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Artificial Root: Development Based on Synthetic Rhizosphere Fertilizers for Agriculture under Environmental Stresses

Galip Akay[1,2]

[1]Blacksea Advanced Technology Research and Application Centre (KITAM), Ondokuz Mayis University, Samsun, Türkiye
[2]School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon Tyne, UK
Email: galip.akay1@gmail.com

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Abstract

Artificial Root (AR) concept for agriculture is introduced following the integration of interdisciplinary research by the present author and the literature survey of the relevant topics in order to achieve sustainable and efficient plant and crop yield under the emerging environmental stresses due to climate change. The AR system utilises the plant's own defence mechanisms through the generation of a protective microenvironment for the plant roots, which results in the protection of the rhizosphere and the enhancement of plant exudate concentration. The bioactive forms of AR can also enhance or provide nitrogen fixation by the plant and bacteria in the protected rhizosphere. The emerging stresses include enhanced CO_2, elevated temperatures, extreme weather, and drought events, which AR can address for soil fertility, CO_2 sequestration, plant response to stressors, and crop productivity. The AR system is administered into the soil as a synthetic rhizosphere (SRS) fertilizer (denoted as SX-fertilizer, X = A, B depending on fertilizer type) and shortly becomes part of the growing plant when the plant roots preferentially ingress into the skeleton of the fertilizer particles through bio-, chemo-, and hydrotropisms. Once associated with the plant roots, AR functions both as rhizosphere and rhizosheath. At this stage, the skeleton of the SX-fertilizer particles is a microporous, interconnected, elastic, hydrophilic, bioactive, and functionalized material, such as PolyHIPE Polymer (PHP). PolyHIPE is chosen because of its biological, chemical, and morphological versatility, which allows the evaluation of the prevailing mechanisms in AR. The skeleton of the bioactive SB-fertilizers contains suitable bacteria/fungi for root infection and nitrogen fixation in legumes or nitrogen-fixing bacteria for non-legumes. SA-fertilizers without bacteria are produced *in situ* during the low temperature and pressure ammonia production by plasma catalytic synthesis with reactive separation using PHP. SX-fertilizers not only improve soil fertility, but also enhance plant productivity/yield under water and nutrient stress by 50% - 300%. The enhancement of root function, including root hair and exudate production, and bacterial ingrowth from the soil is dependent on the biochemical and physical structure of PHP. The available literature on the use of PHP in medicine, biotechnology, and tissue engineering is reviewed for the optimal design of the SB-fertilizers' biochemical and physical structures. SB-fertilizers can replace the use of Haber Bosch ammonia-fertilizers. SX-fertilizers' use represents negative carbon emission as they can sequester carbon over a long-time scale. Other emerging fertilizers include the use of nano-silica particles as a sub-class of quantum-(QX) fertilizers. Highly porous QX-fertilizers, based on nano-SiO_2 with B, Ca, Mg, Mn, Fe, Co, Ni, Cu, Zn, Mo, V, Se nano-spinel oxides are obtained readily when high/medium entropy supported quantum catalysts, QCs (primarily for use in plasma catalytic reactions), reach their service life, thus providing a circular bio-economy. In the case of nitrogen fixation through catalytic plasma activated water technique using QCs, the resulting NH_4^+ NO_3^- solution can be used without catalyst removal.

Keywords

Artificial Root, Advanced Fertilizers, Agriculture, Environmental Stressors, Polyhipe, Rhizosphere, Rhizosheath, Quantum Catalysts, Quantum Fertilizers

1. Introduction

Based on the performance of biological and non-biological symbiotic rhizosphere fertilizers, an Artificial Root (AR) system is proposed. This AR system has three critical components: (1) A highly porous, hydrophilic, elastic, ionic polymeric support/skeleton/scaffold with a bioactive and micro-, and nano-porous surface acting as a rhizosheath; (2) The basic rhizosheath is filled with nutrients (such as ammonium nitrate), which can take place during the manufacture of such fertilizers; (3) Suitable microorganisms (such as plant growth-promoting rhizobacteria and mycorrhizal fungi) are cultivated in the rhizosheath for a biofertilizer system which can be self-generative. Depending on the plant type and the prevailing soil and environmental conditions, the variants of these AR systems are administered into the soil in particulate form. Due to the presence of hydro-, chemo- and bio-tropisms (which act as a driving force for the roots to grow towards the source of water, nutrients and microorganisms) provided by the AR particles, roots selectively ingress into them, thus creating a micro-environment for root, water, nutrient and bacterial interactions. The AR system can now be considered as a combined rhizosheath and rhizosphere, acting as an interaction facilitator and protector of the root functions, in particular root exudates, so that plants can respond to permanent or transient biotic and abiotic stresses. The proposed AR system becomes part of the plant, rather than an independent production platform.

It aims to redesign/modify the existing biological system, imparting the means to achieve more efficient, robust and predictable novel functionalities through the supply of water, nutrients and functional microorganisms to the rhizosphere.

In the following review, the available patent and literature are critically examined to provide the basis of the AR-design together with greenhouse data associated with various plants and bacteria, as well as the behavior of cells within the AR-scaffolds and their desired characteristics.

This research was motivated by the 2023 UN Emissions Gap, Climate Change Report [1] and the 2024 UN Environmental Programme's waste management outlook report [2]. Firstly, a technology transfer roadmap was recently proposed for the establishment of small-scale (distributed) production of green ammonia, nitric acid, advanced (symbiotic) fertilizers, and electricity [3] [4]. This roadmap proposal describes the electrification of integrated-intensified biorefinery (IIBR) technology powered by biomass and unavoidable biowaste, which have a global energy capacity of some 7-8-fold of global energy demand [4]. It is important to note that electrically powered IIBR technology using biomass/waste is only feasible at a small-scale distributed production scale dictated by the supply chain and the nature of the intensified technology [2]-[4].

The critical elements of the IIBR technology include: (1) Novel gasification for syngas generation [4] [5]; (2) Syngas cleaning [4] [5] (3) Electricity generation [3] [4]; (4) Novel plasma catalytic reactors [6] [7] for syngas cleaning and syngas conversion to NH_3, fertilizers, fuels, alcohols, with important byproducts, such as bio-ash and bio-tar; (5) Novel plasma generating supported plasma catalysts with high activity due to quantum effects under plasma [8] [9]; (6) Porous hydrophilic polymers [10] [11] for in-situ ammonia sequestration, advanced symbiotic fertilizer support and AR-systems in the form of Synthetic RhizoSphere-RhizoSheath (SRS) [12]-[14].

The IIBR represents a circular economy, diagrammatically represented in Figure 1. The input materials are biomass/waste, catalysts, microporous materials [3] [4] [10]-[17]. The intermediate chemicals are syngas, CH_4, and H_2. The primary products include electricity for powering the IIBR process and the national grid, while ammonia, urea, and advanced fertilizers are for agriculture. Here, we are concerned with two types of advanced fertilizers, which are denoted as SX-fertilizers and QX-fertilizers. SX-fertilizers are based on the establishment of an artificial rhizosphere/rhizosheath. Currently, for reasons of cost and technology readiness level, the only SRS medium (as a skeletal structure of SX-fertilizers) available is a functionalized PolyHIPE Polymer (PHP), which is also known as PolyHIPE [15]-[17]. PHP used as a fertilizer support is based on a highly porous, crosslinked, elastic, styrene–divinyl benzene copolymer. The basic PHP can be produced and subsequently functionalized to obtain sulfonated s-PHP [10]-[14].

QX-fertilizers are based on suitable grades of quantum catalysts used in plasma catalytic synthesis in energy conversion processes, including ammonia and fertilizer production as illustrated diagrammatically in **Figure 1**. The use of quantum catalysts [3] [4] as fertilizers (as well as agrochemicals for above-ground applications) makes IIBR economically circular and productive. Byproducts include bioash (as a catalyst for gasification and as an energetically/exergetically better alternative to bio-char as a soil additive) and bio-tar as a natural agro-chemical [4]. Together with NH_3 and its derivatives (urea, ammonium-based fertilizers), the other primary products, Fischer-Tropsch fuels and alcohols, can be used as sustainable fuels and chemicals.

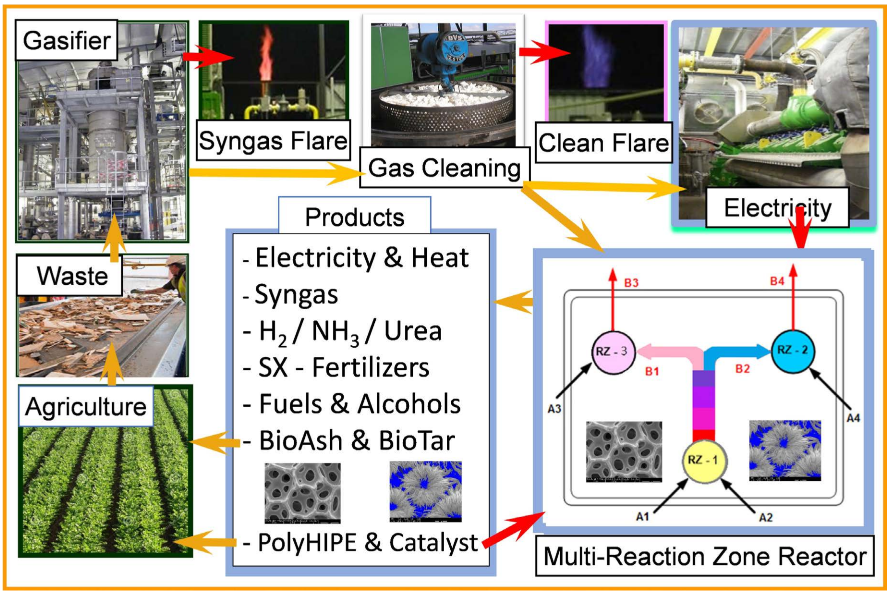


Figure 1. Integrated intensified biorefinery (IIBR) illustrating the critical elements and circularity of the technology. The current status of IIBR is illustrated through the technology readiness levels of its critical components. Adopted from reference [4].

QX-fertilizers are based on suitable grades of quantum catalysts used in plasma catalytic synthesis in energy conversion processes, including ammonia and fertilizer production, as illustrated diagrammatically in **Figure 1**. The use of quantum catalysts [3] [4] as fertilizers (as well as agrochemicals for above-ground applications) makes IIBR economically circular and productive. Byproducts include bioash (as a catalyst for gasification and as an energetically/exergetically better alternative to bio-char as a soil additive) and bio-tar as a natural agrochemical. Together with NH_3 and its derivatives (urea, ammonium-based fertilizers), the other primary products, Fischer-Tropsch fuels and alcohols, can be used as sustainable fuels and chemicals.

The purpose of this review is to introduce the background science for SX-fertilizers and the reasons why such fertilizers are necessary for the emerging world of Enhanced CO_2 (eCO_2), Elevated Temperatures (eTe), and Extreme Weather Events (eWe), including extreme drought events (eDe). The biological SB-fertilizers represent the most important form of the SX-fertilizers. Here, the biochemical and architectural structure of the SRS-medium is critical for the functional efficiency of SX-fertilizers. PHP is preferentially used as the skeletal frame of the SX-fertilizers. Therefore, the advances made in medicine, bio- and tissue-engineering based on PHP should be utilized in the design of SX-fertilizers. This study provides a critical review of the biological applications of PolyHIPE relevant to SB-fertilizers and sets the fundamentals of a fertilizer design which forms the AR system in soil.

1.1. Emerging Fertilizers for Agriculture in the Changing Environment

SX-fertilizers (X = A): The skeletal fertilizer (nitrogen based) support structure is known as the Synthetic RhizoSphere (SRS)-medium [12]-[14]. As part of the circular economy, suitable mineral acids (or their mixtures) are absorbed within the pores of s-PHP and used as a sequestration medium for ammonia during low temperature (≈ 100˚C) and atmospheric pressure direct plasma catalytic synthesis of fertilizer in the form of sulfonated neutralized PHP (sn-PHP). This in situ product sequestration lowers the ammonia and fertilizer production costs to make emerging SX-fertilizers competitive with classical Haber-Bosch fertilizers [3] [4]. Over a period of time (in perennials), soil bacteria and fungi also colonize the SRS-medium, creating a protective microbiome with a high concentration of root exudate.

SB-fertilizers (X = B): These fertilizers are the biological version of SA-fertilizers. The skeletal structure of the SA-fertilizers is inoculated with useful soil bacteria for direct nitrogen fixation from air (for legumes) or nitrogen-fixing bacteria for non-legumes. Arbuscular mycorrhizal fungi (See Ahammed *et al.*, [18] and Rennel *et al.*, [19]) containing sn-PHP can be used for the enhancement of plant growth and suppression of plant disease through the provision of pathogen and parasite resistance.

1.2. QX-Fertilizers: Quantum Catalysts and Quantum Fertilizers

A novel catalyst system has been developed [4] [5] [8] [9] [20] for use in several plasma catalytic syntheses, including NH_3, CO_2 dry reforming, CO_2 conversion to CO, Fischer-Tropsch reactions, and nitrogen fixation from air and water [21]-[25]. These catalysts are highly porous piezoelectric spinel oxides supported by silane coated silica molecules and nano-silica particles (≈ 1 - 7 nm), thus possessing semiconductor characteristics, represented as $M^{(1)}_{3-j}M^{(2)}_kO_{4-m}\{\#\}_nN_r/SiO_2$ (unary (k = 0) or binary (k > 0) catalyst) with oxygen vacancies {#} and nitrogen substitution. The perovskite version of these catalysts is black piezoelectric $BaTiO_3$ (bp-{BTO}) with oxygen vacancies, nitrogen substitution, and a variable Ba/Ti ratio within micron-sized domains, represented as $BaTi_{1-v}\,O_{3-x}\{\#\}_yN_z$. Previously, ferroelectric $BaTiO_3$ has been used in nonthermal plasma reactions as a plasma catalysis promoter (PCP) [5]-[7] [20] and as a catalytic packing material over which plasma could be generated for combined plasma and surface catalysis. This process, in turn, converted the PCP surface structure, making it acquire a piezoelectric state, hence suitable as an effective plasma catalyst or co-catalyst with supported spinel oxides [5] [7]. Due to their physicochemical structures, both catalysts show quantum effects in plasma and generate plasma in air when irradiated with microwave radiation [3] [4] [8] [9]. These quantum catalysts are processed using a high-intensity power (HIP) processing technique, such as microwave radiation with plasma generation and solution combustion [3] [4] [8] [9] [20]. Plasma generation under microwave irradiation of perovskites and their dual use as a PCP [3] [4] [8] [9] [20] catalyst has been confirmed recently [26] [27]. We note that the quantum catalysts in the piezoelectric state can also be used in photosynthesis subject to external activation such as ultrasound or physical stress/strain imposition. In plasma processing, piezo-catalyst activation is achieved through thermal fluctuations, especially through plasma power pulsations, which also enhance energy efficiency of plasma synthesis [3] [4]. The physical nanostructures of these quantum catalysts are shown in **Figure 2** for bp-{BTO}. Here, the step- and terrace-structures [3] [4] are present on the 2D-banded platelet domains separated by lattice exudates, which are generated during microwave-induced plasma generation in air. As in bp-{BTO}, in the quantum catalyst Fe/Mn/SiO_2, the nanostructures responsible for quantum effects (due to Casimir forces [28]) are the presence of 2D-plates and ribbons with bar-code structures as shown in **Figure 2(b)** [3].

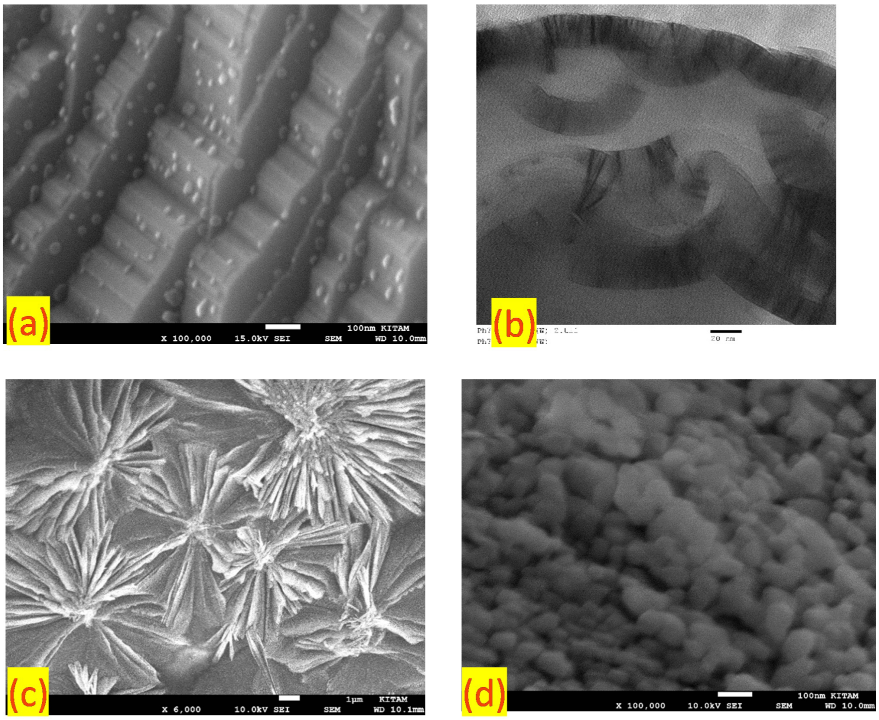


Figure 2. Nano-structure of the quantum catalysts. (a) SEM image of the black piezoelectric barium titanate (Scale bar = 100 nm); (b) TEM image of Fe/Mn/SiO_2 silica-supported spinel catalyst (Scale bar = 20 nm); (c) Surface structure of Co/Cu/SiO_2 silica-supported catalyst (Scale bar = 1 μm); (d) Nano-particulate nature of the catalyst surface decorations of Co/Cu/SiO_2 catalyst (Scale bar = 100 nm).

Another quantum effect observed in these catalysts is due to dusty plasma

(Havnes effect [29]) as a consequence of porogenesis in bp-{BTO} [3] [4] [8] [9] and the nano-particulate nature of the pore walls of silanized silica-supported (at the molecular level) spinel catalysts, as shown in **Figures 2(c,d)**. The nano-particulate nature of the quantum spinel catalysts is common to all of the catalysts investigated by the author [3] [4] [8] [9]. This property is useful in plasma catalysis (prevention of plasma-induced product dissociation in plasma catalytic synthesis [3] [4] [25] [30] [31]) and can be utilized as nano-fertilizers after their activity decays because they not only have nano-silica but also essential micronutrients for plants, such as Mg, Mn, Fe, Ni, Cu, and Zn, as a catalyst and catalyst promoter.

Over a period of time, thermochemical catalysts become deactivated [32]. There are currently no long-term service data available for plasma catalysts. The only available plasma catalyst stability data (over a period of 175 hours of continuous operation) in plasma catalytic NH_3 synthesis [21] and Fischer-Tropsch syngas-to-liquid conversion [23] using quantum catalysts, indicate that there is no loss of catalyst activity. However, in terms of industrial applications, these experimental conditions are too short. Nevertheless, in thermochemical applications, these quantum catalysts may also deactivate. The deactivated catalysts can then be used as fertilizers, provided the catalyst is not toxic to the environment and plants (*i.e.*, the catalysts are restricted to Mn, Fe, Ni, and Cu and catalyst promoters; Ca, Mg, and Zn).

In recent years, nano-structured catalysts have been used as quantum fertilizers, in particular silicon, in order to alleviate abiotic and biotic stresses, including water, salinity, metal toxicity, thermal, and nutrient stresses [33]. Sheng and Chen [34] reviewed the mechanism of silicon metabolization by plants and have shown that in addition to non-covalent interactions through amorphous silica, Si can form covalent bonds with plant cell components via Si–O–C linkages between monosilicic acid (H_4SiO_4) and *cis*-diols of cell wall polysaccharides or lignin. The covalently bound organosilicon, independent of amorphous inorganic silica, may play a crucial role in plant cell wall structure, leading to enhanced plant growth and resistance against biotic and abiotic stresses [34].

In their review, Ullah *et al.*, argue [33] that the environmentally friendly Si application is the replacement of synthetic toxic chemicals for sustainable agriculture to gain maximum yield under limited resources and unpredictable environmental conditions, as well as regulate gene expression to mitigate biotic and abiotic stresses [33]. Similar conclusions are reached by Zhu *et al.*, [35] that Si can regulate Na^+, polyamine salinity-induced osmotic stress, antioxidant defence, and polyamine metabolism [35]. Jiang *et al.*, [36] used a new type of 2 nm silicon quantum dots (SiQDs) and showed that they could significantly improve the growth of rice seedlings by increasing the uptake of nutrient elements and activating the antioxidative defence system. Furthermore, metabolomics revealed that the supply of SiQDs could significantly up-regulate several antioxidative metabolites by reprogramming the nitrogen- and carbon-related biological pathways [36].

However, the use of nano-structures is not confined to silicone. Liu *et al.*, [37] used biomass-derived quantum carbon dots in agriculture to increase plant salt tolerance through enhanced photosynthesis. Wang *et al.*, [38] used salicylic acid ZnO quantum dots to activate plants' defence response against disease. In their review of carbon quantum dots, Chaudhary *et al.*, [39] concluded that the applications of QDs are yet to be explored significantly for innovation and technology-based agriculture.

In the above studies, primarily, silicon is used for the delivery of these benefits. More recently, silica nanoparticles were shown to have the same effects as silicon because these small particles can be metabolized by the plants [40]. Hoang *et al.*, [41] synthesized SiO_2 nanoparticles (NPs) in the size range of 16 - 37 nm and demonstrated their potential as a plant stimulant with increased quantity and quality of maize crops. Cuong *et al.*, [42] used combined SiO_2 and CeO_2 NPs and showed that the growth rate of cultivated strawberry (Fragaria × ananassa) had a synergistic effect at an optimum concentration of the NPs. A comparative study of 28.8 nm SiO_2 NPs foliar spray with silicic acid was carried out at field scale over two consecutive rice cultivation seasons [43]. It was found that silica NPs increased grain yield by 45.53% and straw yield by 45.73% compared with the silicic acid. Further, the protein content of grains (8.82%) increased significantly with a benefit-cost ratio of 2.68 over other treatments tested [43].

The above cited studies illustrate that the use of NP SiO_2 in certain applications can be highly productive, although some reports suggest otherwise in the case of MoS_2 nanosheets [44] and Fe_2O_3 NPs in aquatic applications [45]. The quantum catalysts, such as $M^{(1)}{}_{3-j}M^{(2)}{}_kO_{4-m}\{\#\}_nN_r/SiO_2$, contain both SiO_2 and catalysts/catalyst promoters, $M^{(1)}$ and $M^{(2)}$. The number of metals can be increased to obtain high entropy supported catalysts when the number of metal components increases up to five [4]. Clearly, these catalytic components must be non-toxic and function well in plasma catalytic reactions and subsequently can be utilised as quantum fertilizers.

Although a welcome advance, it is unlikely that QX-fertilizers can replace the classical Haber-Bosch fertilizers. However, HB-fertilizers need to be produced and utilized in such a way that they do not contribute to global warming. As shown recently, this is highly possible, and the SRS-based advanced fertilizers can even achieve negative CO_2 emission [3]. Our interest in QX-fertilizers is the establishment of an integrated food-energy-water production technology through a circular economy in which QX-fertilizers and quantum-catalysts are part of this economy.

2. Structure of PolyHIPE Polymers

PolyHIPE Polymer (PHP) was discovered and developed during the 1980s at the Unilever Research Port Sunlight Laboratory, England; the responsible team included the present author. This material was then named PolyHIPE Polymer and acronymed as PHP (Polymerized High Internal Phase Emulsion Polymer, to differentiate PHP from emulsion polymers). PHPs offer unprecedented and unparalleled controllable physical and chemical structures over a very broad range of variables. The key advantage of PHPs is that they can be produced with sizes ranging from ca. 1 μm to 1 cm, with a very narrow pore size distribution and a range of chemical/biochemical functionalizations, including biodegradability [3] [4] [10]-[17]. The pore and interconnecting hole sizes, as well as the surface biochemical functionality, are the most important properties of PHPs in biological applications when the "Confinement Phenomenon" (CP) is the underlying driving force for biochemical transformations involving microorganisms [46] [47]. It is therefore important to understand the PHP structure and control the desired structures through processing.

Based on the availability of such a medium as functionalized PHP (f-PHP), the present author developed the theoretical bases of CP, according to which the behaviour of matter, including the living, is dependent on the size, biochemistry, and the dynamic nature of the environment in which they are confined [3] [46] [47]. This conclusion is based on entropic considerations, but it can in fact be construed as a statement of fact, which has been utilized as an entropic driving force for Process Intensification (PI) [46] in agriculture (A-PI) [12]-[14], biology, including tissue engineering (B-PI) [48]-[56], chemistry and environmental remediation (C-PI) [57]-[62] and energy (E-PI) [63]-[66] technologies. However, later studies indicate an intense level of publications on the utilization of PolyHIPE in agriculture [67]-[69], bioprocess intensification [70] [71], and in particular in medical applications and tissue engineering as apparent from the recent publications [72]-[80].

2.1. Functionalization and Macro-Nano Structuring of PolyHIPE for Biological Applications

In 1998, Akay *et al.*, [48] published the first ever study on 3D tissue engineering (applied to in vitro cartilage cell growth) using well-characterized PolyHIPE polymers with nanopores on pore walls to provide the uninterrupted passage of messenger molecules, nutrients, and metabolites. PolyHIPEs with uniform pore and interconnecting sizes as well as varying degrees of pore surface bioactivity were used. These surface-functionalized PolyHIPEs (f-PHPs) were used as a flow micro-bioreactor. In some cases, a 2D or 3D network of capillaries (1 mm - 10 μm in diameter) [48] was established within the reactors for local nutrient feeding, oxygenation, and metabolite collection in order to produce artificial organs such as lungs as represented in **Figure 3**. The interface between the channels and the bulk can be open or closed by surface modification of the sacrificial capillaries through solubility parameter difference between the capillaries and the bulk PHP [48] [57]. Monoliths with capillaries were also used in the agricultural applications of sn-PHP to allow large roots to branch out within the SRS-medium [12] [13]. These reactors were applied to membrane separations of surfactant molecules or polymers from water [57] [58]. Metallic versions of these reactor systems are also available for catalyst applications in micro-chemical reactors [62]. More recently, Du *et al.*, [81] also used to facilitate cell infiltration and osteogenic differentiation.

In the PHP functionalization, it is necessary to start the process at the emulsification stage because the absorption of chemicals necessary for functionalization is difficult when thick monolithic PHPs are to be processed. Instead, the relevant chemicals are included either in the aqueous phase or the oil phase at the emulsification stage and the polymerization is carried out. In some cases, no further action is required after polymerization, but in other cases, further chemical modifications may be needed.

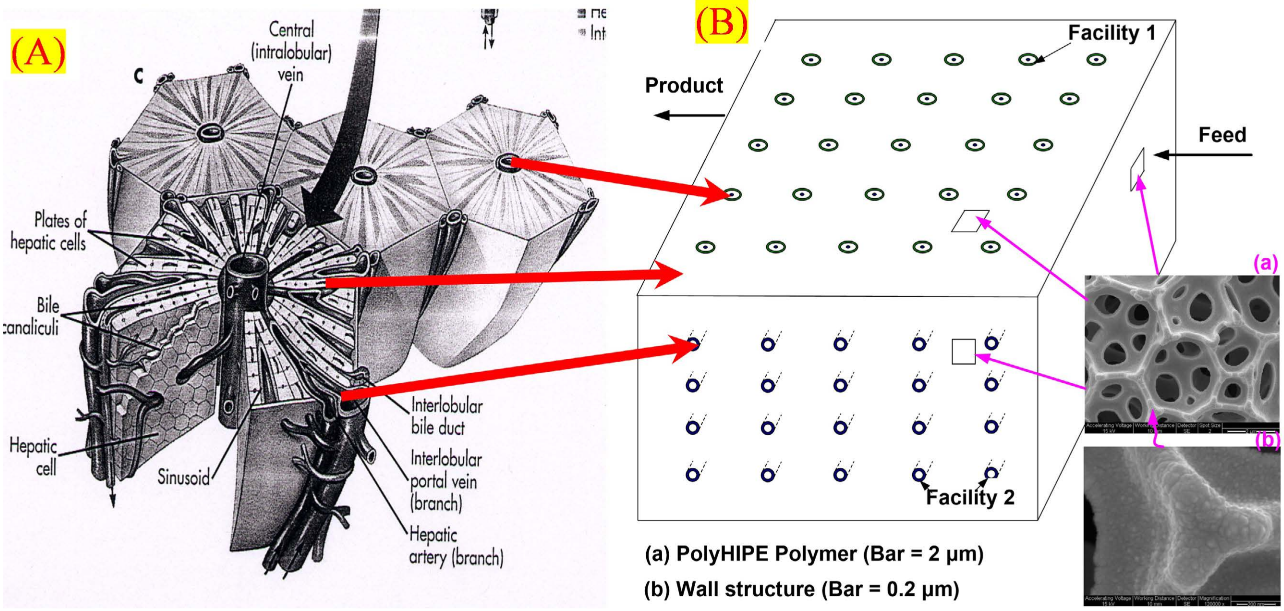


Figure 3. Diagrammatic representation of an artificial organ system or facilitated microbioreactor using PolyHIPE Polymer with channels for various functions such as the central vein or hepatic artery branch simulant. The bulk of the PHP is used for the culture of hepatic cells. Additional channels are needed to force the seeding of the cells to start cell growth. Adopted from reference [48].

Irrespective of any post-polymerization action, the inclusion of these additives for f-PHP production resulted in emulsion droplet coalescence during polymerization [48]. Polymerization with coalescence results in enlarged pore size with thicker nano-porous walls dispersed in smaller primary pores. In coalescence pores, the interconnecting pores are numerous per pore, while in the primary pores (which have not undergone coalescence), there are ≈ 12 interconnecting holes per pore. Pickering coalescence is used to obtain large pores when the primary pores are too small for PHP applications [48] [80].

The above-described technique was used for the surface functionalization of PHP with: (1) phosphoric acid containing hydroxyapatite for bioactivity [48]-[66], (2) peptide hydrogel for bioactivity [53]; (3) sulfuric acid, nitric and phosphoric acids for fertilizer generation or microwave-induced sulfonation for enhanced hydrophilicity for agricultural, biological, chemical and energy applications [7]-[14] [48]-[66]; (4) water-soluble polymers for enhanced water uptake [48].

2.2. Primary and Coalescence Pores

Typically, PHPs shown in **Figure 4** have an oil phase composition of: Styrene 78%; Divinyl benzene (DVB) 8%; Non-ionic surfactant (Span 80) 14%. The aqueous phase contains 1% potassium persulphate as an aqueous phase initiator. The following examples in **Figure 4** illustrate the importance of emulsification and polymerization conditions. **Figure 4(a)** shows similar-sized pores (≈40 μm) formed at the beginning of HIPE formation (90% void). At this stage, the emulsion can have a double-emulsion form, as apparent from the presence of droplets within the larger pores of the PHP itself. The pores have a large number of interconnecting holes and give the impression of being coalescent pores (see **Figure 4(e,f)**). However, unlike coalescent pores, this structure does not have any primary pores between the coalescent pores, as seen in **Figures 4(e,f)**.

Figure 4(b) illustrates the appearance of the PHP after the emulsion is fully processed to obtain a desired size [82]. Here, the pore size is ≈ 2 μm with a uniform pore size distribution. Polymerization temperature and time were 60˚C and 8 hours, respectively, with the ratio of the interconnect diameter (d) to pore diameter (D) ratio d/D = 0.26. Note that, due to the 3D nature of the PHP, when the fracture surface is produced for SEM, smaller pores appear due to the location of the fracture line. When the aqueous (dispersed) phase volume is increased, d/D also increases, thus reducing the pore wall area for support. This can be overcome when HIPE is polymerized at high pressure in order to increase the polymerization temperature and hence reduce the polymerization time. **Figure 4(c)** shows the closed pore structure of the 95.5% aqueous phase volume PHP that becomes closed when d/D (ratio of the interconnect diameter to pore diameter) is reduced from 0.26 to 0.12, with fewer holes when compared with atmospheric pressure polymerization [82]. In this case, polymerization temperature was 60˚C and the pressure was 30 bar, with a total polymerization time of 420 min. The reduction of the d/D ratio is due to pressure, as in other experiments carried out at 60˚C, closed pore structures were still evident [82]. It is therefore possible to control the d/D ratio by adjusting the polymerization pressure to reduce the phase volume dependence of d/D while increasing the polymerization temperature.

Depending on the type of cells, large pore size PHPs may be necessary. This can be achieved using coalescence pores, which, however, do not produce uniform pore size, and a large number of primary pores are still present. However, this disadvantage of coalescence pores can be overcome by choosing a suitable additive [48] or by reducing the additive concentration and lowering the polymerization temperature until the gel point is reached [48]. Alternatively, the emulsification temperature can be increased in the absence of any additives [48]. In this case, primary pores with large pore size are obtained, as seen in **Figure 4(d)**. In this figure, the maximum emulsification temperature was 80˚C, with a pore size of ≈ 140 μm. However, emulsification at higher temperatures requires an oil phase polymerization initiator, as the aqueous phase initiator, potassium persulphate, decomposes when the temperature is above 85˚C. Hence, emulsification above

85˚C can be carried out using an oil phase initiator [48].

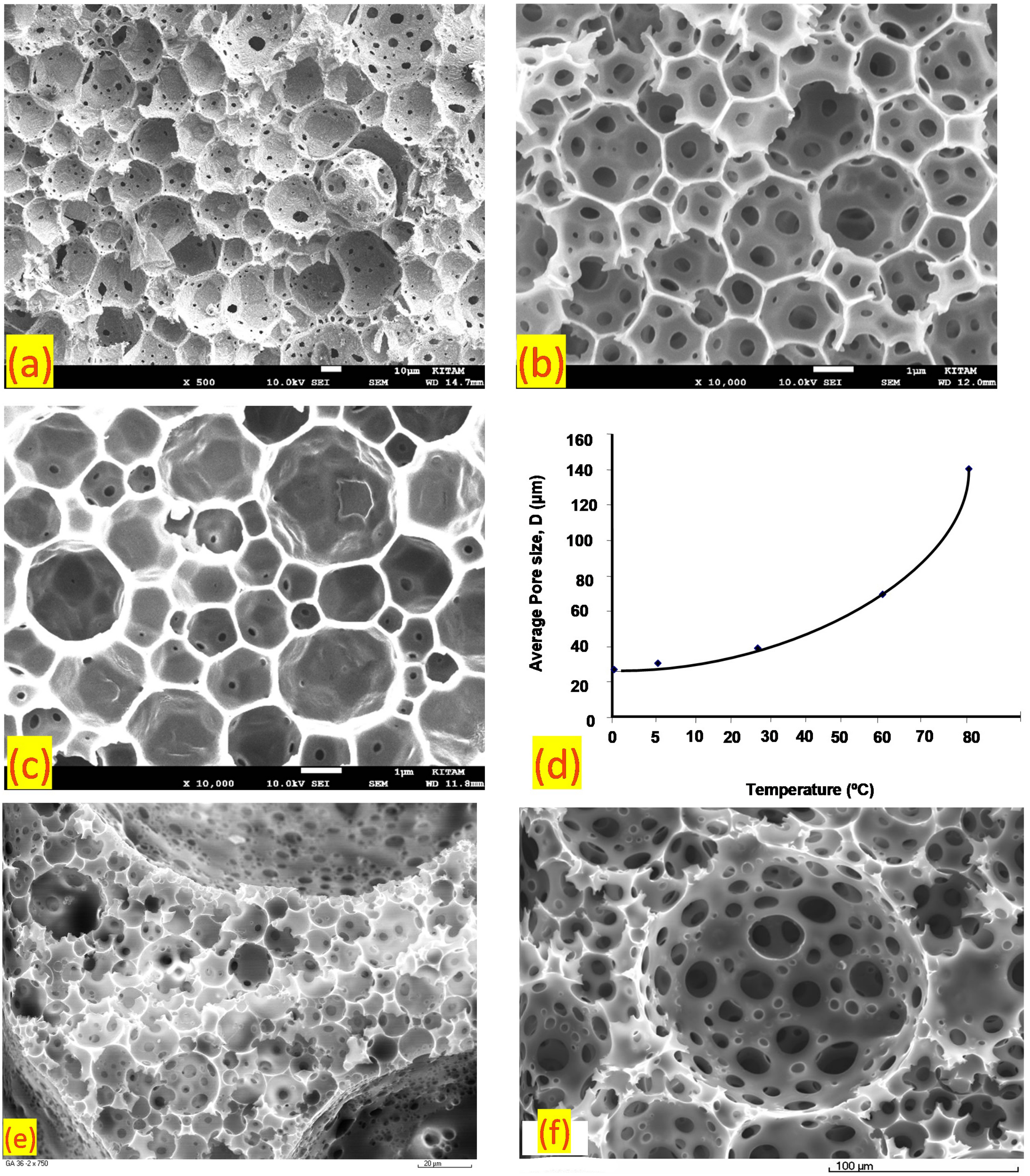


Figure 4. PolyHIPE structures obtained through processing. Unless stated otherwise, aqueous phase volume is 90%. (a) Pore structure at the beginning of emulsion formation at 25˚C, showing coalescence-type pores (Scale bar = 10 μm); (b) Primary pore structure after full emulsion processing (Scale bar = 1 μm); (c) Primary pore structure after polymerization of HIPE (95.5% aqueous phase) at 30 bar (Scale bar = 1 μm); (d) Variation of pore size with HIPE processing temperature; (e) Very large coalescence pores dispersed into primary pores (Scale bar = 20 μm); (f) The structure of a 150 μm coalescence pore (Scale bar = 100 μm).

Figure 4(e) describes the primary pores between three large coalescence pores. Figure 4(f) illustrates the structure of a coalescence pore and the mechanism of its formation from the surrounding primary pores. Several examples are present in reference [48] for the formation of coalescence pores using oil phase or aqueous phase "additives" and their effects on the pore and interconnect size.

2.3. Structure of Coalescent Pores and Nano-Pore Formation

The above-described technique was used for the surface functionalization of PHP with: (a) peptide hydrogel for bioactivity [53]; (b) phosphoric acid-containing hydroxyapatite for surface coating and bioactivity [48]-[66]; (c) sulfuric acid for microwave-induced sulfonation for enhanced hydrophilicity and swelling in agricultural, biological, chemical, and energy applications [7]-[14] [48]-[66], and (d) coalescence pores with highly porous walls [48].

Figure 5 illustrates the formation of coalescence pores and their wall and pore surface structure. Here, the aqueous phase contains 1% potassium persulphate and 10% nitric acid. The oil phase composition is 70% styrene, 8% divinyl benzene, 14% surfactant (Span 80), and 8% vinyl pyridine. The aqueous phase volume is 85%.

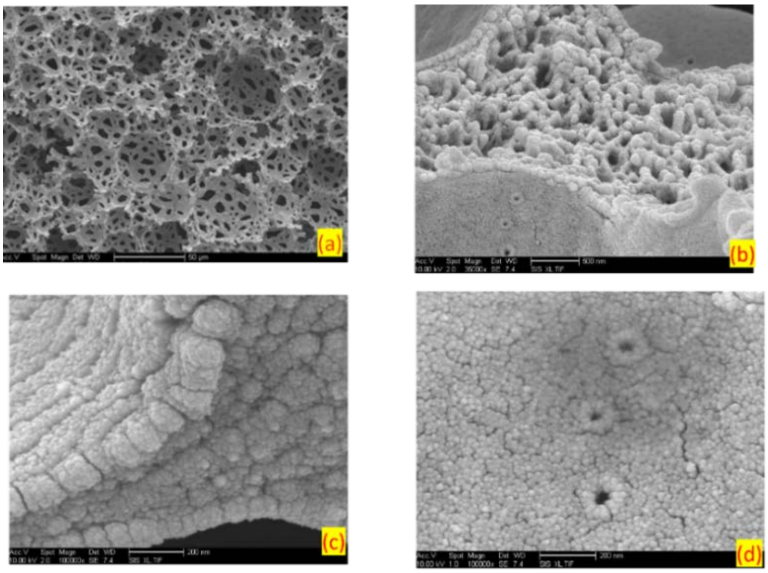


Figure 5. Nano-porous coalescence PHP structure. (a) Coalescence pores (Scale bar = 20 µm); (b) pore wall structure (Scale bar = 500 nm); (c) detail of the wall at higher magnification (Scale bar = 200 nm); surface nano-porosity of the pores (Scale bar = 200 nm).

As seen from Figure 5(a), coalescence pores are formed although the pore size is relatively low. Polymerization is carried out over 24 hours at temperature steps of 40˚C - 50˚C - 60˚C in order to control the coalescence pore size. In Figures 5(b-d), the pore wall and pore surface structures are shown at high magnifications. These PolyHIPEs have a bimodal interconnectivity; both large interconnects and nano-pores, which are formed through the fusion of ca. 20 nm particles with lines of defects acting as interconnecting pores. This type of polymer is useful in micro-bioreactors and SX-fertilizers, providing rapid transport of messenger and metabolite molecules as well as gas diffusion [48]-[56].

2.4. Sulfonation of PolyHIPEs

One of the most functionalised PolyHIPEs is sulfonated s-PHP. It is used in several applications, including agriculture [3] [4] [12]-[14], water [3] [66], and gas cleanup [63] [64] [83], demulsification [56]-[61], as well as bioreactors for the production of enzymes [55] and antibiotics [56]. A process-intensified method of PHP sulfonation is available, which is also suitable for industrial-scale production [7] [10]. In this method, a small amount of sulphuric acid is incorporated into the aqueous phase, and a stable emulsion is formed and subsequently polymerized. If the concentration of the acid is over ≈15 wt%, the emulsion becomes highly unstable and forms very large (> 5 mm) coalescence pores. Therefore, the amount of (sulphuric) acid in the aqueous phase can be used to control the pore size from micrometres to millimetres. In most applications, acid concentration is kept at 10% to obtain the desired pore size. During polymerization, the material undergoes partial sulfonation (≈4%), which is sufficient for rapid absorption of concentrated sulphuric acid for sulfonation [7] [10]. In order to obtain s-PHP with enhanced water uptake associated with enhanced swelling, surfactant (Span 80) is removed by ethanol extraction after polymerization with slight sulfonation [7] [10]. After the concentrated acid (98%) absorption, it is microwave irradiated for ca. 4 minutes for sulfonation at 1 kW power. Clearly, this is a very fast sulfonation technique compared with classical methods such as those applied to PHP by Haq and Johnson [84] in Unilever patents. During microwave irradiation, polymer is swollen and can be neutralised, typically, with ammonia; a process highly suitable during plasma catalytic ammonia production with in situ reactive product separation using Multi-Reaction Zone Reactors (M-RZR) [3] [4]-[9].

Figure 6 illustrates the structure formation in coalescence pores when sulphuric acid containing HIPEs are polymerised, followed by sulfonation using microwave irradiation. Here, the aqueous phase contains 1% potassium persulphate and 10% sulphuric acid with a phase volume of 85%. The oil phase composition is: 78% styrene, 8% divinyl benzene, and 14% Span 80 non-ionic surfactant. As seen in **Figure 6(a)**, the coalescence pores have near-circular interconnectors, similar to the primary pores of the PHPs shown in **Figure 4(a-d)**. Despite its relatively low aqueous phase volume, it has a high level of openness. This is because, during the microwave irradiation, the surface becomes blistered and some of the blisters drop out, forming the interconnects as seen in **Figures 6(b,c)**. The blistered surface structure is shown in **Figure 6(d)**. The surface consists of nanoparticles with hairline cracks. A circular hairline crack separates the region which is a candidate to drop out to form an interconnect, as shown in **Figure 6(d)**. The hairline cracks form approximately 20 nm channels across the wall, thus providing a large amount of nano-connectivity between pores. These structures are specific to the

PHPs prepared through destabilization by acid inclusion in the aqueous phase and subsequent microwave-induced sulfonation.

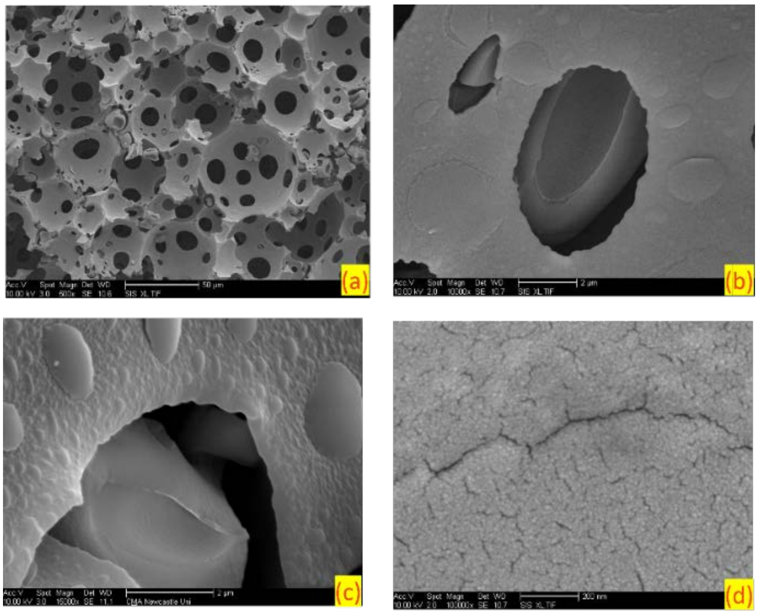


Figure 6. Microwave sulfonated PolyHIPE structure. (a) Presence of coalescent pores with round interconnecting holes due to the formation of extensive blisters; (Scale bar = 20 μm). (b) Interconnecting holes with blisters still intact; (Scale bar = 2 μm); (c) Same as in (b) at a higher magnification; (Scale bar = 2 μm); (d) Pore wall surface structure and the boundary between the fully developed blistered region and bulk; (Scale bar = 200 nm).

2.5. High Surface Area PolyHIPEs and the Effect of Sulfonation

It is possible to obtain very high surface area PolyHIPE by changing the oil phase composition (inclusion of additives in the oil phase) and by decreasing the oil phase volume [10] [48] [85]-[87]. However, when these polymers are sulfonated using thermal methods (with or without acid present at the emulsification stage, using concentrated or dilute acid), the surface area is reduced drastically. On the other hand, using dilute acid at the emulsification stage followed by polymerization, ethanol washing, and microwave sulfonation appears to enhance the surface area.

High surface area PHP was prepared by using an oil phase composition of: 50% DVB, 25% 2-Chloroethylbenzene, and 25% Chlorobenzene. The aqueous phase was: 1.0% potassium persulfate and 5% H_2SO_4. Phase volume was 85%. The surface area of the resulting PolyHIPE was 129 m^2/g. This PHP was thermally sulfonated using the method given by Haq and Johnson [84]. The surface area was reduced drastically to 3.20 m^2/g. When the same polymer was sulfonated through microwave irradiation as described above, the surface area increased to 243 m^2/g. The results are summarised in **Figure 7**.

The scanning electron microscopy study of these PHPs is shown in **Figure 7**, which indicates that the unsulfonated and microwave-induced sulfonated s-PHP have the nano-particulate wall surface structure (**Figures 7(a-d)**, respectively). However, in thermally sulfonated low surface area s-PHP, the original nano-particulate structure is destroyed, as seen in **Figures 7(e,f)**.

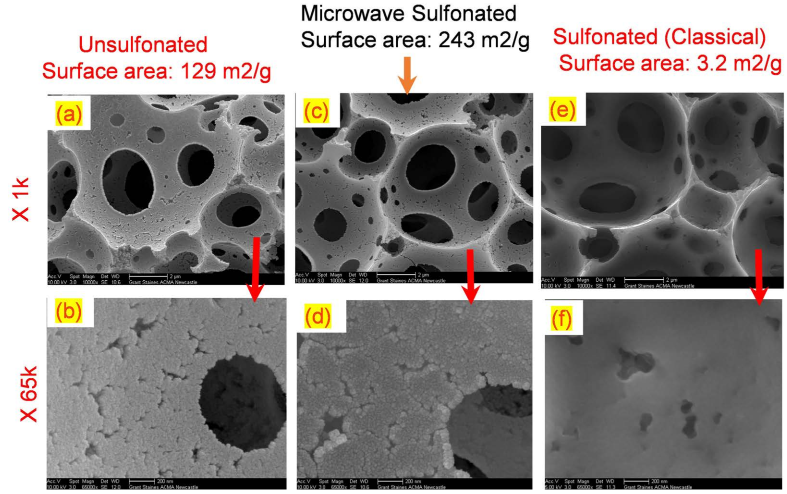


Figure 7. Effect of sulfonation method on the surface area and pore wall structure of high surface area PolyHIPE. (a, b) Unsulfonated polymer; (c,d) Microwave sulfonation polymer; (e, f) Classical thermal sulfonation; (a, c, e) Low magnification (Scale bar = 2 μm); (b,d,f) High magnification (Scale bar = 200 nm).

3. PolyHIPE Pore Size and Biochemical Activity Dependence of Cell and Bacterium Growth

One of the conclusions from the foregoing section is that various variants of PolyHIPE-based materials can be successfully utilized in tissue engineering, leading to the optimization of their biochemical, morphological, and architectural structure for a given application. Several physical and biochemical features of PolyHIPE in agricultural applications have been identified in the "Claims" section of the first patents [12] [88] and publications [3] [4] [14] [67] [68] [69] [89] on this topic. The primary function of PolyHIPE in agriculture is the preferential growth of plant roots towards the PHP particles and the subsequent penetration of roots into the PHP structure. These processes take place through hydrotropism, chemotropism, and biotropism [3] [4]. Without root penetration, the function of PHP is limited. The tropistic mechanisms indicate that the functions of the functionalized f-PHP include: (a) water management through the hydrophilicity of f-PHP (hf-PHP); (b) nutrient source in which nitrate, sulphate, or phosphate-loaded hf-PHP acts as a slow-release fertilizer and absorbent of nutrients in its vicinity; (c) self-sustaining biofertilizer in general and root infection source in legumes in which either pre-cultured hf-PHP biofertilizers are used or, when the nutrients loaded hf-PHP is depleted of fertilizers, ingrown bacteria colonize the hf-PHP. The ingression of the roots thus constitutes an artificial rhizosphere and rhizosheath, which protects the roots from unwanted bacteria as discussed later. The development of hf-PHP into bio-fertilizer (bhf-PHP) represents a clear advantage as it eliminates the use of chemical fertilizers based on Haber-Bosch ammonia. Therefore, it is important to understand the interactions between water, plant roots, and the constituents of bhf-PHP, most importantly, hf-PHP structure and bacteria within it. Therefore, the interactions between hf-PHP and cells and bacteria in other settings are reviewed to provide guidelines in the design of artificial root systems. This review is confined to tissue engineering and micro-bioreactors with supported bacteria.

3.1. The Effects of Pore Size and Biochemical Activity on Cartilage and Bone Tissue Growth Using PolyHIPE

Articular cartilage is composed of cells, chondrocytes, embedded in a resilient matrix of collagen, proteoglycan, and water. In this example [48], chondrocytes, which were primary cells obtained from a bovine metacarpophalangeal joint, were used. Chondrocytes were seeded onto two types of PHP. The first was a plain styrene-2-ethylhexyl acrylate PHP that had not been chemically modified. The second PHP was functionalised with a coating of hydroxyapatite (HA-PHP). The penetration of the chondrocytes into the polymer was determined by histology. The production of glycosaminoglycans (GAG), which are found in the extracellular matrix, was determined by a colorimetric assay, and the type of collagen produced in the matrix was determined with immunocytochemistry. The production of glycosaminoglycans (GAG) is an indication of the production of extracellular matrix. This matrix gives cartilage its load-bearing capacity and is crucial to the development of chondrocytes into cartilage tissue.

To make PHP an ideal scaffold it must be biocompatibility and non-toxic. Biocompatibility is the ability to perform with an appropriate host response in a specific application. PolyHIPE is produced from monomers which are toxic and if any of these monomers are released or the polymer has undergone biodegradation through de-polymerization (re-generation of monomers), it can be potentially toxic. Further, the substrate biochemistry needs to enhance cell functions, including proliferation and differentiation. To assess the biocompatibility, *in vitro* studies were conducted using several cell types but concentrating on macrophages and chondrocytes in PolyHIPE.

Macrophages are responsible for the phagocytosis and digestion of foreign material (both biological and non-biological) in the body. Macrophages are known to have a central role in the inflammatory response to biomaterials and implant failure. Any material that elicits a high response by macrophages would cause the surrounding tissue to become damaged as well as producing an inflammatory response, thereby reducing the biocompatibility of the biomaterial. There are three common ways of assessing the response of macrophages to a biomaterial. They are morphological changes, hydrogen peroxide production and beta glucuronidase production. Morphological changes in the cells are important in cell engineering. Macrophages are spherical *in vitro* and any deviation from this is a sign of a negative response. The performance of the PHP scaffolds with various pore sizes and surface coatings is summarised in Figure 8.

In the SEM micrograph in Figure 8(a), the rounded morphology of the chondrocytes on the surface pores of the polymer can be seen. There is no noticeable effect of the surface bioactivity of the PHP at this point. At later time points, the chondrocytes form a layer on the surface. Figure 8(b) illustrates the effect of the surface biochemistry of various supports. They include the tissue culture plastic (TCP), hydroxyapatite-coated styrene/divinyl crosslinked PolyHIPE (HA-PHP), and the sulfonated-neutralized (with ammonia) hydrophilic PolyHIPE (sn-PHP). As seen sn-PHP is a massively negative control leading to over 10-fold increase in beta-glucuronidase compared to HA-PHP. The tissue culture plastic also provides a positive control with twice the amount of beta-glucuronidase production. As seen in Figure 8(b), the morphology of the chondrocytes for TCP and PHP are rounded while chondrocyte morphology is highly distorted, associated with very high beta-glucuronidase. These results lead overall to a good response by the macrophages to PHP.

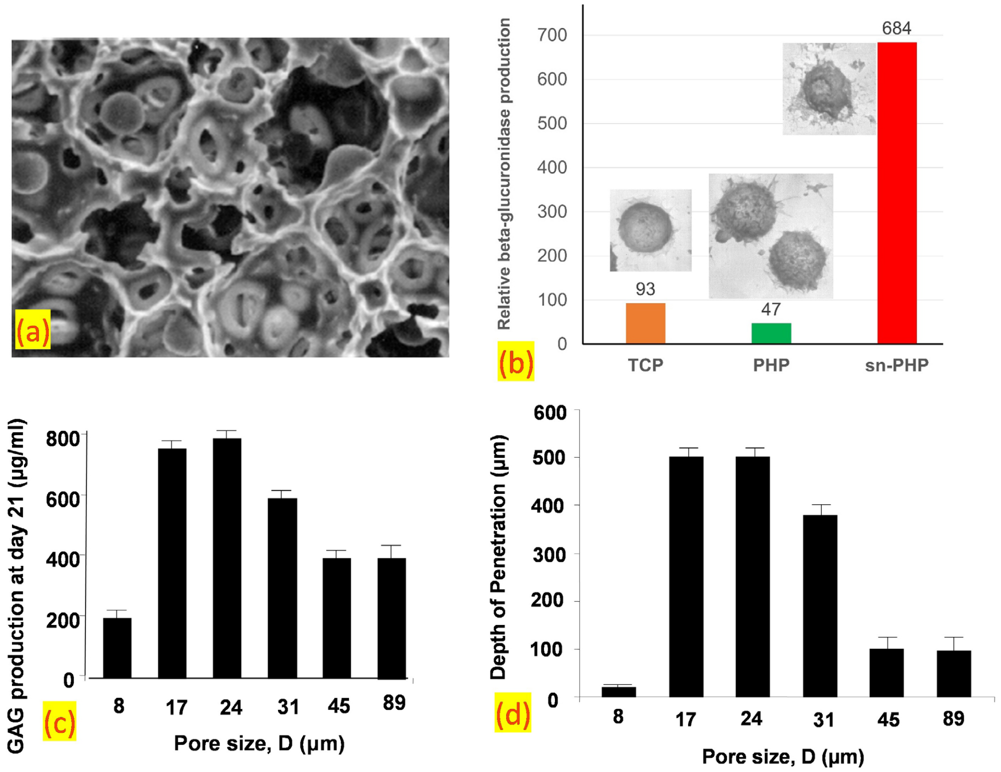


Figure 8. Effect of pore size and pore surface chemistry on chondrocyte growth and performance using functionalized f-PHP. (a) SEM micrograph showing the rounded morphology of chondrocytes on the surface pores of hydroxyapatite-coated PHP; (b) Relative beta-glucuronidase production on tissue culture plastic (TCP), hydroxyapatite-coated HA-PHP (with pore size of 24 µm), and sulfonated, neutralized (with ammonia) PolyHIPE Polymer (sn-PHP) showing the response of the substrate to macrophage morphology; (c) Glycosaminoglycans (GAG) production (cell-associated + released into the medium) showing the response of the substrate to macrophage after 21 days in culture on various pore-sized hydroxyapatite-coated HA-PHPs; (d) Depth of penetration of collagen after 21 days in culture on various pore-sized hydroxyapatite-coated HA-PHPs. Adopted from Reference [48].

Figure 8(c) shows the total GAG production (cell associated + released into the medium) by chondrocytes after 21 days in culture. Figure 8(d) shows the depth of penetration after 21 days. As seen in Figure 8, there is an optimum pore size (≈ 24 μm) to maintain the chondrocyte morphology and to optimise the production of GAG. At lower pore sizes, the cells cannot penetrate the polymer (interconnect size, d = 3 μm when pore size D = 8 μm), and at higher pore sizes (d = 7 μm and D = 89 μm), the cell morphology changes from rounded to flat and fibroblastic in appearance. These fibroblastic-like cells proliferate rapidly and form a layer on the surface rather than penetrating the scaffold.

The importance of the above result is that, when sn-PHPs are used for bacterial support in bioprocessing and agriculture, they produce the most productivity with no biocompatibility issues detected in agricultural applications and antibiotic, enzyme, ethanol production [10]-[14] [48]-[56].

The corresponding experiments with bone (rat osteoblast) cells were also studied using unmodified and HA-modified (HA-PHP) PolyHIPEs with pore sizes of 40, 60 and 100 μm. It was found that the effect of pore size on the phenotype of the cells resulted in few differences, with all polymers supporting osteoblast differentiation and osteogenesis to a similar extent. When comparing all three HA-PHPs by histological analysis, the cells exhibited the same morphology and levels of surface bone formation were not significantly different [52]. However, larger pore-sized polymers promoted more cells to penetrate deeper within the scaffold, as shown in Figure 9(a). The use of the self-assembling peptide hydrogel (RAD 16-1) further improves osteoblast growth compared with HA-PHP [53], as seen in Figure 9(b).

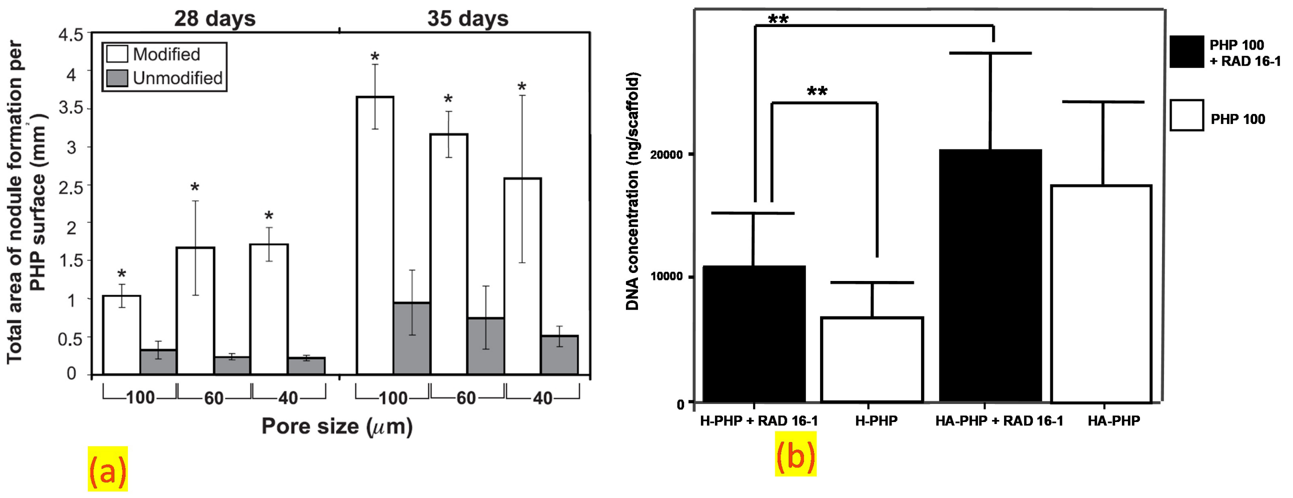


Figure 9. Effect of pore size and pore surface chemistry on rat osteoblast growth in 100 μm sized PolyHIPEs and performance using unmodified, hydrophobic H-PHP and hydroxyapatite-modified HA-PHP, as well as the use of self-assembling hydrogel (RAD 16-1). (a) Total area of nodule formation (cell penetration) as a function of pore size and time for unmodified and modified PHP; (b) The effect of RAD 16-1 on osteoblast growth as determined by DNA concentration after 35 days. From Reference [53].

3.2. Effect of Pore Size in Microbioreactors with Supported Bacteria

Microreactors made from PolyHIPE were used to support phenol-degrading bacteria, *Pseudomonas syringae* [51] [65]. Two pore sizes were used in PHP. The large pore size (100 μm) PHP had a phase volume of 90%, and the second PHP had a pore size of 25 μm with a phase volume of 85%. Bacteria within the 25 μm polymer support remained mono-layered without any apparent production of extracellular matrix during the 30-day continuous experimental period, while the 100 μm formed biofilm (with extracellular matrix) within the pores as shown in **Figure 10(a)**. The monolayer bacterial coverage of the PHP support is shown in **Figures 10(b,c)** at two magnifications. The bulk of the microbioreactor had ≈1.5 bacteria/μm^2. The micro-bioreactor performance was characterized in terms of volumetric utilization rate and compared with the published data, including the case where the same bacteria were immobilized on the surface of micro-porous polymer beads and used in a packed bed during continuous degradation of phenol [65]. It is shown that at the similar initial substrate concentration, the volumetric utilization in the microbioreactor is at least 20-fold more efficient than the packed bed depending on the flow rate of the substrate solution. Under optimized reactor conditions, the efficiency was ca 30-fold [51]. The application of the present technique to other bacterial systems also resulted in similar enhancement levels. These include enzyme [55] and antibiotic [56] production.

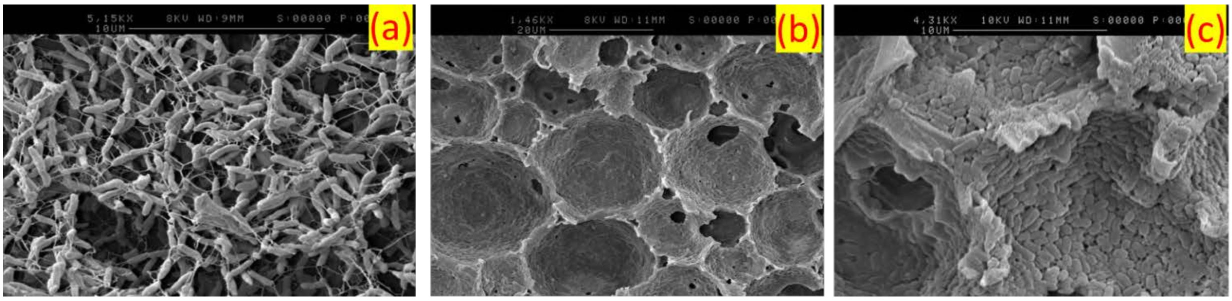


Figure 10. SEM micrograph of the micro-bioreactor at the end of the 30-day continuous cultivation: Cross-section at a distance of 2000 μm from the inlet surface. (a) 100 μm pore size PolyHIPE (Scale bar = 10 μm); (b) 25 μm pore size PolyHIPE polymer in a flow-through micro-bioreactor (Scale bar = 20 μm); (c) Same as (b) at higher magnification (Scale bar = 10 μm). Adopted from Reference [51].

4. Haber-Bosch Fertilizers and Climate Change

Among the essential plant nutrients, nitrogen is one of the most important soil inputs. Since its inception a century ago, Haber-Bosch (HB)-fertilizers (in the form of ammonia or its derivatives) have revolutionized agriculture and have been feeding the growing world population ever since. However, the haphazard overuse of HB-fertilizers, without understanding the mechanisms of interactions between plants, water, soil biodiversity, and microbial communities, has contributed to soil infertility and air pollution, through potent greenhouse gas emissions including NH_3, N_2O, and NO. In addition, partial nitrogen uptake for plant growth, as well as ammonia losses to air, soil, and underground water, contributes to inefficient use of HB-fertilizers. In current agricultural practice, only 30% – 50% of applied nitrogen is used by crops [7] [90]. These ecological and environmental impacts result in soil acidification, eutrophication, nutrient runoff, reduced biological diversity, and greenhouse gas emissions.

With the current understanding of the above-cited impacts, it is now possible to design fertilizer systems that not only address the direct adverse fertilizer impacts on soil and air, but can also, through the use of symbiotic and smart fertilizers (SX-fertilizers), remove carbon and store it in soil by mineralization. However, the production, use, and net carbon removal efficiency of such fertilizers require technological circularity, covering the life cycle of the SX-fertilizers and the food, energy, and water (FEW) nexus in order to achieve sustainability. Due to these constraints, the manufacture of SX-fertilizers is best conducted using process-intensified technologies, capable of utilizing a wide variety of renewable feedstock, such as biomass, bio-waste, sewage sludge, and municipal solid waste, through a small-scale biorefinery concept [3] [4].

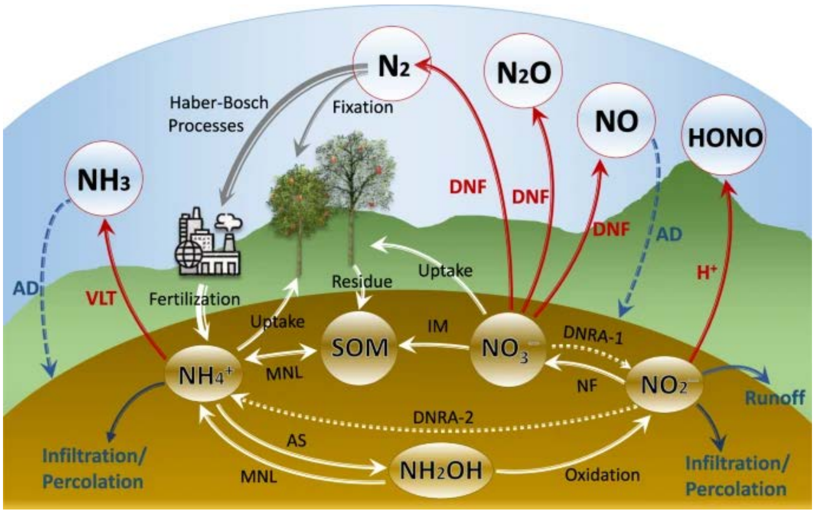


Figure 11. Mechanisms of nitrogen fertilization in soil systems and the associated nitrogen cycles. Reproduced from reference [91]. Acronyms: AD: Atmospheric deposition; AS: Assimilation; DNF: Denitrification; DNRA: Dissimilatory nitrate reduction to ammonia; IM: Immobilization; MNL: Mineralization; NF: Nitrification; SOM: Soil organic matter; VLT: Volatilization.

The potential way forward for the manufacture of SX-fertilizers with technological circularity, advocated by the present author, is based on the conclusion of this review and previous works on various aspects of this interdisciplinary biological-physical-chemistry subject. Technology-circularity advocates the design of processes by manufacturing the maximum number of products within a single reactor system in order to achieve a circular economy and sustainability. In the absence of technology-circularity, each product has to be produced in separate reactors to provide a circular economy with reduced sustainability. In order to establish the science, engineering, and technology of SX-fertilizer production, the mechanisms of nitrogen fertilization in soil and the associated nitrogen cycle are investigated initially. **Figure 11** illustrates well the nitrogen cycle in soil and highlights the important mechanisms which should be considered when designing efficient SX-fertilizers, with high nitrogen use efficiency, carbon sequestration capacity, and reduced greenhouse gas emissions provided by Pan *et al.*, [91].

4.1. Ammonia Fertilizers and CO_2 Emission

Both plant leaves and fertilizers in soil are responsible for ammonia emissions. The crop foliage emission of NH_3 occurs during leaf senescence (the last stage of leaf development) when nutrient assimilation is completed and remobilization starts [92]. Although plant nutrient uptake and environmental stresses affect emissions from foliage, the mechanism is not clear. So, the primary research aims to enhance crop yield, rather than address nutrient loss or greenhouse gas emissions. The second source of NH_3 and CO_2 emissions is volatilization from the soil (assuming urea as the primary N-fertilizer) as a result of farming practices and fertilizer hydrolysis, as noted in the chemistry below.

$(NH_2)_2\,CO + 2\,H_2O \rightarrow (NH_4)_2CO_3 \rightarrow NH_4^+ + NH_3 + CO_2 + OH^-$

This means that the microorganisms present in soil need to convert atmospheric nitrogen into ammonium (NH_4^+) and nitrate (NO_3^-) ionic forms to become plant-available [93]. In **Table 3** of reference [91] a summary of NH_3 and CO_2 emission suppression methods is provided. Pan *et al.*, [91] also suggest practical methods to reduce NH_3 emissions when it is directly used in solution. These methods include fertilization management and the use of bio-fertilizers and slow-release fertilizers with slow-release coatings [94].

4.2. Nitrification, Denitrification, and Fertilizer Loss with Nitrous Oxide Emission

Nitrification is an aerobic process driven by ammonium-oxidizing bacteria or archaea, where ammonium (NH_4^+) is oxidized to NO_3^- for plant availability [93], including more efficient photosynthesis by plant leaves. The conversion of NH_4^+ to NO_3^- also indicates the energy loss in nitrogen fixation through NH_3 production. However, NO_3^- can be further reduced by denitrifying bacteria under anaerobic soil conditions. Both of these ionic species can percolate through soil and contaminate groundwater or undergo further transformation to yield N_2O, NO, and N_2, causing nitrogen loss and emission of the potent greenhouse gas, N_2O, which also causes the depletion of the stratospheric ozone layer [95]-[97]. There are several available methods to prevent nitrogen loss and emission, including the coating of fertilizers for slow release and using synthetic nitrification inhibitors (SNI) [98] [99].

However, SNIs suffer from disadvantages including cost, availability, activity decay over time, and potential toxicity [96]. Therefore, an alternative has recently been exploited through the plants' own natural capacity to suppress microbial nitrification, based on the promotion of root exudates and also by biological nitrification inhibitors (BNI) and biological denitrification inhibitors (BDI) [100] [101]. The root-derived fatty acid amides and sterols, and microbe-derived *N*-acyl-homoserine lactones have been successfully used as biological inhibitions [102], thus raising expectations regarding the potential of crops to directly control nitrification and denitrification in soils [103]. Nevertheless, the cost of these inhibitors, their constant replenishment and loss in soil, and soil-specific selectivity and efficiency are likely to be their primary disadvantage.

Not all the gas emissions to the atmosphere from soil are harmful and undesirable. As seen in **Figure 11**, another nitrous gas emission, nitrous acid (HONO), is generated through NO_2^- formation as a result of nitrification and denitrification, and the bacterial decomposition of soil organic matter (SOM) [104]. In air, nitrous acid undergoes photolysis to produce atmospheric hydroxyl radicals, which are vital for the removal of atmospheric pollutants such as CO and CH_4. Nitrous acid is responsible for the production of some 60% of atmospheric hydroxyl radicals, which are also an essential precursor of cloud formation through organic aerosol generation [105] [106].

Before examining the biochemical pathways as described in **Figure 11** for ammonia loss, greenhouse gas emissions, and carbon sequestration in soil, we summarize the emerging nature of agriculture due to three of the environmental stressors; namely eCO_2, eTe, and eDe. Recent research indicates that, to some extent, the mitigative pathways for the destructive consequences of eCO_2 and eTe are inherent in several plants in the form of root exudation. Further understanding of the root exudation process, its composition, its dependence on environmental stressors, and soil phytomicrobiome (microbial community associated with a plant that constitutes the whole root as well as the shoot parts) and its specificity for a given plant, needs to be evaluated. Here we also consider how to best utilize root exudation pathways using, for example, SRS, which allows the evaluation of the interactions between plant roots, water, nutrients, and beneficial bacteria/fungi as well as root exudates as a function of time, concentrated within the SRS particles in soil. These interactions enhance biomass and crop yields, especially under water and nutrient stresses. The SRS-route is considered to be a suitable process to facilitate root plasticity, but without plant genetic modifications, which require the alteration of multiple genes, and thus remains challenging [107].

4.3. Agriculture in the Emerging Climate of Enhanced CO_2 (eCO_2), Elevated Temperatures (eTe), and Extreme Weather Events (eWe)

The agricultural practices and technology in the emerging climate marked by eCO_2, eTe, and eWe, have to address several global warming impacts on soil, soil microbiota, root system architecture, and rhizosphere functions. For example, according to Vega-Mas *et al.*, [103] eCO_2 climate increases N_2O emissions due to enhanced nitrification and denitrification, because nitrification bacteria use CO_2 as a carbon source for growth and NH_4^+ as energy [108]. Further, a more abundant nitrifying population was found in response to eCO_2, alone or in combination with increased temperature [109] [110]. Vega-Mas *et al.*, [103] indicate that, agriculture under future climatic conditions, with eCO_2 and eTe, biological nitrification inhibitor (BNI) production would be promoted since eCO_2 would boost both nitrogen assimilation and production of carbon-rich secondary metabolites. Another important outcome of global warming is the increase in the relative abundance of soil-borne potential fungal plant pathogens (*i.e.*, plant pathogenic bacteria, fungi, oomycetes, viruses, and nematodes) [111]. These pathogens often cause soil-borne disease complexes, which, due to their complexity, frequently remain undiagnosed and unmanaged, leading to chronic yield and quality losses, estimated at 30% globally [112] [113]. As a result, more efficient pest-pathogen control methods are urgently required. Genetic engineering and breeding of pathogen-resistant plant crops involve the alteration of a large number of genes, making this route highly challenging. Furthermore, plant disease resistance could depend on local biotic environmental factors, including plant-associated microbiota, thus confining the genetic engineering route to local applications [114] [115]. This trait is also true for the growth and health of adjacent plants via specific interactions [116].

The protection against pathogens initially takes place at the root rhizosphere, where the exudate promotes bacteria that reduce pathogen concentration. By way of this dilution, or pathogen-targeting bacteriophages, or by plant-signaling, the state of microbiomes switches from conducive to disease-suppression mode. However, relatively little is known about the underlying plant genes that govern microbiome-mediated disease resistance [117]. Nevertheless, the effect of root exudation is clearly an important route in combating root disease. The synthesis of chemicals mimicking plant exudates, or indeed the development of plant growth promoting rhizobacteria (PGPR)-based inoculants, and their use in soil, is one method of achieving several objectives summarized above [118]. For example, a single small peptide (Thuricin 17) was produced by *Bacillus thuringiensis* NEB17, isolated from soybean nodules as a bactericide (proteins with antimicrobial activity), and has been shown to be extremely effective in mitigating the effects of abiotic stresses on a wide range of crop plants [119].

However, similar to the synthesis and use of biological nitrification/denitrification inhibitors, this method can be costly in terms of production and loss during use. It is not universally applicable, since its composition is dependent upon the soil microbial population, notably PGPR. Therefore, the exudate secretion requires the presence of suitable bacterial communities near the rhizosphere, thus requiring soil bacterial supply [120].

4.4. Bio-Tropism and Quorum Signaling

Another method is to promote the in-situ production of plant exudates and keep their concentrations high over the rhizosphere in order to provide quorum signaling to recruit PGPR. In fact, instead of the production of specific components of the root exudates, PGPR-based colonies can be inoculated with a synthetic rhizosphere (SRS) medium and placed in soil as micro-bioreactors, which act as a source of PGPR, nutrients, and water. An SRS medium (synthetic root system) was introduced by the current author [12] [13], which showed that plant roots are attracted to them through biotropism, chemotropism, and hydrotropism, in which biotropism is based on PGPR–root exudate signaling. The above summary indicates that the colonization of the SRS medium by plant roots is not a random process, but takes place due to a strong entropic driving force. Therefore, the rhizosphere transformations now take place within micro-sized domains, as the SRS medium is an interconnected porous material with a well-defined physical and biochemical structure through which plant roots penetrate and create a new micro-environment. These findings form the basis of a new generation of fertilizers in which the interaction between the rhizosphere and the fertilizer system can be enhanced in order to promote root exudate secretion. This can also protect and confine the rhizosphere, and alter root plasticity and morphology [13]. Therefore, this method has universal applicability, high efficiency, and affordability. Here, we first examine the structure of the rhizosphere and root exudate composition, followed by developments in their effects to suppress emissions from soil and enhance the efficiency of nitrogen use and crop yield.

4.5. Root Exudates

Root exudates are a complex group of organic substances released in the rhizosphere with the potential to recruit, repel, stimulate, inhibit, or kill other organisms, including detrimental ones. An improved understanding of how root exudates affect interspecies and/or inter-kingdom interactions in the rhizosphere, under ongoing climate change, is a prerequisite to effectively manage plant-associated microbes, including those causing diseases [121]. In soil mass transfer, a biochemical reaction involving water, nutrients, microorganisms, and plant roots takes place in the root rhizosphere. This provides a shelter for the reactants that establish an inter-species relationship between the roots and microorganisms necessary for plant growth and physiology. Factors influencing the soil microbial population include soil quality, soil moisture, soil pH, and rhizospheric root exudates. These are responsible for the plant growth-promoting rhizobacteria (PGPR) and mycorrhizal fungi as well as their chemotactic mobility towards the plant root [120] [122].

The functions of PGPR, such as direct and indirect mechanisms, metabolism, chemotaxis, secretion, and antibiotic production, are mediated by the gene cluster that triggers host–PGPR interactions. **Figure 12** illustrates the location of the rhizosphere in the growing root, its functions with the soil bacteria, and the direct and indirect functions of root hair. In order to achieve efficient quorum sensing for PGPR recruitment, root exudate concentration needs to be high [123] [124]. The majority of root exudation is localized at the root tip, which is the first part of the plant to explore the new soil environment. This plays a crucial role in root responses to environmental stimuli [125].

In the case of signal compounds, one can use microbe-to-plant signals for direct effects on the plants, or even plant-to-microbe signals to trigger enhanced production of the microbe-to-plant signals in the soil environment. This assumes the presence of the microbes in the soil. One could also use plant-to-microbe signals to control the composition of the phytomicrobiome in ways that are beneficial to the crop plants [118]. Clearly, the presence of PGPR in soil is necessary near the growing root for this mechanism to be effective. The understanding of the mechanisms involved in plant stress signaling and response by phytomicrobiome species, under spatial and temporal climate changes, has been studied for bacterial and fungal biomes. However, the holistic interactions with other species are also needed [126].

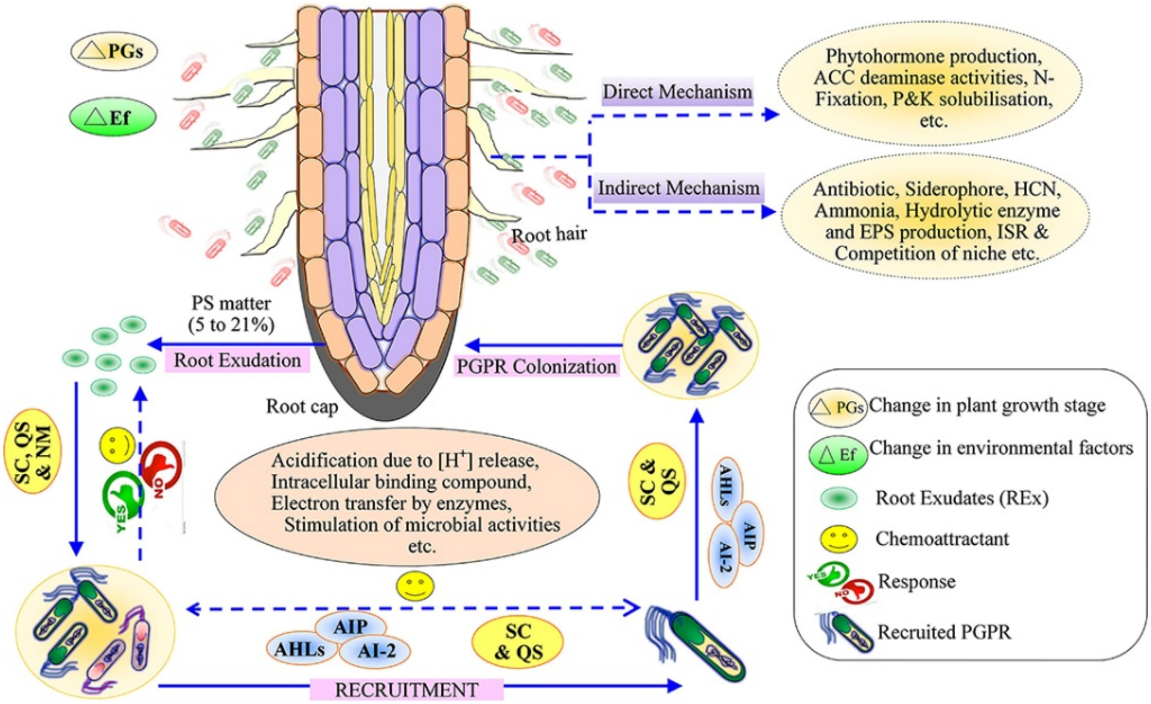


Figure 12. Schematic representation of the mechanism of root exudates for the recruitment of plant growth-promoting rhizobacteria and plant growth-promoting mechanisms (Direct and Indirect). SC, Selected compounds; QS, quorum sensing; NM, nutrient management; AHL, acyl homoserine lactone; AIP, autoinducing peptides; AI-2, autoinducer; PS, photosynthetic matter. Reproduced from reference [120].

4.6. Plant Root System Architecture

Root system architecture is a fundamental component of plant productivity. It determines the capacity of a plant to forage for and acquire resources in the temporal-spatial soil environment. Root system architecture is genetically determined, but the chemical and physical characteristics of the soil environment ultimately shape and size root growth, especially in response to biotic, abiotic, and edaphic stresses. Roots are heterotrophic organs that are metabolically costly to build and maintain. The production of surplus roots diverts the plant from other useful functions, such as photosynthetic production, to support further soil exploration [107] [127].

Plants can respond locally to the spatial-temporal soil environment through several mechanisms and perform functions by minimizing the metabolic cost of soil exploration. This can be accomplished by matching plant investment in root biomass and root function with resource availability in the soil [107]. Recent advances in nutrient uptake and root system architecture can respond to nutrient rich patches that can be used to develop strategies to control root and shoot growth. Common metabolites present in root exudates can be sensed by the roots, to continuously modify the root system architecture, which responds to environmental cues such as nitrogen, phosphorus, and water stress [128] [129].

Here, we confine our attention to the primary functions associated with lateral roots, root hairs, root cluster growth, locally enhanced root proliferation, root tip, rhizosphere, and rhizosheath. The modulation of these functions can be incorporated into symbiotic fertilizers through the synthetic rhizosphere/synthetic root system.

Lateral roots: The density and length of the lateral roots are probably the two most important architectural phenotypes regulating root microbial associations, given that lateral roots comprise the large majority of root systems. They affect the root exudation zones, attachment surfaces, and the location along both vertical and horizontal gradients. Carbon exudation and the prime rhizosphere soil may initiate functions such as nitrification, ammonification, and soil organic matter degradation, either aerobically or anaerobically. Further, following the recruitment of PGPB by root exudation, root architecture can be modified, but the exploitation of such effects in agriculture is limited [127].

Root hairs: The functions of root hairs include changing the area, location, and type of attachment surfaces for microbes to the roots, and affect the composition of the root microbial communities. Longer and denser root hairs can have synergistic effects with microbes participating in nitrification and ammonification of organic matter, by extending the surface area for bacterial support, while increasing soil exploration. Although high root hair density implies increased carbon allocation through root exudation, thus increasing root metabolic costs, it is far outweighed by the benefits provided. These benefits can include plant nitrogen capture, biomass growth, competitiveness for nutrients, dictation of the rhizosheath size, and its protection from all types of stressors, and efficient water and nutrient absorption, especially those with limited mobility such as phosphate [127] [130].

Recently, a significant positive correlation was identified between root hair length and root hair density with relative-water content. This indicates the potential role of root hairs in mediating resilience under water shortages [131].

Root architecture and anatomy: Under low nutrient supply, root architecture and anatomy interact with rhizosphere microbiota in order to optimize nitrogen capture [132]-[134]. Synergies and trade-offs of microbial associations, as influenced by root anatomy and architecture to optimize nitrogen capture by crops, represent promising avenues for crop breeding and microbiome engineering [127].

Long roots and perennial crops: The advantages of long and extensive root systems are well known in accessing nutrients and water, and reducing nitrate leaching, which can justify the increasing root metabolic costs as in root hairs [127] [135]-[137]. Differences in biomass allocation are one major distinction, whereby annual plants allocate proportionately more biomass above-ground, while perennial plants allocate more biomass towards extensive root systems. Currently, annual cereals, oil seeds, and legumes are planted on almost 70% of cropland. This combined area supplies a similar portion (~70%) of all human calories. To provide food security for the increasing world population, in a worsening agricultural environment, perennial cereals and energy crops have been proposed to supersede annual plants [137]-[139]. Perennial energy crops were also advocated for soil carbon sequestration through extended root biomass and enhanced above-ground biomass yield, compared with annuals. It has been shown that perennial polycultures significantly outperform annuals in moderate fertility sites [136] [140].

Despite ongoing critiques that the perceived vision of perennials is unlikely to succeed, and unworthy of expanded investment [141] [142], recent research progress, theoretical considerations, and advances in breeding and genetic technologies have combined to provide justification for an aggressive expansion in perennial grain research in current and future decades, as reported by Olson *et al.*, [142] and DeHaan *et al.* [143].

Annual crops have relatively short growing seasons, shallow rooting depths, and lower root densities. This limits their access to nutrients and water, leaves croplands more vulnerable to degradation, and reduces soil carbon inputs and habitat for wildlife. Perennial crops capture, retain, and utilize more precipitation, have access to soil nutrients deeper within the soil, maintain more plant residues at the soil surface, and have a longer photosynthetic season. All of these benefits increase yearly light interception and enhance productivity. This farming system is resilient to flooding, extreme weather, and storms. In a perennial farming system, some commonly cultivated crops include plantain, banana, wheat, sorghum, and rice. Studies have revealed that axillary buds on perennial rice nodes have the ability to overwinter and subsequently develop into new plants during the following seasons, resulting in lower agricultural inputs [144]-[147].

Perennials prevent the depletion of soil resources in ecosystem restoration; the residual root systems promote the growth characteristics of ratoon crops such as sugar cane, in which their residues (such as sugar cane bagasse) provide a substantial quantity of biomass for annual bioenergy generation [148]. Over a period of time, perennials ultimately require lower rates of fertilizer, pesticide, and labour inputs; symbiotic/smart fertilizers are particularly suitable for these crops [12] [14].

4.7. Rhizosheath and Engineered Rhizosphere

It is clear that the rhizosphere is primarily responsible for regulating most of the plant root functions and interfacing them with microbiota, nutrients, and water, while responding to stressors through root exudation. Therefore, it is important to protect the rhizosphere and facilitate its functions so that plants can respond more efficiently to the rapidly evolving stressors due to climate change. In fact, most plants already have an inherent mechanism to protect and facilitate the rhizosphere through the formation of the rhizosheath. It is a soil-rich cover formed by the aggregation of soil and microbial communities. It is facilitated by a network of gel-forming (mucilage) hydrophilic metabolites (rhizodeposits). These are released by microbes (extracellular matrix responsible for biofilm formation), roots, and root tips in the presence of high root hair density and length. The rhizosheath is rich in water, nutrients, labile carbon, and microbial biomass [149]-[151].

The rhizosheath not only protects the roots and rhizosphere but also provides a protective nutrient-rich micro-environment for the soil microbiome. It is therefore a further manifestation of the symbiotic relationship between plant roots and plant-beneficial microorganisms. This symbiotic platform is particularly important under drought conditions and in deserts where the rhizosphere is an edaphic "mini-oasis" from which other competing microorganisms are excluded [152]. The ingression selectivity is likely to be achieved through the weaponization of antibiotics produced by the beneficial bacteria and mycorrhizal and saprotrophic fungi in the rhizosheath [153]. We can therefore assume that the SX-fertilizers also act as an artificial edaphic barrier for the protection of the mini-oasis generated by the SRS-medium.

Rhizosphere engineering aims to control and manipulate the biophysical properties of the rhizosphere and its components for specific goals, through agronomic, physical, chemical, biological, and genomic approaches [154] [155]. Wang and Kuzyakov [155] provided a recent review of this subject in the enhancement of soil carbon sequestration, and also proposed a number of future research activities to help understand the complex interactions between rhizosphere components and their outcomes. Zhang *et al.*, [156] proposed an entropic approach to rhizosphere engineering in which the nutrient supply administration was localized with improved information exchange, related to root-soil-microbe interactions. This resulted in an increase in nutrient-use efficiency. Localized fertilizer administration (rather than general fertilization of soil) is a known practice. This method is now further refined by on-demand, localized production, fertilizer use, and rhizosphere engineering [110].

Although the understanding of the root exudate composition, secreted under well-defined abiotic and biotic stressors, and associating each of the compounds with a type of stress so that these chemicals can be manufactured and used in the soil to combat plant diseases and improve crop yield, remains highly challenging. This process is somewhat akin to pharmaceutical manufacture and practice. Further complications include cost, loss of manufactured bio-stimulants in soil, and rapidly changing spatiotemporal soil conditions, especially due to weather events. Therefore, robust and cost-effective routes for fertilizer administration and agricultural practice under eCO_2, eTe, and eWe/eDe need to be devised, which should operate through the function of the root rhizosphere.

The synthetic rhizosphere approach is another route for the protection of rhizosheath functions and for crop yield enhancement, especially under water and nutrient stress.

5. Synthetic Rhizosphere/Rhizosheath: Artificial Root System

Synthetic RhizoSphere/RhizoSheat (SRS), which can also be considered a synthetic root system. Due to its mechanism and efficiency in biomass growth and crop yield enhancements (especially under nutrient and water stress), the SRS–method represents another example of phenomenon-based process intensification in agriculture [46].

All of the process intensifications described above were carried out by using highly hydrophilic, elastic, swellable (upon contact with water) micro-molecular porous soil additives (SRS-medium) with a well-prescribed physical-chemical-biological structure. In order to utilise the benefits of size-dependent response, they can also contain nutrients, beneficial bacteria/fungi, and useful chemical moieties for cation or anion exchange capability. This can also control the rate of biodegradability. These characteristics of the SRS-medium are essential in order to direct the growing roots towards the SRS-medium in the soil, and then ingress into the SRS-medium, thus creating a micro-environment for efficient interaction between water, nutrients, bacteria, fungi, and plant rhizosphere/root at the micron scale. This can also protect the micro-organisms and plant roots from soil predators.

It is important to note that, root ingression does not take place in laboratory experiments when model soils such as perlite particles are used. In this case, roots simply grow through the interparticle spaces.

The above summary of the SRS-technology indicates that the wide-ranging abilities of the rhizosphere are not compromised when responding to various temporal-spatial stressors or its communication with other soil components. SRS-medium protect the rhizosphere and facilitate its functions. Therefore, SRS-technology differs substantially from engineering plant genes and rhizosphere/rhizosheath or the identification, isolation, and synthesis of specific chemicals exuded by the roots for a specific function. Nevertheless, all these technologies are useful and fundamental. They can be co-developed and integrated to achieve a highly efficient rhizosphere-technology in the fight against climate change and food security. As summarised next, SRS-technology has been applied to various crops and plants, resulting in process intensification of up to ca. 300% for grass under water-nutrient stress, but lower efficiency of ca. 60% for legume fruits. These productivity enhancements obtained in greenhouse cultivations using PHP-based SRS-medium are far above the enhancements obtained by other published methods. Compared with other porous/semi-porous soil additives (including hydrogels, super absorbent polymers, and biochar), the biological, chemical, and physical versatility of PHP offers an outstanding opportunity to develop an equally versatile synthetic root system. Therefore, we highlight the performance of the SRS-medium and the underlying mechanism for plant productivity enhancement using PHP.

5.1. Performance and Mechanism of SRS-Based Agro-Process Intensification

The performance and mechanism of SRS-medium in agriculture have been evaluated using greenhouse experiments, the details of which are available and closely related to BioProcess Intensification [3] [4] [12]-[14] [46]-[51] [88]. Here, the effects of SRS-medium on biomass and crop yield are demonstrated in three settings: (1) Biomass yield enhancement using ryegrass as a model non-woody, non-leguminous plant and fertilizer containing SRS-medium; (2) Enhancement of fruit (pea pod) yield and its nutritional characteristics using the pea as a model legume and nitrogen-fixing bacteria (*Rhizobium leguminosarum*) inoculated SRS-medium; (3) Enhancement of biomass yield using lawn grass as a model non-leguminous plant and nitrogen-fixing bacterium (*Azospirillum brasilense*) inoculated SRS-medium. In each case, the enhancement levels are provided, and the plant root – SRS medium interactions are demonstrated through SEM images of the root-PHP systems. In all cases, biological samples were prepared using the procedure described previously [12]-[14].

In all cases, sulfonated-neutralised PHP (sn-PHP) was used after washing and drying the samples to remove any acid/ammonia. The SRS-medium constituted 0.5 wt% of the soil in plant pots placed in greenhouses and subjected to various watering and nutrient programs.

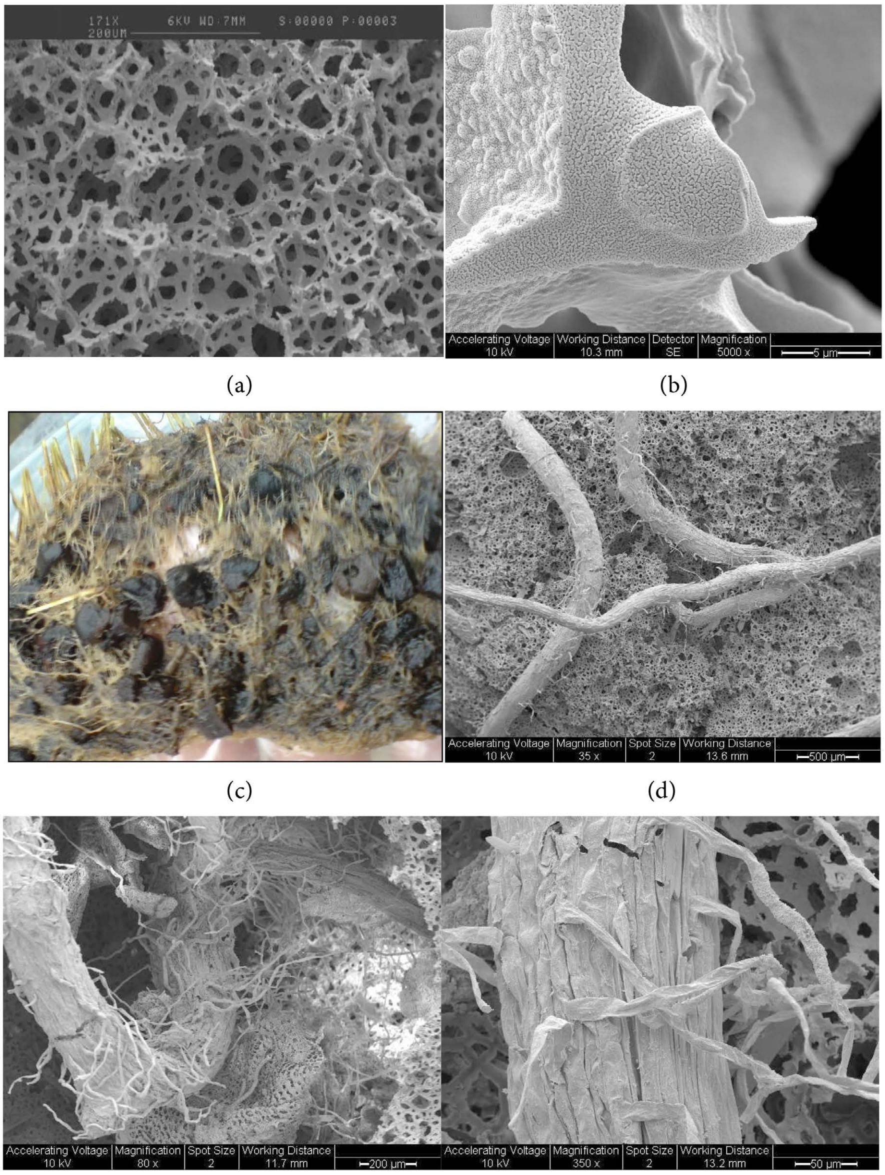
5.2. Biomass Yield Enhancement Using Grass as a Model Non-Woody, Non-Leguminous Plant and Fertilizer Containing SRS-Medium

The use of ryegrass as a model perennial plant is useful because abiotic/biotic stresses can be tested over a long period of time and harvests. In these sets of experiments, root growth is directed to the SRS-medium through hydrotropism and chemotropism driving forces. Washed and dried sn-PHP was mixed with certain amounts of nitrogen fertilizer solution. An equivalent amount of fertilizer solution was added directly to the plant pots after seeding the soil. The results, which demonstrate the merits of the SRS-medium, are shown in **Table 1** and **Figure 13**.

Table 1. Ryegrass growth: Average % change with respect to the control for cubical (5^3 mm^3) sn-PHP with an average pore size of 150 μm and different SRS-medium/fertilizer combinations and harvests under daily watering (25 cm^3/pot-day). From reference [13].

Harvest Time (days)	Significant ($p < 0.05$) changes in yield with respect to the control (%)									
	sn-PHP (no fertilizer)		Miracal-Gro fertilizer (MG)		MG & sn-PHP		Nitram fertilizer (AN)		AN & sn-PHP	
	Fresh	Dry	Fresh	Dry	Fresh	Dry	Fresh	Dry	Fresh	Dry
21	46.9	36.4	21.9	NS	44.1	38.4	NS	NS	35.9	26.3
42	45.6	29.9	NS	NS	59.9	53.8	NS	NS	35.7	NS
63	98.3	99.1	NS	NS	135	123	NS	NS	143	98.3

Fresh = Fresh yield; Dry = Dry yield; NS = No significant ($p > 0.05$) change in yield. For further details (including the commercial fertilizers (MG) and (AN)), see Reference12.



(a) (b)

(c) (d)

(e) (f)

Figure 13. SEM and photo (c) images of elastic/highly swellable sn-PHP illustrating the plant root association. (a) SEM image of sn-PHP used in the experiments; scale bar = 200 µm; (b) Porous structure of the walls, scale bar = 5 µm; (c) Ryegrass root association with sn-PHP after 63 days of cultivation (size of the sn-PHP ca. 5 mm); (d) Fracture surface of the sn-PHP showing several roots, one of which is branching; scale bar = 500 µm; (e) Root structures and sn-PHP environment created by the root and sn-PHP interaction; scale bar = 200 µm; (f) Enlarged view of a root with root hairs penetrating into the sn-PHP; scale bar = 50 µm. Reproduced from references [12] [13].

Table 1 clearly shows that sn-PHP provides enhanced yield (both fresh and dry biomass) in the presence or absence of commercial fertilizers. The relative increase in yield increases with increasing harvest number as the initially administered fertilizer depletes. The maximum yield enhancement over the control is 135% (fresh biomass) and 123% (dry biomass). The dry biomass yield enhancement increases substantially under drought conditions (weekly watering) and reaches 240% provided that sn-PHP is administered in powder form (size range 100 μm – 2000 μm) [13] [88] [89]. Under drought conditions, fresh biomass enhancement is only 109%.

Table 1 also differentiates the performance of two different commercial fertilizers, although their effects in biomass enhancement by sn-PHP only become significant at the third harvest. There are two mechanisms for this behaviour: First, sn-PHP acts as a slow-release fertilizer, and second, by the time of the third harvest (63 days after seeding), roots reach all of the sn-PHP particles and associate with them, as seen in **Figure 13**.

Figures 13(a,b) illustrate the architecture of the SRS-medium. Here, the sn-PHP pore volume is 90%, and the pore walls are nano-porous, with an average pore size of 150 μm, obtained through the method described previously [7] [13] [14]. The photo image of the SRS-medium and root association is shown in **Figure 13(c)**, while the SEM images in **Figures 13(d-f)** illustrate the structure of the roots within the SRS-medium, which itself is modified, compared with **Figure 13(a)**. The open pores of the original sn-PHP structure (**Figure 13(a)**) are substantially filled, and roots with diameter ca. 200 μm are present (d-f), along with root hairs (diameters ca. 20 μm). The roots are able to branch out (**Figure 13(d)**), and the root hairs penetrate into the pores through sn-PHP interconnecting holes. Furthermore, **Figure 13(e)** clearly shows the modification of the root architecture.

5.3. Enhancement of Fruit (Pea Pod) Yield and Its Nutritional Characteristics Using Pea as a Model Legume and Nitrogen-Fixing Bacteria (Rhizobium leguminosarum) Inoculated SRS-Medium

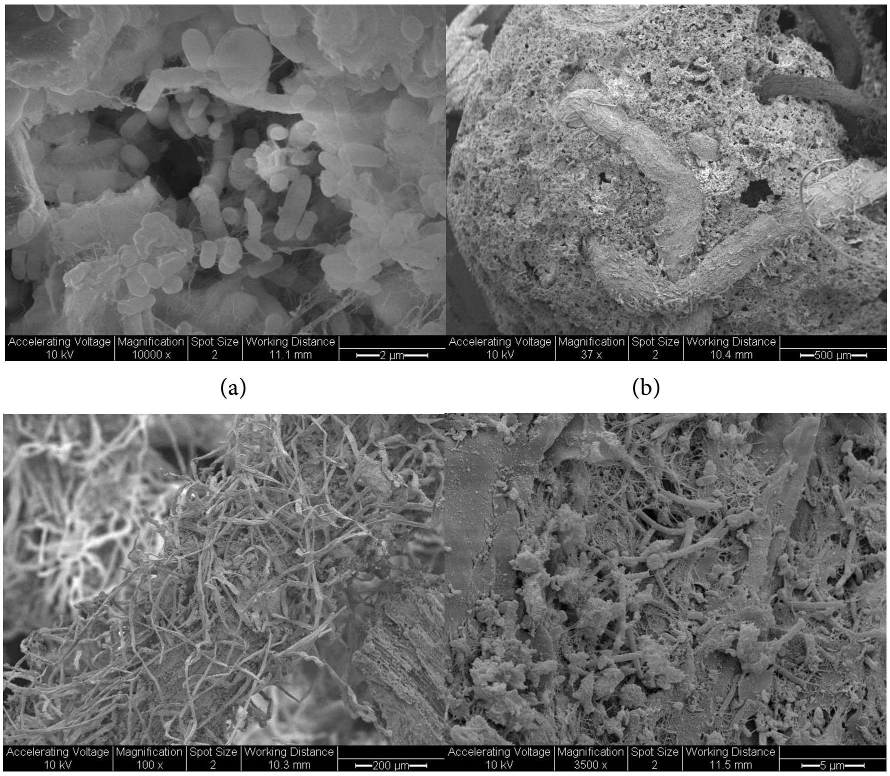
It was shown that non-biological SRS-medium is only useful under nutrient and water stress [12] [13]. In order to demonstrate the effect of supported bacteria in close proximity to plant roots, sn-PHP was inoculated with a nitrogen-fixing bacterium, *Rhizobium leguminosarum* and mixed with soil in plant pots. The equivalent number of bacteria was used in the soil when no sn-PHP was present. Sn-PHP was also used by itself (no bacterium) as a baseline for the inoculated sn-PHP. The final set was the control group, which did not have any bacteria or sn-PHP, and the results were compared with this control group. The structure, dimensions, and the amount of sn-PHP used were identical to the previous example (ryegrass growth). After planting one pea seed per pot, the pots were watered with 50 ml of water for the next 42 days, after which the pea crop and the shoots (biomass) were removed separately and weighed immediately, as well as after drying them.

The results are summarized in **Table 2**. It was found that the only statistically significant enhancement ($p < 0.05$) was when sn-PHP was used with *Rhizobium leguminosarum*. In this case, the dry pea yield was enhanced by 69.6%, whereas dry biomass enhancement was 31.0%.

The reason for this behavior is that as the pea plant roots grow through the *Rhizobium* inoculated sn-PHP, bacterial infection and nodulation take place. The visual examination of inoculated sn-PHP shows that nodulation only took place if the roots passed through the sn-PHP, indicating that the bacteria dispersed freely in soil did not have sufficient concentration to cause extensive infection and nodulation.

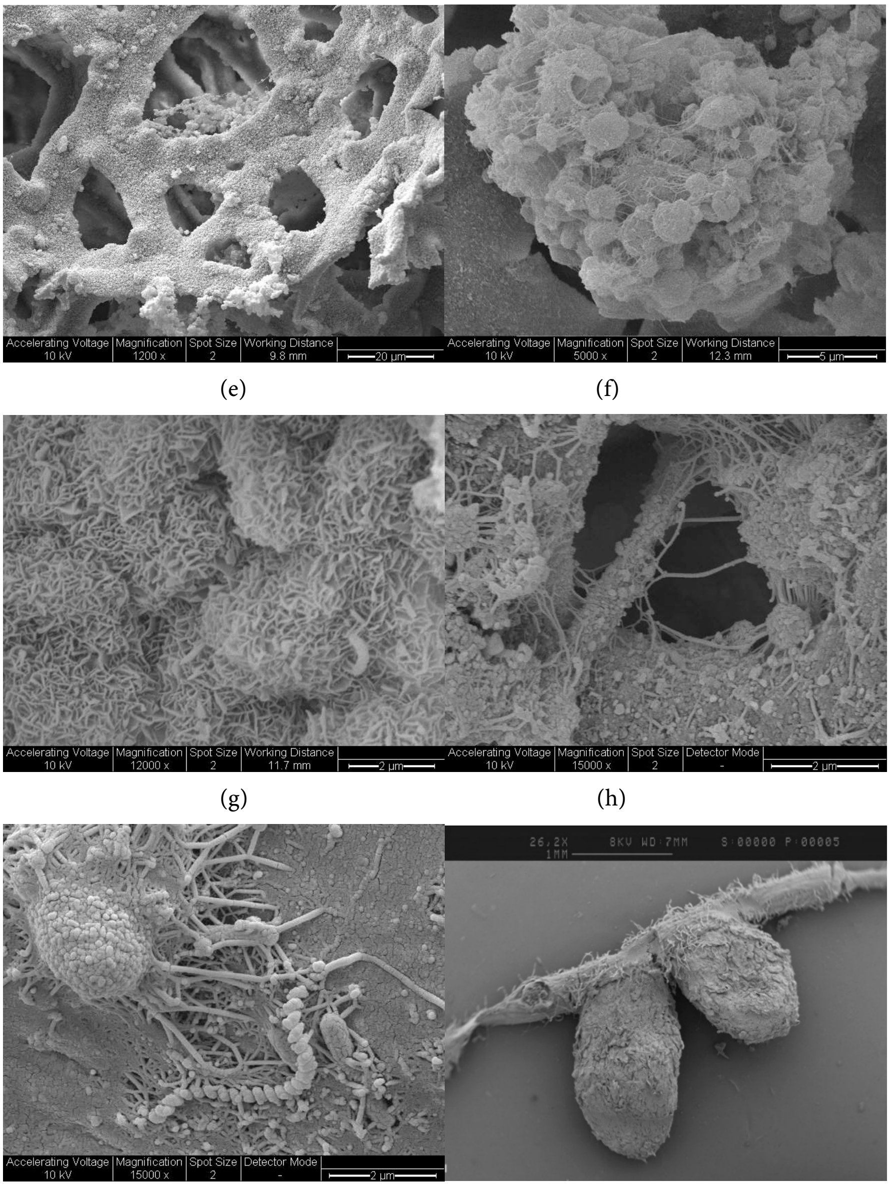
Table 2. Percentage difference in nutrient and mineral content of various growth regimes compared with the control group in which the soil does not contain any sn-PHP or bacterium. From Reference [13].

Element	Relative enhancement/reduction with respect to control pea growth					
	sn-PHP (no bacterium)		Bacteria in soil		Bacteria in sn-PHP	
	Shoot	Pea	Shoot	Pea	Shoot	Pea
Nitrogen	9.63%	20.11%	−45.85%	7.06%	−11.59%	65.49%
Phosphorus	15.01%	16.96%	−41.07%	28.85%	5.61%	90.18%
Potassium	21.87%	11.80%	−36.44%	19.93%	15.84%	81.15%
Magnesium	26.63%	22.67%	−20.16%	10.81%	25.53%	78.11%
Calcium	14.37%	24.55%	−21.12%	9.11%	26.95%	88.72%
Sulphur	−17.36%	9.75%	13.51%	28.31%	13.19%	70.37%
Manganese	44.01%	15.85%	−20.58%	4.66%	−10.95%	7.74%
Copper	35.93%	−10.83%	−33.11%	17.95%	10.71%	25.87%
Iron	156.23%	81.44%	403.78%	106.05%	34.35%	54.03%



(a) (b)

(c) (d)



(e) (f)

(g) (h)

(i) (j)

Figure 14. Biological SRS-medium in the form of *Rhizobium leguminosarum* inoculated sn-PHP illustrating the various aspects of a synthetic rhizosphere after 42 days in soil with pea plant. (a) *Rhizobium leguminosarum* colony in sn-PHP after inoculation and before its deployment in the soil with pea plant (scale bar = 2 μm); (b) Extensive plant roots within the sn-PHP at low magnification (scale bar = 500 μm); (c) Pea plant root and root hairs (scale bar = 200 μm); (d) Micro-environment within the pores containing roots, root hairs, bacteria (scale bar = 5 μm); (e) Surface of a pore with extensive coverage with rhizodeposits (scale bar = 20 μm); (f) Bacterial colony in the SRS-medium after 42 days of cultivation (scale bar = 5 μm); (g) Several bacteria covered with rhizodeposits (scale bar = 2 μm); (h) Presence of a micro-environment showing several features including fungi and rhizodeposits (scale bar = 2 μm); (i) A bacterium covered with rhizodeposits (scale bar = 2 μm); (j) Two root nodules with surface deposits and an emerging third nodule on the same root (scale bar = 1 mm). From references [12] [13].

Another important finding was that *Rhizobium* inoculated sn-PHP had the highest protein content (as apparent from the nitrogen and phosphorus content of the dry pea crop) as well as micronutrient metals. These results are shown in Table 2. Except for iron, when sn-PHP is used with bacteria, the mineral content of both shoots and pea are higher compared with the case when sn-PHP was not used.

Figure 14 illustrates the stages of micro-environment development within the sn-PHP after its inoculation with *Rhizobium leguminosarum* and use as the SRS-medium. Figure 14**a** shows the establishment of a *Rhizobium leguminosarum* colony within the sn-PHP after 14 days of incubation. Here, 2 μm long *Rhizobium leguminosarum* can be identified together with their extracellular matrix building the colony. The inoculated sn-PHP can either be mixed with soil immediately after inoculation or following an incubation period, which ensures extensive colonization within the SRS-medium.

The extensive root coverage in sn-PHP is shown in Figures 14(b-d). In these figures (with increasing magnification) there is extensive coverage of sn-PHP pores with roots (Figure 14(a)), root hairs (Figure 14(c)), and bacteria, as well as what appears to be fungi (Figure 14(d)). As seen in Figure 14(b), the root diameter (ca. 200 μm) is significantly greater than the pore and interconnects, which are shown in Figure 14(e). This figure shows that the surface of the pores is covered with rhizodeposits. Figure 14(f) illustrates a bacterial colony, which however appears to be different from the colony when bacteria are incubated in the laboratory under sterile conditions. Figures 14(g-i) illustrate various types of micro-environments in the SRS-medium. They show the presence of extensive rhizodeposition, which includes secondary metabolites and root exudates [157] [158]. Figure 14(j) shows the presence of two root nodules as well as a third emerging nodule on a small root length. Due to their size, the nodules are always outside the SRS-medium, although the root infection is primarily in the SRS-medium.

5.4. Enhancement of Biomass Yield Using Grass as a Model Non-Leguminous Plant and Nitrogen-Fixing Bacterium (*Azospirillum brasilense*) Inoculated SRS-Medium

Azospirillum are free-living, nitrogen-fixing, plant growth-promoting rhizobacteria which are able to colonize the roots of hundreds of plant species and significantly improve their growth, development, and productivity under field conditions. For example, wheat yield has been increased by approximately 30% by inoculation with *Azospirillum brasilense* [159]-[161]. Several of their functions have been studied, which indicate that there are multiple mechanisms involved in their ability to promote plant growth [161]. They can be used as a bio-fertilizer as well as in the co-inoculation of legumes with rhizobia, which results in enhanced crop yield in the region of 30%. More recently, their applications have been extended to biotechnology [161].

Table 3 summarizes the biomass yield enhancement when sn-PHP was inoculated with *Azospirillum brasilense* and used as an SRS medium, in the same way as described in the previous two sections in greenhouse experiments. There were four groups of soil treatment. 1) Control group: Soil in the plant pots did not contain any bacterium or sn-PHP; 2) Soil contained 0.5 % sn-PHP; 3) Soil contained inoculation medium; 4) sn-PHP had the same amount of bacterial inoculation as in (3) [162]. The ryegrass was watered every day and harvested every 3 weeks when the dry weights were determined. The results were compared with respect to the control group as a percentage of biomass yield enhancement.

Table 3 indicates that sn-PHP provides good biomass growth enhancement after 6 weeks when the root penetration into the SRS-medium is completed. However, when the soil nutrients are depleted (12 weeks of growth period), its performance is reduced, but still above that of the control. When *Azospirillum brasilense* was placed in soil, the best performance of ca. 30% is similar to that observed previously in field trials [160] [161]. Further, when sn-PHP was used as the support for *Azospirillum brasilense*, the highest enhancement was 145% after 12 weeks. Initially, the enhancement was low due to the fact that the grass roots needed to penetrate into the SRS-medium and the bacteria needed to proliferate within the pores. The SEM study of the root association with sn-PHP indicates that the root architecture within the SRS-medium is very similar to those illustrated in **Figure 13** and **Figure 14**.

Table 3. Lawn grass growth using *Azospirillum brasilense*: Average % change with respect to the control (Group-(i)) using cubical (5^3 mm^3) sn-PHP with an average pore size of 150 µm with twice weekly watering (50 cm^3/pot-day).

Harvest time (weeks)	Biomass enhancement with respect to the control (%)		
	Group-(ii) sn-PHP only	Group-(iii) Bacterium only	Group-(iv) bacterium in sn-PHP
3	7.4	11.7	9.6
6	36.2	14.3	9.5
9	70.3	29.7	40.5
12	18.2	18.2	145

5.5. The Effect of Nitrogen Fixing Bacterium (*Bradyrhizobium japonicum*) with or without sn-PHP on Soybean Growth under Nutrient Stress

The effect of sn-PHP containing the bacteria (*Bradyrhizobium japonicum*) was investigated on soybean growth, under both normal and reduced water conditions, but in the presence of reduced soil nutrients. *B. japonicum* is a gram-negative, nitrogen-fixing bacteria that forms a symbiotic relationship with soybean plants. The effect of the biologically active SX-fertilizers in fixing nitrogen from air is not immediately obvious because, in the presence of readily available soil nitrogen, legumes prefer to use the available nitrogen from the soil. In order to accelerate the bacterial effects, the nutrient content of the soil used in the present greenhouse experiments was reduced by successive washings using tap water. Before and after washing, the soil nutrient content was: Nitrogen = 0.22 wt% and 0.14 wt%; Phosphorus = 8.66 μg/ml and 5.87 μg/ml; Potassium = 203 μg/ml and 109 μg/ml, respectively. Sulfonated neutralised PolyHIPE, sn-PHP, was either used without any bacterium or with *B. japonicum.* Each pot contained 500 g soil and sn-PHP use was 2.5 g/pot. *B. japonicum* inoculation with 2.5 g sn-PHP was carried out using Hoagland's nitrogen-free nutrient solution [12]. Two watering regimes were used: (1) Normal watering with 100 ml water per pot twice weekly; (2) Droughted soybean was given 50 ml water per pot, twice weekly.

A summary of the results is shown in **Figure 15**. Dry shoot and root weights obtained under normal and drought watering are presented for: (1) Control (contains no sn-PHP or *B. japonicu*); (2) Same as the "control" with sn-PHP; (3) Same as the "control" with *B. japonicu*; (4) Same as (2) but sn-PHP contains *B. japonicu.* The presence of sn-PHP (without *B. japonicu*) results in a 97% enhancement in shoot dry weight under normal watering. Under drought conditions, the corresponding enhancement was 87%. The enhancement in dry root weights for normal and droughted watering was 54% and −9.9% (which is, however, statistically not significant), indicating that the biomass enhancement in the presence of sn-PHP has been achieved with a lesser amount of root, indicating that sn-PHP does act as an artificial root, especially under drought conditions. These results also indicate that under drought conditions, root dry weight increases, while the reverse is true in the presence of sn-PHP.

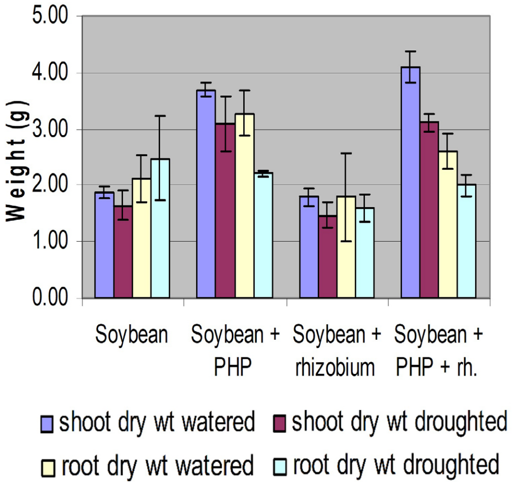


Figure 15. The effect of nitrogen-fixing bacterium, *Bradyrhizobium japonicum*, with or without sn-PHP on soybean growth under water and nutrient stresses. From reference [162].

When *B. japonicum* is administered into the soil, there is no statistically significant change in the dry shoot and root weights. When *B. japonicum* is administered within sn-PHP, the dry shoot and root weight increases in normally watered plants are 121% and 25.6%, respectively. The corresponding shoot and root dry weights for droughted watering are 25.6% and −18%, respectively. These trends are the same as in the previous cases studied here. It is interesting to note that under droughted watering, root weight decreases (or increases slightly) in the presence of sn-PHP compared with the control (no sn-PHP). The increase in shoot weight due to bacteria within sn-PHP is 25% under normal watering. With droughted watering, this increase is 5%. However, the enhancement of SB-fertilizers on biomass and crop yield is more pronounced over a longer time scale as the soil becomes more depleted in nutrients.

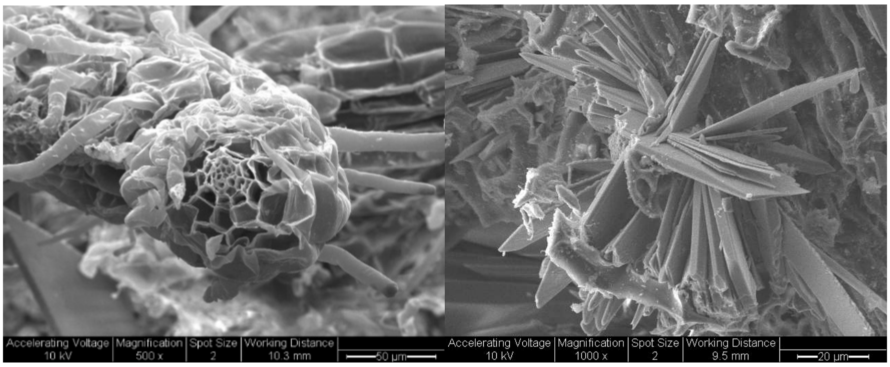
Fertiliser levels fall during plant growth as a result of wash-out and plant metabolism. As shown earlier, for example, in grass growth, the effect of the SRS-medium started to show after the second or third harvest under normal watering. As nutrients were already depleted, the beneficial effects of the SRS-medium became clear immediately even with normal watering. Under water stress, the observed effects are similar to those observed in our previous studies [12]-[14] [162]. Under water stress, although there is substantial enhancement in biomass yield, the increase in root weight in the presence of polymer is not significant, indicating that the available root mass is sufficient to sustain enhanced biomass growth.

The advantages of long and extensive root systems are well known in accessing nutrients and water, and reducing nitrate leaching, which can justify the increasing root metabolic costs as in root hairs [127] [135]-[137] [163] [164]. Differences in biomass allocation are one major distinction, whereby annual plants allocate proportionately more biomass aboveground, while perennial plants allocate more biomass towards extensive root systems. The soil carbon sequestration potential [164] is also affected by the root characteristics [163]. Plants also adapt to environmental stresses through alterations in root morphology and plasticity [164]. It is possible that SRS-medium facilitates such alterations (such as longer root hairs) so that the root system becomes more efficient.

According to DeLisi *et al.*, [165], the difference between atmospheric GHG levels that will be reached if current trends continue, and levels that would be achieved if the goals of the US decarbonization plan are met—even with worldwide implementation—is inconsequential. Therefore, DeLisi *et al.*, [166] and Gidding [167] argue that any mitigation strategy must include the drawdown of atmospheric greenhouse gases and advocate a particular drawdown strategy, agrigenomics, offering the opportunity for a revolutionary trifecta: climate change mitigation, food security, and medical advances. DeLisi *et al.*, [166] thus propose to use synthetic and systems biology techniques to reduce greenhouse gases. These techniques include, among other possibilities, engineering plants to convert CO_2 produced by respiration into a stable carbonate, designing plants with an increased root-to-shoot ratio, and creating plants with the ability to self-fertilize. The foregoing analyses for the AR-system indicate that the feasibility of these aims has already been achieved. For example, the inclusion of nitrogen-fixing bacteria both for legumes (Section 5.3, using *Rhizobium leguminosarum*) and non-legumes (Section 5.4, using *Azospirillum brasilense*) achieves a constant supply of nitrogen and micronutrients. Also, by placing SX-fertilizers at different levels in the soil, roots can grow deeper as a result of hydro-, chemo-, and bio-tropisms [3]. In any case, a switch to perennial crops will achieve this objective. However, the enhancement of the root-to-shoot ratio also means reduced biomass and crop productivity. The long-term mineralization of CO_2 by using the AR-system has also been discussed previously (Section 4, and reference [3]).

One of the important advantages of the proposed AR-system based on bacterial SB-fertilizer is that several different SB-fertilizer grades can be prepared and used in the soil, each grade producing different metabolites in the rhizosphere in order to enhance the root exudate functions, including photosynthesis, plant resource-use efficiency, and facilitating the crosstalk between plant and soil microbes to remedy stresses [168]. For example, the generation of specific metabolites (enzymes) can significantly enhance photosynthesis as shown in artificial photosynthesis [169] [170].

5.6. Calcium Oxalate Formation



(a) (b)

Figure 16. Calcium oxalate crystals and grass root within sn-PHP in soil (Scale bar = 50 µm). (a) Root and root hairs with calcium oxalate crystal; (b) Same as in (a) at a higher magnification, showing several calcium oxalate crystals growing within the pores of sn-PHP (Scale bar = 20 µm). From reference [82].

Calcium oxalate, $Ca(COO)_2$, (denoted as CaO_x), a mineral of low solubility, is found widely in plants, but its fate in soils has been neglected until recently. A comprehensive review by Uren [171] considers the likely forms and reactions in soils that may be significant in the recycling of both calcium (Ca) and carbon (C). In soils, calcium oxalate is both formed by fungi and utilized by saprotrophic microbes and by some mesofauna as a source of energy and C. In acidic soils, the oxidation releases soluble products, the Ca as Ca^{2+} and the C as bicarbonate, whereas in alkaline soils some Ca is released as Ca^{2+} but some C and Ca^{2+} form calcium carbonate, which may contribute to the formation of calcrete, usually in soils found in arid regions. This latter reaction has been considered as a possible major pathway, which may be utilized in the sequestration of carbon dioxide [171]. Calcium carbonate formation is favored by degradation of CaOx by oxalotrophic bacteria accompanied by an increase in soil pH in a process known as the oxalate-carbonate pathway [171] [172]. In their recent review, He *et al*., [173] conclude that CaOx has far-reaching implications in plant physiology, ecology, and human health. Physiological roles include calcium regulation, defense against herbivory, and potential contributions to carbon sequestration, while they have ecological significance in nutrient cycling and plant-soil interactions. However, concerns over human health are due to kidney stone formation and the potential hazards posed by these crystals in human nutrition, particularly in the context of oxalate-rich diets and kidney stone formation [173].

Figure 16 shows that CaO_x is also produced within the sn-PHP either by ingrown fungi or plant roots. It is likely that crystal growth within the pores will have a different crystal structure from that grown from solution or with the soil.

5.7. Hypercrosslinked PolyHIPE Supported Spent Nano Catalysts as Fertilizers for Micronutrient Delivery

5.7.1. Quantum Catalysts for the Delivery of Micronutrients to Plants

Crop yields and nutritional security are extremely dependent on the climatic conditions projected for the future, and consequently, most of the food produced for human consumption is under its menace [174] [175]. Elevated CO_2 is closely related to increased demands for nutrients and water for plant growth [176]. The artificial root system is primarily designed for efficient delivery of the essential (H, C, O) and primary macronutrients (N, P, K) to the plant while promoting the plant's own defence mechanisms against biotic and abiotic stresses. **Figure 17** illustrates the macro- and micro-nutrients, which indicate the hierarchy of the macro- and micro-nutrients. **Figure 17** also indicates that Group 3d transition metals as catalysts ranging from Sc to Zn are also included in the list of micronutrients, including Mn, Fe, Ni, Cu, Zn (primary micronutrients), and Co as the secondary micronutrient [177].

The other primary micronutrients include B, Cl, and Mo (Group 4d catalyst), while the emerging secondary micronutrients include Na, V, Se, Si, and Al. Some of these non-transition metals used as primary/secondary macro/micro-nutrients (K, Ca, Mg, S, B) are also used as catalyst promoters in the QCs [178]. Therefore, in choosing the composition of the QCs, their post-service function as micronutrients should be considered to provide full circular economy.

Compared with the essential and primary macronutrients, the effect of climate change on micronutrients has not been investigated until recently. It is known that when agricultural yields are reduced because of inadequate soil micronutrient concentration, malnutrition may result. Deficits in soil micronutrients can result from a number of variables, such as the use of intensive cropping practices, micronutrient leaching, soil characteristics, and decreased use of farmyard waste [177]. **Figure 18** shows some of the primary micronutrient requirements at various stages of plant growth [179].

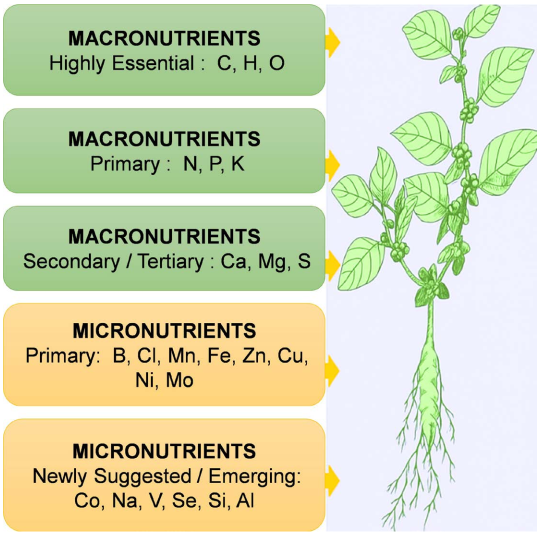


Figure 17. The hierarchy of the essential macro- and micro-nutrients [both minerals and non-minerals] for plant growth. Reproduced from Kerry *et al.*, [177].

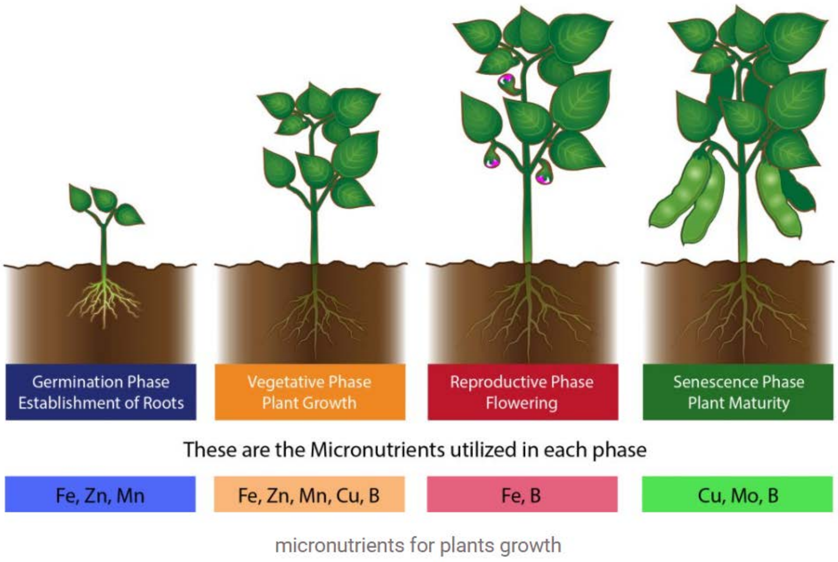


Figure 18. Micronutrient use at various stages of plant growth. Reproduced with permission from Indian Micro Fertilizers Manufacturers Association (IMMA) [180] (See also Tiwari *et al.*, [179]).

The function of these micronutrients was summarised by Marschner [181] as: **B:** Sugar metabolism, flowering, fruit and seed development; **Mn**: Photosynthesis; **Fe**: Chlorophyll synthesis; **Cu:** Enzyme activation and nitrogen metabolism; **Zn:** Early growth and development. This summary clearly indicates the root-leaf connectivity as the availability of B, Mn, and Fe directly affects leaf function. Therefore, micronutrient limitation has particular importance because of their role in key biochemical pathways, which in turn has an impact on the susceptibility of plants to biotic and abiotic stresses. However, the response largely depends on plant genotype, and each mineral element has complex interactions with several changing climate variables [182].

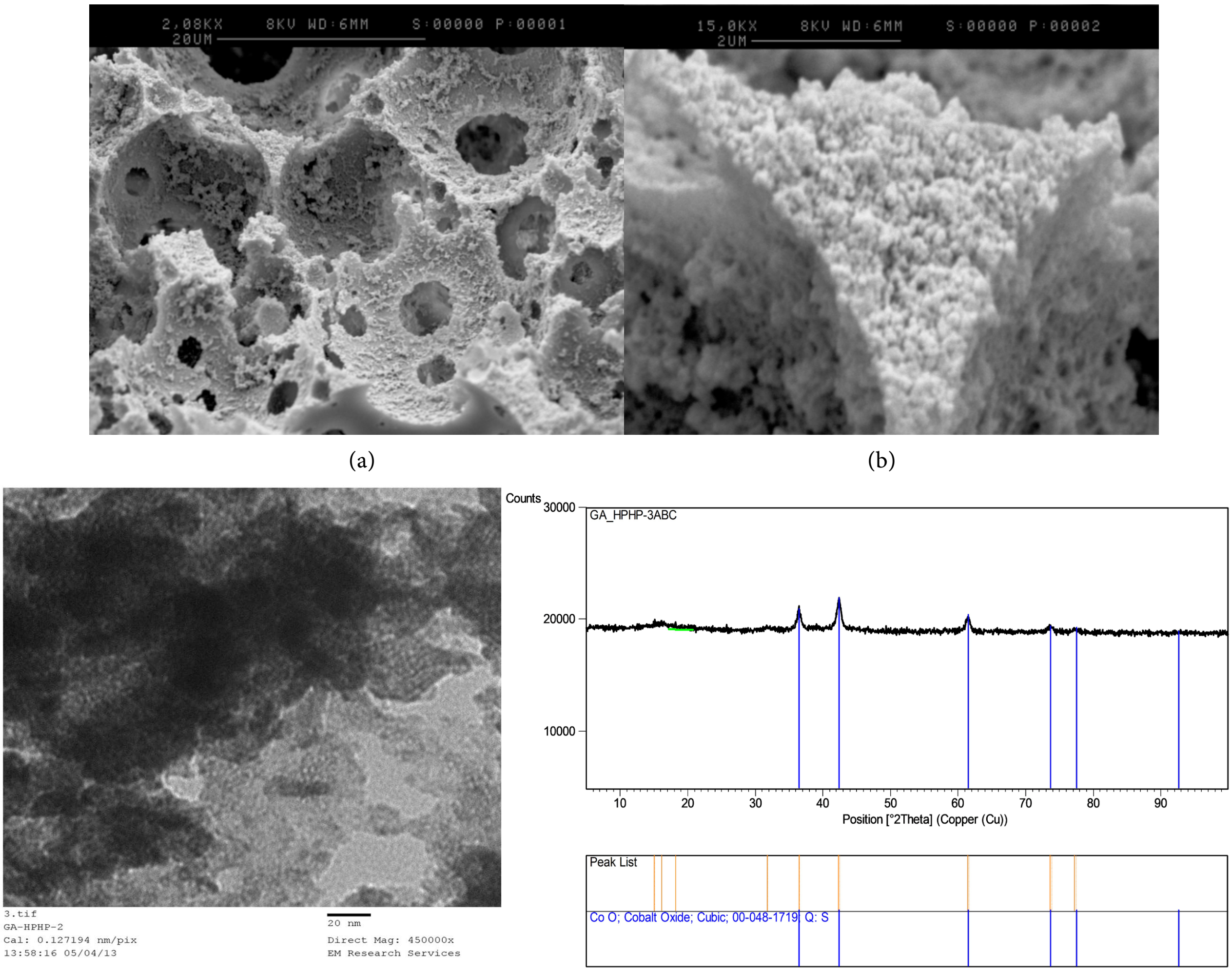
Numerous studies have been carried out to investigate soil micronutrient absorption and bioavailability. In order to improve crop utilization of soil nutrients, Tiwari *et al.*, [179] provided a recent analysis of the relationships between plant functions and soil nutrients. The internalization of micronutrients through the transcellular transport mechanism by plant or mammalian cells is dependent on the biological and dynamic barriers involved, as well as particle characteristics such as size, shape, charge, and surface chemistry [183] [184]. The particle physicochemical properties also determine the biological function of the internalized particles. Further, in plants, there appears to be a defensive biochemical pathway to exclude toxic particles (including nano- and micro-plastics) through the thickening of the cell wall via lignin synthesis, carbohydrate metabolism, and lipid transport [185].

5.7.2. Hypercrosslinked PolyHIPE Polymer as Catalyst Support and Symbiotic Fertilizer

Although the silica-supported QCs can deliver both silica and metals in the micronutrient category (such as B, Mg, V, Mn, Fe, Co, Ni, Cu, Zn, Mo, Si, S, Se) either as a catalyst or catalyst support/promoter, their pore structure (pore and interconnect size) is not suitable for root penetration and their association with the plant. They can be used in porous sachets as particles. Alternatively, Hypercrosslinked PolyHIPE Polymer (HX-PHP) or Sulfonated Hypercrosslinked PolyHIPE (sHX-PHP) supported nano-catalysts can be used as AR at the end of their service life. Hypercrosslinked Polystyrene (HXPs) or Sulfonated Hypercrosslinked Polystyrene (sHXPs) have a very high surface area by virtue of their extensive pores in the nano-to-subnano scale. Due to increased crosslinking density, the start of polymer decomposition increases by about 100˚C [186]. Furthermore, as shown by Mikkelsen *et al.*, [187], the dielectric constant of polymers is similar to that of silica but the dielectric constant of sHXPs increases with the increasing degree of sulfonation by an order of magnitude while its electrical conductivity enhancement reaches three orders of magnitude. Other applications and preparation methods of HXPs and sHXPs are available [188] [189].

Therefore, both HX-PHP or sHX-PHP can be used as catalyst supports instead of SiO_2 or Al_2O_3. Recently, Markova *et al.*, [190] using XHPs, inserted Fe and Ru co-catalysts for Fischer-Tropsch synthesis, obtaining a high yield of high hydrocarbons. However, the synthesis of HX-PHP or sHX-PHP or their use as catalyst supports is not currently available. Catalytic HX-PHP and sHX-PHP can be used as fertilizers at the end of their service life for the delivery of micronutrients. Alternatively, Hypercrosslinked PolyHIPE (HX-PHP) or Sulfonated Hypercrosslinked PolyHIPE (sHX-PHP) supported nano-catalysts can be utilized as AR at the end of their service life, thus providing a circular economy and environmental management.

The preparation of such HX-PHP or sHX-PHP supported catalysts has been conducted recently [82]. **Figures 19(a,b)** illustrate the scanning electron microscopy image of the HX-PHP after synthesis at two magnifications. It can be seen from **Figure 19(a)** that the usual PHP structure is still present, but it is partly obscured by the presence of Friedel-Crafts catalyst ($FeCl_2$) particles, but otherwise, the usual PHP structure is maintained. **Figure 19(b)** illustrates high wall porosity, which is also reflected in its very high surface area (ca. 1000 m^2/g). **Figure 19(c)** illustrates the transmission electron microscopy image of a HX-PHP after the removal of $FeCl_2$ by 1,2 dichloroethane solvent extraction followed by $Co(NO_3)_2$ catalyst precursor insertion and the subsequent decomposition of $Co(NO_3)_2$ under plasma in a H_2 stream. The XRD spectrum of the resulting HX-PHP with cobalt catalysts is shown in **Figure 19(d)**, which shows that $Co(NO_3)_2$ decomposed to CoO. The catalyst particles mainly appear to be located around the nano-sized pores in the form of rings. Therefore, the nano-sized pores are not blocked up with the catalyst.



(a) (b)

(c) (d)

Figure 19. Electron microscopy images and XRD of the HX-PHP at various stages of processing. (a) Scanning electron microscopy (SEM) image of the pore morphology after synthesis (Scale bar = 20 μm); (b) SEM image of the HX-PHP wall structure (Scale bar = 2 μm); (c) Transmission electron microscopy of HX-PHP after catalyst insertion and plasma treatment under hydrogen atmosphere (Scale bar = 20 nm); (d) XRD spectrum of the CoO catalyst containing HX-PHP after treatment in plasma under hydrogen atmosphere. From reference [82].

The catalyst precursor $Co(NO_3)_2$ is inserted into the pores of HX-PHP after dissolving it in ethanol. Following drying, HX-PHP particles were dispersed into 3 mm diameter $BaTiO_3$ spheres, which act as a Plasma Catalysis Promoter (PCP), and placed into the Dielectric Barrier Discharge (DBD) reactor as shown in **Figure 20**.

This reactor unit was then inserted into the general purpose DBD-equipment described previously [5]-[7]. A constant stream of H_2 was passed through the reactor at 50 ml/min at 250˚C. The packed bed of PCP and HX-PHP particles was contained between two perforated stainless-steel electrodes, and plasma was generated between them [5]-[7] [21]-[23]. The composition of the gases from the outlet was periodically checked until no nitrogen oxide was present. The BET surface area of the original HX-PHP (after solvent extraction to remove $FeCl_2$) was reduced from 1020 m^2/g to 433 m^2/g after catalyst precursor insertion and its decomposition and reduction in H_2 atmosphere, which is partly due to the presence of a high density CoO catalyst.

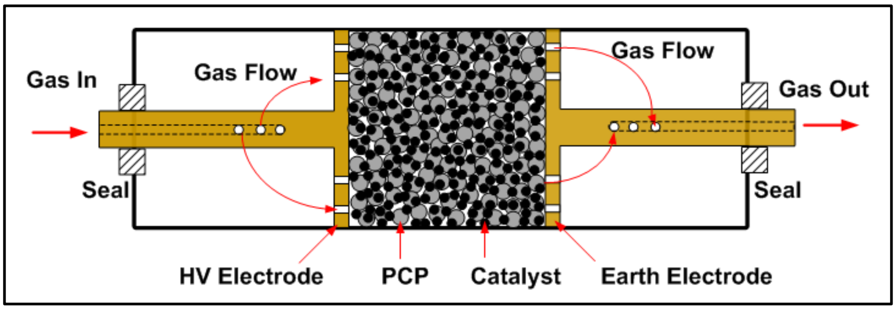


Figure 20. Dielectric barrier discharge (DBD) reactor used in the decomposition of the catalyst precursor salt in the Hypercrosslinked PolyHIPE Polymer (HX-PHP) support. From reference [82].

The use of HX-PHP or sHX-PHP as a support for catalysts has been demonstrated. These catalysts can be used in plasma as well as in thermochemical reactions, followed by use as XA-fertilizers in artificial root applications and the delivery of micronutrients. If the catalyst precursor within the pores of HX-PHP can also act as a Friedel-Crafts catalyst, then the second stage of the catalyst insertion will not be required, thus simplifying the process.

6. Health, Safety, and Environmental Impact of Artificial Root Technology

It is imperative that the health, safety, and environmental impact of AR-technology be assessed before any technology transfer at a large scale. A preliminary assessment should include: (1) Toxicity of styrene monomer; (2) biodegradation of sulfonated/neutralized PolyHIPE, sn-PHP; (3) accumulation and toxicity of micro- and nano-particulate SA- and SB-fertilizers based on sn-PHP and their uptake by plants.

Based on the available data, an assessment of styrene toxicity and biodegradation of PolyHIPE was assessed by Akay and Fleming [14]. Styrene monomer is biodegradable and is consequently excreted in urine from the body as water-soluble metabolites [191]. The metabolic pathways, genetic, and physiological aspects of degradation have been well established [192]-[194]. Further, several large epidemiological studies indicated that styrene was not carcinogenic [195]. The US National Toxicology Programme still classified styrene as anticipated to be a human carcinogen. The carcinogenicity of styrene has finally been settled this year (2025) with an expert panel report for the European Commission [196]. The Panel concluded that there was no evidence that styrene is genotoxic following oral exposure. For substances demonstrated to be non-genotoxic, according to the European Food Safety Authority (EFSA) Note for Guidance for Food Contact Materials (FCM), a specific migration limit (SML) up to 50 μg/kg food would not be of safety concern. Consequently, the use of styrene in the manufacture of FCM respecting the SML of 40 μg/kg food proposed by the European Commission is not of safety concern [196].

It is well known that the degradation rate of plastics is strongly dependent on their processing history, composition, morphology, environment, as well as the source of the degradation process in which radiation and bacteria represent the main determinants [197]-[201]. In the present case, for a given skeletal PolyHIPE in soil, the degradation rate is primarily controlled by the presence of bacteria and possibly by root exudates and the microenvironment generated within the pores, as seen in **Figure 14**. Experimental data on the degradation rates of plastics in soil are very limited. The estimated lifespan of polystyrene is 50 - 80 years [198]. However, due to the physical and biochemical nature of sn-PHP and the prevailing microenvironmental conditions, we can expect a significantly shorter lifespan [197]-[201]. Furthermore, the chemical composition of PolyHIPE can be altered in order to control its lifespan for a given application. It will be prudent to use PolyHIPE initially in perennial crops and non-food applications to gain experience and understanding of the AR network.

The emergence of micro- and nano-plastics in the environment, including soil, water, and air, and their ingestion and inclusion in tissue and cells are of serious concern. Nano-plastics are the main concern in agriculture. Such particles in soil are primarily generated by degradation of the macro- and micro-plastics in soil, and they can accumulate in plants and animals by crossing cellular membranes, thus disrupting cellular functions [202]-[204].

The effects of nano-plastics have been investigated by Sun *et al.*, [205]. It was found that both positively and negatively charged nano-plastics can accumulate in Arabidopsis thaliana (a model plant with a short life cycle). The aggregation promoted by the growth medium and root exudates limited the uptake of amino-modified polystyrene nano-plastics with positive surface charges. Positively charged nano-plastics accumulated at relatively low levels in the root tips. However, these nano-plastics induced a higher accumulation of reactive oxygen species and inhibited plant growth and seedling development more strongly than negatively charged sulfonic-acid-modified nano-plastics. By contrast, the negatively charged nano-plastics were observed frequently in the apoplast and xylem. These findings provided direct evidence that nano-plastics can accumulate in plants, depending on their surface charge. Plant accumulation of nano-plastics can have both direct ecological effects and implications for both agricultural sustainability and food safety.

The clear detrimental effects of nano-plastics on plants indicate that nano-plastic formation should be prevented in AR networks. Such preventive attributes are already present in the skeletal PolyHIPE, especially in bioactive AR networks. Further, very large enhancements observed in biomass (grass) and crop (pea) yield indicate that SA- or SB-fertilizers are not affected by nano-plastics as described by Sun *et al.*, [205]. These inherent preventative attributes are based on the formation of a microenvironment with bacteria, extracellular matrix, and root exudates, which isolates the surface of the PHP skeleton from the plant roots. In view of concerns over nano-plastic formation, further measures can be taken, such as coating the pores with silica or hydroxyapatite at the processing stage [48].

7. Discussion

In line with the expectations based on the performance data of mammalian cells and other bacteria summarized in Section-3, the above results indicate that high levels of plant productivity are delivered by using SRS-medium in soil, especially by those bioactive sn-PHPs. Therefore, the synthetic rhizosphere/synthetic rhizosheath (or synthetic root system) concepts are promising routes to enhance plant productivity, especially under water and nutrient stress, leading to artificial root systems established either as soil additives or used in soilless agriculture [68]. In the absence of these stresses, SRS-medium does not provide any substantial advantage.

As indicated previously, s-PHP can be used for various applications such as syngas or water cleaning (tar removal in the gasification process) and as a medium for in situ ammonia sequestration in plasma processes producing symbiotic fertilizers. These fertilizers can be directly used as the SRS-medium in soil, or they can be inoculated with a suitable bacterium and/or fungus to obtain the bioactive SRS-medium. Once in the soil, through interactions with plant roots and root exudates, the SRS-medium and its components are transformed into a microbiome [206].

As observed by Chen *et al.*, [97] the effect of excessive nitrogen fertilizer on microbial growth in the SRS-medium should be considered, as microbial network complexity can increase [97]. Yuan *et al.*, [207] observed that the molecular ecological networks under warming became significantly more robust, with network stability strongly correlated with network complexity, supporting the central ecological belief that complexity begets stability. Furthermore, warming significantly strengthened the relationships of network structure to community functional potentials and key ecosystem functioning. These results indicate that preserving microbial ‘interactions’ is critical for ecosystem management and for projecting ecological consequences of future global warming [207] [208]. Therefore, it is likely that a number of sn-PHP grades of SRS-medium should be produced with different functionalities and this composite fertilizer system should be added to the soil.

The use of perennial crops (as also advocated by the UN [2]) under eCO_2, eTe, and eWe environment will greatly enhance the techno-economic outlook of the proposed SRS-technology because the SRS-medium in soil need not be disturbed and the frequency of its replenishment is reduced. The high carbon-sequestration potential of perennials is also an important reason for their use in global warming adaptation and abatement.

The technology readiness level (TRL) of the proposed artificial root system based on SX-fertilizers depends on whether it is biologically active or not. Based on his industrial experience in technology development and deployment, the author rates the SA-fertilizers (sn-PHP loaded with nitrogen fertilizers) as an artificial root system at 7. In this case, the technology requires industrial-scale production of PolyHIPE polymers and their sulfonation, followed by in situ or ex-situ loading with fertilizers. PolyHIPEs were produced and sulfonated at an industrial scale using scalable equipment developed by the author and used in syngas and process water cleaning in biomass gasification [3]-[8] [209] [210]. The in situ nitrogen fertilizer loading (such as ammonium nitrate/sulphate/phosphate) of PolyHIPEs can be carried out using the plasma catalytic reactor system [5]-[8] to provide technology circularity and reduce the cost of direct green-fertilizer production to a level competitive with Haber-Bosch fertilizers, but with several added performance and environmental benefits, including sustainability.

In the case of biologically active SB-fertilizers containing useful microorganisms such as bacteria, fungi, archaea, and even viruses, sn-PHP can be used [211] [212]. Currently, we have only experimented with a limited number of bacteria and fungi. As shown in the first part of this review, although the use of PolyHIPEs in medicine, bioengineering, and biotechnology has resulted in some understanding of their function, the same cannot be said about bacteria-loaded PolyHIPE in soil. The inoculation of sn-PHP with suitable bacteria and/or fungi should be carried out a few days before field application. This can be carried out in mobile bioreactors. The use of fertilizers produced at the site of application has been considered [24] [98] [213] [214]. Another suitable at-field fertilizer is plasma catalytic microbubble nitrogen fertigation [24] in which NO_3^- is the primary product. As shown recently by Cao *et al.* [215], NO_3^- is more readily utilized by some crops compared with NH_4^+. Further, Cao *et al.* [215] clearly illustrates the importance of root leaf connectivity. The efficient (and cheap) plasma catalysts used in N-fertigation include Fe/Si quantum catalysts [3] [4] [9] [216] which can also be utilised as quantum-fertilizers without having to remove them from the fertigation fertilizer. After their service life, these catalysts can be utilized as micronutrients.

The use of the catalytic hypercrosslinked PolyHIPE and quantum catalysts (including those used in fertigation), for the delivery of micronutrients, has additional benefits in terms of CO_2 mineralization [3] through the mechanism advanced by Gadikota *et al.*, [217] [218].

As advocated by Srivastava *et al.*, [219], interdisciplinary collaborations between soil science, agronomy, biotechnology, microbiology, and environmental science are necessary for sustainable agriculture. The proposed AR-system was developed through an interdisciplinary, discovery-based approach but requires field trials and long-term assessment. Further enhancement of plant productivity can be achieved by microbiome manipulation using bioengineering tools [220]. The presence of several granted patents (see section on "Conflicts of Interest" declaration by the author) providing connectivity between different strands of AR also indicates that the technology can be utilized at an industrial scale. What has been shown so far is a large crop and biomass yield enhancement when SX-fertilizers are used as an artificial root system under water and nutrient stress in greenhouse experiments. As regards technology readiness levels (TRL), the present author considers the TRL of SB-fertilizers to be 5 compared with the TRL at 7 for SA-fertilizers as an artificial root system. PolyHIPE and its variants have already been produced at industrial scale and used in various applications at industrial scale, including field trials and syngas cleaning (tar and particulate removal) and process water remediation in industrial scale biomass and waste gasification and electricity generation at 1 MWe [3] [4] [83]. There is extensive experience in the use of PolyHIPE in biological applications including tissue engineering, antibiotic, enzyme, and ethanol production [10]-[14] [48]-[56] [67]-[69] [72] [74] [75] [80] [85]-[89]. The use of PolyHIPE and its variants in agriculture is confined to greenhouse experiments and a small-scale field trial.

8. Conclusions

The artificial root concept is introduced as a novel approach to combat emerging water and nutrient stresses in agriculture through the facilitation of efficient macro- and micro-nutrient delivery, as well as geological CO_2 sequestration. This process results in enhanced biomass growth rate, crop yield, and nutrition. These attributes are achieved through the formation of an artificial/synthetic rhizosphere/rhizosheath when the plant roots ingress into the SRS-medium, creating a microenvironment in which plant roots, root exudates, microbiota, water, and nutrients interact within the confines of the artificial root system.

The basic, skeletal AR is formed when highly porous and hydrophilic material, such as sulfonated PolyHIPE Polymer, is placed into soil. PolyHIPE can also contain nutrients/fertilizers, or it can include suitable bacteria and/or fungi. The growing plant roots preferentially ingress into PolyHIPE through a variety of tropistic mechanisms, and eventually, a microbiome is established within them.

The use of PolyHIPE as a preferred platform for AR is almost unavoidable. PolyHIPE is a unique material which can be manufactured with a wide range of pore architectures (pore size, pore connectivity, surface area, wall structure, and pore volume) and biochemical activity. These properties are especially important when useful bacteria are cultivated within the pores of PolyHIPE before they are introduced into the soil. Depending on the pore architecture, proliferation, differentiation, and productivity of the bacterial communities are affected. These properties have been evaluated when bioactive PolyHIPE is used as a support for bacteria or mammalian cells in tissue engineering, bioengineering, and environmental remediation. Therefore, in the absence of directly relevant data, the type of PolyHIPE for use in agriculture can be chosen through the review of similar biological systems. Hence, this review includes the use of PolyHIPE in other biological applications. The industrial-scale application of PolyHIPE in agriculture requires a low cost, which can be achieved through the widening of its use in other areas, such as chemicals, energy, and catalysts.

The macronutrient delivery to plants is the primary function of the AR system. On the other hand, the micronutrient delivery can be achieved by using spent silica or PolyHIPE supported nano-size heterogeneous catalysts, as most micronutrients are catalytic transition metals or catalyst promoters. The use of recently discovered quantum catalysts after their service life as quantum fertilizers is ideal. The silica-supported quantum catalysts provide efficient nitrogen conversion in the development of fertigation fertilizers, even when cheap catalysts such as Fe are used.

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Data Availability Statement

A reasonable amount of data originating from the author’s own research can be requested from the author.

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Conflicts of Interest

The author’s conflicts of interest are based on his patents on the subject and the formation of a charity promoting AR-technology. The author declares that various elements of the proposed artificial root system described in this paper benefited from several granted patents which have been utilized in industry. The author is in the process of establishing a charitable organization (Climate Change Trust) to support technologies leading to climate change mitigation. Granted patents include: US Patents: US2023/0064758 (pending); US11498845; US9416019; US08486168; US07820729; US8898955; US7780854; US08252072; US8177985; US63445907; US08252072. European Patents: EP1183328; EP2349362; EP2342272; EP649867; EP799303.

References

[1] UN (2023) Emissions Gap Report 2023, Broken Record: Temperatures Hit New Highs, Yet World Fails to Cut Emissions (Again), Chapter 1. https://www.unep.org/resources/emissions-gap-report-2023

[2] United Nations, United Nations Environment Programme and International Solid Waste Association (2024) Global Waste Management Outlook 2024- beyond an Age of Waste: Turning Rubbish into a Resource. February. https://www.unep.org/resources/global-waste-management-outlook-2024

[3] Akay, G. (2025) Green Ammonia, Nitric Acid, Advanced Fertilizer and Electricity Production with *in Situ* CO_2 Capture and Utilization by Integrated Intensified Nonthermal Plasma Catalytic Processes: A Technology Transfer Review for Distributed Biorefineries. *Catalysts*, **15**, Article 105. https://doi.org/10.3390/catal15020105

[4] Akay, G. (2023) Hydrogen, Ammonia and Symbiotic/Smart Fertilizer Production Using Renewable Feedstock and CO_2 Utilization through Catalytic Processes and Nonthermal Plasma with Novel Catalysts and in Situ Reactive Separation: A Roadmap for Sustainable and Innovation-Based Technology. *Catalysts*, **13**, Article 1287. https://doi.org/10.3390/catal13091287

[5] Akay, G. (2016) Ammonia Production by Integrated Intensified Processes. US Patent, US9416019. (First published as GB201014304D0 on 13-10-2010). https://patents.google.com/patent/US9416019B2/en14

[6] Akay, G. (2022) Catalytic Multi-Reaction Zone Reactor System. U.S. Patent US11,498,845. https://patents.google.com/patent/US11498845B2/en

[7] Akay, G. (2017) Sustainable Ammonia and Advanced Symbiotic Fertilizer Production Using Catalytic Multi-Reaction-Zone Reactors with Nonthermal Plasma and Simultaneous Reactive Separation. *ACS Sustainable Chemistry & Engineering*, **5**, 11588-11606. https://doi.org/10.1021/acssuschemeng.7b02962

[8] Akay, G. (2023) Synthesis of Plasma Generating-Chemical Looping Catalysts. U.S. Patent Application, 2023/0064758. https://patents.google.com/patent/WO2021145843A3/en

[9] Akay, G. (2020) Plasma Generating—Chemical Looping Catalyst Synthesis by Microwave Plasma Shock for Nitrogen Fixation from Air and Hydrogen Production from Water for Agriculture and Energy Technologies in Global Warming Prevention. *Catalysts*, **10**, Article 152. https://doi.org/10.3390/catal10020152

[10] Akay, G., Noor, Z.Z., Calkan, O.F., Ndlovu, T.M. and Burke, D.B. (2010) Process for Preparing a Functionalized PolyHIPE Polymer. US Patent US07820729. https://patents.google.com/patent/US7820729B2/en

[11] Akay, G., Calkan, B., Hasan, H. and Mohamed R. (2013) Preparation of Nanostruc-

tured Microporous Composite Foams, European Patent EP 2342272. https://patents.google.com/patent/EP2342272A2/en

[12] Akay, G. and Burke, D.R. (2014) Synthetic Symbiotic System as Soil Additives to Deliver Active Ingredients through Plant Roots for Enhanced Plant and Crop Yield. US Patent US8898955. https://patentimages.storage.googleapis.com/30/b8/9b/d1f4fd63f6d601/US8898955.pdf

[13] Akay, G. and Burke, D.R. (2012) Agro-Process Intensification through Synthetic Rhizosphere Media for Nitrogen Fixation and Yield Enhancement in Plants. *American Journal of Agricultural and Biological Sciences*, **7**, 150-172. https://doi.org/10.3844/ajabssp.2012.150.172

[14] Akay, G. and Fleming, S. (2012) Agro-Process Intensification: Soilborne Micro-Bioreactors with Nitrogen Fixing Bacterium *Azospirillum brasilense* as Self-Sustaining Biofertiliser Source for Enhanced Nitrogen Uptake by Plants. *Green Processing and Synthesis*, **1**, 427-437. https://doi.org/10.1515/gps-2012-0041

[15] Zhang, T., Sanguramath, R.A., Israel, S. and Silverstein, M.S. (2019) Emulsion Templating: Porous Polymers and Beyond. *Macromolecules*, **52**, 5445-5479. https://doi.org/10.1021/acs.macromol.8b02576

[16] Kramer, S., Cameron, N.R. and Krajnc, P. (2021) Porous Polymers from High Internal Phase Emulsions as Scaffolds for Biological Applications. *Polymers*, **13**, Article 1786. https://doi.org/10.3390/polym13111786

[17] McKenzie, T.J. and Ayres, N. (2023) Synthesis and Applications of Elastomeric Polymerized High Internal Phase Emulsions (Polyhipes). *ACS Omega*, **8**, 20178-20195. https://doi.org/10.1021/acsomega.3c01265

[18] Ahammed, G.J. and Hajiboland, R. (2024) Introduction to Arbuscular Mycorrhizal Fungi and Higher Plant Symbiosis: Characteristic Features, Functions, and Applications. In: Ahammed, G.J. and Hajiboland, R., Eds., *Arbuscular Mycorrhizal Fungi and Higher Plants*, Springer, 1-17. https://doi.org/10.1007/978-981-99-8220-2

[19] Runnel, K., Tedersoo, L., Krah, F., Piepenbring, M., Scheepens, J.F., Hollert, H., *et al.* (2025) Toward Harnessing Biodiversity–Ecosystem Function Relationships in Fungi. *Trends in Ecology & Evolution*, **40**, 180-190. https://doi.org/10.1016/j.tree.2024.10.004

[20] Akay, G. (2016) Co-Assembled Supported Catalysts: Synthesis of Nano-Structured Supported Catalysts with Hierarchic Pores through Combined Flow and Radiation Induced Co-Assembled Nano-Reactors. *Catalysts*, **6**, Article 80. https://doi.org/10.3390/catal6060080

[21] Akay, G. and Zhang, K. (2017) Process Intensification in Ammonia Synthesis Using Novel Coassembled Supported Microporous Catalysts Promoted by Nonthermal Plasma. *Industrial & Engineering Chemistry Research*, **56**, 457-468. https://doi.org/10.1021/acs.iecr.6b02053

[22] Zhang, K., Zhang, G., Liu, X., Phan, A.N., Luo, K. and Akay, G. (2020) Correction to "A Study on Co_2 Decomposition to CO and O_2 by the Combination of Catalysis and Dielectric-Barrier Discharges at Low Temperatures and Ambient Pressure". *Industrial & Engineering Chemistry Research*, **59**, 502-502. https://doi.org/10.1021/acs.iecr.9b06637

[23] Akay, G., Zhang, K., Al-Harrasi, W.S.S. and Sankaran, R.M. (2020) Catalytic Plasma Fischer-Tropsch Synthesis Using Hierarchically Connected Porous Co/SiO_2 Catalysts Prepared by Microwave-Induced Co-Assembly. *Industrial & Engineering Chemistry Research*, **59**, 12013-12027. https://doi.org/10.1021/acs.iecr.0c01585

[24] Zhuang, C., Long, N.V.D., Tran, N.N., Zhang, T., Cullen, P., *et al.* (2025) Microbubble Plasma Processing for N-Fertigation via Plasma Catalysis. *ChemCatChem*, **17**, e202401838. https://doi.org/10.1002/cctc.202401838

[25] Bogaerts, A., Centi, G., Hessel, V. and Rebrov, E. (2023) Challenges in Unconventional Catalysis. *Catalysis Today*, **420**, Article 114180. https://doi.org/10.1016/j.cattod.2023.114180

[26] Meunier, F.C. and Kaddouri, A. (2024) Microwave-Assisted Oxidation of N_2 into No_x over a La-Ce-Mn-O Perovskite Yielding Plasmas in a Quartz Flow Reactor at Atmospheric Pressure. *Catalysts*, **14**, Article 635. https://doi.org/10.3390/catal14090635

[27] Ruiz-Martín, M., Oliva-Ramírez, M., González-Elipe, A.R. and Gómez-Ramírez, A. (2025) Plasma Catalysis for Gas Conversion—Impact of Catalyst on the Plasma Behavior. *Current Opinion in Green and Sustainable Chemistry*, **51**, Article 100990. https://doi.org/10.1016/j.cogsc.2024.100990

[28] Rodriguez, A.W., Capasso, F. and Johnson, S.G. (2011) The Casimir Effect in Microstructured Geometries. *Nature Photonics*, **5**, 211-221. https://doi.org/10.1038/nphoton.2011.39

[29] Havnes, O., Morfill, G.E. and Goertz, C.K. (1984) Plasma Potential and Grain Charges in a Dust Cloud Embedded in a Plasma. *Journal of Geophysical Research*: *Space Physics*, **89**, 10999-11003. https://doi.org/10.1029/ja089ia12p10999

[30] Patil, B.S., Cherkasov, N., Srinath, N.V., Lang, J., Ibhadon, A.O., Wang, Q., *et al.* (2021) The Role of Heterogeneous Catalysts in the Plasma-Catalytic Ammonia Synthesis. *Catalysis Today*, **362**, 2-10. https://doi.org/10.1016/j.cattod.2020.06.074

[31] Navascués, P., Garrido-García, J., Cotrino, J., González-Elipe, A.R. and Gómez-Ramírez, A. (2023) Incorporation of a Metal Catalyst for the Ammonia Synthesis in a Ferroelectric Packed-Bed Plasma Reactor: Does It Really Matter? *ACS Sustainable Chemistry & Engineering*, **11**, 3621-3632. https://doi.org/10.1021/acssuschemeng.2c05877

[32] Argyle, M. and Bartholomew, C. (2015) Heterogeneous Catalyst Deactivation and Regeneration: A Review. *Catalysts*, **5**, 145-269. https://doi.org/10.3390/catal5010145

[33] Ullah, M.S., Mahmood, A., Ameen, M., Nayab, A. and Ayub, A. (2024) Multidimensional Role of Silicon to Mitigate Biotic and Abiotic Stresses in Plants: A Comprehensive Review. *Silicon*, **16**, 5471-5500. https://doi.org/10.1007/s12633-024-03094-6

[34] Sheng, H. and Chen, S. (2020) Plant Silicon-Cell Wall Complexes: Identification, Model of Covalent Bond Formation and Biofunction. *Plant Physiology and Biochemistry*, **155**, 13-19. https://doi.org/10.1016/j.plaphy.2020.07.020

[35] Zhu, Y., Gong, H. and Yin, J. (2019) Role of Silicon in Mediating Salt Tolerance in Plants: A Review. *Plants*, **8**, Article 147. https://doi.org/10.3390/plants8060147

[36] Jiang, H., Wang, H., Qian, C., Yang, Z., Yang, D. and Cui, J. (2024) A New Type of Quantum Fertilizer (Silicon Quantum Dots) Promotes the Growth and Enhances the Antioxidant Defense System in Rice Seedlings by Reprogramming the Nitrogen and Carbon Metabolism. *Journal of Agricultural and Food Chemistry*, **72**, 2526-2535. https://doi.org/10.1021/acs.jafc.3c08112

[37] Liu, Y., Liu, D., Han, X., Chen, Z., Li, M., Jiang, L., *et al.* (2024) Magnesium-Doped Carbon Quantum Dot Nanomaterials Alleviate Salt Stress in Rice by Scavenging Reactive Oxygen Species to Increase Photosynthesis. *ACS Nano*, **18**, 31188-31203. https://doi.org/10.1021/acsnano.4c09001

[38] Wang, H., Qian, C., Sun, L., Jiang, H., Wang, X., Cui, J., *et al.* (2024) A Novel Type of Quantum-Delivery System (Salicylic Acid Conjugation Based on Zno Quantum

Dots) Alleviates the Bacterial Fruit Blotch Disease of Melon Plants by Activating Defense Response. *Chemical Engineering Journal*, **500**, Article 156901. https://doi.org/10.1016/j.cej.2024.156901

[39] Chaudhary, M., Singh, P., Singh, G.P. and Rathi, B. (2024) Structural Features of Carbon Dots and Their Agricultural Potential. *ACS Omega*, **9**, 4166-4185. https://doi.org/10.1021/acsomega.3c04638

[40] Nguyen, N.N., Nguyen, N.T., Nguyen, P.T., Phan, Q.N., Le, T.L. and Do, H.D.K. (2024) Current and Emerging Nanotechnology for Sustainable Development of Agriculture: Implementation Design Strategy and Application. *Heliyon*, **10**, e31503. https://doi.org/10.1016/j.heliyon.2024.e31503

[41] Hoang, C.V., Thoai, D.N., Cam, N.T.D., Phuong, T.T.T., Lieu, N.T., Hien, T.T.T., *et al.* (2022) Large-Scale Synthesis of Nanosilica from Silica Sand for Plant Stimulant Applications. *ACS Omega*, **7**, 41687-41695. https://doi.org/10.1021/acsomega.2c05760

[42] Cuong, D.M., Mai, N.T.N., Luan, V.Q., Tung, H.T., The Vinh, B.V., Thuy, N.T.T., *et al.* (2024) Optimizing the Combination of SiO2nps and Ceo2nps on Relative Growth Rate of Fragaria × Ananassa Plantlets Cultured *in Vitro*. *Plant Cell, Tissue and Organ Culture* (*PCTOC*), **159**, Article No. 43. https://doi.org/10.1007/s11240-024-02902-6

[43] Gopal, D., Prasad, T.N.V.K.V., Pradeep, T., Bhargava Rami Reddy, C., Nirmal Kumar, A.R., Naseeruddin, R., *et al.* (2025) Synergistic Impact of Foliar Application of Nanoparticulate Silica on the Sustainable Productivity of Low Land Rice. *Journal of Plant Nutrition*, **48**, 222-236. https://doi.org/10.1080/01904167.2024.2399804

[44] Chen, S., Kang, Z., Peralta-Videa, J.R. and Zhao, L. (2023) Environmental Implication of Mos2 Nanosheets: Effects on Maize Plant Growth and Soil Microorganisms. *Science of The Total Environment*, **860**, Article 160362. https://doi.org/10.1016/j.scitotenv.2022.160362

[45] Ding, Y., Bai, X., Ye, Z., Ma, L. and Liang, L. (2019) Toxicological Responses of Fe3O4 Nanoparticles on *Eichhornia crassipes* and Associated Plant Transportation. *Science of The Total Environment*, **671**, 558-567. https://doi.org/10.1016/j.scitotenv.2019.03.344

[46] Akay, G. (2005) Bioprocess and Chemical Process Intensification. In: Lee, S., Ed., *Encyclopedia of Chemical Processing*, Marcel Dekker 183-199. https://books.google.co.uk/books/about/Encyclopedia_of_Chemical_Processing_Onli.html?id=YWC1DwAAQBAJ&redir_esc=y

[47] Akay, G. (2005) Size Dependent Transport Phenomena in Micro-Porous Media and Its Application to the Preparation of Nano-Structured Materials with Arterial Micro-Pores. In: Kasagi, N., Maruyama, S., Yoshida, H. and Inoue, T., Eds., Sixth *World Conference on Experimental Heat Transfer, Fluid Mechanics and Thermodynamics*, University of Tokyo, 14-17. http://fluid.ippt.gov.pl/conference_proceedings/.list/ExHFT-6

[48] Akay, G., Dawnes, S. and Price, V.J. (2002) Microcellular Polymers as Cell Growth Media and Novel Polymers. European Patent EP1183328. http://v3.espacenet.com/textdoc?DB=EPODOC&IDX=EP1183328

[49] Bokhari, M., Birch, M. and Akay, G. (2003) Polyhipe Polymer: A Novel Scaffold For *in Vitro* Bone Tissue Engineering. In: Elçin, Y.M., Ed., *Advances in Experimental Medicine and Biology*, Springer US, 247-254. https://doi.org/10.1007/978-1-4615-0063-6_18

[50] Akay, G., Birch, M.A. and Bokhari, M.A. (2004) Microcellular PolyHIPE Polymer Supports Osteoblast Growth and Bone Formation *in Vitro*. *Biomaterials*, **25**, 3991-

4000. https://doi.org/10.1016/j.biomaterials.2003.10.086

[51] Akay, G., Erhan, E. and Keskinler, B. (2005) Bioprocess Intensification in Flow-through Monolithic Microbioreactors with Immobilized Bacteria. *Biotechnology and Bioengineering*, **90**, 180-190. https://doi.org/10.1002/bit.20376

[52] Akay, G., Bokhari, M.A., Byron, V.J. and Dogru, M. (2005) Development of Nano-Structured Micro-Porous Materials and Their Application in Bioprocess-Chemical Process Intensification and Tissue Engineering. In: Galan, M.A. and Del Valle, E.M., Eds., *Chemical Engineering Trends and Developments*, Wiley, 171-196. https://doi.org/10.1002/0470025018.ch7

[53] Bokhari, M.A., Akay, G., Zhang, S. and Birch, M.A. (2005) The Enhancement of Osteoblast Growth and Differentiation *in Vitro* on a Peptide Hydrogel—Polyhipe Polymer Hybrid Material. *Biomaterials*, **26**, 5198-5208. https://doi.org/10.1016/j.biomaterials.2005.01.040

[54] Akay, E.M., Okumus, Z., Yildirim, O.S., Bokhari, M.A. and Akay, G. (2011) Synthetic Organs for Transplant and Bio-Mimic Reactors for Process Intensification Using Nano-Structured Micro-Porous Materials. In: Brebbia, C.A. and Carpi, A., Eds., *Environmental Health and Biomedicine*, WIT Press, 383-394. https://doi.org/10.2495/ehr110331

[55] Jimat, D.N., Harwood, C. and Akay, G. (2013) Production of A-Amylase by Immobilized Bacillus Subtilis in Polymeric Polyhipe Matrix. In: Pogaku, R., Bono, A. and Chu, C., Eds., *Developments in Sustainable Chemical and Bioprocess Technology*, Springer US, 159-171. https://doi.org/10.1007/978-1-4614-6208-8_21

[56] Ndlovu, T.M., Ward, A.C., Glassey, J., Eskildsen, J. and Akay, G. (2015) Bioprocess Intensification of Antibiotic Production by *Streptomyces coelicolor* A3(2) in Micro-Porous Culture. *Materials Science and Engineering*: *C*, **49**, 799-806. https://doi.org/10.1016/j.msec.2015.01.052

[57] Akay, G., Bhumgara, Z.G. and Wakeman, R.J. (1995) Self-Supported Porous Channel Filtration Modules: Preparation, Properties and Performance. *Chemical Engineering Research and Design* (*Trans. I. Chem. E., Part A*), **73**, 782-797. https://scopus.kisti.re.kr/noregist/viewScopus.jsp?eid=0032104239

[58] Wakeman, R., Bhumgara, Z. and Akay, G. (1998) Ion Exchange Modules Formed from Polyhipe Foam Precursors. *Chemical Engineering Journal*, **70**, 133-141. https://doi.org/10.1016/s1385-8947(98)00088-6

[59] Akay, G., Pekdemir, T., Shakorfow, A.M. and Vickers, J. (2012) Intensified Demulsification and Separation of Thermal Oxide Reprocessing Interfacial Crud (THORP-IFC) Simulants. *Green Processing and Synthesis*, **1**, 109-127. https://doi.org/10.1515/greenps-2011-0510

[60] Akay, G. and Vickers, V. (2010) Methods for Separating Oil and Water, US Patent, US7780854. https://patents.justia.com/patent/7780854

[61] Akay, G. and Vickers, V. (2012) Methods for Separating Oil and Water, US Patent, US8177985. https://patents.google.com/patent/US8177985B2/en

[62] Akay, G. and Jordan, C.A. (2011) Gasification of Fuel Cane Bagasse in a Downdraft Gasifier: Influence of Lignovellulosic Composition and Fuel Particle Size on Syngas Composition and Yield. *Energy and Fuel*, **25**, 2274-2283. https://doi.org/10.1021/ef101494w

[63] Jordan, C.A. and Akay, G. (2012) Occurrence, Composition and Dew Point of Tars Produced during Gasification of Fuel Cane Bagasse in a Downdraft Gasifier. *Biomass and Bioenergy*, **42**, 51-58. https://doi.org/10.1016/j.biombioe.2012.03.014

[64] Dogru, M. and Akay, G. (2012) Catalytic Gasification. US Patent US08252072. https://patentimages.storage.googleapis.com/20/5b/0b/9569366d6473fd/US8252072.pdf

[65] Erhan, E., Yer, E., Akay, G., Keskinler, B. and Keskinler, D. (2004) Phenol Degradation in a Fixed-Bed Bioreactor Using Micro-Cellular Polymer-Immobilized *Pseudomonas syringae*. *Journal of Chemical Technology & Biotechnology*, **79**, 195-206. https://doi.org/10.1002/jctb.938

[66] Barlık, N., Keskinler, B., Kocakerim, M.M. and Akay, G. (2016) Functionalized Polyhipe Polymer Monoliths as an Anion-Exchange Media for Removal of Nitrate Ions from Aqueous Solutions. *Desalination and Water Treatment*, **57**, 26440-26447. https://doi.org/10.1080/19443994.2016.1164083

[67] Preechawong, J., Chindacharin, S., Sapsrithong, P. and Nithitanakul, M. (2017) Mesoporous Water Adsorbent Material from Poly High Internal Phase Emulsion for Agriculture Application. *Journal of Applied Polymer Science*, **134**, Article 45509. https://doi.org/10.1002/app.45509

[68] Kovačič, J.M., Ciringer, T., Ambrožič-Dolinšek, J. and Kovačič, S. (2022) Use of Emulsion-Templated, Highly Porous Polyelectrolytes for *in Vitro* Germination of Chickpea Embryos: A New Substrate for Soilless Cultivation. *Biomacromolecules*, **23**, 3452-3457. https://doi.org/10.1021/acs.biomac.2c00593

[69] Zowada, R. and Foudazi, R. (2023) Macroporous Hydrogels for Soil Water Retention in Arid and Semi-Arid Regions. *RSC Applied Polymers*, **1**, 243-253. https://doi.org/10.1039/d3lp00117b

[70] Ebrahimzadeh Kouchesfahani, M. and Babaeipour, V. (2020) Micro Bioreactor Scale-Up and Industrialization: A Critical Review of the Methods, Their Prerequisites, and Perquisites. *Minerva Biotecnologica*, **32**, 64-78. https://doi.org/10.23736/s1120-4826.19.02595-3

[71] Chaichol, P. and Weeranoppanant, N. (2023) Advances in *in Situ* and *in-Line* Liquid-Liquid Extraction for Bioprocess Intensification. *Reaction Chemistry & Engineering*, **8**, 2387-2402. https://doi.org/10.1039/d3re00266g

[72] Aldemir Dikici, B. and Claeyssens, F. (2020) Basic Principles of Emulsion Templating and Its Use as an Emerging Manufacturing Method of Tissue Engineering Scaffolds. *Frontiers in Bioengineering and Biotechnology*, **8**, Article ID: 875. https://doi.org/10.3389/fbioe.2020.00875

[73] Kovačič, S., Schafzahl, B., Matsko, N.B., Gruber, K., Schmuck, M., Koller, S., *et al.* (2022) Carbon Foams via Ring-Opening Metathesis Polymerization of Emulsion Templates: A Facile Method to Make Carbon Current Collectors for Battery Applications. *ACS Applied Energy Materials*, **5**, 14381-14390. https://doi.org/10.1021/acsaem.2c02787

[74] Ozkendir, O., Karaca, I., Cullu, S., Erdoğan, O.C., Yaşar, H.N., Dikici, S., *et al.* (2023) Engineering Periodontal Tissue Interfaces Using Multiphasic Scaffolds and Membranes for Guided Bone and Tissue Regeneration. *Biomaterials Advances*, **157**, Article 213732. https://doi.org/10.1016/j.bioadv.2023.213732

[75] Touchet, T.J., Horelica, M., Gruenbaum, R., Lewy, K., Hines, E., Stranahan, L., *et al.* (2024) Fabrication and *in Vivo* Assessment of Oxidatively Responsive PolyHIPE Scaffolds for Use in Diabetic Orthopedic Applications. *Macromolecular Bioscience*, **24**, Article 2300393. https://doi.org/10.1002/mabi.202300393

[76] Wu, J., Li, F., Yu, P., Yu, C., Han, C., Wang, Y., *et al.* (2024) Transcriptomic and Cellular Decoding of Scaffolds-Induced Suture Mesenchyme Regeneration. *International Journal of Oral Science*, **16**, Article No. 33.

https://doi.org/10.1038/s41368-024-00295-y

[77] Rahimnejad, M., Makkar, H., Dal-Fabbro, R., Malda, J., Sriram, G. and Bottino, M.C. (2024) Biofabrication Strategies for Oral Soft Tissue Regeneration. *Advanced Healthcare Materials*, **13**, Article 2304537. https://doi.org/10.1002/adhm.202304537

[78] Shlomo-Avitan, B., Machour, M., Ahmad, S.S., Friedler, Y., Levenberg, S. and Silverstein, M.S. (2025) Emulsion-Templated Macroporous Polycaprolactone: Synthesis, Degradation, Additive Manufacturing, and Cell-Growth. *Polymer*, **320**, Article 127971. https://doi.org/10.1016/j.polymer.2024.127971

[79] Li, H., Li, D., Wang, X., Zeng, Z., Pahlavan, S., Zhang, W., *et al.* (2025) Progress in Biomaterials-Enhanced Vascularization by Modulating Physical Properties. *ACS Biomaterials Science & Engineering*, **11**, 33-54. https://doi.org/10.1021/acsbiomaterials.4c01106

[80] Durgut, E. and Claeyssens, F. (2025) Pickering Polymerized High Internal Phase Emulsions: Fundamentals to Advanced Applications. *Advances in Colloid and Interface Science*, **336**, Article 103375. https://doi.org/10.1016/j.cis.2024.103375

[81] Du, S., Huynh, T., Lu, Y., Parker, B.J., Tham, S.K., Thissen, H., *et al.* (2024) Bioactive Polymer Composite Scaffolds Fabricated from 3D Printed Negative Molds Enable Bone Formation and Vascularization. *Acta Biomaterialia*, **186**, 260-274. https://doi.org/10.1016/j.actbio.2024.07.038

[82] Akay, G. (2025) Processing, Functionalization of PolyHIPE Polymers for Artificial Root System for the Delivery of Macro- and Micro-Nutrients. British Patent Application.

[83] Akay, G., Jordan, C.A. and Mohamed, A.H. (2013) Syngas Cleaning with Nano-Structured Micro-Porous Ion Exchange Polymers in Biomass Gasification Using a Novel Downdraft Gasifier. *Journal of Energy Chemistry*, **22**, 426-435. https://doi.org/10.1016/s2095-4956(13)60056-x

[84] Haq, Z. and Johnson, R.S. (1986) Highly Absorbent Substrate Article. US Patent 4606958. https://patents.google.com/patent/WO1985000111A1/en

[85] Ahmad, S. and Silverstein, M.S. (2025) Emulsion Templating: DIY Versatility for the Creative Design of Macroporous Polymers. *Progress in Polymer Science*, **165**, Article ID: 101970. https://doi.org/10.1016/j.progpolymsci.2025.101970

[86] Aldemir Dikici, B., Dikici, S. and Claeyssens, F. (2022) Synergistic Effect of Type and Concentration of Surfactant and Diluting Solvent on the Morphology of Emulsion Templated Matrices Developed as Tissue Engineering Scaffolds. *Reactive and Functional Polymers*, **180**, Article 105387. https://doi.org/10.1016/j.reactfunctpolym.2022.105387

[87] Mert, H.H. and Mert, E.H. (2021) Emulsion Templated Hierarchical Macroporous Polymers. In: Uthaman, A., Thomas, S., Li, T. and Maria, H., Eds., *Engineering Materials*, Springer International Publishing, 43-86. https://doi.org/10.1007/978-3-030-85397-6_3

[88] Akay, G. and Burke, D.R. (2015) Synthetic Symbiotic System as Soil Additives to Deliver Active Ingredients Through Plant Roots for Enhanced Plant and Crop Yield. European Patent, EP2349362. https://patents.google.com/patent/EP2349362B1/zh

[89] Burke, D.R., Akay, G. and Bilsborrow, P.E. (2010) Development of Novel Polymeric Materials for Agroprocess Intensification. *Journal of Applied Polymer Science*, **118**, 3292-3299. https://doi.org/10.1002/app.32640

[90] Raghuram, N., Aziz, T., Kant, S., Zhou, J. and Schmidt, S. (2022) Editorial: Nitrogen Use Efficiency and Sustainable Nitrogen Management in Crop Plants. *Frontiers in*

Plant Science, **13**, Article ID: 862091. https://doi.org/10.3389/fpls.2022.862091

[91] Pan, S., He, K., Lin, K., Fan, C. and Chang, C. (2022) Addressing Nitrogenous Gases from Croplands toward Low-Emission Agriculture. *npj Climate and Atmospheric Science*, **5**, Article No. 43. https://doi.org/10.1038/s41612-022-00265-3

[92] Guo, Y., Ren, G., Zhang, K., Li, Z., Miao, Y. and Guo, H. (2021) Leaf Senescence: Progression, Regulation, and Application. *Molecular Horticulture*, **1**, Article No. 5. https://doi.org/10.1186/s43897-021-00006-9

[93] Liu, X., Hu, B. and Chu, C. (2021) Nitrogen Assimilation in Plants: Current Status and Future Prospects. *Journal of Genetics and Genomics*, **49**, 394-404. https://doi.org/10.1016/j.jgg.2021.12.006

[94] Cameron, K.C., Di, H.J. and Moir, J.L. (2013) Nitrogen Losses from the Soil/Plant System: A Review. *Annals of Applied Biology*, **162**, 145-173. https://doi.org/10.1111/aab.12014

[95] Huérfano, X., Estavillo, J.M., Torralbo, F., Vega-Mas, I., González-Murua, C. and Fuertes-Mendizábal, T. (2022) Dimethylpyrazole-Based Nitrification Inhibitors Have a Dual Role in N_2O Emissions Mitigation in Forage Systems under Atlantic Climate Conditions. *Science of The Total Environment*, **807**, Article 150670. https://doi.org/10.1016/j.scitotenv.2021.150670

[96] Coskun, D., Britto, D.T., Shi, W. and Kronzucker, H.J. (2017) Nitrogen Transformations in Modern Agriculture and the Role of Biological Nitrification Inhibition. *Nature Plants*, **3**, Article No. 17074. https://doi.org/10.1038/nplants.2017.74

[97] Chen, Y., Li, Y., Qiu, T., He, H., Liu, J., Duan, C., *et al.* (2024) High Nitrogen Fertilizer Input Enhanced the Microbial Network Complexity in the Paddy Soil. *Soil Ecology Letters*, **6**, Article No. 230205. https://doi.org/10.1007/s42832-023-0205-3

[98] Yin, M., Gao, X., Kuang, W. and Zhang, Y. (2023) Meta-Analysis of the Effect of Nitrification Inhibitors on the Abundance and Community Structure of N_2O-Related Functional Genes in Agricultural Soils. *Science of The Total Environment*, **865**, Article 161215. https://doi.org/10.1016/j.scitotenv.2022.161215

[99] García-Gutiérrez, S., Guardia, G., Montoya, M., Vallejo, A., Cardenas, L.M. and García-Marco, S. (2023) Dry Rainfed Conditions Are Key Drivers of the Effect of Conservation Tillage and a Nitrification Inhibitor on N Fate and N_2O Emissions: A Field 15N Tracing Study. *Geoderma*, **432**, Article 116424. https://doi.org/10.1016/j.geoderma.2023.116424

[100] Lata, J., Le Roux, X., Koffi, K.F., Yé, L., Srikanthasamy, T., Konaré, S., *et al.* (2022) The Causes of the Selection of Biological Nitrification Inhibition (BNI) in Relation to Ecosystem Functioning and a Research Agenda to Explore Them. *Biology and Fertility of Soils*, **58**, 207-224. https://doi.org/10.1007/s00374-022-01630-3

[101] Saud, S., Wang, D. and Fahad, S. (2022) Improved Nitrogen Use Efficiency and Greenhouse Gas Emissions in Agricultural Soils as Producers of Biological Nitrification Inhibitors. *Frontiers in Plant Science*, **13**, Article ID: 534. https://doi.org/10.3389/fpls.2022.854195

[102] Lu, Y., Kronzucker, H.J., Yu, M., Shabala, S. and Shi, W. (2024) Nitrogen-Loss and Carbon-Footprint Reduction by Plant-Rhizosphere Exudates. *Trends in Plant Science*, **29**, 469-481. https://doi.org/10.1016/j.tplants.2023.09.007

[103] Vega-Mas, I., Ascencio-Medina, E., Bozal-Leorri, A., González-Murua, C., Marino, D. and González-Moro, M.B. (2023) Will Crops with Biological Nitrification Inhibition Capacity Be Favored under Future Atmospheric CO_2? *Frontiers in Plant Science*, **14**, Article ID: 1245427. https://doi.org/10.3389/fpls.2023.1245427

[104] Fang, Q., Lu, A., Hong, H., Kuzyakov, Y., Algeo, T.J., Zhao, L., *et al.* (2023) Mineral Weathering Is Linked to Microbial Priming in the Critical Zone. *Nature Communications*, **14**, Article No. 345. https://doi.org/10.1038/s41467-022-35671-x

[105] Bhattarai, H.R., Wanek, W., Siljanen, H.M.P., Ronkainen, J.G., Liimatainen, M., Hu, Y., *et al.* (2021) Denitrification Is the Major Nitrous Acid Production Pathway in Boreal Agricultural Soils. *Communications Earth & Environment*, **2**, Article No. 54. https://doi.org/10.1038/s43247-021-00125-7

[106] Maier, S., Kratz, A.M., Weber, J., Prass, M., Liu, F., Clark, A.T., *et al.* (2022) Water-driven Microbial Nitrogen Transformations in Biological Soil Crusts Causing Atmospheric Nitrous Acid and Nitric Oxide Emissions. *The ISME Journal*, **16**, 1012-1024. https://doi.org/10.1038/s41396-021-01127-1

[107] Dunbabin, V.M., Postma, J.A., Schnepf, A., Pagès, L., Javaux, M., Wu, L., *et al.* (2013) Modelling Root-Soil Interactions Using Three-Dimensional Models of Root Growth, Architecture and Function. *Plant and Soil*, **372**, 93-124. https://doi.org/10.1007/s11104-013-1769-y

[108] Wendeborn, S. (2020) The Chemistry, Biology, and Modulation of Ammonium Nitrification in Soil. *Angewandte Chemie International Edition*, **59**, 2182-2202. https://doi.org/10.1002/anie.201903014

[109] Waqas, M.A., Li, Y., Ashraf, M.N., Ahmed, W., Wang, B., Sardar, M.F., *et al.* (2021) Long-Term Warming and Elevated CO_2 Increase Ammonia-Oxidizing Microbial Communities and Accelerate Nitrification in Paddy Soil. *Applied Soil Ecology*, **166**, Article 104063. https://doi.org/10.1016/j.apsoil.2021.104063

[110] Diao, T., Peng, Z., Niu, X., Yang, R., Ma, F. and Guo, L. (2020) Changes of Soil Microbes Related with Carbon and Nitrogen Cycling after Long-Term CO_2 Enrichment in a Typical Chinese Maize Field. *Sustainability*, **12**, Article 1250. https://doi.org/10.3390/su12031250

[111] Delgado-Baquerizo, M., Guerra, C.A., Cano-Díaz, C., Egidi, E., Wang, J., Eisenhauer, N., *et al.* (2020) The Proportion of Soil-Borne Pathogens Increases with Warming at the Global Scale. *Nature Climate Change*, **10**, 550-554. https://doi.org/10.1038/s41558-020-0759-3

[112] Chen, Y., Yao, Z., Sun, Y., Wang, E., Tian, C., Sun, Y., *et al.* (2022) Current Studies of the Effects of Drought Stress on Root Exudates and Rhizosphere Microbiomes of Crop Plant Species. *International Journal of Molecular Sciences*, **23**, Article 2374. https://doi.org/10.3390/ijms23042374

[113] Savary, S., Willocquet, L., Pethybridge, S.J., Esker, P., McRoberts, N. and Nelson, A. (2019) The Global Burden of Pathogens and Pests on Major Food Crops. *Nature Ecology & Evolution*, **3**, 430-439. https://doi.org/10.1038/s41559-018-0793-y

[114] Vannier, N., Agler, M. and Hacquard, S. (2019) Microbiota-Mediated Disease Resistance in Plants. *PLOS Pathogens*, **15**, e1007740. https://doi.org/10.1371/journal.ppat.1007740

[115] Yang, K., Fu, R., Feng, H., Jiang, G., Finkel, O., Sun, T., *et al.* (2023) RIN Enhances Plant Disease Resistance via Root Exudate-Mediated Assembly of Disease-Suppressive Rhizosphere Microbiota. *Molecular Plant*, **16**, 1379-1395. https://doi.org/10.1016/j.molp.2023.08.004

[116] Zhou, X., Zhang, J., Khashi u Rahman, M., Gao, D., Wei, Z., Wu, F., *et al.* (2023) Interspecific Plant Interaction via Root Exudates Structures the Disease Suppressiveness of Rhizosphere Microbiomes. *Molecular Plant*, **16**, 849-864. https://doi.org/10.1016/j.molp.2023.03.009

[117] Escudero-Martinez, C., Coulter, M., Alegria Terrazas, R., Foito, A., Kapadia, R., Pie-

trangelo, L., *et al.* (2022) Identifying Plant Genes Shaping Microbiota Composition in the Barley Rhizosphere. *Nature Communications*, **13**, Article No. 3443. https://doi.org/10.1038/s41467-022-31022-y

[118] Backer, R., Rokem, J.S., Ilangumaran, G., Lamont, J., Praslickova, D., Ricci, E., *et al.* (2018) Plant Growth-Promoting Rhizobacteria: Context, Mechanisms of Action, and Roadmap to Commercialization of Biostimulants for Sustainable Agriculture. *Frontiers in Plant Science*, **9**, Article ID: 1473. https://doi.org/10.3389/fpls.2018.01473

[119] Nazari, M. and Smith, D.L. (2020) A PGPR-Produced Bacteriocin for Sustainable Agriculture: A Review of Thuricin 17 Characteristics and Applications. *Frontiers in Plant Science*, **11**, Article ID: 916. https://doi.org/10.3389/fpls.2020.00916

[120] Upadhyay, S.K., Srivastava, A.K., Rajput, V.D., Chauhan, P.K., Bhojiya, A.A., Jain, D., *et al.* (2022) Root Exudates: Mechanistic Insight of Plant Growth Promoting Rhizobacteria for Sustainable Crop Production. *Frontiers in Microbiology*, **13**, Article ID: 916488. https://doi.org/10.3389/fmicb.2022.916488

[121] Lamichhane, J.R., Barbetti, M.J., Chilvers, M.I., Pandey, A.K. and Steinberg, C. (2024) Exploiting Root Exudates to Manage Soil-Borne Disease Complexes in a Changing Climate. *Trends in Microbiology*, **32**, 27-37. https://doi.org/10.1016/j.tim.2023.07.011

[122] Gupta, V., Kumar, G.N. and Buch, A. (2020) Colonization by Multi-Potential Pseudomonas Aeruginosa P4 Stimulates Peanut (*Arachis hypogaea* L.) Growth, Defence Physiology and Root System Functioning to Benefit the Root-Rhizobacterial Interface. *Journal of Plant Physiology*, **248**, Article 153144. https://doi.org/10.1016/j.jplph.2020.153144

[123] Bashir, S., Iqbal, A., Hasnain, S. and White, J.F. (2021) Screening of Sunflower Associated Bacteria as Biocontrol Agents for Plant Growth Promotion. *Archives of Microbiology*, **203**, 4901-4912. https://doi.org/10.1007/s00203-021-02463-8

[124] South, K.A., Nordstedt, N.P. and Jones, M.L. (2021) Identification of Plant Growth Promoting Rhizobacteria That Improve the Performance of Greenhouse-Grown Petunias under Low Fertility Conditions. *Plants*, **10**, Article 1410. https://doi.org/10.3390/plants10071410

[125] Canarini, A., Kaiser, C., Merchant, A., Richter, A. and Wanek, W. (2019) Root Exudation of Primary Metabolites: Mechanisms and Their Roles in Plant Responses to Environmental Stimuli. *Frontiers in Plant Science*, **10**, Article ID: 157. https://doi.org/10.3389/fpls.2019.00157

[126] Khan, A.L. (2023) The Phytomicrobiome: Solving Plant Stress Tolerance under Climate Change. *Frontiers in Plant Science*, **14**, Article ID: 1219366. https://doi.org/10.3389/fpls.2023.1219366

[127] Lynch, J.P., Galindo-Castañeda, T., Schneider, H.M., Sidhu, J.S., Rangarajan, H. and York, L.M. (2024) Root Phenotypes for Improved Nitrogen Capture. *Plant and Soil*, **502**, 31-85. https://doi.org/10.1007/s11104-023-06301-2

[128] Karlova, R., Boer, D., Hayes, S. and Testerink, C. (2021) Root Plasticity under Abiotic Stress. *Plant Physiology*, **187**, 1057-1070. https://doi.org/10.1093/plphys/kiab392

[129] Han, C., Wang, L., Lyu, J., Shi, W., Yao, L., Fan, M., *et al.* (2023) Brassinosteroid Signaling and Molecular Crosstalk with Nutrients in Plants. *Journal of Genetics and Genomics*, **50**, 541-553. https://doi.org/10.1016/j.jgg.2023.03.004

[130] Burak, E., Quinton, J.N. and Dodd, I.C. (2021) Root Hairs Are the Most Important Root Trait for Rhizosheath Formation of Barley (*Hordeum vulgare*), Maize (*Zea mays*) and *lotus Japonicus* (Gifu). *Annals of Botany*, **128**, 45-57. https://doi.org/10.1093/aob/mcab029

[131] Qiao, M., Sun, R., Wang, Z., Dumack, K., Xie, X., Dai, C., *et al.* (2024) Legume Rhizodeposition Promotes Nitrogen Fixation by Soil Microbiota under Crop Diversification. *Nature Communications*, **15**, Article No. 2924. https://doi.org/10.1038/s41467-024-47159-x

[132] Yu, P., He, X., Baer, M., Beirinckx, S., Tian, T., Moya, Y.A.T., *et al.* (2021) Plant Flavones Enrich Rhizosphere Oxalobacteraceae to Improve Maize Performance under Nitrogen Deprivation. *Nature Plants*, **7**, 481-499. https://doi.org/10.1038/s41477-021-00897-y

[133] Salas-González, I., Reyt, G., Flis, P., Custódio, V., Gopaulchan, D., Bakhoum, N., *et al.* (2021) Coordination between Microbiota and Root Endodermis Supports Plant Mineral Nutrient Homeostasis. *Science*, **371**, eabd0695. https://doi.org/10.1126/science.abd0695

[134] Galindo-Castañeda, T., Rojas, C., Karaöz, U., Brodie, E.L., Brown, K.M. and Lynch, J.P. (2023) Influence of Root Cortical Aerenchyma on the Rhizosphere Microbiome of Field-Grown Maize. Biorxiv. https://doi.org/10.1101/2023.01.31.525837

[135] Bacher, H., Montagu, A., Herrmann, I., Walia, H., Schwartz, N. and Peleg, Z. (2023) Stress-Induced Deeper Rooting Introgression Enhances Wheat Yield under Terminal Drought. *Journal of Experimental Botany*, **74**, 4862-4874. https://doi.org/10.1093/jxb/erad059

[136] Sprunger, C.D., Culman, S.W., Peralta, A.L., DuPont, S.T., Lennon, J.T. and Snapp, S.S. (2019) Perennial Grain Crop Roots and Nitrogen Management Shape Soil Food Webs and Soil Carbon Dynamics. *Soil Biology and Biochemistry*, **137**, Article 107573. https://doi.org/10.1016/j.soilbio.2019.107573

[137] Glover, J.D., Reganold, J.P., Bell, L.W., Borevitz, J., Brummer, E.C., Buckler, E.S., *et al.* (2010) Increased Food and Ecosystem Security via Perennial Grains. *Science*, **328**, 1638-1639. https://doi.org/10.1126/science.1188761

[138] Glover, J.D. (2005) The Necessity and Possibility of Perennial Grain Production Systems. *Renewable Agriculture and Food Systems*, **20**, 1-4. https://doi.org/10.1079/raf200499

[139] DeHaan, L.R., Van Tassel, D.L. and Cox, T.S. (2005) Perennial Grain Crops: A Synthesis of Ecology and Plant Breeding. *Renewable Agriculture and Food Systems*, **20**, 5-14. https://doi.org/10.1079/raf200496

[140] Sprunger, C.D. and Philip Robertson, G. (2018) Early Accumulation of Active Fraction Soil Carbon in Newly Established Cellulosic Biofuel Systems. *Geoderma*, **318**, 42-51. https://doi.org/10.1016/j.geoderma.2017.11.040

[141] Loomis, R.S. (2022) Perils of Production with Perennial Polycultures. *Outlook on Agriculture*, **51**, 22-31. https://doi.org/10.1177/00307270211063910

[142] Olsson, L., Andersson, E., Ardö, J., Crews, T., David, C., DeHaan, L., *et al.* (2024) What Is the Prospect of a Perennial Grain Revolution of Agriculture? *Global Sustainability*, **7**, e35. https://doi.org/10.1017/sus.2024.27

[143] DeHaan, L.R., Anderson, J.A., Bajgain, P., Basche, A., *et al.* (2023) Discussion: Prioritize Perennial Grain Development for Sustainable Food Production and Environmental Benefits. *Science of The Total Environment*, **895**, Article 164975.

[144] Guo, C., Lin, W., Gao, W., Lan, C., Xu, H., Zou, J., *et al.* (2023) Physiological Properties of Perennial Rice Regenerating Cultivation in Two Years with Four Harvests. *Plants*, **12**, Article 3910. https://doi.org/10.3390/plants12223910

[145] Zhang, S., Huang, G., Zhang, Y., Lv, X., Wan, K., Liang, J., *et al.* (2022) Sustained Productivity and Agronomic Potential of Perennial Rice. *Nature Sustainability*, **6**, 28-38. https://doi.org/10.1038/s41893-022-00997-3

[146] Vico, G., Tang, F.H.M., Brunsell, N.A., Crews, T.E. and Katul, G.G. (2023) Photosynthetic Capacity, Canopy Size and Rooting Depth Mediate Response to Heat and Water Stress of Annual and Perennial Grain Crops. *Agricultural and Forest Meteorology*, **341**, Article 109666. https://doi.org/10.1016/j.agrformet.2023.109666

[147] Taylor, K.M., Nelsen, T.S., Scow, K.M. and Lundy, M.E. (2024) No-Till Annual Wheat Increases Plant Productivity, Soil Microbial Biomass, and Soil Carbon Stabilization Relative to Intermediate Wheatgrass in a Mediterranean Climate. *Soil and Tillage Research*, **235**, Article 105874. https://doi.org/10.1016/j.still.2023.105874

[148] Andrea Jordan, C. and Akay, G. (2012) Speciation and Distribution of Alkali, Alkali Earth Metals and Major Ash Forming Elements during Gasification of Fuel Cane Bagasse. *Fuel*, **91**, 253-263. https://doi.org/10.1016/j.fuel.2011.05.031

[149] York, L.M., Carminati, A., Mooney, S.J., Ritz, K. and Bennett, M.J. (2016) The Holistic Rhizosphere: Integrating Zones, Processes, and Semantics in the Soil Influenced by Roots. *Journal of Experimental Botany*, **67**, 3629-3643. https://doi.org/10.1093/jxb/erw108

[150] Mo, X., Wang, M., Zeng, H. and Wang, J. (2023) Rhizosheath: Distinct Features and Environmental Functions. *Geoderma*, **435**, Article 116500. https://doi.org/10.1016/j.geoderma.2023.116500

[151] Ani, M., Schaumann, G.E. and Diehl, D. (2023) Influence of Nanoscale Spatial Architecture of Seed and Root Mucilage on Its Wettability. *Rhizosphere*, **28**, Article 100803. https://doi.org/10.1016/j.rhisph.2023.100803

[152] Marasco, R., Fusi, M., Ramond, J., Van Goethem, M.W., Seferji, K., Maggs-Kölling, G., *et al.* (2022) The Plant Rhizosheath-Root Niche Is an Edaphic "Mini-Oasis" in Hyperarid Deserts with Enhanced Microbial Competition. *ISME Communications*, **2**, Article 47. https://doi.org/10.1038/s43705-022-00130-7

[153] Lucas, J.M., Gora, E., Salzberg, A. and Kaspari, M. (2019) Antibiotics as Chemical Warfare across Multiple Taxonomic Domains and Trophic Levels in Brown Food Webs. *Proceedings of the Royal Society B*: *Biological Sciences*, **286**, Article 20191536. https://doi.org/10.1098/rspb.2019.1536

[154] Ahmadi, K., Zarebanadkouki, M., Ahmed, M.A., Ferrarini, A., Kuzyakov, Y., Kostka, S.J., *et al.* (2017) Rhizosphere Engineering: Innovative Improvement of Root Environment. *Rhizosphere*, **3**, 176-184. https://doi.org/10.1016/j.rhisph.2017.04.015

[155] Wang, C. and Kuzyakov, Y. (2024) Rhizosphere Engineering for Soil Carbon Sequestration. *Trends in Plant Science*, **29**, 447-468. https://doi.org/10.1016/j.tplants.2023.09.015

[156] Zhang, K., Rengel, Z., Zhang, F., White, P.J. and Shen, J. (2023) Rhizosphere Engineering for Sustainable Crop Production: Entropy-Based Insights. *Trends in Plant Science*, **28**, 390-398. https://doi.org/10.1016/j.tplants.2022.11.008

[157] Dlamini, S.P., Akanmu, A.O. and Babalola, O.O. (2022) Rhizospheric Microorganisms: The Gateway to a Sustainable Plant Health. *Frontiers in Sustainable Food Systems*, **6**, Article ID: 925802. https://doi.org/10.3389/fsufs.2022.925802

[158] Mitter, E.K., Tosi, M., Obregón, D., Dunfield, K.E. and Germida, J.J. (2021) Rethinking Crop Nutrition in Times of Modern Microbiology: Innovative Biofertilizer Technologies. *Frontiers in Sustainable Food Systems*, **5**, Article ID: 606815. https://doi.org/10.3389/fsufs.2021.606815

[159] de Souza, J.E.B. and de Brito Ferreira, E.P. (2017) Improving Sustainability of Common Bean Production Systems by Co-Inoculating Rhizobia and Azospirilla. *Agriculture, Ecosystems & Environment*, **237**, 250-257. https://doi.org/10.1016/j.agee.2016.12.040

[160] Elnahal, A.S.M., El-Saadony, M.T., Saad, A.M., Desoky, E.M., El-Tahan, A.M., Rady, M.M., *et al.* (2022) The Use of Microbial Inoculants for Biological Control, Plant Growth Promotion, and Sustainable Agriculture: A Review. *European Journal of Plant Pathology*, **162**, 759-792. https://doi.org/10.1007/s10658-021-02393-7

[161] Cassán, F., Coniglio, A., López, G., Molina, R., Nievas, S., de Carlan, C.L.N., *et al.* (2020) Everything You Must Know about Azospirillum and Its Impact on Agriculture and Beyond. *Biology and Fertility of Soils*, **56**, 461-479. https://doi.org/10.1007/s00374-020-01463-y

[162] Akay, G. and Fleming, S. (2011) Engineered Ecosystem Development for Agro-Process Intensification. *WIT Transactions on Ecology and the Environment*, **114**, 485-495. https://doi.org/10.2495/eco110421

[163] Srivastava, R.K. and Yetgin, A. (2024) An Overall Review on Influence of Root Architecture on Soil Carbon Sequestration Potential. *Theoretical and Experimental Plant Physiology*, **36**, 165-178. https://doi.org/10.1007/s40626-024-00323-6

[164] Yetgin, A. (2024) Exploring the Dynamic Nature of Root Plasticity and Morphology in the Face of Changing Environments. *Ecological Frontiers*, **44**, 112-119. https://doi.org/10.1016/j.chnaes.2023.07.008

[165] DeLisi, C. (2024) An Agrigenomics Trifecta: Greenhouse Gas Drawdown, Food Security, and New Drugs. *Cold Spring Harbor Perspectives in Biology*, **16**, a041676. https://doi.org/10.1101/cshperspect.a041676

[166] DeLisi, C., Patrinos, A., MacCracken, M., Drell, D., Annas, G., Arkin, A., *et al.* (2020) The Role of Synthetic Biology in Atmospheric Greenhouse Gas Reduction: Prospects and Challenges. *BioDesign Research*, **2020**, Article 1016207. https://doi.org/10.34133/2020/1016207

[167] Giddings, L.V. (2023) Overcoming Obstacles to Gene-Edited Solutions to Climate Challenges. *Cold Spring Harbor Perspectives in Biology*, **16**, a041677. https://doi.org/10.1101/cshperspect.a041677

[168] Chai, Y.N. and Schachtman, D.P. (2022) Root Exudates Impact Plant Performance under Abiotic Stress. *Trends in Plant Science*, **27**, 80-91. https://doi.org/10.1016/j.tplants.2021.08.003

[169] DeMirci, H., Rao, Y., Stoffel, G.M., Vögeli, B., Schell, K., Gomez, A., *et al.* (2022) Intersubunit Coupling Enables Fast CO_2-Fixation by Reductive Carboxylases. *ACS Central Science*, **8**, 1091-1101. https://doi.org/10.1021/acscentsci.2c00057

[170] Erb, T.J. (2024) Photosynthesis 2.0: Realizing New-to-Nature CO_2-Fixation to Overcome the Limits of Natural Metabolism. *Cold Spring Harbor Perspectives in Biology*, **16**, a041669. https://doi.org/10.1101/cshperspect.a041669

[171] Uren, N.C. (2018) Calcium Oxalate in Soils, Its Origins and Fate—A Review. *Soil Research*, **56**, 443-450. https://doi.org/10.1071/sr17244

[172] Nel, T., Clarke, C.E., Francis, M.L., Stone, W., Cowan, D.A., Botha, A., *et al.* (2024) Efficient Quantification of Soluble and Insoluble Oxalates in Clay Mineral Mixtures. *Communications in Soil Science and Plant Analysis*, **55**, 1985-1999. https://doi.org/10.1080/00103624.2024.2336574

[173] He, H., Li, D., Li, X. and Fu, L. (2024) Research Progress on the Formation, Function, and Impact of Calcium Oxalate Crystals in Plants. *Crystallography Reviews*, **30**, 31-60. https://doi.org/10.1080/0889311x.2024.2309486

[174] Burritt, D.J. (2019) Crop Plant Adaption to Climate Change and Extreme Environments. In: Melton, L., Shahidi, F. and Varelis P., Eds., *Encyclopedia of Food Chemistry*, Academic Press, 196-201. https://doi.org/10.1016/b978-0-08-100596-5.22333-0

[175] Soares, J.C., Santos, C.S., Carvalho, S.M.P., Pintado, M.M. and Vasconcelos, M.W. (2019) Preserving the Nutritional Quality of Crop Plants under a Changing Climate: Importance and Strategies. *Plant and Soil*, **443**, 1-26. https://doi.org/10.1007/s11104-019-04229-0

[176] Briat, J., Dubos, C. and Gaymard, F. (2015) Iron Nutrition, Biomass Production, and Plant Product Quality. *Trends in Plant Science*, **20**, 33-40. https://doi.org/10.1016/j.tplants.2014.07.005

[177] Kerry, R.G., Mahapatra, G.P., Patra, S., Sahoo, S.L., Pradhan, C., Padhi, B.K., *et al.* (2018) Proteomic and Genomic Responses of Plants to Nutritional Stress. *BioMetals*, **31**, 161-187. https://doi.org/10.1007/s10534-018-0083-9

[178] Tripathi, D.K., Singh, S., Singh, S., Mishra, S., Chauhan, D.K. and Dubey, N.K. (2015) Micronutrients and Their Diverse Role in Agricultural Crops: Advances and Future Prospective. *Acta Physiologiae Plantarum*, **37**, Article No. 139. https://doi.org/10.1007/s11738-015-1870-3

[179] Tiwari, H., Bhatt, R., Singh, P.K., Das, D., Vihan, S., Tomar, T., *et al.* (2024) Micronutrients in the Plant-Soil-Environment Continuum: A Comprehensive Review. *European Journal of Nutrition & Food Safety*, **16**, 171-178. https://doi.org/10.9734/ejnfs/2024/v16i71465

[180] Indian Micro Fertilizers Manufacturers Association (IMMA) (2024) Micronutrients for Plants Growth. https://imma.co.in/micronutrients-for-plants

[181] Marschner, H. (2012) Marschner's Mineral Nutrition of Higher Plants. Vol. 89, Academic Press. https://doi.org/10.1016/C2009-0-63043-9

[182] Nakandalage, N. and Seneweera, S. (2018) Micronutrients Use Efficiency of Crop-Plants under Changing Climate. In: Hossain, M.A., Kamiya,T., Burritt, D.J., Phan, T. L.-S. and Fujiwara, T., Eds., *Plant Micronutrient Use Efficiency*, Academic Press, 209-224. https://doi.org/10.1016/b978-0-12-812104-7.00015-0

[183] Mok, Z.H. (2024) The Effect of Particle Size on Drug Bioavailability in Various Parts of the Body. *Pharmaceutical Science Advances*, **2**, Article 100031. https://doi.org/10.1016/j.pscia.2023.100031

[184] Foroozandeh, P. and Aziz, A.A. (2018) Insight into Cellular Uptake and Intracellular Trafficking of Nanoparticles. *Nanoscale Research Letters*, **13**, Article No. 339. https://doi.org/10.1186/s11671-018-2728-6

[185] Xu, G., Li, X., Zhu, T., Wang, F. and Yin, J. (2025) When Nano- and Microplastics Meet Taro (*Colocasia esculenta*) Roots: Their Size-Dependent Adsorption, Penetration, and Promotion on Secondary Wall Reinforcement. *Environmental Science & Technology*, **59**, 8345-8356. https://doi.org/10.1021/acs.est.4c11230

[186] Wang, Z., Jiang, D.D., McKinney, M.A. and Wilkie, C.A. (1999) Cross-Linking of Polystyrene by Friedel-Crafts Chemistry to Improve Thermal Stability. *Polymer Degradation and Stability*, **64**, 387-395. https://doi.org/10.1016/s0141-3910(98)00159-1

[187] Mikkelsen, A., Wojciechowski, J., Rajňák, M., Kurimský, J., Khobaib, K., Kertmen, A., *et al.* (2017) Electric Field-Driven Assembly of Sulfonated Polystyrene Microspheres. *Materials*, **10**, Article 329. https://doi.org/10.3390/ma10040329

[188] Li, C., Che, W., Liu, S.-Y. and Liao, G. (2023) Hypercrosslinked Microporous Polystyrene: From Synthesis to Properties to Applications. *Materials Today Chemistry*, **29**, Article 101392. https://doi.org/10.1016/j.mtchem.2023.101392

[189] Manaenkov, O., Nikoshvili, L., Bykov, A., Kislitsa, O., Grigoriev, M., Sulman, M., *et al.* (2023) An Overview of Heterogeneous Catalysts Based on Hypercrosslinked Polystyrene for the Synthesis and Transformation of Platform Chemicals Derived from

Biomass. *Molecules*, **28**, Article 8126. https://doi.org/10.3390/molecules28248126

[190] Markova, M.E., Stepacheva, A.A., Bykov, A.V., Larichev, Y.V., Doluda, V.Y., Sulman, M.G., *et al.* (2025) Fe/Ru Synthesized by Hydrothermal Deposition on Hyper-Cross-linked Polystyrene as Promising Fischer-Tropsch Catalyst. *Frontiers of Chemical Science and Engineering*, **19**, Article No. 28. https://doi.org/10.1007/s11705-025-2529-2

[191] Wigaeus, E., Lof, A., Bjurström, R. and Nordqvist, M.B. (1983) Exposure to Styrene. Uptake, Distribution, Metabolism and Elimination in Man. *Scandinavian Journal of Work, Environment & Health*, **9**, 479-488. https://doi.org/10.5271/sjweh.2385

[192] Mohamadyan, M., Moosazadeh, M., Borji, A., Khanjani, N. and Moghadam, S.R. (2019) Occupational Exposure to Styrene and Its Relation with Urine Mandelic Acid, in Plastic Injection Workers. *Environmental Monitoring and Assessment*, **191**, Article No. 62. https://doi.org/10.1007/s10661-019-7191-z

[193] Gąszczak, A., Bartelmus, G. and Greń, I. (2011) Kinetics of Styrene Biodegradation by *Pseudomonas* Sp. E-93486. *Applied Microbiology and Biotechnology*, **93**, 565-573. https://doi.org/10.1007/s00253-011-3518-6

[194] Tan, G.A., Chen, C., Ge, L., Li, L., Tan, S.N. and Wang, J. (2015) Bioconversion of Styrene to Poly(Hydroxyalkanoate) (PHA) by the New Bacterial Strain *Pseudomonas putida* Nbus12. *Microbes and environments*, **30**, 76-85. https://doi.org/10.1264/jsme2.me14138

[195] Anon (2012) CLH Report for Styrene. Danish Environmental Protection Agency. https://echa.europa.eu/documents/10162/e7c7d1a1-b42a-410b-8afe-62b8ada88ca5

[196] Lambré, C., Crebelli, R., Da Silva, M., Grob, K., Lampi, E., Milana, M.R., *et al.* (2025) Reassessment of the Risks to Public Health Related to the Genotoxicity of Styrene Present in Plastic Food Contact Materials. *EFSA Journal*, **23**, e9473. https://doi.org/10.2903/j.efsa.2025.9473

[197] Zumstein, M.T., Schintlmeister, A., Nelson, T.F., Baumgartner, R., Woebken, D., Wagner, M., *et al.* (2018) Biodegradation of Synthetic Polymers in Soils: Tracking Carbon into CO_2 and Microbial Biomass. *Science Advances*, **4**, eaas9024. https://doi.org/10.1126/sciadv.aas9024

[198] Glaser, J.A. (2019) Biological Degradation of Polymers in the Environment. In: Gomiero, A., Ed., *Plastics in the Environment*, IntechOpen, Chapter 5. https://doi.org/10.5772/intechopen.85124

[199] Chamas, A., Moon, H., Zheng, J., Qiu, Y., Tabassum, T., Jang, J.H., *et al.* (2020) Degradation Rates of Plastics in the Environment. *ACS Sustainable Chemistry & Engineering*, **8**, 3494-3511. https://doi.org/10.1021/acssuschemeng.9b06635

[200] Samir, A., Ashour, F.H., Hakim, A.A.A. and Bassyouni, M. (2022) Recent Advances in Biodegradable Polymers for Sustainable Applications. *npj Materials Degradation*, **6**, Article No. 68. https://doi.org/10.1038/s41529-022-00277-7

[201] Silva, R.R.A., Marques, C.S., Arruda, T.R., Teixeira, S.C. and de Oliveira, T.V. (2023) Biodegradation of Polymers: Stages, Measurement, Standards and Prospects. *Macromol*, **3**, 371-399. https://doi.org/10.3390/macromol3020023

[202] Brun, N.R., van Hage, P., Hunting, E.R., Haramis, A.G., Vink, S.C., Vijver, M.G., *et al.* (2019) Polystyrene Nanoplastics Disrupt Glucose Metabolism and Cortisol Levels with a Possible Link to Behavioural Changes in Larval Zebrafish. *Communications Biology*, **2**, Article No. 382. https://doi.org/10.1038/s42003-019-0629-6

[203] Dhada, I., Periyasamy, A., Sahoo, K.K., Manojkumar, Y. and Pilli, S. (2023) Microplastics and Nanoplastics: Occurrence, Fate, and Persistence in Wastewater Treatment Plants. In: Tyagi, R.D., Pandey, A., *et al.*, Eds., *Current Developments in Biotechnology and Bioengineering*, Elsevier, 201-240.

https://doi.org/10.1016/b978-0-323-99908-3.00016-6

[204] Biao, W., Hashim, N.A., Rabuni, M.F.B., Lide, O. and Ullah, A. (2024) Microplastics in Aquatic Systems: An In-Depth Review of Current and Potential Water Treatment Processes. *Chemosphere*, **361**, Article 142546. https://doi.org/10.1016/j.chemosphere.2024.142546

[205] Sun, X., Yuan, X., Jia, Y., Feng, L., Zhu, F., Dong, S., *et al.* (2020) Differentially Charged Nanoplastics Demonstrate Distinct Accumulation in Arabidopsis Thaliana. *Nature Nanotechnology*, **15**, 755-760. https://doi.org/10.1038/s41565-020-0707-4

[206] Compant, S., Cassan, F., Kostić, T., Johnson, L., Brader, G., Trognitz, F., *et al.* (2024) Harnessing the Plant Microbiome for Sustainable Crop Production. *Nature Reviews Microbiology*, **23**, 9-23. https://doi.org/10.1038/s41579-024-01079-1

[207] Yuan, M.M., Guo, X., Wu, L., Zhang, Y., Xiao, N., Ning, D., *et al.* (2021) Climate Warming Enhances Microbial Network Complexity and Stability. *Nature Climate Change*, **11**, 343-348. https://doi.org/10.1038/s41558-021-00989-9

[208] Liu, S., Wu, J., Cheng, Z., Jin, Z., Zhang, X., *et al.* (2025) Microbe-Mediated Stress Resistance in Plants: The Roles Played by Core and Stress-Specific Microbiota. *Microbiome*, **13**, Article 111. https://doi.org/10.1186/s40168-025-02103-z

[209] Akay, G. and Irving, N. (2002) Dynamic Mixing Apparatus for the Production of Liquid Compositions. US Patent US63445907. https://patents.google.com/patent/US6345907B1/en

[210] Akay, G. (2011) Integrated Process Intensification: The Development of Intensified Integrated Biorefinery Technology to Help Combat Global Warming. *Public Service Review*: *UK Science and Technology*, **3**, 148-152. https://portal.issn.org/resource/ISSN/2045-3884

[211] Roossinck, M.J. (2015) A New Look at Plant Viruses and Their Potential Beneficial Roles in Crops. *Molecular Plant Pathology*, **16**, 331-333. https://doi.org/10.1111/mpp.12241

[212] Chen, Q., Song, Y., An, Y., Lu, Y. and Zhong, G. (2024) Soil Microorganisms: Their Role in Enhancing Crop Nutrition and Health. *Diversity*, **16**, Article 734. https://doi.org/10.3390/d16120734

[213] Nguyen, M.T.P., Knowling, M., Tran, N.N., Burgess, A., Fisk, I., Watt, M., *et al.* (2023) Space Farming: Horticulture Systems on Spacecraft and Outlook to Planetary Space Exploration. *Plant Physiology and Biochemistry*, **194**, 708-721. https://doi.org/10.1016/j.plaphy.2022.12.017

[214] Butler, C., Fan, Y., Grewal, S. and Winter, L.R. (2023) At-Field and On-Demand Nitrogenous Fertilizer Synthesis. *ACS Sustainable Chemistry & Engineering*, **11**, 5803-5818. https://doi.org/10.1021/acssuschemeng.2c06551

[215] Cao, Y., Pan, Y., Yang, Y., Liu, T., Wang, M., Li, Y., *et al.* (2024) Variation of Mesophyll Conductance Mediated by Nitrogen Form Is Related to Changes in Cell Wall Property and Chloroplast Number. *Horticulture Research*, **11**, uhae112. https://doi.org/10.1093/hr/uhae112

[216] Ruiz-Martín, M., Oliva-Ramírez, M., González-Elipe, A.R. and Gómez-Ramírez, A. (2025) Plasma Catalysis for Gas Conversion—Impact of Catalyst on the Plasma Behavior. *Current Opinion in Green and Sustainable Chemistry*, **51**, Article 100990. https://doi.org/10.1016/j.cogsc.2024.100990

[217] Gadikota, G. (2021) Carbon Mineralization Pathways for Carbon Capture, Storage and Utilization. *Communications Chemistry*, **4**, Article No. 23. https://doi.org/10.1038/s42004-021-00461-x

[218] Katre, S., Ochonma, P., Mamidala, A., Sahu, S., Nair, A.M., Ravi, K., *et al.* (2025) Organic Ligands and CO_2 Unlock the Potential for Energy Relevant Metals Recovery and Carbon Mineralization from Mafic Rocks. *Scientific Reports*, **15**, Article No. 10882. https://doi.org/10.1038/s41598-025-94153-4

[219] Srivastava, R.K., Purohit, S., Alam, E. and Islam, M.K. (2024) Advancements in Soil Management: Optimizing Crop Production through Interdisciplinary Approaches. *Journal of Agriculture and Food Research*, **18**, Article 101528. https://doi.org/10.1016/j.jafr.2024.101528

[220] Joshi, D., Kaushik, A., Kumar, R., Arya, A., Santoyo, G., Singh, V.K., *et al.* (2025) Improving Plant Performance through Microbiome Manipulation: The Potential Role of Current Bioengineering Approaches. *Bacteria*, **4**, Article No. 12. https://doi.org/10.3390/bacteria4010012