二相厌氧消化工艺硫酸盐还原细菌的研究*

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摘 要 采用厌氧操作技术和 MPN 法测定表明, 产酸相中的 SRB 含量为 2.0– 5.7×10⁶ 个/ml, 产甲烷相中含量为 0.93– 9.3×10⁷ 个/ml, 2 者之差一般约为 1 个数量级. 单相 UASB 反应器的 SRB 含量与产甲烷相类似. 在产酸相与产甲烷相的上部悬浮液中 SRB 含量分别为 7.5×10⁵ 和 4.3×10⁵ 个/ml, 底部污泥中 SRB 含量分别为 2.5×10⁶ 和 2.5×10⁷ 个/ml. SRB 与产甲烷细菌相比, 具有较强的环境适应能力和较小的附着能力. 此外, 分析讨论了 SRB 的生长和分布特性对反应器中硫酸盐还原作用和产甲烷作用的影响与控制.

关键词 硫酸盐还原细菌, 二相厌氧消化, UASB 反应器.

厌氧反应器中硫酸盐还原菌[1-2]的生长条件和代谢途径与产甲烷细菌非常相似. 它对厌氧消化过程和出水后处理有重大影响, 高浓度硫酸盐废水的处理也由此成为一大难题[2-4]. 为了寻求经济有效的高浓度硫酸盐废水的治理技术, 笔者提出二相厌氧消化工艺具有较大的应用开发潜力[5]. 本文报道以二相 USAB 工艺为试验装置, 分析测定硫酸盐还原细菌(Sulphate Reducing Bacteria, SRB) 的生态分布结果, 同时对 SRB 进行形态鉴定, 指出二相厌氧消化工艺可以处理高浓度硫酸盐废水的微生物学依据, 并讨论了与产甲烷细菌的相互竞争关系及运行控制要点.

1 材料和方法

试验装置采用实验室二相 UASB 工艺. 研究中另设单相 UASB 反应器作为对照. 反应器的具体结构和运行控制见参考文献[6]. SRB 的计算采用三管最可能数法(MPN), 操作过程如下:

取反应器混合液数 10ml, 放入 Warning 匀浆器的小杯子中, 低速档搅碎 45s, 此时包括颗粒污泥在内都能得到很好的悬浮分散. 收集搅碎后的均匀悬浮液作为原液, 用玻璃或塑料无菌注射器, 在无氧蒸馏水中进行 10 倍梯度稀释, 再分别接种到相应的硫酸盐还原细菌液体培养基中, 置于 35℃恒温箱内培养 2 周, 然后观察并计算结果.

SRB 是较严格的厌氧细菌, 为了保证较高的厌氧状态并得到较好的测定结果, SRB 培养基的配制均采用 Hungate 严格厌氧操作技术[7]. SRB 培养基的配方为[8]: 乳酸钠 3.5g, NH_4Cl 1.0g, $NaSO_4$ 1.0g, $MgSO_4 \cdot 7H_2O$ 0.1g, K_2HPO_4 0.5g, $Fe(NH_4)_2(SO_4) \cdot 7H_2O$ 0.65g, $CaCl_2$ 0.1g, 蒸馏水 1000ml, pH7.0–7.2。

固体培养基再加 2% 琼脂. 菌落的观察和分离培养采用滚管法[7]. 所有培养基配制后都以 0.11MPa 的压力灭菌 20min, 冷却后取出待用. 一般现配现用.

2 试验结果

2.1 不同运行条件下硫酸盐还原细菌的分布

不同运行负荷下, 二相及单相 UASB 反应器中硫酸盐还原细菌的测定结果见图 1. 从图 1 中可以看出:

(1) 二相 UASB 工艺中产甲烷相反应器的 SRB 含量在不同的运行负荷下变化不大, 均在 0.93–9.3×10⁷ 个/ml 范围之内. 单相 UASB 反应器的 SRB 含量与产甲烷相反应器类似 (1.5–7.3×10⁷ 个/ml), 而且 2 者的SRB 含量

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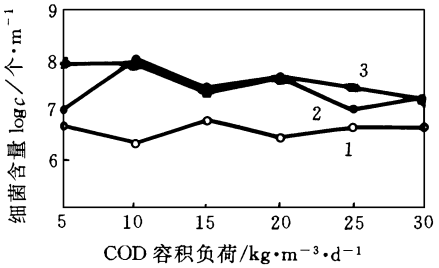

图 1 硫酸盐还原细菌在不同负荷下的生态分布
产酸相反应器 2. 产甲烷相反应器 3. 单相反应器

基本一致.

(2) 产酸相反应器的SRB 含量在不同的运行负荷下也变化很小(2.0– 5.7×10⁶ 个/ml). 与产甲烷相反应器相比, 其含量约低一个数量级. 由于产酸相和产甲烷相反应器的运行条件相差极大, 而 2 者的 SRB 含量却差异较小, 这说明 SRB 具有较强的环境适应能力.

SRB 在不同运行负荷下含量基本不变的特性可能与基质有关. 本试验中, 进水硫酸盐含量保持不变, 因此, SRB 也维持在一定的数量不变.

2.2 硫酸盐还原细菌的垂直分布

SRB 在反应器中的垂直分布着重考虑颗粒污泥与悬浮液中细菌的分布差异. 取样口 1 和 4 分别代表颗粒污泥床底部和上部, 取样品 6 为反应器上部悬浮液. 测定结果见图 2.

从图 2 可以看出, 产酸相反应器中上下层的SRB 含量分别为 7.5×10⁵ 和 2.5×10⁶ 个/ml, 相差不到 1 个数量级. 这与该反应器流态——完全混合态是一致的. 在产甲烷相反应器中, 颗粒污泥的 SRB 含量为 2.5×10⁷ 个/ml, 比悬浮液的含量(4.3×10⁵) 要高约 2 个数量级。单相 UASB 反应器表现出类似的情况(4.3×10⁷/2.5×10⁵). 如果与产甲烷细菌的生态分布相比(颗粒污泥比悬浮液的含量高 3– 4 个数量级)[6], 可以得到这样的结论: SRB 的附着能力和在颗粒污泥中的富集作用相对比较弱.

2.3 酸化状态下硫酸盐还原细菌的生态分布

酸化状态下 SRB 的生态分布见图 3. 测定结果表明, 在酸化状态下各反应器的 SRB 含量

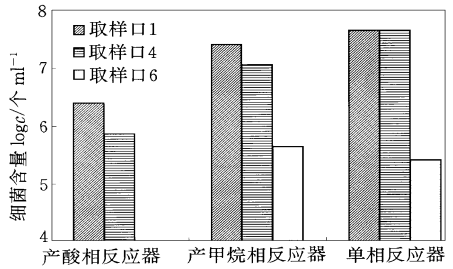

图 2 硫酸盐还原细菌的垂直分布

与正常状态相比均变化不大, 计数值差异小于 1 个数量级, 由此进一步说明 SRB 比产甲烷细菌具有更强的环境适应能力, 在不利的环境条件(包括酸性条件) 下 SRB 比产甲烷细菌具有生长优势. 根据这一特性, 可以通过控制运行条件, 达到控制硫酸盐还原作用的目的, 即采用二相厌氧消化工艺, 在产酸相反应器中, 人为地富集SRB 含量, 强化SRB 的活性, 通过SRB 的硫酸盐还原作用将 SO_4^{2-} 转化为气态硫化氢(H_2S) 去除, 减轻产甲烷相反应器受到的 SO_4^{2-} 负荷, 从而为高浓度硫酸盐废水的处理提供一条新途径.

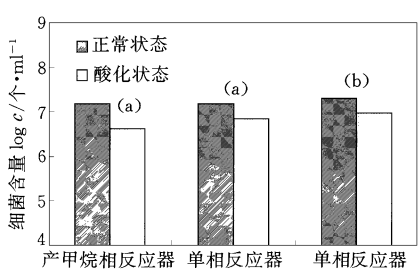

图 3 正常和酸化状态下的硫酸盐还原细菌分布
(a) COD 容积负荷约 30kg/(m³·d)
(b) COD 容积负荷约 18kg/(m³·d)

2.4 硫酸盐还原细菌的形态观察

进行硫酸盐还原作用的优势细菌是一种能运动的小细菌, 大小为 0.4– 0.8×1.0–2.0μm. 革兰氏染色阳性, 不形成芽孢, 在以乳酸盐为碳源的培养基中生长良好, 并可与亚铁离子生成黑色的硫化物沉淀, 借此能很方便地观察和判断 SRB 的生长. 不能利用葡萄糖, 但能利用乙酸盐和 H_2 作生长基质. 根据这些特性, 笔者初步确定反应器中的硫酸盐还原细菌

为脱硫弧菌属(*Desulfovibrio*). 滚管中生长的SRB 菌落外观黑色, 锥瓶形, 直径 0.5– 1.5mm (照片略). 采用电子显微镜观察颗粒污泥的细菌, SRB 细菌呈微弯的细小弧菌(照片略).

3 结果讨论

3.1 SRB 分布特性及其应用

产酸相中 SRB 含量较高, 比产甲烷细菌要高 2– 3 个数量级[6]. 因此, 可考虑在产酸相中强化硫酸盐还原作用(包括富集培养 SRB 和控制最适的 SRB 生长条件等), 减轻产甲烷相反应器受到的 SO_4^{2-} 负荷, 这样, 利用二相工艺中产酸相和产甲烷相分离的特点, 就能减消进水的高 SO_4^{2-} 含量对产甲烷过程的抑制影响, 实现这类有机废水的有效处理.

影响SRB 生长的条件, 除了进水的硫酸盐含量及 COD/SO_4^{2-} 的比值之外[9], 主要的工艺运行参数是 pH 值和 HRT. 通常, 纯培养的 SRB 在中性 pH 下生长较好. Widell 报道在 pH 小于 6.0 时生长不易进行并失去部分活性[10]; 而且某些脱硫弧菌培养物的最小倍增时间约 17h. 实际运行条件已大大超过纯培养物能承受的极限, 但 SRB 的计数分析表明, 可以生长良好并发挥代谢活性. 存在这些差异的原因有: 细菌本身在一定的环境条件下发生驯化适应作用, 反应器中的营养和生长因子比较适宜, 细菌之间有互营共生作用, 细菌互相粘连而以絮状体形式存在等. 但是, 细菌的适应也是有限度的. 实际运行中应注意控制产酸相反应器的 pH 大于 5.0, 一般以 6.0 左右为宜. 同时也要注意适宜的进水 COD/SO_4^{2-} 比值, 一般应控制这一比值大于 5, SO_4^{2-} 绝对值浓度小于 4000mg/L.

3.2 SRB 的生长特性及与产甲烷细菌之间的竞争

SRB 既可利用乳酸盐或乙酸盐, 也可利用 H_2 或 NADH+ H^+ 还原 SO_4^{2-} 获取生长所需的能量. 这就和产甲烷细菌发生明显的竞争性基质利用. 从热力学上分析硫酸盐还原作用更易进行, 见下式:

$$SO_4^{2-} + 4H_2 \rightarrow H_2O + H_2S + 2OH^-$$

($\Delta G^{0'} = -151.9$kJ/mol 反应)

$$CO_2 + 4H_2 \rightarrow 2H_2O + CH_4$$

($\Delta G^{0'} = -135.6$kJ/mol 反应)

因此, SRB 具有竞争优势. 在自然生态环境中, 例如江河、湖泊、海洋等的沉积物, SRB 确实比产甲烷细菌占优势, 但厌氧消化反应器中却是产甲烷细菌占优势, 产甲烷作用是主导反应. 不少研究者从生长动力学参数来解释这一现象[2,11]. 另一方面, 细菌的附着性能和环境适应能力也是一个重要因素. 本试验结果表明, 产甲烷细菌比 SRB 的附着成球能力要高, 但对环境的适应能力稍弱, 这也有利于产甲烷细菌在厌氧反应器正常运行过程中的富集和生长.

硫酸盐还原作用和产甲烷作用的竞争, 必须考虑的因素还有代谢产物及其影响[12]. 产甲烷细菌的形成产物是 CH_4 和 CO_2, 2 者都可以气体的形式释放, 因而不会造成常见的产物抑制, 有利于生化反应过程的连续进行. 可是, SRB 的最终还原产物是 H_2S 或其它硫化物, 它们会抑制许多细菌的生长. 这也是 SRB 对产甲烷作用带来的负面影响. 由于这一影响, 也促使产甲烷细菌在厌氧反应器中比 SRB 更具有生长竞争优势. 根据这些特性, 应用二相 UASB 工艺处理高浓度硫酸盐废水时, 使 SRB 和产甲烷细菌分别在产酸相和产甲烷相反应器中生长良好, 发挥各自的最大活性, 实现高浓度硫酸盐废水的有效治理.

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azo-dye aqueous solutions. The photodegradation products of phenol were also determined.

Keywords: photochemistry, photodegradation, wastewater treatment, oil refinery wastewater, coking industry wastewater, phenol.

The Preliminary Study on The Mechanism of Dyes Waste Water Treatment with ACF Electrode. Jia Jinping et al. (Dept. of Applied Chem., Shanghai Jiao Tong Univ., Shanghai, 200240): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 31—34

In this article, a new type of electrode made of ACF to treat several simulated dye waste water was studied. Under the electrolytic voltage ranged from 15V to 25V, all the wastewater's chromaticity removals are near 100%, with COD removals within 30%- 80%. And the reaction mechanism were figure out preliminarily by various characterization means such as IR、UV、spectrofluorimetry and TOC. Mainly, it may be that the treating processes involve radical reaction and coagulation simultaneously. The radical reaction can combine several organic molecules by radical coupling, so the larger molecule can be coagulated easily.

Keywords: active carbon fiber, electrode, electrochemistry, dyes waste water, reaction mechanism.

Determination and Discussion of Hydraulic Retention Time in Membrane Bioreactor System.

Zhang Shaoyuan, Wang Jusi et al. (Research Center for Eco-Environ. Sci., Chinese Academy of Sci., Beijing 100085): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 35—38

Based on the microorganism kinetic model the formula for computing the hydraulic retention time in the membrane bioreactor system (MBR) is derived, and then influencing factors of MBR are discussed. The results showed that the influencing factors are listed in order from strength to weakness as maximum specific removal rate K, saturation constant K_S, maintenance coefficient m, net bacteria yield coefficient Y_G and maximum specific growth rate μ_m. Finally, the formula is simplified and its simple form is as follows: $T = 1.1 \times (1/\beta - 1)(K_S + L)/KS_0$.

Keywords: membrane bioreactor, wastewater treatment, hydraulic retention time, microbial kinetic model, kinetic constant, operation constant.

The Pilot Test of Electrostatics-cyclone Precipitation Technology. Xu Dexuan and Qu Zhihe (Institute of Electrostatics, Northeast Normal University, Changchun 130024): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 39—41

The mechanism of electrostatics-cyclone precipitation technology has been researched in this paper. The pilot demonstration showed that this technology, using to improve the wet cyclone precipitator of power station, can heighten the precipitation efficiency from 92.55% to 98.4%. The precipitation efficiency for different concentration of flue gas is quite stable. When the gas flow is 10600 Nm^3/h, the resistance is 800- 920 Pa and the consumption per unit flow of high voltage power supply is 0.2 $W \cdot h/(m^3 \cdot h)$.

Keywords: electrostatics-cyclone precipitation technology, wet cyclone precipitation, high voltage power.

A Study of Sulfate Reducing Bacteria in Two Phase Anaerobic Process of UASB Reactors. Zhu Jianrong et al. (Dept. of Environ. Eng. Tsinghua Univ., Beijing 100084): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 42—44

This paper described the properties of numeration and distribution of sulfate reducing bacteria (SRB) in two phase process of UASB reactors. Using Hungate anaerobic technique and MPN determination method, it was showed that SRB of acidogenic phase are 2.0～5.7× 10^6 cells/ml, and the population of SRB in methanogenic phase are 0.93～9.3× 10^7 cells/ml. The difference of SRB between acidogenic and methanogenic phase is about 1 order of magnitude. The numeration of SRB in single UASB reactor is similar to that of methanogenic phase. The distributions of SRB exhibited that the bacterial population of acidogenic and methanogenic phase are 7.5× 10^5 and 4.3× 10^5 in upper layer of suspended mixed liquids, and 2.5× 10^6 and 2.5× 10^7 cells/ml in lower layer of anaerobic sludge, re-

spectively. These measurements revealed that SRB can better adapt to conditional changes, and has less attachment ability to granules compared with methanogenic bacteria, which certify the possibility to treat high strength organic wastewater containing sulfate using two phase anaerobic digestion process in microbiological aspects. The effects of sulfate reduction on methanogeneses in anaerobic reactor based on the SRB growth and distribution were discussed.

Keywords: SRB, two phase anaerobic digestion, UASB reactor.

Simulating Toxicity Tests of Methamidophos Pesticide to Soil Animals. Li Zhongwu and Wang Zhenzhong et al. (Dept. of Resource and Environment, Hunan Normal University, Changsha 410081): *Chin. J. Environ. Sci.*, **18** (6), 1997, pp. 45—49

Results of simulating experiments on methamidophos pesticide to soil animals showed that the methamidophos pesticide has an obvious effect on soil animals, the species and the amount of soil animals decrease obviously with increasing of methamidophos pesticide treating concentration; the diversity indexs are 3. 7596, 5. 7962 and 8. 5714 for 0. 54ml/L, 0. 01ml/L and control of methamidophos pesticide treating concentration respectively. Toxicity test of earthworm showed that the methamidophos pesticide influences obviously earthworm, their LC_{50} are 13. 7ml/L, 5. 4ml/L and 3. 9ml/L for 24 hours, 48 hours and 72 hours respectively. Safe concentration calculated of earthworm living is 0. 2517ml/L.

Keywords: soil animal, earthworm, methamidophos, simulating experiment.

Bioaccumulation of Two Speciations of Rare Earth Elements in Rice Seedling. Wang Qin, Sun Hao et al. (State Key Lab of Pollution Control and Resources Reuse, Dept. of Environ. Sci. & Engin., Nanjing Univ., 210093): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 50—52

Bioaccumulation of light, medium, and heavy rare earth elements and their EDTA-complexes by rice seedling was investigated simutaneously. The results showed that the bioaccumulation values in the root and above ground parts (stem & leave) of the rice seedling were positively correlated with the concentration of the rare earth elements in the culture solution. The results all showed that the ion speciation of the rare earth elements was the effective speciation for the root of plant, the order of bioaccumulation values was: root > stem & leave; the bioaccumulation values of EDTA-complexe in the root decreased obviously, while in the stem & leave the value increased evidently, so the speciation of EDTA-complexe was the effective speciation for the above ground parts of plant.

Keywords: rare earth ion, rare earth-EDTA complexe, bioaccumulation, rice, seedling.

A Study on the Characteristics of Reaction of Dichloramine and Bromide at Water Chlorination. Huang Xuejuan and Zhang Danian (Research Institute of Environ. Eng., East China Univ. of Sci. and Tech., Shanghai 200237): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 53—57

Monochloramine and dichloramine can be formed at water chlorination which containing ammonia. The chloramine react with bromide contained in water. The reaction rate increases with pH elevating and decreases with descent of bromide concentration. There is an introducing period in the reaction, and this period are inverse proportion with logarithm of bromide concentration. The reaction rate is first order reaction for dichloramine. Reaction products are studied by UV spectrum, gas chromatograph and polytetrafluoroethylene micro porous permeation, and Br_3^- and N_2 have been affirmed. The reaction formula can be infered.

Keywords: dichloramine water, chlorination, bromide, introducing period, UV spectrum, gas chromatograph, polytetrafluoroethylene micro porous permeation.

Study on SO_2 Absorption with Manganese Waste Slag to Produce $MnSO_4 \cdot H_2O$. Ning Ping et al. (Dept. of Environ. and Che. Eng., Kunming Univ. of Science and Techology, Kunming 650093): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 58—60

The experimental research of SO_2 desulphurization with manganese waste slag from a $MnSO_4 \cdot H_2O$ production plant has been done