

微生物胞外活性氧的产生及其促进有机污染物降解的研究进展

陈丽娇¹, 聂红云^{*1,2}, 王磊^{1,2}, 聂麦茜^{1,2}, 第五振军^{1,2}, 张建¹, 陈婧¹

1 西安建筑科技大学环境与市政工程学院, 陕西 西安 710055

2 陕西省膜分离重点实验室, 陕西 西安 710055

陈丽娇, 聂红云, 王磊, 聂麦茜, 第五振军, 张建, 陈婧. 微生物胞外活性氧的产生及其促进有机污染物降解的研究进展[J]. 微生物学通报, 2022, 49(1): 323-335

Chen Lijiao, Nie Hongyun, Wang Lei, Nie Maiqian, Diwu Zhenjun, Zhang Jian, Chen Jing. Advances in the production of extracellular reactive oxygen species and its promotion on the biodegradation of organic pollutants[J]. Microbiology China, 2022, 49(1): 323-335

摘 要: 生物法处理是环境中有机污染物去除的主要途径, 具有费用低、环境影响小等特点, 其不足之处在于所需处理时间长, 尤其当有机污染物难降解时, 处理时间长达数十年甚至数百年。胞外活性氧(extracellular reactive oxygen species, EROS)是微生物代谢时产生的一类含氧活性基团, 对难降解有机物的生物降解具有很好的促进作用。近年来, 相关研究报道剧增, 但目前尚未见综述报道。本文总结了 EROS 产生及其促进有机污染物降解领域的最新研究成果, 主要从 EROS 的简介、产生的微生物和机理、对有机污染物降解的促进作用、未来研究方向及面临的挑战等几个方面展开论述, 以期为研究者提供参考。

关键词: 胞外活性氧; 产生机理; 难降解有机物; 胞外酶; 胞外非酶物质

基金项目: 陕西省科技计划重点创新产业链项目(2019ZDLSF05-04); 中国博士后科学基金(2018M633479); 陕西省科技厅自然科学基金基础研究计划项目(2019JQ-759)

Supported by: Key Innovation Industry Chain of Science and Technology Project of Shaanxi Province (2019ZDLSF05-04); China Postdoctoral Science Foundation (2018M633479); Natural Science Basic Research Program of Shaanxi Provincial Science and Technology Department (2019JQ-759)

*Corresponding author: E-mail: nie0212@126.com

Received: 2021-05-07; Accepted: 2021-07-29; Published online: 2021-09-07

Advances in the production of extracellular reactive oxygen species and its promotion on the biodegradation of organic pollutants

CHEN Lijiao¹, NIE Hongyun^{*1,2}, WANG Lei^{1,2}, NIE Maiqian^{1,2}, DIWU Zhenjun^{1,2}, ZHANG Jian¹, CHEN Jing¹

1 School of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, Shaanxi, China

2 Key Laboratory of Membrane Separation of Shaanxi Province, Xi'an 710055, Shaanxi, China

Abstract: Biological treatment, with the characteristic of low cost and slightly environmental impact, has become a main removal pathway of environmental organic pollutants. The disadvantage is that the treatment time is long, especially for refractory organic pollutants, which may need several decades or even hundreds of years. Extracellular reactive oxygen species (EROS), with the ability of promoting biodegradation of refractory organic pollutants, were oxygen-containing active group generated from the metabolism of microorganisms. Recently, researches related to the effect of EROS on biodegradation of refractory organic pollutants increased sharply. However, no relative review has been reported yet. In this paper, the latest research achievements on the production of EROS and its promotion on biodegradation of refractory organic pollutants have been summarized, mainly from the aspects of introduction of EROS, producing microbes, generation mechanism, promotion on the degradation of refractory organic pollutants, future direction and challenges, aiming at providing a guidance for the following researchers.

Keywords: extracellular reactive oxygen species; generation mechanism; refractory organic pollutants; extracellular enzyme; extracellular non-enzymatic substances

随着经济的快速发展和人们生活方式的改变,大量个人护理产品、阻燃剂、杀虫剂、内分泌干扰物(endocrine disrupting chemical, EDC)等^[1-3]新兴污染物(emerging contaminant, EC)被排放到各类环境主体,虽然在环境中水平低(一般在纳克到微克级别),但因其具有较高的生物活性、易积累、毒性大、难降解等特性,严重威胁环境安全和人类健康,因此受到高度关注^[4-7]。生物法因处理费用低、环境影响小且控制管理方便,已经成为污水处理领域中应用最广的处理技术^[8]。然而传统的生物处理工艺难以完全去除 EC,在城市污水厂的二级出水甚至三级出水中常检测到一定浓度的 EC,包括 EDC

和多环芳烃(polycyclic aromatic hydrocarbon, PAH)等,浓度在纳克到微克级别^[9-11]。近年来,研究者发现微生物在代谢过程中能产生一类胞外活性氧(extracellular reactive oxygen species, EROS),可加速难降解有机物的生物降解^[12-15]。由于此类活性氧种类与高级氧化中起作用的活性氧种类相同,而且其随微生物代谢过程产生,所以不需要额外添加化学物质或增加能耗,从而避免了高级氧化过程带来的能耗高、副产物多、易产生二次污染等不足^[16-19],因此,EROS 在促进难降解有机物生物降解中具有重要的研究价值^[20-21]。近年来,关于 EROS 产生机理及其在生物降解中作用的研究

较多。为了更好地理解微生物 EROS 的形成,了解其对难降解有机物去除的促进作用,本文从 EROS 简介、产生的微生物和机理、对有机污染物降解的促进作用、未来研究方向及面临的挑战等方面进行了总结和论述,以期为研究者提供参考。

1 胞外活性氧简介

活性氧(reactive oxygen species, ROS)泛指一类化学性质活泼、具有强氧化活性的含氧自由基或含氧的非自由基衍生物,如羟基自由基($\cdot\text{OH}$)、超氧阴离子自由基($\cdot\text{O}_2^-$)、单线态氧($^1\text{O}_2$)、过氧化氢(H_2O_2)和碳酸盐自由基($\cdot\text{CO}_3^-$)等^[22-23]。EROS 是指特定条件下,在生物胞外产生的含氧活性基团^[24]。EROS 种类包括 $\cdot\text{OH}$ 、 $\cdot\text{O}_2^-$ 、 $^1\text{O}_2$ 和 H_2O_2 , 在所有 ROS 中, $\cdot\text{OH}$ 氧化能力最强,反应活性最高,几乎可与所有生物分子和有机物发生不同类型的化学反应^[21]。 $\cdot\text{O}_2^-$ 有一定的反应活性,可作为氧化剂或转化成其他高活性的 ROS 自由基,提高有机污染物降解效率^[25]。 $^1\text{O}_2$ 是分子氧处于激发态的高能状态,反应活性高,可与一些有机分子发生化学反应^[26]。 H_2O_2 是唯一相对稳定的 ROS,作为氧化剂可降解一些无机或有机污染物,而且在光、电、催化剂等条件下极易分解,产生 $\cdot\text{OH}$ 、 $\cdot\text{O}_2^-$ 等 ROS^[27]。

ROS 产生方式主要分为两大类,一是在光、电等催化条件下产生的非生物方式,二是生物方式,也就是生物代谢过程中产生的胞外或胞内活性氧,如好氧生物代谢、过氧化物酶及胞外分泌物等在反应过程中产生 ROS^[28]。本文重点论述微生物代谢过程中产生的 EROS。

EROS 在生物体系的作用可分为正负两方面。其负面作用主要指 ROS 的产生会导致人体诱发基因突变、肿瘤、细胞衰老和癌变、降低

免疫功能等疾病或抑制微生物生长^[29-30];正面作用主要指 EROS 可促进难降解有机物生物降解,加强植物化感作用、生长调控、理化防御系统和元素循环等^[31-32]。

2 产胞外活性氧的微生物

目前已报道了大量能产生 EROS 的微生物,主要可分为藻类、真菌、细菌等^[33-34]。在海洋水体中,氧气是 ROS 的主要来源,其产生依赖于光照^[35],驱动着金属和碳的生物化学循环。Plummer 等^[36]探究了海洋浮游植物球石藻产生 $\cdot\text{O}_2^-$ 的调控及所产 $\cdot\text{O}_2^-$ 的生物学功能。海洋中 EROS 的产生是黑暗和光照协同调节的。Sutherland 等^[37]发现原绿球藻、聚球藻和棕囊藻在黑暗条件下产生 EROS 可作为细胞的信号转导,其变化与细胞数量变化相关。Diaz 等^[38]研究了海洋硅藻产生的 EROS 是跨质膜电子传递系统的副产物,在光合作用和 NADP 的协同下平衡细胞的氧化还原状态。因此,藻类 EROS 在维持生态平衡中具有重要作用。

真菌中关于 EROS 的研究与应用相对较多,其所产生的过氧化物酶,如木质素过氧化物酶(lignin peroxidase, LiP)、锰过氧化物酶(manganese peroxidase, MnP)和漆酶等,在降解过程中调节 EROS 的产生及催化酚类、芳香类等有机污染物的氧化分解。冯义平等^[39]总结了白腐真菌胞外分泌 LiP 和 MnP 在自由基作用下对水体中酚类干扰物的去除情况。Shi 等^[40]研究利用合适褐煤比例和培养基混合培养白腐真菌,其中 LiP、MnP 和漆酶的分泌量较对照组显著增加,酶活力得到极大提升,加快了煤的催化解聚。田乔鹏等^[41]针对白腐真菌、ROS 和漆酶三者的关系,进一步研究发现真菌产生的 ROS 中, $\cdot\text{O}_2^-$ 抑制白腐真菌产漆酶,而 H_2O_2 和 $\cdot\text{OH}$ 起促进作用,它们对漆酶的合成调控起

到关键作用。

近年来,细菌中 EROS 的研究日渐增多,其对难降解有机物的降解作用日渐被重视。目前报道能产生 EROS 的细菌多是海洋假交替单胞菌、铜绿假单胞菌等。Huang 等^[42]报道了铜绿假单胞菌在降解四溴双酚 A (tetrabromobisphenol A, TBBPA) 时胞外分泌大量绿脓菌素 (pyocyanin, Pyo), 其介导产生的 H_2O_2 和 $\cdot\text{OH}$ 是促进降解的主要动力,但在能源消耗下,细胞防御作用下降,过量的 ROS 易产生细胞自毒性。Diaz 等^[43]发现海洋硅藻海链藻产生的 $\cdot\text{O}_2^-$ 与其他 EROS 可调节细胞的氧化还原状态,从而促进其健康生长。郭定环等^[44]也研究了无光条件下海洋 *Pseudoalteromonas* sp. GCY 产 EROS 的特性,发现与蛋白胨相比,牛肉膏培养基中菌体产 H_2O_2 和 $\cdot\text{O}_2^-$ 量较多,添加典型有机污染物后,不同典型有机污染物对菌体产胞外 H_2O_2 和 $\cdot\text{O}_2^-$ 的影响存在差异。

3 微生物胞外活性氧的产生机理

3.1 胞外酶类前体物产生活性氧的作用机理

产生 EROS 的酶(后文简称 E)主要包括 LiP^[45]、漆酶^[46]、MnP^[47]、辣根过氧化物酶(horseradish peroxidase, HRP)^[47]等。如图 1 所示,过氧化物酶产生 EROS 的途径主要有 2 种。通常好氧微生物体系存在丰富的 H_2O_2 ^[48-49], 其可与产生 EROS 的酶反应生成一种具有高氧化活性的中间体(compound I), 然后细分为 2 种反应途径。第 1 种反应途径是生成的 compound I 再与 1 分子的 H_2O_2 反应, 生成 O_2 、 H_2O 和 E, 反应终止。第 2 种是生成的 compound I 与具有还原性的有机污染物(AH_2)反应, 生成含自由基的有机污染物 ($\text{AH}\cdot$) 和另外一种中间体 (compound II), $\text{AH}\cdot$ 继续与 AH_2 反应, 使 AH_2 通过自由基链反应降解; 此外, 生成的 compound II 也可与 AH_2 反应, 生成 H_2O 和 E^[50]。

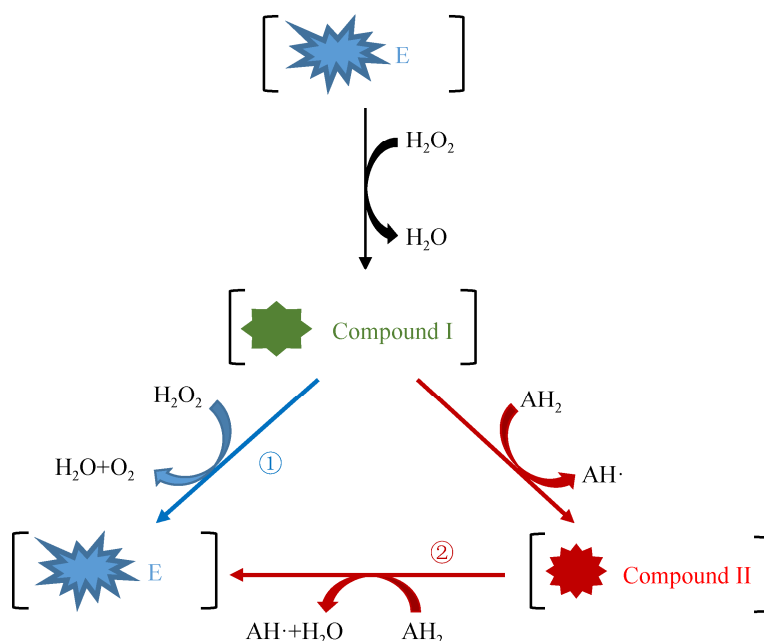


图 1 过氧化物酶催化机理

Figure 1 Catalytic mechanism of peroxidase.

Li 等^[51]发现胞外 HRP 可通过 H_2O_2 介导实现有机污染物降解; 在含 HRP 的降解天然雌激素体系中, 羟基化中间产物被 H_2O_2 催化氧化, 加快酶促降解, 而无 HRP 的体系中中间产物大量积累。梁念^[52]探究了丛毛单胞菌中的染料脱色过氧化物酶(dye-decolorizing peroxidase 35, DyP35)对木质素的降解机理, DyP35 攻击苯环侧链, 脱除甲氧基形成羟基化中间产物, 继续作用于木质素, 将其裂解成低分子化合物和简单有机酸等。刘鸿^[53]在 HRP 体系中加入 H_2O_2 和亚铁盐, 亚铁离子与酶竞争 H_2O_2 形成芬顿反应, 芬顿-酶耦合体系氧化性增强, 对磺胺甲噁啉的处理效果显著提升。

漆酶是一种含有多个铜离子的多酚氧化酶, 催化底物主要为酚类^[54-55]。其中细菌漆酶和真菌漆酶在污水处理领域的应用广泛^[56]。其催化降解机理如图 2 所示, 在好氧条件下, 污染物将羟基上的电子传递给铜离子活性中心, 自身生成自由基类中间体(如酚类自由基、胺类自由基), 这类中间体极不稳定, 可在氧气存在下继续被氧化, 最终产物为 H_2O 和 CO_2 ^[57]; 同

时一小部分自由基类中间体发生自身的偶联反应, 形成聚合物^[58]。

Morsi 等^[59]研究表明, 微生物漆酶根据铜离子活性中心可分为 I 型、II 型和 III 型铜离子, 生物催化效果依赖于 I 型铜离子的氧化还原电位, 首先底物与 I 型铜离子活性位点结合, 并将电子转移到三核铜簇(1 个 II 型铜离子与 2 个 III 型铜离子形成三核铜簇), 最后该电子与活性中心处的氧气分子反应, 将底物氧化为 H_2O 和 CO_2 。陈明雨等^[60]认为, 漆酶催化氧化机理主要为漆酶夺取底物电子产生底物自由基中间体和漆酶将电子传递给氧气分子将其还原成水; 当应用到 EC 降解反应时, 微生物漆酶较植物漆酶具有更高的活性和催化效率。Zeng 等^[61]利用枯草芽孢杆菌 CotA 分泌漆酶产生的 ROS 降解 PAH, 发现漆酶的氧化还原电位越高, 氧化效率越好。Samak^[62]以菌株 CotA 的漆酶为例, 针对大肠杆菌 BL21 提出微需氧培养策略, 菌株 CotA 的漆酶产 ROS 水平显著提高。靳洁^[63]研究发现海洋细菌 IOB-7 可分泌胞外漆酶, 其产生的 ROS 可氧化分解 4-氯苯酚和 2,4-二氯酚。

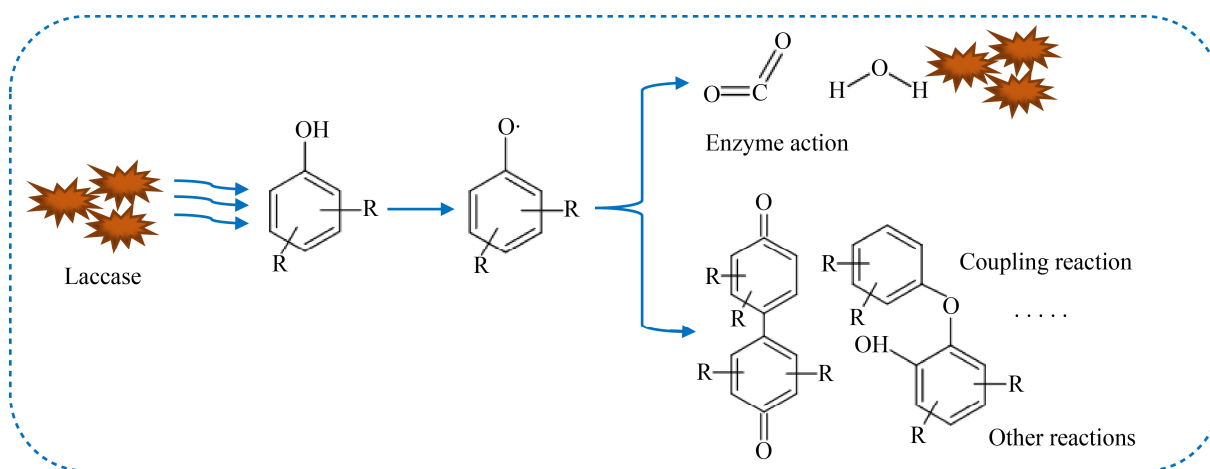


图 2 漆酶催化机理

Figure 2 Mechanism of laccase catalysis.

3.2 胞外非酶物质产生活性氧的作用机理

已报道能产生 EROS 的非酶类物质主要有吩嗪和螯铁蛋白两类。吩嗪类是假单胞菌产生的一种蓝绿色或黄绿色、含有氮杂环的小分子次生代谢物^[64]，其种类主要包括绿脓菌素(pyocyanin, Pyo)、吩嗪-1-酰胺(phenazine-1-carboxamide, PCN)、吩嗪-1-羧酸(phenazine-1-carboxylic acid, PCA)和 1-羟基吩嗪(1-hydroxyphenazine, HPE)。假单胞菌在碳源和氧气充足的情况下产生吩嗪类物质，添加适当促进剂(戊二酸、草酸、葡萄糖等)可提高吩嗪类物质的分泌量，该类物质易与胞外烟酰胺腺嘌呤二核苷酸(nicotinamide adenine dinucleotide, NADH)、还原型谷胱甘肽(glutathione, GSH)及其他含有巯基的物质、过氧化物酶等还原性或氧化性物质发生反应，产生 ROS，攻击 C-C 键或 C-R 键，使直链烃或 PAH 断裂成低分子物质，最终氧化为 H₂O 和 CO₂^[65-67]。其作用机理如图 3 所示。

黄璐等^[68]利用铜绿假单胞菌 NY3 从种子液中提取胞外小分子物质，研究表明，这类小分子物质主要包括 Pyo、PCN 及 2 种异咯嗪系列化合物，在降解底物过程中可产生 ROS，而且其属于氧化还原类物质，可加快底物之间电子传递速度，促进十四烷降解；当在 NY3 菌降解体系中加入戊二酸后，Pyo 分泌量增加^[69-70]，促进有机污染底物十六烷与氧气之间的电子传递速率；当在 NY3 降解体系中加入草酸时，胞

外吩嗪类物质的分泌量增加，尤其是 PCA 的分泌量显著提高，其可与胞外液中存在的 NADH、GSH、铁离子结合，产生 ROS，促进十六烷降解^[71-72]。

螯铁蛋白是假单胞菌胞外分泌的能螯合铁离子与一些过渡金属离子的载体物，主要包括脓青素(pyoverdine, PVD)和绿脓杆菌螯铁蛋白(pyochelin, PCH)这 2 种，除此之外还有一些少见的铁载体^[73]。铁和一些金属是细胞生长所必需的营养元素，是启动烷烃降解关键氧化酶的活性中心。细胞缺铁时，分泌螯铁蛋白来捕获周围环境中的铁离子，螯合形成铁的复合物，为细胞提供必要的铁元素，同时催化产生·OH，氧化降解底物污染物^[73]。螯铁蛋白催化机理如图 4 所示。

假单胞菌分泌的胞外螯铁蛋白在有机锡降解方面发挥重要作用。Inoue 等^[74]发现假单胞菌 CNR15 可分泌胞外 PVD，推测降解机理可能为 PVD 螯合金属离子发生金属络合反应，产生·OH 导致有机锡化合物 Sn-C 裂解键。Sun 等^[75]在深入解析 Inoue 等^[74]的推测后，发现铜绿假单胞菌胞外可分泌另一种螯铁蛋白 PCH，其与 Fe 螯合后催化产生·OH，·OH 攻击 Sn-C 键导致三苯基锡(triphenyltin, TPT)分解；在加入 H₂O₂后·OH 产生量增加，提高了 TPT 降解率。这与 Inoue 等^[74]研究螯铁蛋白作用机理一致。此外，螯铁蛋白在烃类有机污染物降解等方面也有许多有关机

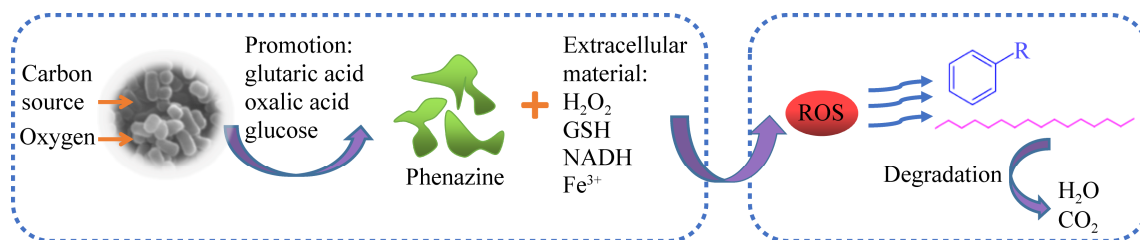


图 3 吩嗪类物质催化机理

Figure 3 Catalytic mechanism of phenazine compounds.

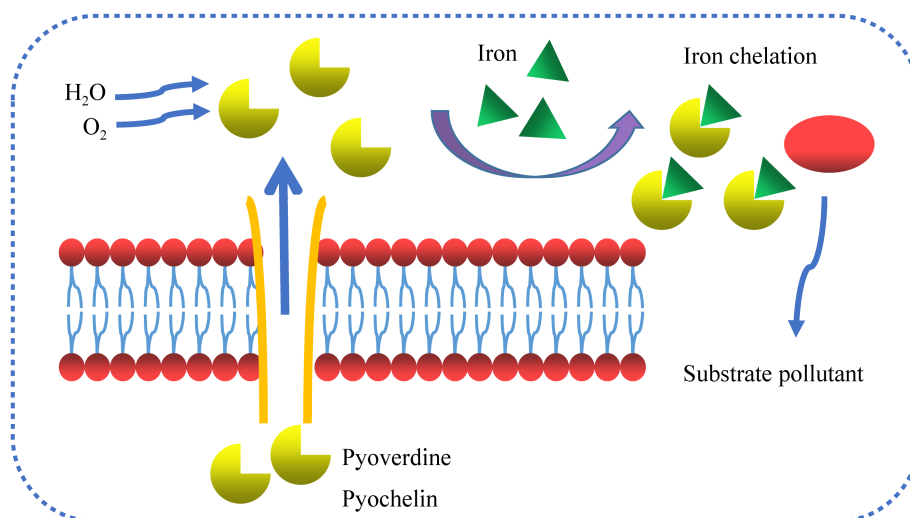


图4 螯铁蛋白催化机理

Figure 4 Catalytic mechanism of cheloferritin.

理的报道。Gu 等^[76]发现铜绿假单胞菌 fz 能分泌胞外 PCH, PCH 可与 Fe^{3+} 螯合产生 $\cdot\text{OH}$, 进而加速 TBBPA 的降解。赵碧洁等^[77]进一步探究十六烷促降解机理, 发现铜绿假单胞菌 NY3 分泌胞外物质 PCH, 其与 FeCl_3 螯合, 反应体系中有明显 $\cdot\text{OH}$ 产生, $\cdot\text{OH}$ 攻击 C-C 键促进十六烷裂解, 与 Gu 等^[76]揭示的机理一致。

4 微生物胞外活性氧的促降解作用

微生物 EROS 在多种有机污染物的降解转化中都发挥重要作用, 对未来难降解有机污染物和 EC 的去除提供了研究方向。在近几年的研究中, 报道较多的是 EROS 对直链烃、芳香烃和含杂原子的烃类有机污染物生物降解的促进作用。

4.1 EROS 对烃类污染物生物降解的影响

研究发现, 铜绿假单胞菌 NY3 能分泌吩嗪类和绿脓杆菌螯铁蛋白类等胞外活性物质, 这类物质可产生 EROS, 进而引起十六烷、十四烷、菲等直链烃和芳香烃的降解^[65,67,69,71,78-79]。当菌株 NY3 胞外液中吩嗪类物质的浓度为

0.2 $\mu\text{mol/L}$ 时, 相较于空白对照(吩嗪类浓度为 0), 与等浓度(40 $\mu\text{mol/L}$)的 NADH、GSH 反应 8 h 可使 20 mmol/L 十六烷的降解率分别达到 30%–50%、10%–40%^[65]。在含高浓度吩嗪的菌株 NY3 胞外液中, Pyo 与 NADH 结合, 72 h 内可使菲的降解率达到 46.13%^[78]。对于纯吩嗪含量的菌株 NY3 胞外液体系, 8 h 内菲在 Pyo 和 NADH 催化作用下降解率达到了 30%–50%^[67]。进一步研究发现, 在胞外添加戊二酸、草酸等小分子时, 有利于胞外吩嗪类物质的分泌; 当在体系中加入戊二酸时, 胞外 Pyo 的分泌量较无戊二酸体系增加了 86.6%, 在 16 h 内体系中 NY3 菌胞外液对十六烷的降解率与未加戊二酸相比提高了 16.29%^[69]。当在体系中加入草酸(最佳浓度为 1 g/L)时, 与未加草酸体系相比, 胞外 PCA 的浓度提高了 38.9%, 在 8 h 内可使菌株 NY3 胞外液对十四烷降解率与未加草酸相比提高 15.2%^[71]。除吩嗪类物质外, 菌株 NY3 分泌的螯铁蛋白物质 PCH 也可以引起烃类污染物的降解。当体系中 PCH 与 Fe^{3+} 浓度比为 1:2–1:1 时, 对十六烷降解效果最佳, 降解

率最高可达 28.42%^[79]。胞外酶类物质产生的 EROS 对烃类污染物也具有较好的降解效果。Xu 等^[80]利用枯草芽孢杆菌分泌的过氧化物酶降解木质素,发现在 37 °C 微氧条件下作用 24 h,木质素降解率可达 23%,与空白相比提高了 17.23%。Zeng 等^[81]利用大肠杆菌漆酶氧化多环芳烃,与真菌漆酶相比,其对蒽和苯并[a]芘的催化效果相同,但表现出更好的热稳定性,在 60 °C 作用 24 h,蒽和苯并[a]芘的降解率分别为 80%和 97%。以上研究结果表明,EROS 可有效提高烃类污染物的生物降解效率。同时,降解过程中的中间产物鉴定与废水可生化性研究结果表明,上述胞外活性物质的降解作用可使母体污染物转化为一类降解中间产物,进而提高其可生化性。

4.2 EROS 对含杂原子烃类污染物生物降解的影响

刘沙沙等研究假单胞菌 fz 胞外液中降解 TBBPA 的活性组分,并对胞外液中活性组分的降解机理进行探究^[82]。胞外液中的一类活性物质与 Fe^{3+} 结合可产生自由基,引起 TBBPA 通过 β 断裂和脱溴这 2 个途径进行降解^[76]。对这一类活性物质进一步表征,结果表明,这类物质是一种铁载体,其结构中主要含有甘氨酸、脯氨酸和丙氨酸^[83]。Huang 等^[42]研究了绿脓杆菌对 TBBPA 的降解,发现在最优条件下体系分泌大量 Pyo,24 h 内绿脓杆菌 OD_{600} 提高了 7 倍,总有机碳(total organic carbon, TOC)下降了 78%,7 d 时 TBBPA 降解率约 50%。马建鹏等^[84]利用假单胞菌探索高效降解五氯苯的方法,发现将纳米零价铁与假单胞菌耦合,体系中可产生 $\cdot\text{OH}$,36 h 内五氯苯的降解率可达 55.4%。靳洁^[63]利用海洋细菌 IOB-7 降解酚类污染物,发现 IOB-7 细菌可分泌胞外漆酶,添加 3-乙基苯并噻唑-6-磺酸[2,2'-azino-bis(3-ethylbenzothiazoline-

6-sulfonic acid), ABTS]作为电子传递介质,漆酶与 ABTS 协同促进氯酚类物质降解,24 h 内苯酚降解率为 5.11%,4 h 内 4-氯酚和 2,4-二氯酚降解率分别为 1.33%和 2.76%。张杰等^[85]利用白腐真菌降解氯酚类物质,发现白腐真菌分泌的胞外漆酶与体系中产生的自由基协同催化,可使氯酚类物质达到较好的降解效果,其中 2,5-二氯苯酚、2,6-二氯苯酚、2,4,5-三氯苯酚和 2,4,6-三氯苯酚降解率分别为 86.2%、45.3%、98.7%和 84.8%。周鑫等^[86]探究了毛栓菌 27-1 漆酶对酚酸类化合物的降解效能,发现毛栓菌 27-1 漆酶能完全降解酚酸类化合物中的香草酸、咖啡酸和芥子酸,加入介质物质 ABTS 后,可使浓度在 100 mg/L 的丁香酸完全降解。漆酶对双酚 A (bisphenol A, BPA)具有很好的降解效果, *Trametes versicolor* 产生的漆酶与 BPA 可自发反应,24 h 降解率达到 88.76%,条件优化后,44.6 °C、初始 BPA 浓度 5 mg/L、pH 值为 5.20 条件下反应 1 h, BPA 降解率最佳,为 97.68%^[87]。综上所述,胞外活性氧可有效提高含杂原子烃类污染物的生物降解效率。

5 存在问题及展望

EROS 是伴随微生物代谢产生的,其产生过程低能耗、无污染,而且能显著提高有机污染物尤其是难降解有机污染物的生物降解效率,在有机污染环境的生物修复中有着巨大的应用潜力。基于现有研究结果仅限于 EROS 的产生机理,距离应用 EROS 提高难降解有机物的生物修复能力还有一定距离。为尽快将 EROS 的促进作用实际应用于难降解有机污染物的生物修复,今后的研究应从以下几个方面着手:(1) 因微生物胞外分泌物成分复杂,应在目前的研究基础上探索不同分泌物在 EROS 形成中所扮演的角色,深入解析 EROS 的形成机理;(2) 在生物降解体系中,

EROS 不仅能促进难降解有机物的降解, 也可产生生物自毒性, 因此, 应研究 EROS 与微生物细胞代谢之间的相互关系, 寻求 EROS 与胞内酶协同作用的高效降解状态。

REFERENCES

- [1] Ahmed SF, Mofijur M, Nuzhat S, Chowdhury AT, Rafa N, Uddin MA, Inayat A, Mahlia TMI, Ong HC, Chia WY, et al. Recent developments in physical, biological, chemical, and hybrid treatment techniques for removing emerging contaminants from wastewater[J]. *Journal of Hazardous Materials*, 2021, 416: 125912
- [2] Pires VL, Novais SC, Lemos MFL, Fonseca VF, Duarte B. Evaluation of multivariate biomarker indexes application in ecotoxicity tests with marine diatoms exposed to emerging contaminants[J]. *Applied Sciences*, 2021, 11: 3878
- [3] Peng Y, Gautam L, Hall SW. The detection of drugs of abuse and pharmaceuticals in drinking water using solid-phase extraction and liquid chromatography-mass spectrometry[J]. *Chemosphere*, 2019, 223: 438-447
- [4] Celis-Hernandez O, Cundy AB, Croudace IW, Ward RD, Busquets R, Wilkinson JL. Assessing the role of the “estuarine filter” for emerging contaminants: pharmaceuticals, perfluoroalkyl compounds and plasticisers in sediment cores from two contrasting systems in the southern U.K.[J]. *Water Research*, 2021, 189: 116610
- [5] Škufca D, Kovačič A, Prosenc F, Griessler Bulc T, Heath D, Heath E. Phycoremediation of municipal wastewater: removal of nutrients and contaminants of emerging concern[J]. *Science of the Total Environment*, 2021, 782: 146949
- [6] Gomes IB, Maillard JY, Simões LC, Simões M. Emerging contaminants affect the microbiome of water systems — strategies for their mitigation[J]. *npj Clean Water*, 2020, 3: 39
- [7] Richardson SD, Ternes TA. Water analysis: emerging contaminants and current issues[J]. *Analytical Chemistry*, 2005, 77(12): 3807-3838
- [8] Rempel A, Gutkoski JP, Nazari MT, Biolchi GN, Cavanhi VAF, Treichel H, Colla LM. Current advances in microalgae-based bioremediation and other technologies for emerging contaminants treatment[J]. *Science of the Total Environment*, 2021, 772: 144918
- [9] Saidulu D, Gupta B, Gupta AK, Ghosal PS. A review on occurrences, eco-toxic effects, and remediation of emerging contaminants from wastewater: special emphasis on biological treatment based hybrid systems[J]. *Journal of Environmental Chemical Engineering*, 2021, 9(4): 105282
- [10] Dominguez JR, Núñez-Delgado A, García-Rodríguez J. Treatment technologies for emerging contaminants in water[J]. *Journal of Environmental Management*, 2021, 286: 112256
- [11] Gosset A, Wiest L, Fildier A, Libert C, Giroud B, Hammada M, Hervé M, Sibeud E, Vulliet E, Polomé P, et al. Ecotoxicological risk assessment of contaminants of emerging concern identified by “suspect screening” from urban wastewater treatment plant effluents at a territorial scale[J]. *Science of the Total Environment*, 2021, 778: 146275
- [12] Chung J, Lee G, Chung S, Lee YW. Removal of 1,4-dioxane in water using specific microbe immobilization cells[J]. *Water, Air, and Soil Pollution*, 2019, 230(6): 1-8
- [13] Awfa D, Ateia M, Fujii M, Yoshimura C. Photocatalytic degradation of organic micropollutants: inhibition mechanisms by different fractions of natural organic matter[J]. *Water Research*, 2020, 174: 115643
- [14] Khalid S, Yamazaki H, Socorro M, Monier D, Beniash E, Napierala D. Reactive oxygen species (ROS) generation as an underlying mechanism of inorganic phosphate (Pi)-induced mineralization of osteogenic cells[J]. *Free Radical Biology and Medicine*, 2020, 153: 103-111
- [15] Song N, Bai LL, Xu HC, Jiang HL. The composition difference of macrophyte litter-derived dissolved organic matter by photodegradation and biodegradation: role of reactive oxygen species on refractory component[J]. *Chemosphere*, 2020, 242: 125155
- [16] Belghit A, Merouani S, Hamdaoui O, Alghyamah A, Bouhelassa M. Influence of processing conditions on the synergism between UV irradiation and chlorine toward the degradation of refractory organic pollutants in UV/chlorine advanced oxidation system[J]. *Science of the Total Environment*, 2020, 736: 139623
- [17] Gagol M, Cako E, Fedorov K, Soltani RDC, Przyjazny A, Boczkaj G. Hydrodynamic cavitation based advanced oxidation processes: studies on specific effects of inorganic acids on the degradation effectiveness of organic pollutants[J]. *Journal of Molecular Liquids*, 2020, 307: 113002
- [18] Luo HW, Cheng Y, Zeng YF, Luo K, Pan XL. Enhanced decomposition of H₂O₂ by molybdenum disulfide in a

- Fenton-like process for abatement of organic micropollutants[J]. *Science of the Total Environment*, 2020, 732: 139335
- [19] Sun B, Wang Y, Xiang YY, Shang C. Influence of pre-ozonation of DOM on micropollutant abatement by UV-based advanced oxidation processes[J]. *Journal of Hazardous Materials*, 2020, 391: 122201
- [20] Kohtani S, Yoshida K, Maekawa T, Iwase A, Kudo A, Miyabe H, Nakagaki R. Loading effects of silver oxides upon generation of reactive oxygen species in semiconductor photocatalysis[J]. *Physical Chemistry Chemical Physics*, 2008, 10(20): 2986-2992
- [21] Nosaka Y, Nosaka AY. Generation and detection of reactive oxygen species in photocatalysis[J]. *Chemical Reviews*, 2017, 117(17): 11302-11336
- [22] Zhang T, Hansel CM, Voelker BM, Lamborg CH. Extensive dark biological production of reactive oxygen species in brackish and freshwater ponds[J]. *Environmental Science & Technology*, 2016, 50(6): 2983-2993
- [23] Lepez A, Pirnay T, Denanglaire S, Perez-Morga D, Vermeersch M, Leo O, Andris F. Long-term T cell fitness and proliferation is driven by AMPK-dependent regulation of reactive oxygen species[J]. *Scientific Reports*, 2020, 10: 21673
- [24] Korshunov SS, Imlay JA. A potential role for periplasmic superoxide dismutase in blocking the penetration of external superoxide into the cytosol of Gram-negative bacteria[J]. *Molecular Microbiology*, 2002, 43(1): 95-106
- [25] Ding X, Wang SY, Shen WQ, Mu Y, Wang L, Chen H, Zhang LZ. Fe@Fe₂O₃ promoted electrochemical mineralization of atrazine via a triazinon ring opening mechanism[J]. *Water Research*, 2017, 112: 9-18
- [26] Di Mascio P, Martinez GR, Miyamoto S, Ronsein GE, Medeiros MHG, Cadet J. Singlet molecular oxygen reactions with nucleic acids, lipids, and proteins[J]. *Chemical Reviews*, 2019, 119(3): 2043-2086
- [27] 徐晓, 杨祥龙, 陈婷, 丁星, 陈浩. 活性氧物种在环境污染物降解转化中的应用研究进展[J]. *华中农业大学学报*, 2020, 39(5): 1-8
- Xu X, Yang XL, Chen T, Ding X, Chen H. Application of reactive oxygen species in environmental pollutants degradation and transformation[J]. *Journal of Huazhong Agricultural University*, 2020, 39(5): 1-8 (in Chinese)
- [28] Li H, Shang J, Yang ZP, Shen WJ, Ai ZH, Zhang LZ. Oxygen vacancy associated surface Fenton chemistry: surface structure dependent hydroxyl radicals generation and substrate dependent reactivity[J]. *Environmental Science & Technology*, 2017, 51(10): 5685-5694
- [29] Wang PF, Gong QJ, Hu JB, Li X, Zhang XJ. Reactive oxygen species (ROS)-responsive prodrugs, probes, and theranostic prodrugs: applications in the ROS-related diseases[J]. *Journal of Medicinal Chemistry*, 2021, 64(1): 298-325
- [30] Wang WW, Zhai DS, Bai YQ, Xue K, Deng LL, Ma LR, Du TS, Ye ZC, Qu D, Xiang A, et al. Loss of QKI in macrophage aggravates inflammatory bowel disease through amplified ROS signaling and microbiota disproportion[J]. *Cell Death Discovery*, 2021, 7: 58
- [31] Diaz JM, Plummer S. Production of extracellular reactive oxygen species by phytoplankton: past and future directions[J]. *Journal of Plankton Research*, 2018, 40(6): 655-666
- [32] Zhang MX, Chiang YH, Toruño TY, Lee D, Ma MM, Liang XX, Lal NK, Lemos M, Lu YJ, Ma SS, et al. The MAP4 kinase SIK1 ensures robust extracellular ROS burst and antibacterial immunity in plants[J]. *Cell Host & Microbe*, 2018, 24(3): 379-391.e5
- [33] Zakaria BS, Dhar BR. Characterization and significance of extracellular polymeric substances, reactive oxygen species, and extracellular electron transfer in methanogenic biocathode[J]. *Scientific Reports*, 2021, 11: 7933
- [34] Han RX, Lv J, Zhang SH, Zhang SZ. Hematite facet-mediated microbial dissimilatory iron reduction and production of reactive oxygen species during aerobic oxidation[J]. *Water Research*, 2021, 195: 116988
- [35] Zinser ER. The microbial contribution to reactive oxygen species dynamics in marine ecosystems[J]. *Environmental Microbiology Reports*, 2018, 10(4): 412-427
- [36] Plummer S, Taylor AE, Harvey EL, Hansel CM, Diaz JM. Dynamic regulation of extracellular superoxide production by the coccolithophore *Emiliania huxleyi* (CCMP 374)[J]. *Frontiers in Microbiology*, 2019, 10: 1546
- [37] Sutherland KM, Coe A, Gast RJ, Plummer S, Suffridge CP, Diaz JM, Bowman JS, Wankel SD, Hansel CM. Extracellular superoxide production by key microbes in the global ocean[J]. *Limnology and Oceanography*, 2019, 64(6): 2679-2693
- [38] Diaz JM, Plummer S, Hansel CM, Andeer PF, Saito MA, McIlvin MR. NADPH-dependent extracellular superoxide production is vital to photophysiology in the marine diatom *Thalassiosira oceanica*[J]. *PNAS*, 2019, 116(33): 16448-16453
- [39] 冯义平, 毛亮, 董仕鹏, 高士祥. 过氧化物酶催化去除水体中酚类内分泌干扰物的研究进展[J]. *环境化学*, 2013, 32(7): 1218-1225

- Feng YP, Mao L, Dong SP, Gao SX. Peroxidase-catalyzed removal of phenolic endocrine disrupting chemicals from water[J]. Environmental Chemistry, 2013, 32(7): 1218-1225 (in Chinese)
- [40] Shi KY, Liu Y, Chen P, Li Y. Contribution of lignin peroxidase, manganese peroxidase, and laccase in lignite degradation by mixed white-rot fungi[J]. Waste and Biomass Valorization, 2021, 12(7): 3753-3763
- [41] 田乔鹏, 汪新悦, 张永, 管政兵, 蔡宇杰, 廖祥儒. 活性氧对白腐真菌漆酶合成的影响[J]. 食品与生物技术学报, 2019, 38(5): 103-110
- Tian QP, Wang XY, Zhang Y, Guan ZB, Cai YJ, Liao XR. Effect of reactive oxygen species on laccase synthesis of white-rot fungus[J]. Journal of Food Science and Biotechnology, 2019, 38(5): 103-110 (in Chinese)
- [42] Huang WT, Yin H, Yu YY, Lu GN, Dang Z, Chen ZH. Co-metabolic degradation of tetrabromobisphenol A by *Pseudomonas aeruginosa* and its auto-poisoning effect caused during degradation process[J]. Ecotoxicology and Environmental Safety, 2020, 202: 110919
- [43] Diaz JM, Hansel CM, Voelker BM, Mendes CM, Andeer PF, Zhang T. Widespread production of extracellular superoxide by heterotrophic bacteria[J]. Science, 2013, 340(6137): 1223-1226
- [44] 郭定环, 王竞, 顾晨, 郭雅丽. 海洋假交替单胞菌产胞外活性氧特性研究[J]. 大连理工大学学报, 2020, 60(6): 555-561
- Guo DH, Wang J, Gu C, Guo YL. Study of characteristics of extracellular reactive oxygen species produced by a marine *Pseudoalteromonas* sp.[J]. Journal of Dalian University of Technology, 2020, 60(6): 555-561 (in Chinese)
- [45] Khatoon N, Jamal A, Ali MI. Lignin peroxidase isoenzyme: a novel approach to biodegrade the toxic synthetic polymer waste[J]. Environmental Technology, 2019, 40(11): 1366-1375
- [46] Shi YF, Zhu KC, Dai YC, Zhang C, Jia HZ. Evolution and stabilization of environmental persistent free radicals during the decomposition of lignin by laccase[J]. Chemosphere, 2020, 248: 125931
- [47] Vos AM, Jurak E, Pelkmans JF, Herman K, Pels G, Baars JJ, Hendrix E, Kabel MA, Lugones LG, Wösten HAB. H₂O₂ as a candidate bottleneck for MnP activity during cultivation of *Agaricus bisporus* in compost[J]. AMB Express, 2017, 7(1): 1-9
- [48] Verspecht T, Ghesquière J, Bernaerts K, Boon N, Teughels W. Evaluating the intrinsic capacity of oral bacteria to produce hydrogen peroxide (H₂O₂) in liquid cultures: interference by bacterial growth media[J]. Journal of Microbiological Methods, 2021, 182: 106170
- [49] Hasebe Y, Fukuzawa M, Matsuhisa H. Quantitative determination of *Escherichia coli* based on the electrochemical measurement of bacterial catalase activity using H₂O₂-selective organic/inorganic-hybrid sol-gel film-modified Pt electrode[J]. Journal of Environmental Sciences, 2009, 21: S44-S47
- [50] 朱寅灿. 固定化辣根过氧化物酶对金橙 I 废水的脱色降解及生物毒性研究[D]. 福州: 福州大学硕士学位论文, 2018
- Zhu YC. The decolorization and degradation of wastewater containing orange I catalyzed by immobilized horseradish peroxidase and biotoxicity study[D]. Fuzhou: Master's Thesis of Fuzhou University, 2018 (in Chinese)
- [51] Li JH, Zhang Y, Huang QG, Shi HH, Yang Y, Gao SX, Mao L, Yang X. Degradation of organic pollutants mediated by extracellular peroxidase in simulated sunlit humic waters: a case study with 17 β -estradiol[J]. Journal of Hazardous Materials, 2017, 331: 123-131
- [52] 梁念. 细菌来源漆酶 lacc 和染料脱色过氧化物酶 DyP35 对木质素的降解作用及机理研究[D]. 镇江: 江苏大学硕士学位论文, 2020
- Liang N. The role and its mechanism on lignin degradation by bacteria-derived laccase and dye-decoloring peroxidase DyP35[D]. Zhenjiang: Master's Thesis of Jiangsu University, 2020 (in Chinese)
- [53] 刘鸿. 辣根过氧化物酶对磺胺甲噁啉降解的研究[D]. 济南: 山东大学硕士学位论文, 2019
- Liu H. Study on the degradation of sulfamerazine by horseradish peroxidase[D]. Jinan: Master's Thesis of Shandong University, 2019 (in Chinese)
- [54] 宁甲练, 陈志莉, 汪楚依, 谢文静. 固定化漆酶降解水中酚类污染物的研究进展[J]. 水处理技术, 2019, 45(2): 13-17
- Ning JL, Chen ZL, Wang CY, Xie WJ. Research progress of immobilized laccases for phenolic contaminants degradation in water[J]. Technology of Water Treatment, 2019, 45(2): 13-17 (in Chinese)
- [55] Xu PF, Du H, Peng X, Tang Y, Zhou YY, Chen XY, Fei J, Meng Y, Yuan L. Degradation of several polycyclic aromatic hydrocarbons by laccase in reverse micelle system[J]. Science of the Total Environment, 2020, 708: 134970
- [56] 张泽雄, 刘红艳, 邢贺, 马钰. 漆酶可降解底物种类的研究进展[J]. 生物技术通报, 2017, 33(10): 97-102
- Zhang ZX, Liu HY, Xing H, Ma Y. Research progress on

- substrate species degraded by laccase[J]. *Biotechnology Bulletin*, 2017, 33(10): 97-102 (in Chinese)
- [57] 王馥丽, 赵鹏, 裴承新, 黄启斌, 蒋辉, 习海玲. 漆酶及其应用研究进展[J]. *生命科学仪器*, 2017, 15(5): 19-24
Wang FL, Zhao P, Fei CX, Huang QB, Jiang H, Xi HL. Research progress of laccase and its application[J]. *Life Science Instruments*, 2017, 15(5): 19-24 (in Chinese)
- [58] Zhang SQ, Lin FF, Yuan QP, Liu JW, Li Y, Liang H. Robust magnetic laccase-mimicking nanozyme for oxidizing o-phenylenediamine and removing phenolic pollutants[J]. *Journal of Environmental Sciences*, 2020, 88: 103-111
- [59] Morsi R, Bilal M, Iqbal HMN, Ashraf SS. Laccases and peroxidases: the smart, greener and futuristic biocatalytic tools to mitigate recalcitrant emerging pollutants[J]. *Science of the Total Environment*, 2020, 714: 136572
- [60] 陈明雨, 倪烜, 司友斌, 孙凯. 固定化真菌漆酶在环境有机污染修复中的应用研究进展[J]. *生物技术通报*, 2021, 37(6): 244-258
Chen MY, Ni X, Si YB, Sun K. Advances in the application of immobilized fungal laccase for the bioremediation of environmental organic contamination[J]. *Biotechnology Bulletin*, 2021, 37(6): 244-258 (in Chinese)
- [61] Zeng J, Zhu QH, Wu YC, Lin XG. Oxidation of polycyclic aromatic hydrocarbons using *Bacillus subtilis* CotA with high laccase activity and copper independence[J]. *Chemosphere*, 2016, 148: 1-7
- [62] Samak NAA. 重组大肠杆菌发酵产漆酶及其催化应用[D]. 北京: 中国科学院大学(中国科学院过程工程研究所)博士学位论文, 2017
Samak NAA. CotA laccase production from recombinant *Escherichia coli* for efficient bio-catalytic[D]. Beijing: Doctoral Dissertation of University of Chinese Academy of Sciences (Institute of process engineering, Chinese Academy of Sciences), 2017 (in Chinese)
- [63] 靳洁. 海洋细菌 IOB-7 漆酶的生产纯化及其降解污染物的研究[D]. 哈尔滨: 哈尔滨工程大学硕士学位论文, 2016
Jin J. The study on production and purification of laccases produced by *Roseovarius* sp. IOB-7 and biodegradation of pollutants by it[D]. Harbin: Master's Thesis of Harbin Engineering University, 2016 (in Chinese)
- [64] 马霞, 聂麦茜, 卢剑, 聂红云, 王琰, 田晓婷, 侯宝卫. 鼠李糖脂对铜绿假单胞菌 NY3 表面特性及其降解效率的影响[J]. *环境科学学报*, 2014, 34(10): 2462-2468
Ma X, Nie MQ, Lu J, Nie HY, Wang Y, Tian XT, Hou BW. Effects of rhamnolipid on the properties of cell surface of strain *Pseudomonas aeruginosa* NY3 and its degradation efficiency of hydrocarbons[J]. *Acta Scientiae Circumstantiae*, 2014, 34(10): 2462-2468 (in Chinese)
- [65] 聂红云. 铜绿假单胞菌 NY3 胞外小分子活性物及其促进烃类降解的作用机理研究[D]. 西安: 西安建筑科技大学博士学位论文, 2017
Nie HY. Studies on characteristics of the secretion of extracellular small active compounds by *P. aeruginosa* NY3 and their promotion mechanisms to the efficiency of biodegradation of hydrocarbon[D]. Xi'an: Doctoral Dissertation of Xi'an University of Architecture and Technology, 2017 (in Chinese)
- [66] Nie HY, Nie MQ, Wang L, Diwu ZJ, Xiao T, Qiao Q, Wang Y, Jiang X. Evidences of extracellular abiotic degradation of hexadecane through free radical mechanism induced by the secreted phenazine compounds of *P. aeruginosa* NY3[J]. *Water Research*, 2018, 139: 434-441
- [67] Nie HY, Nie MQ, Diwu ZJ, Wang L, Qiao Q, Zhang B, Yang XF. Homogeneously catalytic oxidation of phenanthrene by the reaction of extracellular secretions of pyocyanin and Nicotinamide Adenine Dinucleotide[J]. *Environmental Research*, 2020, 191: 110159
- [68] 黄璐, 聂麦茜, 胡睿, 肖婷, 聂红云, 王琰. 铜绿假单胞菌 NY3 胞外分泌物对降解烃类的影响作用[J]. *微生物学杂志*, 2017, 37(1): 36-42
Huang L, Nie MQ, Hu R, Xiao T, Nie HY, Wang Y. Effects of extracellular polymer on alkanes degradation by *Pseudomonas aeruginosa* NY3[J]. *Journal of Microbiology*, 2017, 37(1): 36-42 (in Chinese)
- [69] 张波, 聂麦茜, 聂红云, 田晓婷, 乔琦. 绿脓菌素促进铜绿假单胞菌 NY3 降解烃的作用机理[J]. *中国环境科学*, 2019, 39(7): 3088-3093
Zhang B, Nie MQ, Nie HY, Tian XT, Qiao Q. The effects of pyocyanin on alkanes degradation by *Pseudomonas aeruginosa* NY3[J]. *China Environmental Science*, 2019, 39(7): 3088-3093 (in Chinese)
- [70] Nie HY, Nie MQ, Xiao T, Wang Y, Tian XT. Hexadecane degradation of *Pseudomonas aeruginosa* NY3 promoted by glutaric acid[J]. *Science of the Total Environment*, 2017, 575: 1423-1428
- [71] 肖婷, 聂麦茜, 聂红云, 朱洪胜, 乔琪, 陈军. 草酸对铜绿假单胞菌 NY3 降解烃的作用研究[J]. *微生物学杂志*, 2018, 38(2): 70-76
Xiao T, Nie MQ, Nie HY, Zhu HS, Qiao Q, Chen J. Effects of oxalic acid on hydrocarbon degradation by *Pseudomonas aeruginosa* NY3[J]. *Journal of Microbiology*, 2018, 38(2): 70-76 (in Chinese)

- [72] Nie HY, Nie MQ, Wang L, Diwu ZJ, Zhang J, Chen J, Xiao T. Promotion effect of extracellular abiotic degradation of hexadecane by co-existence of oxalic acid in the culture medium of *Pseudomonas aeruginosa* NY3[J]. Environmental Technology & Innovation, 2021, 22: 101415
- [73] Braud A, Geoffroy V, Hoegy F, Mislin GLA, Schalk IJ. Presence of the siderophores pyoverdine and pyochelin in the extracellular medium reduces toxic metal accumulation in *Pseudomonas aeruginosa* and increases bacterial metal tolerance[J]. Environmental Microbiology Reports, 2010, 2(3): 419-425
- [74] Inoue H, Takimura O, Kawaguchi K, Nitoda T, Fuse H, Murakami K, Yamaoka Y. Tin-carbon cleavage of organotin compounds by pyoverdine from *Pseudomonas chlororaphis*[J]. Applied and Environmental Microbiology, 2003, 69(2): 878-883
- [75] Sun GX, Zhong JJ. Mechanism of augmentation of organotin decomposition by ferripyochelin: formation of hydroxyl radical and organotin-pyochelin-iron ternary complex[J]. Applied and Environmental Microbiology, 2006, 72(11): 7264-7269
- [76] Gu C, Wang J, Liu SS, Liu GF, Lu H, Jin RF. Biogenic Fenton-like reaction involvement in cometabolic degradation of tetrabromobisphenol A by *Pseudomonas* sp. fz[J]. Environmental Science & Technology, 2016, 50(18): 9981-9989
- [77] 赵碧洁, 聂麦茜, 聂红云, 肖婷, 蒋欣, 赵元寿. 绿脓杆菌螯铁蛋白分泌及其对铜绿假单胞菌 NY3 降解烃类的影响作用[J]. 微生物学杂志, 2018, 38(1): 76-82
- Zhao BJ, Nie MQ, Nie HY, Xiao T, Jiang X, Zhao YS. Secretion of pyochelin & its effects on alkanes degradation by *Pseudomonas aeruginosa* NY3[J]. Journal of Microbiology, 2018, 38(1): 76-82 (in Chinese)
- [78] 聂红云, 聂麦茜, 第五振军, 王磊, 乔琦, 张波. 铜绿假单胞菌胞外液对菲的降解特性研究[J]. 安全与环境学报, 2020, 20(5): 1895-1901
- Nie HY, Nie MQ, Diwu ZJ, Wang L, Qiao Q, Zhang B. Degradation of phenanthrene through the cell-free extracellular fluid of *P. aeruginosa* NY3[J]. Journal of Safety and Environment, 2020, 20(5): 1895-1901 (in Chinese)
- [79] 赵碧洁. 铜绿假单胞菌 NY3 分泌绿脓杆菌螯铁蛋白及其对烃类降解特性的影响作用[D]. 西安: 西安建筑科技大学硕士学位论文, 2017
- Zhao BJ. The secretion of pyochelin and its effects on alkanes degradation by *Pseudomonas aeruginosa* NY3[D]. Xi'an: Master's Thesis of Xi'an University of Architecture and Technology, 2017 (in Chinese)
- [80] Xu WY, Fu SF, Yang ZM, Lu J, Guo RB. Improved methane production from corn straw by microaerobic pretreatment with a pure bacteria system[J]. Bioresource Technology, 2018, 259: 18-23
- [81] Zeng J, Lin XG, Zhang J, Li XZ, Wong MH. Oxidation of polycyclic aromatic hydrocarbons by the bacterial laccase CueO from *E. coli*[J]. Applied Microbiology and Biotechnology, 2011, 89(6): 1841-1849
- [82] 刘沙沙, 王竞, 吕红, 柳广飞, 范真真, 周集体. *Pseudomonas* sp. fz 胞外分离物降解四溴双酚 A[J]. 环境工程学报, 2015, 9(4): 1631-1638
- Liu SS, Wang J, Lv H, Liu GF, Fan ZZ, Zhou JT. Degradation of tetrabromobisphenol-A by extracellular isolates of *Pseudomonas* sp. fz[J]. Chinese Journal of Environmental Engineering, 2015, 9(4): 1631-1638 (in Chinese)
- [83] Gu C, Wang J, Guo MF, Sui M, Lu H, Liu GF. Extracellular degradation of tetrabromobisphenol A via biogenic reactive oxygen species by a marine *Pseudoalteromonas* sp.[J]. Water Research, 2018, 142: 354-362
- [84] 马建鹏, 马安周, 王榆琬, 王锋, 庄国强. 纳米零价铁耦合假单胞菌协同高效降解五氯苯[J]. 微生物学通报, 2019, 46(11): 2857-2864
- Ma JP, Ma AZ, Wang YW, Wang F, Zhuang GQ. Integrated zero-valent ironnanoparticles and *Pseudomonas* sp. strains system enhance degradation of pentachlorobenzene[J]. Microbiology China, 2019, 46(11): 2857-2864 (in Chinese)
- [85] 张杰, 吴姗姗, 杨园媛, 谭雪梅. 漆酶对水中氯酚类物质的去除[J]. 环境化学, 2019, 38(9): 2101-2107
- Zhang J, Wu SS, Yang YY, Tan XM. Removal of chlorophenols in aqueous solution by laccase[J]. Environmental Chemistry, 2019, 38(9): 2101-2107 (in Chinese)
- [86] 周鑫, 缪晓磊, 余学军. 毛栓菌 27-1 漆酶对酚酸类化合物降解的效能分析[J]. 中国农学通报, 2021, 37(13): 35-41
- Zhou X, Miao XL, Yu XJ. The degradation efficiency of *Trametes hirsuta* 27-1 laccase on phenolic acids[J]. Chinese Agricultural Science Bulletin, 2021, 37(13): 35-41 (in Chinese)
- [87] Liu HY, Zhang ZX, Xie SW, Xing H, Zhu YN, Li HY, Yi ZS. Study on transformation and degradation of bisphenol A by *Trametes versicolor* laccase and simulation of molecular docking[J]. Chemosphere, 2019, 224: 743-750