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# SPG 膜表面润湿性对膜污染和化学耐受性的影响

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**摘要:** SPG 膜微气泡曝气系统可应用于废水好氧处理, SPG 膜污染以及其对化学清洗的耐受性是影响其应用的重要因素。本研究在采用在线化学清洗的微气泡曝气生物膜反应器中, 考察了 SPG 膜表面性质对膜污染及化学耐受性的影响。结果表明, 在长期运行过程中, SPG 膜表面润湿性对膜污染和化学耐受性具有明显影响。膜表面污染层主要是有机污染, 而疏水性膜抗有机污染能力较强。使用在线化学清洗时, 碱性次氯酸钠溶液对亲水性膜腐蚀严重, 膜孔径和孔隙率显著增大。疏水性膜抗碱性次氯酸钠溶液化学腐蚀能力较强, 膜孔结构仅有轻微改变, 但是疏水性膜表面疏水官能团易被氧化, 使得膜表面润湿性下降。同时, 疏水性膜在氧传质、污染物去除和降低能耗等方面具有优势。因此, 疏水性 SPG 膜适用于微气泡曝气废水好氧生物处理。

**关键词:** 微气泡曝气; SPG 膜; 表面润湿性; 膜污染; 化学耐受性

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## Effect of Membrane Wettability on Membrane Fouling and Chemical Durability of SPG Membranes

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**Abstract:** Shirasu porous glass (SPG) membranes have been applied for microbubble aeration in aerobic wastewater treatment. In the present study, both hydrophilic and hydrophobic SPG membranes were used in a microbubble-aerated biofilm reactor with online chemical cleaning, and their membrane fouling and chemical durability were determined to be strongly dependent on the membrane wettability. The fouling layer formed on the surface of both membranes was confirmed to be mainly organic fouling, and the hydrophobic membrane showed a relatively stronger resistance to the organic fouling. The severe chemical corrosion of the hydrophilic membrane was observed due to exposure to the alkaline sodium hypochlorite solution used for chemical cleaning, which resulted in significant increases in the median pore diameter and the porosity. On the other hand, the pore structure of the hydrophobic membrane changed slightly when exposed to the alkaline sodium hypochlorite solution, suggesting its strong alkali-resistance due to the non-wetting surface. However, the surface hydrophobic groups of hydrophobic membrane could be oxidized by sodium hypochlorite solution, resulting in more wettable membrane surface. The hydrophobic membrane also showed better performance in the respects of oxygen transfer, contaminant removal and energy-saving. Therefore, the hydrophobic membrane seemed more appropriate to be applied for microbubble aeration in aerobic wastewater treatment process.

**Key words:** microbubble aeration; SPG membrane; surface wettability; membrane fouling; chemical durability

微气泡通常是指直径为 10 ~ 50  $\mu\text{m}$  的微小气泡, 微气泡曝气技术在废水处理领域受到关注<sup>[1]</sup>。目前, 微气泡曝气在废水处理中应用多为废水物化处理过程, 且已经证实微气泡曝气能够增强臭氧和氧气的气液传质速率<sup>[2-4]</sup>。微气泡曝气也已应用于废水好氧生物处理, 以提高氧传质速率<sup>[5]</sup>。微气泡曝气会破坏活性污泥絮体, 导致污泥絮体破碎、粒径减小和污泥沉降性降低<sup>[5, 6]</sup>, 因此难以应用于活性污泥反应器。而在生物膜反应器中, SPG 膜微气泡曝气系统可以实现连续稳定运行, 且氧利用率接近 100%, 显著高于传统曝气系统<sup>[7]</sup>。

SPG 膜是一种多孔玻璃膜, 通过相分离及酸沥过程制备<sup>[8]</sup>。SPG 膜作为一种气相分散介质, 可以应用于微气泡产生过程<sup>[9-11]</sup>, 而 SPG 膜表面润湿性对微气泡形成和气液传质均有影响<sup>[10, 12]</sup>。

SPG 膜污染是其应用中的主要问题之一。当亲水性 SPG 膜用于微气泡曝气生物膜反应器时, 膜污

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染会影响微气泡形成并导致氧传质效果恶化<sup>[13]</sup>。因此,需要在线化学清洗控制 SPG 膜污染的发展。但是化学清洗对膜材料具有腐蚀作用,导致膜性能和寿命降低<sup>[14, 15]</sup>。长期运行中,SPG 膜对化学清洗的耐受性目前仍不清楚。

本研究在微气泡曝气生物膜反应器中采用亲水性和疏水性 SPG 膜,观察长期运行后膜污染现象,探究膜表面润湿性对膜污染影响。此外,在长期运行时,使用次氯酸钠和盐酸溶液进行在线化学清洗,观察和分析长期化学清洗后,两种 SPG 膜表面性质和膜孔结构变化,分析膜表面润湿性对其化学耐受性的影响,以期对未来 SPG 膜的实际应用提供理论和技术支持。

## 1 材料与方法

### 1.1 SPG 膜

本研究采用管式亲水性(接触角  $27^\circ$ )和疏水性(接触角  $107^\circ$ )SPG 膜(SPG 技术有限公司,日本),膜孔径均为  $0.6 \mu\text{m}$ 。SPG 膜组分为 70% 的  $\text{SiO}_2$ 、10% ~ 15% 的  $\text{Al}_2\text{O}_3$  和其他成分<sup>[9]</sup>。SPG 膜自身为亲水性,疏水性 SPG 膜通过使用有机硅烷化合物进行膜表面化学改性制备。

### 1.2 实验装置

SPG 膜微气泡曝气生物膜反应器实验装置如图 1 所示。利用亲水性或疏水性 SPG 膜进行微气泡曝气。控制 SPG 膜内液体流速为  $0.73 \sim 1.08 \text{ m}\cdot\text{s}^{-1}$ 。利用空气压缩机提供  $0.6 \sim 0.8 \text{ MPa}$  的压缩空气,通过调节跨膜压差(膜外侧气压与内侧液压之差)控制空气通量,空气通量控制在  $1.15 \times 10^{-3} \sim 1.51 \times 10^{-3} \text{ m}^3 \cdot (\text{m}^2 \cdot \text{s})^{-1}$ 。通过显微镜观察和测量,确定产生微气泡直径范围为  $20 \sim 60 \mu\text{m}$ ,亲水膜和疏水膜产生的微气泡平均直径分别为  $31.1 \mu\text{m}$  和  $41.7 \mu\text{m}$ <sup>[2]</sup>。

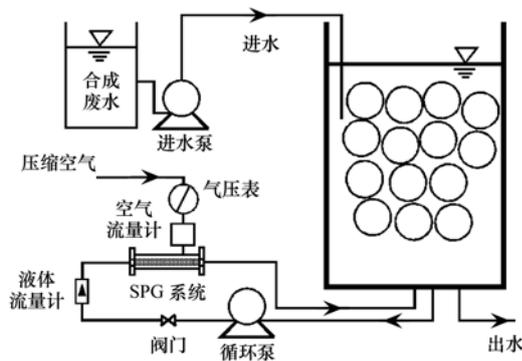


图 1 实验装置示意

Fig. 1 Schematic diagram of experimental apparatus

生物膜反应器直径和高分别为  $250 \text{ mm}$  和  $600 \text{ mm}$ ,有效容积为  $15 \text{ L}$ 。反应器内填充组合填料床层,组合填料为聚丙烯球(直径  $80 \text{ mm}$ )中填充聚氨酯多孔填料(平均孔径  $0.5 \sim 1 \text{ mm}$ ),填料填充率为 27%。

### 1.3 实验过程

向反应器中接种城市污水处理厂二沉池回流污泥,接种初始污泥浓度(MLSS)约为  $0.8 \text{ g}\cdot\text{L}^{-1}$ ,以促进填料上生物膜的形成。采用传统气泡曝气,待填料上生物膜生物量达到  $1.0 \text{ g}\cdot\text{L}^{-1}$ 左右时,挂膜过程完成。后续运行采用亲水性或疏水性 SPG 膜进行微气泡曝气。挂膜过程及后续运行过程均采用模拟生活污水<sup>[10]</sup>。

连续运行期间 2 种膜的运行条件完全相同,如表 1 所示。模拟废水的平均 COD 浓度为  $385.7 \text{ mg}\cdot\text{L}^{-1}$ 。连续进水,出水通过反应器底部的阀门控制。实验温度为室温。

长期运行中,每 2 d 对 SPG 膜进行在线清洗,清洗方法为:依次使用次氯酸钠溶液( $1000 \text{ mg}\cdot\text{L}^{-1}$ ,  $\text{pH} > 11$ )、盐酸溶液( $0.5 \text{ mol}\cdot\text{L}^{-1}$ )和蒸馏水,清洗时间分别为 30、30 和 15 min。

测定采用亲水性和疏水性 SPG 膜微气泡曝气生物膜反应器运行性能,包括空气渗透阻力、污染物去除和能耗。运行前后,测定膜表面特性和膜孔结构,以分析其膜污染和膜化学耐受性。

表 1 运行条件

Table 1 Operating conditions

项目	数值
运行时间/d	97
SPG 膜面积/ $\text{m}^2$	$1.57 \times 10^{-3}$
水力停留时间(HRT)/h	12
平均进水 COD 浓度/ $\text{mg}\cdot\text{L}^{-1}$	385.7
平均进水氨氮浓度/ $\text{mg}\cdot\text{L}^{-1}$	49.3
SPG 膜清洗方式	在线清洗

### 1.4 分析方法

SPG 膜污染及表面结构采用扫描电镜(SEM)(S-4800-I, Hitachi, 日本)观察,同时进行能谱(EDS)分析,以确定 SPG 膜表面  $1 \sim 2 \mu\text{m}$  处元素分布<sup>[17, 18]</sup>。采用压汞仪(Poresizer 9320, Micromeritics, 美国)测定膜孔径及孔隙率。SPG 膜样品压片后,采用红外(FTIR)光谱法(Nicolet6700, ThermoFisher, 美国)测定表面官能团。溶解氧(DO)通过溶氧仪(WTW cellOx 325, 德国)测定。采用压力表测定 SPG 膜外侧空气压力和内侧液体压力,确定跨膜压差。空气流量通过气体流量计测定。反应器进出水

COD 和氨氮浓度均采用国标方法测定. 采用电能表测定系统运行能耗.

## 2 结果与讨论

### 2.1 SPG 膜表面 SEM 观察

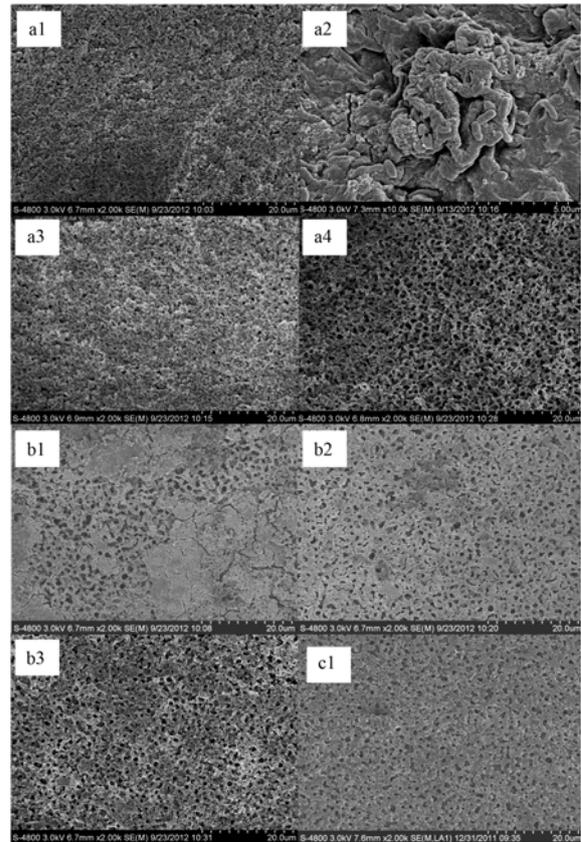
亲水性和疏水性 SPG 新膜表面膜孔结构相同, 如图 2(c1) 所示. 图 2(a1) 和(b1) 分别为长期使用后的亲水性和疏水性 SPG 膜污染后表面 SEM 图像, 亲水膜表面污染层均匀密实, 而疏水膜表面污染层相对松散. 在亲水膜表面污染层中可观察到微生物细胞, 如图 2(a2) 所示. 可见, 尽管采用了在线化学清洗, 长期运行后并不能完全控制膜污染发展.

利用酸浸处理 ( $0.5 \text{ mol} \cdot \text{L}^{-1}$  盐酸溶液, 室温, 4 h) 和热处理 ( $550^\circ\text{C}$ , 2 h) 对污染膜进行离线清洗<sup>[13]</sup>. 酸浸处理对疏水膜表面污染层去除明显[图 2(b2)], 但对亲水膜表面污染层去除效果不佳[图 2(a3)], 这表明亲水膜更易形成不可逆污染. 可见, 疏水膜表面的非润湿性显著降低了污染物在膜表面的附着, 因而膜污染相对较轻. 同时采用酸浸处理和热处理时, 亲水膜和疏水膜表面污染层几乎被全部去除[图 2(a4) 和(b3)].

长期使用后, 亲水膜表面膜孔结构[图 3(a)] 与新膜[图 3(c)] 相比发生了显著变化, 膜孔侵蚀明显, 孔径显著增大; 而疏水膜表面膜孔结构仅有轻微破坏[图 3(b)]. 可见, 疏水膜比亲水膜具有更强的抗污染和化学耐受特性. 在线化学清洗可能是导致膜表面膜孔结构破坏的主要原因.

### 2.2 SPG 膜表面元素分布

新膜和污染膜表面元素分布如图 4 所示. 亲水性和疏水性新膜表面主要元素为 O 和 Si, 这与膜的主要组分为  $\text{SiO}_2$  是一致的<sup>[9]</sup>. 利用有机硅烷化合物进行表面疏水改性后, 疏水膜表面 C 元素含量明显提高. 覆盖污染层后, 亲水膜[图 4(a)] 和疏水膜[图 3(b)] 表面 C 元素含量均显著增加, 而 O、Si 元素和金属元素含量减少. 去除污染层后, 膜表面元素分布与新膜基本相同. 可见, 有机污染是造成膜



a1 ~ a4, 亲水膜表面, 分别为污染膜、污染层中的微生物、酸浸处理和酸热联合处理; b1 ~ b3, 疏水膜表面, 分别为污染膜、酸浸处理和酸热联合处理; c1, 新膜

图 2 亲水性和疏水性 SPG 膜表面结构 SEM 观察

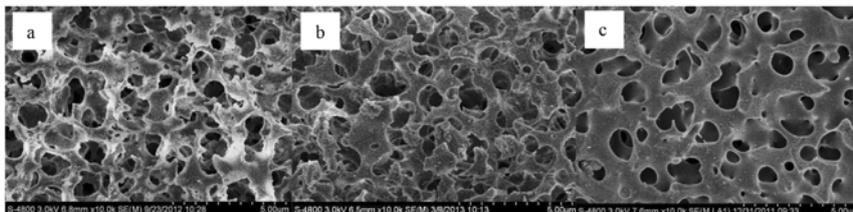
Fig. 2 SEM observation of surface microstructure of hydrophilic and hydrophobic SPG membranes

污染的主要因素.

### 2.3 红外(IR)光谱分析

新膜和污染膜 IR 光谱如图 5 所示. 由于 SPG 膜主要组分为  $\text{SiO}_2$ , 因此所有光谱中均出现 Si—O 伸缩振动强吸收峰 ( $1055 \text{ cm}^{-1}$ )<sup>[19]</sup> 和 O—Si—O 弯曲振动强吸收峰 ( $470 \text{ cm}^{-1}$ )<sup>[20]</sup>.

与亲水膜相比, 疏水膜在  $2930 \text{ cm}^{-1}$  和  $2850 \text{ cm}^{-1}$  处出现较强吸收峰, 这是由于膜表面疏水改性后, C—H 非对称振动和对称振动造成的<sup>[10]</sup>.



(a) 使用后的亲水膜; (b) 使用后的疏水膜; (c) 新膜

图 3 膜表面孔结构破坏 SEM 观察

Fig. 3 SEM observation of surface pore destruction of the membranes

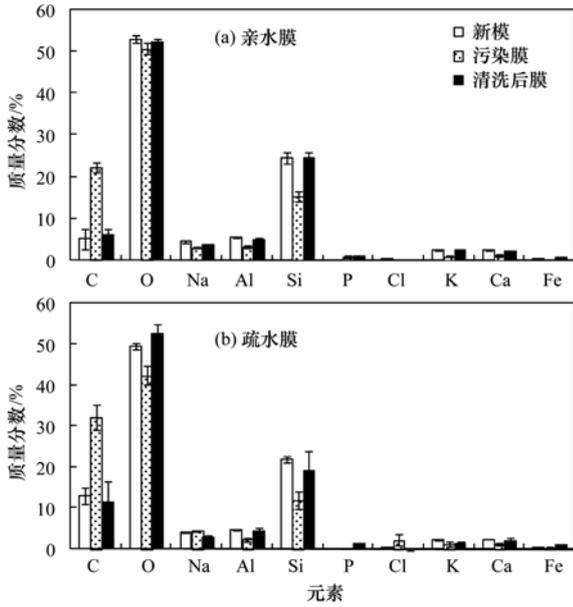


图4 新膜、污染膜和清洗后膜的表面元素分布  
Fig. 4 Surface elemental distributions of new, fouled and cleaned membranes

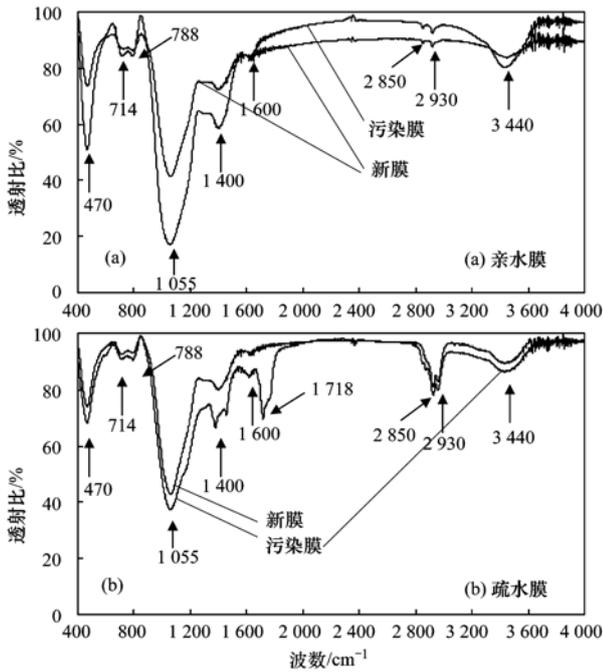


图5 新膜和污染膜的红外光谱

Fig. 5 Infrared spectra of new and fouled membranes

污染亲水膜 IR 光谱中没有出现新吸收峰和峰的位移. 而在污染疏水膜 IR 光谱 $1718\text{ cm}^{-1}$ 处, 出现新的强吸收峰. 此吸收峰是由于疏水膜表面 C—H 被次氯酸钠溶液氧化为 C=O 的伸缩振动造成的<sup>[21]</sup>, 同时使得疏水膜表面极性和润湿性增强.

2.4 膜孔结构

利用酸浸处理和热处理<sup>[13]</sup>去除膜表面污染层

后, 长期使用的 SPG 膜孔径分布与累积膜孔体积变化如图 6 所示. 由于膜孔结构不受表面疏水改性的影响, 疏水膜与亲水新膜膜孔结构相同<sup>[12]</sup>. 2 种新膜的平均孔径和累积膜孔体积分别约为  $0.52\ \mu\text{m}$  和  $0.53\text{ cm}^3\cdot\text{g}^{-1}$ .

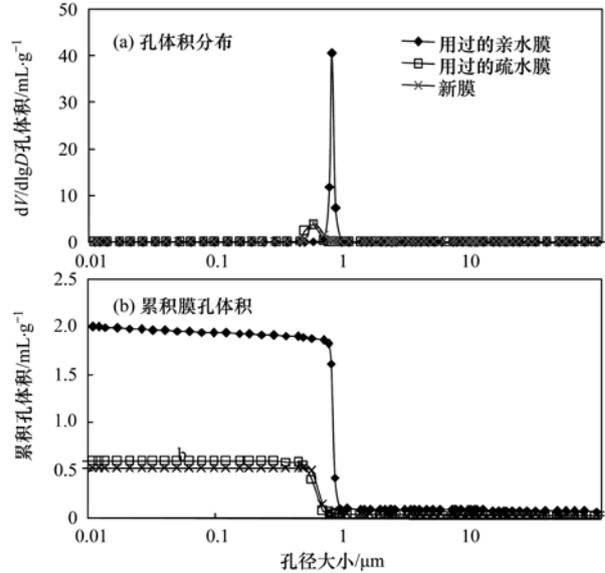


图6 新膜、使用后的(污染的和清洗过的)亲水和疏水 SPG 膜的孔体积分布和累积膜孔体积

Fig. 6 Pore size distribution and cumulative pore volume of new and used (fouled and cleaned) hydrophilic and hydrophobic SPG membranes

使用后的亲水膜孔径和累积膜孔体积显著增加, 分别为  $0.80\ \mu\text{m}$  和  $2.06\text{ cm}^3\cdot\text{g}^{-1}$ . 此外, 膜容积密度从  $1.04\text{ g}\cdot\text{cm}^{-3}$  减少到  $0.40\text{ g}\cdot\text{cm}^{-3}$ , 意味着膜重量损失高达 61.5%. 可见, 在线化学清洗对亲水膜具有强烈的化学侵蚀作用, 造成膜组分大量溶出. 这是由于 SPG 膜作为一种玻璃膜抗碱性较弱, 当膜接触碱性次氯酸钠溶液时,  $\text{OH}^-$  离子使得膜骨架 Si—O 键断裂,  $\text{SiO}_2$  网络结构逐渐被破坏, 膜组分大量溶出, 膜孔径增大. 由于碱性溶液常用于有机污染控制<sup>[22]</sup>, 其对 SPG 膜化学腐蚀是 SPG 膜应用的一个问题, 已有研究者尝试开发耐碱性 SPG 膜<sup>[23]</sup>.

另一方面, 疏水膜有较强的耐化学腐蚀性. 使用后的疏水膜孔径和累积孔体积略有变化, 分别为  $0.59\ \mu\text{m}$  和  $0.60\text{ cm}^3\cdot\text{g}^{-1}$ . 疏水性表面可以阻止碱性溶液进入膜孔内, 有效避免化学腐蚀. 因此, SPG 膜表面疏水改性是一种有效抵抗膜内化学腐蚀的方法. 值得注意的是, 次氯酸钠溶液能够氧化膜表面疏水基团, 增强膜表面润湿性, 降低疏水膜化学耐受性. 这可能是疏水膜表面孔结构轻微破坏的原因.

## 2.5 空气通透性

长期运行时,利用 Darcy 定律计算亲水膜和疏水膜的空气渗透阻力<sup>[24]</sup>,如图 7 所示. 初始阶段,由于亲水膜表面润湿和膜孔中水的存在,其空气渗透阻力远远大于疏水膜. 在随后的运行过程中,尽管膜污染有所发展,但亲水膜空气渗透阻力逐渐降低. 此时,由于化学侵蚀,膜孔隙率从 54.8% 增大至 81.9%,这可能是造成空气渗透阻力降低的主要原因.

疏水膜较大的接触角有利于促进气相扩散和微气泡的形成<sup>[10]</sup>,因此疏水膜初始空气渗透阻力很低. 然而,随着次氯酸钠溶液对表面疏水基团的破坏,疏水膜的表面亲水性增强,造成空气渗透阻力显著提高.

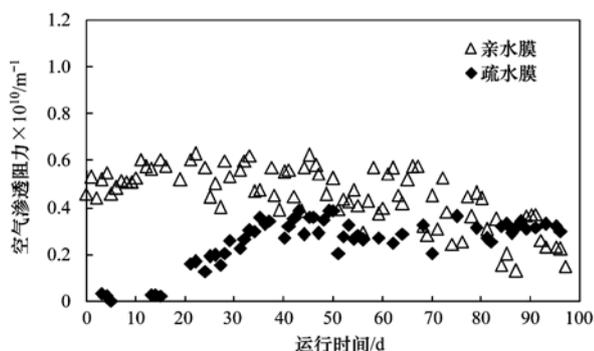


图 7 长期运行时亲水性和疏水性 SPG 膜的空气通透性

Fig. 7 Air permeation resistance of hydrophilic and hydrophobic SPG membranes during long-term operation

## 2.6 运行性能

相同运行条件下,亲水膜和疏水膜处理系统的运行性能如表 2 所示. 可以看到,使用疏水膜可以获得略高的 DO 浓度和污染物去除效率,可能的原因是其氧传质阻力较低<sup>[12]</sup>. 此外,由于疏水膜空气渗透阻力较低,其空压机能耗比亲水膜低 33.6%.

表 2 亲水膜、疏水膜处理系统性能

Table 2 Performance of the treatment system using hydrophilic or hydrophobic membrane

名称	亲水膜	疏水膜
平均溶解氧浓度/ $mg \cdot L^{-1}$	2.13	2.84
平均 COD 出水浓度/ $mg \cdot L^{-1}$	45.6	34.7
平均 COD 去除率/%	88.2	91.0
平均氨氮出水浓度/ $mg \cdot L^{-1}$	16.2	13.5
平均氨氮去除率/%	67.1	72.6
平均 COD 去除负荷/ $kg \cdot (m^3 \cdot d)^{-1}$	0.68	0.70
空压机平均能耗/ $kW \cdot h \cdot d^{-1}$	0.053	0.035

以上结果表明,膜表面润湿性对 SPG 膜微气泡曝气废水好氧处理中膜污染和化学耐受性有重要影

响. 疏水膜具有较强的抗污染能力和化学耐受性,以及更高效的运行性能,因此,疏水膜更适用于微气泡曝气废水好氧处理.

## 3 结论

(1) SPG 膜表面润湿性对膜污染和化学耐受性具有重要影响. 亲水性和疏水性 SPG 膜表面污染层主要为有机污染. 疏水膜比亲水膜具有更强的抗有机污染能力.

(2) 使用碱性次氯酸钠溶液在线清洗时,对亲水膜造成严重化学侵蚀,导致膜孔径和孔隙率显著增大. 疏水膜有较强耐化学侵蚀能力,膜孔结构变化较小,但膜表面疏水基团易被氧化,导致膜表面疏水性降低和空气渗透阻力增加.

(3) 在氧传质、污染物去除和能耗方面,疏水膜比亲水膜具有更好的运行性能. 疏水膜具有较强的抗污染能力和化学耐受性,以及较好的运行性能,因此更适用于微气泡曝气废水好氧处理.

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