

# 锌对厌氧体系的影响及 5 种重金属离子抑制作用的比较\*

王菊思 赵丽辉 贾智萍 王正兰 郭 珩

(中国科学院生态环境研究中心,北京 100085) (北京市太阳能研究所,北京 100083)

**摘要** 研究在混合式厌氧消化器中锌离子对厌氧生物的抑制作用和不同的日加入量对厌氧体系的影响。实验结果表明,日加入锌低于 40mg/L,对体系无影响;日加入量为 70mg/L 和高于 109mg/L 时,对体系分别造成轻微抑制和严重抑制。同时,以体系中溶解态金属离子的浓度(mol/L)与体系中污泥含量(kgVS/L)的比值为依据,比较了 5 种金属离子对体系的抑制性强弱,其顺序为:Pb>Cu>Ni>Cr(VI)>Cr(III)>Zn。

**关键词** 抑制作用,厌氧消化,重金属。

厌氧发酵处理高浓度有机废水已被实践证明是一种有效的技术。一些研究表明,无机离子、特别是重金属离子对厌氧微生物有很大的影响<sup>[1-3]</sup>。在很多废水中,如某些食品加工废水和制药废水中常含有锌离子,其对厌氧过程影响的报道尚不多见。因而,研究锌对厌氧过程的影响规律,找出厌氧过程允许的最高的锌离子浓度,对把厌氧技术成功地应用在废水处理中有着重要的参考价值。本文采用混合式厌氧反应,以酒精液为基质,研究锌对厌氧过程的影响规律;比较了锌、铜、铬、镍和铅对厌氧体系的抑制作用。

现出来。

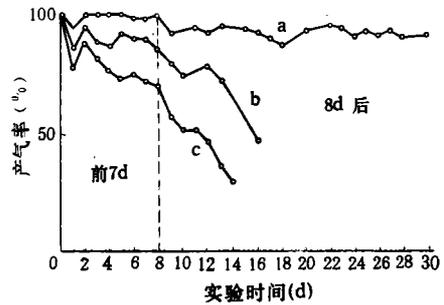


图 1 各反应器的相对产气率随时间的变化情况  
前 7d 加入锌离子浓度:a. 1 号反应器:36.4mg/L  
b. 2 号反应器:72.7mg/L c. 3 号反应器:109.0mg/L  
第 8d 以后加入锌离子浓度:a. 1 号反应器:72.7mg/L  
b. 2 号反应器:109.1mg/L c. 3 号反应器:145.5mg/L

图 1、2 和 3 分别给出了在试验周期内,3 个反应器的产气率、有机酸含量和 COD 去除率随时间的变化情况。比较 3 个图可看出,1 号反应器日加入锌量为 36.4mg/L,在试验周期内,产气率、COD 去除率和有机酸含量均未发生明显变化,表明此时厌氧体系未受任何影响;2 号反应

## 1 实验

厌氧生物实验在混合式厌氧反应器中进行。实验方法及条件同文献[4]。1、2 和 3 号反应器为试验组,每日的进料中加入硝酸锌。3 个反应器的日加入锌量分别为 36.4mg/L、72.7mg/L 和 109mg/L。4 和 5 号反应器为对照组。试验温度为 35±1℃,抑制试验期间,每 24h 测量产气体积,每 48h 测量出料中的 COD 值、有机酸含量和溶解态锌离子浓度,见文献[4]。

## 2 结果与讨论

### 2.1 锌加入量与体系受抑制程度的关系

厌氧生物过程受到的影响和抑制可由体系中产气率、COD 去除率和有机酸含量的变化表

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器的日加入量为 72.7mg/L,在前 10d,厌氧体系运行较稳定,3 个参数虽有变化,但不明显,但 10d 后,产气率下降至 47%,COD 去除率也下降至 80%,有机酸含量升至 2500mg/L,表明此时厌氧体系受到中度抑制;3 号反应器的日加入量为 109mg/L,比较 1 号和 2 号反应器,它的变化最为明显,在试验周期的前 10d,产气率和 COD 去除率有明显下降,分别为 69%和 83%,在以后的 5d 里,产气率急剧降至 28.8%,COD 去除率降至 68.4%,有机酸含量上升,高达 4180mg/L,表明此时厌氧体系受到严重的抑制。

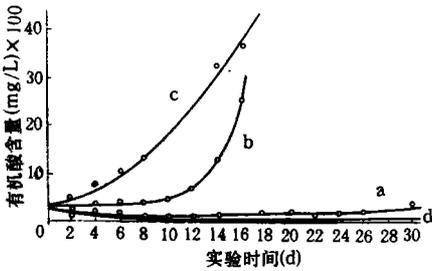


图 2 各反应器中的有机酸累积量随时间的变化情况  
a. 1 号反应器 b. 2 号反应器  
c. 3 号反应器 d. 4 号反应器

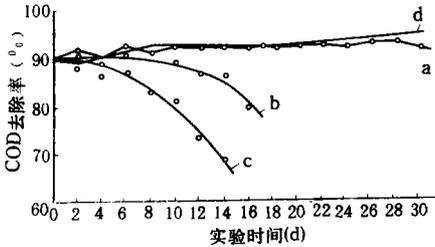


图 3 各反应器中的 COD 去除率随时间的变化情况  
a. 1 号反应器 b. 2 号反应器  
c. 3 号反应器 d. 4 号反应器

**2.2 厌氧体系中溶解态锌离子浓度与受抑制程度的关系**

有些研究者认为,金属离子对厌氧过程的抑制作用主要是溶解态的金属离子,厌氧体系中溶解态金属离子的浓度不仅与日加入量有关,也与厌氧体系本身的缓冲能力(使金属离子形成沉淀)有关。本研究发现,日加入锌量低于 40.0mg/

L 时,体系中的溶解态的锌离子浓度在 1.2mg/L 以下,并能持续地维持这一浓度,对体系几乎不产生不良影响。消化液中的溶解态离子的浓度远远低于日加入的浓度,说明厌氧体系有使锌生成沉淀(碳酸盐和硫化物)的能力,但这种能力是有限的,当日加入锌浓度为 109mg/L 时,体系中的溶解态的锌离子含量随锌的逐渐加入呈明显递增趋势,表明加入的锌量超过了厌氧体系能使其生成沉淀的容量,消化液中大量的溶解态的锌离子对厌氧微生物产生不良影响,使体系受到严重的抑制,图 4 给出了厌氧体系中溶解态锌离子浓度与产气率、有机酸含量和 COD 去除率变化的关系,体系中溶解态锌离子浓度的增加造成产气率线性下降,表明厌氧体系受抑制程度与溶解态锌离子浓度成正比。

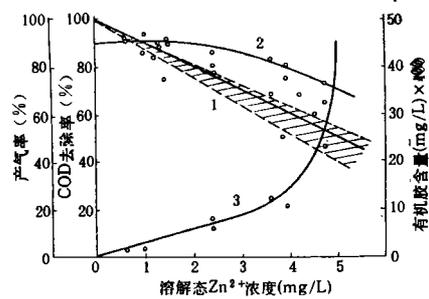


图 4 溶解态锌离子浓度与产气率、COD 去除率  
和有机酸含量的关系  
1. 产气率 2. COD 去除率 3. 有机酸含量

**2.3 锌的污泥负荷与抑制作用的关系**

厌氧体系对金属离子的承受能力与污泥含量有直接的关系,表 1 给出了污泥含量与日加入锌量的关系以及在不同的污泥负荷下,厌氧体系受到抑制的情况。当日加入锌量与污泥干重的比值低于 0.12%(1178mg/kgVS)时,对厌氧过程没有影响(产气率下降 5%);当该比值为 0.30%(3110mg/kgVS)时,产生中度抑制(产气率下降 20%—40%);该比值超过 0.4%(4150mg/kgVS)时,对厌氧过程产生严重的抑制(产气率下降 > 40%)。维持厌氧体系的正常运行应控制锌引入浓度小于 0.1%(1000mg/kgVS)。

表 1 厌氧体系中污泥对锌离子的负荷

反应器编号	污泥干重 (%)	日加入锌离子 / 污泥干重 (%)	溶解态金属离子浓度 (mg/L)	产气率下降 (%)	抑制程度
1	17.0	0.12	0.68	<5	无抑制
		0.24	0.89	5—20	轻度抑制
2	18.2	0.22	1.18	5—20	轻度抑制
		0.33	1.96	20—40	中度抑制
3	19.3	0.31	2.82	20—40	中度抑制
		0.41	4.23	>40	重度抑制

2.4 铜、锌、镍、铅、铬(Ⅲ)和铬(Ⅵ) 6 种金属离子对厌氧消化体系的抑制作用的比较

这种比较是以引起厌氧体系相同抑制程度所加入的金属离子量,消化液中溶解态金属离子量和厌氧消化污泥的金属离子负荷量为指标.关于厌氧体系受抑制程度 4 个等级的划分标准和表达方式见文献[4].为了使不同的厌氧反应器

之间有相对可比性,本文引入了污泥(干重)对体系中溶解态金属离子负荷这一概念来比较不同的金属离子对厌氧微生物毒性的大小,由于金属离子对厌氧微生物是以一个个离子起作用的,因此以毫摩尔数来表示金属离子负荷的实际含量为每单位重量干重污泥(kgVS)平均承受的溶解态的金属离子的毫摩尔数即:mmol/kgVS.表 2

表 2 铜、锌、镍、铅和铬对厌氧体系抑制作用的比较

金属离子名称	日加入量		溶解态金属离子/污泥干重 (mmol/kgVS)	产气率下降 (%)	抑制情况
	(mg/L)	(mmol/L)			
铜	<20	<0.32	<0.1	<5	无抑制
	20—60	0.32—0.95	0.1—1.6	5—20	轻度抑制
	60—90	0.95—1.42	1.6—2.5	20—40	中度抑制
	>90	<1.42	>2.5	>40	重度抑制
锌	<36	<0.56	<0.3	<5	无抑制
	36—109	0.56—1.67	0.3—0.6	5—20	轻度抑制
	109—145	1.67—2.22	0.6—1.3	20—40	中度抑制
	>145	>2.22	>1.3	>40	重度抑制
镍	<30	<1.51	<1.6	<5	无抑制
	30—60	0.51—1.02	1.6—2.5	5—20	轻度抑制
	60—109	1.02—1.86	2.5—3.5	20—40	中度抑制
	>109	>1.86	>3.5	>40	重度抑制
铅	<10	<0.05	<0.02	<5	无抑制
	10—109	0.05—0.53	0.02—0.04	5—20	轻度抑制
	109—181	0.53—0.87	0.04—0.09	20—40	中度抑制
	>181	>0.87	>0.09	>40	重度抑制
三价铬	<30	<0.58	<0.43	<5	无抑制
	30—72	0.58—1.39	0.43—0.77	5—20	轻度抑制
	72—145	1.39—2.79	0.77—1.37	20—40	中度抑制
	>145	>2.79	>1.37	>40	重度抑制
六价铬	<15	<0.29	<0.4	<5	无抑制
	15—73	0.29—1.40	0.02—0.45	5—20	轻度抑制
	73—109	1.40—2.10	0.45—1.53	20—40	中度抑制
	>109	>2.10	>1.53	>40	重度抑制

给出了几种金属离子引起厌氧体系不同抑制程度时的日加入浓度和溶解态金属离子的污泥负荷。从表 2 所列实验结果看到,在其它条件相同的厌氧体系中,引入不同种类的重金属离子,抑制作用各异,以其引起相同程度抑制作用所加入的金属离子量作比较,其作用强弱的顺序为:  $Pb > Cu, Ni > Cr(VI) > Cr(III), Zn$ ; 在相同的实验条件下,如果只考虑金属离子引入带来对厌氧体系的影响,则这种影响的大小即与日加入金属离子浓度有关,又直接与体系中存在的溶解态的金属离子有关,这是真正对厌氧微生物起毒害作用的因素。在大多数厌氧体系中,溶解态的金属离子与日加入的金属离子量有正相关性,即日加入金属离子越多,体系中存在的溶解态金属离子浓度也越高。以引起相同抑制程度各种金属溶解态离子浓度数值进行比较,离子浓度越低,说明其抑制作用越强,几种金属离子对厌氧微生物的抑制作用强弱顺序为:  $Pb > Cr(VI), Cr(III) > Zn > Cu > Ni$ 。这个顺序与以日加入量相比较的顺序是不同的。这种差异说明,厌氧微生物可以耐受较高浓度的镍离子,而对铬和铅离子的耐受浓度很低。因此,以溶解态离子浓度为依据作比较,镍离子的抑制作用最小,然而由于硫化镍的溶度积明显高于其它几种金属的硫化物,因此在消化液中的溶解态的镍离子浓度就远远高于其它金属的溶解态离子。随着试验时间的延长,体系中镍离子的浓度逐渐升高,并很快达到或超过厌氧微生物所能承受的浓度,与其它反应器相比,加入镍的厌氧体系更快地进入到抑制状态,即镍日加入

量较少的情况下,已对体系产生抑制作用,因此,以日加入量作比较,镍的抑制作用排在了前面。在应用厌氧生物技术处理废水的操作中,为保证厌氧体系的正常运行,较易控制的是金属离子的日加入浓度,因此以日加入浓度做为抑制作用的比较依据更有实用价值。为维持厌氧体系的正常运行,6 种金属离子在消化液中的浓度与污泥干重之比应分别控制在: 锌  $< 0.3 \text{ mmol/kgVS}$ ; 铜  $< 0.1 \text{ mmol/kgVS}$ ; 镍  $< 1.6 \text{ mmol/kgVS}$ ; 铅  $< 0.02 \text{ mmol/kgVS}$ ; 三价铬  $< 0.43 \text{ mmol/kgVS}$  和六价铬  $< 0.4 \text{ mmol/kgVS}$ 。

### 3 结 论

(1) 锌离子对厌氧体系的抑制程度随日加入量的增加而加重。维持厌氧体系正常运行的锌离子的日加入量应不高于  $40 \text{ mg/L}$ 。污泥对锌离子的负荷应抑制在  $1000 \text{ mg/kgVS}$  以下。体系中溶解态锌离子浓度低于  $1.0 \text{ mg/L}$  时,对厌氧生物过程基本上无抑制作用。

(2) 以日加入各种金属离子的浓度 ( $\text{mmol/L}$ ) 作为抑制作用强弱的比较依据,评价 6 种重金属离子产生相同程度抑制作用时的强弱顺序为:  $Pb > Cu > Ni > Cr(III) > Cr(VI) > Zn$ 。

### 参 考 文 献

- 1 Mosey F E. Water Poll. Control. 1976, 75, 10
- 2 Thomas D H et al. J. Water Poll. Control Fed. 1978, 50, 61
- 3 Alexandra Kouzell- Kaetsiri et al. Environmental Technology Letters. 1988, 9, 261
- 4 王菊思. 环境科学. 1991, 12(6), 2
- 5 王菊思. 环境化学. 1990, 9(6), 49

# Abstracts

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## Analysis of the Effects of Biofilm Thickness on Fluidised Bed Bio-Reactor (FBBR) Performance.

Zhou Ping et al. (Dept. of Environmental Engineering, Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, 15(2), 1994, pp. 1—5

A mathematical model of fluidised bed bio-reactor has been established and a large amount of experiment has been carried out to verify the validity of the model. The analysis of organic matter concentration profile in biofilm and the effects of biofilm thickness ( $\delta = 30\text{--}400\mu\text{m}$ ) on biomass concentration, effectiveness factor, effluent quality and the degradation rate of organic matter have been conducted in detail. The results show that the maximum organic degradation rate per unit volume of biofilm is 0.52kg COD/(L · d) when influent COD is 530mg/L and the optimal biofilm thickness is about 180 $\mu\text{m}$  in the experiment.

**Key words:** fluidised bed bio-reactor, effectiveness factor, biomass concentration, biofilm thickness.

## Study on the Treatment of Monosodium Glutamate Processing Wastewater in an External Air Lift Reactor.

Cheng Shupe, Cui Yibing et al. (Dept. of Environmental Science & Engineering, Nanjing University, Nanjing 210008); *Chin. J. Environ. Sci.*, 15(2), 1994, pp. 6—10

The biotechnique of external air lift reactor (EALR) was used for the treatment of monosodium glutamate processing wastewater to produce a single cell protein (SCP) with *Rhodospseudomonas sphaeroides*. The removal of BOD<sub>5</sub> was 92% under the following conditions; BOD<sub>5</sub>, 2750mg/L in the influent; K<sub>La</sub>, 242h<sup>-1</sup>; HRT, 12h; and the concentration of charcoal particle as a carrier, 10g/L. The species of microorganism, *R. sphaeroides*, has a protein content of up to 67.2% and a coefficient of SCP yield of 0.59kg (cell)/(kgBOD<sub>5</sub> · d). The process has a biological load of 1.68kg BOD<sub>5</sub>/(kg MLSS · d), which is higher than that either in an activated sludge process or in a PSB 4-stage system.

**Key words:** external air lift reactor, *Rhodospseudomonas sphaeroides*, monosodium glutamate processing wastewater, BOD<sub>5</sub>, biological load, oxygen transfer coefficient, single cell protein.

## Reclamation Treatment of Chrome Leather Scraps IX. The Molecular Weight and molecular Weight Distribution of Collagen Protein.

Jiang Tingda et al. (Research Center For Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 15(2), 1994, pp. 11—14

The molecular weight and its distribution of the

collagen protein were determined with a water-phase gel chromatography (WPGC). The collagen protein was separated from chrome leather scraps under different reaction conditions. In WPGC, distilled water was used as solvent, containing 0.02% NaN<sub>2</sub>, and dextran with a broad molecular weight distribution as standard. In the designed reaction time and pH value range, the number average molecular weight (M<sub>n</sub>) of collagen protein was below 4000, and the molecular weight distribution proves to be wide ( $d = \overline{M}_w/\overline{M}_n = 3.19\text{--}8.35$ ).

**Key words:** chrome leather scrap, molecular weight, gel chromatography.

## Assessment on the Biodegradability of Organics in Municipal Wastewater and the Measures for Controlling Its Refractory Organics.

Huang Xia, Zhang Xiaojian et al. (Dept. of Environmental Engineering, Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, 15(2), 1994, pp. 15—19

The organic compounds in a municipal wastewater were analysed by using GC-MS method and the biodegradability of the organics was discussed by calculating the first order reaction rate constant K<sub>b</sub> (20°C) for each of the organic compounds present in an aerobic biological treatment process. The results showed that 38 and 16 kinds of main organics existed in the influent and in the effluent, respectively, of the aeration tank in a municipal sewage treatment plant. The main refractory organics were found to be dibutyl phthalate and diisooctyl phthalate. Their effective control should be made by strengthening the pollution management at source or carrying out a pretreatment of wastewater before discharge into the public sewerage system.

**Key words:** GC-MS, biodegradability, municipal wastewater, refractory organics.

## Inhibitory Effect of Zinc on Anaerobic System and a Comparison with Other Four Heavy Metal Ions.

Wang Jusi, Zhao Lihui et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 15(2), 1994, pp. 20—23

The inhibition of zinc on an anaerobic biological system was studied. The results indicated that no effect was observed when a daily addition of zinc was less than 40mg/L, and a significant or serious inhibition was found when a daily addition of zinc was 70mg/L and over 109mg/L, respectively. In a comparison, the inhibition of five heavy metals to an anaerobic digestion can be ranked in a decreasing order of Pb > Cu > Ni > Cr(VI) > Cr(III) > Zn, in

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terms of the ratio of the concentration of dissolved ion (mg/L) to the activated sludge (kg VS/L).

**Key words:** anaerobic system, heavy metal, zinc.

**Analysis and Prediction on the Traffic Noises from an Elevated Express Compound Highway.** Chen Ziming, Lu Deming et al. (Dept. of Physics, Qingdao University of Oceanography, Qingdao 266003); *Chin. J. Environ. Sci.*, 15(2), 1994, pp. 24—28

Based on a section of the Jinan-Qingdao Express Highway in the suburbs of Qingdao City which is a typical compound highway of elevated structure, an analysis has been made on the relationship between its traffic noises and the factors involved. A mathematical model has been also established for predicting the traffic noises from an elevated express compound highway. It is found that the theoretical calculations based on this model are generally coincident with the actually simulated measurements.

**Key words:** elevated express compound highway, insonified zone, peak volume hour, running noise of a single vehicle.

**Influence of Different Carbon Sources on Denitrification.** Xu Yatong. (Dept. of Environmental Science, East China Normal University, Shanghai 200062); *Chin. J. Environ. Sci.*, 15(2), 1994, pp. 29—32

In a suspended sludge system, the rates of denitrification and carbon uptake can follow a zero-order reaction when the carbon supply was from an unlimited, single kind of carbon source at a suitable pH and temperature. It was found that a mixed volatile fatty acid (VFA) C-source resulted in a higher rate of denitrification than any of the individual VFA C-sources which formed the mixed one. Of the VFAs, acetate gave the highest rate of denitrification. The VFAs gave a higher rate of denitrification than their corresponding alcohols. The means of reducing the carbon consumption and the cost of treatment in a denitrification system had been also discussed.

**Key words:** biological denitrification, suspended sludge, carbon source, rate of denitrification, C-uptake rate.

**Simulation of Thermal Structure and Evaporation for Lakes.** Congzhi Zhou et al. (Teaching and Research Section for Water & Heating Logistic Engineering University, Chongqing 630041); *Chin. J. Environ. Sci.*, 15(2), 1994, pp. 33—37

An one-dimensional eddy diffusion model was used

for prediction of the annual vertical temperature profile and evaporation rate of a lake. The governing equation was a non-linear heat transfer equation assuming horizontal homogeneity. No lake-specific fitting of the parameters of the model was necessary. Eddy diffusivities were computed with Richardson Number. The heat exchange at the water surface was formulated by the energy balance approach, and the bottom of the lake was considered to be insulated. The governing equation was solved by finite difference. Computation was made for Lakes Colorado City and Calhoun. Quantitative and qualitative agreement between computed and measured temperature profiles was very good, with an error of less than 2°C. The computed annual evaporation capacity approached the one measured and the difference between them was only 5% of the measurement value.

**Key words:** lake, thermal structure, evaporation.

**Promoting the Electrolysis Efficiency of a Bipolar Electrolyser by Adding a Coated Activated Carbon.** Zhou Kanghan, Zhou Ding. (Harbin Institute of Technology, Harbin 150006); *Chin. J. Environ. Sci.*, 15(2), 1994, pp. 38—40

It has been found that improving the conditions of contact between particles in a bipolar electrolyser is a key to promoting its electrolysis efficiency. Such an improvement has been achieved by adding a coated activated carbon to the electrolyser and the satisfactory results were obtained. With a Proper formulation, the addition of a coated activated carbon at a ratio of 100 : 30 allowed the electrolysis efficiency to increase from 130% to 245% and a stable, uniform distribution could be kept during an operation for about 300h.

**Key words:** electrolysis efficiency, bipolar electrolyser, coated activated carbon.

**Ozone Layer Depletion, Aerosol Pollution and Solar UV-B Radiation at the Ground.** Wang Shaobin (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 15(2), 1994, pp. 41—44

Ozone layer depletion and aerosol pollution have an influence on the solar ultraviolet radiation reaching the ground. A computation indicates that the radiation amplification factor (RAF) for a DNA damage varies from 2.3 to 4.2 when a reduction in column ozone goes from 1% to 30%. Since the industrial revolution, the daily UV-B radiation in urban and rural areas has decreased by about 45% and 10%, respectively, that can be attributed to aerosol pollution. The computed UV-B radiation due to the ozone reduction in Beijing shows an increasing