• 45 •

庆大霉素和金霉素废水的处理试验研究

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摘要 对庆大霉素、金霉素及其混合废水的厌氧、好氧处理进行静态试验。结果表明,对于 COD 为 19240 mg/L 的庆大霉素废水,当厌氧反应时间为 3 d, 好氧 10 h 时, COD 去除率为 98.4%; COD 为 7740 mg/L 的庆大霉素和 金霉素混合废水(1:2),厌氧处理 2 d, 好氧 10 h 时, COD 去除 95.8%; 庆大霉素废水厌氧处理 3 d, 金霉素废水 厌氧处理 6 h,再将这 2 种废水混合进行好氧处理 4 h,其最终出水 COD 可小于 300 mg/L。 关键词 庆大霉素废水,金霉素废水,厌氧-好氧静态试验。

庆大霉素和金霉素属广谱抗生素,可抑制 多种(G⁺、G⁻)微生物。抗生素废水中含有发酵 的残余培养基质、发酵中间产物、被破坏的或 残余的抗生素、微生物菌丝体以及溶解于水中 的有机溶剂等。此类废水具有有机物浓度高、 悬浮物多、可生化性差的特点,一般须先与其 它有机废水混合或进行预处理以降低毒性和杀 菌力后再进行生物降解^[1-2],本文直接进行了 厌氧-好氧处理试验(静态),最终出水 COD 降 至 300 mg/L 以下,达到了制药行业排放标准, 为中试和生产性试验研究创造了条件。

1 试验概况

试验用废水是某抗生素厂多种生产废水中 选出的 COD 高、水量大的 2 股废水,其水质如 表 1 所示。由表 1 可见,这 2 种废水的 BOD₅/ COD 值均很低,属生物难降解废水。庆大霉素 废水呈暗红色浆状,悬浮物含量高且难以沉淀 分离,金霉素废水呈黄色,较为清澈。

表	1	试验	废水	质
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废水	pH	COD	BOD ₅	SS	NH ⁺ -N
		(mg/L)	(mg/L)	(mg/L)	(mg/L)
庆大霉素废水	6.5-6.8	20000	3700	12000	47
金霉素废水	33.6	1500	100	30	500

试验采用间歇进料方式,反应瓶容积5L, 接种污泥取自工厂排水沟底,试验温度为 30C--34C。

2 试验结果分析与讨论

2.1 废水可生化性试验

因原废水中含有残余的庆大霉素和金霉素, 对于微生物可能具有抑制作用,为此本试验采 用史氏发酵管进行厌氧产气试验,试验废水的 pH 均调至 7,污泥 VSS 浓度 12 g/L,发酵温度 40 C,试验结果如图 1 所示。



图1 厌氧产气试验结果

1. 葡萄糖 2. 金霉素废水 3. 庆大霉素废水 4. 污泥空白

由图 1 可见, 庆大霉素和金霉素废水的累 计产 CH4 曲线均在不投加底物的污泥空白产气 曲线之上, 这表明虽然这 2 种废水的降解速度 远小于葡萄糖, 但对微生物并没有抑制作用, 也可看出庆大霉素废水较金霉素废水难降解。

2.2 庆大霉素废水处理试验

2.2.1 厌氧静态试验

庆大霉素废水悬浮物含量很高,以前曾进

环境科学

行过混凝沉淀、气浮、板框压滤等预处理,但试 水直接进行厌氧消化的方法,结果如表2所示。 验结果均很不理想,故本试验采取庆大霉素废 在反应最初 0.5 d, COD 变化不大,而 SS

表 2 庆大霉素废水厌氧试验

累计时间 (d)	COD	COD 去除	SS (mg/L)		SS 去除	pН	VFA	BOD ₅ /COD
	(iiig/ 11/	(70)	(1.1.6, 2.)		(707		(ing/L)	
0	19240		11640			6.8	513	0.18
0.5	15630	18.8	1720		85.2	6.2		0.41
1	9755	49.3	860		92.6	6.4	662	0.43
1.5	3062	84.1					573	
2	2300	88.0	570	,	95.1	7.1		0.39
3	1380	92.8	550		95.3	7.1		0.28
4	969	95.0	409		96.5	7.1	525	0.15

的去除率高达 85.2%,表明在这一段时间内, 主要是废水中的悬浮物在微生物胞外酶的作用 下转化成溶解性的 COD 并水解产酸,致使 pH 下降而 VFA 上升,废水的可生化性得到了较为 明显的改善。SS 的去除基本在 1 d 内完成,而 COD 的去除作用主要是在 3 d 内完成的。随着 反应时间的延长,COD 及 SS 的去除效果均变 化不大,而 BOD₅/COD 值则逐渐下降。pH 值 2 d 后逐渐回升,VFA 下降,这是由于反应进入 了产 CH₄ 阶段,大量的 VFA 转化成 CH₄ 的缘 故。试验中污泥浓度为 20.9 g/L,庆大霉素废 水的产气率为去除 1 kgCOD 产沼气 0.45 m³。

2.2.2 好氧静态试验

厌氧预处理虽然大大降低了废水的 COD 和 SS,但残余的 COD 仍很高,故还必须进行好氧 后处理。好氧静态试验采用容积为 2 L 的反应 瓶处理厌氧出水,试验中污泥浓度为 2.7 g/L, COD 降解历时结果如表 3 所示。

表 3 庆大霉素废水好氧后处理 COD 历时变化(mg/L)

好氧后处理	厌	、氧处理时间(c	D	
时间(h)	2	3	4	
0	2300	1380	969	
2	875	543	579	
4	610	470	510	
6	594	413	460	
8	573	348	295	
10	551	303	260	
24	569	310	252	

$$\ln \frac{c-c_{\rm n}}{c_{\rm o}-c_{\rm n}} = -XKt \tag{1}$$

式中, c₀: t=0 时有机物浓度(mg/L); c: t 时有 机物浓度(mg/L); c_n:不可生物降解有机物浓度 (mg/L); X: VSS 浓度(g/L); K: 反应速率常 数[L/(gVSS • h)]。

可以认为废水经长时间曝气后,其残余的 COD 即为不可生物降解的部分,故经过 2、3、 4d 的厌氧处理和 24 h 好氧处理后,废水中残余 的不可生物降解量 c_n 约为 500、300、250 mg/ L。根据式(1)可求得其对应的好氧反应速率常 数 K 为 0.266、0.196、0.120 L/(gVSS · h)。 可见,随着厌氧时间的延长, c_n 逐渐减少,但好 氧反应速率也随之降低。

2.3 金霉素废水处理试验

2.3.1 好氧试验

因金霉素废水 COD 相对较低,故首先考虑 不经厌氧直接进行好氧静态和动态处理试验。 动态试验采用一总容积为 12 L 的完全混合曝气 池,进水 COD 维持在 1500 mg/L 左右。试验结 果如表 4 所示。

表 4 金霉素废水好氧试验结果

静态	<i>t</i> (h)	2	5	7	22
	COD(mg/L)	960	776	531	415
动态	HRT(h)	4.2	5.1	9.0	20
	COD(mg/L)	672	495	441	430

由表4可见,金霉素废水中含有较多的难降解物质,直接进行好氧处理,即使时间长达20h以上,最终COD仍高于400mg/L,不能达

到制药行业的排放标准(COD<300 mg/L)。 2.3.2 厌氧-好氧静态试验

厌氧-好氧处理静态试验所用金霉素原水 COD为1530 mg/L,用 NaOH 将其 pH 调至 7,

表5 金霉素废水厌氧-好氧静态处理结果(mg/L)

好氧时间(h)		0	2	4
厌氧时间	3h	829	509	245
	6h	792	341	188

试验条件与结果如表 5 所示。

由表 5 可见,金霉素废水只需短时间的厌

氧预处理,再经过4h的好氧后处理,COD即 可降至250 mg/L以下,厌氧预处理可大大提高 金霉素废水的可生化性。

2.4 混合抗生素废水处理试验

根据实际废水的组成, 按庆大霉素废水: 金霉素废水=1:2的比例配制混合废水, 进行 厌氧-好氧处理静态试验, 结果如表 6、7 所示。

由此可见, 混合废水经过 2 d 的厌氧处理, 再经过 10 h 的好氧后处理, 最终 COD 仍未达 到 300 mg/L 以下。

表 6 混合废水厌氧静态处理结果

<i>t</i> (d)	COD(mg/L)	COD 去除(%)	SS(mg/L)	SS 去除(%)	pН	VFA(mg/L)
0	7740		5376		7.0	864
1	3215	58.5	2417	55.0	6.7	912
2	875	88. 7	410	92.4	6.7	631

表 7 好氧静态后处理结果

<i>t</i> (h)	0	2	4	6	8	10
COD(mg/L)	875	405	410	392	354	326

2.5 治理方案的选择

从上述试验结果看,在实际工程中若混合 废水采用厌氧-好氧处理,当厌氧停留时间为2 d时,要使好氧出水 COD 小于 300 mg/L 是比 较难的。但试验发现金霉素废水经短时间的厌 氧反应和好氧处理后,COD 可低于 300 mg/L, 且金霉素废水量大,故可考虑将其作为稀释水: 首先将较难降解的庆大霉素废水单独进行较长 时间的厌氧处理,因其水量较小,所需反应器 容积不大;金霉素废水进行短时间的厌氧处理 后2股废水混合进行好氧处理。对于庆大霉素 废水,随着厌氧反应时间的延长,厌氧段 COD 去除率增大,而好氧段去除率下降,故可适当 延长厌氧停留时间,而缩短好氧处理时间,这 样在实际工程中可降低投资与运行费用。

综上所述,建议庆大霉素废水厌氧停留时间3d,金霉素废水厌氧停留时间6h,分别进行厌氧处理后再混合,进行停留时间为4h的 好氧后处理,此时总出水 COD 约为:

$$470 \times \frac{1}{3} + 188 \times \frac{2}{3} = 282 \text{ mg/L}$$

3 结论

(1)采用厌氧工艺可大大改善抗生素废水 的可生化性。

(2) 对于 SS 含量极高且难以沉淀的庆大霉 素废水, 厌氧工艺对 SS 的去除是有效的。

(3) COD 为 19240 mg/L 的庆大霉素废水, 当厌氧反应时间 3 d、好氧反应时间 10 h 时, COD 总去除率为 98.4%。

(4) COD 为 7740 mg/L 的混合抗生素废水,当厌氧反应时间 2 d、好氧反应时间 10 h 时,COD 总去除率为 95.8%。

(5) 庆大霉素废水与金霉素废水分别进行 厌氧处理较 2 种废水混合进行厌氧处理更为合 理。

(6) 庆大霉素废水厌氧处理时间 3 d、金霉 素废水厌氧处理 6 h、再将 2 种废水混合进行好 氧处理 4 h,其最终出水 COD 可能小于 300 mg/L。

参考文献

1 郭耀基.化工环保.1990,10(4):199
2 林锡伦.化工环保.1991,11(2):95

management and decision-making.

Key words: river basin management, model, QUAL2EU, non-point sources pollution, river water quality, reservoir.

Study on the Thermal Effects of Cooling Water from Power Plants on Young Mullet (*Liza* haematochlia Temminck and Schlegel). Ru Shaoguo (Marine Life College, Qingdao Ocean University, Qingdao 266003), Hou Wenli et al. (Dept. of Environ. Sciences, Northeast Normal University, Changchun 130024); Chin. J. Environ. Sci., 16(5), 1995, pp. 30-32

The title study was carried out by measuring various critical temperatures for young mullet. The results show that under the condition of a natural water temperature of 25°C, young mullet had its acvoidance temperature, TL₅₀, UILT, MWAT, CTM and short-term exposure maximum temperature of 34℃, 36.7℃, 38.75℃, 30.52℃, 40.82°C and 35.32°C, respectively. The areas where young mullet was sensitive to a thermal effect were mapped, and a temperature-time equation log $t(\min) = 17.9422 + 0.4202 T(C)$ and a safe temperature equation $T(C) = (\log 1440$ a)/b-2 were established. A high temperature shock of $\Delta T = 15^{\circ}$ C for 2 minutes led to a mortality of 25%, that of $\Delta T = 14^{\circ}$ for 5 minutes led to a mortality of 15% and the maximum tolerable ΔT was less than 15 °C.

Key words: cooling water from power plant, young mullet, thermal effect.

Comparative Study on Ecological Suitability of Cities Within a Region. Yang Yongtai (Foshan City's EPA, Foshan 528000): Chin. J. Environ. Sci., 16(5), 1995, pp. 33-37

The principles and specific indicators for urban ecological suitability were described. Based on the natures of urban ecosystems, the factors composition analysis and fuzzy maximum tree method were suggested to estimate the homogeneity and heterogeneity of the ecological suitabilities among cities within a region. By exemplifying the group of cities in the Pearl River Delta, the scores of compositional factors and the fuzzy sub-tree sets for the ecological suitabilities of cities were calculated. The results show that the method gave reasonable conclusions and was more practical.

Key words: urbon ecological suitability, composition factor, fuzzy maximum tree, comparative study.

Development of a Multifunctional Swell and Permeability Apparatus and Its Application to

the Permeability Test of Compacted Bentonite.

Zhou Kanghan, Li Guoding and Yu Ke (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): Chin. J. Environ. Sci., 16(5), 1995, pp. 38-40

A multifunctional swell and permeability apparatus has been developed and can be used for many different purposes, for example, the tests of soil for solidifiability, permeability and swellability. It was found that it is particularly useful in the study on a highly compacted and less permeable bentonite of $\rho > 1.5$ g/cm³. With this apparatus, a sample of a permeability in the range of 10^{-12} — 10^{-6} cm/s was precisely measured under the condition of a hydraulic gradient in the range of (2- $4) \times 10^3$. It is also useful to study those highly compacted, less permeable and swellable clays.

Key words: permeability apparatus, permeability, compacted bentonite.

Experimental Studies on Firing a Glazed Colored Glass-Brick from Chromic Slag. Wang Yongzeng et al. (Tangshan Longge Ceramic and Rere Farth Development Corp. Tangshan 063000): Chin. J. Environ. Sci., 16(5), 1995, pp. 41-44

Firing a glazed colored glass-brick from chromic slag was carried out as a high-level research on processing chromic slag harmlessly in ceramic industry. The experiment results show that the leaching amount of hexavalent chromium was lower than the national standard, with its physical and chemical properties conforming to the relative national standard requirements under the conditions of adding 20% chromic slag and a certain amount of fluxing agent into the base materrial, and controlling the shaping pressure, technological parameters and condition in the firing processes.

Key words: chromic slag, glazed colored glassbrick, hexavalent chromium.

Study on the Treatment of Gentamycin and Aureomycin Wastewaters and the Measures for Pollution Control. Zhou Ping and Qian Yi (Dept. of Envrion. Eng., Tsinghua University, Beijing 100084), Su Chengyi (Chinese Research Academy of Environ. Sciences, Beijing 100012); Chin. J. Environ. Sci., 16(5), 1995, pp. 45– 47

A gentamycin wastewater, an aureomycin wastewater and a mixture of both wastewaters were subjected to an anaerobic treatment, an aerobic treatment or a combination of both treat-

ments in batch experiments. A COD removal of 98. 4% was given when a gentamycin wastewater with a COD concentration of 19240 mg/L was subjected to an anaerobic treatment for 3 d and then to an aerobic treatment for 10 h. A COD removal of 95.8% was given when a mixture of gentamycin wastewater and aureomycin wastewater (1:2) with a COD concentration of 7740 mg/L was subjected to an anaerobic treatment for 2 d and then to an aerobic treatment for 10 h. The COD concentration in final effluent could be reduced to less than 300 mg/L when the gentamycin wastewater after an anaerobic treatment for 3 d was combined with the aureomycin wastewater after an anaerobic treatment for 6 h and then subjected to an aerobic treatment for 4 h.

Key words: gentamycin wastewater, aureomycin wastewater, refractory organics, anaerobic-aerobic treatment.

Chemical Valence States of Sulfur Measured with a High Resolution Two Crystal X-ray Fluorescence Method. Wang Qingguang et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085), Ji Ang (Shanghai Institute of silicates, Chinese Academy of Sciences, Shanghai 200050), Ma Guangzu (Institute of Rock and Mineral Analysis, Ministry of Geology and Mineral Resources, Beijing 100037); Chin. J. Environ. Sci., 16 (5), 1995, pp. 48-50

With a high resolution two crystal X-ray fluorescence (HRXRF) method, the chemical valence states of sulfur in pure elemental sulfur, sulfites, sulfates and sulfides and in some of unknown samples were determined, the range of energy differences of the spectral peaks for sulfur in different valence states were identified, and then the range of energy differences was used to identify the chemical valences of sulfur in unknown samples. Each of chemical valence states of sulfur in standard samples had essentially no change after they had been subjected to repeated HRXRF measurements. Sulfur in various chemical valence states had the following ranges of energy differences for spectral peaks: S^{6+} , +1.10 to +1.25 eV; S^{4+} , +0. 61 to +0. 93 eV; and S^{2-} , -0.12 to -0.21 eV. This method was found useful in the measurement of sulfur in a single chemical valence state, and in the identification of different chemical valence states of sulfur.

Key words: HRXRE, chemical valence state, sulfur, sulfur-bearing compounds, energy

change.

Application of Black-box Theory to GC Analysis of Waste Containing Methanol. Qin Jinping et al. (Nanjing Institute of Chemical Technology, Nanjing 210009): Chin. J. Environ. Sci., 16 (5), 1995, pp. 51-53

The GC optimal conditions were estimated based on black-box theory. GC/MS was used for qualitative analysis of methanol wastewater. On the GPX-203 (60-80 mesh) coated with 5% PEG-20 M, $C_1 - C_5$ alcohols in methanol wastewater were quantitatively analyzed by means of FID. The detection limits were 1 μ /ml for $C_1 - C_3$ alcohols, 3 μ g/ml for C₄ alcohols, and 4 μ g/ml for C₅ alcohols.

Key words: methanol, wastewater, $C_1 - C_5$ alcohols, black-box theory, gas chromatography.

Flame Atomic Absorption Spectrometric Determination of Copper, Lead, Cadmium, and Manganese in Natural Waters Using a Flow Injection System with On-line Ion Exchange Preconcentration. Wang Peng et al. (Dept. of Applied Chemistry, Harbin Institute of Technology, Harbin 150006): Chin. J. Environ. Sci., 16 (5), 1995, pp. 54-56

The title method was developed, and some practical considerations in the design of on-line column preconcentration FIA system for FAAS were studied. The relative standard deviation was about 2.0% (n=11) at a sampling frequency of 45 h⁻¹ with an enrichment of around 20 times. The advantages, such as high-efficiency, on-line, accuracy, precision, micro-amount of sample, automation et al., made it possible to be applied to the routine analysis of natural waters.

Key words: flow injection analysis (FIA), ion exchange preconcentration, atomic absorption spectrometry, copper, lead, cadmium, manganese.

Study on the Seasonal Variations in the Atmospheric Particulate Nitrate and Sulfate Concentrations in the Yanshan District of Beijing. Li Xin, Guo Huajie et al. (Dept. of Technical Physics, Peking Univ., Beijing 100871); Chin. J. Environ. Sci., 16(5), 1995, pp. 57-60

The title study was carried out in summer and autumn, in which the seasonal variations were aslo related to the atmospheric concentration of ozone as a major photochemical oxidant. The results show that the concentrations of nitrate and sulfate in atmospheric particulates varied significantly with seasons, and were higher in summer that in