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Review Article

Review on advances in bio-based admixtures for concrete

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ABSTRACT

Bio-based admixtures (BBAs) are emerging as a promising class of additives for concrete, offering a more sustainable and environmentally friendly alternative to conventional chemical admixtures. Derived from various natural or biological sources, including plants, animals, and microorganisms, BBAs have shown potential in enhancing the performance characteristics of concrete in several key areas. This review article provides an in-depth exploration of BBAs, beginning with a detailed classification of the different types of BBAs based on their source material and production methods. It then delves into the various characterization techniques used to assess the properties and performance of BBAs, providing insights into their impact on the workability, strength, durability, and rheology of concrete. The article also discusses the diverse application areas of BBAs, highlighting their versatility and potential for wide-ranging use in the construction industry. It further identifies and discusses the challenges associated with the use of BBAs, such as issues related to compatibility with different types of cement and concrete, storage and shelf-life considerations, quality control and standardization concerns, and cost-effectiveness. In conclusion, the review emphasizes that while BBAs hold great promise as an alternative to conventional chemical admixtures for concrete, there is a need for more interdisciplinary collaboration and research to overcome the identified challenges and fully realize their potential. The paper calls for further studies focusing on optimizing the production and application processes of BBAs, as well as developing standardized testing and quality control procedures.

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1. INTRODUCTION

Currently, over 50% of the global population lives in urban areas, according to The World Bank [1]. The report estimates that by 2045, there will be 6 billion more people living in cities worldwide. This population growth demands for the basic services, infrastructure, and affordable housing. As a result, the construction sector will need to expand rapidly in order to meet the demand. On the other hand, environmental concerns are increasing as the population grows and the built environment expands. One sector with a significant adverse impact on the environment is the construction industry [2]. Environmental challenges such as global warming, natural resource depletion and ecosystem destruction which are caused by the construction industry, have put the construction sector under a spotlight [3]. Manufacturing of construction materials, transportation, on-site erection, use, maintenance, and demolition of the built structure at the end of its service life, in general from cradle to grave, the construction industry poses environmental repercussions.

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The main environmental effects of the construction of concrete structures are the carbon footprint of concrete and the massive consumption of natural resources. Out of the concrete-making materials, admixtures make up the smallest proportion when compared to the other ingredients (aggregates, cement, and water). However, these chemicals or minerals (admixtures) have a significant role in getting the desired fresh and hardened concrete properties. In addition, admixtures have an unwanted environmental impact that mainly arises from their production process and the feedstock materials that are used in the manufacturing processes. For instance, condensation products of formaldehyde such as naphthalene sulfonated formaldehyde condensates, sulfonated melamine formaldehyde polymers, and aminosulfonic acid series are used in the production of several conventional water-reducing admixtures [4]. Furthermore, it is known that these items produce formaldehyde, a chemical that is extremely hazardous to living things, into the environment. Additionally, because the raw materials used to make polycarboxylates, which are used to make water-retarding admixtures, are obtained from petroleum, there would be a potential shortage of these materials [4, 5]. Superplasticizers contribute between 0.4 and 10.4% of dthe total environmental effect of concrete, according to Sabbagh & Esmatloo [6].

Academic and industrial research on admixture is concentrating on creating novel, environmentally friendly, and biodegradable products that are made from renewable natural resources as environmental concerns increase. This review paper thoroughly summarizes and presents the state of knowledge concerning bio-admixtures which are based on natural or biological sources which are non-petrochemicals. Detailed systematic review was conducted on potential bio-admixture making materials, their production process, and application areas. Additionally, gaps that have not been covered in the literature are noted and suggested for additional research. This study also provides a brief overview of the chemical admixtures currently used in the building sector.

2. ADMIXTURES

Occurring naturally or in manufacture, admixtures can be defined as additives or chemicals that are often added when the concrete is mixed, with an aim to enhance specific properties of the concrete, either in plastic or hardened form, such as durability, workability, early or final strength [7]. They offer several benefits to concrete including increased workability, reduced water requirement, better durability, improved strength, volume changes and desired coloration, among others.

However, due to limitations in understanding their mechanism of interaction with concrete, admixtures are often utilized on trial-and-error basis. In this regard, studies have often focused on understanding the interaction between admixtures and the hydrating components of cement [8]. Out of this, it has been observed that the admixtures can occur freely in the concrete matrix as solids or solutions, achieve surface interactions or combine chemically with cement components or the cement paste itself. The consequence of the interaction is therefore the influence on the mechanical and physico-chemical properties of the concrete as durability, strength, setting time, microstructure, kinetics of hydration, water demand and products composition [9].

2.1. Classification of Admixtures

Admixtures are majorly classified into mineral and chemical. Mineral admixtures are also known as Secondary Cementitious Materials (SCMs). SCMs include, fly ash, limestone, shale, calcined clay, pozzolana and many others. These are often added in large amounts to the concrete with the aim to improve the workability conditions of fresh concrete; improve its resistance to sulfates attack, alkali-aggregate expansion and thermal cracking; and reducing the cement content in the mixture [10]. Chemical admixtures are often applied in very small amounts to improve the quality of concrete during transportation, mixing, curing or placement [11]. More specifically, they are tasked with air entraining, plasticizing concrete mixtures, reducing water requirements and in control of the setting time. Some special admixtures are designed to control shrinkage, inhibit alkali-silica reaction or corrosion [12]. According to ASTM C494 and AASHTO M194, chemical admixtures fall into 8 types according to their physical and general requirement; water reducing (Type A), retarding (Type B), accelerating (Type C), water reducing and retarding (Type D), water reducing and accelerating (Type E), water reducing, high range (Type F), water reducing, high range, and retarding admixture (Type G), and specific performance admixtures (Type S) [13].

In practical use, chemical admixtures will be incorporated often in the range of less than 1–2%, and rarely up to 5% against the weight of cement [10]. The normal water reducing or plasticizing admixtures are designed to increase workability of concrete while decreasing water content consistently up to 10%. Ready mix companies use this type of admixtures for performance optimization of normal concretes.

The sole purpose of retarding admixture is to slow down the hydration process of the cement, thereby preventing setting before placement and compaction. This is usually a necessary method in places characterized by hot climatic conditions, when extensive concrete pours are required. Retarding admixtures are known to cause a retardation effect on concrete by either of these ways: (i) through adsorption of the retarding compound on the surface of the particles of cement, thereby forming a protective skin that prevents further reaction, thus slowing down hydration, (ii) through the adsorption of the retarding compound onto the nuclei of calcium hydroxide, thereby poisoning their growth, (iii) forming complexes with calcium ions that exist in solution thus increasing their solubility and consequently discouraging formation of calcium hydroxide nuclei, or (iv) by precipitation around cement particles of insoluble derivatives of the retarding compounds formed by reaction with the highly alkaline aqueous solution, thereby forming a protective skin [14].

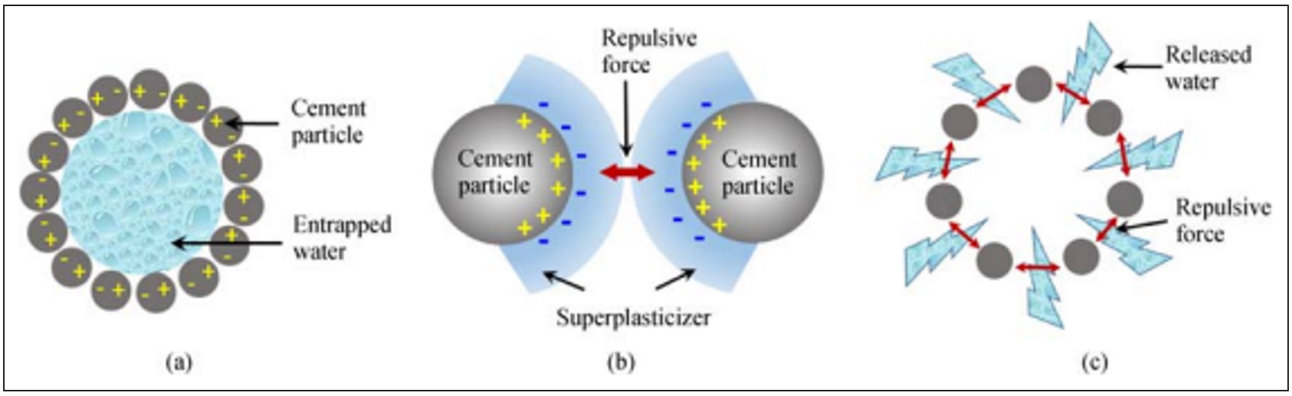

Figure 1. Effect of superplasticizer on cement particles [15]. **(a)** entrapment of water by cement particles, **(b)** repulsion of superplasticizer coated cement particles, **(c)** release of entrapped water.

High range water reducing superplasticizers are used when high water reduction with high workability is required, up to 30%, from about 12%. Such use cases include projects involving steel fiber reinforcement, precast and self-compacting concretes. When a superplasticizer is added to cement mortar, negative charges due to the superplasticizer cause dispersion of cement particles through repellence, thereby improving the flow characteristics [15]. This is illustrated in Figure 1. Previous X-ray Diffraction and Scanning Electron Microscopy analysis have shown that superplasticizers affect the crystallinity of the cement hydrates, instead of altering the types of hydration products [16].

Air entraining admixtures are used especially in frost prone areas to improve the concrete by introducing stable air bubbles of less than 0.3 mm in diameter in the concrete, that reduce scaling and cracking due to frost action. The advantage of this type of admixture is that beyond the aforementioned application, the entrapped air improves cohesion in concrete mix, which improves segregation and bleeding of water before rest. Common agents of air entraining admixtures include sulfonated compounds, polymers of polyethylene oxide, resins of natural wood and neutralized vinsol resins [11]. The mechanism of air entrainment is characterized by critical requirements for air development and stability is concrete; introduction of air, surface tension reduction at water/air interface, shell strength and elasticity at water/air interface, and development of matrix viscosity [17]. Mixing action introduces air into the concrete. Without the air entraining admixture, the volume of air in concrete ranges approximately 1–3% with voids greater than 0.5 mm. The admixture is necessary for fine air bubbles distributed evenly throughout the concrete. 0.5 seconds of exposure to a hydrating mixture of cement with air entraining admixtures, the bubbles will be covered in particulates, leading to formation of a shell characterized by sufficient strength and density as to withstand coalescence forces, rupture and gas exchange [18]. The bubbles will remain spread throughout the cement matrix if the paste has enough viscosity. According to Stoke's law, however, if the viscosity of the admixture is too low, air bubbles will escape from the paste as a result of the force of buoyancy [19].

Accelerating admixtures are aimed at increasing early hydration rate in the cement. These admixtures are often used in cold conditions, where they accelerate the early strength development or setting or the concrete. It has been noted that both inorganic and organic additives can quicken the hydration of Portland cements. The compounds can be conveniently separated into two categories: soluble inorganic salts and compounds, and soluble organic salts and compounds, with the first category being the larger [20]. Compounds from both classes are combined to create many commercial accelerators. Insoluble solid substances, such as silicate minerals, cementitious materials, and finely ground magnesium and calcium carbonates, have been employed as accelerators to a considerably lesser extent [21]. Soluble inorganic salts based on alkali or alkali earth metals as hydroxides, chlorides, nitrites and nitrates, carbonates, among others, are often employed in the accelerated setting of Portland cement. Both anion and cationic salts of alkali and alkali earth metals partake in the acceleration reaction on tri-calcium silicate (C_3A) hydration [21]. Calcium chloride for instance, is a known accelerator of the aluminate phases-gypsum system hydration. The Cl^- enhance ettringite formation until consumption of gypsum. If there is free C_3A remaining, calcium monochloroaluminate ($C_3A.CaCl_2.10H_2O$) is formed [22].

Water resisting admixtures, also referred to as waterproofing admixtures, expel, impede or block natural flow of water in hardened concrete capillaries. This is applicable and indispensable for structures below the water table for water retaining structures.

The classification of admixtures is summarized in Figure 2.

2.2. Base Materials for Admixture Production

There are multitude of admixtures which are classified based on benefit-orientated classification. Some of these admixtures are water-reducers, superplasticizers, Air-entrainers, and accelerators. A variety of chemicals are used for the production of those admixtures and the chemicals that are basis for the production are summarized in Table 1.

Lignosulphonates (LS) as water reducers are mostly applied in ready mix concrete. These chemicals are usually biproducts of bisulphite pulping of wood during the separa-

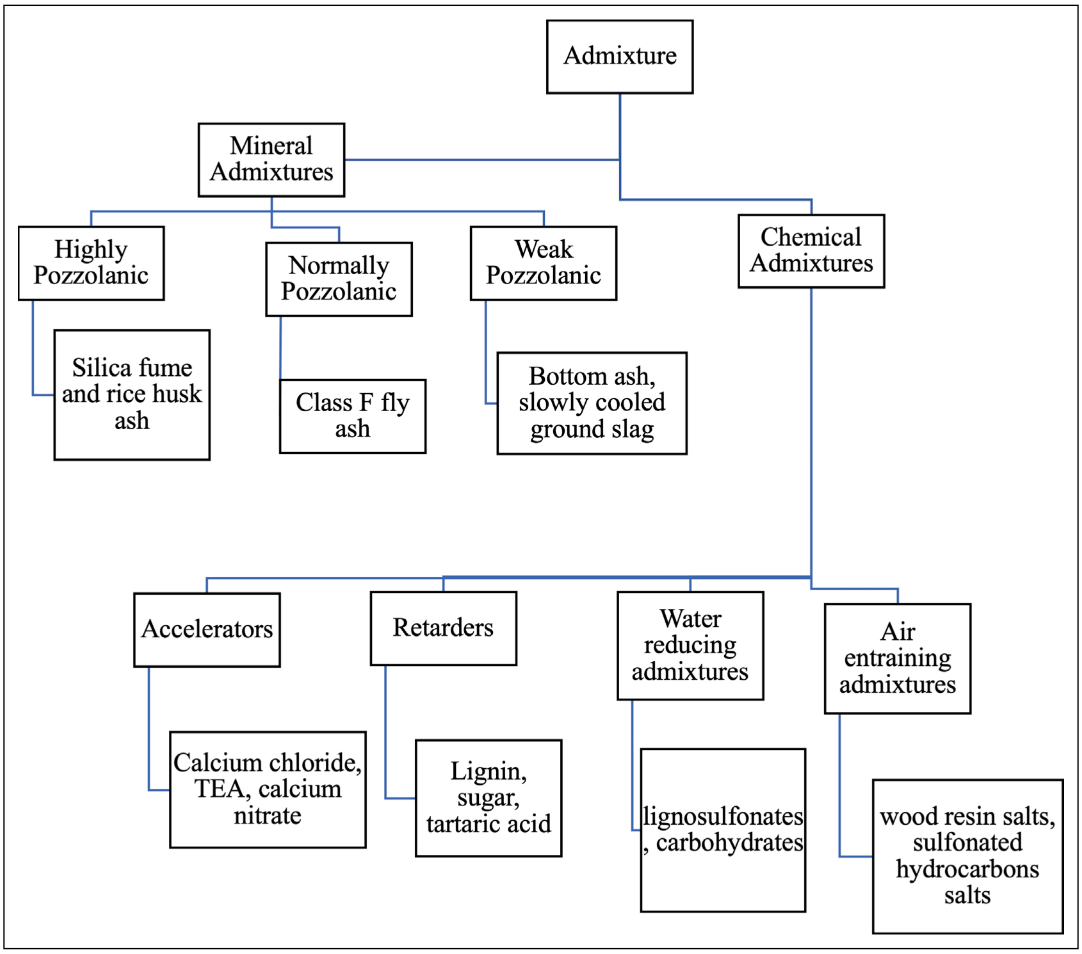

Figure 2. Classification of admixtures [7].

tion of lignin from cellulose fibres. Natively, lignin is insoluble in water, presenting a complex three-dimensional network of randomly crosslinked monolignos like conyferil, coumaryl and synapyl alcohols. Sulphate based delignification involves use of bisulphites and sulphites of magnesium, sodium, calcium or ammonium at elevated temperatures [24]. Hereby, low molecular weight lignin is achieved due to molecules fragmentation occurring over breaking of ester bonds. In addition to this, the sulphonic groups attached to the aliphatic chains are added, making the molecule water soluble. Through this, the LS is separated from the insoluble cellulose through filtration. However, for application to concrete, the lignosulphonate produced through this method needs further modification [25]. This is because about 25% of its total solid's composition is made up of sugars with strong concrete setting retardation. It therefore undergoes precipitation, which removes the sugars, then alkaline heat treatment, amine extraction or ultrafiltration as necessary. Despite their large application in ready mix concrete, LS show minimal water reduction capability of approximately 8–10%, at an average dose of 0.1–0.3% the weight of cement. It is due to this reason that LS is not applied in high-performance concrete [26]. Lignosulfonates are made up of various functional groups as carboxylic acids, phenolic hydroxyls, methoxyl, cathechol, sulphonicacids and various combinations of these, as shown in Figure 3. The dispersing effect of lignosulfonate on cementitious materials has been observed to be a function of its degree of adsorption on the surface of cement grains and hydrates. Thereby, the two main dispersing mechanisms are steric hindrance, and electrostatic repulsion, both portrayed by lignosulfonates [27]. During electrostatic repulsion, the LS, through its functional groups, renders the surface of the cement particle negatively charged. Such particles, on approaching each other, are repelled electrostatically, thus formation of agglomerates is prevented [28]. LS has also been observed to have an adsorption preference to aluminate and ferrite over silicate phases [28]. In a study by Danner [29], the authors discuss that the hydration of aluminate phases C_3A and C_4AF, and silicate phases, C_3S and C_2S, are observed to be retarded by Ca-lignosulfonate. This was observed to occur through retardation of the transformation of hexagonal C_2AH_{13} and $C4AH_{14}$ to the cubic hydrogarnet phase C_3AH_6 [29].

Monosaccharides are other components regarded as an important aspect in retardation, due to the effect of sugars stereochemistry on the ability of the chemical to complex with metal ions on solutions and surfaces on which such cations have an affinity. This complexation, although not a sufficient condition, is necessary for concrete retardation to occur. Thereby, to increase the complexation activity of aldehyde sugars, partially oxidizing them to carboxylic acids

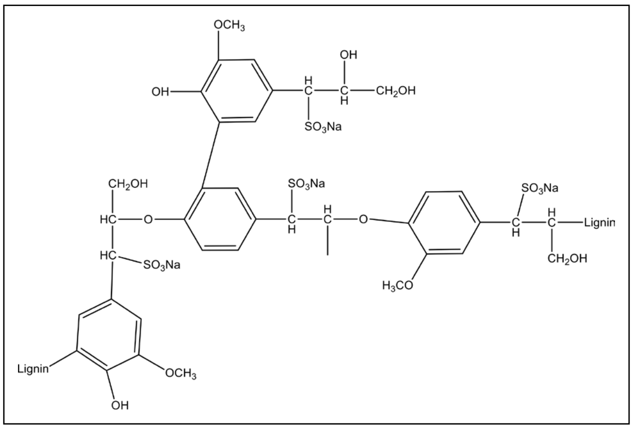

Figure 3. Chemical structure of lignosulfonate [24].

Table 1. Basis of chemical admixtures [23]

Type of admixture	Chemical materials forming the basis for the admixture
Water-reducing	Lignosulphonate
	Hydroxycarboxylic acid
	Hydroxylated polymers
Superplasticizers	Sulfonated naphthalene formaldehyde
	Sulfonated melamine formaldehyde
	Polyacrylates
Air-entraining	Neutralized wood resins
	Fatty-acid salts
	Alkyl-aryl sulfonates
	Alkyl sulfates
	Phenol ethoxylates
Accelerators	Calcium chloride
	Calcium formate
	Triethanolamine

can be done. This is usually a spontaneous reaction, which can be slow, but the alkaline nature of cementitious systems has been seen to catalyze the process. This leads to many different degradation products, that carry carboxylate function. A glucosidic bond between two monosaccharides can influence redox reactivity of sugars, and their reactivity in alkaline conditions as those in cementitious products [24].

Polysaccharides are often utilized as viscosity-modifying admixtures (VMA) in concrete. Through microbial fermentation, high molecular weight welan and diutan polysaccharides (Fig. 4) are produced, for use as VMAs [30]. With a molecular weight of about 10^6 g/mol, welan gum is made of tetrasaccharide backbone chain made up of L-rhamnose, L-mannos, D-glucurinic acid and D-glucose. The backbone of welan gum hosts side chains with either L-mannose or L-rhumnose single units substituting third carbon of every 1, 4 linked glucose. Diutan only differs from welan gum with two units of L-rhamnose and a higher

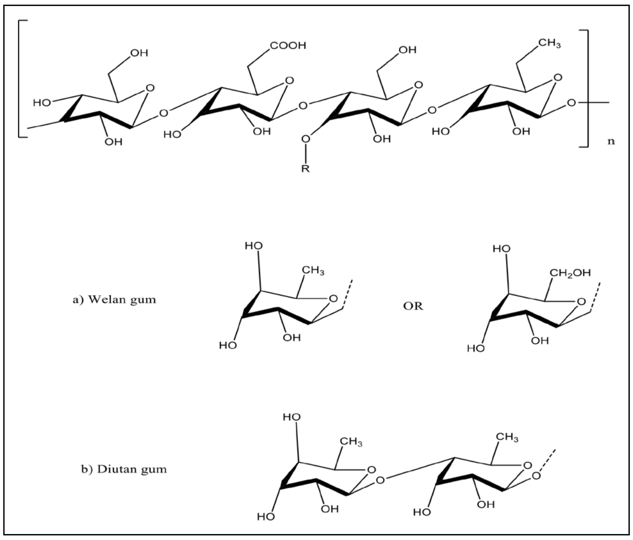

Figure 4. Structure of welan and diutan gum polysaccharides.

molecular weight of 3–5 x 10^6 g/mol. These gums are seen to have high stability even under elevated temperatures and pH up to 11 [31]. When used in cement, they adopt double helical conformation, whereby side chains screen the backbone thus preventing cross-linking of the carboxylate groups on the backbone by calcium ions in concrete. Therefore, high Ca^{2+} concentrations do not destabilize them, making them the ideal VMAs [32].

3. BIO-BASED ADMIXTURES

In general biomaterials are defined as processed or engineered products that are used in different application areas and obtained partially or fully from renewable biobased resources [33]. Bio-admixtures, in that sense, are admixtures that are derived from renewable biobased resources. Others define bio-admixtures as molecules that contain natural or modified biopolymers and biotechnological and biodegradable products [31]. Plank [34] defines bio admixtures as a functional molecule used in building products to optimize material properties.

3.1. Bio-Based Sources for Bio-Admixture

Natural polymers such as lignosulfonate, starch, chitosan, and protein hydrolysates can be found in bio-admixtures that are used for concrete application. For different reasons, bacteria or fungi can also be used in combination with those natural polymers [35]. From this, it can be inferred that bio-admixture can be sourced from plants, animals or microorganisms.

Several plant and plant derivatives have been used as a bio-admixture. Even in the ancient times, during the Roman Empire, vegetable fat used to be added in lime mortar [35]. Many studies have been done recently on the usage of various plant kinds and plant derivatives as admixtures in concrete. Some of the plants/plant derivatives which have been investigated for their pertinence for concrete application are:- Acacia Karro gum [36], starch from cassava and maize [37], arrowroot [5], corn [4], molasses from sugar

Table 2. Microbial-based admixtures and their production process [60]

Admixture	Biotechnological process	Function/application	Application	Dosage	References
Sodium gluconate	Biooxidation of glucose by bacteria Gluconobacter oxydans, filamentous fungi Aspergillus niger, or yeastlike fungi Aureobasidium pullulans	Superplasticizer, retarder, corrosion inhibitor, water reducer	Gypsum plaster, mortars, grouts, concrete mix	0.1–04%	[34, 61]
Xanthan gum	Biosynthesis by bacteria Xanthmonas campestris	Thickener, retarder in self-consolidating concrete	Paints, floor screeds	0.2–0.5%	[62]
Welan gum	Biosynthesis by bacteria Alcaligenes sp.	Thickener, retarder in self-consolidating concrete	Paints, floor screeds	0.1–0.5%	[63, 64]
Scleroglucan	Biosynthesis by fungi from genera Sclerotium, Corticium, Sclerotinia, Stromatinia	Thermostable viscosifier	Paints, floor screeds	0.2–0.5%	[63]
Succinoglycan	Biosynthesis by bacteria Alcaligenes sp.	High-shear thinning, temperature induced viscosity breakback	Soil stabilization	1–15 g/L of water	[63]
Curdlan gum	Biosynthesis by bacteria from genera Agrobacterium or Alcaligenes	Set retarder, viscosifier	Self-consolidating concrete	Up to 10 g/L of water	[32, 65]
Polyaspartic acid	Chemical synthesis	Dispersant, corrosion inhibitor, air-entraining agent	Set retarder in gypsum	–	[60]
Dextran	Biosynthesis by lactic acid bacteria	Rheology modifier	Portland cement, grouts (self-leveling)	–	
Pullulan	Biosynthesis by yeastlike fungi Aureobasidium pullulans	Viscosifier, set retarder	Self-consolidating concrete	–	
Sewage sludge	Waste biomass of municipal wastewater treatment plants	Viscosifier, set retarder	Sintered light-weight aggregate for nonstructural concrete	1:1–1:3 ratio of clay to sewage sludge ratio	[66]
Bacterial cell walls	Aerobic cultivation of bacteria	Microstructural filler	Concrete production	0.03–3.3%	[60]

production [38], aqueous extract from okra [39], grape and mulberry extracts [40], gram-flour and triphala [41], gum of triumfetta pendrata [42], guar gum [43], palm liquor [44], seaweed [45], Black tea extract [46], cypress tree extract [47], pine tree bark extract [48], vegetable cooking oil [49–52].

Animal products have been utilized for a very long time as an admixture in the construction of buildings and other structures, much as plants and their derivatives. For instance, the Romans used dried blood as an air-entraining agent and biopolymers such as proteins as set retarders for gypsum [53]. Similarly, the Chinese have used egg white, fish oil, and blood-based mortars when constructing the Great Wall [35]. Recent studies have looked at concretes that feature natural admixtures made from animal products. Such animal products include: ghee [41], broiler hen egg [54] and animal protein [55].

Microorganisms can improve the properties of concrete [56]. The addition of microbial biopolymers to concrete and dry-mix mortars is one of their main uses in the building sector. The examples of microbial admixtures that are used in concrete are protein hydrolysates and welan gum; and in case of dry-mix mortar these admixtures are succinoglycan and xanthan gum [57]. In addition, sodium gluconate, xanthan gum, curdlan, or gellan gum are also such kind of admixtures [35]. The other is, a consortium of certain species of beneficial microorganisms which are known as effective microorganisms (EM). These include lactic acid bacteria (LAB), yeast, photosynthetic bacteria (PSB), and Actinomyces which are more effective than only one type of microorganism because their coexistence allows their metabolites to be used as food, hence extending their life span [56].

4. BIO-ADMIXTURE PRODUCTION PROCESS

4.1. Plant-Based Admixture Production

With the use of portable water, plant parts are properly cleansed of dust and other contaminants. To obtain a gel, the stem or leaves are filleted. Other chemical extracts are obtained from dissolving pulverized powder such as gum in water and filtered to obtain liquid extracts such as aloe vera gel.

Mbugua et al. [36] produced a bio-admixture from Acacia Karroo Gum by collecting the tears (exudates) from the tree bark and dried it at room temperature. Following the removal of bark bits and other foreign objects, the cleaned ooze was crushed, sieved through a 200 µm sieve, and then stored in a cold, dry area until it was needed. On the other hand, Schmidt et al. [42] prepared bio-admixtures from acacia gums and gum of the *triumfetta pendrata* A. Rich. The gums were initially dissolved in tap water at room temperatures, then the solution was filtered to separate the coarse impurities, and finally, the filtrate was dried and ground. The same researchers have also prepared cassava starch-based admixture by dissolving the cassava starch in a tap water at a temperature of 70 °C. Then the residue of coarse particles was sieved off, and the remainder was dried and ground to obtain the admixture [42].

Another study utilized four litters of water to boil one kilogram of cypress bark, which was chopped into tiny pieces and heated under pressure for two hours. Another investigation involved boiling a kilogram of cypress bark, which was broken up into tiny pieces, for two hours while under pressure. After 24 hours it was shaken vigorously for 5 minutes and the admixture was collected [58]. Similar to this, in a study on a bio-admixture composed of okra extract, the seed and pod of the okra were broken up into small pieces and added to tap water in a predetermined ratio (weight of okra to volume of water), then swirled for five minutes, and left undisturbed for an hour. The viscous extract was then filtered using a 300 µm sieve. The okra bits were further crushed by hand for more extraction before being passed through a 150 µm sieve. The extracted material was subsequently used within a day of storage [39].

Water hyacinth plant extract was made by Okwadha & Makomele [51] after they harvested and cleaned the plant under flowing water. Once the muddy debris and impurities had been removed, it was spread out on a clean, absorbent piece of cloth and dried in the shade. The dry plant was then finely cut into small pieces of about 5 mm, and then ground into fine powder. Followed by a moistening of 500 g of the powder with a liter of tap water, and soaked in 30 ml of ethanol for 24 hr. Then the filtered extract was stored for use.

In relation to the preparation of starches used in construction materials Schmidt et al. [59] suggested that the starch needs to be cold water soluble. And when it is used in cementitious materials where the pH environment is high, the starches have to be stabilized by ether or ester bond in the hydroxyl groups. As the stabilization typically reduce the tendency for retrogradation and to minimize intermolecular interactions.

4.2. Microbial-Based Admixture Production

Microbial based admixtures can be made by using bacteria or fungi, by employing biotechnological processes. These types of admixtures are getting attention because of their high biosynthesis rate as compared to plant-based products. And these admixtures can be produced in biotechnological factories, in industrial level [57]. Some of the microbial-based admixtures with their production processes are summarized in Table 2.

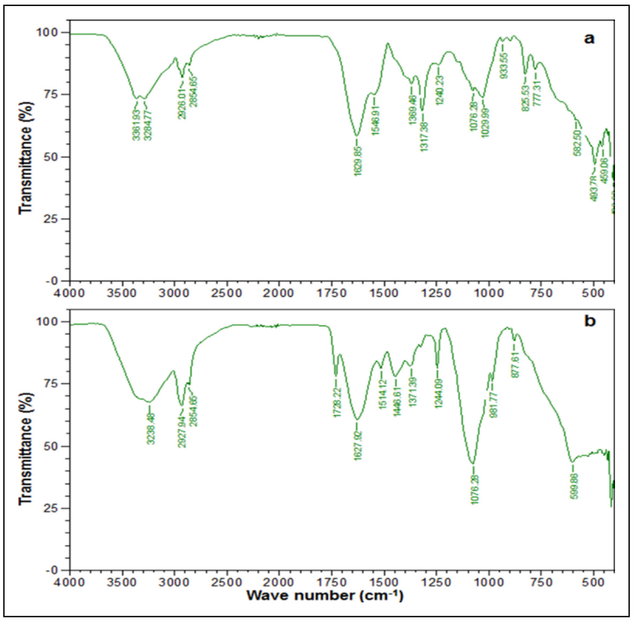

Figure 5. FTIR studies of: **(a)** Spincea oleracea and **(b)** Calatropis gigantea [69].

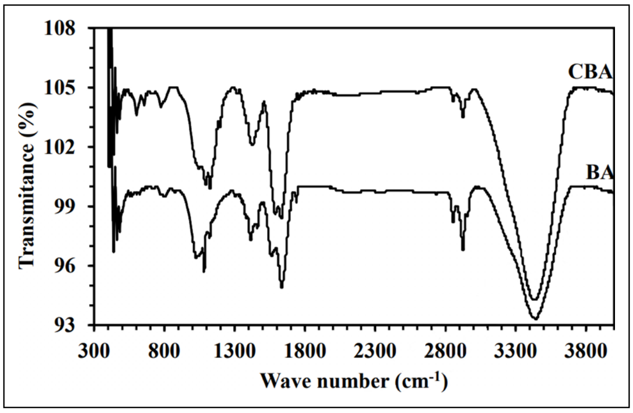

Figure 6. FTIR Spectra of aqueous bio-admixture (BA) and cement treated bio-admixture (CBA) [39].

5. CHARACTERIZATION OF BIO-ADMIXTURES

Chemical and ionic composition, type of organic functional groups, structure of the polymer and distribution of molecular weight of different polymers affect the behavior of admixtures. These property-defining parameters can be examined using different techniques or methods of characterizations [67]. Some of the methods are; Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Fourier transform Raman spectroscopy (FT-Raman), ionic chromatography, ultraviolet-visible spectroscopy (UV-VIS), nuclear magnetic resonance spectroscopy (H-RMN and C-RMN), gel permeation chromatography (GPC) [40, 67].

5.1. Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR was used to characterize a starch-based chemical admixture used to reduce heat of hydration. The spectra analysis mainly showed the presence of is starch-based –OH hydrophilic, functional group [68]. Malathy et al. [69], have conducted FTIR on a dried plant extracts produced from

Table 3. Summary of FTIR studies in bio-admixture characterization

Admixture	Active chemical	Property	Application	Dosage	FTIR observations	References
Aqueous okra extract	Acidic hetero polysaccharide (pectin)	Viscosity enhancement	White cement paste	15 ml of 10% cement paste blended with 100 ml plant extract	Broad bands in 1500–1700 cm^{-1} and two absorption minimums near 1634 cm^{-1} and 1565 cm^{-1} suggested presence of pectin and proteins as major chemical constituents in admixture 1640–1660 cm^{-1} – amide I present in protein of plant extract. 1550 cm^{-1} – amide II due to protein.	[39]
Egg albumen	Protein (hydrophilic and hydrophobic aminoacids)	Improve workability	Natural hydraulic lime mortar	0.1–0.3% by weight of water	3293 cm^{-1} – OH stretch due to proteins, illustrating the hydrophilic character of egg albumen, thus could generate more bond moisture 1031 cm^{-1} – carboxyl groups corresponding to cell wall pectin	[71]
Natural sugars (molasses/ palm jaggery/ honey) and Terminalia chebula	Polysaccharides	Rheology alteration and retarding	Fly ash and ground granulated blast furnace slag-based mortars	0.8% by weight of aluminosilicate materials.	881 cm^{-1} – presence of beta-glucosidic linkages between monosaccharides. 1390 (R-NH_2), 1270 (–C–O–H bending) and 1120 (Ph–NH_2) due to chebulagic acid, chebulinic acid and hydrolyzable tannoids in terminalia chebula.	[72]
Spinacea oleracea and Calatropis gigantea plant extracts	Polyphenols	Self-curing agent (water retention)	Fly ash-based concrete	0.6% (S. oleracea) and 0.24% (C. gigantea) by binder weight	3435.12 cm^{-1} - –OH stretch vibrations due to adsorbed water molecules. 875.63 (C–O bending) and 1421 (C–O stretching) attributed to CO_3^{2-}	[69]

Spincea oleracea (*S. oleracea*) and *Calatropis gigantea* (*S. oleracea*), to test the existence of hydroxyl (–OH) and ether (–O–) functional groups in a bio admixture used as internal curing agent The peaks as observed are illustrated in Figure 5.

According to Figure 5, the peaks observed at wavenumbers 3361.93 and 3284.71 cm^{-1} confirmed the presence of -OH groups as in the *S. Oleracea* and 3238.48 cm^{-1} as in *C. Gigantea*. This feature indicated the water retention capability of the plant extract and thus qualified them as concrete bioadmixtures.

Hazarika et al. [39], prepared the test sample of okra aqueous extract which is treated (CBA) and untreated (BA) with filtrate of cement water suspension. The FTIR spectra, as observed, are shown in Figure 6.

The results of the FTIR spectrum indicated the chemical composition of bio-admixtures. Some of the functional groups that were found from the observation are O-H, CH_2, C=O groups. According to Silverstein et al. [70], the presence of these functional groups is an indication for the presence of galactose, rhamnose and galacturonic acid of pectin. In the study, it was also observed that some peaks shifted to higher frequency, while others increased in intensity, when the bio-admixture was applied to cement matrix. This indicates that FTIR technique, in addition to fingerprinting the chemical composition of the bio-admixture, can also give an insight on the interaction of the admixture and the cement phases.

Abd El-Rehim et al. [4], performed FTIR to confirm the starch modification by chlorosulfonic acid and interpret the structure of sulfonated starch which was proposed to be used as water-retarding agent in cement industry. Other studies whereby FTIR has been applied in bio-admixture characterization are summarized in Table 3.

5.2. X-ray Diffraction (XRD)

X-ray powder diffraction (XRD) is a technique widely used in material science to investigate crystalline materials in finely divided or powder form, it can also be applied to non-crystalline solids. On the contrary, studies have shown that structural information about liquid crystalline phases can be obtained from XRD. Qualitative or quantitative analysis can be used to characterize the material properties. Each crystalline phase is individually characterized by the specific distribution and intensity of diffraction peaks, which is similar to a fingerprint. On this basis, qualitative analysis is founded. On the other hand, because the diffraction intensities are directly related to crystal structure and the amounts of each phase, quantitative analysis, which is the determination of the amounts of more than one phase in a mixture, is possible.

Table 4. Summary of XRD characterization

Admixture	Type/feature	Application	Dosage	XRD observations	References
Cactus (Opuntia ficus indica) mucilage	Water repellent	Hydraulic lime mortar + sand mixture	25–100% of lime-sand mixture	High intensity peaks of CH in hydraulic lime, decreasing in reference mortar to medium intensity and trace amounts in cactus-based mortar. Medium intensity peaks peaks of CSH and geh Medium intensity peaks peaks of CSH and gehlenite identified in both reference and cactus modified mortars indicating hydraulic nature of lime used.	[73]
Bilwa (Aegle marmelos) fruit extract	Water retention and air entraining agent	Hydraulic lime mortar	1–3% by weight of water	Portlandite peaks were observed at higher intensity, along with moderate brucite and calcite peaks	[74]
Cactus extract	Water retention	OPC 53 grade cement-based concrete	2–10% by weight of water	Portlandite was observed to reduce in cactus modified samples indicating early consumption of portlandite to form CSH phases Higher intense peaks of C_2S and C_3S phases were observed in 10% cactus concrete compared to reference, which supported observed enhanced mechanical properties	[75]
Black tea extract	Dispersant/ workability enhancement	Metakaolin blended cement mortar	0.5–2% by weight of water.	Content of CH Content of CH significantly higher when black tea extract is used, indicating potential facilitation of hydration of cement in production pf CH, suppression of pozzolanic reaction of metakaolin thus consume less CH at 7 days curing	[46]

Using XRD Mahmood et al. [40] directly examined grape and mulberry extracts which were used as natural admixtures. Others have studied cement paste, mortar or concrete that contain a variety of bio admixtures to infer the effects of a given bio-admixture on mineralogy of the mix. This implicitly gives some idea about the characteristics of the admixture. Table 4 summarizes some studies that used XRD in characterization of bio-admixtures.

5.3. Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) is the response of atomic nuclei to magnetic fields. Many nuclei have a magnetic moment and behave like a spinning bar magnet. These spinning magnetic nuclei can interact with external magnetic fields, producing a detectable signal [50].

Although the most common application of NMR is the structural determination of molecules, the technique has the advantage of direct mixture analysis, and thus, NMR has demonstrated a unique potential to be used for metabolic mixture analysis. This technique has also been used for easy and quick recognition of microorganisms, antimicrobial susceptibility tests, and other applications [76]. NMR can also be utilized to study the degree of hydration, the reactivity of pozzolanic materials, clinker composition, interaction of organic admixtures with cement minerals, the different states of water in concrete, among others [77].

Mota et al. [78], have used ^1H NMR to study the impact of sodium gluconate on white cement-slag systems with Na_2SO_4. The authors stated that ^1H NMR is highly advantageous to analyses the distribution of water in the sample among the different pore sizes. A summary of studies that characterized admixtures with NMR is given in Table 5.

5.4. Gas Chromatography–Mass Spectrometry (GC-MS)

When gas chromatograph (GC) and mass spectrometer (MS) are combined into one GC-MS system, the resulting capabilities of the system are not simply the sum of the two instruments however it increases the analytical capabilities exponentially [83]. One of the common applications of GC-MS is for identification of key small molecules such as fatty acids, amino acids, and organic acids in biofluids [84]. For instance, Okwadha & Makomele, [51] conducted GC-MS to identify the components of water hyacinth extract. From the analysis, minute fragments of dissolved lignocelluloses, fatty acid groups, alcohols, aldehydes, and ketones were observed. Similarly, Sathya et al. [52], examined water hyacinth using GC-MS, and reported similar findings as saturated and unsaturated fatty acids, in addition to lignocellulose, which had the admixture classified as a retardant. More studies are summarized in Table 6.

5.5. Rheology

The study on how concrete paste or slurry deform or behave under a given water/powder ratio is rheology. The study of rheology is known as rheometry. Many fluids depict simplest form of linear deformation referred as Newtonian flow [88]. However, complex fluids such as mortar and concrete show plastic behavior explained by Bingham model [89]. In the Bingham model, flow initiates on some level of stress (yield stress) following a linear relationship of stress and strain [90]. Concrete as a material demonstrates yield stress properties to obtain a specific level of viscosity. Although, flow depends on other factors such as concentrations, temperature and many more. The concrete or mortar parameters like workability include mobility, stability and compatibility [88]. The fresh concrete workability

Table 5. Summary of NMR characterization in bio admixture studies

Admixture	Dosage	Application	Analysis conditions	NMR observations	References
Latex admixture	0.1–0.5%	Tile mortar	^{13}C, ^{27}Al and ^{29}Si NMR spectra were acquired at Magnetic field of 7.05 and 11.74 T, Spinning speeds of 8 kHz and Temperatures of 233 – 243 K	Only minor differences in ^{13}C spectra at slightly heightened admixture concentrations before and after 14 days of hydration. After hardening, signal ratios of CHO and CH_2 to the CO and CH_3 groups were observed to change, indicating polymer decomposition due to partial hydrolysis.	[79]
Chitosan based admixture	5–20% the weight of water	OPC mortar	^{1}H NMR spectroscopy	Approximately 27% and 7% of the total amino groups were transformed into amides attached with 3,4 – dihydroxyhydrocinnamic acid groups	[80]
Basalt fiber	1.3% of the cementitious material	Recycled aggregate concrete	Porosity was measured with NMR of magnetic field of 0.3 T, resonance frequency of 50–60 Hz and coil diameter of 60 mm	It was observed that internal pores of the specimens were mainly micropores.	[81]
Organic corrosion inhibitors (OCI) (easter-, alcoholamine-, and carboxylic acid- based)		OCI-modified concrete		OCIs used were observed not to affect the hydration product species. Easter-based OCIs significantly decreased the proportion of larger pores, thereby enhanced compressive and reduced capillary absorption rate. Concrete frost resistance was observed to improve on addition of alcoholamine-, and carboxylic acid based OCIs.	

Table 6. Summary of researches utilizing GC-MS in admixture characterization

Admixture	Active chemical	Property	Application	Dosage	GC-MS cbservations	References
Olive oil and milk	Fatty acids	Hydrophobic admixture	Standard CEM I mix	–	The total fatty acid value measured was appreciably higher for the olive oil, due to the significantly lower fatty acid content of milk.	[85]
Kadukkai (Terminalia chebula) and jaggery	Fatty acids	Antimicrobial activity	Air Lime mortar	1–5% the weight of water	Peaks of 2-piperidinone (antimicrobial quality), ethybenzene (formation of styrene), and cyclobutenes(antioxidant) were observed.	[86]
Water hyacinth (Eichornia crassipes) extract	Lignin	Water reduction	Portland cement concrete	0.25–0.75% hyacinth extract the weight of concrete	Lignocellulose, saturated and unsaturated fatty acids were observed in the extracts, which were concluded to play a role in the improvement of cement workability.	[87]
Water hyacinth (Eichornia crassipes) extract	Fatty acids and lignin	Retarder	Self-compacting concrete	0–25% partial replacement to commercial superplasticizer	Concentrations of octanoic acid, hexadecenoic acid, heptane, phycol, 1-ethyl-2-pyrrolidinone, among other compounds were observed in GC-MS peaks	[51]

is measured by flowing ability, passing ability, segregation and bleeding resistance and viscosity [91]. Special concrete rheology is evaluated through slump tests ranging from Abram's cone slump test, slump table flow test, V-funnel, U-box test, J-ring test and L-box test [92]. Introducing bio-admixtures into fresh mixes interfere with thixotropy and viscoelasticity of the slurry particles with the aim of improving pumpability and shooting flow [93].

Table 7. Water Hyacinth utilization as a bio-admixture

Mix design	Bio-admix/ superplasticizer replacement%	Rheology	Mechanical properties	Micro-structure analysis	References
A mix of 1:2:4 (Class M15) with water/ cement ratio 0.45 under OPC	The water hyacinth was replaced at 0%, 10%, 15%, 20% and 25% by volume of commercial admixture, Auramix 40	The increase in the percentage of Water Hyacinth increased workability. WH extract retained SCC slump flow of 2–5 seconds and a diameter of 500–700 mm on T_{500} slump flow test	The compressive strength was checked on the 7th, 14th and 28th days. At 20% of WH, the highest compressive strength on the 28th day.	On the 7th day, there was an optimum 2.8% water absorption rate with 25% WH extract dosage. On the 28th day, the water absorption rate significantly increased to 6.3%	[51]
A mix of 1:2:4 (M class M15)	The water hyacinth was replaced at 0%, 0.5% and 1%.	The addition of 0.5% WH decreased the initial setting time to 172.2 from 187.2 minutes. However, the final time increased from 255 minutes to 270 minutes. Further addition of WH to 1% reduced both the initial and final setting times significantly. The results recommended for further percentage increase to ascertain the yielding point of WH as an admixture	Compared with the standard concrete increasing WH from 0.5% to 1% increased the compressive strength from 21.4 to 21.7 on the 28th day.	–	[99]
A design of 1:1.78:2.77 (cement: sand: coarse aggregate) and Water/ cement ratio of 0.45	A powder form of WH on percentage replacement was done at 1%, 2%, 5% and 10% on cement. Solution form of WH was done at 0.25%, 0.5%, 0.75% and 1% on cement	Increasing the WH extract in percentage dosing, increase workability. This was attributed to fragments of lignocellulose dissolved in the extract. On the 7th day cubes with 5% and 10%, WH had not set. Similarly, they noted that WH solution retained slump flow and recommended it for a superplasticizer.	The compressive strength increases from 0 to 0.25% but further dosing was reduced and was assimilated to the uneven fineness of WH powder and cement.	–	[98]
Normal concrete	0%, 0.5%, 1%, 1.5% & 2% by mass of aggregate	–	Compressive strength (IS 516-1959) and Tensile strength	Water absorption	[101]
Mortar at 1:3	0.38 w/c at 0%, 10, 15 and 20% mass replacement of cement	Increased workability with retard effect	Increased compressive strength with% increase of WH	Decreased water absoption with% increase	[52]

5.6. Mechanical Properties

Special concrete (SP) is a modern concrete for wide applications in the laboratory and practical world. Selecting SP components and ratios depends on the physical and mechanical properties required in the project [94]. The mechanical characteristics include compressive strength, split tensile strength, flexural strength and modulus of elasticity [95]. There are many types of biological agents used to retard, accelerate, or remove air in mortar and/or concrete improving workability, curing and hardened properties [52]. The study on mechanical properties of bio-concrete enhances awareness on optimal use of available biological agents for sustainable concrete production.

5.7. Microstructure Analysis

Concrete is categorized into three heterogeneous components, cement paste, pore structure and interfacial transition zone that enhance mechanical strength and durability [96]. Microstructure study seeks to interpret the behavior of concrete in exposure conditions during the serviceability period [97]. Introducing bio-admixtures to fresh mix of concrete and mortars enhance packing ability. The hardened property of the enhanced mortar can be porous of impervious to chemical and water ingression (SLO). Microstructure study establishes the behavior of bio-concrete when exposed to various environmental aspects. This is discussed further in the section of Bio-Admixtures.

6. BIO-ADMIXTURES

6.1. Plant-Based Bio-Admixtures (Pb2A)

6.1.1. Water Hyacinth

Water hyacinth (WH) is an aquatic plant classified under weeds from its high regenerative rate of 2 tons per acre [51]. Its scientific name is *Eichhornia crassipes*. The weed is highly invasive, which makes it difficult for aquatic species to survive. Physical extraction is the only method to physically stop its spread [98]. Utilizing the weed for additional purposes, such as the manufacturing of concrete, aids in sustainable waste management as shown in Table 7. The utilization of water hyacinth in concrete is attractive in relation to its composition. The use of the plant's extracts as a concrete retarder has been made possible by the presence of cellulose, saturated fatty acids, and unsaturated fatty acids, according to Gas Chromatography analysis [51]. According to a second study using biomass from pulverized water hyacinths, the effect on concrete varied depending on the replacement ratio of the additive, with 0.5 percent replacement causing an acceleration effect and 1 percent replacement causing a retardation effect [99]. According to a different study, water hyacinth liquid extract, which according to Gas Chromatography analysis was found to include lignin, improved water reduction in the concrete created [100].

6.1.2. Gum Arabic

Gum Arabic is a yellow exudate from acacia trees, such as Acacia Senegal, also known as chaar gund, acacia gum, or meska [102]. The discharge is produced by a wounded bark. Water can dissolve the gum [103]. It is composed of polysaccharides and glycoproteins with adhesive or binder characteristics [104]. Some applications of Gum Arabic are discussed in Table 8.

6.1.3. Starch

Starch is a natural biopolymer classified as a homo-polysaccharide. It forms a basic unit of glucose constituting amylopectin and amylose, given in Figure 7 [111]. Starch is hydrolyzed in presence of water components that delay the hydration process in cement. The formation of nanocrystals is influenced by the presence of amylopectin [112]. Starch applications in enhancing concrete properties are discussed in Table 9.

6.1.4. Aloe Vera Gel

Aloe vera plant is a tropical climate plant believed to originate from the Arabian Peninsula. It grows to a height of between 60–100 cm [119]. The plant is collected from the field, thoroughly cleaned under moving water. The green layer is peeled off and the white part grained to a gel. The chemical constituents of aloe vera gel are given in Figure 8. The gel is added to concrete during fresh mixing at the percentage weight of cement. In concrete, the major application of aloe vera gel is to act as a plasticizer, since it contains above 95% water content [120]. Studies based on aloe vera utilization are summarized in Table 10.

6.2. Microbial Based Bio-Admixtures

The effects of three microbial based bio-admixtures are summarized in Table 7. These are Sodium gluconate (SG), Welan gum (WG) and Xanthan gum (XG). SG, given in Figure 9, is a crystalline powder that can be produced under properly controlled conditions [124]. And it is one kind of typical hydroxycarboxylic acid salt [125].

Both WG and XG, given previously in Figure 4, are industrially produced microbial polysaccharides [60]. Xanthan gum (XG) is obtained by aerobic fermentation by Xanthmonas campestris [126]. Whereas WG is high molecular microbial polysaccharides produced by the fermentation of Alcaligenes species [68]. Further studies are summarized in Table 11.

7. APPLICATIONS OF BIO-BASED ADMIXTURES

Chemical admixtures have a plethora of applications in the construction sector. Similarly, bio-admixtures are expected to have such a broad application with even more sustainable manner. However, there are limited number of researches which examine the applicability of bio-based admixtures in different types of concretes. The two types of concretes which were found in literatures and use bio-admixtures are self-compacting (SCC) and self-healing concrete (SHC). SCC is a special type of concrete obtained by adding plasticizers and superplasticizers to the normal concrete. SCC flows under its self-weight to fill congested reinforcement in sophisticated formwork. Scholars and interested companies have carried research on alternative organic admixtures for producing SCC [51]. have used water hyacinth extract as a bio-admixture and improve the rheological property of SCC. And Xanthan Gum was used by [126].

The other is self-healing concrete, a type of concrete which has the ability to repair its cracks automatically. Among the various methods of self-healing, biological self-healing is the most common one. Biological self-healing works by adding bacteria to the concrete. In self-healing concrete, bacteria are used along with calcium nutrients known as calcium lactate. This product is added in the concrete mix in wet condition. The bacteria that are introduced in the concrete can be in inactive stages for up to 200 years and become active as soon as it comes in contact with water seeping through the cracks in concrete. Then germination of bacterial spores will be initiated, which feeds on the calcium lactate consuming oxygen. This process transforms the soluble calcium lactate into insoluble limestone. When this limestone gets hardened, the crack is being filled up [131].

Different microbials are used to produce self-healing concrete. Provided that appropriate conditions, sufficient nutrients and a calcium source are available, several strains of bacteria can induce the precipitation of calcium carbonate. And this precipitation has been known for its ability to improve the mechanical properties and durability of construction materials. In this regard, encapsulated bacterial spores have shown the ability to self-heal cracks in concrete. These days self-healing concrete based on mi-

Table 8. Gum Arabic studies on producing bioconcrete

Mix design	Bio-admix/ superplasticizer replacement%	Rheology	Mechanical properties	Micro-structure analysis	References
SCC mix design according to EFNARC guidelines at 2% air content and water-powder ratio (w-p) from 0.65–0.8	GA at 2%, 4%, 6%, 8% 10% and 12%	The spread flow ranges from 660-750 mm falling under the SF2 flow class. Spread flow increased with an increase in dosage where the optimum spread flow at 1.8% wt% of 680 mm. At 1.1 w-p, spread-flow reduce due to an increase in yield stress. The lowest yield stress 2%	–	–	[105]
The control mix design had a water/ cement ratio of a controls 0.5 and 0.45 of SCC. under Dangote OPC cement	Gum Arabic as a superplasticizer	In dosing of Gum Arabic, the initial time increased from 1.8 hours to 5.3 hours while the final setting time increased from 3.6 hours to 8.36 hours for control and SCC respectively.	The compressive strength increased over the age from 7 days to 90 days. At the 28-day normal concrete obtained higher compressive strength but SCC gradually gained strength to the 90 days and obtained a higher value of 32.34 N/mm^2	–	[104]
		The slump retention for the control was 25 mm. The flowability of SCC confirmed to Class 1 at 582 mm. the L-box achieved 7.2 seconds,			
		Viscosity through V-funnel was recorded as 5.48 sec which is less than 8 seconds.			
SCC design mix as per the European Guidelines for Self-Compacting Concrete (EFNARC) in the provision of BS-EN 12350-1 and BS-EN 12350-2.	0.9% and 1.5%	SCC1 records a slump flow of 560 mm thus Class SF_1. The V-funnel is 8 sec adequate for SCC. L-box, U-box and Fill-box have low values hence low passing ability but no segregation.	–	–	[106]
–	–	SCC2 had a V-funnel value of 7s good flowability with 590 mm. L-box, U-box and Fill-box have low values hence low passing ability but no segregation	–	–	
–	–	SCC3 V funnel the flow of 5.5 s with a flowability diameter of 660 mm. L-box, U-box and Fill-box have good values recommended passing ability. Thus SCC class SF_1	–	–	
–	–	SCC4 has a slump value of 680 mm Class SF_1. V-funnel flowability value of 5s thus Class VF_1 of satisfying viscosity of SCC. L-box, U-box and Fill-box	–	–	

Table 8 (cont). Gum Arabic studies on producing bioconcrete

Mix design	Bio-admix/ superplasticizer replacement%	Rheology	Mechanical properties	Micro-structure analysis	References
		have good values recommended passing ability			
OPC grade 52.5 is used at a Water/cement ratio of 0.5	Gum Arabic Karoo at 0%, 0.3%, 0.4% 0.5%, 0.7%, 0.8%, 0.9%, 1% and 1.1% of cement	The setting times are according to EN-03 2005. The highest initial setting time for Gum Arabic Karoo is 0.5% dosage. It was higher than 3.18 hours to control but reduced at 0.9% dosage. The final setting time higher at 0.6% dosage	The value of compressive strength decreases with an increase in gum Arabic Karoo dosage across 2 days, 7 days and 28 days.	Thermogravimetric analysis was done at 7 days curing	[36]
–	–	The flow test according to ASTM C-330:2003 and water/cement ratio 0.7. Flowability increased by 19% between 0.4% and 0.7% dosage but beyond 0.8% flowing increased by 70.3%.			
–	–	Bleeding was controlled at 0.8% dosage. But excess dosage caused bleeding			
OPC used with ASTM C 14737 and ACI-211.1	Gum Arabic dosage at 0.0%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5% and 0.7%.	There significant increase in initial setting time from 0.4% to 0.7%. The final setting times increased in the same manner	There is an average increase of compressive strength over age (7 days, 28 days and 90 days) with a maximum value at 0.7% dosing which is attributed to prolonged curing.		[103]
–	–	The slump increased by 205.7% and 500% with a dosage of Gum Arabic.			
A concrete mix ratio of 1:1.7:2.5 and water ratio of 0.5 with characteristic strength of 20 KN/m^3	GA at 0.00%, 0.25%, 0.5%, 0.75% to 1.00% wt% by cement Cured between 3 days to 90 days	The slump ranged between 30 to 180 mm. Under OPC, GA reduced apparent viscosity and shear rate thus high fluidity.	According to ASTM C192/C192M the compressive strength increases with increasing GA% dosage with optimum value at 0.5% wt% dosing.	The density and water absorption according to ASTM C 642-13. Density values are normal at 2537 kg/m^3 to 2842 kg/m^3	[107]
–	–	–	–	Water absorption increases with increased GA% dosage hence increase in porosity with curing age.	
Normal concrete	GA powder and liquid 0.1%, 0.2%, 0.4%, 0.6%, 0.8%, 1.0%, and 1.2% of cement content	In presence of GA powder slump values remain constant across percentage dosage (wt%). Optimum at 0.2% of GA-Powder	Compressive strength decreases with an increase in percentage dosage of GA powder	–	[108]
		In presence of GA liquid slump values increase with the increase in GA liquid.	Compressive strength decreases with an increase in percentage dosage of GA powder	–	
SCC mix design as according	0.2% while varying cement kg/m^3	Reducing cement from 400 kg/ GA to 370 kg/Ga and 350 kg	–	–	[109]

Table 8 (cont). Gum Arabic studies on producing bioconcrete

Mix design	Bio-admix/ superplasticizer replacement%	Rheology	Mechanical properties	Micro-structure analysis	References
to BS EN 480		slump flow increase satisfying BS EN 206-9-201 -Flow rate for SCC increases in presence of 0.2% GA.			
–	–	0.2% GA enhances SCC resist bleeding, segregation and surface settlement	–	–	
–	–	GA in reducing cement weight per meter cubic increases air content	–	–	
Standard mix of 1:2:4 and cured at 7 days, 14 days, 21 days and 28days	GA at 0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0% by weight of cement	-Initial setting time increase with the increase in% dosage of GA (from 88 min at 0% to 387 min at 1% GA) -Workability through slump test as per BS 8110: 1970. Slump reduces with increase in% GA. Workability reduces from high to medium thus improving	The compressive strength increases with age at a particular GA content but reduces with increasing dosage.	Shrinkage increase with the increase in dosage of GA. Weight reduces with an increase in GA content.	[110]

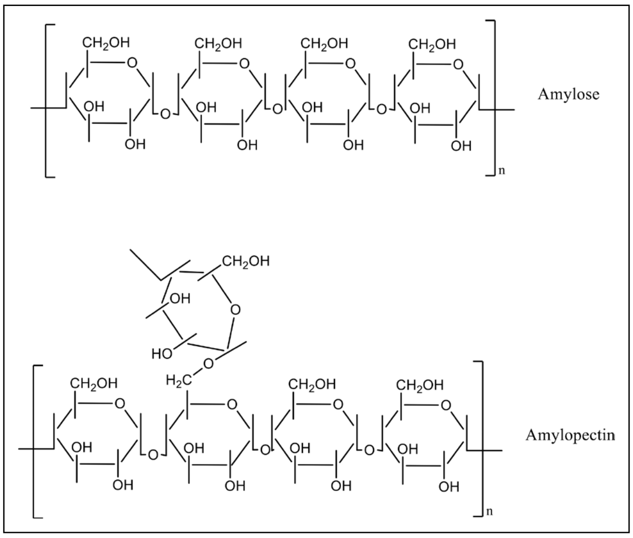

Figure 7. Chemical structure of starch.

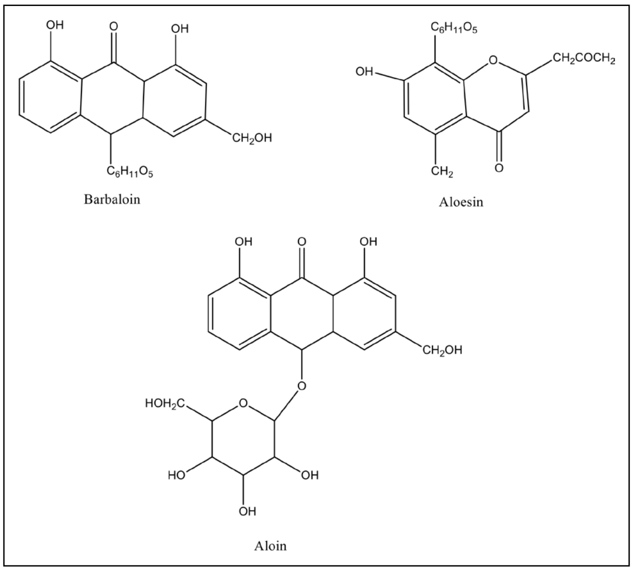

Figure 8. Chemical constituents in aloe vera gel [121].

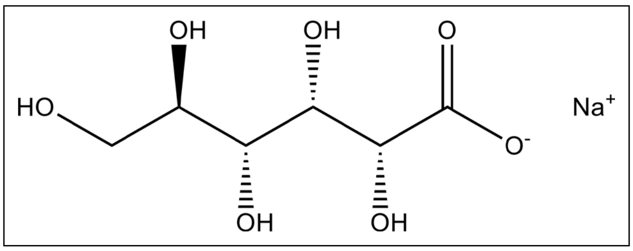

Figure 9. Chemical structure of sodium gluconate.

crobial mineralization has become a promising technology to enhance the durability of concrete structures.

8. OPPORTUNITIES AND CHALLENGES IN USING BIO-BASED ADMIXTURES

8.1. Sustainability Studies

Environmental aspects or potential impacts result from material inputs and environmental releases associated with the manufacturing, transportation, construction and demolition of concrete. Out of the total environmental load of concrete, the contribution of admixtures or superplasticizers is minimal. However, in the production of superplasticizers crude oil and natural gas are used both as raw material and as fuel. Thus, to reduce the environmental impact of superplasticizers in the concrete the raw materials as well as the way of production have to change [6].

Table 9. Starch applications in bioconcrete

Mix design	Bio-admix/ superplasticizer replacement%	Rheology	Mechanical properties	Micro-structure analysis	References
SCC mix design under OPC	0%, 0.25% and 0.5%	Allows slump retention	–	–	[112]
		Low slump retention with an increase in dosage	–	–	
Normal concrete (BS EN 8500-2)	0.4, 0.8, 1.2, 1.6 and 2.0%	Slump test according to (BS EN 12350-2) and reduced with addition of Cassava starch	–	Water absorption (BS 1881-122), sorptivity, resistance to sulphates, sodium and chloride penetration	[113]
Mortar w/c of 0.5 under OPC	0%, 0.5%, 1.5%, 2.0% and 2.5%	Initial and final setting times as per ASTM C187 and ASTM C191	–	Absorption test as per ASTM C1403	[114]
–	–	Flowing ability as per ASTM C1437	–	–	
–	–	Normal consistency	–	–	
Mix proportion of 1.5:3:4	0%, 0.5%, 1% and 1.5% maize starch and cassava starch	Deteriorate slump with increase starch	Compressive strength	Durability increased	[115–117]
Mix design was at ratio of 1:2:3 at 0.47 w/c	Percent weight of cement at 0%, 1%, 3% and 5%	Corn starch improves workability at optimum 1%	Corn starch improves workability, increase compressive strength and density up to the optimum 1% dosage	–	[118]

Table 10. Aloe vera gel studies on producing bioconcrete

Mix design	Bio-admix/ superplasticizer replacement%	Rheology	Mechanical properties	Micro-structure analysis	References
M30 at 0.45 w/c	1%, 1.5%, 2%, 2.5%	Workability increased with percentage dosage of admixture	Compressive strength reduced with increase dosage	–	[122]
	–	–	Flexural strength as per IS 516-1959 increased by 7.9% and optimum at dosage of 1%	–	
M25	0%, 10%, 20% ad 30%	–	Compressive and flexural strength increased by 30% over conventional concrete	Aloe is a good corrosion inhibitor	[119]
	–	–	Split tensile does not change with pc. dosage		
	0.5%, 0.7% and 1% of cement weight	2% workability of Aloe Juice was comparable to Rheobuild chemical admixture	% Dosage increase, reduced compressive strength. But compressive strength was at par by the 28 days with the normal concrete.		
M25 as per IS 10262-2009	0.5%, 1%, 1.5%, 2% and 2.5%		In presence of jute fiber, both the tensile, compressive and flexural strength increase in all ages (3, 7, 14 and 28 days)		[123]

Regarding raw materials usage bio-admixtures use renewable natural resources which can easily be cultivated and grow. And this makes bio-admixtures environmentally friendly solution. In relation to the production process, plant-based bio-admixtures have almost a net zero environmental impact. These days the question of sustainability is an alarming issue. Thus, uses of bio-admixtures have to go beyond laboratory application or research and should be made widely available for the construction industry.

Table 11. Summary of three microbial based bio-admixtures and their effect on concrete property

Bio-admixture	Bio-admixture dosage	Tested physical/ mechanical properties	Conclusions drawn on the resulting cement paste/ mortar / concrete properties	References
Sodium gluconate (SG)	0.00–0.05% with the increment of 0.01% by weight of cement	Compressive strength, Normal consistency and setting time, Fluidity of cement mortars, Hydration kinetics and hydration products, Microstructural analysis	At 3 and 10 days, 10% and 6% of compressive strength increase observed as compared to the blank cement mortar Initial and final setting time were prolonged and the difference between the two decreased with the increase in SG. For fluidity, the "saturation dosage" of SG was 0.01% SG prolongs the induction period and delays the reaction of C_3S.	[124]
	0.02 wt.%, 0.06 wt.%, 0.10 wt.%, and 0.15 wt.% by cement mass	Setting time at 20 °C and 35 °C curing temperature, Compressive strength, Fluidity, Zeta potential Hydration behavior using isothermal calorimetry measurements, X-ray diffraction (XRD), and thermogravimetric analysis (TGA)	For the dosage of SG in the range of 0.02%–0.15%, setting time has a linear relationship with that of the amount of SG used (at 20 °C). At a higher temperature (>35 °C) is difficult to maintain significant retarding effect using SG SG reduce the cement cumulative heat of hydration and delay the occurrence time of heat evolution peak at some degrees, but with a little impact on reducing the cement evolution rate peak. Mechanical and dispersion properties of cement pastes added with SG are depending on their additions. At the dosage less than 0.15%, SG has positive effects on the compressive strength, and the negative effects occur if the dosages exceed 0.15% Compressive strength is highest when the SG addition dosage is 0.06%	[125]
Welan gum (WG)	0, 0.03, 0.05, 0.075 and 0.10 percent by mass of cement WG and 0.4, 0.8, 1 1.5, 2, and 2.5% of naphthalene-based HRWR	Fluidity, rheological properties, washout mass loss bleeding setting time	Losses in fluidity due to the use of WG can be regained without significant effect on the resistance to washout and forced bleeding, by using adequate dosage of HRWR, increase in WG content and the reduction in the HRWR dosage increase the degree of pseudo-plasticity of cement grout washout resistance is enhanced by the increase in WG dosage and reduction in HRWR content. However, with a proper use of WG-HRWR, highly flowable, yet washout resistant mixtures can be secured Combinations of WG and HRWR can secure high resistance to forced bleeding since The coupled effect of WG-HRWR delays the onset of initial setting of cement grout. Such delay seems to be more affected by the dosage of WG	[127]
	0.00 (blank), 0.025, 0.05, 0.075, 0.10 and 0.25% (the mass ratios to water).	Setting time at normal consistency Compressive strength Hydration characterization Microstructural analysis (XRD, TG-DSC, SEM)	WG slightly increases the water demand for normal consistency With the increase in concentration of WG, time period from initial to final setting also slightly increases 0.05% WG solution promotes the compressive strength development at longer ages and reduces the pore size of the cement paste. The induction period and the second reaction of the aluminate phase have delayed due to the WG, but has very limited influence on the total heat release of cement paste. The hydration of C_3S was also a little retarded at early hydration time; meanwhile, WG affects the formation of $Ca(OH)_2$ but not AFt.	[68]

Table 11 (cont). Summary of three microbial based bio-admixtures and their effect on concrete property

Bio-admixture	Bio-admixture dosage	Tested physical/ mechanical properties	Conclusions drawn on the resulting cement paste/ mortar / concrete properties	References
			From SEM analysis, WG does not affect the morphologies of hydration products, but there are many gel-like particles stick on the surface of the hydration product, which can be a reason for the higher porosity in hardened cement pastes with high dose of WG.	
	0.01, 0.03, 0.05, 0.075, 0.1% by weight of cement	Compressive- flexural strength tests mini-slump, and mini-V funnel tests	WG caused an increase in compressive strength up to 0.05%. Beyond this dosage it caused a decrease on the mechanical strength and negatively affect flexural strength	[128]
Xanthan gum (XG)	Welan gum and superplasticizers β-FDN (naphthalene) or PCE (polycarboxylate) were set to 0.1 wt%, 1 wt% and 0.2 wt%	Bleeding rate Rheological properties of cement slurry, Fluidity Mechanical properties Hydration heat Zeta potential	A good anti- segregation and anti-bleeding properties was obtained because of WG Cement slurries containing WG with superplasticizer show non-Newtonian fluid behavior, For WG combined with β-FDN, no significant differences observed on the workability, mechanical properties, hydration heat and zeta potential of the slurries For WG combined with PCE, the workability, rheological properties and zeta potential are significantly affected by the two mixing methods, implying significant competitive adsorption of WG and PCE.	[129]
	0.0%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% of cement	On the fresh concrete, slump flow, V-funnel, U-box, L-box, J-ring tests On the hardened concrete, compressive, tensile and flexure tests	Using XG 1% of cement binder, improved fresh properties like as Slump- flow, V-funnel, L-box, U-box and J-ring compared to conventional SCC. Optimum dosage of XG for M-25 and M-40 grade concrete was1%. With the addition of optimum dosage in SCC maximum values of fresh properties were achieved The compressive strength of SCC M-25 decreases by 17% on addition of 3% of XG. While for M-40 it decreases by 14%. The flexure strength of SCC M-25 and M-40 decreases by 24% on addition of 3% of Xanthan gum. The Tensile strength of SCC M-25 and M-40 decreases by 18% on addition of 3% of Xanthan gum.	[126]
	XG was used in seven different proportions from 0.0–1.2% with 0.2% increment in combination with 0.5% and 1% of Sulphonated Naphthalene superplasticizer	Slump flow, flow time, L-box tests on the fresh Self Compacting concrete Compressive strength, Split tensile strength and, Flexural strength	To increase flowability Super plasticizers are required with XG. Workability results shows that T50 time is increasing with increasing dosage of XG along with superplasticizer. However, slump flow decreases with increasing dosage of XG. At 7- and 28-Days Compressive strength, split tensile strength and flexural strength increased up to 0.6% of XG along with super plasticizer. After adding more than 0.6% of XG along with superplasticizer compressive strength and split tensile strength decreased. At 7 and 28 days (0.6% XG and 0.5% SP) and (0.6% XG and 1.0% SP) gives higher compressive strength, split tensile strength and flexural strength	[130]
	0.01, 0.03, 0.05, 0.075, 0.1% by weight of cement	Compressive and flexural strength mini-slump, and mini-V funnel tests	XG reduced the compressive strength in all ratios Negatively affect flexural strength XG was effective in terms of fresh state behavior activity.	[128]

8.2. Codes and Standards

For the traditional chemical admixtures there exist standard specifications which cover the materials, the test methods and other requirements in relation to the use of chemical admixtures to be added to hydraulic-cement concretes. Some of these standards are ASTM C494/C494M-17, ACI 212.3R-10, IS:9103 and IS:2645. However, to the authors acknowledgement, such kind of specifications are lacking for the case of bio-based admixtures especially for Plant-based bio-admixtures. And this a challenge which hinders a large-scale production and application of bio-admixtures and it has to be addressed. To assure the quality of the product and wide range applicability of bio-based admixtures especially plant-based bio-admixtures, codes and standards need to be developed. In addition, codes and standards help to standardize the production process, handling and storage mechanisms of the bio-admixtures.

9. CONCLUSION

1. Bio-based admixtures are promising alternatives to conventional chemical admixtures for concrete, as they can improve the rheological, mechanical, and durability properties of concrete while reducing the environmental impact of the construction industry. However, there is a lack of comprehensive and systematic studies on the sources, production, performance, and compatibility of bio-based admixtures with different types of cement and concrete. More research is needed to optimize the bio-admixture production processes, standardize the characterization methods, and evaluate the long-term effects of bio-admixtures on concrete structures
2. Bio-based admixtures can be derived from various renewable sources, such as plants, animals, or microorganisms, and can be produced by different biotechnological processes, such as biosynthesis, bio-oxidation, or bio-fermentation. For the manufacture of admixtures, there are, however, only a limited number of bio-based sources that are available and diverse, particularly in some areas where natural resources are in short supply or in danger of becoming endangered. More research is needed to explore new and sustainable bio-based sources, such as agricultural or industrial wastes, that can be used for admixture production.
3. Bio-based admixtures can be characterized by various techniques, such as FTIR, XRD, NMR, GC-MS, and rheology, to determine their chemical composition, functional groups, molecular structure, interaction with cementitious materials. Standardization and harmonization of characterization methods for bio-admixtures across different studies and applications has not been identified. More research is needed to develop and validate reliable and comparable characterization methods for bio-admixtures that can provide consistent and accurate results.
4. Bio-based admixtures have been reported to provide various functions and benefits to concrete, such as water reduction, rheology modification, retardation, acceleration, air entrainment, self-curing, self-healing, corrosion inhibition, and antimicrobial activity. However, there is a need for more research on the mechanisms and effects of bio-based admixtures on the hydration, microstructure, and properties of concrete.
5. Although, the fresh and hardened concrete property that results from the usage of plant-based bio-admixtures is of acceptable quality, there are a number of bottlenecks that hinder industrial application of Pb2A. Some of the reasons are lack of standard manufacturing, handling, and storage mechanisms.

10. AREAS FOR FURTHER RESEARCH

1. Concerning plant-based bio-admixtures (PB2A), the majority of studies identified fail to specify or denote the age of the source plant. However, it is imperative to recognize that the age of the plant constitutes a potential factor influencing the properties and performance of the derived bio-admixture. Thus, dedicated research efforts are warranted to systematically investigate the impact of plant age on the quality and characteristics of bio-admixtures.
2. Furthermore, for PB2A, it is essential to acknowledge that the handling and storage mechanisms are expected to exert a significant influence on their properties. Therefore, comprehensive evaluations of PB2A under diverse environmental exposure conditions are imperative. For instance, inquiries should explore the consequences of storing bio-admixtures in temperate zones, arid regions, or cold environments. Additionally, research should address how direct sunlight exposure affects the properties and performance of these bio-admixtures.
3. A notable observation is that the majority of studies pertaining to PB2A employ the produced bio-admixture for its intended purpose within a relatively short timeframe post-production. To ensure the longevity of bio-admixtures when extended storage is necessary, proactive measures must be considered. Consequently, investigations into the potential use of preservative chemicals to maintain the functionality of the product over an extended period are warranted.
4. It is noteworthy that the studies conducted on bio-admixtures predominantly employ Ordinary Portland Cement (OPC). Consequently, there is a pressing need to examine the compatibility and applicability of bio-admixtures with various types of cement, including blended cements, cement composites, and low-carbon cements.
5. In addition, the applicability of bio-admixtures in various types of concrete has not received adequate attention in current research endeavors. Therefore, it is imperative to conduct comprehensive investigations into the suitability of bio-admixtures for different concrete types, encompassing high-performance concrete, lightweight concrete, air-entrained concrete, prestressed concrete, reinforced concrete, precast concrete, polymer concrete, and digital fabrication techniques employing bio-admixtures.

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ETHICS

There are no ethical issues with the publication of this manuscript.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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