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综述

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微藻固定化培养材料的构建策略及应用进展

李晓意,隆宇欣,谭魏葳,江民文,周加境*,杜晓声*

(四川大学 轻工科学与工程学院,四川 成都 610065)

摘要:微藻因具备较高的光合固碳效率和多样化产物合成能力,已被广泛应用于废水处理、碳捕集、生物能源开发及高价值化学品生产等研究领域。相比传统悬浮培养,固定化培养更有利于细胞富集和体系稳定运行,同时也能在一定程度上简化生物量回收过程,并提高系统对外界环境波动的耐受性。以微藻固定化培养材料为核心,综述了天然高分子、合成高分子、复合材料及功能化材料的构建方式和应用进展,并比较了包埋法与附着法在操作特点和适用场景上的差异。进一步归纳了固定化微藻在环境治理、能源转化、食品制造和农业资源化方面的潜在应用。总体来看,该技术仍面临传质效率受限、长期稳定性有待提高以及工程化放大较为困难等问题,后续研究仍需围绕材料优化、反应器设计和运行调控等方面展开。

关键词:微藻;固定化培养;载体材料;资源利用

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Construction strategy and application progress of immobilized culture materials for microalgae

LI Xiaoyi, LONG Yuxin, TAN Weiwei, JIANG Minwen, ZHOU Jiajing*, DU Xiaosheng*

(College of Biomass Science and Engineering, Sichuan University, Chengdu 610065, Sichuan, China)

Abstract: Microalgae have attracted extensive attention in wastewater treatment, carbon capture, bioenergy production, and the synthesis of high-value chemicals owing to their efficient photosynthetic carbon fixation capacity and potential for the production of diverse metabolites. Compared with conventional suspended cultivation, immobilized cultivation exhibits significant advantages in increasing cell density, enhancing system stability, simplifying biomass recovery, and improving resistance to environmental fluctuations. Focusing on the construction and application of materials for microalgal immobilized cultivation, this paper reviews the research progress of natural polymers, synthetic polymers, composite materials, and functional materials in this field, and compares the operational characteristics and applicable scenarios between the embedding method and the attachment method. On this basis, the application potential of microalgal immobilization in environmental remediation, energy conversion, food production, and agricultural resource utilization is further outlined. Meanwhile, mass transfer limitations, insufficient long-term stability, and difficulties in scale-up remain key challenges restricting its further development. Subsequent research still needs to focus on material optimization, reactor design, and operational regulation.

Key words: microalgae; immobilized cultivation; carrier materials; resource utilization

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作者简介:李晓意(1997-),女,博士,研究方向为微藻在能源与环境领域的应用,E-mail:lixiaoyi320@163.com

*通信作者:周加境,男,博士,研究员,E-mail:jjzhou@scu.edu.cn;杜晓声,男,博士,副研究员,主要从事功能高分子材料、生物质材料、低介电电子树脂及光热存储材料的设计、合成及应用,E-mail:thomasdu@sina.cn

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0 引 言

微藻是一类广泛分布于水生环境中的光合微生物,在全球碳循环和初级生产力中具有重要作用。微藻具有生长周期短、光合效率高以及代谢产物类型丰富等特点,因此在生物能源、食品、医药及环境修复等领域展现出广阔的应用前景[1-4]。然而,微藻资源的规模化开发仍受到培养效率、收获成本和工艺经济性等因素的制约[5]。

悬浮培养是目前较为常用的微藻培养方式,但在规模化过程中存在生物量浓度低、培养体积大、收获与分离成本高以及易受污染等问题,限制了其应用[6]。固定化技术通常是将微藻细胞附着在载体表面,或包埋于一定的材料结构中,使其能够在相对稳定的空间内生长和富集。与悬浮培养相比,这种方式有利于提高局部细胞浓度,也可在一定程度上降低后续生物量回收的难度,并改善体系在环境波动或外源污染条件下的运行稳定性[7-8]。同时,固定化体系在传质效率、资源回收和长期运行稳定性方面具有潜在优势。基于此,本文从材料构建和应用发展的角度,对微藻固定化培养体系的相关研究进行梳理。围绕固定化材料的设计思路,综述天然高分子、合成高分子、复合材料及功能化材料在微藻培养中的应用进展;对包埋法、附着法等主要构建方式的特点及适用场景进行归纳分析。在此基础上,进一步总结固定化微藻材料在环境治理、能源转化、食品生产和农业资源化等领域的研究现状,并讨论传质受限、长期稳定性不足和工程放大难度较高等问题。相关内容可为后续固定化培养体系的材料优化、结构设计和实际应用提供参考。

1 微藻固定化培养材料体系

1.1 天然高分子材料

天然高分子材料因来源广泛、成本较低、环境友好且生物相容性良好,在微藻固定化培养中应用广泛。该类材料通常可在温和的条件下形成含水网络结构,既能固定微藻细胞,又能保持物质交换,为细胞生长提供相对稳定的环境。当前应用较多的天然高分子材料主要包括海藻酸盐、壳聚糖、卡拉胶、琼脂(糖)及纤维素类材料等(表1)。

在天然高分子材料中,海藻酸盐是应用最广泛的一类。海藻酸盐来源于褐藻,可在Ca^{2+}等二价金属离子作用下迅速形成凝胶,因制备条件温和、操作简便、细胞毒性低且能提供相对稳定的微环境,常用于构建固定化微藻凝胶微球,并广泛应用于废水处理、营养盐去除及光生物反应器培养等领域。研究表明,海藻酸盐固定化体系的处理效果与藻种密切相关,不同微藻在固定化条件下的营养盐吸收能力存在差异,从而影响整体处理效率[9]。工程应用方面,海藻酸盐固定化微藻已被用于CO_2捕集、生物质生产及真实食品工业废水处理[10-11]。同时,基于海藻酸钠/卡拉胶构建的三维固定化水凝胶体系还能在近无液体条件下实现高效培养,并持续生产蛋白质、脂类和类胡萝卜素等营养成分[12],见图1(a)。

壳聚糖是另一类常用于微藻固定化的天然高分子材料,主要由几丁质脱乙酰化制得。其分子结构中含有较多氨基基团,具有较好的生物相容性、成膜性和一定机械强度[13-14]。由于壳聚糖表面带正电,能够与带负电的微藻细胞发生静电相互作用,因此有利于细胞附着和固定。相关研究表明,壳聚糖基载体可用于固定化微藻,并促进废水中营养盐的捕

表1 微藻固定化培养中不同材料体系的比较

Table 1 Comparison of different material systems in microalgal immobilized cultivation

材料类别	主要材料体系	主要优势	关键局限性	成本	微藻培养效率	适用场景
天然高分子材料	海藻酸盐、壳聚糖、卡拉胶、琼脂、纤维素	生物相容性好、成本低、制备温和	强度和稳定性不足、易传质受限	偏低	适于常规固定化培养和营养盐去除,部分体系可维持较好生长与产物积累	废水处理、营养盐去除、食品培养
合成高分子材料	PVA、PEG/PEGDA、PU	强度高、稳定性好、结构可调	成本较高,部分体系传质仍受限	中等	培养稳定性较好,适于连续培养,优化后可提升生长和氮磷去除	废水处理、附着培养、功能载体
复合材料	天然/合成高分子复合、多孔生物质基复合	性能协同,兼顾强度与传质	体系复杂,制备与优化难度较高	中等	有助于提高细胞密度、生长效率及复杂废水处理表现	复杂废水处理、CO_2捕集、资源回收
功能化与智能化材料	3D打印、仿生结构、供氧水凝胶、响应型活体材料	光/质传递优化,功能集成度高	技术门槛高,放大应用受限	偏高	在优化光照、传质和固定稳定性方面表现突出,适合高密度与功能化培养	生物制造、创面修复、碳固定

获，同时有助于维持细胞活性和提高生物量回收效率[15]。构建的交联壳聚糖/明胶微球负载小球藻体系，可用于双酚A去除，体现出载体吸附与微藻代谢协同去除污染物的潜力[16]，见图1(a)。

此外，卡拉胶、琼脂和琼脂糖也常用于微藻固定化培养，具有良好的成胶性能和生物相容性。研究表明，卡拉胶复合水凝胶有助于提升体系机械稳定性和污染物去除效率；琼脂基固定化体系在重复使用和长期保存后仍能保持较高的氮、磷去除能力，显示出较好的应用潜力[17-18]。近年来，纤维素及其衍生材料也被用于微藻固定化体系。该类材料来源丰富、可再生性强且结构稳定。通过引入纳米纤维素或与其他天然高分子复合，可改善水凝胶的机械强度和长期运行稳定性。相关研究表明，纤维素基复合水凝胶在养殖废水处理中具有良好的营养盐去除效果和重复使用潜力，同时也可作为微藻附着培养的三维支架，用于结构化培养和3D打印生物墨水开发[19-20]。

1.2 合成高分子材料

与天然高分子材料相比，合成高分子材料通常具有更高的机械强度、化学稳定性和结构可调控性，因此，在微藻固定化培养中逐渐受到关注。可以通过调控聚合方式、交联密度和孔结构，构建稳定的三维网络，为微藻细胞提供适宜的附着位点和生长微环境。目前，聚乙烯醇、聚乙二醇及其衍生物、聚氨酯等是相关研究中较常见的合成高分子材料。

聚乙烯醇(polyvinyl alcohol，PVA)是微藻固定化中常用的合成高分子载体，具有较好的成胶性和机械稳定性。通过冷冻-融化处理，PVA可形成孔道相对连通的多孔凝胶结构，有助于改善体系内物质传递。相关研究显示，PVA固定化微藻体系在废水处理中可实现较好的总氮和总磷去除效果，并具有一定连续运行稳定性[21]，见图1(b)；在凝胶珠中引入光纤结构后，内部光照分布可得到一定改善，从而缓解光遮蔽并促进微藻生长和营养盐去除[22]。PVA/海藻酸盐杂化水凝胶还可用于微藻-硝化细菌共固定化，有助于提高载体稳定性和废水脱氮效果[23]。总体来看，PVA基载体具有较好的力学性能和运行稳定性，但仍可能受到传质阻力限制，后续可通过复合改性和孔结构调控进一步优化。

近年来，聚乙二醇(polyethylene glycol，PEG)及其衍生物也逐渐被用于微藻固定化培养，其中聚乙二醇二丙烯酸酯(polyethylene glycol diacrylate，PEGDA)受到较多关注。PEG类材料通常具有较好的亲水性和透光性，其交联结构可通过光聚合方式进行调节。因此，适合构建具有一定结构稳定性的固定化体系。研究显示，PEGDA/海藻酸盐双网络水凝胶结合表面包覆策略，有助于减少细胞泄漏并提高载体稳定性，同时在抗生素污染物降解和重复利用方面具有一定应用潜力[24]；Pluronic F127二丙烯酸酯(F127-DA)/PEGDA光合活体水凝胶能够改善凝胶基体的力学性能和结构稳定性，有利于微藻在三维体系中的长期固定和功能保持[25]，见图1(b)。总体来看，PEGDA及其光固化体系便于结构调控和功能整合，在模块化微藻固定化平台构建中具有一定应用潜力。

另一类具有应用潜力的合成高分子材料是聚氨酯(polyurethane，PU)，通常以多孔泡沫形式作为载体。其较高的孔隙率和比表面积有利于微藻细胞附着，但孔径和尺寸差异也会影响细胞生长及污染物去除效果。相关研究显示，PU泡沫可促进营养盐同化和生物量回收，并在提高氢气产率及维持体系稳定性方面具有一定作用[26-28]。

1.3 复合材料体系

相比单一载体，复合材料可通过不同高分子、增强组分或多孔基质的组合，改善固定化体系的结构和功能表现。研究表明，天然高分子之间或其与合成高分子的复合，可在保持较好生物相容性的同时，提高凝胶稳定性和营养盐去除效果[23, 29]；引入气泡结构或无机增强组分后，还可改善局部微环境，促进细胞生长和氮磷去除[30]，见图1(c)。总体来看，复合材料体系为提升固定化微藻在复杂废水环境中的运行稳定性提供了一种可行思路。

1.4 功能化与智能固定化材料

随着微藻固定化研究的推进，材料设计逐渐从单一载体支撑转向更精细的结构调控。通过引入光调控或环境响应等功能，固定化体系的光利用和物质传递过程有望得到改善，其应用也开始向生物制造等方向延伸。仿生结构设计是其中的重要方向，例如，3D(生物)打印可用于构建类珊瑚微环境，调节光传输并改善局部传质，为高密度微藻培养提供条件[31-32]，见图1(d)。此外，结合3D打印和合成生物学方法，可构建具有环境响应能力的复杂结构，并用于耦合光合碳固定与矿化过程，以提升碳封存效果[33-34]。

供氧型微藻固定化水凝胶近年来也被用于生物医学研究。该体系可依靠微藻光合作用持续释放氧气，改善创面局部缺氧状态，并促进组织修复。结合3D生物打印后，可进一步形成结构可控的光

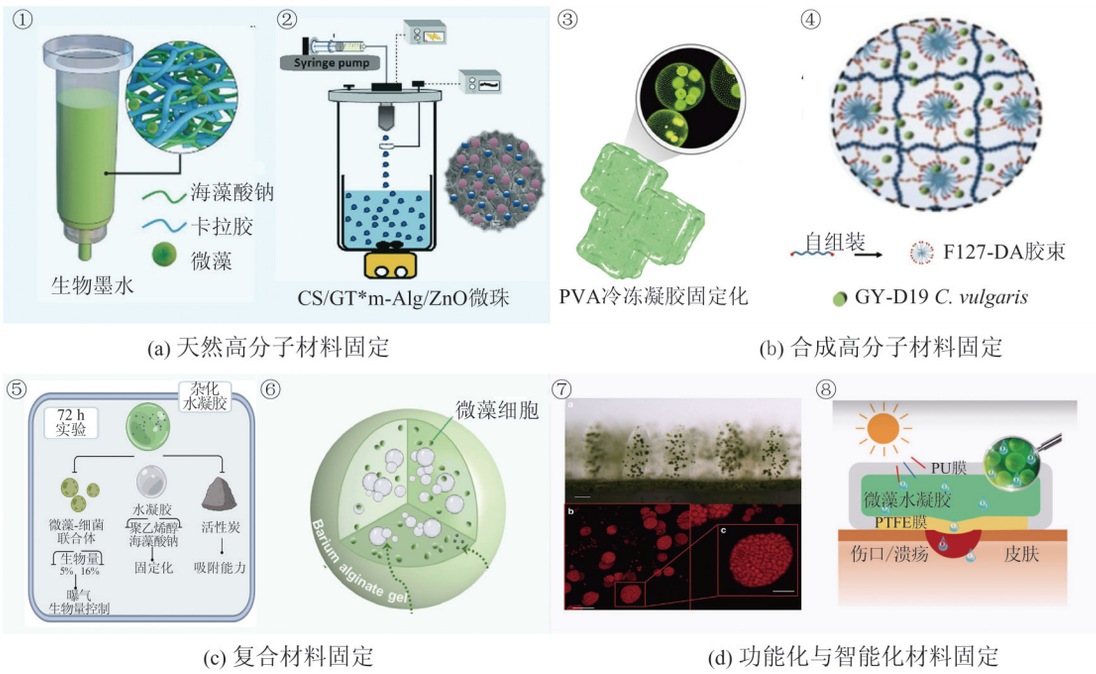


图 1　微藻固定化培养材料体系

Figure 1　Immobilized culture material systems for microalgae

①:海藻酸钠/卡拉胶构建的三维固定化水凝胶体系[12];②:壳聚糖/明胶交联微球负载小球藻体系用于双酚 A 去除[16];③:聚乙烯醇固定化微藻体系[21];④:Pluronic F127 二丙烯酸酯(F127-DA)/PEGDA 固定化微藻体系[25];⑤:PVA/海藻酸盐杂化水凝胶体系[23];⑥:浮性钡藻酸盐气泡珠固定化微藻体系[30];⑦:仿生珊瑚固定微藻[31];⑧:用于慢性伤口治疗的微藻水凝胶贴片[35]

①: three-dimensional immobilized hydrogel system constructed with sodium alginate/carrageenan[12]; ②: chitosan/gelatin crosslinked microsphere-loaded chlorella system for bisphenol A removal[16]; ③: polyvinyl alcohol (PVA) immobilized microalgal system[21]; ④: pluronic F127 diacrylate (F127-DA)/PEGDA immobilized microalgal system[25]; ⑤: PVA/alginate hybrid hydrogel system[23]; ⑥: floating barium alginate bubble bead immobilized microalgal system[30]; ⑦: biomimetic coral-inspired immobilized microalgal system[31]; ⑧: microalgal hydrogel patch for chronic wound treatment[35]

合支架,用于创面供氧和修复等场景[35-39],见图 1(d)。初步临床研究也表明,含微藻的光合支架具有较好的生物安全性,显示出向实际应用转化的潜力[40]。

2　微藻固定化构建方式

2.1　包埋法

包埋法是微藻固定化中较常用的方法,通常将微藻细胞限制在聚合物网络或多孔基质内部,使其在局部空间内维持生长和代谢,并保持物质交换,见图 2(a)。该方法可通过离子交联、冷冻-融化或光聚合等方式构建凝胶体系,操作较简单,条件温和,对细胞活性的影响相对较小[41-42]。但包埋体系仍存在传质受限和光遮蔽等问题,在高细胞密度条件下尤为明显。海藻酸盐是常用的基础材料,近年来研究逐渐转向复合材料构建和结构优化。将其与羧甲基纤维素、果胶或明胶等材料复合,可提高藻珠稳定性,并改善细胞生长、产氧和废水处理效果[29,43]。此外,为缩短扩散路径、缓解细胞生长不均,薄层包埋、核壳结构和微胶囊等形式也被用于固定化体系中,使包埋法从单纯细胞固定逐渐扩展到局部微环境调控[44-46]。

随着先进制造技术的发展,包埋法开始向结构化构建方向拓展,其中 3D 打印技术被认为是其重要发展路径之一。该体系本质上仍是将微藻细胞包埋在水凝胶网络中,但可通过数字化设计调节支架形貌、孔隙和厚度,从而改善光照分布和物质传递条件,减轻高密度培养中的自遮蔽和传质受限问题[47-48]。

近年来,3D 打印包埋体系已逐步发展到面向再生食品、废水处理和生物医用材料的多场景应用。例如,仿生“3D 打印珊瑚”可通过结构设计改善微藻的高密度培养效果[31];空间集约型三维培养支架则有助于提高资源利用效率和单位体积产出[12];在环境治理方面,3D 打印小球藻生物载体和双网络可回收水凝胶已用于废水处理及抗生素降解,表现出一定稳定性和重复使用潜力[24,49]。此外,中空纤维、管

状水凝胶及微藻负载支架也被探索用于持续供氧和组织修复[36, 50-51]。总体来看，3D打印为包埋法从单纯细胞固定转向微环境设计和功能化应用提供了新的思路。

2.2 附着法

附着法是微藻固定化培养中常用的一种方式，主要利用微藻在固体表面的自然附着能力，使细胞固定在载体表面并逐渐形成生物膜。微藻细胞通常先在重力、流体扰动或表面相互作用下接近载体，随后完成初始附着，见图2(b)。在附着逐渐稳定后，细胞分泌的胞外聚合物(EPS)可增强其与载体之间的黏附作用，并促进细胞聚集和生长，最终形成具有一定厚度的附着型固定化体系[52-54]。与包埋法相比，附着法通常不需要额外的交联或凝胶化过程，操作较简单，且有利于光照和物质传递，也便于后续生物量收获。不过，其固定化效果容易受到载体表面性质及界面稳定性的影响。

附着型固定化的关键在于载体表面能否为微藻提供稳定的黏附环境。表面沟槽、粗糙度、疏水性以及胞外聚合物(EPS)等因素，都会影响细胞初始附着和后续生物膜形成[53, 55-56]。目前，松树皮、土工布等低成本天然材料已被用于微藻附着培养，并在废水氮、磷和有机物去除中表现出一定效果[57-58]。同时，陶瓷基底、砂浆板和棕榈废弃物等载体也受到关注，可通过调节表面结构和光照条件改善附着培养性能[59-61]。

3 微藻固定化培养体系的应用进展

3.1 食品与生物活性产物

微藻富含蛋白质、不饱和脂肪酸、类胡萝卜素及多糖等多种生物活性物质，是重要的功能食品与天然产物来源。近年来，固定化培养体系通过构建稳定的三维微环境，有效提高了微藻细胞密度及目标产物积累效率，在食品及生物活性产物开发中展现出独特优势。

与传统悬浮培养相比，固定化培养能够为微藻提供相对稳定的生长环境，有利于调节细胞代谢，并调节蛋白质、脂质、类胡萝卜素和多糖等活性成分的积累。研究表明，固定化微藻在低液体投入或受限液相条件下仍可保持较高的营养产出，因此在可持续食品和新型食品生物质开发中具有一定潜力[12, 62]，见图3(a)。此外，固定化过程还可能影响细胞生理状态和物质分配，从而提高生物量及部分目标产物的积累，如脂肪酸、胞外多糖和氨基酸等[63-65]。在高附加值产物开发方面，固定化技术不仅有助于强化脂质生产与资源回收，还可促进虾青素等天然色素积累；固定化微藻提取物还表现出较强的抗氧化活性，并在活性包装材料中具有应用潜力[66-69]。总体来看，固定化培养为微藻营养成分和活性产物的积累提供了一种可行方式。

3.2 固定化微藻在能源领域的应用

在能源领域，固定化微藻主要用于生物制氢、生物柴油前体生产以及沼气净化等方向。相比悬浮培养，固定化体系更有利于细胞保留，可减少培养过程

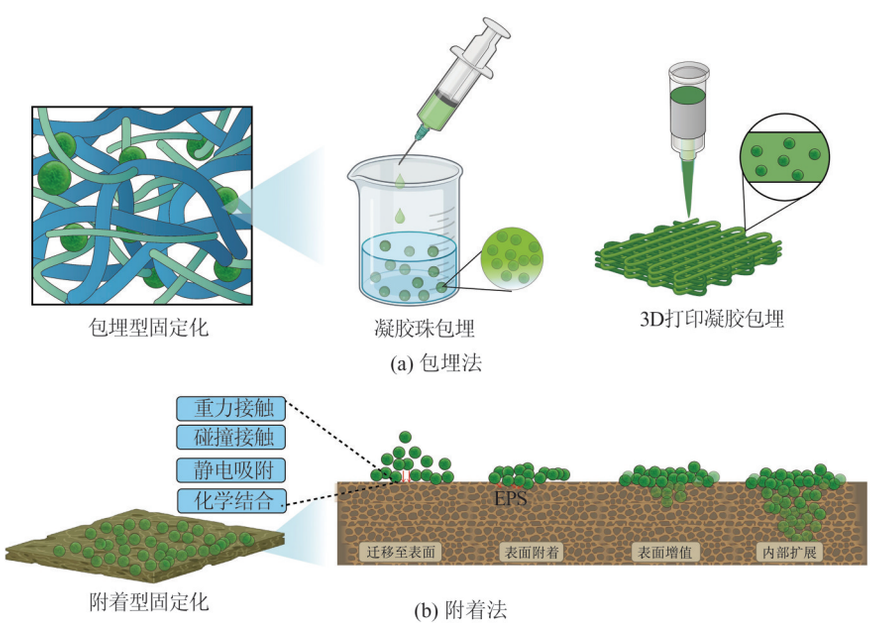


图2 微藻固定化的主要技术途径

Figure 2 Main technical approaches for microalgal immobilization

中的生物量流失。同时,载体形成的局部微环境也有助于改善光照和底物传递条件,从而提高能源转化过程的稳定性。

近年来,固定化微藻在生物制氢方面已有较多研究。普通小球藻和斜生栅藻在固定化条件下可利用人工废水持续产氢,且海藻酸盐珠的聚合程度会影响扩散过程、藻珠寿命和产氢表现[70-71]。在含酚废水体系中,固定化海藻酸盐微藻珠也可兼顾污染物去除和产氢[72]。附着型固定化同样具有一定优势,例如负载于聚氨酯泡沫上的微藻可用于市政废水处理和绿氢生产,光周期调节还能改善产氢及污染物去除效果[27,73]。在脂质及生物柴油前体生产方面,固定化产油微藻可作为两相净化单元,在沼气提纯和厌氧消化液处理过程中同步实现二氧化碳去除、营养盐回收和脂质积累[74];此外,采用两阶段固定化生物反应器将小球藻与市政废水活性污泥分区固定化,可在部分共培养模式下显著提升生物氢产量[75],见图3(b)。固定化培养有利于提高细胞保留率和体系稳定性,也为废水处理与能源产物回收的结合提供了新的思路。

3.3 固定化微藻在环境污染治理中的应用

固定化微藻因细胞易保留、抗冲击能力较强,在环境污染治理中受到较多关注。相关研究已将其用于富营养化水体、养殖废水、食品工业废水和市政污水处理,并取得了一定的营养盐去除效果[76-79]。对于有机污染物和难降解工业废水,固定化微藻同样展现出良好应用潜力,可用于纺织染料废水、抗生素和17β-雌二醇等污染物的去除,并在无机污染控制方面表现出优于悬浮培养的处理效果[24,80-84],见图3(c)。

固定化微藻在碳捕集和烟气CO_2利用中也具有一定应用潜力。固定化微藻光生物反应器证明,固定化载体可用于直接捕集尾气中的CO_2,并通过提高局部细胞密度提升固碳效率[10]。近年的研究还发现,将附着培养与CO_2吸收过程结合,可提高碳固定能力和生物质生产效率[85]。此外,活体微藻/丝瓜络生物复合材料也被用于从富CO_2三乙醇胺溶液中再捕集CO_2,拓展了固定化微藻在碳捕集中的应用形式[86]。总体而言,固定化微藻的应用已逐渐从营养盐去除延伸到污染物治理和碳资源回收,在细胞保留和抗冲击方面表现出一定优势。

3.4 固定化微藻在农业领域的应用

固定化培养有助于维持微藻细胞活性,并促进废水中氮、磷等养分的回收利用。近年来,固定化微藻逐渐被用于生物肥料、土壤改良和植物生长促进等方向,为环境治理与农业利用之间的结合提供了一种思路。

固定化微藻及其与功能菌构建的共固定化体系,可用于废水养分回收,并进一步转化为农业利用资源[17,77]。这类体系既能承担一定的废水处理功能,也可作为农业接种载体,为植物微生物互作研究提供参考[87-88]。废水处理后的藻菌珠残余物还可用于土壤改良,改善退化土壤肥力和微生物群落结构[89-90]。此外,海藻酸钙凝胶珠共固定化微藻与植物促生菌后,可促进植物在荒漠土壤中的生长[91],见图3(d)。

4 微藻固定化面临的主要挑战与发展方向

尽管微藻固定化培养在细胞富集、体系稳定运行和应用拓展方面具有一定优势,但其进一步应用仍受到多种因素限制。对于包埋型体系而言,光照、CO_2和营养盐在材料内部的传递容易受阻,可能造成局部缺光、缺氧或代谢产物积累,从而影响细胞生长及目标产物形成。附着型体系则更多受初始黏附效率、生物膜过度增厚和界面稳定性等问题影响。此外,反应器结构、流体条件、光照分布、运行方式和成本控制等因素,也会增加固定化技术工程放大的难度。

针对上述问题,未来微藻固定化培养体系仍需在材料、结构和运行调控方面进一步优化。材料方面,可开发机械强度较高、传质性能较好且具有生物相容性的复合载体,并结合3D打印凝胶等成型方法,提高固定化结构的可设计性和运行稳定性。结构方面,可通过引入有序孔道、分级结构或仿生形态,改善光照分布和物质传递,同时提高空间利用效率。无液体培养和垂直培养等方式也可作为降低运行成本的探索方向。同时,藻菌共培养、酶催化、新型反应器设计以及传感监测等技术,可进一步提升体系的连续运行能力和过程可控性。总体而言,微藻固定化培养仍需加强材料设计、反应器构建和运行策略之间的匹配,才能更好地服务于能源、环境、食品和农业等领域的实际应用。

5 小 结

微藻固定化培养已由早期单一载体和传统包埋方式,逐步发展为材料复合化、结构精细化和功能集成化协同推进的研究方向。不同材料体系和构建方式各具优势,也分别受到传质效率、力学稳定性、细胞泄漏及工程放大的制约。随着高性能复合材料、3D打印、仿生结构设计及智能调控技术的不断发展,微藻固定化体系有望在环境治理、能源转化、食

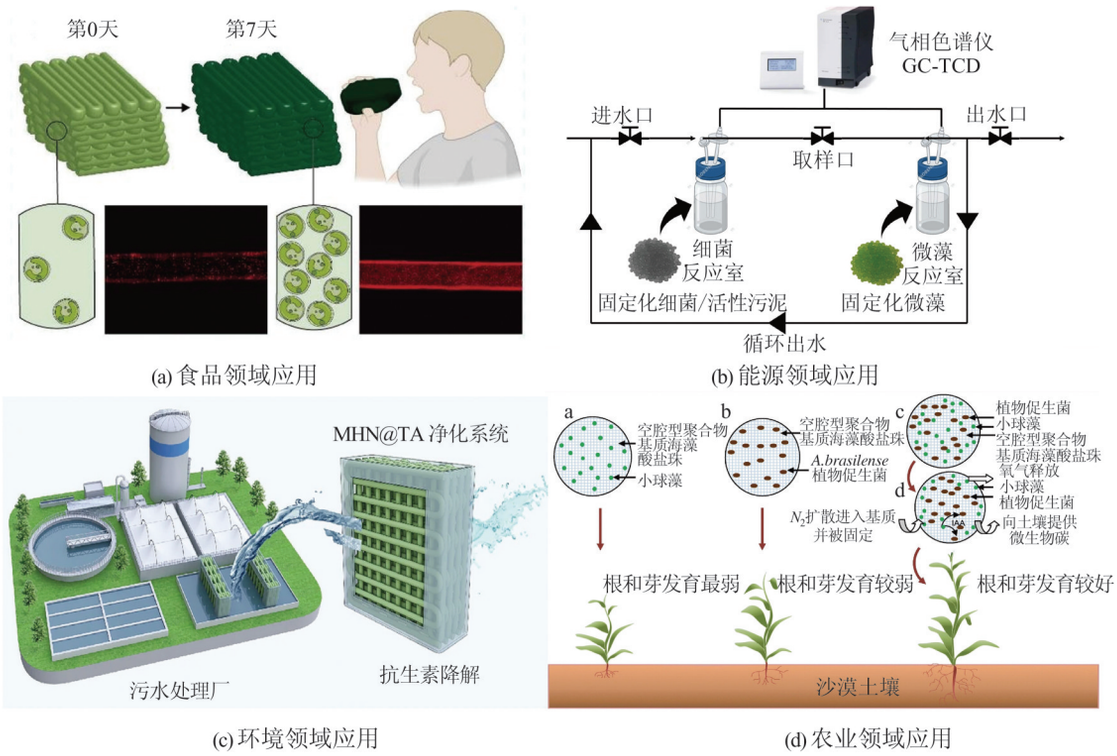


图 3　微藻固定化培养体系的应用

Figure 3　Applications of immobilized culture systems of microalgae

(a)，生物打印的微藻多糖水凝胶用于易吞咽型替代食品[62]；(b)，微藻-细菌共培养的新型两阶段固定化生物反应器用于生物制氢[75]；(c)，3D打印微藻水凝胶用于抗生素降解[24]；(d)，固定在藻酸盐中的微藻和植物促生菌对沙漠土壤中植物生长的影响[91]

(a)，bioprinted microalgal polysaccharide hydrogel for easy-to-swallow alternative food products[62]; (b), novel two-stage immobilized bioreactor with microalgae-bacteria co-culture for biohydrogen production[75]; (c), 3D-printed microalgal hydrogel for antibiotic degradation[24]; (d), effects of microalgae and plant growth-promoting microbes immobilized in alginate on plant growth in desert soil[91]

品制造和农业资源化等领域展现更大的应用潜力，并进一步推动其由实验室研究走向实际应用。

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