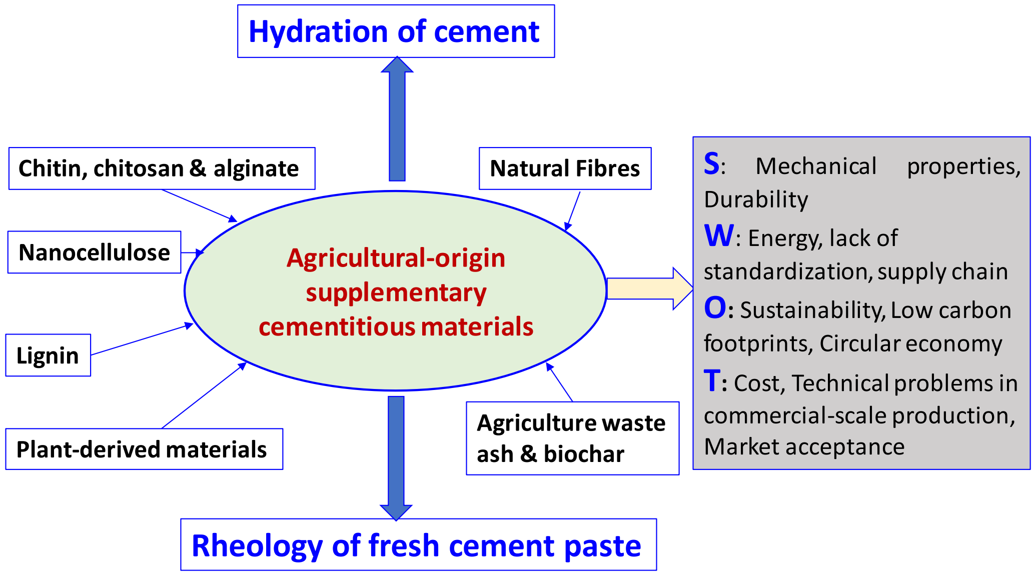

Fig. 9. SWOT analysis of the use of agricultural-origin cementitious materials for partially replacing clinker in cement.

water-reducing efficiency, tunable setting time, and enhanced mechanical and durability properties make xylonic acid a promising alternative to traditional lignosulfonate-based water-reducing agents. Johnson et al. provided a comprehensive review of various types of bio-based concrete water reducers, their working mechanisms, and their influence on the rheological and mechanical properties of concrete [263]. This review deals with both synthetic and bio-based water reducers, highlighting advancements in their production and application. They have highlighted the challenges in developing bio-based water reducers from renewable resources, including issues related to raw material variability, process scalability, and performance consistency in concrete formulations.

3. Sustainability

Portland cement manufacturing is one of the most CO_2-emitting processes. Therefore, major efforts are being made to decarbonise the cement and construction industry [264–267]. In the coming decades, Portland cement (PC) demand is expected to rise in India and developing regions of sub-Saharan Africa, Asia-Pacific, and the Middle East [268]. In contrast, demand in China, Europe, and North America will plateau or decline [268]. To align with net-zero greenhouse gas emissions by 2050, the cement industry must adopt medium-term strategies such as improving energy efficiency, advancing technologies, using alternative fuels and raw materials, and increasing clinker substitution. Among these, CCUS (carbon capture, utilization, and storage) and clinker substitution offer the greatest decarbonization potential. However, a one-size-fits-all approach is impractical given the diverse market demands, raw material availability, production technologies, and infrastructure across countries. Instead, strategic frameworks should be customized to each country's specific context and needs, guided by SWOT analysis, life cycle assessment, and techno-economic evaluation.

3.1. SWOT analysis and techno-economic assessment

Strengths, Weaknesses, Opportunities, and Threats (SWOT) analyses for the different cementitious materials may vary depending on the origin and nature of agricultural-origin supplementary cementitious materials. However, this is a good method to understand the sustainability probability of agricultural-origin supplementary cementitious materials for partially replacing Portland cement, coarse/fine aggregates and reinforcement. Clinker is the main component of Portland cement, with no viable alternative, but it is a major source of greenhouse gases. Khan et al. have carried out a SWOT analysis on biochar, obtained from locally available agricultural waste (date palm fronds) [269]. The SWOT analysis carried out by Khan et al. suggested that biochar in Portland cement exhibits improved performance in concrete than ordinary concrete, with probability for circular economy and applications in various construction designs. The major challenges are cost and technical bottlenecks in the standardized production and applications of biochar in concrete. Nasir et al. carried out a SWOT analysis of the use of nanostructured cellulose, such as cellulose nanocrystals (CNCs), cellulose nanofibers (CNFs), and bacterial nanocellulose (BNC) in cement [270]. This SWAOT analysis suggested strengths in the circular economy, sustainable and durable construction, weaknesses in energy and eco-toxicity, opportunities in green building and low carbon footprints, and identified threats in low energy-efficient technology. SWOT analysis of mortar utilizing Arabic gum suggested that this can expand the market for farmers, reduce material costs and contribute to the circular economy [271].

The SWOT analysis was carried out based on the review of the literature on agriculture-origin materials as supplementary cementitious materials for partially replacing clinker up to 10–20 % in cement and summarized in Fig. 9. It is seen that the major strengths of using agricultural-origin cementitious materials are the enhanced mechanical properties and durability, which originate from facilitation of hydration of C_3S (the main component of clinker). This results in the formation of a denser microstructure of C-S-H, leading to lower permeability and, hence, corrosion resistance. The natural fibres and nanofibres also provide reinforcement and crack bridging, leading to autogenous healing. In addition to this, lignin and plant extracts improve the rheology of the freshly prepared cement paste. However, the major weakness of using these materials in construction is related to energy consumption, lack of standardization of preparation and uses, and problems in the supply chain, as most of these materials are generated in localized areas. The major advantages are the valorisation of agricultural waste, various regulatory compliance due to the use of green materials, processes and the possibility to make ultrahigh-performance cement composites with an appropriate choice of agricultural-origin cementitious materials [265].

3.2. Life cycle assessment

The process of assessing the environmental consequences of a

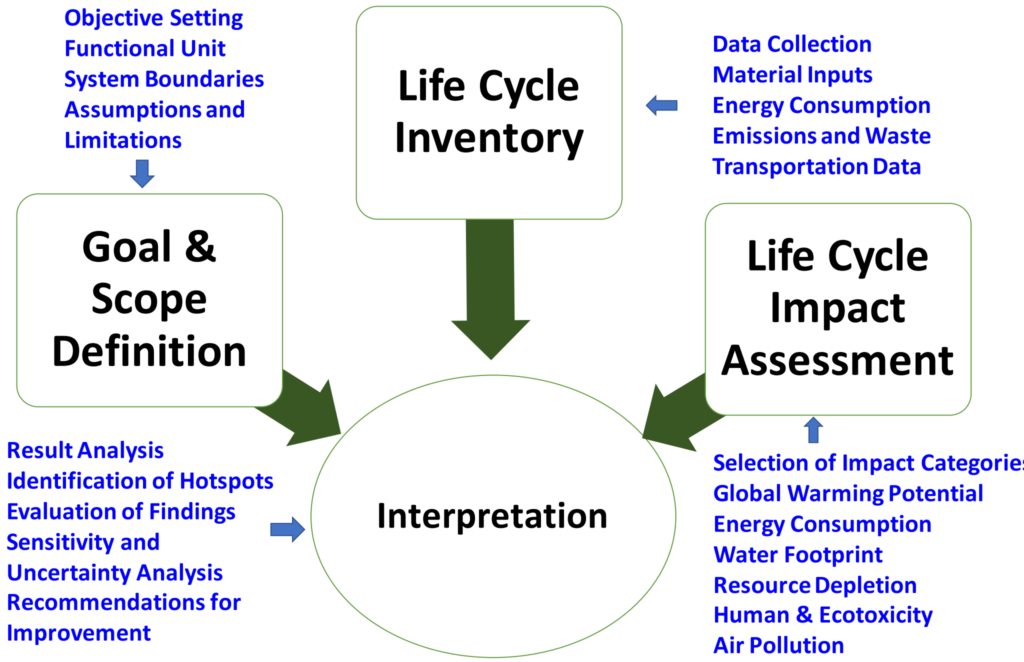

Fig. 10. Framework of LCA based on International Standard Organization (ISO) 14040.

product over every stage of its life to reduce liability and increase resource efficiency is referred to as life-cycle assessment (LCA). An LCA using agricultural-origin cementitious supplementary materials evaluates the environmental impacts associated with each stage of their life cycle, from raw material extraction to end-of-life disposal. This also involves the stages in the production of cement such as: (i) environmental impact and energy consumption of raw material extraction and processing, (ii) greenhouse gas emissions, energy use, carbon sequestration, and by-product utilization during the production of Portland cement and concrete, (iii) transportation, (iv) durability and longevity during use phase, and (v) end-of-life (disposal or recycling). Based on these evaluations, the overall life cycle assessment is done in terms of carbon footprint, resource efficiency and potential trade-offs involving agriculture waste utilization. Therefore, LCA plays an important role in the decarbonisation of Portland cement production and in understanding the sustainability of cementitious infrastructure. The framework of LCA generally has four steps as shown in Fig. 10 [272].

As shown in Fig. 10, LCA applications are based on a framework involving four steps: (i) goal and scope definition, (ii) life cycle inventory (LCI), (iii) life cycle impact assessment (LCIA), and (iv) interpretation. The first step, Goal and scope, deals with the objectives of LCA, the system of the product and/or process, the functional unit, system boundaries, and the validity of the assumptions [273]. The impact of selecting different functional units on the LCA of green concrete was studied by Panesar et al., who indicated that functional units significantly affect the LCA results [274]. In general, the functional units are required to quantify the function of a product or process and are employed for comparison with other systems. In many studies, 1 Kg is taken as the functional unit, which is uniformly employed in all datasets, analysis and interpretation. The LCA is conducted from cradle to gate, i. e., from the extraction of components to the production of cement.

Life Cycle Inventory (LCI) involves the compilation of relevant input and output inventory data, such as data on energy inputs, raw materials, emissions, water usage, and transportation for each life cycle stage. For green cement using supplementary cementitious materials, LCI includes quantifying the raw materials used, such as clinker substitutes like slag or agricultural-origin materials, energy consumption in kilns and grinding processes, and emissions like CO_2, NO_x, and particulate matter. Data collection forms the basis for understanding the material flows and energy demands in Portland cement production. The dataset from Ecoinvent is employed for construction materials in many studies [275]. Ecoinvent contains detailed data on materials, energy flows, and emissions associated with cement production and its related activities. It covers global and regional energy use, waste management, and transportation datasets.

Life cycle impact assessment (LCIA) evaluates the environmental effects based on various indicators of potential environmental impacts. This assessment addresses several environmental issues, such as the global warming potential of CO_2-equivalent emissions, energy consumption involving both renewable and non-renewable energy used, and water footprint across the life cycle. Other crucial indicators include resource depletion, human and ecotoxicity, and air pollution. In green cement production, reducing clinker content through supplementary materials leads to lower emissions and resource depletion, helping to mitigate climate change impacts. LCIA is a comprehensive evaluation process involving the grouping of all inventories into their various impact categories. Thus, the LCIA results in the impact of the product. SimaPro is the most employed LCA software tool, which allows for detailed modelling of the cement life cycle, from raw material extraction to waste management. Olagunju et al. have compared software packages for LCA of the cement industry, such as GaBi, OpenLCA, SimaPro, and Umberto, and observed that SimaPro is the best software tool based on the required standards [276]. It supports databases like Ecoinvent and helps to assess environmental impacts such as carbon footprint, resource depletion, and water use. Cement CO_2 and Energy Protocol (WBCSD) developed by the World Business Council for Sustainable Development (WBCSD) could be used to calculate direct and indirect CO_2 emissions and assess energy efficiency measures across cement production stages. A comprehensive approach involving a combination of LCA with Building Information Modelling (BIM) has been used to evaluate the environmental costs of material manufacturing. LCA analyze the environmental impacts of different scenarios, and BIM software (Autodesk Revit) provides information on the building materials for LCA input [277,278].

Following the LCIA, the interpretation is the last step in which the most significant environmental impacts are identified. This stage helps to pinpoint the life cycle stages, such as raw material extraction or manufacturing, where impacts are highest. ReCiPe is a life cycle impact assessment method used to evaluate the effects of cement production on ecosystems, human health, and resource depletion. It provides indicators for various environmental categories, which help in understanding the broader impact of cement manufacturing. Recommendations are then made to further reduce ecological footprints. For green cement, this might involve increasing the use of alternative fuels, improving energy efficiency in production, or maximizing the recycling of materials. A sensitivity and uncertainty analysis should also be performed to evaluate how changes in key parameters, such as different types of alternative materials or energy sources, affect the outcomes. This ensures that the conclusions drawn are significant and account for uncertainties in the data. An extensive review of Life Cycle Assessment (LCA) techniques and their use in the construction sector has been given by Chau et al. [279]. The study has covered the significance of life cycle assessment (LCA) in encouraging sustainable growth in the construction sector and emphasises the need for more investigation to improve the methods used for assessment. Ige and Olanrewaju have done a comparative LCA of different Portland cement types in South Africa and identified the clinkering process as the primary cause of atmospheric impacts [280]. The raw materials required in clinkering were found to be major contributors to the resource depletion impacts and toxicity impacts. They showed lower environmental impacts in configurations having lower clinker-to-cement ratios. This seems to suggest that the partial replacement of clinker with agricultural-origin supplementary cementitious materials would lower the environmental impacts. Though there are not many studies on using agricultural-origin materials in cement, LCA studies have been carried out for partially replacing clinker with supplementary cementitious materials.

Ali has compared the LCA of polymeric and conventional concrete for sustainable construction [281]. SimaPro V9.5 software was used to conduct this life cycle assessment (LCA) from raw material extraction to the production stage (cradle to gate). The midpoint and endpoint data were used to analyse the environmental impacts, and the results indicated that polymeric concrete had a lower impact on global warming, acidification, and eutrophication potential than conventional concrete. Climate change significantly affected both regular and polymer concrete in terms of single-score outcomes; the former scored 0.90 mPt, while the latter recorded a far lower 0.14 mPt, suggesting a 75 % decline. For regular concrete and polymer concrete, the global warming potential was determined to be 8.95 kg CO_2 equivalent and 1.38 kg CO_2 equivalent, respectively. Last but not least, an overall reduction of 84.24 % in the endpoint outcome indicated that the greatest impact was on human health. According to this study, polymeric concrete may be a more environmentally friendly option for some applications than traditional concrete. Because polymer concrete is more expensive than ordinary concrete, one of the biggest challenges in using it in the infrastructure industry is to address the techno-economic problems. LCA of rice husk ash (RHA) as a viable substitute material in cement has been carried out by Gursel et al. [282]. This study revealed that RHA decreased the environmental impact of producing concrete and its carbon footprint at every stage of the life cycle, from the procurement of raw materials to disposal at the end of the process. Therefore, RHA could be a sustainable supplementary material for Portland cement, and using it can lessen the environmental impact of the construction industry. Manjunatha et al. carried out the LCA of concrete prepared with conventional cement (OPC) and sustainable cement (ground granulated blast furnace slag (GGBS) and Portland pozzolana cement (PPC)) to compare the environmental impact [283]. They concluded, based on the LCA model, that concrete prepared with OPC has greater impacts on climate change and carbon footprints as compared to GGBS cement and PPC cement. Navaratnam et al. conducted an LCA of mortar containing 15% (by weight) fly ash, blast furnace slag, bottom ash, recycled glass, ferronickel slag, expanded polystyrene, and wood ash. [284]. This study showed that fly ash had lower environmental impacts across most categories, including human health, ecosystems, and natural resources.

Fly ash can be used to replace higher amounts ($>$ 60 %) of sand or cement in conventional mortar as compared with other wastes, indicating it is a sustainable option for producing greener mortar. Al-Gheethi et al. have studied the LCA of bio-cementitious materials production for comparison with conventional cement production [285]. The LCA analysis showed that, in comparison to the production of conventional cementitious materials, the production of bio-cementitious materials had a greater environmental impact. This is because both inorganic substances (calcium nitrate) and organic substances (urea and molasses) are present. The worker may be at risk due to the bacterial presence. Nonetheless, the majority of the research employs non-pathogenic types of bacteria. A life cycle assessment of the repurposing of biomass ash as a secondary cementitious material in cement mortars was carried out by Tosti et al. [286]. LCA was conducted by considering not only the reduction of CO_2 but also the effects on all non-toxic categories, and the carcinogenicity and toxicity to humans during the service and second life stages. This was based on the fact that biomass ash does contain elevated levels of elements that could be harmful to humans or the environment. These LCA studies show that reusing biomass ash as a secondary cement material benefits most impact categories and does not cause harmful leaching during cement use or its second life..

Georgiades et al. assessed the life cycle impact of European cement production, exploring decarbonisation strategies such as clinker substitution, alternative fuels, kiln efficiency improvements, and carbon capture [287]. By 2050, clinker substitution (42 %), alternative fuels (25 %), and kiln efficiency (12 %) could collectively cut CO_2-eq. emissions by ~58 % (excluding carbon capture) and ~88 % (including it) compared to 2020. These measures would reduce emissions to 0.09 kg CO_2-eq. per kg of cement. Decarbonising the electricity input could further lower emissions by ~10 %. This study highlights multiple viable pathways for the cement sector to align with global climate targets. However, it is seen from the available literature on LCA of cementitious materials that there are several local factors, and therefore cannot be generalized. Major challenges appear to be the techno-economic considerations in using supplementary cementitious materials in cement for sustainable construction activities.

3.3. Circular economy

The United Nations (UN) sustainable development goals (SDGs) are dependent on waste management and the circular economy related to life below water (SDG 14), life on land (SDG 15), climate action (SDG 13), and responsible consumption and production (SDG 12). Apart from the aforementioned objectives, the construction industry is also closely associated with sustainable cities and communities (SDG 11) and industry, innovation, and infrastructure (SDG 9), which aim to achieve sustainable, resilient, eco-friendly, and affordable housing and infrastructure by 2030, respectively [288,289]. The circular economy is built upon six core principles: reuse, recycle, redesign, remanufacture, reduce, and recover (6Rs). It serves as a conceptual framework focused on decoupling economic growth from environmental impact [290–292]. The value of resources is maximised through these cycles, and the materials are continuously maintained in an endless cycle that decreases the demand for raw material utilisation through reproduction and remanufacturing [293]. Nodehi et al. have reviewed circular economy in the construction industry through the use of waste materials such as supplementary cementitious materials, construction and demolition waste, and plastic wastes, which was found to be encouraging in life cycle assessment, including durability [294]. A review on sustainability, durability, and structural properties of green concrete made by partial replacement of clinker by using supplementary cementitious materials suggested its promising potential for a circular economy [295]. Based on these reviews and in the present context, the plausible circular economy model is illustrated in Fig. 11.

The circular economic model for the construction industry mainly focuses on minimizing waste and making the most of resources by

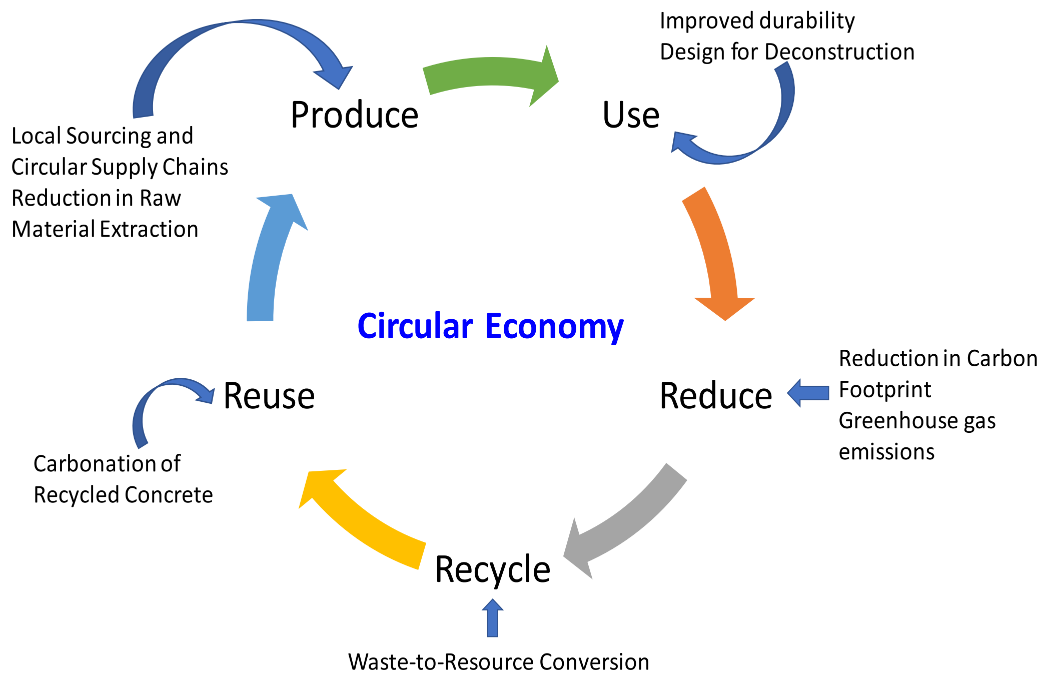

Fig. 11. Illustration of the circular economy model in the sustainable construction industry.

reusing, recycling, and repurposing materials throughout the lifecycle of a structure. Unlike the traditional linear economy (take, make, use, dispose), the circular economy aims to keep materials and products in use for as long as possible, thus reducing the demand for raw materials and lowering the environmental impact. Thus, the circular economy model in construction is dependent on: (i) low-carbon and sustainable materials such as agricultural-origin supplementary cementitious materials, (ii) recycling construction and demolition waste, (iii) process efficiency, (iv) durability and adaptive reuse, and (v) closed-loop systems. Thus, this circular economy model would promote resource conservation, energy savings, and a significant reduction in greenhouse gas emissions and carbon footprints, making it a crucial part of sustainability efforts in the cement and construction sectors.

Usually viewed as environmental contaminants, paper mills and agro-industrial waste can be transformed into valuable resources in cement manufacture, fostering a closed-loop economy. Black liquor, or Kraft lignin, is produced as a by-product of Kraft pulping. It has been observed that adding black pulp liquor to fresh concrete at varying dosages improves the concrete's mechanical qualities and delays setting [296]. Several studies proposed paper mill effluent as an admixture in cementitious materials to develop a circular economy [297–300]. There is a possibility of using agro-industrial waste ash for the circular economy as pozzolanic materials in cement, as discussed in the section dealing with agricultural waste ash and biochar. The use of paper mill sludge ash, rice husk ash, and sugarcane bagasse ash in cement production has been widely explored in India due to the ease of availability, promoting sustainable construction practices. Countries like Malaysia and Indonesia are increasingly using palm oil fuel ash in cement, creating value from the palm oil industry's waste products. Rice husks are grown for roughly 750 million tonnes a year, yielding about 160 million tonnes of garbage that is finally discarded into the environment, filling up a sizable landfill and contributing to pollution issues. After rice husk undergoes combustion, a significant quantity of silica content is still present after the lignin and cellulose content are removed. Cement content ranges from 900 to 1000 kg/m^3 in ultrahigh-performance concrete (UHPC), one of the newest innovations in concrete manufacturing. Rice husk ash added to cementitious materials exhibits improved UHPC performance, according to a review by Mosaberpanah et al. [301]. The use of rice husk ash as a cementitious ingredient in recycled aggregate concrete has been investigated by Rattanachu et al. [302]. The steel corrosion and chloride resistance of the recycled aggregate concrete were greatly enhanced by adding ground rice husk ash to the concrete at a weight percentage of 20–50 % of regular Portland cement. The recycled aggregate concrete exhibited better resistance to chloride penetration and the least amount of steel corrosion when 50 % ground rice husk ash was substituted for OPC.

Climate and resource footprint assessment and visualization of recycled concrete for the circular economy were carried out by Mostert et al. [303]. Based on this study, recycling concrete can reduce its material footprint by up to 50 %. However, wet processing of concrete waste can increase its water footprint by up to 10 times and has limited potential to reduce its climate impact. Cerchione et al. have done LCA of concrete production from a circular economy perspective and concluded that recycled aggregates could contribute to reducing the impacts of construction and demolition waste management and disposal [304]. Carbon mineralisation in concrete is also important for sustainable and eco-friendly solutions to support the circular economy [305]. Strategies for the circular economy cannot be evaluated exclusively from the standpoint of materials or goods. System-level assessments are required to avoid the dangers of harmful technical lock-in and/or the early failure of innovations, as well as to discover potential synergies and trade-offs when various circularity techniques are combined [306].

4. Conclusions

The decarbonization of Portland cement production has become increasingly urgent due to rising consumption and, consequently, higher production levels. Extensive efforts are being made to reduce the carbon footprint of cement and concrete through innovative strategies, advanced technologies, policy interventions, case studies, and economic considerations. However, significant challenges remain in effectively addressing this critical issue. The agricultural-origin supplementary cementitious materials are expected to a big role in green and durable construction aligned with UN sustainable development goals encompassing life below water (SDG 14), life on land (SDG 15), climate action (SDG 13), responsible consumption and production (SDG 12), sustainable cities and communities (SDG 11) and industry, innovation, and infrastructure (SDG 9). The possibilities of using different agricultural-

Table 5
Summary of agricultural-origin supplementary materials employed in construction with their merits and demerits.

Agro-materials	Functions in cement & concrete	Merits	Demerits
Jute Fibre	Enhances workability and tensile strength (reinforcement)	Economical	Susceptible to decay, requires treatment
Coir Fibre	Improves ductility, resists crack propagation (reinforcement)	Strong natural fibre, renewable	Requires chemical or alkali pre-treatment
Flax Fibre	Improves tensile and flexural performance (reinforcement)	Strong natural fibre, renewable	Alkaline degradation, needs coating
Ramie Fibre	Enhances strength, moisture regulation (reinforcement)	High mechanical strength, renewable	Susceptible to microbial decay
Alginate	Retains moisture, improves internal curing and crack resistance	Forms hydrogels, enhances durability	Sensitive to alkaline conditions, higher cost and sourcing from marine biomass
Chitin (Shellfish exoskeletons)	Binds with cement phases; modifies microstructure	Renewable, enhances barrier properties	Requires pretreatment, insoluble in water. Its deacetylated product, chitosan, is a better corrosion inhibitor but costly
Sawdust (wood industry waste)	Fine aggregate substitute	Reduces density, improves thermal performance.	Reduces strength, variable composition
Coconut Shell	Coarse aggregate substitute	Reduces density; provides lightweight concrete with good impact resistance	Lower strength, high water absorption
Rice husk ash (Rice milling waste)	Pozzolanic material for partial replacement of clinker	Improves strength and sulfate resistance, abundant, high silica content	Needs controlled combustion to avoid crystalline silica formation
Sugarcane bagasse ash (Sugar industry waste)	Pozzolanic material for partial replacement of clinker	Improves strength and sulfate resistance, abundant, good silica content, and presence of lime	Needs controlled combustion to avoid crystalline silica formation
Biochar (Pyrolyzed biomass)	Filler and carbon-rich supplementary cementitious material	Enhances thermal and mechanical properties, captures carbon	Affects workability and setting
Nanocellulose (obtained from cotton, hemp and other cellulosic materials)	Nano-reinforcement enhances mechanical strength, reduces shrinkage	Excellent strength-to-weight, crack resistance	High production cost and dispersion difficulty
Lignin / Lignosulfonates (Wood/paper industry)	Superplasticiser, water reducer, and set retarder	Cost-effective plasticizer	Lower efficiency than synthetic superplasticizers, costly
Plant Extracts (tannins, gums, etc.)	Alters hydration, acts as a retarder	Admixtures, corrosion inhibitors	Inconsistent composition, shelf-life issues
Xylonic / Gluconic Acid (Fermented agricultural sugars)	Improves flowability, delays setting	Competitive with synthetic plasticisers	It may not be cost-effective if used in purified form, bioreactor-related issues

origin supplementary cementitious materials in cement and concrete such as natural fibres, nanocellulose, lignin, natural polymers (chitin, chitosan and alginate), plant extract mostly containing polysaccharides, and agricultural waste ashes and biochar were examined in this manuscript. The agriculture-origin nanofibers could be effective for reinforcement in concrete and preventing microcracks by bridging effects. It is also interesting to note that fine and coarse aggregates in concrete could also be partially replaced with agriculture-origin materials with minimum processing. Many studies suggested that most of these agricultural-based supplementary cementitious materials affect the chemistry of hydration of Portland cement and subsequent nucleation and growth of C-S-H, which results in a denser microstructure and improved mechanical properties of the concrete. The agricultural waste ashes and biochar exhibit, especially rice husk and sugarcane bagasse ashes, considerable pozzolanic activity due to the presence of amorphous nano-silica, and could replace as high as 20 wt% of clinker in cement with the improvement of the performance of concrete. The different agricultural cementitious materials are summarized in Table 5.

The sustainability of agricultural-origin supplementary cementitious was analysed and reviewed in terms of SWOT analysis, life cycle assessment and circular economic model. SWOT analyses suggested opportunities for sustainability by reducing carbon footprints and the possibility of a circular economy. There are threats also due to techno-economic considerations and acceptance in the infrastructure industries. Life cycle assessment indicated the possibility of significant decarbonization of construction activities with durability by using the agricultural origin supplementary cementitious materials. However, there are bottlenecks, such as the techno-economic considerations and supply chain, in using agricultural-orign supplementary cementitious materials in Portland cement for sustainable construction activities.

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.

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