膜生物反应器处理抗生素废水研究进展

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摘要　综述了膜生物反应器(MBR)对抗生素的去除效果,剖析了去除抗生素的生物降解和吸附途径,讨论了温度、pH、污泥浓度、污泥龄、水力停留时间、氧化还原电位等因素对 MBR 中抗生素去除效果的影响,介绍了膜生物反应器组合工艺对抗生素的强化去除效果,旨在为 MBR 去除抗生素的工艺设计与运行条件的优化提供参考。

关键词　膜生物反应器;抗生素;去除效果;去除途径;影响因素
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Research Progress of Treatment of Antibiotic Wastewater by MBR

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Abstract　Removal efficiency of antibiotics from wastewater by membrane bioreactor (MBR) was reviewed,and removal pathways (biodegradation and adsorption) were deeply analyzed. Meanwhile,the effects of influencing factors including temperature,pH,mixed liquor suspended solids (MLSS),sludge retention time (SRT),hydraulic retention time (HRT) and redox potential on the removal effect of antibiotics were emphatically discussed,and the strengthening removal effect of antibiotics by MBR combined processes was introduced,aiming to provide a reference for the design and optimization of operating condition of MBR processes for treating antibiotic wastewater.

Key words　Membrane bioreactor; Antibiotics; Removal effect; Removal ways; Influencing factors

近年来,抗生素被广泛应用于人类疾病治疗、畜禽养殖和农业生产中,其大量使用所引发的人类健康和环境安全问题备受社会关注。由于传统活性污泥法无法有效去除生活污水[1-3]、畜禽养殖污水[4-5]及制药废水[6]中的抗生素,从而使得大量抗生素经由城市污水厂排放到河流水沙[7-9]、土壤[10-11]、地下水[12]等天然环境中。我国每年抗生素使用量达 16.20 万 t,经污水处理厂处理后排放到天然环境中的抗生素仍然高达 5.38 万 t[13]。可见,城市污水处理厂排水已成为天然环境中抗生素的重要来源,城市污水厂升级改造问题亟需解决。膜生物反应器(MBR)是将膜的高效分离与生物降解作用相结合的一种高效污水处理工艺,与传统的活性污泥系统相比,其具有污泥浓度高、固液分离能力强、污泥龄长、菌群多样性高等特点,因此越来越多的学者将 MBR 应用于含抗生素废水处理的研究中。笔者综述了 MBR 对抗生素的去除效果,剖析了 MBR 中去除抗生素的生物降解和吸附途径,讨论了温度、pH、污泥浓度、污泥龄、水力停留时间和氧化还原电位等因素对 MBR 中抗生素去除效果的影响,介绍了 MBR 组合工艺对抗生素的强化去除效果,旨在为 MBR 去除抗生素的工艺设计与运行条件的优化提供参考。

1　MBR 对抗生素的去除效果

目前,绝大多数城市污水厂采用的是活性污泥法工艺。由于抗生素的理化性质各异及生物降解性的不同,因而不同种类的抗生素在传统城市污水处理厂的进水、出水中的浓度存在较大差异。抗生素在传统城市污水厂进水和出水中的浓度水平在 ng/L ~ μg/L,但在污泥中却可以达到 mg/g 的浓度水平。这表明传统的活性污泥法对抗生素的去除效果有限,从而导致大量的抗生素随着传统城市污水厂出水进入到天然环境中。主要类型抗生素在城市污水厂传统活性污泥法工艺进水、出水和污泥中的存在浓度见表 1。

几大类抗生素在传统活性污泥法工艺(CAS)与 MBR 中的去除效果如表 2 所示。磺胺类在城市污水厂出水和污泥中的浓度较低(表 1),表明 CAS 对磺胺类有一定去除效果,然而其去除效果不够稳定,由表 2 可以看出,其去除率范围为 -138.0% ~96.0%。CAS 对大环内酯类的去除效果一般,大部分低于 50.0%。与 CAS 相比,MBR 可将磺胺类和大环内酯类抗生素的去除率提升至 50.0% ~90.0%,显示出其明显的去除优势。喹诺酮类和四环素类在 CAS 中的去除率可达 70.0% 以上,其在污泥中较高的浓度表明这 2 类抗生素很有可能是通过排泥而去除的;这 2 类抗生素经 MBR 去除其去除率可以提升至 90.0% 以上,比 CAS 去除率高约 20.0%。在整体去除率方面,MBR 对各类抗生素的去除效果较佳,虽然各研究结果有所差异,但基本可达 80.0% ~ 90.0% 的去除效果。

由于不同的研究中 MBR 所在的环境条件及运行条件不同,因此得出的去除率范围有较大差异。即使是同一种抗生素,在不同研究中其去除效果也不尽相同,这是因为其去除率受到多种因素的影响。以磺胺甲恶唑为例,它是在各类环境中被检出频率最高的 1 种抗生素,因此研究者对磺胺甲恶唑的研究最多[46]。MBR 对磺胺甲恶唑的去除效果见表 3。由表 3 可以看出,污泥龄、水力停留时间、污泥浓度等因素均会影响 MBR 对磺胺甲恶唑的去除效果。此外,MBR 中抗生素去除率出现较大差异的原因还有以下几种:进水浓度差异较大,这与进水来源中居民抗生素使用量及是否含有制药废水密切相关;水质具有波动性,取样不能完全反映整个过程的去除情况[15],采样方式不同也会导致数据差异较大;吸附于进水中颗粒物上的抗生素在整个处理过程中脱附[47],或着进水中一些代谢或中间产物转化造成出水抗生素浓度升高[48]。此外,也有磺胺甲恶唑去除率为负值的报道[20],其原

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因可能是污水中存在的 N^4 - 乙酰化磺胺甲恶唑重新转化为　　母体导致出水浓度增高。

表 1　抗生素在城市污水厂进水、出水和污泥中的存在浓度

Table 1　Concentrations of antibiotics in influent, effluent and sludge in urban wastewater treatment plants

分类 Classification	抗生素 Antibiotic	进水浓度 Influent concentration//ng/L	出水浓度 Effluent concentration//ng/L	泥相浓度 Sludge concentration//ng/g	参考文献 Reference
磺胺类 Sulfonamides	磺胺甲恶唑	52.0 ~ 1 000.0	65.2 ~ 680.0	0 ~ 45.0	[14 - 18]
	磺胺嘧啶	14.4 ~ 1 300.0	1.1 ~ 36.0	0 ~ 70.0	[14 - 15,17]
	磺胺甲基嘧啶	7.8 ~ 18.0	1.6 ~ 23.3	2.4 ~ 5.3	[14,17]
	磺胺吡啶	30.0 ~ 530.0	7.1 ~ 330.0	0 ~ 68.0	[14,17]
四环素类 Tetracyclines	四环素	59.8 ~ 535.0	10.3 ~ 290.0	199.0 ~ 1 650.0	[14,16,18]
	氧四环素	40.0 ~ 107.0	2.6 ~ 20.5	117.0 ~ 1 680.0	[14,18]
	氯四环素	7.5 ~ 178.0	0 ~ 53.5	83.0 ~ 455.0	[14,18]
喹诺酮类 Quinolones	环丙沙星	15.0 ~ 1 380.0	7.2 ~ 851.0	40.0 ~ 1 150.0	[2,14,16 - 18]
	诺氟沙星	30.3 ~ 1 978.0	0.1 ~ 200.0	430.0 ~ 7 550.0	[2,14 - 15,17 - 18]
	氧氟沙星	80.0 ~ 3 100.0	1.2 ~ 1 200.0	330.0 ~ 21 000.0	[2,14 - 15,17 - 18]
大环内酯类 Macrolides	脱水红霉素	25.2 ~ 942.0	105.0 ~ 695.0	20.5 ~ 102.0	[14,18]
	红霉素	170.0 ~ 1 978.0	51.0 ~ 2 054.0	38.0 ~ 720.0	[15,17]
	罗红霉素	4.2 ~ 164.0	17.6 ~ 360.0	1.8 ~ 170.0	[15,17]
	克拉霉素	118.0 ~ 861.0	40.4 ~ 277.0	23.4 ~ 76.8	[14]
β - 内酰胺类	氨苄西林	34.4 ~ 383.0	0.9 ~ 17.4	—	[18]
β - lactams	头孢氨苄	65.7 ~ 1 718.0	142.0 ~ 1 176.0	—	[18]
	头孢噻肟	38.4 ~ 93.0	24.1 ~ 57.6	—	[18]
其他 Others	林可霉素	106.0 ~ 129.0	0 ~ 21.1	11.2 ~ 31.1	[14]
	氯霉素	0 ~ 57.0	0 ~ 43.0	—	[15,18]

表 2　CAS 与 MBR 对抗生素的去除效果比较

Table 2　Removal effects of antibiotics by CAS and MBR

分类 Classification	抗生素 Antibiotics	CAS 去除率 Removal rate by CAS//%	参考文献 References	MBR 去除率 Removal rate by MBR//%	参考文献 References
磺胺类 Sulfonamides	磺胺甲恶唑	-138.0 ~ 96.0	[15,19 - 21]	53.0 ~ 91.9	[20,22 - 32]
	磺胺嘧啶	50.0 ~ 87.0	[15,18]	48.0 ~ 93.8	[20,29 - 30]
	磺胺吡啶	-107.0 ~ 72.0	[20]	75.0 ~ 90.0	[30]
β - 内酰胺类	氨苄西林	23.0 ~ 82.0	[18,33]	>99.4	[29]
β - lactams	青霉素	0 ~ 29.0	[34 - 36]	>90.0	[37]
大环内酯类 Macrolides	红霉素	15.0 ~ 56.0	[15,38]	57.3 ~ 91.0	[24 - 25,28]
	罗红霉素	53.0 ~ 76.0	[15,39]	62.0 ~ 81.0	[20,24 - 25,28]
	阿奇霉素	37.0 ~ 49.0	[40 - 41]	50.0 ~ 78.0	[26,30]
	克拉霉素	13.0 ~ 43.0	[20 - 21,40]	50.0 ~ 95.0	[6,20,25 - 26,30]
喹诺酮类 Quinolones	诺氟沙星	31.0 ~ 78.0	[34,36]	47.0 ~ 90.0	[6,26,42]
	环丙沙星	66.0 ~ 87.0	[21]	51.0 ~ 89.0	[6,26,43]
	氧氟沙星	26.0 ~ 77.0	[21,44]	85.0 ~ 91.3	[27,42]
四环素类 Tetracyclines	四环素	43.0 ~ 73.0	[34 - 35,45]	>83.6	[26,29]
	氧四环素	44.0 ~ 88.0	[18,45]	>79.7	[29]

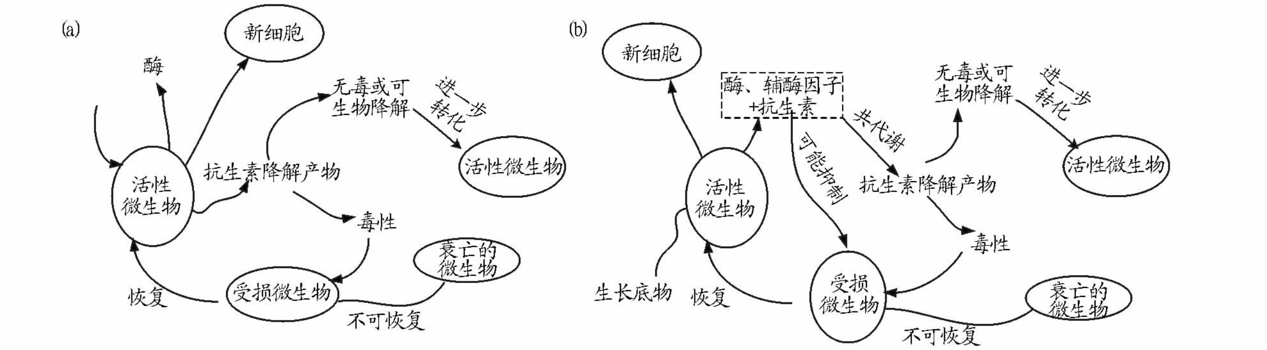
表 3　MBR 对磺胺甲恶唑的去除效果

Table 3　Removal effects of sulfamethoxazole by MBR

进水类型 Types of influent	进水浓度 Influent concentration//μg/L	污泥龄 SRT//h	水力停留时间 HRT//h	污泥浓度 MLSS//g/L	去除率 Removal rate//%	参考文献 References
市政污水 Municipal wastewater	>0.100	10 ~ 15	24.0	7.5 ~ 8.5	59.0	[22]
医院污水 Hospital wastewater	3.476	30 ~ 50	19.0	2.0	7.0	[6]
市政污水 Municipal wastewater	—	6 ~ 8	11.0	5.7	66.0	[26]
人工配水 Artificial wastewater	100.000	>100	24.0	—	56.5	[24]
市政污水 Municipal wastewater	0.367	40	9.0	4.0/6.0/8.0/10.0	70.0	[25]
市政污水 Municipal wastewater	0.850 ~ 1.600	16/33/60 ~ 80	13.0	—	95.0	[20]
人工配水 Artificial wastewater	10.000	72	12.0	—	53.0	[28]
人工配水 Artificial wastewater	2.000	70	2.4	8.6 ~ 10.0	91.9	[31]
市政污水 Municipal wastewater	0.093	—	7.2/15.0	1.4 ~ 8.4/6.7 ~ 26.0	78.3/80.8	[27]
人工配水 Artificial wastewater	500.000	3/10/30/60	6.0/12.0/24.0	0.3 ~ 6.3	>88.5	[29]
人工配水 Artificial wastewater	0.500 ~ 1.000	100	—	—	75.0 ~ 90.0	[30]
人工配水 Artificial wastewater	50.000	15/30	9.0/13.0	—	55.0/86.0	[32]

2 抗生素去除途径

2.1 生物降解 抗生素的生物降解过程与抗生素自身性质、污泥特性、运行条件等因素有关[49]，这些条件通过影响微生物的生长、抗生素的代谢途径来影响细胞生物降解过程。抗生素的物化性质显著制约其自身去除效果，抗生素内部多样的分子结构也使得抗生素的生化性差异巨大。酯类、腈类、芳族醇结构可以提高其生化性，而芳香胺类、卤基、硝基和偶氮基、长支链以及复杂芳环等基团可降低其生化性[50-52]。例如，大环内酯类抗生素一般具有带有支链和糖类的环，而磺胺类具有 2 个被—SO_2NH—结构联结的小环，这使得磺胺类极性和亲水性更强，从而决定了磺胺类抗生素比大环内酯类抗生素更易通过生物降解作用去除[24]。抗生素的代谢途径也会影响到生物降解过程。毒性较小、在环境中浓度存在较高的抗生素可以作为碳源被微生物通过直接代谢途径降解，毒性大、浓度低的抗生素则需通过微生物的共代谢作用得以去除[53]。共代谢是指微生物在主要底物存在条件下，对非生长底物进行降解的代谢方式[54]。微生物可以通过共代谢作用将抗生素转变成能够易生物降解的中间产物参与到主要代谢途径中去。某些种类的微生物如自养氨氧化菌被认为具有共代谢多种抗生素的能力[55]，其在硝化条件下会生成氨单加氧酶[56]，这种酶能够羟基化抗生素从而达到降解抗生素的目的。抗生素生物降解途径如图 1 所示。



注：a. 直接代谢；b. 共代谢。

Note：a. Direct metabolism；b. Co-metabolism.

图 1 抗生素生物降解途径[53]

Fig. 1 Biodegradation ways of antibiotics[53]

目前公认的生物降解模型主要为假一级模型，其用来解释抗生素生物降解行为。学者通过质量平衡算式计算 K_{biol}（降解速率常数）值作为抗生素生物降解性能的指标。生物降解模型：

$$\frac{dC_t}{dt} = -K_{biol} \times X_{bh} \times C_0 \quad (1)$$

式中，$\frac{dC_t}{dt}$ 为反应速率[mg/(L·s)]，C_t 为 t 时刻水相浓度(mg/L)，t 为反应时间(s)，K_{biol} 为降解速率常数[L/(mg·s)]，X_{bh} 为活性污泥浓度(mg/L)，C_0 为起始浓度(mg/L)。

2.2 污泥吸附 吸附在絮体、悬浮物以及污泥中的抗生素会随着沉淀作用以及排泥去除，这也是 MBR 去除抗生素的重要途径。吸附作用主要从 2 个方面来进行：①分子脂肪链和芳香基团与微生物亲脂细胞膜间的疏水作用；②组分的带正电基团与污泥负电表面的静电作用[57]。抗生素的亲疏水性是影响污泥吸附的重要指标。Rogers[58] 提出用辛醇－水分配系数(K_{ow})值判断抗生素亲疏水性，由于未考虑到抗生素的 pKa 以及 pH 对抗生素的影响，lgK_{ow} 在评价亲疏水性上存在一定缺陷。通常学者利用表观分配系数 K_d 来对抗生素吸附作用进行评估[59]，其计算公式为：

$$K_d = \frac{C_s}{C_w} \quad (2)$$

式中，C_s 为平衡条件下水相浓度(μg/L)；C_w 为泥相浓度(μg/g)。

Li 等[57] 认为，对于 $K_d < 500$ L/kg ($\lg K_d < 2.7$) 的抗生素，其吸附作用影响很小。对于 K_d 较大的抗生素，其通过吸附作用去除的比重很大。喹诺酮类抗生素如环丙沙星和诺氟沙星($K_d > 15\ 000$ L/kg)难以生物降解，其去除效果与 K_d 间有明显的正相关关系，且需通过与污泥絮体的静电作用来去除，而非疏水作用[2,60]。与活性污泥法相比，MBR 中惰性物质含量较高，污泥粒径小且表面积大，有利于吸附[61]。但由于 MBR 排泥量较少，因此通过吸附去除的抗生素总量不一定高[62-63]。MBR 中抗生素的吸附和生物降解途径已经得到绝大多数学者的公认，且 MBR 中抗生素的吸附过程较为迅速，而抗生素的生物降解是其去除过程的限速步骤。Dorival-García 等[42] 在研究中考查喹诺酮类抗生素的降解行为，发现吸附在 60 min 内快速完成，抗生素浓度从 24 h 后随着污泥生物降解而缓慢下降。Fernandez-Fontaina 等[24] 也发现，吸附过程结束后 MBR 水相和泥相中的抗生素浓度以相近的速度降低，表明水相和泥相中抗生素存在相似的生物降解行为。

总之，一方面 MBR 中较小尺寸絮体的存在增大了吸附接触面积，提高了吸附效果，另一方面复杂的微生物菌群有利于生物降解[63]。MBR 反应器突出的泥水分离效果归结于膜组件的间接截留作用，它可以使得出水中基本不含污泥，保证了出水中不会有污泥携带抗生素排放到环境中[64]。此外，对于那些疏水性强且含有吸电子基团的抗生素，虽然其

在水相中去除率高,但其会积累在污泥中并随之进入环境,因此污泥的安全处置问题亦需要学者更多的关注。

3　影响因素

3.1　温度　温度的改变能够导致抗生素物化性质、微生物活性、增殖速率等受到影响,进而导致出水水质及系统稳定运行受到影响[65]。

过高或过低的温度条件会降低抗生素的去除效果。低温条件下微生物的活性减弱会影响微生物对抗生素的生物降解过程,导致抗生素去除效率降低[66]。高温条件下,污泥会分解释放出污染物造成出水浓度的增加[65],物质的去除率同样会变低。温度的改变也会带来混合液特性的变化。Hai 等[65]观察到污泥浓度会随着温度的升高而变低,胞外聚合物特性表现稳定,而溶解性微生物代谢产物中蛋白质的含量在低于 20 ℃和高于 45 ℃时明显增加。混合液特性与 MBR 中污泥絮体结构、沉降性能以及膜污染有着非常密切的关系,因此温度对混合液特性的改变会影响 MBR 的稳定运行。温度还会影响吸附作用,从而影响抗生素的去除效果。一般来说,温度的改变对带有强吸电子功能团、亲水性强的组分影响更大[65]。对于大多数物质来说,吸附等温线随着温度升高而降低[67],因此温度的升高会造成吸附能力的降低。对于喹诺酮类抗生素来说,其通过污泥吸附去除的效果会随着温度的升高而明显降低,但由于温度升高有利于生物降解,因此整体的去除率随温度升高依然呈现增大的趋势[42]。

3.2　pH　pH 能够显著影响抗生素的去除,在不同的 pH 条件下,抗生素可能为中性、阴性或两性的,随之其物化性质及生化性质也会相应发生改变[68]。

对于能够发生电离的组分,其在 pH 较低的条件下以疏水形式存在,而在 pH 较高的条件下其会带上负电不利于吸附于污泥上。对于不可电离组分,pH 的影响很小。磺胺甲恶唑在 pH = 5 时主要以中性形式存在,疏水性强,有利于其吸附作用,去除效率最高[69]。Tadkaew 等[69]还发现可电离组分受 pH 的影响非常大,且辛醇水分配系数的改变与去除率的变化非常一致。Watkinson 等[34]研究发现,当 pH < 7 时,红霉素能够脱去一个水分子生成脱水红霉素,从而使其无法被检测到。pH 条件不仅影响吸附作用,而且还影响微生物活性和菌群结构[70]。

3.3　污泥浓度　与 CAS 相比,较高的污泥浓度是 MBR 反应器的一大特点。体系中的污泥浓度升高意味着有更多的微生物可以参与到抗生素的去除中,这不仅可以使总体的生物降解能力得到增强,而且可以使得抗生素在污泥上的吸附总量得到增加,从而减小出水中抗生素浓度[42]。

污泥浓度高也意味着有较低的食微比(F/M),体系中可产生更多复杂的微生物菌群,这些微生物需要代谢难降解组分以维持其生长,因此整体上可以提高其降解抗生素的能力。MBR 系统能够减少微生物的流失,因此也有利于难降解组分的降解。高浓度的污泥浓度还可使 MBR 拥有更高的抗冲击负荷的能力[71]。

Sahar 等[72]观察污泥浓度积累过程(3.8 ~ 10.4 g/L)中抗生素的去除率变化,发现磺胺甲恶唑去除效果随污泥浓度增加而增大,而大环内酯类的去除率大小与污泥浓度无关。Dorival-Garcia 等[42]发现将污泥浓度从 7 g/L 增大到 15 g/L 时,喹诺酮类抗生素的去除率和生物降解途径占比均有显著提高。他还指出,较高的污泥浓度虽然使微生物对抗生素的吸附能力降低,但其可为抗生素提供更多的吸附位点,从而使得抗生素的吸附总量增加。Fernandez-Fontaina 等[24]比较了 MBR 和 CAS 的吸附和生物降解能力,发现 MBR 中抗生素的 K_{biol} 和 K_d 值并无明显提高,因此他认为 MBR 的去除优势主要在于高浓度的污泥浓度使得去除总量增大。

3.4　污泥龄　污泥龄是污水处理厂工艺设计的重要指标,它影响着污泥浓度、生物多样性、微生物的活性和优势菌群,同时它也是影响 MBR 去除抗生素效果的重要因素。在较长的污泥龄下,慢速生长自养菌(如硝化细菌)能够缓慢增殖,同时微生物种类更为复杂,其可通过直接代谢或共代谢的方式加强抗生素的降解[29]。一般来说,MBR 的污泥龄比 CAS 的要大,MBR 对抗生素的去除效果更好。长泥龄、较低污泥负荷能够提高污泥生物多样性,有助于抗生素在污泥共代谢作用下的去除;短泥龄会导致污泥浓度下降、絮体尺寸变大以及比表面积减小,从而降低抗生素的去除效果[29]。因此,适当延长污泥龄可以提高 MBR 对抗生素的去除率。然而,也有学者观察到在相同污泥龄条件下,与 CAS 相比,MBR 对抗生素的去除并无优势,这可能与其他因素(如污泥浓度、食微比等)的影响有关[73]。

3.5　水力停留时间　一般来说,提高水力停留时间能够增加微生物和污水的接触时间,从而提高抗生素的去除效果。

当水力停留时间过短时,污泥生物降解抗生素速率的提高无法抵消增大的进水负荷,此时去除效率就会下降。Fernandez-Fontaina 等[66]在研究中观察到红霉素随着水力停留时间的缩短,其通过生物降解作用去除的比例先是增大,随后随进水负荷的提高而减小,而罗红霉素随着水力停留时间的缩短,其生物降解去除率减小,表明不同抗生素在相同水力停留时间下有着不同的动力学和计量学限制。Gros 等[61]和 García-Galán 等[74]基于伪一级动力学模型,提出处理工艺需要满足最小水力停留时间($t_{1/2}$)来保证足够的时间进行吸附和生物降解以达到去除效果。K_{biol} 值较高及 K_d 值较低的抗生素(即疏水性较差)更易受到水力停留时间的影响,而 K_{biol} 值较低及 K_d 值较高的抗生素更易受到污泥龄的影响。

3.6　氧化还原电位　诸多文献报道了抗生素在好氧硝化、缺氧反硝化以及厌氧条件下的去除效率,对于大多数抗生素来说好氧条件下其去除率较高。Suarez 等[75]对好氧硝化条件和缺氧反硝化条件下 MBR 对抗生素的去除效果进行了比较,结果表明罗红霉素、红霉素在硝化条件下去除率分别为 91% 和 89% 左右,而在缺氧条件下其去除率分别仅为 15% 和 20% 左右。也有文献报道在厌氧条件下某些抗生素去除效果较佳的情况,如 Suarez 等[75]研究发现,好氧条件下磺胺甲恶唑去除率仅为 22% 左右,而 Monsalvo 等[76]和 Wijekoon 等[52]的研究结果显示,磺胺甲恶唑在厌氧 MBR 中几乎被完

全去除。Xue 等[77]在研究中也发现甲氧苄氨嘧啶在厌氧池中几乎被完全去除。分析原因可能是：①回流使厌氧池抗生素浓度下降；②污泥吸附造成的下降；③厌氧污泥自身具有较强的降解抗生素的能力。而红霉素在污泥相的浓度在好氧池达到最低，这可能是由于好氧池下生物降解的作用。

4 MBR 组合工艺

MBR 对绝大多数抗生素具有较佳的去除效果，但出水中依然有相当的残余。因此许多学者研究 MBR 组合工艺对抗生素的强化去除效果，如粉末活性炭－膜生物反应器工艺（PAC－MBR）[43]、膜生物反应器－臭氧工艺（MBR－O_3）[43]、膜生物反应器－紫外光/H_2O_2 工艺（MBR－UV/H_2O_2）[78]、膜生物反应器－反渗透/纳滤工艺（MBR－RO/NF）[79]等。MBR 及其组合工艺对抗生素的去除效果见表 4。由表 4 可以看出，MBR 组合工艺比单独的 MBR 具有更佳的去除效果。此外，还有学者将酶催降解与 MBR 结合用于去除微量有机污染物[80]。

表 4 MBR 及其组合工艺对抗生素的去除效果

Table 4 Removal effects of antibiotics by MBR and its combined processes

抗生素 Antibiotics	去除率 Removal rate//%					参考文献 References
	MBR	PAC－MBR	MBR－O_3	MBR－RO/NF	MBR－UV/H_2O_2	
磺胺甲恶唑 Sulfamethoxazole	85.0	—	—	100.0	90.5	[81,82]
红霉素 Erythromycin	42.0～64.0	100.0	—	97.7	—	[26,83]
罗红霉素 Roxithromycin	71.0～86.0	100.0	—	—	—	[83]
环丙沙星 Ciprofloxacin	73.0	96.5	97.9	—	96.2	[43,82]
恩诺沙星 Enrofloxacin	56.0	97.5	98.8	—	—	[43]
克拉霉素 Clarithromycine	50.0	—	—	—	85.6	[82]

粉末活性炭－膜生物反应器工艺主要利用活性炭的吸附能力以提高去除效果。Baumgarten 等[43]在研究中将粉末活性炭（投加量＜50 mg/L）加入到 MBR 反应器，环丙沙星、恩诺沙星和莫西沙星的去除率分别从 73%、56%、78% 提高到 96% 左右。Serrano 等[83]研究发现，粉末活性炭的加入可使反应器内氨氧化菌增多，从而提高了生物降解抗生素的能力；MBR 中加入 1 g/L 的粉末活性炭便几乎可以完全去除红霉素和罗红霉素。活性炭加入初期能够提高去除效果，但运行一段时间后活性炭吸附能力丧失，去除效果就会下降；对于难降解的物质，活性炭有限的吸附容量是限制其去除效果的重要因素[84]。活性炭的加入需要定期再生或更换，会增大产泥量。反渗透/纳滤膜的去除原理主要为分子截留[48,85]，静电作用也发挥一定作用。大量研究表明反渗透/纳滤膜有去除微量有机污染物的能力[86]，MBR 与反渗透/纳滤膜的互补结合能够强化处理效果、拓宽工艺的适用范围。Alturki 等[81]研究发现，膜生物反应器－反渗透/纳滤工艺几乎能够完全去除磺胺甲恶唑，其中 MBR 反应器对磺胺甲恶唑的去除率可达 85% 以上，其余部分主要为反渗透/纳滤膜发挥作用；Alturki 等[81]认为 MBR 能够去除疏水性强和生物降解能力强的物质，而对于亲水性强的组分去除率则比较分散，这一部分随后被反渗透/纳滤膜有效去除。臭氧、紫外光、二氧化钛光催化等高级氧化技术历来被认为是处理难降解有机物的有效方法，其可帮助去除 MBR 无法有效去除的抗生素。紫外光或二氧化钛光催化氧化受到水质条件（如浊度）和有机物的影响较为严重[87]，MBR 较好的出水水质能够有效解决这一问题。然而，采用高级氧化技术强化去除抗生素的过程中，抗生素的毒性可能会增强[88]。需要指出的是，有关 MBR 与高级氧化联用技术去除抗生素的应用研究依然较少，副产物的产生以及毒性增强的问题依然存在，这也成为其应用的一大限制。

5 结语

抗生素的大量使用所引发的人类健康和环境安全问题不容忽视。大量文献报道了城市污水厂进水、出水和污泥中抗生素的检出，表明传统活性污泥法不能有效去除抗生素。MBR 对各类抗生素的去除效果较佳，其在城市污水厂中的应用必将大大降低天然环境中抗生素的流入。MBR 中抗生素主要通过生物降解和吸附这 2 种途径去除，二者受到抗生素的分子结构、亲疏水性的制约。影响因素研究是提高 MBR 对抗生素去除效果的前提和基础，对于优化 MBR 运行条件具有重要的理论和现实意义。去除效果受到温度、pH、污泥浓度、污泥龄、水力停留时间、氧化还原电位等多方面的影响，其中学者应重点关注污泥浓度、污泥龄。此外，MBR 组合工艺的开发和应用能够完善城市污水厂的处理工艺，从而进一步增强抗生素的去除效果，这也值得学者进行更深入地研究。

目前，学者对 MBR 去除抗生素的去除机理、影响因素研究仍然不够全面、深入。抗生素种类繁多、性质各异，学者应着眼于更大种类范围的抗生素，进一步研究其在 MBR 的去除机理与效果。有关 MBR 中抗生素通过生物降解和吸附途径去除的比例的相关报道依然较少，以吸附为主要途径的抗生素依然会残留在泥相中，从而造成污泥安全处置问题，因此有必要开展泥相中抗生素的行为和归趋研究。

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