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污水处理厂厌氧氨氧化工艺小试

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摘要: 在市政污水处理厂进行厌氧氨氧化工艺小试实验。试验以 A/O 除磷和亚硝化工艺处理后的生活污水为基质, 室外启动并运行上向流厌氧氨氧化生物滤柱。第 109 d 时, 连续 15 d 氨氮和亚硝氮去除率大于 90%, 总氮去除率大于 70%, 厌氧氨氧化生物滤柱启动成功。第 245 ~ 333 d, 运行进入冬季, 滤料生物量 (以 VSS 计, 下同) 为 $12.24 \text{ mg} \cdot \text{g}^{-1}$, 平均总氮去除率为 54.3%。第 461 d 对滤柱进行反冲洗, 滤料生物量降低至 $8.01 \text{ mg} \cdot \text{g}^{-1}$ 。第 605 ~ 693 d, 运行再次进入冬季, 滤料生物量为 $10.41 \text{ mg} \cdot \text{g}^{-1}$, 平均总氮去除率为 69.7%。生物量小于去年同期水平, 但总氮去除负荷提高了 23%。在整个运行过程中, 高温 (30℃) 污泥厌氧氨氧化速率基本保持不变, 低温 (15℃) 厌氧氨氧化速率 (以 MLSS 计) 从 $1.5 \text{ kg} \cdot (\text{kg} \cdot \text{d})^{-1}$ 增长到 $3.6 \text{ kg} \cdot (\text{kg} \cdot \text{d})^{-1}$ 。结果表明, 长期低温驯化有利于提高厌氧氨氧化工艺低温处理效果, 实现冬季厌氧氨氧化工艺高效运行。

关键词: 生活污水; 低温; 厌氧氨氧化; 滤柱; 生物膜

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Lab-scale ANAMMOX Process in a Wastewater Treatment Plant

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Abstract: A lab-scale, completely anaerobic ammonium oxidation (ANAMMOX) process was operated in a municipal wastewater treatment plant (WWTP). Sewage effluent treated by an A/O process and nitrification process was input as the substance to start up the up-flow ANAMMOX filter reactor. After the 109th day, the ammonia removal rate and nitrite removal rate were greater than 90% for 15 successive days and the nitrogen removal rate was higher than 70%. The ANAMMOX filter reactor successfully started up. From days 245 to 333, the reactor was running during the winter. The weight of biomass reached $12.24 \text{ mg} \cdot \text{g}^{-1}$, and the average nitrogen removal rate was 54.3%. Backwash was adopted at day 461, and the weight of biomass decreased to $8.01 \text{ mg} \cdot \text{g}^{-1}$. From days 605 to 693, the reactor was running in the winter again. The weight of biomass was $10.41 \text{ mg} \cdot \text{g}^{-1}$, and the average nitrogen removal rate was sustained at 69.7%. Compared with the previous winter, the weight of biomass was lighter but the total nitrogen removal loading was 23% greater. For the entire operation, the ANAMMOX rate at high temperature was stable but that at low temperature increased from $1.5 \text{ kg} \cdot (\text{kg} \cdot \text{d})^{-1}$ to $3.6 \text{ kg} \cdot (\text{kg} \cdot \text{d})^{-1}$. The results show: Long-term domestication at low temperature was in favor of improving treatment efficiency of ANAMMOX process in cold environment and realized ANAMMOX process operated efficiently in winter.

Key words: sewage; low temperature; ANAMMOX; filter; biomembrane

与传统脱氮工艺相比, 厌氧氨氧化工艺节省了 62.5% 曝气量、脱氮途径短、无需外加碳源、温室气产量低^[1], 成为目前最具前景的污水脱氮工艺^[2]。

厌氧氨氧化菌适合处理高温、高氨氮污水^[3~6], 而城市生活污水是典型的低温、低氨氮水质^[7], 如何将厌氧氨氧化工艺应用于市政污水处理厂是长久以来的难点^[8]。在国外, 厌氧氨氧化工艺已成功应用于污水处理厂中, 以处理垃圾渗滤液^[9]、消化上清液^[10]、养殖业废水^[11, 12]等高氨氮废水, 而市政污水处理厂厌氧氨氧化工艺的研究仍处于小试阶段^[13]。国内, 厌氧氨氧化工艺主要局限

于实验室研究^[14~16], 在实际污水处理厂中长期运行厌氧氨氧化工艺的报道鲜见。

常温低氨氮环境中, 厌氧氨氧化工艺处理负荷低^[17, 18]。通常认为, 常温驯化可以使厌氧氨氧化菌逐步适应低温环境^[19~21]。前人的研究在实验室内进行, 以人工配水为基质, 氨氮浓度为 $100 \sim 350 \text{ mg} \cdot \text{L}^{-1}$, 运行温度为 $18 \sim 25^\circ\text{C}$, 且驯化时间较短。而实际生活污水成分复杂, 亚硝化后的生活污水氨氮浓度为 $10 \sim 25 \text{ mg} \cdot \text{L}^{-1}$, 水温为 $10 \sim 24^\circ\text{C}$ 。因此,

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在市政污水处理厂中,研究长期常低温驯化对厌氧氨氧化菌的影响有着重大的意义.

基于此,本研究在污水处理厂中,将 A/O 除磷和亚硝化工艺串联作为预处理工艺,以预处理后的生活污水为基质,启动并长期运行厌氧氨氧化工艺的小试,分析长期运行过程中厌氧氨氧化菌的活性.

1 材料与方法

1.1 试验装置

试验采用上向流生物滤柱反应器(图 1).装置由有机玻璃制成,内径 20 cm,承托层装填 5 cm,滤料装填 45 cm,反应器有效容积为 18 L.承托层采用粒径为 4~8 mm 的砾石填料,滤料为直径 5~10 mm 的黑色火山岩.最下端取样口距滤柱底部 10 cm,由下向上每隔 25 cm 设置一个取样口.反应器底部设曝气装置以进行反冲洗,外部缠绕黑色保温棉以避免光和保温.

1.2 试验用水和接种污泥

将 A/O 除磷和亚硝化工艺串联作为预处理工艺,以预处理后的生活污水为厌氧氨氧化工艺的基质,具体水质指标如表 1 所示.

反应器启动时接种 4 L 厌氧氨氧化絮状污泥,

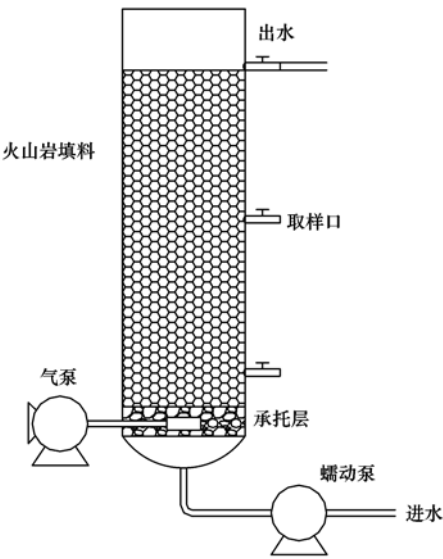


图 1 反应器装置示意

Fig. 1 Schematic diagram of the experimental equipment

污泥浓度为 $2\,200\text{ mg}\cdot\text{L}^{-1}$.厌氧氨氧化絮状污泥来自于稳定运行的厌氧氨氧化 SBR 反应器, SBR 反应器总氮去除率稳定在 85% 左右,总氮去除负荷为 $0.5\text{ kg}\cdot(\text{m}^3\cdot\text{d})^{-1}$.

1.3 运行参数

整个运行阶段,进水基质及滤速保持不变,运行所处的季节及进水温度如表 2 所示.

表 1 A/O 除磷出水水质

Table 1 Characteristics of the effluent from the A/O process

序号	检测项目	单位	结果	序号	检测项目	单位	结果
1	NH_4^+-N	$\text{mg}\cdot\text{L}^{-1}$	14~20	5	COD	$\text{mg}\cdot\text{L}^{-1}$	15~45
2	NO_2^--N	$\text{mg}\cdot\text{L}^{-1}$	17~24	6	pH	—	7.0~7.8
3	NO_3^--N	$\text{mg}\cdot\text{L}^{-1}$	4~7	7	TP	$\text{mg}\cdot\text{L}^{-1}$	<1.5
4	SS	$\text{mg}\cdot\text{L}^{-1}$	<20	8	温度	$^{\circ}\text{C}$	10~22

表 2 各阶段反应器参数变化情况

Table 2 Parameter variations of each stage

序号	时间/d	季节	水温/ $^{\circ}\text{C}$	序号	时间/d	季节	水温/ $^{\circ}\text{C}$
1	1~61	春	15.1~18.3	6	425~509	夏	16.4~21.6
2	62~152	夏	16.5~21.9	7	510~604	秋	13.2~19.6
3	153~244	秋	12.6~18.9	8	605~695	冬	10.1~14.7
4	245~333	冬	10.2~14.3	9	696~784	春	13.8~18.8
5	335~424	春	14.1~18.6	10	785~869	夏	17.1~20.6

1.4 化学分析方法及反应速率的测定

水样分析中 NH_4^+-N 测定采用纳氏试剂光度法, NO_2^--N 采用 *N*-(1-萘基)乙二胺光度法, NO_3^--N 采用紫外分光光度法, COD 采用快速测定仪, DO、pH 和水温通过 WTW 便携测定仪测定,其余水质指标的分析方法均采用国标方法.

反应速率的测定:从反应器中取滤料,刮下生物膜,放入 2 个烧杯中,分别测定 30°C 和 15°C 时的厌氧氨氧化反应速率,代表高温厌氧氨氧化速率和低温厌氧氨氧化速率.烧杯设置机械搅拌,氨氮和亚硝氮基质浓度为 $50\text{ mg}\cdot\text{L}^{-1}$,使碱度与氨氮之比为 5, pH 为 7.6~8.0,整个运行过程中水中 DO 维

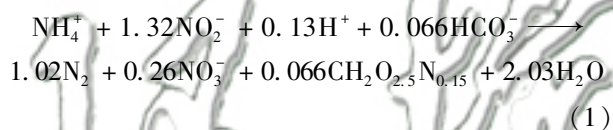
持在 $0.3 \text{ mg} \cdot \text{L}^{-1}$ 以下。

2 结果与分析

2.1 厌氧氨氧化滤柱的启动

春季进行厌氧氨氧化工艺的启动。反应器装填火山岩填料后, 接种 3.5 L 污泥浓度为 $2200 \text{ mg} \cdot \text{L}^{-1}$ 的厌氧氨氧化絮状污泥进行挂膜。挂膜阶段, 采用较低的水力负荷以减小对滤料表面微生物的冲击, 滤速定为 $0.10 \text{ m} \cdot \text{h}^{-1}$ 。同时, 反应器出水进行收集并循环进水, 以减少厌氧氨氧化菌的流失。运行 5 d 后, 出水 SS 浓度小于 $20 \text{ mg} \cdot \text{L}^{-1}$, 表明厌氧氨氧化菌已基本被截留在反应器中。此时反应器改为连续进水出水, 滤速提高到 $0.15 \text{ m} \cdot \text{h}^{-1}$, HRT 为 3.3 h 。

连续运行阶段反应器氨氮, 亚硝氮和硝氮变化如图 2 所示, 进水温度及总氮去除率如图 3 所示。为了研究脱氮途径, 引入厌氧氨氧化反应方程式, 如式(1)所示。厌氧氨氧化菌按 $1:1.32$ 的比例消耗氨氮和亚硝氮。厌氧氨氧化工艺生成的氮气量与硝氮量之比为 8 , 该值称为特征比。试验亚硝氮氨氮消耗比和特征比如图 4 所示。



反应器改为连续进水出水的第 1 d , 总氮去除

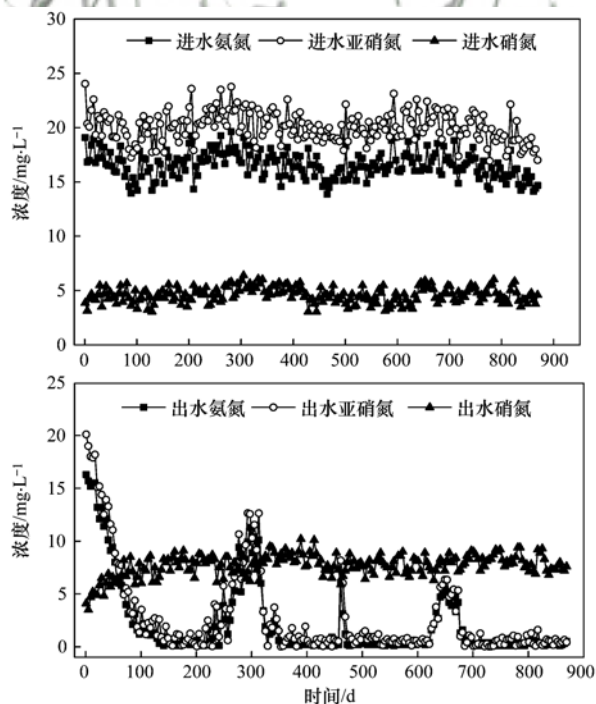


图 2 氨氮、亚硝氮和硝氮浓度的变化

Fig. 2 Concentration variations of ammonia, nitrite, and nitrate

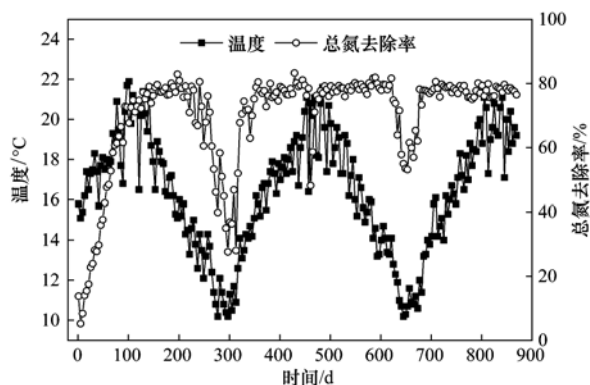


图 3 温度和总氮去除率

Fig. 3 Temperature and total nitrogen removal rate

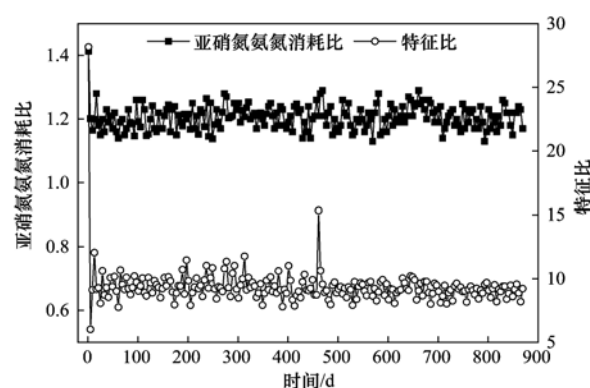


图 4 亚硝氮氨氮消耗比和特征比

Fig. 4 Consumption ratio of nitrite to ammonia and characteristic ratio

率为 13.8% 。但亚硝氮氨氮消耗比为 1.41 , 特征比为 28.17 , 不满足厌氧氨氧化方程式。分析其原因, 可能是由于火山岩填料对基质的吸附作用。随着吸附达到饱和, 总氮去除率明显降低, 第 4 d 时, 总氮去除率由 13.8% 降低到 5.2% 。反应器继续运行, 氨氮和亚硝氮去除效果逐渐提高, 出水硝氮浓度逐步增加。第 109 d 时, 连续 15 d 氨氮和亚硝氮去除率大于 90% , 总氮去除率大于 70% , 亚硝氮氨氮消耗比稳定在 $1.17 \sim 1.26$, 特征比稳定在 $8.76 \sim 10.21$, 符合厌氧氨氧化反应方程式, 表明上向流厌氧氨氧化生物滤柱启动成功。

Zekker 等^[22]在 20°C 条件下以发酵厂高氨氮污水为基质, 历时 186 d 成功启动厌氧氨氧化工艺。进水温度 $20 \sim 25^\circ\text{C}$, 氨氮和亚硝氮基质浓度为 $30 \sim 50 \text{ mg} \cdot \text{L}^{-1}$, Bao 等^[23]在 224 d 启动厌氧氨氧化生物滤柱。Zhang 等^[24]以含 $25 \sim 35 \text{ mg} \cdot \text{L}^{-1}$ 氨氮和亚硝氮的配水为基质, 23°C 条件下 90 d 成功启动厌氧氨氧化 SBR 反应器。与前人研究成果相比, 本试验以更低浓度的实际生活污水为基质, 在 $15.1 \sim 21.9^\circ\text{C}$ 的条件下, 成功启动厌氧氨氧化反应器, 较前人的研究成果有所进步。

2.2 厌氧氨氧化滤柱的低温运行

第 153 ~ 244 d 时, 反应器在秋季运行, 进水温度为 12.6 ~ 18.9℃. 温度在 14℃ 以上时, 反应器氨氮、亚硝氮去除率大于 95%, 温度小于 14℃ 时, 氨氮和亚硝氮去除率明显降低. 第 245 d, 反应器运行进入冬季, 进水温度为 10.2 ~ 14.3℃. 由图 3 可知, 反应器总氮去除率与进水温度密切相关. 进水温度在 10 ~ 12℃ 时, 总氮去除率为 25% ~ 60%. 进水温度为 12 ~ 14℃ 时, 总氮去除率为 55% ~ 75%. 第 245 ~ 334 d, 反应器最大出水总氮浓度为 30.1 $\text{mg} \cdot \text{L}^{-1}$, 平均总氮去除率为 54.3%.

为了避免生物膜过度增殖导致滤柱堵塞, 第 461 d 对滤柱进行反冲洗. 反冲洗时, 采用较大的水力负荷以达到削减生物膜厚度的目的. 以气水联合的方式进行反冲洗, 气水比为 3, 水冲强度为 2.0 $\text{L} \cdot (\text{s} \cdot \text{m}^2)^{-1}$, 反冲洗时间为 3 min. 反冲洗后, 氨氮去除率从 98.6% 降低到 59.7%, 亚硝氮去除率从 97.3% 降低为 57.2%, 总氮去除率由 78.4% 降为 48.1%. 运行 8 d 后, 氨氮去除率恢复至 90% 以上, 总氮去除率提高到 71%. 相比于其他生物膜^[25, 26], 本试验厌氧氨氧化生物膜反冲洗后恢复速度较快. 有研究表明, 成熟的厌氧氨氧化菌生物膜结构紧凑, 分泌较多的胞外多聚物, 对水力负荷冲击的抵抗能力强^[27], 因此成熟厌氧氨氧化生物膜受反冲洗影响较小.

第 510 ~ 604 d, 运行季节为秋季, 进水温度为 13.2 ~ 19.6℃, 反应器氨氮和亚硝氮去除率大于 90%, 总氮去除率大于 75%. 相比于去年同期水平, 进水温度在 14℃ 以下时, 依然有着良好的处理效果. 第 605 d, 运行再次进入冬季, 进水温度为 10.1 ~ 14.7℃. 进水温度在 10 ~ 12℃ 时, 总氮去除率为 50% ~ 65%. 进水温度为 12 ~ 14℃ 时, 总氮去除率为 70 ~ 80%. 第 605 ~ 695 d, 反应器最大出水总氮浓度为 19.7 $\text{mg} \cdot \text{L}^{-1}$, 平均总氮去除率为 69.7%. 总氮去除率比去年同期相比增长了 29%, 总氮去除负荷增长率为 23%.

Guillén 等^[19]通过 1 048 d 的低温驯化, 提高了低温厌氧氨氧化工艺的处理效果. Trojanowicz 等^[20]从低温驯化 3 a 的厌氧氨氧化反应器中取泥, 在低温时成功启动反应器并取得了良好的处理效果. 前人的研究主要表明, 长期的低温驯化可以提高低温厌氧氨氧化菌活性, 但对于长期驯化对厌氧氨氧化活性提高并未量化. 在本试验中, 从第 245 ~ 334 d 到第 605 ~ 695 d, 历时 1 a, 总氮去除负荷增长率

为 23%, 长期低温驯化明显地提高了反应器低温处理效果.

2.3 生物学特性研究

每个季节从反应器中取出滤料, 测定滤料生物量及反应速率, 结果如图 5 所示. 生物量单位以 VSS/滤料计, 为 $\text{mg} \cdot \text{g}^{-1}$.

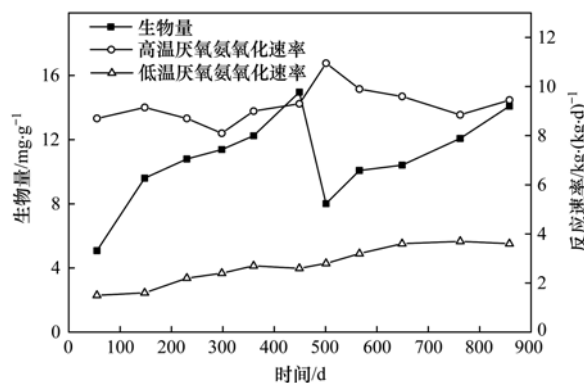


图 5 生物膜厚度及反应速率

Fig. 5 Thickness of biofilm and reaction rate

第 55 ~ 148 d, 进水温度为 16.5 ~ 21.9℃, 反应器生物量从 5.08 $\text{mg} \cdot \text{g}^{-1}$ 增长到 9.61 $\text{mg} \cdot \text{g}^{-1}$, 增长幅度较大. 第 230 ~ 298 d, 进水温度为 10.2 ~ 13.8℃, 生物量由 10.20 $\text{mg} \cdot \text{g}^{-1}$ 提高为 11.38 $\text{mg} \cdot \text{g}^{-1}$, 低温环境中生物量增长速度较慢, 表明温度对厌氧氨氧化菌生物膜的增长有较大影响. 第 461 d 滤柱进行反冲洗, 生物量从 14.96 $\text{mg} \cdot \text{g}^{-1}$ 降低至 8.01 $\text{mg} \cdot \text{g}^{-1}$, 反冲洗可以有效地剪切生物膜, 将滤料生物量维持在较低水平. 第 360 d, 运行处于冬季, 生物量为 12.24 $\text{mg} \cdot \text{g}^{-1}$, 第 649 d, 反应器再次处于冬季, 生物量为 10.41 $\text{mg} \cdot \text{g}^{-1}$. 与去年同期相比, 生物量处于较低水平, 但反应器总氮去除率负荷提高了 23%. 其原因是经过长期的常温驯化, 低温条件下厌氧氨氧化菌活性显著提高.

反应速率测定时的温度、基质浓度均相同, 因此高温厌氧氨氧化反应速率代表了不同阶段污泥中厌氧氨氧化菌比例. 由图 5 可知, 高温厌氧氨氧化速率基本相同. 进水温度几乎不会影响生物膜中厌氧氨氧化菌所占比例.

低温反应速率与高温反应速率的比值可以有效地反映低温厌氧氨氧化菌的活性. 由图 5 可见, 第 55 d 时, 低温厌氧氨氧化反应速率(以 MLSS 计, 下同)为 1.5 $\text{kg} \cdot (\text{kg} \cdot \text{d})^{-1}$, 与高温反应速率的比值为 0.17. 随着反应器的继续运行, 低温厌氧氨氧化速率明显提高, 第 858 d 时, 低温厌氧氨氧化速率达到了 3.6 $\text{kg} \cdot (\text{kg} \cdot \text{d})^{-1}$, 与 30℃ 厌氧氨氧化速率比

值为 0.38. 与第 55 d 相比, 第 858 d 时高温厌氧氨氧化反应速率基本相同, 低温厌氧氨氧化速率增长 140%, 低温反应速率与高温反应速率的比值增长率达 123%. 结果表明, 长期低温驯化有利于提高低温厌氧氨氧化菌活性.

3 结论

(1) 试验以 A/O 除磷和亚硝化工艺处理后的生活污水为基质, 室外启动厌氧氨氧化生物滤柱. 第 109 d 时, 连续 15 d 氨氮和亚硝氮去除率大于 90%, 总氮去除率大于 70%, 厌氧氨氧化生物滤柱启动成功.

(2) 第 245 ~ 333 d, 运行进入冬季, 滤料生物量为 $12.24 \text{ mg} \cdot \text{g}^{-1}$, 平均总氮去除率为 54.3%. 第 605 ~ 693 d, 运行再次进入冬季, 滤料生物量为 $10.41 \text{ mg} \cdot \text{g}^{-1}$, 平均总氮去除率为 69.7%. 滤料生物膜厚度小于去年同期水平, 但总氮去除负荷提高了 23%.

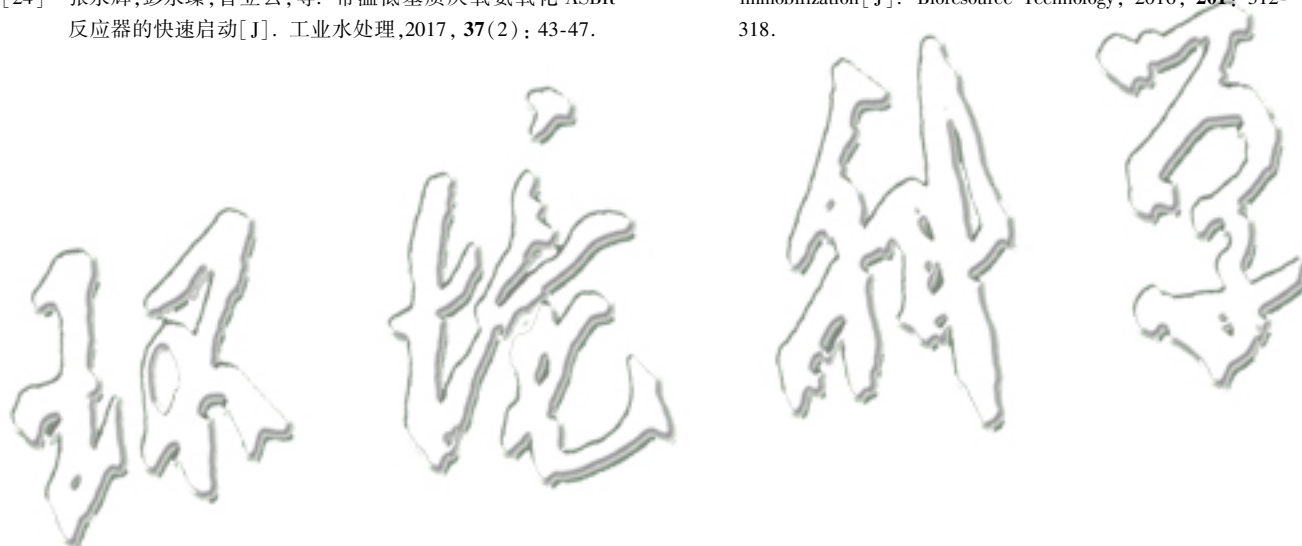
(3) 在整个运行过程中, 高温厌氧氨氧化速率基本保持不变, 低温厌氧氨氧化速率从 $1.5 \text{ kg} \cdot (\text{kg} \cdot \text{d})^{-1}$ 增长到 $3.6 \text{ kg} \cdot (\text{kg} \cdot \text{d})^{-1}$, 增长率达 140%. 长期低温驯化有利于提高厌氧氨氧化工艺低温处理效果, 实现冬季厌氧氨氧化工艺高效运行.

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