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典型药物与个人护理品(PPCPs)的厌氧降解转化研究进展

孙悦宏[1,2], 熊倩[3,#], 吴亨宇[1,2], 陈铨乐[1,2], 吴丹[1,2], 刘有胜[1,2,*], 应光国[1,2]

1. 华南师范大学环境学院,广州 510006
2. 华南师范大学广东省化学品污染与环境安全重点实验室,环境理论化学教育部重点实验室,广州 510006
3. 中国水产科学研究院南海水产研究所/农业农村部南海渔业资源环境科学观测实验站/广东省渔业生态环境重点实验室,广州 510300

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摘要: 药物与个人护理品(pharmaceuticals and personal care products, PPCPs)的污染和环境归趋问题备受关注。其中厌氧降解转化作为疏水性 PPCPs 在自然环境介质中的主要消解方式尤为重要。本文以典型 PPCPs 为例,分析了城市污水处理厌氧工艺对 PPCPs 的去除情况,主要包括污泥吸附和厌氧生物转化;总结了化学结构、微生物、碳源和氧化还原电位等多种因素对 PPCPs 厌氧降解转化效率的影响,其中氧化还原电位发挥重要作用,因其与氧化还原酶密切相关;同时,重点归纳了磺胺甲噁唑、苯并三唑和三氯生等 3 种典型 PPCPs 在不同氧化还原电位下的厌氧降解转化途径,并对 PPCPs 厌氧微生物降解的未来研究重点和发展方向进行展望:(1)强化 PPCPs 的有机质-厌氧微生物共代谢降解机制研究;(2)聚焦 PPCPs 厌氧降解菌群筛选及其功能研究;(3)深入开展厌氧降解菌群培养体系构建和原位厌氧降解研究。本研究相关结果有望为 PPCPs 的污染防治提供科学依据。

关键词: 药物及个人护理品;环境归趋;影响因素;厌氧降解转化
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Research Advances on Anaerobic Microbial Degradation of Typical Pharmaceuticals and Personal Care Products (PPCPs)

Sun Yuehong[1,2], Xiong Qian[3,#], Wu Hengyu[1,2], Chen Quanle[1,2], Wu Dan[1,2], Liu Yousheng[1,2,*], Ying Guangguo[1,2]

1. School of Environment, South China Normal University, Guangzhou 510006, China
2. Guangdong Provincial Key Laboratory of Chemical Pollution and Environmental Safety, Key Laboratory of Theoretical Chemistry of Environment, South China Normal University, Guangzhou 510006, China
3. South China Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences/Scientific Observing and Experimental Station of South China Sea Fishery Resources and Environment, Ministry of Agriculture and Rural Affairs/Key Laboratory of Fishery Ecology and Environment, Guangzhou 510300, China

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第一作者:孙悦宏(1999—),男,硕士研究生,研究方向为典型药物与个人护理品的厌氧降解,E-mail: yuehong.sun@m.scnu.edu.cn
* **通信作者**(Corresponding author), E-mail: yousheng.liu@m.scnu.edu.cn
\# **共同通信作者**(Co-corresponding author),E-mail: qian.xiong010@163.com

Abstract: The contamination and environmental fate of pharmaceuticals and personal care products (PPCPs) have raised great concerns. Anaerobic degradation and transformation as the main natural reduction for hydrophobic PPCPs in environment is particularly important. Here we reviewed the anaerobic removal fate of typical PPCPs in the municipal wastewater treatment plants, mainly including sludge adsorption and anaerobic biodegradation. Subsequently, the effects of chemical structure, microorganisms, carbon source, and redox potential on the anaerobic degradation and transformation efficiency of PPCPs were summarized, of which redox potential played an important role due to its special relationship with redox enzymes. Then, we focused on the anaerobic degradation and transformation pathways of three typical PPCPs (sulfamethoxazole, benzotriazole and triclosan) under different redox potential conditions. Finally, we presented the forward research challenges and proposed the future research priorities in PPCPs anaerobic biodegradation: (1) Exploring the anaerobic co-metabolism mechanisms of PPCPs; (2) Focusing on the isolation of PPCPs anaerobic degradation bacteria and the associated function analysis; (3) Investigating the construction of anaerobic degradation bacteria culture system and in-situ anaerobic degradation of PPCPs. This systematic review provides scientific basis for the management and control of PPCPs contamination.
Keywords: pharmaceuticals and personal care products; environmental fate; influence factors; anaerobic biodegradation

Daughton 和 Ternes[1]于 1999 年首次提出药物与个人护理品(pharmaceuticals and personal care products, PPCPs)概念,主要包括:人用和兽用药物,例如抗生素、类固醇、止痛药和降压药等;以及化妆品、防晒霜、洗发水和染发剂等个人护理品。作为一类与人类日常生活密切相关的化学物质,PPCPs 生产和使用量巨大,并在生产、使用过程中不断地向环境介质中释放。研究发现,PPCPs 在废水[2]、表层水[3]、地下水[4]、土壤[5]和饮用水[6]等多种环境介质中广泛检出。大部分 PPCPs 的化学结构稳定,进入受纳环境后长期残留,其在水环境中的检出浓度通常介于 $ng\cdot L^{-1}$ 到 $\mu g\cdot L^{-1}$ 水平,土壤或沉积物中检出浓度一般在 $ng\cdot g^{-1}$ 水平。环境中残留的 PPCPs,不仅会对生态系统造成潜在的风险,还会影响人类健康,如抗生素污染会诱导耐药菌和耐药基因的传播扩散,对人类健康造成潜在威胁[7]。最近 *Science* 杂志的封面论文研究发现典型紫外吸收剂羟苯甲酮会在珊瑚体内富集和代谢,产生危害珊瑚生存的光毒素,加速濒危生态系统的消失[8]。另外,还有研究发现典型杀生剂三氯生对鱼类具有发育毒性和神经毒性[9]。因此,PPCPs 的污染防控引起国内外广泛关注,我国也提出将抗生素等新污染物作为重点管控新污染物进行系统监测和污染防控。

现阶段针对 PPCPs 的常用去除方法包括物理法(吸附法、膜分离法)、化学氧化法(辐射分解、芬顿氧化法、臭氧氧化法、电化学氧化和过硫酸盐氧化等)、微生物降解法(好氧降解、厌氧降解)以及物化法-生物法组合技术等[10]。其中,微生物降解法因其环境友好、成本低等优势而受到广泛关注。PPCPs 好氧微生物降解因其条件易于控制,目前已有大量相关研究。表 1 中列举了药物、苯并三唑、激素和抗生素等 4 类常见的 PPCPs,研究发现这些 PPCPs 如萘普生、5-氯代苯并三氮唑、磺胺甲噁唑的好氧微生物降解效率和降解半衰期显著低于厌氧微生物降解(表 1)[11-15]。通常疏水性的 PPCPs 进入受纳环境后,倾向于分布在厌氧或者缺氧环境中,厌氧微生物降解可能是其主要的消解方式,而目前针对 PPCPs 厌氧微生物降解机制研究仍很有限。因此,深入开展 PPCPs 的厌氧降解研究具有重要意义,了解其在环境中的厌氧降解转化过程、影响因素与制约因子,有助于系统认识 PPCPs 的污染过程与环境归趋,从而针对性地研发污染阻断和控制技术。本研究以典型 PPCPs 为例介绍了其在污水处理厂中的厌氧去除情况,并总结了 PPCPs 厌氧降解的主要影响因素,重点归纳了磺胺甲噁唑、苯并三唑和三氯生等 3 种典型 PPCPs 类化合物的厌氧降解转化途径,以期为 PPCPs 的污染防治提供科学依据。

1　城市污水处理厂中 PPCPs 的厌氧去除途径(Anaerobic removal pathways of PPCPs in urban sewage treatment plants)

疏水性 PPCPs 受辛醇/水分配系数(K_{ow})、解离常数(pK_a)等物化性质,环境温度、pH 值等外界因素影响,容易吸附于污泥中[16]。如三氯生、舍曲林、奥

克立林和 UV-326 等化合物因 K_{ow} 值较高,在污泥相的占比分别可达 41%、90%、92% 和 54% (图 1)[17-19]。此外,还有研究发现污泥吸附也是部分亲水性 PPCPs 在污水处理厂中的主要去除途径。依诺沙星、诺氟沙星、环丙沙星和恩诺沙星等 K_{ow} 在-0.2 ~0.46 之间的氟喹诺酮类抗生素,在污水处理厂或实验室模拟污水处理实验中高达 73.9% ~ 86.2%可吸附到污泥相(图 1)[20-25]。污泥对氟喹诺酮类抗生素的强吸附作用可能是由带电的化合物基团与微生物及惰性颗粒表面发生的静电作用所引起[26]。而污泥对四环素、土霉素等低 K_{ow} 的四环素类抗生素的吸附作用则与阳离子交换机制密切相关。污泥相通常处于厌氧或缺氧环境,吸附在污泥中的 PPCPs 会进一步发生厌氧降解转化。Martín 等[27]研究发现低浓度对乙酰氨基酚、双氯芬酸、水杨酸、苯扎贝特和氟喹诺酮类抗生素等 PPCPs 在厌氧消化工艺中的去除率显著高于好氧处理工艺。此外,文拉法辛、泛影酸和曲马多等在好氧工艺过程中去除效率极低的化合物,进入厌氧工艺后其去除率有显著提升[28-29]。相比于好氧工艺,厌氧消化工艺已经成为污水处理厂去除一些难降解 PPCPs 的有效手段。

2 PPCPs 厌氧降解转化的主要影响因素(Main influence factors of anaerobic biodegradation of PPCPs)

2.1 化学结构(Chemical structure)

PPCPs 的化学结构决定了其理化性质和生物可降解性,官能团会影响 PPCPs 的生物可降解性[30-35]。对于含有苯环的化合物,苯环上连接的—COOH、—OH 等官能团能够促进其羟基化并增加生物可降解性,而卤素则会降低化合物的生物可降解性[35]。Musson 等[32]对比研究了 4 种化学结构不同 PPCPs 的厌氧降解效率,发现乙酰水杨酸>酒石酸美托洛尔>对乙酰氨基酚>布洛芬。乙酰水杨酸因苯环上含—COOH、—OH 官能团,呈现出较高的生物可降解性;而酒石酸美托洛尔苯环上含有醚键和氨基、对乙酰氨基酚苯环上侧链分支含酰胺键、布洛芬侧链高度分支,这些特征官能团可能在一定程度上影响了 3 种化合物的生物可降解性,导致其厌氧降解效率显著低于乙酰水杨酸[32]。

2.2 微生物(Microorganisms)

微生物是 PPCPs 厌氧降解转化的主要执行者,其组成、稳定性和功能微生物丰度等均会影响 PPCPs 的厌氧降解[36]。Sella 等[37]研究发现 3 种不同污泥中磺胺甲噁唑的降解效果有差异,微生物群落结构相对稳定的污泥体系中磺胺甲噁唑降解效果最好。Wolfson 等[38]对比研究发现添加目标化合物苯海拉明后,丛毛单胞菌科、共生细菌科和厌氧绳菌科细菌明显富集,说明该类细菌可能是苯海拉明降解功能菌群。大量研究证实,厌氧降解功能单菌的筛选可有效促进特定污染物的降解效果。Chopra 和 Kumar[39]从印度哈里亚纳邦污水中分离获得厌氧菌株德伦特杆菌 S1(*Bacillus drentensis* strain S1),其对乙酰氨基酚(初始浓度为 300 mg·L^{-1})的厌氧降解效率高达 93%。Ouyang 等[40]在初始浓度 100 μmol·L^{-1}磺胺甲噁唑的硫酸盐还原体系中加入富集培养

表 1 典型药物与个人护理品(PPCPs)的好氧与厌氧降解效率差异

Table 1 Difference between aerobic and anaerobic degradation of typical pharmaceuticals and personal care products (PPCPs)

化合物 Compound	条件 Condition	降解半衰期/d Degradation half-life/d	降解效率/% Degradation efficiency/%	参考文献 Reference
萘普生 Naproxen	好氧 Aerobic	75.00	100	[11]
	厌氧 Anaerobic	24.00	100	
对乙酰氨基酚 Acetaminophen	好氧 Aerobic	2.54	100	[12]
	厌氧 Anaerobic	1.16	100	
5-氯代苯并三氮唑 5-chlorobenzotriazole	好氧 Aerobic	86.00	52	[13]
	厌氧 Anaerobic	26.00	86	
17β-雌二醇 17β-estradiol	好氧 Aerobic	2.10	>96	[14]
	厌氧 Anaerobic	1.60	>96	
磺胺甲噁唑 Sulfamethoxazole	好氧 Aerobic	3.99	>97	[15]
	厌氧 Anaerobic	4.75	>97	

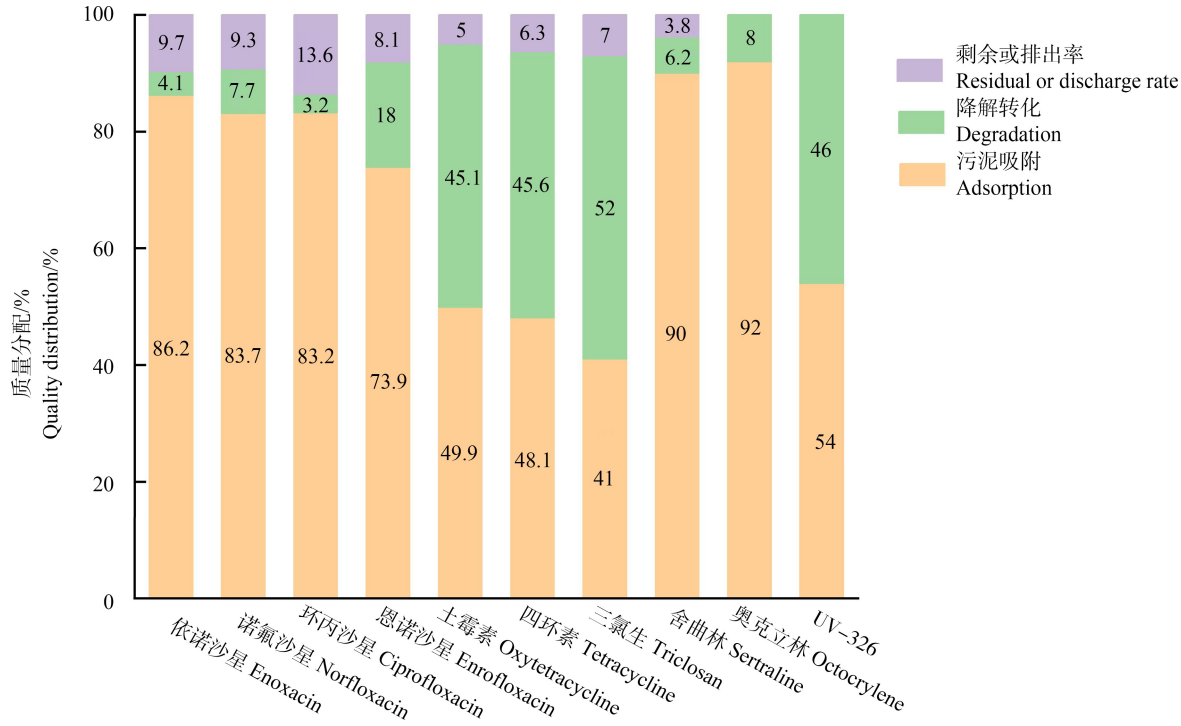

图 1　典型 PPCPs 在城市污水厂中的主要去除途径及贡献[17-25]

Fig. 1　Main removal pathways and contributions of typical PPCPs in municipal sewage treatment plants[17-25]

的希尔登伯勒普通脱硫弧菌(*Desulfovibrio vulgaris* Hildenborough),磺胺甲噁唑的降解效果高达 90%。吴丹等[41]从某市政污水处理厂厌氧消化污泥中分离得到柠檬酸盐杆菌属 BP3-1(*Citrobacter amalonaticus* strain BP3-1),对 BP-3(2 mg·L^{-1})的降解效率高达 98.3%。

此外,研究还发现温度、pH 和腐殖酸等多种环境因素会影响微生物活性,进而影响 PPCPs 的厌氧降解转化效率。在一定温度范围内,微生物活性随温度改变而变化,影响 PPCPs 的厌氧降解速率[42]。然而,也有研究发现温度对部分 PPCPs 的厌氧降解无明显影响。Carballa 等[43-44]研究发现除了布洛芬和罗红霉素外,佳乐麝香、吐纳麝香、卡马西平、地西泮、萘普生、双氯芬酸、碘普罗胺、磺胺甲噁唑、雌酮、17β-雌二醇和 17α-乙炔雌二醇等 11 种 PPCPs 的厌氧降解均不受温度的影响。另一方面,不同微生物的最适生长 pH 不同,通常当微生物处于最适生长 pH 值时,其对 PPCPs 的厌氧降解效率较高。Mao 等[45]研究发现,不同的 pH 条件下希瓦氏菌属对磺胺吡啶和磺胺甲噁唑的降解效率有显著差异,当 pH 值为 7 ~ 8 时 2 种抗生素的降解效率均最高。

腐殖酸物质(humic substances, HS)作为自然环境中存在的动物、植物和微生物残骸及其降解产物中经过高度转化的而成的有机物质[46],能够影响多种 PPCPs 的厌氧生物降解,研究发现五氯苯酚的微生物还原性脱氯受其影响显著[47-49];此外,多种 HS 可作为氧化还原中间介质影响 2,4-二氯苯氧乙酸的厌氧微生物降解[50]。HS 影响 PPCPs 厌氧微生物降解的方式可能存在多种:(1)HS 可作为电子供体或者受体,在 HS 还原微生物和一些不溶的电子受体(如三价铁氧化物)之间穿梭传递电子,通过影响微生物的无氧呼吸改变微生物对 PPCPs 的降解活性[51];(2)HS 能够改变微生物的生长活性;(3)HS 可将部分 PPCPs 转化为低毒产物或充当疏水性化合物的表面活性剂以增加 PPCPs 的生物可利用性。然而,目前关于 HS 对 PPCPs 厌氧微生物降解的影响机制尚未明确,有待进一步研究。

2.3　外加条件(Additional conditions)

2.3.1　碳源(Carbon source)

通过添加外源碳源,促进 PPCPs 的厌氧共代谢转化已被广泛报道,其共代谢降解机理主要包括:(1)降解菌更易于利用外源碳源,释放酶非特异性作用于 PPCPs 促进其降解;(2)降解菌利用外源碳源促进其自身生长,提高特定降解酶的分泌从而促进 PPCPs 降解。不同碳源对 PPCPs 的厌氧共代谢降解转化效果影响差异显著。控制外加碳源为单一变量,当蛋白胨作为共代谢碳源时,磺胺甲噁唑的厌氧

降解半衰期为 4.53 d,而可溶淀粉作为共代谢碳源时,磺胺甲噁唑的厌氧降解半衰期缩短至 1.61 d[52]。然而,Baquero 等[53]研究发现当醋酸钠作为共代谢碳源时,卡马西平和双氯芬酸的去除效率降低。添加合适的碳源构建共代谢体系可有效提高 PPCPs 的厌氧降解效率,而不同碳源对其厌氧降解的影响机制仍有待深入研究。

2.3.2 氧化还原电位(Redox potential)

氧化还原条件也会对 PPCPs 的厌氧降解产生影响,部分难降解化合物只能在特定的条件下有效降解。由表 2 可知,咖啡因、萘普生、阿替洛尔、普萘洛尔、苯并三唑、5-甲基苯并三唑、5-氯代苯并三唑、

表 2 PPCPs 在不同厌氧降解条件下的降解情况

Table 2 Degradation of PPCPs under different anaerobic condition

化合物 Compound	条件 Condition	降解半衰期/d Degradation half-life/d	降解效率/% Degradation efficiency/%	参考文献 Reference
咖啡因 Caffeine	硫酸盐还原 Sulfate-reducing	–[a]	100	[54]
	硝酸盐还原 Nitrate-reducing	–[a]	100	
	产甲烷 Methanogenic	–[a]	<20	
萘普生 Naproxen	锰还原 Manganese-reducing	66	100	[11]
	铁还原 Iron-reducing	24	100	
	硫酸盐还原 Sulfate-reducing	87	100	
	硝酸盐还原 Nitrate-reducing	n.d.[b]	−2[c]	
阿替洛尔 Atenolol	锰还原 Manganese-reducing	n.d.[b]	18	
	铁还原 Iron-reducing	381	52	
	硫酸盐还原 Sulfate-reducing	n.d.[b]	19	
	硝酸盐还原 Nitrate-reducing	192	100	
普萘洛尔 Propranolol	锰还原 Manganese-reducing	n.d.[b]	20	
	铁还原 Iron-reducing	n.d.[b]	12	
	硫酸盐还原 Sulfate-reducing	n.d.[b]	−2[c]	
	硝酸盐还原 Nitrate-reducing	258	66	
苯并三唑 Benzotriazole	厌氧对照 Anaerobic control	144	36	[13]
	铁还原 Iron-reducing	239	31	
	硫酸盐还原 Sulfate-reducing	165	18	
	硝酸盐还原 Nitrate-reducing	315	24	
5-甲基苯并三唑 5-methylbenzotriazole	厌氧对照 Anaerobic control	57	61	
	铁还原 Iron-reducing	41	76	
	硫酸盐还原 Sulfate-reducing	88	47	
	硝酸盐还原 Nitrate-reducing	128	35	
5-氯代苯并三唑 5-chlorobenzotriazole	厌氧对照 Anaerobic control	44	71	
	铁还原 Iron-reducing	26	86	
	硫酸盐还原 Sulfate-reducing	96	45	
	硝酸盐还原 Nitrate-reducing	78	53	
美托洛尔 Metoprolol	硫酸盐还原 Sulfate-reducing	–[a]	56	[55]
	硝酸盐还原 Nitrate-reducing	–[a]	−9[c]	
	产甲烷 Methanogenic	–[a]	52	
环丙沙星 Ciprofloxacin	发酵 Fermentation	–[a]	n.d.[b]	[56]
	硫酸盐还原 Sulfate-reducing	–[a]	80	
	硝酸盐还原 Nitrate-reducing	–[a]	82	

注:[a]“–”表示文献中未给出数据;[b]“n.d.”表示在实验周期内未被检测到;[c]降解效率为负数可能是由于污泥解吸附作用或是较小的分析偏差导致。

Note: [a] “–” indicated that no data was given in the reference; [b] “n.d.” indicated that it was not detected during the experimental period; [c] The negative degradation efficiency may be caused by sludge desorption or small analysis deviation.

美托洛尔和环丙沙星在不同氧化还原条件下降解效率差异显著[11,13,54-56]。如萘普生在硝酸盐还原条件下难降解,在硫酸盐还原条件下降解效率较高;而普萘洛尔则呈现出相反的降解规律。咖啡因在产甲烷条件下降解效率较低,而在硫酸盐还原和硝酸盐还原条件下均呈现较高的降解效率[55]。

目前,关于 PPCPs 厌氧降解效率的影响因素研究普遍以控制单一变量为主,然而不同因素之间具有相互作用。如不同的氧化还原条件会影响 PPCPs 降解菌群的组成[56],温度变化对降解菌生理活性产生影响进而导致降解菌最适 pH 值发生改变等。因此,未来开展 PPCPs 厌氧微生物降解研究时应尽可能模拟复杂自然环境体系,考虑多因素相互作用对其降解转化规律的影响。

3　典型 PPCPs 的厌氧降解转化途径(Anaerobic biodegradation pathways of typical PPCPs)

本文以使用量大、检出率高、具有潜在生态毒性和健康风险的磺胺甲噁唑、苯并三唑以及三氯生 3 种典型的 PPCPs 为例,归纳总结了其在不同氧化还原条件下的厌氧降解转化途径。

3.1　磺胺甲噁唑(Sulfamethoxazole)

磺胺甲噁唑(sulfamethoxazole, SMX)是一种磺胺类的抗生素,由氨基取代的苯环通过磺酰胺与甲基化异噁唑环相连组成(图 2),常用于人类和动物疾病预防和治疗,使用量大,且被人和动物服用以后不能完全代谢,其在环境中广泛分布,对人、动物和环境造成潜在危害。相比于传统的去除工艺,研究发现厌氧序批生物膜反应器、横流式厌氧固定化生物量反应器等厌氧工艺对 SMX 的去除效果较好[57]。目前,针对 SMX 在硫酸盐还原条件和铁还原条件下的厌氧降解转化机理已展开了一系列深入的研究[23,40,58-59],普遍认为 SMX 的厌氧降解途径起始于异噁唑环 O—N 键断裂。在铁还原条件下,铁循环功能微生物将 Fe(Ⅲ)还原为 Fe(Ⅱ),进而 Fe(Ⅱ)诱导 SMX 中的异噁唑环 O—N 键断裂[59]。而 SMX 并不与硫化物反应,推测 SMX 在硫酸盐还原条件和铁还原条件下的异噁唑环 O—N 键断键机制不同。Jia 等[23]研究进一步发现 SMX 在硫酸盐还原条件下异噁唑环 O—N 键断裂很可能是由 DNHP 依赖性还原酶(NADH-dependent reductases)所诱导,例如亚硫酸盐还原酶的催化反应。此外,学者研究发现 SMX 在硫酸盐还原条件发生降解,而其在氧化还原电位较高的硝酸盐还原条件下并未发生降解[40,60],可能是由于低氧化还原电位蛋白酶在高氧化还原电位下被抑制导致。虽然 SMX 在硫酸盐还原条件和在硝酸盐还原条件下断键机制不同,但其在不同氧化还原条件下的厌氧降解均与 DNHP 依赖性还原酶等酶催化作用有密切关系。这类酶可能属于低氧化还原点位还原酶,在低氧化还原条件下起作用,而在高氧化还原电位下被抑制。总之,SMX 在不同氧化还原条件下的厌氧降解途径差异较大,涉及的机理也相对复杂,有待进一步研究。

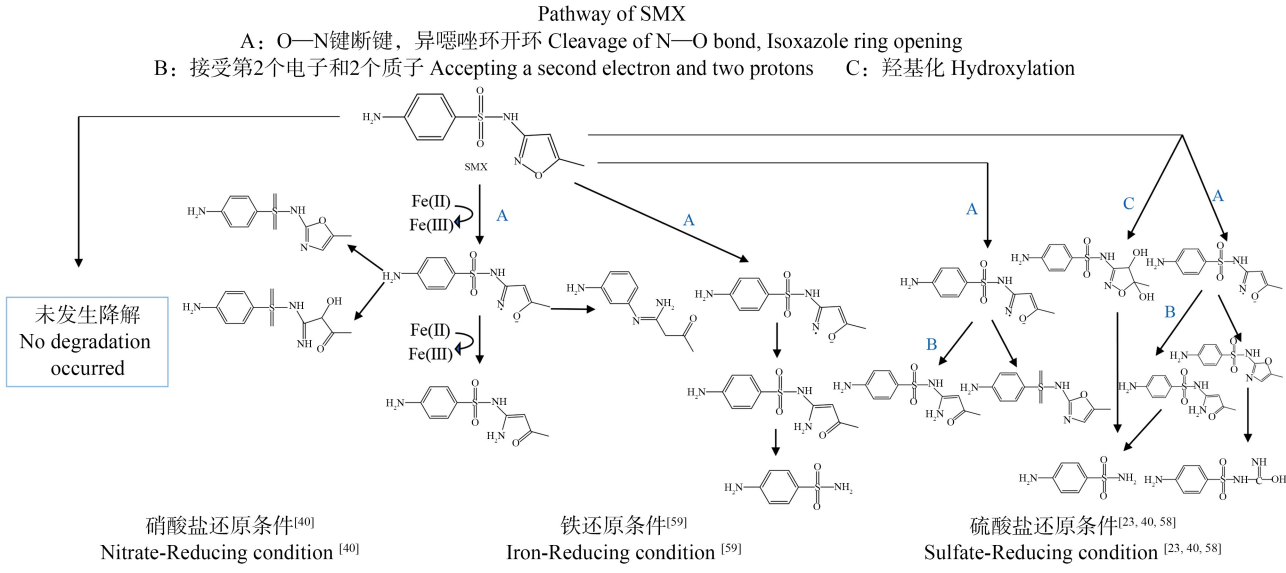

图 2　磺胺甲噁唑(SMX)在不同氧化还原条件下可能的厌氧降解途径[23,40,58,59]

Fig. 2　Possible anaerobic degradation pathways of sulfamethoxazole (SMX) under different redox condition [23,40,58,59]

3.2 苯并三唑(1H-benzotriazole)

苯并三唑类是生产量和使用量最大的一类紫外吸收剂,广泛添加于防晒霜、杀菌剂、洗涤剂、药物、轮胎橡胶防腐蚀剂和制冷剂等产品中[61]。苯并三唑(1H-benzotriazole, BT)结构如图 3 所示,由苯环和三唑环连接组成。伴随着 BT 的大规模使用,其在地下水[62]、城市雨水径流[63],甚至人体尿液[64]中均有检出。已有研究表明,BT 会造成鱼类内分泌系统絮乱,存在潜在环境风险[65]。目前针对 BT 的厌氧降解转化研究并不多,有限的研究发现 BT 的微生物降解与氧化还原条件相关,且其在不同的氧化还原条件下的降解途径不尽相同(图 3):硝酸盐还原条件下,BT 仅发生甲基化形成 1-甲基苯并三唑(B);硫酸盐和铁还原条件下,BT 能够发生 N—N 键的断裂,紧接着甲基化形成二甲基苄胺(C)或聚合形成咔唑(D)[13,66-67]。在不同氧化还原条件下,BT 的降解转化产物均有苯酚生成,但其降解途径不同。硝酸盐还原条件下,BT 首先发生甲基取代反应,而硫酸盐和铁还原条件下经由 N—N 键断裂后开环。分析其可能的原因,不同氧化还原条件下发挥作用的酶不同,进而导致 BT 的降解转化途径不同。

3.3 三氯生(Triclosan)

三氯生(triclosan, TCS)是一种人工合成的广谱类杀菌剂,由一个间位被 2 个氯元素取代的苯环和一个间位分别被氯元素、羟基取代的苯环通过醚键相连接(图 4)。TCS 具有较好的杀菌作用,在生产生活中广泛应用于牙膏、肥皂和洗发水等个人护理品。TCS 因具有生物累积性、生物毒性及环境毒性[68],其去除研究受到广泛关注。虽然有研究认为 TCS 在厌氧条件下一般难以降解[69],但 Gangadharan Puthiya Veetil 等[70]研究发现其在硫酸盐还原条件和产甲烷条件下均会发生厌氧降解。在低氧化还原电位的硫酸盐还原条件和产甲烷条件下,TCS 能够发生二苯醚键断裂和还原性脱氯反应,这可能是由低氧化还原电位酶介导。而 Ying 等[69]发现 TCS 在厌氧土壤中难以降解,可能是因为样品氧化还原电位较高抑制了低氧化还原电位酶发挥作用。

综合上述典型 PPCPs 降解途径发现:不同氧化还原条件对 PPCPs 的厌氧降解途径存在显著影响,酶是 PPCPs 厌氧降解中的重要参与者[71],而不同的氧化还原电位会促进或抑制酶活性,进而影响 PPCPs 的降解转化途径。

4 总结与展望(Conclusion and prospect)

PPCPs 是一类具有生态毒性、可在环境介质中迁移转化的新污染物,其在受纳环境中的分配和降解转化决定其环境持久性和影响。探究 PPCPs 在环境中的降解转化过程、影响因素和制约因子等,可为针对性地研发 PPCPs 污染阻断和管控技术提供科学依据和技术指导。多种 PPCPs 属于疏水性化合物,进入受纳环境后,往往分布在厌氧或者缺氧环境,厌氧微生物降解是其主要的降解转化方式。近年来,针对 PPCPs 的厌氧降解研究取得了一定的进展,揭示了化学结构、微生物、外加条件如碳源和氧化还原条件等是其重要影响因素,也发现了厌氧降解过程中可能涉及一些还原酶活性的变化,并筛获

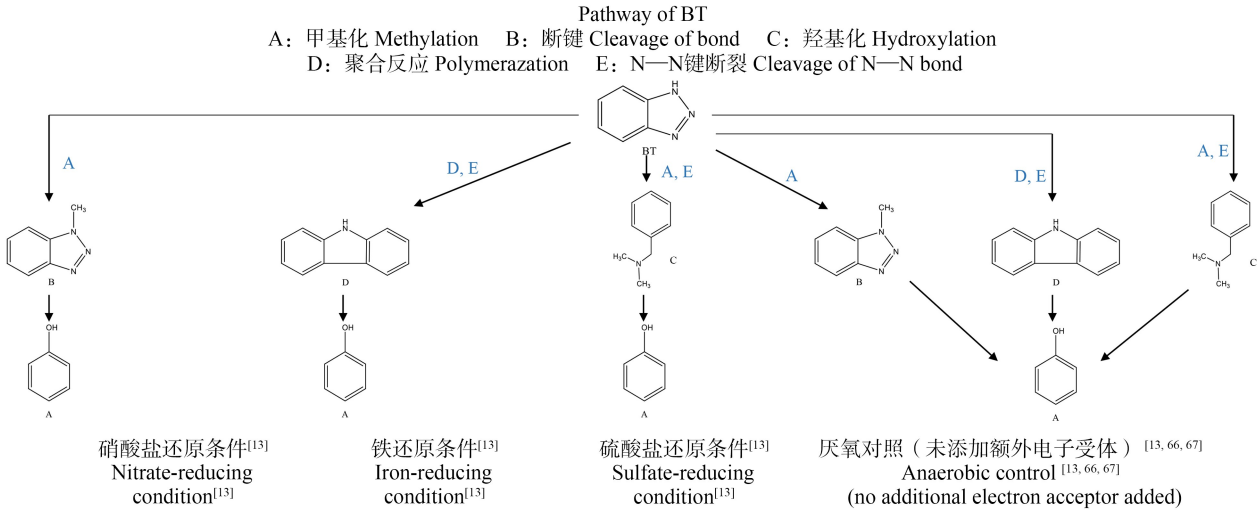

图 3 苯并三唑(BT)在不同氧化还原条件下可能的厌氧降解途径[13,66,67]

Fig. 3 Possible anaerobic degradation pathways of 1H-benzotriazole (BT) under different redox condition [13,66,67]

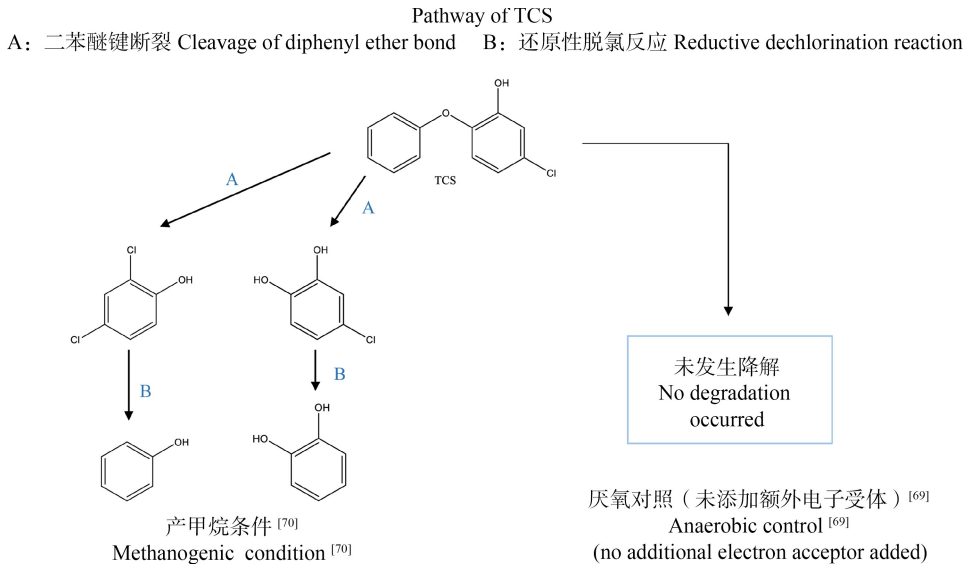

图 4　三氯生(TCS)在不同氧化还原条件下可能的厌氧降解途径 [69-70]

Fig. 4　Possible anaerobic degradation pathways of triclosan (TCS) under different redox condition [69-70]

了一些特定的降解微生物。然而,自然环境中PPCPs 的厌氧微生物降解是一个复杂体系,现阶段对于严格厌氧条件的模拟、多因素条件组合筛查、降解功能菌群的相互作用机理等方面仍存在许多挑战,需要进一步研究。

(1)强化 PPCPs 的有机质-厌氧微生物共代谢降解机制研究。前期研究多以单一环境因素下的模拟厌氧降解研究为主,而自然环境因子复杂多样,其中有机质-厌氧共代谢是 PPCPs 非常重要的厌氧降解过程,未来有必要深入研究有机质-厌氧微生物降解协同作用机理,可通过理论计算和高分辨质谱技术等手段准确筛查 PPCPs 厌氧降解中间产物,并结合基因组学、蛋白组学和代谢组学等技术,从多水平分析有机质-厌氧微生物共代谢机制。

(2)聚焦 PPCPs 厌氧降解菌群筛选及其功能研究,前期研究虽已筛获特定的降解菌株,但针对其功能基因相关研究较少,降解作用机理尚不清楚。有鉴于此,通过基因组学和转录组学等多组学手段揭示降解功能基因,为后续 PPCPs 特定厌氧降解工程菌研制做储备。另一方面,在实际环境中,PPCPs 的厌氧降解转化通常是依赖功能菌群间的相互作用完成。因此,有必要加强对 PPCPs 具有高效降解能力的功能菌群评价与筛选研究。

(3)突破厌氧降解菌群培养体系构建和原位厌氧降解研究。模拟自然环境中的厌氧条件、厌氧培养基的单一性和选择性、厌氧培养过程中极易发生污染等是制约厌氧降解研究突破的重要因素。开发和模拟自然环境中的厌氧条件将有助于揭示污染物的厌氧降解转化过程;而研发广谱的厌氧微生物培养基则有助于降解功能菌的筛选。因此,未来有必要进一步开展污染场地原位的厌氧降解实验和修复验证实验研究。

通信作者简介:刘有胜(1981—),男,博士,研究员,主要研究方向为典型新污染物的环境行为、归趋和污染防控。

共同通信作者简介:熊倩(1988—),女,博士,助理研究员,主要研究方向为污染物化学行为和环境毒理学。

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