



## 专论与综述

## 含氮有机物在污水处理过程中的生物转化机制与模型研究进展

汪杰<sup>1</sup> 郑芳<sup>1</sup> 柴文波<sup>1</sup> 邢德峰<sup>2</sup> 逯慧杰<sup>\*1</sup><sup>1</sup> 浙江大学环境与资源学院 浙江 杭州 310058<sup>2</sup> 哈尔滨工业大学城市水资源与水环境国家重点实验室 黑龙江 哈尔滨 150090

**摘要:** 随着市政污水处理厂的提标改造,出水总氮浓度逐渐降低,但溶解性有机氮(Dissolved Organic Nitrogen, DON)在总氮中的占比却越来越高,对含氮消毒副产物的生成和受纳水体富营养化的潜在贡献不可忽视。正因如此,近年来有关污水处理系统中 DON 的研究不断增加。本文重点综述了污水处理厂 DON 特征、生成转化规律及其生态影响。目前通过混凝沉淀、消毒等物理化学工艺的联合最高可去除 70%左右的进水 DON,但生物处理单元的微生物代谢活动会生成新的 DON,主要包括氨基酸、聚胺等,其藻类生物可利用性较高。在已有 DON 模型基础上,本文提出了更加完善的 ASM3-DON 模型,纳入了包括内源呼吸、细胞生长、微生物产物再利用在内的 6 个过程,可用于对 DON 生成转化进行更加精确的模拟。未来围绕污水处理过程的 DON 研究应重点关注 DON 的快速精确定量分析、生成转化规律探究以及高效去除方法开发。

**关键词:** 污水处理, 溶解性有机氮, 物理化学转化, 微生物生成, 数学模型

**Biotransformation and modeling of nitrogenous organic matter in wastewater treatment processes**WANG Jie<sup>1</sup> ZHENG Fang<sup>1</sup> CHAI Wenbo<sup>1</sup> XING Defeng<sup>2</sup> LU Huijie<sup>\*1</sup><sup>1</sup> Department of Environmental and Resource Sciences, Zhejiang University, Hangzhou, Zhejiang 310058, China<sup>2</sup> State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin, Heilongjiang 150090, China

**Abstract:** In many countries around the world, it is necessary to upgrade municipal wastewater treatment plants (WWTPs) to meet the more stringent discharge limits of nutrients. However, with the decreased total dissolved nitrogen (TDN) in the effluent, the proportion of dissolved organic nitrogen (DON) in TDN is increasing, which potentially contributes to the synthesis of more nitrogenous disinfection byproducts (N-DBP) and the eutrophication of receiving water bodies. As a result, studies on WWTP DON have been increasing in recent years, and this article systematically reviews its characteristics, transformation and ecological consequences. At present, up to 70% of the influent DON can be removed by coagulation, precipitation, disinfection and other combined physical and chemical processes. However, metabolic activities in the biological treatment units generate new DON, including small molecular amino acids and

**Foundation item:** Fundamental Research Funds for the Central Universities (2020FZZX001-06)

**\*Corresponding author:** Tel: 86-571-88982004; E-mail: luhuijie@zju.edu.cn

**Received:** 01-08-2020; **Accepted:** 20-09-2020; **Published online:** 13-04-2021

**基金项目:** 中央高校基本科研业务费专项资金(2020FZZX001-06)

**\*通信作者:** Tel: 0571-88982004; E-mail: luhuijie@zju.edu.cn

**收稿日期:** 2020-08-01; **接受日期:** 2020-09-20; **网络首发日期:** 2021-04-13

polyamines, which have a relatively high algal bioavailability. We propose a more comprehensive ASM3-DON model, involving six major processes associated with DON biotransformation, including endogenous respiration, cell growth, and reuse of soluble microbial products. The model can be used to predict wastewater effluent DON concentration with increased accuracy. Future research on wastewater DON should focus on developing more rapid and accurate quantification methods, unraveling its formation and transformation mechanisms, as well as developing more efficient removal techniques to reduce effluent DON.

**Keywords:** wastewater treatment, dissolved organic nitrogen, physiochemical transformation, microbial formation, mathematical model

污水处理工艺提标增效一直是国内外水处理研究领域的前沿。我国污水处理厂提标改造对改善水环境产生了重大和积极的作用。截至 2019 年 12 月, 全国共有 2 913 座城镇污水处理厂执行污染物一级 A 排放标准, 占总数的 53.2%, 其中太湖、巢湖等重点流域对于氮磷等营养盐的排放控制更加严格。虽然污水处理厂升级改造显著降低了氨氮和总氮负荷, 但某些近海区域的富营养化问题并没有得到解决。类似情况在美国等国家也有出现, 例如在过去 15 年中, 污水处理厂排入长岛海湾(Long Island Sound Estuary, USA)的氮负荷减少, 但富营养化仍然是一个严重的问题<sup>[1]</sup>。有研究人员推测污水处理厂出水中的有机氮具有比无机氮更高的藻类可利用性, 可能是导致富营养化持续发生的重要因素之一<sup>[1-4]</sup>。

有机氮可按粒径划分为颗粒态有机氮(Particulate Organic Nitrogen, PON, >1.2  $\mu\text{m}$ )、胶体态有机氮(Colloidal Organic Nitrogen, CON, 0.1–1.2  $\mu\text{m}$ )和溶解态有机氮(Dissolved Organic Nitrogen, DON, <0.1  $\mu\text{m}$ ), 其中 DON 是有机氮的主要生物可利用形态<sup>[2,5-7]</sup>。污水生物处理过程中的微生物代谢活动可生成大量有机含氮化合物, 而且随着污水处理厂出水溶解性总氮(Total Dissolved Nitrogen, TDN)浓度的降低, DON 的占比最高可达 50%–80%<sup>[2,8]</sup>。低分子量、亲水性的 DON 具有较高的生物利用度, 能够刺激浮游植物生长而引起水体富营养化<sup>[1-2,5]</sup>, 也是形成消毒副产物的重要前体物<sup>[9-12]</sup>。DON 在污水处理厂内不易通过简单的吸附、沉淀等工艺去除, 有报道显示排入某些敏感水域的污水中 90%以上含氮物质

为 DON<sup>[2,13]</sup>。由此可见, DON 是一类浓度低但生态风险较大的污染物, 已经成为制约污水处理厂出水总氮进一步削减的瓶颈之一。

以往针对 DON 的研究多集中于海洋和地表水两大生境<sup>[14-20]</sup>, 但近年来有关污水处理厂中 DON 的研究逐渐增多, 主要关注 DON 组分、迁移转化规律以及生态风险等<sup>[6,10,21-24]</sup>。有报道显示污水在流经生物处理单元时 DON 浓度经常不降反升, 说明微生物群落可能生成了较多的 DON<sup>[25]</sup>。微生物对 DON 生成和转化的贡献及其模型模拟受到越来越多的关注<sup>[26-30]</sup>, 但已有的文献综述未能详尽说明<sup>[31]</sup>。本文综述了污水处理厂中 DON 的特征、生成与转化以及生态影响, 重点关注了 DON 的重要组分并综述了它们的微生物生成转化机制, 为进一步削减出水 DON 提供参考。

## 1 污水处理厂中 DON 的特征

DON 在全球污水处理厂进水中的浓度范围为 2.2–15.4 mg-N/L<sup>[12,32-33]</sup>, 在出水中的浓度范围为 0.42–5.00 mg-N/L<sup>[2,5,7,34-37]</sup>。当污水处理设施出水总氮浓度降至 10 mg-N/L 以下时(我国部分地方标准已达 10 mg-N/L 甚至更低), DON 的浓度通常在 0.1–3.0 mg-N/L 之间<sup>[2]</sup>。污水处理厂出水 DON 主要成分为游离和结合性的氨基酸、尿素、核酸、腐殖酸等, 其中大部分为低分子量和亲水性组分<sup>[5,12]</sup>。污水生物处理反应器进水中的小分子量 DON (<1 kD, Low Molecular Weight DON)浓度范围为 4.2–4.4 mg-N/L, 出水浓度约为 1.5–3.5 mg-N/L, 总体去除率在 17%–66%之间<sup>[5]</sup>。另一方面, 出水

中亲水性 DON 的浓度范围为 0.5–1.5 mg-N/L, 而疏水性 DON 较低, 约为 0.1–0.5 mg-N/L<sup>[2]</sup>。

表 1 总结了不同污水处理工艺的出水 DON 特征。生物脱氮工艺出水 DON 的浓度平均为 1.36±0.18 mg-N/L, 而普通活性污泥法为 1.08±0.31 mg-N/L, 未发现二者有显著差异。另一方面, 脱氮工艺(如 A<sup>2</sup>O 等)的平均出水 DON/TDN 为 27.3%±5.4%, 普通活性污泥法的平均出水 DON/TDN 却仅为 8.2%±4.0%, 最高的出水 DON/TDN 出现在某 4 阶段 Bardenpho 工艺中(83.5%)。上述 2 方面综合导致脱氮工艺出水 DON/TDN 值较高。单独采用 A<sup>2</sup>O 工艺时, 出水 DON 的浓度平均值为 1.8±0.3 mg-N/L, 当添加膜过滤进行深度处理后, DON 的浓度降至 0.69±0.11 mg-N/L, 推测为大分子 DON 被膜截留。剩余的小分子 DON 主要组分为溶解性总氨基酸

(Dissolved Total Amino Acid, DTAA), 其在污水处理厂进水中的浓度范围为 11.0–17.5 μmol-N/L, 出水中的浓度范围为 1.5–7.0 μmol-N/L<sup>[32]</sup>。生物脱氮、膜深度处理等工艺对于无机氮的高效生物去除, 以及在此过程中小分子、溶解性有机氮的生物生成导致其出水 DON/TDN 较高。表征不同污水处理工艺的 DON 总量、组成、亲疏水性等为研究其生物转化规律及控制方法奠定了基础。

2 污水处理过程中 DON 的生成与转化

2.1 DON 的物理化学转化

污水中的 DON 可通过吸附、混凝和离子交换等物理化学方法得到去除。生物活性炭具有独特的孔隙结构和高吸附性, 针对深度处理后的市政污水, 粉末活性炭(Powdered Activated Carbon, PAC)可去除 72%的 DON<sup>[38]</sup>。常规的混凝工艺通过双电层作用和化学架桥作用可以去除部分 DON,

表 1 污水生物处理不同工艺的出水溶解性有机氮特征  
Table 1 DON in the effluent from different wastewater biological treatment processes

工艺类型 Process types	出水浓度 Effluent concentration (mg-N/L)		溶解性有机氮占 总溶解性氮比例 DON/TDN (%)	参考文献 References
	总溶解性氮 Total dissolved nitrogen (TDN)	溶解性有机氮 Dissolved organic nitrogen (DON)		
4 stage Bardenpho	1.21±0.25	1.01±0.23	83.5	[2]
5 stage Bardenpho	10.28±0.33	1.83±0.18	17.8	
5 stage Bardenpho+ Denitrification filter	2.83±0.23	1.02±0.10	36.0	
Activated sludge	15.90±3.80	1.00±0.20	6.2	[5]
A <sup>2</sup> O	10.40±3.10	1.80±0.30	17.3	
AO+Ozone	16.11±0.20	1.43±0.05	8.9	
Oxidation ditch+Filtration+UV	12.32±0.37	0.87±0.07	7.1	[7]
SBR+Biological filter	11.55±0.17	1.32±0.07	11.4	
AO	6.00±2.20	1.70±0.40	28.3	
Activated sludge	8.80±4.50	1.00±0.90	11.4	[35]
UCT	8.40	1.20	14.3	
A <sup>2</sup> O	6.80	1.50	22.1	
A <sup>2</sup> O+Membrane filtration	1.71±0.62	0.55±0.17	33.0	[34]
Biological filter+ Denitrification fluidized bed	6.73±0.99	1.42±0.33	20.0	
A <sup>2</sup> O+Dual media filter	3.06±0.48	0.42±0.05	14.0	
A <sup>2</sup> O+Denitrification filter	3.64±0.54	1.11±0.11	30.0	

但效率不高。例如明矾对水源水中 DON 的去除率仅为 15%左右<sup>[39]</sup>, 而使用硫酸铝作为混凝剂时 DON 去除率为 30%–35%<sup>[40–41]</sup>。强酸性的阳离子交换树脂对污水中 DON 的去除率为 33%–56%<sup>[38]</sup>, 其强酸性基团如磺酸基( $-\text{SO}_3\text{H}$ )在溶液中解离出  $\text{H}^+$ , 氨基酸等 DON 组分可与之结合形成新的阳离子得到去除。

除上述常规工艺之外, 联合多种物理化学处理工艺对 DON 的去除效果更佳。例如臭氧氧化可先将难降解 DON 转化为易生物降解的 DON, 然后通过生物活性炭滤池进行吸附和生物降解<sup>[42–44]</sup>。该联合工艺对 DON 的去除率(48.3%)显著高于单独的臭氧处理工艺(31%), 而且芳香类蛋白是主要的 DON 组分<sup>[45]</sup>。此外, 臭氧氧化与混凝结合也可强化 DON 的去除<sup>[46–48]</sup>, 一方面臭氧可以直接氧化 DON, 另一方面臭氧与水反应产生具有更强氧化性的羟基自由基降解 DON<sup>[49]</sup>。臭氧氧化结合混凝工艺对市政污水处理厂出水 DON 的去除率可高达 71%<sup>[13]</sup>。

## 2.2 DON 的微生物生成

脱氮除磷是污水处理系统中 DON 生成和转化最为活跃的过程。微生物能够通过胞外聚合物(Extracellular Polymeric Substance, EPS)的释放和微生物代谢产物(Soluble Microbial Products, SMP)的溶出增加 DON<sup>[12,30]</sup>。氨氮是硝化微生物的电子供体, 也是合成 DON 尤其是小分子氨基酸类物质的重要底物<sup>[50]</sup>, 其先由  $\alpha$ -酮戊二酸经胺化形成谷氨酸, 进而合成谷氨酰胺、脯氨酸、赖氨酸和鸟氨酸等。但在污水脱氮微生物中只有典型反硝化菌(如 *Paracoccus denitrificans*)中有完整的苯丙氨酸和酪氨酸合成途径, 而污水处理中典型的氨氧化菌(如 *Nitrosomonas europaea*)、亚硝酸盐氧化菌(如 *Nitrobacter winogradskyi*)、厌氧氨氧化菌(如 *Candidatus Kuenenia stuttgartiensis*)等均不能合成苯丙氨酸和酪氨酸<sup>[51–52]</sup>。另有关于宏基因组的研究发现, 短程硝化-厌氧氨氧化反应器中脯氨酸合成酶 I 基因(*proS I*)仅在主导的异养反硝化菌的基因组

中出现, 而脯氨酸合成酶 II 基因(*proS II*)在几类主要自养微生物(氨氧化菌、亚硝酸盐氧化菌、厌氧氨氧化菌)基因组内均存在, 所以脱氮群落中的自养微生物与异养微生物间可能在脯氨酸合成上具有合作关系<sup>[53]</sup>。由此可知, 脱氮微生物群落存在基于部分氨基酸的紧密代谢互作关系(图 1), 这也是微生物生成氨基酸以进行物质交换的重要驱动力之一, 并对微生物群落结构的组装起到重要调控作用。

近年来, 大量有关污水处理微生物群落基因组及转录组的研究发现, 与氨基酸及其衍生物代谢相关的基因及其转录本的检出丰度较高, 通常占总量的 10%–20%左右, 而且与主要污染物 COD、氮、磷等去除率显著相关<sup>[55–56]</sup>。氨基酸的代谢对运行工况的响应较灵敏, 溶解氧、底物浓度以及碳氮源种类等均会影响污水处理群落的氨基酸合成及消耗。例如聚磷菌在厌氧条件下会积累甘氨酸, 胞内积累浓度可达 3 mmol/L, 而在好氧且无外加碳源的条件下会消耗储存的甘氨酸作为碳源<sup>[57–59]</sup>。含有氯化铵的污水可促进序批式反应器(Sequencing Batch Reactor, SBR)活性污泥群落中天冬氨酸转氨酶基因(*ast*)、谷氨酸合成酶基因(*glr*)的富集, 而氨基酸降解相关基因谷氨酰胺酶基因(*glsA*)、天冬氨酸酶基因(*aspQ*)的丰度降低<sup>[60]</sup>。碳源种类的改变会影响反硝化微生物的碳代谢途径, 氨基酸合成通路的表达水平也会发生显著变化<sup>[61]</sup>。在使用混合碳源进行异养菌培养时, 不同碳源进入氨基酸合成通路的位置不同, 在很大程度上决定了微生物对碳源的利用方式(依次或同时消耗)及其供应氨基酸库的百分比<sup>[62]</sup>。在不同进水氮源(氯化铵、尿素、丙氨酸)条件下, SBR 反应器出水中的缬氨酸、天冬氨酸、谷氨酸等含量显著不同<sup>[60]</sup>。在饥饿条件下, 氨氧化菌的氨基酸合成通路表达下调, 氨基酸的生物合成量减少<sup>[63]</sup>。另一研究发现, 厌氧氨氧化反应器生物膜脱落时会伴随着部分氨基酸合成和转运基因(*cysS*、*artQ*)转录活性的降低, 而氨基酸代谢基因(*gcvH*)活性升高<sup>[64]</sup>。

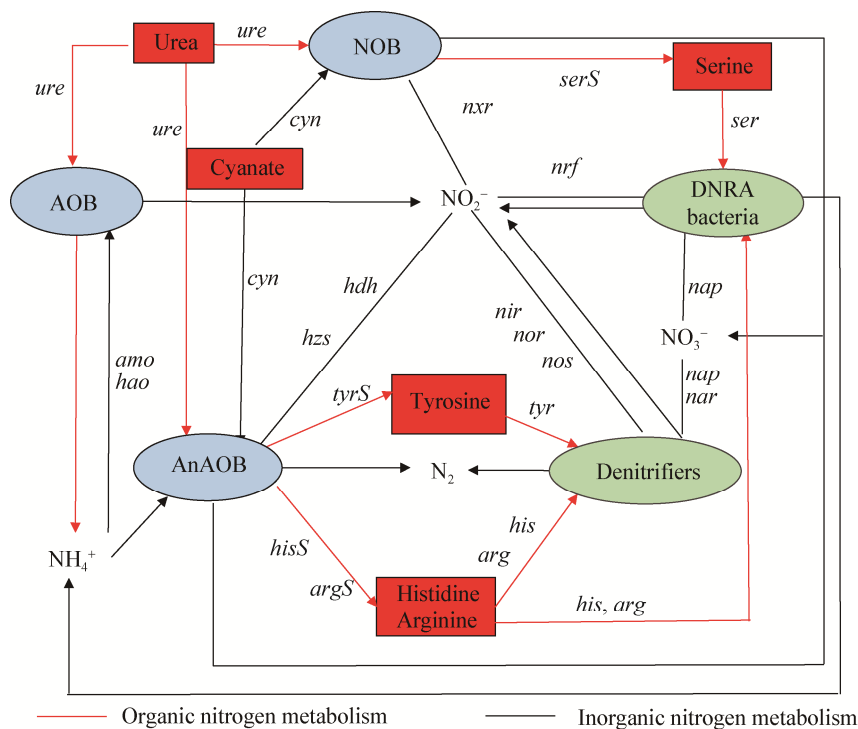


图 1 脱氮微生物基于无机氮和部分氨基酸的代谢互作关系

Figure 1 Metabolic interactions between nitrogen removal microorganisms based on inorganic nitrogen and amino acids

注: *amo*、*hao*、*cyn*、*hdh*、*hzs*、*nir*、*nor*、*nos*、*nrf*、*ure*、*his*、*tyr*、*ser*、*arg* 分别编码氨单加氧酶、羟胺氧化还原酶、氰酸酯酶、联氨脱氢酶、联氨合成酶、同化硝酸盐还原酶、一氧化氮歧化酶、氧化亚氮还原酶、亚硝酸盐还原酶、脲酶、组氨酸解氨酶、酪氨酸酶、丝氨酸转氨酶、精氨酸酶<sup>[54]</sup>

Note: *amo*, *hao*, *cyn*, *hdh*, *hzs*, *nir*, *nor*, *nos*, *nrf*, *ure*, *his*, *tyr*, *ser*, *arg* encoded respectively ammonia single oxygenase, hydroxylamine oxidoreductase, cyanate ester, hydrazine dehydrogenase, hydrazine synthase, assimilation of nitrate reductase and nitric oxide dismutase, nitric oxide reductase, nitrite reductase, urease, histidine ammonia enzyme, tyrosinase, serine transaminase, arginase<sup>[54]</sup>

除氨基酸外, 胺也是一类重要的小分子 DON。由鸟氨酸脱羧而产生的腐胺(丁二胺)广泛存在于细胞中, 其含量变化可以有效调控细胞 pH 值。通过代谢组学研究发现, 氨氧化菌在饥饿条件下会大量积累腐胺和亚精胺等聚胺类物质, 从而加速生物膜的形成<sup>[63]</sup>。综上所述, 氨基酸、聚胺等小分子 DON 物质的微生物生成是污水处理工艺中重要的 DON 来源。

### 2.3 DON 的微生物转化

在污水生物处理单元中, DON 的微生物转化通常需要先水解形成氨氮, 再被微生物作为氮源或电子供体利用。当游离氨缺乏时, 尿素和氰酸盐等 DON 化合物可被多种硝化微生物用作替代氮源和能源, 包括部分氨氧化菌、氨氧化古菌、亚

硝酸盐氧化菌以及新发现的完全氨氧化菌 (Comammox Bacteria) 等<sup>[65]</sup>。上述微生物的基因组中大多同时编码脲酶和氰化酶, 可将尿素和氰酸盐水解后产生游离氨作为电子供体, 因此它们不仅能够合成氨基酸类 DON, 也对 DON 的转化有重要贡献<sup>[66-67]</sup>。厌氧氨氧化反应器在进水含有乙酸钠的条件下氨基糖和核苷酸糖代谢途径被激活, 进水 C/N 的改变会导致天冬氨酸和谷氨酸的合成通路下调<sup>[68]</sup>。

除了从实验角度揭示污水处理系统中 DON 的微生物转化外, 还可以通过构建数学模型来模拟和预测 DON 的微生物生成与转化。Simsek 等建立了 DON 的生物转化模型, 包括生物量衰减、PON 水解为 DON、DON 氨化为氨氮 3 个过程, 并给出

了相关的动力学和化学计量学参数<sup>[67]</sup>。但该模型无法计算微生物产生的 DON (Microorganism-Derived DON, mDON) 的浓度, 这部分 DON 大多为低分子量、亲水性 DON, 具有较高的生态风险。Hu 等在此模型基础上补充了自、异养菌生长释放 mDON 的过程, 通过模型计算得出 mDON 约占污水处理厂出水 DON 的 36%–50%<sup>[69]</sup>。这在一定程度上解决了目前难以通过实验方法将 mDON 与来自进水的 DON 组分进行区分的问题。然而现有模型均未考虑来源于 EPS 和 SMP 的 DON, 具体来说包括基质利用相关产物(Utilization Associated Product, UAP) 和 EPS 进一步水解产生生物物质相关产物(Biomass Associated Product, BAP)中的含氮有机物。因此, 本文在活性污泥法 ASM3 模型基础上, 提出了 ASM3-DON 生成转化模型, 纳入了包括内源呼

吸、细胞生长、SMP 再利用在内的共计 6 个过程(表 2), 以期为 DON 的生成转化研究提供更多的参考, 并指导污水生物处理过程的 DON 削减控制。

### 3 污水处理厂出水 DON 的生态影响

#### 3.1 富营养化潜力

DON 主要成分氨基酸、尿素、核酸、腐殖酸等对大部分绿蓝藻, 包括有毒微囊藻的生长具有显著促进作用, 是导致富营养化的重要物质。可以用可生物降解性 DON (Biodegradable DON, BDON) 和可生物利用性 DON (Bioavailable DON, ABDON) 来描述 DON 的生物利用程度<sup>[25]</sup>。BDON 是指 DON 中能被细菌降解并矿化的部分, 以一定时间内的 DON 降解量来表示; ABDON 是指直接或间接被浮游植物所利用作为氮源的 DON

表 2 ASM3-DON 模型中主要微生物过程的反应速率方程

Table 2 Process kinetics and stoichiometry in the ASM3-DON model

DON 转化过程 DON conversion processes	微生物 Microbes	DON 系数 DON coefficient	过程反应速率 Process rate
细胞生长 Cell growth	氨氧化菌 AOB	$i_{N,UAP,A} \cdot f_{UAP,A}$	$\mu_{max}^{AOB} \cdot \frac{S_{O_2}}{K_{O_2}^{AOB} + S_{O_2}} \cdot \frac{S_{NH_4}}{K_{NH_4}^{AOB} + S_{NH_4}} \cdot X_{AOB}$
	亚硝酸盐氧化菌 NOB	$i_{N,UAP,N} \cdot f_{UAP,N}$	$\mu_{max}^{NOB} \cdot \frac{S_{O_2}}{K_{O_2}^{NOB} + S_{O_2}} \cdot \frac{S_{NO_2}}{K_{NO_2}^{NOB} + S_{NO_2}} \cdot X_{NOB}$
	异养反硝化菌 HDB	$i_{N,UAP,H} \cdot f_{UAP,H}$	$\eta_{HET} \mu_{max}^{HET} \cdot \frac{K_{O_2}^{HET}}{K_{O_2}^{HET} + S_{O_2}} \cdot \frac{S_S}{K_S + S_S} \cdot \frac{S_{NO_3}}{K_{NO_3} + S_{NO_3}} \cdot X_H$
细胞内源呼吸 Endogenous respiration	氨氧化菌 AOB	$i_{N,BAP} \cdot f_{BAP,A}$	$b_{AOB} \cdot \frac{S_{O_2}}{K_{O_2}^{AOB} + S_{O_2}} \cdot X_{AOB}$
	亚硝酸盐氧化菌 NOB	$i_{N,BAP} \cdot f_{BAP,N}$	$b_{NOB} \cdot \frac{S_{O_2}}{K_{O_2}^{NOB} + S_{O_2}} \cdot X_{NOB}$
	异养反硝化菌 HDB	$i_{N,BAP} \cdot f_{BAP,H}$	$b_H \cdot \frac{S_{NO_3}}{K_{NO_3} + S_{NO_3}} \cdot X_H$
EPS 水解作用 EPS hydrolysis		$i_{N,BAP} \cdot (1 - f_{SS})$	$k_{H,EPS} \cdot \frac{X_{EPS}}{K_X + X_{EPS}} \cdot \frac{X_H}{X_H} \cdot X_H$
DON 氨化作用 DON ammonification		-1	$k_a \cdot \frac{S_{ND}}{K_{H,ND} + S_{ND}} \cdot X_H$
异养菌利用 UAP 生长 Heterotrophic bacteria use UAP to grow		$-i_{N,UAP} / Y_{UAP}$	$\eta_{HET} \mu_{max}^{HET} \cdot \frac{K_{O_2}^{HET}}{K_{O_2}^{HET} + S_{O_2}} \cdot \frac{S_{UAP}}{K_{UAP} + S_{UAP}} \cdot \frac{S_{NO_3}}{K_{NO_3} + S_{NO_3}} \cdot X_H$
异养菌利用 BAP 生长 Heterotrophic bacteria use BAP to grow		$-i_{N,BAP} / Y_{BAP}$	$\eta_{HET} \mu_{max}^{HET} \cdot \frac{K_{O_2}^{HET}}{K_{O_2}^{HET} + S_{O_2}} \cdot \frac{S_{BAP}}{K_{BAP} + S_{BAP}} \cdot \frac{S_{NO_3}}{K_{NO_3} + S_{NO_3}} \cdot X_H$

注:  $i$ : 含氮量;  $f$ : 组分;  $Y$ : 生长得率;  $\mu$ : 最大比增长率;  $K$ : 生物亲和常数;  $b$ : 内源呼吸速率;  $\eta$ : 缺氧情况下的换算系数

Note:  $i$ : Nitrogen content;  $f$ : Component;  $Y$ : Growth yield;  $\mu$ : Maximum specific growth rate;  $K$ : Biological affinity constant;  $b$ : Endogenous respiratory rate;  $\eta$ : Conversion coefficient under anoxic condition

含量,以一定时间内的 DON 消耗量来表示<sup>[67]</sup>。Simsek 等研究发现,在二级生物滴滤池出水中,BDON 和 ABDON 分别占总 DON 的 62%和 71%;而在活性污泥法中,两者分别占总 DON 的 26%和 47%,这表明与活性污泥法相比,生物膜法能够产生更多容易被生物降解和利用的 DON<sup>[25]</sup>。Hu 等通过实验测得污水处理厂出水中的 ABDON 为总 DON 的  $38.5\% \pm 12.4\%$ <sup>[7]</sup>,推测 DON 是导致富营养化的重要因素<sup>[70]</sup>。

DON 组成对其生物利用度有显著影响,例如利用亲水性和疏水性 DON 组分分别进行藻类生长实验,14 d 后测得亲水性 DON 组的藻类叶绿素 a 浓度为 240  $\mu\text{g/L}$ ,而疏水性 DON 组的藻类叶绿素 a 浓度仅有 5  $\mu\text{g/L}$ <sup>[2]</sup>。由于亲水性和低分子量 DON 会刺激微生物和藻类的生长并消耗溶解氧,从而威胁受纳水体的水质安全<sup>[2,5,21]</sup>,因此应开展对污水处理厂出水 DON 的富营养化潜能评估,并在污水排放或回用前对其进行针对性处理。

### 3.2 消毒副产物生成

含氮消毒副产物(N-Disinfection By-Products, N-DBPs),如卤乙腈(Haloacetonitriles, HANs)、卤代硝基甲烷(Halonitromethanes, HNMs)、二甲基亚硝胺(Nitrosodimethylamine, NDMA)等均具有较强的细胞毒性。污水中的 DON 是一类重要的 N-DBPs 前体物质,在氯消毒过程中 DON 与消毒剂反应,生成含硝基、腈基、酰胺基的 N-DBPs<sup>[9,71]</sup>。Pehlivanoglu-Mantas 等研究发现市政污水出水 NDMA 生成势为 320 ng-NDMA/mg-DON<sup>[12]</sup>,而工业废水的 NDMA 生成势更高,为 374.8 ng-NDMA/mg-DON<sup>[7]</sup>。此外,亲水性 DON 的 HNMs 生成势高于疏水性 DON (36.8 nm-HNMs/mg v.s. 26.2 nm-HNMs/mg)<sup>[72]</sup>。C/N 比和 pH 是影响 N-DBP 生成势的关键因子<sup>[73]</sup>。

## 4 总结与展望

污水处理厂出水 DON 在总氮中的占比较高,能够刺激藻类生长引起富营养化,而且是形成含氮

消毒副产物的重要前体物,在污水处理厂提标改造过程中应关注此类污染物。本文综述了污水处理厂 DON 的特征、生成与转化以及生态影响,并提出了 ASM3-DON 模型,对 DON 的微生物生成转化过程进行了更加精确的描绘。未来围绕污水处理系统中溶解性有机氮应重点开展 2 方面研究:(1) 工艺方面,在保证无机氮去除效率的前提下,优化包括脱氮除磷在内的典型污水处理工艺,从减少 DON 微生物生成和促进其物理化学转化利用上降低 DON,如吸附、混凝和高级氧化等联合去除工艺的开发;(2) 机理方面,采用多组学手段开发基于 DON 关键组分如氨基酸类的生物标志物,可以用于指示污水微生物群落的组装过程、种群代谢互作关系、对环境胁迫的响应机制,为揭示 DON 在污水处理系统中的微生物生成和转化规律提供指导。

## REFERENCES

- [1] Suter EA, Lwiza K, Rose JM, Rose JM, Gobler C, Taylor GT. Phytoplankton assemblage changes during decadal decreases in nitrogen loadings to the urbanized Long Island Sound estuary, USA[J]. Marine Ecology Progress Series, 2014, 497: 51-67
- [2] Liu HZ, Jeong J, Gray H, Smith S, Sedlak DL. Algal uptake of hydrophobic and hydrophilic dissolved organic nitrogen in effluent from biological nutrient removal municipal wastewater treatment systems[J]. Environmental Science & Technology, 2012, 46(2): 713-721
- [3] Hu HD, Ren HQ. Removal of bioavailable dissolved organic nitrogen in wastewater by membrane bioreactors as posttreatment: implications for eutrophication control[J]. Bioresource Technology, 2019, 271: 496-499
- [4] Yao XL, Zhang YL, Zhang L, Zhu GW, Qin BQ, Zhou YQ, Xue JY. Emerging role of dissolved organic nitrogen in supporting algal bloom persistence in Lake Taihu, China: emphasis on internal transformations[J]. Science of the Total Environment, 2020, 736: 139497
- [5] Eom H, Borgatti D, Paerl HW, Park C. Formation of low-molecular-weight dissolved organic nitrogen in predenitrification biological nutrient removal systems and its impact on eutrophication in coastal waters[J]. Environmental Science & Technology, 2017, 51(7): 3776-3783
- [6] Fan L, Brett MT, Li B, Song MM. The bioavailability of different dissolved organic nitrogen compounds for the freshwater algae *Raphidocelis subcapitata*[J]. Science of the Total Environment, 2018, 618: 479-486

- [7] Hu HD, Ma HJ, Ding LL, Geng JJ, Xu K, Huang H, Zhang YY, Ren HQ. Concentration, composition, bioavailability, and N-nitrosodimethylamine formation potential of particulate and dissolved organic nitrogen in wastewater effluents: a comparative study[J]. *Science of the Total Environment*, 2016, 569/570: 1359-1368
- [8] Nam SN, Amy G. Differentiation of wastewater effluent organic matter (EfOM) from natural organic matter (NOM) using multiple analytical techniques[J]. *Water Science and Technology*, 2008, 57(7): 1009-1015
- [9] Ma CX, Xu HZ, Zhang L, Pei HY, Jin Y. Use of fluorescence excitation-emission matrices coupled with parallel factor analysis to monitor C- and N-DBPs formation in drinking water recovered from cyanobacteria-laden sludge dewatering[J]. *Science of the Total Environment*, 2018, 640/641: 609-618
- [10] Tan YW, Lin T, Jiang FC, Dong J, Chen W, Zhou DJ. The shadow of dichloroacetonitrile (DCAN), a typical nitrogenous disinfection by-product (N-DBP), in the waterworks and its backwash water reuse[J]. *Chemosphere*, 2017, 181: 569-578
- [11] Bond T, Huang J, Templeton MR, Graham N. Occurrence and control of nitrogenous disinfection by-products in drinking water: a review[J]. *Water Research*, 2011, 45(15): 4341-4354
- [12] Pehlivanoglu-Mantas E, Sedlak DL. Measurement of dissolved organic nitrogen forms in wastewater effluents: concentrations, size distribution and NDMA formation potential[J]. *Water Research*, 2008, 42(14): 3890-3898
- [13] Liu B, Gu L, Li QF, Yu GZ, Zhao CM, Zhai HM. Effect of pre-ozonation-enhanced coagulation on dissolved organic nitrogen in municipal wastewater treatment plant effluent[J]. *Environmental Technology*, 2019, 40(20): 2684-2694
- [14] Cao XY, Mulholland MR, Helms JR, Bernhardt PW, Duan P, Mao JD, Schmidt-Rohr K. A major step in opening the black box of high-molecular-weight dissolved organic nitrogen by isotopic labeling of *Synechococcus* and multibond two-dimensional NMR[J]. *Analytical Chemistry*, 2017, 89(22): 11990-11998
- [15] Chang NB, Wen D, McKenna AM, Wanielist MP. The impact of carbon source as electron donor on composition and concentration of dissolved organic nitrogen in biosorption-activated media for stormwater and groundwater co-treatment[J]. *Environmental Science & Technology*, 2018, 52(16): 9380-9390
- [16] Knapp AN, Casciotti KL, Prokopenko MG. Dissolved organic nitrogen production and consumption in eastern tropical south Pacific surface waters[J]. *Global Biogeochemical Cycles*, 2018, 32(5): 769-783
- [17] Fernández-Castro B, Álvarez M, Nieto-Cid M, Zunino P, Mercier H, Álvarez-Salgado XA. Dissolved organic nitrogen production and export by meridional overturning in the eastern subpolar north Atlantic[J]. *Geophysical Research Letters*, 2019, 46(7): 3832-3842
- [18] Kang J, Liu SL, Ma TF, Gao X. Production mechanism and characteristics of dissolved organic nitrogen derived from soluble microbial products (SMPs-DON) in a drinking water biological aerated filter[J]. *Water Supply*, 2019, 19(7): 1994-2000
- [19] Osburn CL, Handsel LT, Peierls BL, Paerl HW. Predicting sources of dissolved organic nitrogen to an estuary from an agro-urban coastal watershed[J]. *Environmental Science & Technology*, 2016, 50(16): 8473-8484
- [20] Lu DL, Kang ZJ, Yang B, Dan SF, Zhang D, Zhang P, Huang HF, Zhong QP. Compositions and spatio-temporal distributions of different nitrogen species and lability of dissolved organic nitrogen from the Dafengjiang River to the Sanniang Bay, China[J]. *Marine Pollution Bulletin*, 2020, 156: 111205
- [21] Qin C, Liu HZ, Liu L, Smith S, Sedlak DL, Gu AZ. Bioavailability and characterization of dissolved organic nitrogen and dissolved organic phosphorus in wastewater effluents[J]. *Science of the Total Environment*, 2015, 511: 47-53
- [22] Hu HD, Jiang C, Ma HJ, Ding LL, Geng JJ, Xu K, Huang H, Ren HQ. Removal characteristics of DON in pharmaceutical wastewater and its influence on the N-nitrosodimethylamine formation potential and acute toxicity of DOM[J]. *Water Research*, 2017, 109: 114-121
- [23] Hu HD, Ren HQ. Can fluorescence spectrometry be used as a surrogate for predicting the dissolved organic nitrogen and its bioavailable portion in wastewater effluents?[J]. *Chemosphere*, 2016, 164: 299-303
- [24] Saunders JF, Yu Y, McCutchan JH, Rosario-Ortiz FL. Characterizing limits of precision for dissolved organic nitrogen calculations[J]. *Environmental Science & Technology Letters*, 2017, 4(11): 452-456
- [25] Simsek H, Kasi M, Ohm JB, Blonigen M, Khan E. Bioavailable and biodegradable dissolved organic nitrogen in activated sludge and trickling filter wastewater treatment plants[J]. *Water Research*, 2013, 47(9): 3201-3210
- [26] Sattayatewa C, Pagilla K, Pitt P, Selock K, Bruton T. Organic nitrogen transformations in a 4-stage Bardenpho nitrogen removal plant and bioavailability/biodegradability of effluent DON[J]. *Water Research*, 2009, 43(18): 4507-4516
- [27] Liao KW, Hu HD, Ma SJ, Ren HQ. Effect of microbial activity and microbial community structure on the formation of dissolved organic nitrogen (DON) and bioavailable DON driven by low temperatures[J]. *Water Research*, 2019, 159: 397-405
- [28] Xu H, Lin CS, Chen W, Shen Z, Liu ZG, Chen TY, Wang YT, Li Y, Lu CH, Luo J. Effects of pipe material on nitrogen transformation, microbial communities and functional genes in raw water transportation[J]. *Water Research*, 2018, 143: 188-197



- [29] Zengler K, Zaramela LS. The social network of microorganisms: how auxotrophies shape complex communities[J]. *Nature Reviews Microbiology*, 2018, 16(6): 383-390
- [30] Ni BJ, Zeng RJ, Fang F, Xie WM, Sheng GP, Yu HQ. Fractionating soluble microbial products in the activated sludge process[J]. *Water Research*, 2010, 44(7): 2292-2302
- [31] Zheng F, Wang J, Xiao R, Chai WB, Xing DF, Lu HJ. Dissolved organic nitrogen in wastewater treatment processes: transformation, biosynthesis and ecological impacts[J]. *Environmental Pollution*, 2021, 273: 116436
- [32] Huo SL, Xi BD, Yu HL, Qin YW, Zan FY, Zhang JT. Characteristics and transformations of dissolved organic nitrogen in municipal biological nitrogen removal wastewater treatment plants[J]. *Environmental Research Letters*, 2013, 8(4): 044005
- [33] Sattayatewa C, Pagilla K, Sharp R, Pitt P. Fate of organic nitrogen in four biological nutrient removal wastewater treatment plants[J]. *Water Environment Research*, 2010, 82(12): 2306-2315
- [34] Fan L, Brett MT, Jiang WJ, Li B. Dissolved organic nitrogen recalcitrance and bioavailable nitrogen quantification for effluents from advanced nitrogen removal wastewater treatment facilities[J]. *Environmental Pollution*, 2017, 229: 255-263
- [35] Westgate PJ, Park C. Evaluation of proteins and organic nitrogen in wastewater treatment effluents[J]. *Environmental Science & Technology*, 2010, 44(14): 5352-5357
- [36] Czerwionka K, Makinia J, Pagilla KR, Stensel HD. Characteristics and fate of organic nitrogen in municipal biological nutrient removal wastewater treatment plants[J]. *Water Research*, 2012, 46(7): 2057-2066
- [37] Simsek H, Wadhawan T, Khan E. Overlapping photodegradable and biodegradable organic nitrogen in wastewater effluents[J]. *Environmental Science & Technology*, 2013, 47(13): 7163-7170
- [38] Parkin GF, McCarty PL. A comparison of the characteristics of soluble organic nitrogen in untreated and activated sludge treated wastewaters[J]. *Water Research*, 1981, 15(1): 139-149
- [39] Pramanik BK, Choo KH, Pramanik SK, Suja F, Jegatheesan V. Comparisons between biological filtration and coagulation processes for the removal of dissolved organic nitrogen and disinfection by-products precursors[J]. *International Biodeterioration & Biodegradation*, 2015, 104: 164-169
- [40] Lee W, Westerhoff P. Dissolved organic nitrogen removal during water treatment by aluminum sulfate and cationic polymer coagulation[J]. *Water Research*, 2006, 40(20): 3767-3774
- [41] Dotson A, Westerhoff P. Occurrence and removal of amino acids during drinking water treatment[J]. *Journal - American Water Works Association*, 2009, 101(9): 101-115
- [42] Reungoat J, Escher BI, Macova M, Argand FX, Gernjak W, Keller J. Ozonation and biological activated carbon filtration of wastewater treatment plant effluents[J]. *Water Research*, 2012, 46(3): 863-872
- [43] Chu WH, Gao NY, Yin DQ, Deng Y, Templeton MR. Ozone-biological activated carbon integrated treatment for removal of precursors of halogenated nitrogenous disinfection by-products[J]. *Chemosphere*, 2012, 86(11): 1087-1091
- [44] Chen BY, Kim Y, Westerhoff P. Occurrence and treatment of wastewater-derived organic nitrogen[J]. *Water Research*, 2011, 45(15): 4641-4650
- [45] Liu B, Gu L, Yu X, Yu GZ, Zhao CM, Li QF, Zhai HM. Profile of dissolved organic nitrogen (DON) in full-scale ozone and biological activated carbon filter[J]. *Desalination and Water Treatment*, 2015, 55(8): 2069-2078
- [46] Rahman MF, Jasim SY, Yanful EK, Ndiongue S, Borikar D. Advanced oxidation treatment of drinking water: Part II. turbidity, particles and organics removal from lake Huron water[J]. *Ozone: Science & Engineering*, 2010, 32(5): 295-304
- [47] Sadrnourmohamadi M, Gorczyca B. Effects of ozone as a stand-alone and coagulation-aid treatment on the reduction of trihalomethanes precursors from high DOC and hardness water[J]. *Water Research*, 2015, 73: 171-180
- [48] Sadrnourmohammadi M, Gorczyca B. Effects of ozone as a stand-alone and coagulation-aid treatment on the reduction of trihalomethanes precursors from water with high DOC and low calcium hardness[J]. *Desalination and Water Treatment*, 2017, 78: 117-126
- [49] Jin X, Jin PK, Hou R, Yang L, Wang XC. Enhanced WWTP effluent organic matter removal in hybrid ozonation-coagulation (HOC) process catalyzed by Al-based coagulant[J]. *Journal of Hazardous Materials*, 2017, 327: 216-224
- [50] Pehlivanoglu-Mantas E, Sedlak DL. Wastewater-derived dissolved organic nitrogen: analytical methods, characterization, and effects: a review[J]. *Critical Reviews in Environmental Science and Technology*, 2006, 36(3): 261-285
- [51] Lucker S, Wagner M, Maixner F, Pelletier E, Koch H, Vacherie B, Rattei T, Damste JSS, Spieck E, Le Paslier D, et al. A *Nitrospira* metagenome illuminates the physiology and evolution of globally important nitrite-oxidizing bacteria[J]. *Proceedings of the National Academy of Sciences of the United States of America*, 2010, 107(30): 13479-13484
- [52] Chain P, Lamerdin J, Larimer F, Regala W, Lao V, Land M, Hauser L, Hooper A, Klotz M, Norton J, et al. Complete genome sequence of the ammonia-oxidizing bacterium and obligate chemolithoautotroph *Nitrosomonas europaea*[J]. *Journal of Bacteriology*, 2003, 185(9): 2759-2773
- [53] Speth DR, In't Zandt MH, Guerrero-Cruz S, Dutilh BE,

- Jetten MSM. Genome-based microbial ecology of anammox granules in a full-scale wastewater treatment system[J]. *Nature Communications*, 2016, 7: 11172
- [54] Kuypers MMM, Marchant HK, Kartal B. The microbial nitrogen-cycling network[J]. *Nature Reviews Microbiology*, 2018, 16(5): 263-276
- [55] Yu K, Zhang T. Metagenomic and metatranscriptomic analysis of microbial community structure and gene expression of activated sludge[J]. *PLoS One*, 2012, 7(5): e38183
- [56] Chao YQ, Mao YP, Yu K, Zhang T. Novel nitrifiers and comammox in a full-scale hybrid biofilm and activated sludge reactor revealed by metagenomic approach[J]. *Applied Microbiology and Biotechnology*, 2016, 100(18): 8225-8237
- [57] Nguyen HTT, Kristiansen R, Vestergaard M, Wimmer R, Nielsen PH. Intracellular accumulation of glycine in polyphosphate-accumulating organisms in activated sludge, a novel storage mechanism under dynamic anaerobic-aerobic conditions[J]. *Applied and Environmental Microbiology*, 2015, 81(14): 4809-4818
- [58] Kong YH, Nielsen JL, Nielsen PH. Identity and ecophysiology of uncultured actinobacterial polyphosphate-accumulating organisms in full-scale enhanced biological phosphorus removal plants[J]. *Applied and Environmental Microbiology*, 2005, 71(7): 4076-4085
- [59] Nguyen HTT, Le VQ, Hansen AA, Nielsen JL, Nielsen PH. High diversity and abundance of putative polyphosphate-accumulating *Tetrasphaera*-related bacteria in activated sludge systems[J]. *FEMS Microbiology Ecology*, 2011, 76(2): 256-267
- [60] He S, Ding LL, Li K, Hu HD, Ye L, Ren HQ. Comparative study of activated sludge with different individual nitrogen sources at a low temperature: effluent dissolved organic nitrogen compositions, metagenomic and microbial community[J]. *Bioresource Technology*, 2018, 247: 915-923
- [61] Lu HJ, Kalyuzhnaya M, Chandran K. Comparative proteomic analysis reveals insights into anoxic growth of *Methyloversatilis universalis* FAM5 on methanol and ethanol[J]. *Environmental Microbiology*, 2012, 14(11): 2935-2945
- [62] Wang X, Xia K, Yang XJ, Tang C. Growth strategy of microbes on mixed carbon sources[J]. *Nature Communications*, 2019, 10: 1279
- [63] Lu HJ, Ulanov AV, Nobu M, Liu WT. Global metabolomic responses of *Nitrosomonas europaea* 19718 to cold stress and altered ammonia feeding patterns[J]. *Applied Microbiology and Biotechnology*, 2016, 100(4): 1843-1852
- [64] Chen ZJ, Meng YB, Sheng BB, Zhou ZB, Jin C, Meng FG. Linking exoproteome function and structure to anammox biofilm development[J]. *Environmental Science & Technology*, 2019, 53(3): 1490-1500
- [65] Yang YC, Daims H, Liu Y, Herbold CW, Pjevac P, Lin JG, Li M, Gu JD. Activity and metabolic versatility of complete ammonia oxidizers in full-scale wastewater treatment systems[J]. *mBio*, 2020, 11(2): e03175-19
- [66] Mekinia J, Stensel HD, Czerwionka K, Drewnowski J, Zaperro D. Nitrogen transformations and mass balances in anaerobic/anoxic/aerobic batch experiments with full-scale biomasses from BNR activated sludge systems[J]. *Water Science and Technology*, 2009, 60(9): 2463-2470
- [67] Simsek H, Kasi M, Wadhawan T, Bye C, Blonigen M, Khan E. Fate of dissolved organic nitrogen in two stage trickling filter process[J]. *Water Research*, 2012, 46(16): 5115-5126
- [68] Feng Y, Zhao YP, Guo YZ, Liu ST. Microbial transcript and metabolome analysis uncover discrepant metabolic pathways in autotrophic and mixotrophic anammox consortia[J]. *Water Research*, 2018, 128: 402-411
- [69] Hu HD, Liao KW, Xie WM, Wang JF, Wu B, Ren HQ. Modeling the formation of microorganism-derived dissolved organic nitrogen (mDON) in the activated sludge system[J]. *Water Research*, 2020, 174: 115604
- [70] Bronk DA, See JH, Bradley P, Killberg L. DON as a source of bioavailable nitrogen for phytoplankton[J]. *Biogeosciences*, 2007, 4(3): 283-296
- [71] Ma DF, Meng YJ, Xia CF, Gao BY, Wang Y. Fractionation, characterization and C-, N-disinfection byproduct formation of soluble microbial products in MBR processes[J]. *Bioresource Technology*, 2015, 198: 380-387
- [72] Hu J, Song H, Addison JW, Karanfil T. Halonitromethane formation potentials in drinking waters[J]. *Water Research*, 2010, 44(1): 105-114
- [73] Chu WH, Gao NY, Deng Y. Formation of haloacetamides during chlorination of dissolved organic nitrogen aspartic acid[J]. *Journal of Hazardous Materials*, 2010, 173(1/2/3): 82-86