

固定化细胞厌氧-好氧工艺处理四环素结晶母液的实验研究*

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摘要 用 PVA 固定化球和厌氧-好氧 IMC 技术处理四环素结晶母液, 结果表明: 当总停留时间为厌氧 24h(35℃), 好氧 6h 时, COD 和四环素的去除率分别为 96%。容积负荷(COD)2.07kg/(m³·d), 较普通法容积负荷提高 16.3%, 产气量提高 4.57 倍。此方法具有系统运行稳定, 容积负荷高, 产泥量少等优点。

关键词 厌氧-好氧处理系统, 四环素结晶母液, 固定化细胞。

固定化微生物细胞(Immobilized Microbial Cell, 简称 IMC)技术是 60 年代从固相酶基础上发展起来的, 在废水处理领域, 日益受到国内外专家和学者的重视, 并进行了较为广泛的研究^[1-5]。将 IMC 技术应用于制药废水的处理目前还鲜见报道。本文就制药废水有代表性的四环素结晶母液作为研究对象, 进行了 PVA 固定化球的性能和用厌氧-好氧 IMC 技术处理四环素结晶母液的研究。目的在于不仅对新包埋剂的性能进行初步研究, 还为处理四环素结晶母液提供一种可能的方法, 也将为 IMC 技术应用于其它难生物降解的特种废水处理提供某些技术上、方法学上的参考。

1 试验装置及方法

1.1 试验装置

IMC 厌氧-好氧两段法实验装置见图 1。

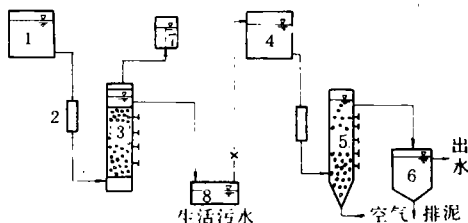


图 1 IMC 厌氧-好氧两段法试验装置

1. 4. 8. 贮水池 2. 进水流量调节器 6. 沉淀池
3. 厌氧反应器 5. 好氧反应器 7. 沼气贮气瓶

IMC 在厌氧反应器内以固定床式存在, 填充率约 50%; 好氧反应器内以流化态存在, 填充率约 10%; 2 个反应器容积分别为 400ml 和 450ml。总停留时间 30h, 其中厌氧段 24h, 好氧段 6h, 采用 V-0.1/10 型空气压缩机曝气。厌氧段采用 35℃ 中温发酵, 好氧段为常温。

1.2 IMC 的制备

选择包埋方式制作固定化细胞, 包埋剂经优化选择定为聚乙烯醇^[6](Polyvinyl Alcohol, 简称 PVA)。由于 IMC 的活性、强度决定于细菌包埋量、PVA 浓度和聚合时间, 本实验首先应用正交试验法, 以降解 COD、四环素(Tetracycline 简称 TC)的活性为指标, 参考球的强度、成球性能等因素, 选择出最佳、优化组合的包埋条件, PVA 的最终浓度为 7%—9%, 交联时间为 16—18h, 最高包菌量为 50%。

将 15%PVA 水溶液与用四环素废水驯化成熟的厌氧和好氧污泥(离心 3000r/min, 10min)按 1:1 分别充分混合后, 滴加到饱和硼酸溶液中, 室温下聚合 24h, 取出冲洗, 分别得到直径为 2—5mm 的厌氧和好氧固定化细胞小球。

1.3 废水水质

四环素结晶母液经回收草酸**后的废液,

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** 李振瑜, 清华大学环境工程系硕士论文。1989

COD 为 12000mg/L 左右,pH 为 3—5。经一定稀释、并对 pH 调整后作为试验水样。

2 结果和讨论

2.1 包菌量与 COD、TC 去除率的关系

厌氧菌固定化小球包菌量不同,COD、TC 去除率及达到最大去除率所需时间不同。见图 2、3。

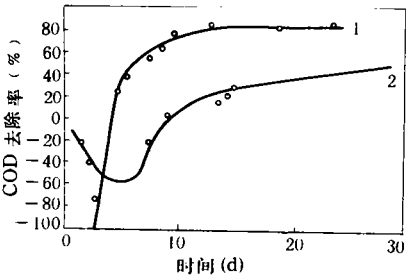


图 2 固定化小球包菌量与 COD 去除率的关系
1. 包菌量 50% 2. 包菌量 13%

低包菌量(13%)的 PVA 小球的 COD 去除率分不同阶段,达最大去除率 40%—50%需时间长约 14d。高包菌量(50%)PVA 小球,只需 6d 去除率达 40%,14d 时去除率高达 75%,维持此状态运行了 3 个月。无论低包菌量还是高包菌量,运行初期的 COD 去除率均为负值,它是由于 PVA 未交联的单体溶出造成出水 COD 值增高。

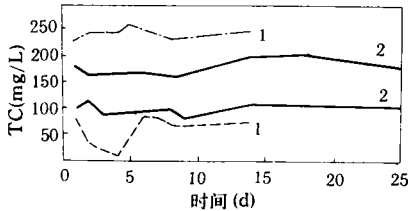


图 3 固定化小球包菌量对 TC 去除率的影响
1. 包菌量 50% 2. 包菌量 13%

从图 3 可见,运行 25d,包菌量为 13%的小球 TC 去除率维持在 30%—50%,而运行 15d,50%包菌量的小球 TC 去除率在 80%—90%。停留时间 1d。

因此,在保证球的强度不受影响的前提下,

提高包菌量是提高去除率行之有效的方法。

2.2 运行中 PVA 球重量变化

将做好的 PVA 球,在未投入运行前,用滤纸吸干表面水分,天平称重,再测小球体积,得到小球比重见表 1。将此小球投入运行,球的重量变化见图 4。

表 1 PVA 菌球运行前物理性能

条件	细胞湿重 (g)	IMC 湿重 (g)	IMC 体积 (cm ³)	IMC 湿比重 (g/cm ³)
厌氧 50% 包菌	35.8	71.5	67.5	1.06
好氧 50% 包菌	17.3	34.5	33.8	1.02

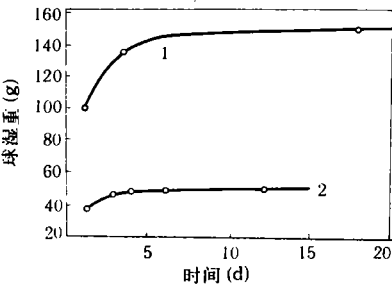


图 4 PVA 包菌小球运行过程中重量变化
1. 包菌量 50%厌氧 2. 包菌量 50%好氧

PVA 包菌小球,在废水中体积膨胀率较大,厌氧小球和好氧小球的膨胀率分别为 83%和 43%。膨胀率达一定限度后维持恒定。取出室温风干,又可恢复原状。运行中小球重量增长缓慢,原因一是受小球内部空隙空间限制,二是抗生素抑菌作用使细菌增殖较小。

2.3 厌氧-好氧工艺连续运转

厌氧-好氧反应器连续运转处理四环素废水,系统达稳定处理效果见表 2、3。可见固定化细胞的厌氧-好氧工艺运行稳定,厌氧 COD、TC 去除率分别在 75%和 85%。好氧 COD、TC 去除率在 80%和 60%左右。没有污泥上浮和跑泥现象,系统的耐受冲击负荷的能力明显加强。

2.4 普通 A/O 系统^[7]和 IMC A/O 系统比较

2 系统处理四环素废水有较大差异(表 4)。由于固定化细胞提高了反应器内的菌体浓度,因

表 2 IMC 厌氧反应器运行结果¹⁾

运行日期	进水	COD 出水	去除率	进水	TC 出水	去除率
1989 年	(mg/L)	(mg/L)	(%)	(mg/L)	(mg/L)	(%)
11-02	1775.1	501.3	71.4	238.0	43.3	81.8
11-03	1842.3	497.1	73.0	241.0	39.7	83.5
11-05	2012.3	513.7	74.5	239.6	36.3	84.9
11-07	2356.6	625.3	73.5	249.7	35.3	85.9
11-09	2614.1	670.3	74.3	253.0	35.0	86.5
11-14	2081.6	424.5	79.6	245.0	17.1	93.0
11-17	1918.4	493.6	74.3	240.0	16.8	93.0
11-21	2537.6	667.5	73.7	251.5	32.7	87.0

1) $V=400\text{cm}^3$ HRT=24h $t=35^\circ\text{C}$ pH=8.5

表 3 IMC 好氧反应器运行结果¹⁾

运行日期	进水	COD 出水	去除率	进水	TC 出水	去除率
1989 年	(mg/L)	(mg/L)	(%)	(mg/L)	(mg/L)	(%)
11-02	501.3	110.2	78.0	43.3	16.1	62.8
11-03	497.1	112.4	77.4	39.7	14.8	62.7
11-05	513.7	109.5	78.7	36.3	17.3	52.3
11-07	625.3	103.7	83.4	35.3	15.4	56.4
11-09	670.3	120.6	82.0	35.0	14.0	60.0
11-14	424.5	93.6	78.0	17.1	7.3	58.0
11-17	493.6	91.7	81.0	16.8	7.0	58.0
11-21	667.5	107.3	83.9	32.7	15.1	53.8

1) $V=45\text{cm}^3$ HRT=6h 常温

表 4 普通 A/O 系统和 IMC A/O 系统实验结果
与运行参数比较

项目	普通 A/O 系统	IMC A/O 系统
停留时间(h)	24/6	24/6
温度(℃)	35/常温	35/常温
COD 进水(mg/L)	2000—2400	2000—2600
COD 出水(mg/L)	90—150	90—120
COD 去除率(%)	93	96
COD 体积负荷 $[\text{g}/(\text{m}^3 \cdot \text{d})]$	1.78	2.07
TC 进水(mg/L)	170—250	250
TC 出水(mg/L)	20	<10
TC 去除率(%)	92	96
TC 体积负荷 $[\text{g}/(\text{m}^3 \cdot \text{d})]$	0.16	0.17
NH ₄ -N 进水(mg/L)	334.6	334.6
NH ₄ -N 出水(mg/L)	130.7	43.8
NH ₄ -N 去除率(%)	61	86.9
产气率 $[\text{CH}_4\text{ml}/\text{lg 湿泥} \cdot \text{d}]$	2.8	15.6
$[\text{CH}_4\text{ml}/(\text{m}^3 \cdot \text{d})]$	226.2	400.4
污泥沉降性能	差(上浮及跑泥)	好
气、液、固三相分离	难	容易
产泥量	少	极少

此处理能力提高,容积负荷(COD)由 1.77kg/($\text{m}^3 \cdot \text{d}$)增加到 2.07kg/($\text{m}^3 \cdot \text{d}$),提高了 16%。

同时,IMC 法是一种固定化增殖细胞的方法,产泥量小,PVA 的多孔结构对污染物有吸附作用,使得四环素去除率提高并稳定维持在 96%左右。

IMC 法与普通 A/O 法相比,避免了运行中经常出现的污泥上浮问题,有效地防止了菌体流失。气、固和液三相分离良好,便于管理和操作。

甲烷产率成倍增长,这是 IMC 法的又一优势,多孔结构的固定化小球为甲烷菌提供了适宜的生长环境,并减缓了外部不利条件对球内甲烷菌生长的影响。同时氨氮去除率增加 25.9%,这是由于 IMC 特殊多孔结构造成的污染物质在球内的累积,致使硝化、反硝化反应更趋完全。

但是由于时间关系和实验条(下转第 77 页)

表 8 叠氮化钠溶液排除 NO₂⁻ 干扰的结果¹⁾

NaNO ₂ (mg/L)	0.00	0.10	0.20	0.50	1.00	2.00	3.00	4.00	5.00
吸光度	0.273	0.268	0.269	0.272	0.276	0.270	0.272	0.271	0.270

1) 胂含量 0.100mg/L, 加 1% 叠氮化钠 1ml

1ml 叠氮化钠摇匀, 再进行测定, 可排除 NO₂⁻ 的干扰。

4 结论

含胂废水用对二甲氨基苯甲醛分光光度法测定, 操作简便, 分析速度快, 灵敏度高, 干扰物质少。经 8 个实验室对 0.100、0.500、0.800mg/L 标准溶液的验证, 实验室内标准偏差为 3.7%、

0.9%、0.6%。实验室间相对偏差 4.4%、1.3%、0.9%。加标回收率在 88%—110% 之间。符合水和废水监测的要求。

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(上接第 31 页) 件限制, IMC 菌球充填率没有达到最佳水平, 若提高此项指标, 预计 COD 去除率将会大大提高。

3 结论

(1) 应用固定化细胞技术, 采用厌氧-好氧工艺处理四环素结晶母液(经回收草酸并稀释约 4 倍和调整 pH 值) 是可行的。效果优于普通 A/O 法, 容积负荷提高 16%。

(2) 固定化 PVA 小球内部的多孔结构对污染物有吸附作用, 有利于四环素的降解。同时, 甲

烷菌在球内部生长良好, 由于固定化对外界条件的耐受压力增大。

(3) 固定化法防止了污泥的上浮, 菌体流失, 同时气、液、固三相易于分离, 便于管理。

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(上接第 47 页) 洗涤剂(ABS)、总铬(Cr_T) 等污染物的净化率可达 50%—70% 以上。

(2) 污水在粗粒沉积物中的渗透属氧化条件。间歇式污水注入有利于产生较多的腐殖质, 腐殖质对 Mn(Ⅰ) 有较强的离子交换吸附和螯合作用, 使 Mn(Ⅰ) 的转化率达 76.15%; 而连续注入试验对 Mn(Ⅰ) 的转化率只有 24.7%。

(3) 污水在粗粒沉积物中的入渗有利于硝化作用进行, 使污水中的 NH₄⁺-N 大部分转化为 NO₃⁻-N, 渗出液中 NO₃⁻ 浓度大于污水供给液。尤其是间歇式污水注入, 经 1.5m 厚的粗粒沉积层, 渗出液中 NO₃⁻ 浓度增长近 1 倍。

(4) 尽管薄层粗粒松散沉积物对污水具有净化能力, 但净化率是有限的, 加之粗粒沉积物易

于污水入渗, 随着污水入渗时间的延续, 其净化能力还会降低。因此, 在地下水浅埋的粗粒沉积物分布地区, 应严格限制污水直接排放和渗入, 以保证地下水源免遭污染。

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Abstracts

Chinese Journal of Environmental Science

maximum pb^{2+} uptake capacity was 88mg/g. *R. nigricans* can be eluted and regenerated with a 0.5mol/L HCl solution and a NaOH solution.

Key words: *Rhizopus nigricans*, adsorption, heavy metals, wastewater treatment.

Adsorption Behaviour of Herbicide Linuron in Soils. Liu Weiping et al. (Dept. of Chem. Zhejiang Univ., Hangzhou 310027); *Chin. J. Environ. Sci.*, 16(1), 1995, pp. 16—18

The adsorption behaviour of herbicide linuron in four soils differing in their physico-chemical properties, has been studied using a batch technique. Adsorption data could be fitted to a Freundlich-type equation. The value of the exponent in the fitted Freundlich isotherms varied from 1.11 to 1.28, and K_f varied widely for four soils (from 3.88 to 93.84). Adsorption was found to be better correlated with five times OM% plus Clays% after dividing soil pH value ($r=0.996$). The adsorption from chloroform solution of linuron on Fe^{3+} , Al^{3+} , Ca^{2+} and K^+ exchanged bentonite sample was also investigated. The some bonding mechanisms, hydrogen-bond, coordination bond and ionic bond, between herbicide to soil components were supposed.

Key words: linuron, soil, bentonite, humic acids, bonding mechanism.

Application of Ferrous-Hydrogen Peroxide Process for the Treatment of Wastewater from Dye Intermediate DSD Acid Manufacturing Processes. Zhu Wanpeng, Yang Zhihua et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, 16(1), 1995, pp. 19—22

A pretreatment method for the biological treatment of wastewater from DSD acid manufacturing processes, a refractory dye intermediate wastewater, based on combined Fe^{2+} - H_2O_2 oxidation and coagulation-flocculation, has been developed. When the wastewater was treated with Fe^{2+} - H_2O_2 oxidation ($[\text{Fe}^{2+}] = 150\text{mg/L}$, $[\text{H}_2\text{O}_2] = 7\text{g/L}$) after a flocculation using an organic flocculant TS-1 at a dosage of 3g/L, the overall COD and colour removals were 64% and 62%, respectively. BOD_5/COD value of the treated wastewater was 0.3. Fe^{2+} - H_2O_2 oxidation treatment can reduce the solubility of organic molecules with sulfonic group and increase the efficiency of coagulation treatment. The COD and colour removals were both more than 90% when FeCl_3 was used as a coagulant which dosages of two stages coagulation were 5g/L and 2g/L after a Fe^{2+} - H_2O_2 oxidation pretreatment at a H_2O_2 dosage of 2g/L.

Key words: ferrous-hydrogen peroxide, DSD acid,

dye intermediate, wastewater treatment.

Study on the Interaction between *Chlorella pyrenoidosa* Chick and Diethyl Phthalate. Yan Hai, Ye Changming et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 16(1), 1995, pp. 23—25

The standard method of algal bioassay for evaluating toxicity of toxic chemicals was applied and the 96h- EC_{50} of diethyl phthalate (DEP) inhibiting the growth of *Chlorella pyrenoidosa* was calculated as 80mg/L. It was found that *C. pyrenoidosa* was able to accumulate and biodegrade DEP. Accumulated amount of DEP and biological concentration factors (BCF) reached maximum values (9.83 mg/g, 205) at 12 h. As time went on afterward, accumulated amount declined gradually with time and reached a minimum value (1.8 mg/g) at 96 h, and BCF also decreased gradually with time before 72 h and reached minimum (80) at 72 h, but after 72 h, BCF increased gradually with time and reached 91 at 96h. Average biodegraded amount of DEP per day was 7.3 mg/L and average biodegradation rate per day was 14.6%. If using kinetic equation of $-dc/dt = K N r$ to fit the biodegradation process, the average relative deviation between calculated values and observed values was 4.0%.

Key words: *chlorella pyrenoidosa* chick, diethyl phthalate, algal bioassay, accumulation, biodegradation.

Joint Toxicity of Selenium and Fluoride ions to Harpacticoida copepod, *Nitocra spinipes*. Xiu Ruiqin et al. (Institute of Environ. Health and Eng., Chinese Academy of Preventive Medicine, Beijing 100050); *Chin. J. Environ. Sci.*, 16(1), 1995, pp. 26—28

The toxicity of selenium and fluoride ions were determined on bioassay of harpacticoida copepod, *Nitocra spinipes*. Median lethal concentration (96h LC_{50}) of selenium and fluoride were 9.2 (7.4—15) mg/L and 290 (284—296) mg/L, respectively. Three combinations of selenium and fluoride were tested (1:10, 1:20, 1:30 ratio of selenium to fluoride). The methods of toxic unit analysis and Marking's additive index were used to evaluate the joint toxicity. The results showed that the joint toxicity of selenium with fluoride ions were antagonism on the harpacticoida copepod.

Key words: selenium, fluoride, joint toxicity, *Nitocra spinipes*.

Treatment of Spent Tetracycline Liquor by Using an

Abstracts

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Immobilized-Microbial-Cell A/O Process. Wang Lei . (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085), Yu Yuxin (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, **16** (1), 1995, pp. 29—31

Immobilized-microbial-cell (IMC) technology, a new technique for biological wastewater treatment, was used to treat a spent tetracycline liquor. The experimental results showed that the removals of both COD and tetracycline were 96% at a COD loading of 2.07 kg/(m³ · d). As compared with a conventional A/O process, there was an increase of COD loading by 16.3% and of gas production by 4.57 times. The IMC technology was found to have some further advantages, including a more stable operation and allowing a higher pollutant loading and less sludge generation.

Key words: anaerobic-aerobic process, tetracycline, immobilized microbial cell.

Flux of N₂O Emission from the Fields in a Wheat and Maize Rotation System. Zeng Jianghai et al. (Institute of Agricultural Modernization, Chinese Academy of Sciences, Shijiazhuang 050021), Song Wenzhi et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 32—35

Nitrous oxide fluxes from the fields in a wheat and maize rotation system were studied in the North China Plain from September 25, 1992 to September 21, 1993. The total emission of N₂O was also estimated according to the fluxes of nitrous oxide measured in a year period. The fluxes of N₂O are 10.6—24.2 μg N/(m² · h) with the correspondingly annual emission of 0.93—2.11 kg N/(hm² · a). The N₂O emissions from urea-fertilized and organic-fertilized plots account for about 0.54% and 0.70% of the amount of applied fertilizers, respectively.

Key words: N₂O, flux, emission, environmental factor.

Study on the Removal of Odor Gas H₂S by a Coaxial Streamer Corona. Liu Linmao et al. (Dept. of Environ. Sci., Northeast Normal Univ., Changchun 130024); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 36—38

The pulsed streamer corona have been used to remove odor (H₂S). The H₂S removal efficiency and power utilization efficiency were compared in the cases of negatively pulsed voltage, positively pulsed voltage and DC voltage. The results show that the

pulsed streamer corona is effective to remove H₂S. The negatively pulsed streamer corona was found to have a H₂S removal efficiency of 88% and a power utilization efficiency of 6.74g/(kw · h). In the same operating condition with negatively pulsed streamer corona, the positively streamer corona was found to have a H₂S removal efficiency of 45% and a power utilization efficiency of 2.27g/(kw · h).

Key words: coaxial streamer corona, H₂S, removal efficiency, power utilization efficiency.

Study on the Cultivation of Granular Sludge in a UASB reactor with a Foaming Porous Calcium Alginate Colloid. Xu Dandong and Xiao Hong (Dept. of Environ. Eng., Lanzhou Railway Institute, Lanzhou 730070); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 39—41

Based on the experiment, this paper describes the effects of foaming porous calcium alginate colloids, as the nucleus of biological granula and the promoter of granular sludge, on the acceleration of operation at the beginning of upflow in an anaerobic sludge bed reactor. It also indicates the process of producing calcium alginate colloids. In the reactor, sludge was cultivated immediately after the microorganisms were introduced, then the produced colloids were taken to mix with the microorganisms. After a continuous 20 day operation, the measurements showed that the content of CH₄ decreased to 70% and the removal rate of TOC reached 70% when calcium alginate colloids, as the nucleus of granula, were replaced by microorganisms with the sedimentation of biological granula at a rate of 300mm/min and a number of about 700 particles/ml. A satisfactory result was obtained by giving a granular sludge of high activities and better sedimentation performance.

Key words: granular sludge, UASB reactor, alginic acid, anaerobic treatment.

Hydrogen production from soybean wastewater by Immobilized Photosynthetic Bacteria. Liu Shuangjiang et al. (Institute of Microbiology, Chinese Academy of Sciences, Beijing 100080); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 42—44

This paper presents the results of hydrogen production from soybean wastewater by immobilized photosynthetic bacteria (IPSB). The results showed that the IPSB in sodium alginate could produce hydrogen from a wide range of the concentrations of soybean wastewater. When the concentrations of wastewater ranged from 7560 to 12600 mgCOD/L, the IPSB could maintain stable hydrogen production for 260 hours, with an average gas production rate