

氯代苯类有机物生物降解性能的研究

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摘要 采用连续、完全混合活性污泥法, 对重点污染物中六种氯代苯类有机物(氯苯、1,2-二氯苯、1,3-二氯苯、1,4-二氯苯、1,2,4-三氯苯、六氯苯)的生物降解性能进行了研究。试验表明, 除六氯苯外, 其它五种氯代苯均能被驯化后的微生物所降解。随着苯环上氯取代基的增加, 氯代苯的生物降解速率降低。在 28 天的连续试验中, 六氯苯基本上不能被微生物所降解。

关键词 氯代苯, 生物降解, 活性污泥法。

随着化学工业的迅猛发展, 人工合成的有机物种类日益增多。美国环保局于 1977 年公布法令, 规定了 129 种重点污染物(Priority Pollutants)作为重点控制对象。近年来, 许多学者^[1-4]对这些重点污染物的生物降解性能做了研究, 所采用的方法是 1967 年 Buch 和 Chamber 提出的三角瓶静培养筛选技术。其基本原理是, 在静止状态下, 将试验有机物与微生物混合接种经七天的培养, 测定其好氧条件下的降解效果, 然后再进行比较筛选和进一步培养。由于三角瓶静培养法与生产实际运用的活性污泥法差距甚远, 因此, 不能确切地反映有机物在环境中的生物降解规律。氯代苯类有机物作为重要的化工原料, 广泛地用于农药、医药和材料合成等行业。本文采用连续、完全混合活性污泥法, 对重点污染物中六种氯代苯类有机物的生物降解性能进行了研究。

一、材料与试验方法

连续、完全混合活性污泥反应器采用直径 20cm 塑料管, 有效高度 10cm, 有效容积为 3.14 L。每天 24h 连续进水, 流量控制在 300ml/h, 水力停留时间为 10.5h。细胞平均停留时间(Q_c)由排放反应器内的混合液来调节, 每天排放一次, 分别排放混合液体积的 1/2、1/4 和 1/6, 则 Q_c 分别为 2、4 和 6 天。反应器内曝气量控制在 2L/min。活性污泥取自上海曲阳污水处理厂回流污泥, 首先用含苯 200mg/L 的溶液进行

驯化(控制条件同上)二周, 使出水苯的含量小于 0.5mg/L(表明微生物已能顺利地利用以苯作为唯一碳源的基质), 用驯化后的污泥作为试验的接种污泥。

氯代苯的分析采用毛细管气相色谱法, 配以电子捕获监测器。水溶液中的氯代苯用分析纯异辛烷萃取分离。取 50ml 含氯代苯的水样于 200ml 分液漏斗中, 加入 20ml 异辛烷, 振荡、静止分层, 分离出有机相。水相再用 20ml 异辛烷萃取一次, 将有机相合并测定。采用标准加入法分析氯代苯的浓度。毛细管直径 0.25 mm, 长度 25m, 填料 OV-101。监测室、进样室和毛细管柱温度分别为 320、190 和 175°C, 毛细管入口分流器的分流比调节在 1:150 和 1:90 范围内。

二、结果与分析

采用连续、完全混合活性污泥反应器研究了重点污染物中六种氯代苯类有机物的生物降解性能。图 1—6 是 Q_c 为 6d 时, 六种氯代苯的生物降解试验结果。由图可知, 除六氯苯外, 其它五种氯代苯均能被微生物有效地降解。其中氯苯的降解最容易, 可被经苯驯化后的微生物直接降解, 去除率达 95% 以上。而 1,2-二氯苯, 1,3-二氯苯, 1,4-二氯苯和 1,2,4-三氯苯在试验最初的一周内, 去除率不到 50%, 但

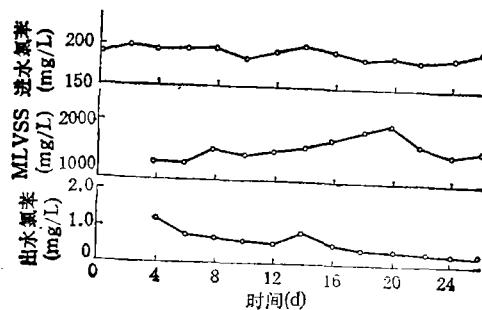


图1 氯苯的活性污泥试验结果
MLVSS 为反应器内混合液的挥发性
悬浮固体浓度(下同)

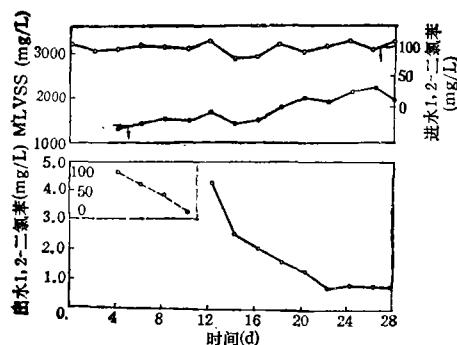


图2 1,2-二氯苯的活性污泥试验结果

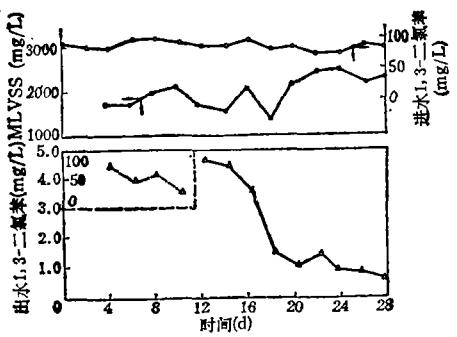


图3 1,3-二氯苯的活性污泥试验结果

经过3个污泥龄(18d)的试验后,微生物得到驯化,使其去除率达到95%以上。说明上述四种氯代苯需要经驯化后的微生物才能有效地被降解。从四周的试验结果还可知,六氯苯基本上不能被微生物所降解,属于难以生物降解的有机物。

活性污泥法的细胞平均停留时间为2、4和6d时,各氯代苯有机物进出水浓度、MLVSS及去除率列于表1中。由表1可知,除六氯苯之外,其它五种氯代苯在Q₀为2、4和6d时均

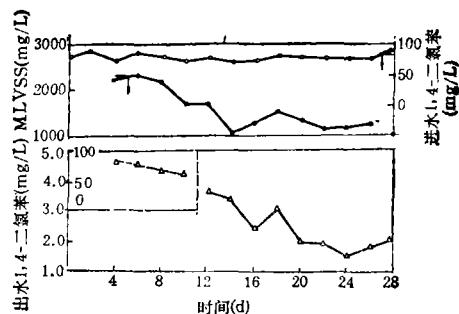


图4 1,4-二氯苯的活性污泥试验结果

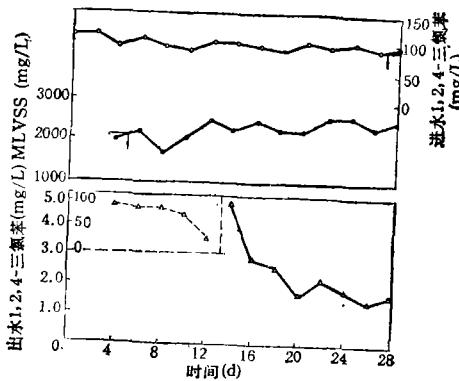


图5 1,2,4-三氯苯的活性污泥试验结果

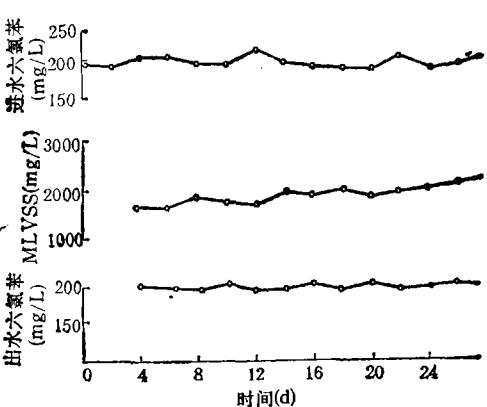


图6 六氯苯的活性污泥试验结果

能很好地被微生物去除。根据各氯代苯有机物进出水的浓度、活性污泥反应器内MLVSS及水力停留时间(10.5h),可计算出各有机物的生物降解速率R(见表1),此值表征了有机物的生物降解难易程度。由表1中R值可知,在六种氯代苯有机物中氯苯最容易被微生物降解;1,2-二氯苯、1,3-二氯苯、1,4-二氯苯的生物降解难易程度基本相同,但1,2,4-三氯苯的生

表1 活性污泥法处理氯代苯有机物结果

| 有机物 | $Q_c(d)$ | 进水浓度 (mg/L) | 出水浓度 (mg/L) | 去除率(%) | MLVSS(mg/L) | R (mg/g污泥·h) |
|-----------|----------|----------------|----------------|--------|-------------|-------------------|
| 氯苯 | 2 | 193 | 0.9 | 99.5 | 1550 | 11.80 |
| | 4 | 199 | 0.5 | 99.7 | 1670 | 11.09 |
| | 6 | 201 | 0.5 | 99.8 | 1650 | 11.57 |
| 1,2-二氯苯 | 2 | 102 | 3.2 | 96.9 | 1490 | 6.32 |
| | 4 | 97 | 1.2 | 98.8 | 1785 | 5.11 |
| | 6 | 98 | 0.8 | 99.2 | 2125 | 4.36 |
| 1,3-二氯苯 | 2 | 100 | 2.4 | 97.6 | 2065 | 4.50 |
| | 4 | 103 | 1.6 | 98.4 | 1750 | 5.52 |
| | 6 | 96 | 0.7 | 99.3 | 2430 | 3.74 |
| 1,4-二氯苯 | 2 | 101 | 5.0 | 95.0 | 2180 | 4.19 |
| | 4 | 97 | 3.0 | 96.9 | 1525 | 5.87 |
| | 6 | 99 | 2.7 | 97.3 | 1320 | 6.95 |
| 1,2,4-三氯苯 | 2 | 92 | 4.7 | 94.9 | 1820 | 4.57 |
| | 4 | 101 | 2.5 | 97.5 | 2210 | 4.24 |
| | 6 | 94 | 1.9 | 98.0 | 2475 | 3.54 |
| 六氯苯 | 2 | 196 | 192 | 2.0 | 1855 | 0.21 |
| | 4 | 205 | 178 | 13.2 | 1640 | 1.57 |
| | 6 | 199 | 189 | 5.0 | 2010 | 0.47 |

物降解较二氯苯为难；六氯苯属于难以生物降解的氯代有机物。

生物降解速率降低。

3. 六氯苯基本上不能被微生物降解。

三、结 论

1. 除六氯苯外，其它五种氯代苯均能被驯化后的微生物降解，当 Q_c 为 2、4 和 6d 时，其去除率均可达 95% 以上。

2. 随着苯环上氯取代基的增加，氯代苯的

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大庆石化空气污染区树木叶片内蛋白质、核酸、游离氨基酸及过氧化物酶同工酶含量的变化

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摘要 石化空气污染区树木叶片内的蛋白质、核酸、游离氨基酸及过氧化物酶同工酶含量较对照区有明显的变化，变化

Abstracts

Chinese Journal of Environmental Science

Key Words: Anaerobic Fluidized Bed Reactor(AFBR), Steady theoretical model, Model of parameter estimation.

Characterization of Distribution of Carbon in Haihe River Valley. Liu Quanyou, Sun Jianzhong, Wang Zijian (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences): *Chin. J. Environ. Sci.*, 13(2), 1992, pp.26—32

This paper approaches the distribution of carbon content in different types of soil in Haihe River valley and the horizontal and vertical changes of various forms of carbon in the soils, studies the ways of natural enrichment, increasing or decreasing, the environment for self-cycling and characteristics of carbon in soil under given conditions and therefore lays a foundation for the study of inventory and flux cycling system of carbon in this region.

Key Words: carbon distribution in soil, carbon cycling.

Characteristics of Temperature Profile in the Polluted Urban Atmosphere of Lanzhou. Wang Haixiao, Gao Huiwang, Chen Changhe (Atmospheric Science Department of Lanzhou University): *Chin. J. Environ. Sci.*, 13(2), 1992, pp.33—35

Based on the comparison of temperature profiles of Polluted urban atmosphere in Lanzhou with those of rural atmosphere in Gaolan, the urban island effect and the influence of air pollutants on lower atmospheric layer at different altitudes were analysed. An analysis of regression was carried out with the data of temperature increment in middle lower atmosphere and lower atmospheric turbidity during daytime. A linear correlation was observed.

Key Words: urban island effect, atmospheric temperature profile

Study on Biodegradability of Benzene Chlorides. Zhao Jianfu (School of Environmental Engineering, Tongji University, Shanghai): *Chin. J. Environ. Sci.*, 13(2), 1992, pp.36—38

Biodegradability of six benzene chloride compounds (chlorobenzene, 1, 2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, hexachlorobenzene) in the priority pollutants were studied with continuous, completely mixed flow activated sludge reactors. Results showed that, except hexachlorobenzene, all the other five benzene chlorides could be biodegraded by domesticated microorganisms. Biodegradation rates of the compounds decreases with the increase of chlorine substituents in the benzene ring, and hexachlorobenzene could not be degraded by the microorganisms in the test during a period of 28 days.

Key Words: priority pollutants, Benzene Chlorides, biodegradability, activated sludge process.

Changes of Content of Protein, Nucleic Acid, Free Amino Acid and Peroxide Isoenzyme in Woody Plant Leaves in Petrochemical Air Pollution Area of Daqing, Heilongjiang Province. He Shimin, He

Yanling (Department of Biology, Qiqihar Teachers College): *Chin. J. Environ. Sci.*, 13(2), 1992, pp.38—40

Obvious changes were observed in the content of protein, nucleic acid, free amino acid and peroxide isoenzyme in woody plant leaves in petrochemical air pollution area compared to the trees in unpolluted areas. The trees with small change in content of above chemicals possess strong pollution-resistant ability. Among the compounds mentioned above, Protein and nucleic acid content decreased and free amino acid and peroxide isoenzyme content increased in the polluted tree leaves. The order of pollution-resistant ability of the trees observed is as follows; *Picea koraiensis*, *Salix matsudana*, *Populus betulinensis*, *Ulmus pumila*, *Syringa obvata* and *Acer negundo*.

Key Words: air pollution, petrochemical plant pollution, pollution indicator, protein, nucleic acid, free amino acid, peroxide isoenzyme.

Studies on Mixed Oxide Catalysts for Automobile Exhaust Control Yang Hanpei, Qiu Fali (Chengdu Institute of Organic Chemistry, Academia Sinica): *Chin. J. Environ. Sci.*, 13(2), 1992, pp.41—44

Non-noble metal containing mixed oxide catalysts used for automobile exhaust control were investigated. Results indicated that, among the mixed oxide catalysts under study, ASC(mixed oxides of rare earth, Pb, Mn, Cu, Cr, and additives) has the highest activity and a prolonged resistance to thermal shocks, carbon deposit, and poisoning of sulphur, lead and phosphorous compounds, and therefore possesses certain prospect of application under vehicle operation conditions.

Key Words: automobile exhaust control, mixed oxide catalysts, catalyst of non-noble metal.

RS-1 Type Catalyst for the Combustion of Sulphur-Containing Organic Waste Gases Jiang Xiaoyuan, Yu Qingrui, Jin Songshou (Hangzhou University, Department of Chemistry): *Chin. J. Environ. Sci.*, 13(2), 1992, pp.44—46

In this paper, The oxidation activity of RS-1 type catalyst for ethyl mercaptan, n-butyl mercaptan, carbon disulfide, dimethyl sulfate, ethyl alcohol, and xylene etc. was discussed. Experimental results showed that the catalytic activity was excellent for those sulphur-containing organic waste gases. Oxidation product SO_x from organic sulphur did not react with the catalyst. Analytical results showed that the emission efficiency SO_x was nearly 100%. At reaction temperature of 380°C, space velocity of 10000h⁻¹, and concentrations of ethyl mercaptan and n-butyl mercaptan equal to 4000—8000 mg/m³ and 6000—8000 mg/m³, respectively, purification efficiency reached as high as 99%. This catalyst is mainly applied to purify industrial exhaust sulphur-containing waste gases from pharmaceutical and agricultural chemical factories.

Key Words: sulphur-containing organic waste gases, combustion catalyst, ethyl mercaptan, butyl mercaptan, carbon disulfide, dimethyl sulfate.

Kinetics of Reaction in the Process of Simulta-