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水环境中尼泊金酯类防腐剂的赋存及生物降解研究进展*

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摘　要　尼泊金酯类防腐剂(parabens)具有潜在内分泌干扰效应,近年来开始受到环境学者关注.这类化合物使用广泛且具有亲脂性,易通过污水排放进入水体/沉积物体系.本文综述了 parabens 在水环境中的赋存特征,以及在水环境中的生物降解转化行为,并对今后研究趋势进行了展望.国内外最新文献总结表明,parabens 在水环境介质中分布广泛,检出率高,母体化合物虽然可以被生物降解,但在污水处理系统中仍不能被完全去除,尤其 parabens 卤代转化产物的半衰期及潜在毒性不容忽视.此外,对于 parabens 在水体/沉积物中好氧及厌氧降解过程中的功能微生物鉴定及群落结构分析还有待深入揭示.因此利用功能微生物开发出污水中尼泊金酯类防腐剂高效痕量去除工艺将是今后研究主要方向,后续研究工作的开展将为今后针对水体/沉积物中这类痕量污染物利用微生物群落进行污染场地原位修复提供基础科学依据.

关键词　尼泊金酯, 赋存, 生物降解, 废水, 转化, 修复.

Occurrence and biodegradation of parabens in aquatic environment- a state-of-the-arts review

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Abstract: Parabens have attracted wide attention in recent years due to their potential endocrine disrupting effects. These substances are widely-used and lipophilic, thus readily discharged into water/sediment environment through sewage flows. This paper reviews the occurrence and microbial degradation behavior of parabens in aquatic environment, and proposes the future research trends. It shows that parabens are widely distributed and frequently detected in aquatic compartment. Although they are biodegradable, they can not be completely removed in wastewater treatment plants. Notably, the half-life and potential toxicity of halogenated products should not be neglected. In addition, functional microbiological identification and community structure analysis during the aerobic and anaerobic degradation process of parabens have yet to be revealed. Hence, the assistance of functional microbes on the development of high efficient trace removal techniques of parabens in wastewater should be the main research field in future. These follow-up research work will provide basic data for

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in-situ remediation on those trace pollutants with the utilization of microbial communities.

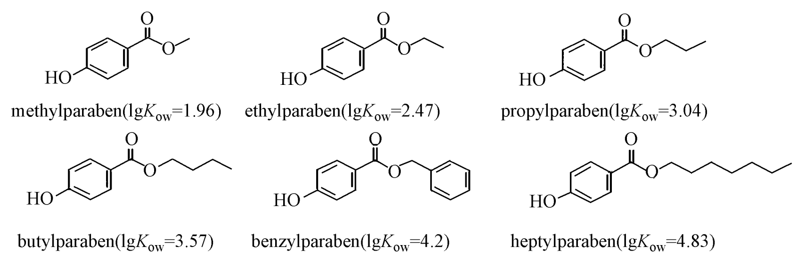
Keywords: parabens, occurrence, biodegradation, wastewater, transformation, remediation.

尼泊金酯类(parabens)作为广谱高效防腐剂,自 20 世纪 30 年代通过化工合成制得以来,在全球被广泛应用于化妆品、护发品、喷雾剂、牙膏、香皂、沐浴露、药物、动物饲料和食品中,属于药物及个人护理品中的一类常用化合物[1-2].近年来,国内外研究人员在各国人群服用的药物、尿液、血液及母乳及其他食物中频繁检出各种 parabens[3-8],且发现在经常使用个人护理品人群中的检出频率及水平比起其他新兴环境痕量污染物要高很多[2,9-10].另外,在河流、污水污泥、农用土壤、沉积物、废水、泳池用水,甚至室内灰尘及空气中也被检出[11-21].Xue 等[22]对美国沿海水域海洋哺乳动物体内 parabens 浓度测定发现,尼泊金甲酯(methylparaben)在大多数哺乳动物体内均被检出,其中在海豚肝脏组织中富集浓度高达 865 $ng \cdot g^{-1}$,表明这类化合物已广泛分布于水环境中.

目前针对 parabens 的研究,国内外主要集中在不同环境介质中的存在水平调查及母体化合物对于生物受试体的毒性测试[23-28]、不同非生物处理方法对母体化合物的降解效果考察,如电化学、臭氧氧化、辐射、光催化及芬顿氧化等其他高级氧化联合处理,取得了一些丰硕的研究成果[29-36],但对其在不同环境条件下的降解转化过程机制及产物毒性等仍缺乏深入认识,尤其对其水环境中的生物降解研究行为较少,而实际上生物降解相对其他化学处理方法来说成本更加低廉、环保,易于投入应用.过去数十年中,parabens 在各种产品中的使用一直被认为是安全无害的,然而近年来报道指出这类化合物具有潜在内分泌干扰效应,可模拟女性雌激素功能,与男性精子 DNA 损伤呈现正相关关系,从而影响男性生殖机能,并可能与女性乳腺癌的形成有一定联系,已被视为新兴污染物[37-43].基于 parabens 的环境实际污染水平的风险评价,截止目前相关报道匮乏.当前已有的关于 parabens 的雌激素效应及水生生物毒性的数据报道均来自于全球各实验室室内的体外和体内实验研究,各类受试体的 parabens 暴露浓度水平显著高于在环境中的实际检出水平,因此这也造成了国际上对于 parabens 在使用安全性上的争议.但不可忽略的是,parabens 属于亲脂性化合物,排放进入环境后较易在水体有机颗粒物、污泥、生物固体、沉积物及有机体组织中富集,且富集程度随着烷基取代基的链长呈比例增加,可通过食物链产生生物放大[44].我国作为 parabens 生产使用大国,人群暴露机会和接触水平较高、摄入途径日趋复杂,如果长期接触此类物质,势必造成人体内浓度水平不断攀升,因此应高度重视,全面展开这类防腐剂的环境行为研究,这对于深入评价其生态安全性,维护人群健康具有重要现实意义.

1　尼泊金酯类防腐剂的种类(Types of parabens)

尼泊金酯类主要包括 methylparaben(甲酯)、ethylparaben(乙酯)、propylparaben(丙酯)、isopropylparaben(异丙酯)、butylparaben(丁酯)、isobutylparaben(异丁酯)、benzylparaben(苄酯)、heptylparaben(庚酯)、octylparaben(辛酯)等 9 种,通常随着其烷基碳链的增大而抗菌作用增强[23-24].环境中最常见的 6 种 parabens 主要为 methyl-、ethyl-、propyl-、butyl-、benzyl-和 heptyl-,其化合物的化学结构如下:



2　尼泊金酯类防腐剂的水环境赋存特征(Occurrence and characteristics of parabens in aquatic environment)

水环境是 parabens 的重要载体,而生活废水排放是进入主要途径.在化妆品使用过程中,主要通过直接和间接两种过程进入到水环境中,直接过程主要体现在人类活动与天然水体直接接触(如游泳、清

洗等淋洗活动)将肥皂、牙膏或染发剂、防晒霜、塑发定型品中含有的 parabens 直接排放,间接排放主要是进入污水处理系统中的各种 parabens 经处理后仍有残留流入水环境中.国内外研究数据表明,污水处理厂进水中的各种 parabens 在各工艺处理区段不能被完全去除,剩余污泥及出水中仍有痕量残留.Canosa 等[45]在对西班牙北部污水处理厂水样检测中发现,methylparaben 和 propylparaben 残留含量最高.Albero 等[46]对西班牙的 3 个污水处理厂进行历时 4 年采样分析也发现,整个研究期间污泥中 methylparaben 和 propylparaben 检出频率较高,methylparaben 检出水平在 5.1—26.2 $ng \cdot g^{-1}$,而 propylparaben 检出水平最高达到 44.1 $ng \cdot g^{-1}$.Liao 等[17]最新研究发现美国、日本和韩国的河流沉积物、污水处理厂污泥中均可检出不同水平的 6 种 parabens,methylparaben 整体贡献率最高.Yamamoto 等[25]对日本城市河流中 7 种 parabens 进行研究评估发现,methylparaben、propylparaben 和 butylparaben 的最高浓度分别为 670、207、163 $ng \cdot L^{-1}$.

近年来关于对我国 parabens 在水环境体系中的赋存水平报道也日趋增多,刘祖发等[47]于 2012 年 12 月采集了广州市航道和河涌水体样品,指出 paraben 已普遍存在于广州河流水体中,且主要以溶解态存在,含量最高的 3 种 paraben 均为 propylparaben、butylparaben 及 methylparaben.Chen 等[48]对广州周边水库地表水和沉积物、生活污水处理厂进出水和脱水污泥及山东德州某地土壤中的 4 种 parabens 进行了测定,发现 methylparaben 在生活污水处理厂中的进水浓度最高,为 372±25 $ng \cdot L^{-1}$,出水浓度为 7.5±0.4 $ng \cdot L^{-1}$,脱水污泥中含量为 30.7±2.3 $ng \cdot g^{-1}$.赵雪等[49]于 2016 年秋冬季采集了哈尔滨某污水处理厂样品,检测结果发现 parabens 污染较普遍,methylparaben、ethylparaben 及 propylparaben 为主要目标污染物,但污染程度与发达国家相比较轻.Sun 等[50]对厦门 3 座污水处理厂进行为期长达 1 年的调研发现,在进水、出水及污泥中,methylparaben 和 propylparaben 的进水中值浓度为 238、280 $ng \cdot L^{-1}$,出水中值浓度为 3.8、2.2 $ng \cdot L^{-1}$,污泥中值浓度为 20.4、3.5 $\mu g \cdot kg^{-1}$.Li 等[51]在北京 35 处地表水样品中检出了 7 种 parabens 及 4 种氯代 parabens,其中 methylparaben 最大检出浓度达 920 $ng \cdot L^{-1}$,检出中值为 6.45 $ng \cdot L^{-1}$,检出率为 100%.Yang 等[52]在珠江流域选取了 9 座采取不同处理工艺的污水处理厂、13 处地表水及 1 处背景地表水的水样进行分析发现,methylparaben、ethylparaben 及 propylparaben 在各污水厂进水中检出率较高,在背景地表水样中未检出,而在地表水中也均被检出,指出 parabens 可被视为珠江三角洲流域污废水中可靠的目标指示污染物.Sun 等[50,53]在福建九龙江口的水样中检出 parabens,并通过对厦门 3 座污水处理厂药物与个人护理品(PPCPs)的季节性时空分布特征的调研结果分析同样提出,methylparaben 和 propylparaben 可用来作为地表水污染的指示化合物[54].

进入水体,经处理或未经处理的 parabens 可进一步迁移进入沉积物中.Viglino 等[55]发现远离人类活动的区域,沉积物没有受到 parabens 污染,而对有人类活动区域的柱状沉积物采样分析则呈现出浓度水平区域分布差异,这表明 parabens 人为排放是主要贡献源.目前沉积物中检出频率较高的 parabens 主要为 methyl 和 propyl-.Gorga 等[56]在伊比利亚河流沉积物中检测到 methylparaben 和 propylparaben,最高浓度分别达到 435、5.98 $ng \cdot g^{-1}$.Liao 等[17]对美、日、韩三国沉积物中 6 种 parabens 残留分布的调研发现,总含量水平为 0.680—95.7 $ng \cdot g^{-1}$,其中 methylparaben 为首要种类,其总含量水平为 0.312—45.5 $ng \cdot g^{-1}$,在该三国 6 种 parabens 总含量水平中所占比例分别为 89%±8%、94%±14%、77%±16%.Liu 等[57]对长江沉积物进行枯水和丰水两季采集检测发现,methylparaben 在所有沉积物样品中被检出,丰水季中值浓度为 5.10 $ng \cdot g^{-1}$,枯水季中值浓度为 4.14 $ng \cdot g^{-1}$;propylparaben 丰水季检出率为 65%,中值浓度为 0.06 $ng \cdot g^{-1}$,枯水季检出率为 100%,中值浓度为 0.58 $ng \cdot g^{-1}$.Peng 等[58]对珠江流域的沉积物调研发现,methylparaben 在整个流域采集的沉积物柱样中均被检出,表明了其持久性特征,指出处理后的废水出水是主要来源,最大检出浓度干重水平为 8.8 $ng \cdot g^{-1}$.

当前在水体环境沉积界面污染物迁移研究领域,国内外较多关注的是河流、河口、近岸和浅海等水域的沉积界面污染物迁移过程,对于湖泊尤其是浅水湖泊水体沉积界面污染物迁移的行为研究相对薄弱.我国华东地区如太湖、巢湖流域湖泊属于典型浅水湖泊,水体交换不畅,近几十年由于周边人类活动直接或间接向湖泊输入了大量无机及有机污染物,已构成组分复杂的纳污湖泊沉积物体系.笔者在 2015 年夏季[59]采集 8 个代表性点位对巢湖表层沉积物样品进行检测分析,结果发现 methylparaben 检出率为 100%,检出范围为 1.35±0.31—5.20±0.79 $ng \cdot g^{-1}$,propylparaben 最高检出水平为

1.29±0.49 $ng \cdot g^{-1}$.这些数据也证实了 parabens 在我国浅水湖泊(巢湖)表层沉积物中的广泛分布性,而浅水湖泊相对自净能力较弱,因此今后对于控制浅水湖泊中如 parabens 这类有机微污染物的输入及原位高效去除修复工作值得研究学者重视.

以上水环境中赋存数据报道充分表明,parabens 作为防腐剂在化妆品、食品、药品等其他产品中的广泛使用导致其通过各种废物流进入到水环境中,造成水环境体系残留已无处不在,需引起高度关注.而与国外相比,我国对 parabens 在水环境体系中赋存水平的系统化调研评估数据相对不足,多数报道只是将 parabens 作为 PPCPs 研究对象中的一个微小部分,因而并未从深层次角度去剖析数据背后所反映的微观流过程.尽管如此,还是不难从中发现,我国有人类活动的水体均已存在显著 parabens 污染,因此今后有必要全面展开其环境归趋行为研究,以为今后适时构建污水处理系统中针对 parabens 的排放标准提供参考依据.

3 尼泊金酯类防腐剂在水环境中的生物降解(Biodegradation of parabens in aquatic environment)

文献表明,当 parabens 释放进入水体中,可发生生物降解.Madsen 等[60]指出 parabens 在好氧条件下易发生生物降解,methylparaben、propylparaben 及 ethylparaben 的生物降解能力(即生物降解需氧量)相当于理论需氧量的 90%.Eriksson 等[61]取样检测了丹麦某小型污水处理及回用厂的进水和出水 parabens 浓度,发现 parabens 可通过旋转式生物接触池中附着微生物的生物膜作用发生明显降解,而没有通过生物膜的水体样品直至实验结束仍能检测到一定浓度的 parabens,证实生物降解发挥了重要作用.Jonkers 等[62]报道了瑞士某污水处理厂序批式活性污泥处理工艺段 parabens 的去除率在 72%以上,Gonzúlez-Mariño 等[63]进一步指出活性污泥中 5 种 parabens(methyl-、ethyl-、propyl-, butyl-和 benzyl-)及 3 种卤代产物的降解主要通过生物路径,而非非生物过程或吸附作用,指出该类化合物的持久性与烷基链长度及卤化程度相关,如 methylparaben 的二卤代产物半衰期远高于母体[24],其卤代产物的毒性可能比母体更强.由于氯作为常见卤素被广泛用于水体杀菌处理,通常污水处理厂进出水等水体中都含有游离氯(指水中 ClO^-、HClO 等),parabens 较易与水体中游离氯反应生成氯代有机物[23-24,64],参与生物降解,增加了水环境中 parabens 生物降解负担.Wang 等[65]报道指出,起始浓度为 10 $mg \cdot L^{-1}$的 methylparaben 的典型氯代产物 methyl 3,5-dichloro-4-hydroxybenzoate (MDHB)在实验时间内,好氧活性污泥中的降解率仅为 14.5%.

质量平衡计算是当前已有文献报道中判定污水处理工艺流程中,污染物生物降解效率的重要手段.Li 等[66]通过对北京某污水处理厂进行质量衡算显示,91.8%的起始输入 parabens 主要通过降解消除,通过吸附、初沉污泥和剩余污泥携带排放所占比小于 7.5%,指出生物降解在传统处理过程中起到重要作用,进一步解析发现 parabens 降解主要发生在厌氧消化池内.同时他们发现对于氯代产物,生物降解和吸附去除作用所占贡献比较低,通过传统处理仅能达到 33.9%—40.7%,深度处理率为 59.2%—82.8%.Sun 等[50]通过计算分析发现,methylparaben 和 propylparaben 在厦门 3 座污水处理厂的去除率高达 97%以上,虽然在污泥中的检出水平表明污泥吸附作用对废水中去除率有一定贡献,但生物降解仍起到主导作用.Wang 等[67]对美国纽约州两座污水处理厂的 parabens 及代谢转化产物调研计算发现,parabens 母体去除率为 89.6%—99.9%,比其代谢转化产物去除率 25.9%—90.6%要高.通过进水中相对较低的母体浓度水平及可检测到的代谢产物水平,进而判定 parabens 在污水系统中可发生快速生物降解.Ashfaq 等[68]通过质量平衡计算也指出 parabens 在污水处理厂中的去除主要通过生物降解.

笔者以城市污水处理厂的活性污泥为研究对象,进一步从微生物处理单元考察验证了环境中两种典型 parabens(methyl-和 propyl-),在浓度水平为 1 $mg \cdot L^{-1}$和 10 $mg \cdot L^{-1}$时的好氧与厌氧生物降解行为[69],结果发现 methylparaben 和 propylparaben 在活性污泥混合菌群中,好氧条件下降解最快,降解半衰期均小于 20 min, 而在不同厌氧条件下,methylparaben 和 propylparaben 的降解半衰期相对好氧条件下较长(8.6—99.0 h), 但具有较长烷基链结构的 propylparaben 降解半衰期又显著低于短链烷基链结构的 methylparaben,实验结果证实了生物降解是 parabens 在污水处理厂中的重要去除手段.苯甲酸为 methylparaben 和 propylparaben 在好氧活性污泥降解中的主要降解产物,但不论是好氧还是厌氧降解,这 2 种化合物仍不能被完全去除,导致在污水处理厂出水中仍可被检出.根据实验结果推测如果污水处理

厂水力停留时间较短,则排放入污水处理厂的 parabens 的去除则可能主要发生在好氧阶段,这与上述 Li 等[66]的报道结果存在差异,Li 等[66]研究结论主要以每个处理单元检测的浓度为依据,通过理论质量平衡计算判断去除率,而这不一定能较准确地反映出 parabens 在污水中的实际生物降解过程,此外其研究样品采集以短暂性瞬时采样为主,未进行较长周期性连续采样,这也需要引起注意.关于 parabens 的微生物降解实验研究,Song 等[70]研究报道也指出了好氧生物膜的存在对于 propylparaben 在灰水中发生较强生物降解的重要性.此外,Fan 等 [71]的最新研究报告也证实了城市污水处理过程中,随着水力停留时间增加,parabens 的去除率有所提高.

上述关于生物降解文献总结发现,不同处理工艺下,水环境中 parabens 的生物去除率报道有所差异,共同点是其转化产物(卤代)持久性比母体更强,但其毒性还有待深入了解,不够明晰.此外,当前已有生物降解报道主要通过生物处理工艺前后质量衡算进行判定,且主要针对污水处理系统,多数文献报道采样周期短,仅反映出瞬时性,而持续性不强,这可能会造成在质量平衡计算中并不能反映出污水处理中的长期性生物降解特征.微生物降解虽然是 parabens 在污水处理厂中的重要去除方式,但如何进一步提升痕量去除工艺还有待强化.此外,目前对于水体/沉积物体系中 parabens 的实质性生物降解过程及机理研究较少.污水处理系统中功能性微生物如何高效利用,水体中藻类与微生物的协同作用对于 parabens 这类新兴污染物的去除研究还存在研究空白[72].

4 结论与展望(Conclusions and perspectives)

近几十年来,人类活动已导致 parabens 在水环境体系中广泛赋存,而研究报道已指出 parabens 在水环境中可被微生物降解,但不能被完全有效去除,目前关于水环境中土著微生物降解母体 parabens 能力与环境条件的关联性、降解路径等还缺乏详实报道.此外,环境介质中污染物衰减常以起始和最终母体化合物浓度进行比较判定,尽管这是被广泛接纳的污染物衰减评估方法,但却忽视了某些污染物可能存在的转化产物比起母体化合物的负面环境影响更大.对于 parabens 来说,水体沉积物中游离态卤素(如游离氯、溴等)存在下反应形成的卤代物生物降解能力、水生毒性影响更不容忽视.

基于以上文献总结发现,对于 parabens 母体及其在环境中的卤代物分布调研性报告分析研究偏多,对其在污水处理系统中的降解效率也多数基于前后段构筑物采样检测数据进行计算判定,而实质性的对于水体/沉积物中好氧及厌氧降解过程中的功能微生物鉴定及群落结构分析还未有效开展,因此后续研究有必要将生物技术与现代仪器分析技术相结合来揭示降解微生物菌群结构、功能演替、降解代谢转化产物,进而阐明生物降解机理,并对转化产物(尤其卤代产物)毒性进行评估.在后续深入研究中,有必要综合微生物学、现代分子生物学、环境地球化学与仪器分析相关知识,如通过稳定同位素探针(SIP)、新一代高通量测序(HTS)及高分辨质谱(HRMS)等手段原位表征 parabens 在水体/沉积物中的生物降解过程及机理,从同位素效应角度阐明微生物在 parabens 降解转化过程中的作用机制,开发痕量去除工艺,同时评估转化产物对整个水环境生态系统的影响.这些研究工作的开展必将为今后针对水体/沉积物中这类痕量污染物利用微生物群落进行污染场地原位修复提供基础科学依据.

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