

硝酸盐对降解对苯二甲酸厌氧 污泥驯化的影响*

李小明 陈 坚 伦世仪

(无锡轻工大学生物工程系, 无锡 214036)

摘要 硝酸盐在通过反硝化作用加速菌体生长的同时, 对污泥中降解 TA 菌群的形成有进一步的诱导作用. 经过 6 周的驯化其对 TA 的比降解能力达到 18.75 mg/(gVSS · d), 而对照组为 10.28 mg/(gVSS · d). 研究结果还显示, 经过 2—3 周可以完成从反硝化作用到产甲烷作用的转化.

关键词 硝酸盐, 对苯二甲酸, 驯化, 厌氧降解.

对苯二甲酸(Terephthalic Acid, 简称 TA)作为一种重要的化工原料, 属于有毒性难降解一类物质, 许多研究发现 TA 对水中微生物的再生有抑制作用, 对一些动物有致癌和致突变作用^[1,2], 现被美国 EPA 列为优先监控的污染物. 采用厌氧的方法来处理含 TA 的有机废水时, 除要经历传统厌氧处理工艺较长的启动时间外, 还面临着如何在尽可能短的时间内获得具有高效率降解 TA 能力的厌氧菌群, 从现有的文献报道看^[3], 对于一般的难降解性有机物, 其厌氧驯化的周期都比较长. 本文通过研究硝酸盐对 TA 厌氧降解污泥驯化进程的影响, 以探索一种能缩短驯化周期同时快速启动厌氧反应器的方法.

1 材料与方法

1.1 实验材料

驯化用培养基组成见表 1. 培养基在使用前先加热煮沸, 冷却后通入 N₂ 以去除其中的氧气.

接种污泥来源: 絮状污泥分别取自无锡市第二制药厂的厌氧消化池, 上海闸北豆制品厂废水处理车间及本实验室原保存厌氧污泥.

对苯二甲酸: 纯度为 99.98%, 购自 Schuchardt, 8011 Hohenbunn bei Munchen 公

表 1 驯化培养基组成/g · L⁻¹

反硝化驯化培养基		产甲烷驯化培养基	
TA	0.5—1	TA	0.5—1
磷酸二氢钾	0.2	磷酸二氢钾	0.7
氯化氨	0.5	氯化氨	0.5
硫酸镁	0.2	硫酸镁	0.2
酵母膏	0—2	酵母膏	0—2
微量元素溶液	5 ml	微量元素溶液	5 ml
硫化钠	0.5	硫化钠	0.5

司.

1.2 方法

(1) 实验方法 厌氧污泥的驯化在 250 ml 三角瓶中分 3 组平行进行. 驯化温度为 36℃ ± 1; 每天摇动 2—3 次. 总的驯化时间约为 2 个月, 约每周更新 1 次培养基, 其间每隔 1—2 d 取样分析其中的 TA 含量, 并记录产气量.

(2) 分析方法 化学需氧量(COD_{Cr}): 半微量快速烘箱法^[4]. 对苯二甲酸: 采用比色法^[5]. pH 值: 用 pH-2C 型精密酸度计测定. 产气量: 采用史氏发酵管测定. 气体成分分析: 气相色谱法^[6]. 挥发性悬浮固体(VSS, 即菌体浓度): 采用标准方法^[7].

* 美国 Amoco 公司资助项目

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2 结果与讨论

2.1 硝酸盐对驯化过程的促进作用

图 1 是加硝酸盐驯化到第 2 周时, TA 降解、产气及 COD 去除的影响, 图 2 是对照组驯化到第 4 周时的情况. 从图 1, 2 中可以看出硝酸盐加入后到第 2 周已表现出较强的降解 TA 能力, TA 的去除率达到 77.1%; 而对照组在第 4 周时去除率仅为 17.6%. 要达到相近的降解水平, 对照实验通常要进行到第 6 周以后. 硝酸盐对驯化过程的促进作用是反硝化作用与 TA 降解(开环)作用偶联的必然结果. 笔者认为, 硝酸盐的存在首先起到了提供能源的作用, 通过反硝化方式, 加速了微生物群体的生长, 促进了降解 TA 微生物群的生长. 产气中含有大量的氮气, 这证明驯化体中进行的是反硝化作用.

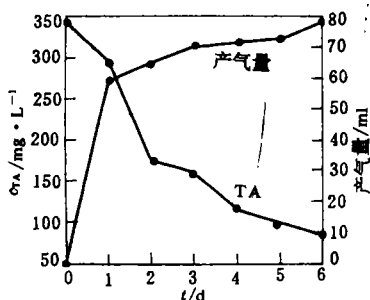


图 1 反硝化驯化至第 2 周时 TA、COD 及产气变化

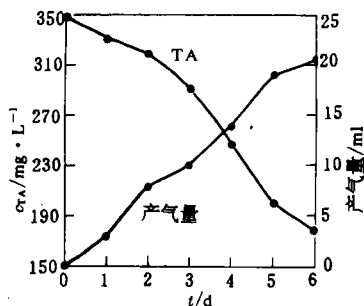


图 2 不加硝酸盐驯化至第 4 周时 TA、COD 及产气变化

解速度增长的对照图. 从图 3 中可看出, 一方面, TA 比降解速度的增加要高于对照组, 另一方面, 其污泥的生长速度也同时提高了. 这说明硝酸盐在加速菌群生长的同时, 也加强了对菌群降解 TA 能力的诱导作用.

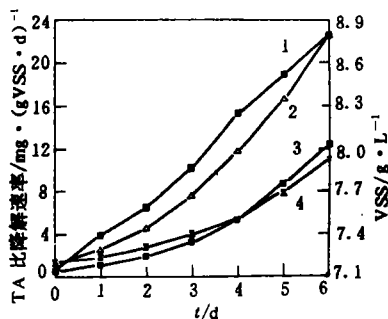


图 3 反硝化作用和产甲烷作用驯化过程中 COD 及 TA 比降解速率的变化

反硝化: 1. $R/\text{mg} \cdot (\text{gVSS} \cdot \text{d})^{-1}$ 2. $\text{VSS}/\text{g} \cdot \text{L}^{-1}$

产甲烷: 3. $R/\text{mg} \cdot (\text{gVSS} \cdot \text{d})^{-1}$ 4. $\text{VSS}/\text{g} \cdot \text{L}^{-1}$

2.2 硝酸盐促进驯化的本质

为进一步研究硝酸盐促进驯化作用的本质, 对驯化过程中比降解速率的变化做了分析(如表 2).

从表 2 中可以看出, 随着菌体绝对量的增加, 其对 TA 的降解能力也逐渐增强. 其中 $\Delta R/\Delta \text{VSS}$ 项反映在一定时间内, 体系降解 TA 速度的增加与菌体浓度增加的比值, 该值的大小反映了单位新增菌体中对降解能力增加的贡献, 值越大表明贡献越多, 增加的菌体中含具有降解 TA 能力的比率也越高. 表 2 表明, 单位时间里降解速度的增加量与菌体的增加量的比值在不同阶段是不同的, 在前 4 周, 该值是逐渐增加的, 第 5 和第 6 周则表现出下降的趋势.

到达第 5、第 6 周时, 该值表现出下降的趋势, 则表明菌体在生长的同时对 TA 的降解能力不再被进一步诱导, 与此同时, 体系中其它菌群得到了生长. 由此可以推断, 在驯化的起始阶段、硝酸盐对驯化过程的影响并不仅仅限于对增加菌体绝对量的贡献, 同时对降解能力的形成也有诱导作用; 当降解 TA 的微生物群达到一定浓度时, 硝酸盐的进一步诱导作用逐

图 3 为驯化 6 周后污泥生长量和 TA 比降

表 2 硝酸盐加入后驯化各阶段的实验结果

时间 (周)	VSS /g · L ⁻¹	R /mg · (L · d) ⁻¹	ΔVSS /g · L ⁻¹	ΔR /mg · (L · d) ⁻¹	ΔR/ΔVSS /g(gVSS · d) ⁻¹
0	7.1941				
1	7.2932	28.57	0.0991		
2	7.4401	47.54	0.1469	18.97	0.1291
3	7.6589	77.09	0.2188	29.55	0.1351
4	7.9742	121.65	0.3103	44.56	0.1436
5	8.3439	156.78	0.3697	35.13	0.0950
6	8.8010	198.95	0.4571	42.17	0.0923

渐减弱，只是随着菌体绝对量的增加，降解 TA 的绝对速度也有所增加。

2.3 从反硝化作用到产甲烷作用的转化

硝酸盐驯化进行到一定阶段后，体系中可能已存在较为完整的 TA 开环微生物群，为促进产甲烷菌的生长和恢复活性，从第 4 周起逐渐降低硝酸盐的浓度使反硝化作用完成后能进行一定的产甲烷作用，以促进污泥中原有的产甲烷菌的活性恢复。至第 6 周完全不加硝酸盐，其对 TA 的降解能力如图 4 所示，图 4 中给出了从第 4 周起完全停加硝酸盐和逐渐少加硝酸盐在第 6 周时降解 TA 的情况；并与普通产甲烷驯化的结果作了对照。结果表明它们对 TA 的

比降解能力分别达到 18.75 mg/(gVSS · d)，15.64 mg/(gVSS · d)和 10.28 mg/(gVSS · d)。

3 结论

(1) 硝酸盐对厌氧降解 TA 污泥的驯化过程有促进作用。这种促进作用可以分成两个方面，一是通过反硝化作用提供的能量直接促进菌体生长，使降解 TA 的微生物群体在绝对数量增加上占优势；另一方面，与此同时，对 TA 降解能力的形成有诱导作用。这种诱导作用并不是直接的，而是由于反硝化作用提供的较高的能量使得微生物群为满足生长要求而造成的对碳源底物的利用的进一步推动力造成的。

(2) 从反硝化作用到产甲烷作用的转化约需 2—3 周时间，逐渐减少硝酸盐更为有利。

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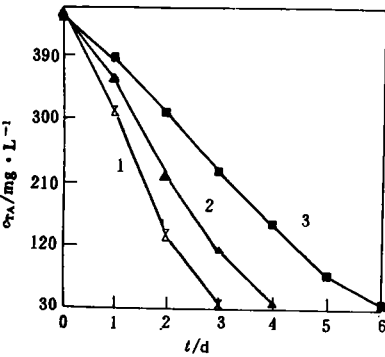


图 4 不同驯化方法进行至第 6 周时 TA 的降解情况
1. 逐渐停止加硝酸盐 2. 停止加硝酸盐 3. 产甲烷驯化

Sci., **17**(4), 1996, pp. 39—40

To study an interaction between *S. obliquus* and N-(2, 4-dimethylphenyl)-N'-methylformamidine, a standard method of algal bioassay for evaluating the toxicity of toxic chemicals was applied and 96 h-EC₅₀ of N-(2, 4-dimethylphenyl)-N'-methylformamidine on inhibition of *S. obliquus*'s growth was calculated as 6.5 mg/L. It was found that N-(2, 4-dimethylphenyl)-N'-methylformamidine can not be biodegraded by *S. obliquus* at the initial concentration of 2, 4 and 8 mg/L respectively.

Key words: *Scenedesmus obliquus*, N-(2, 4-dimethylphenyl)-N'-methylformamidine, algal bioassay, biodegradation.

A Study on the Selective Inhibition of Immobilized Acetyl Cholinesterases of Different Biosources by Organophosphorus insecticides.

Yu Xiaoying (Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002); *Chin. J. Environ. Sci.*, **17**(4), 1996, pp. 41—43

The enzyme electrode method was used to study the selective inhibition of acetyl cholinesterases (AChE) extracted from three different biosources by organophosphorus insecticides. It was found that the inhibition extent of AChE by DDVP follows the order of fly, electric fish, chicken liver. In addition the capacity of five kinds of insecticides to selective inhibition AChE extracted from electric fish was studied. It was found that 9.8×10^{-8} mol/L phoxim is sufficient enough to inhibit 10% of AChE's mobility of electric fish. The detection limits of various kind of insecticides are also presented in this paper. The experiment also showed that in the range of 20—45°C temperature would exert almost no influence on the mobility of AChE. The optimum pH value, ionic strength and the mechanism of selective inhibition which affect the mobility of AChE were discussed.

Key words: organophosphorus insecticides, acetyl cholinesterases, selective inhibition, enzyme electrode.

Research of Upflow Solid Reactor (USR) Treating Chicken farm wastewater at Anaerobic Digestion Condition. Zhou Mengjin et al. (Dept. of Biology, Capital Normal University, Beijing 100037); *Chin. J. Environ. Sci.*, **17**(4), 1996, pp. 44—46

The paper presents the result of Chicken farm

wastewater anaerobic digestion in upflow solid reactor (USR) at 35°C. The influent concentration was as follows: COD: 41900—61500 mg/L, SS: 50—60 g/L, TVA: 3174 mg/L, pH = 6.61. After 67 days of USR proceeding, the loading rate of USR reached to 10.45 g/(L·d), gas production rate achieved 4.88 L/(L·d), and average amount of CH₄ was 59.75% in which, the COD removing rate increased to 86.62%. At 5 days of HRT, the SRT was 24.8 d, SS removing rate was 66.16%.

Key words: upflow solid reactor (USR), Chicken farm wastewater, anaerobic digestion.

Preparation of Compound Granulated Adsorbent of Attapulgit and Studies on Its Adsorbability to Lead.

Qin Fei, Xu Ouyong (Dept. of Environ. Sci. and Eng., Nanjing University, Nanjing 210093), Jiang Tingda (Research Center for Eco-Environmental Sciences, Chinese Academy of sciences, Beijing 100085); *Chin. J. Environ. Sci.*, **17**(4), 1996, pp. 47—50

The granulated adsorbent of Attapulgit (AT) with some additive which includes cement (SN), quartz sands (SS) and steel crumbs (CS) was researched in order to produce a practical adsorbent for removal of lead in the waste water. The manufacture progress of granulated adsorbent and its adsorbability were discussed in detail. Optimum adsorbent is AT-SS among adsorbent of AT-SS, AT-SN and AT-CS. It has a capacity of adsorbing lead of 500 mg/g under the static conditions and of 60 mg/g under the dynamic conditions when it was manufactured at a AT-SS mixing ratio of 5 : 1 and by roasting at a temperature of 700°C for 120 min. The penetration time is 20 h and the regeneration rate is 48.3% with the current velocity of 1.5 ml/min. The Pb concentration of effluence is lower than standard within 236 times bed volume at the intake concentration of 200 mg/L.

Key words: wastewater treatment, adsorbent, lead, attapulgit, cement, quartz sands, steel crumbs.

Effect of Nitrate on Acclimatic Process for Terephthalic Acid Anaerobic Degradation. Li Xiaoming et al. (Dept. of Biotechnology, Wuxi University of Light Industry, Wuxi 214036); *Chin. J. Environ. Sci.*, **17**(4), 1996, pp. 51—53

Nitrate can promote the acclimatic process for

terephthalic acid (TA) anaerobic degradation. Experiment results indicated that nitrate accelerated sludge growth by denitrification and at the same time, more microorganisms or groups degrading TA were induced and formed. After six-week, the specific TA degradation rate reached 18.75 mg/(gVSS · d) and 10.28 mg/(gVSS · d) respectively by denitrify and methanogenic acclimation. The results also showed that it is possible to transfer TA degradation from denitrification to methane fermentation smoothly within 2—3 weeks.

Key words: nitrate, terephthalic acid (TA), acclimation, anaerobic degradation.

Reclamation Treatment of the Oil Refinery Wastewater Sludges by Sulphuric Acid Catalytic Carbonification. Yang Runchang and Zhou Shutian (Dept. of Chem. Eng., Xiangtan Univ., 411105); *Chin. J. Environ. Sci.*, 17(4), 1996, pp. 54—56

The results from the study showed that the sulphuric acid may allow sludges in the wastewater to carbonize and then separate from the wastewater under the conditions of applied pressure of 0.5—0.7 MPa, temperature of 150—170°C and pH of 1.7—1.8. The granular activated carbon can be produced using the carbon cinder carbonized from wastewater sludges by KHCO_3 activation. The main quality indices of the product are better than GB/T 13804-92 (China) secondary granular activated carbon. It was found that catalytic carbonification of sludges is lower cost approach of treating wastewater sludges from oil refinery with waste acid.

Key words: wastewater sludge, reclamation, activated carbon, oil refinery wastewater treatment.

Performance of Ultrafine Fe_2O_3 for High Temperature Removal of H_2S . Hou Xianglin et al. (State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001); *Chin. J. Environ. Sci.*, 17(4), 1996, pp. 57—58

High temperature removal of H_2S is very important in IGCC process. Using ultrafine particles of Fe_2O_3 as H_2S sorbent at high temperature was described in this paper, influences of particle size and temperature were studied, performance of Fe_2O_3 particles prepared by supercritical fluid drying was compared with analytical reagent and

Fe_2O_3 particles prepared by amorphous citrate precursors. Sulfur capacity increased as particle size decreased. Breakthrough time became shorter with increase of temperature. Compared with other metal oxides, sulfur capacity of Fe_2O_3 was higher.

Key words: ultrafine Fe_2O_3 , high temperature desulfurization, H_2S sorbent.

Preparation of Flocculant PFCS and Study on Its Properties. Sun Jianhui et al. (Environ. Sci. Institute of Henan Normal University, Xinxiang 453002); *Chin. J. Environ. Sci.*, 17(4), 1996, pp. 59—61

New inorganic polymeric flocculant poly sulfuric chloride ferri ferrous (PFCS) has been prepared by using dissolving rolling waste steel residue with mixing acid H_2SO_4 -HCl as raw material. The flocculating effect of PFCS has been tested and compared with that of poly sulfuric ferri ferrous (PFS). The experimental results showed that the flocculating effect and removing turbidity are very good in pH range of 6—9. The quantity of PFCS was only 10 mg/L when Yellow River water was treated from 425 turbidity degree to below 5 degree, but the least quantity of PFS was 25 ml/L at the same flocculating conditions. The flocculating effect of PFCS is much better than that of PFS at the same conditions.

Key words: poly sulfuric chloride ferri ferrous, flocculant, rolling waste steel residue, resource recovery.

Study on the Preparation of Polyaluminum Ferric Chloride from Gangue. Gao Baoyu et al. (Dept. of Environ. Eng., Shandong University, Jinan 250100); *Chin. J. Environ. Sci.*, 17(4), 1996, pp. 62—63

Poyaluminum ferric chloride (PAFC), a new type of inorganic flocculant, was prepared by gangue, a kind of waste from coal-mine, and hydrochloric acid as raw materials. The structure of PAFC was studied by transmission electron microscope (TEM), IR spectroscopy and X-ray diffraction. The effect of PAFC in industrial wastewater treatment was tested. The experimental results showed that it is feasible to prepare PAFC from gangue; PAFC produced is the compound of polyaluminum chloride and polyferric chloride. After the wastewaters from coal-mine and oilfield were treated with PAFC in 40 mg/L, the removal ratios of COD, SS and oil are about