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有机物好氧生物降解性二氧化碳生成量测试法的研究*

蒋展鹏　师绍琪　买文宁　顾夏声

（清华大学环境工程系，北京　100084）

摘要　为了探讨测试有机污染物生物降解性方法的通用性和可比性，建立了用二氧化碳生成量来测试有机污染物好氧生物降解性的合理方法. 生物反应瓶容积2 L，受试有机物浓度100 mg/L(以溶解性有机碳计)，接种污泥浓度500 mg/L，反应温度25℃，反应时间14 d. 通过有机物生物降解性的分析，提出了一个生物降解性的评价标准——生物降解性指数(*IB*). 采用本文建立的方法对25种有机物的生物降解性进行了研究，并按生物降解性指数对这些有机物的生物降解难易程度进行了分类.

关键词　有机物，生物降解，二氧化碳生成量.

目前已建立的多种有机污染物生物降解性的测试方法[1,2]，每种方法各有其优缺点，对于同一种有机污染物采用不同的方法往往会得出不同、有时甚至相反的结果[3,4]，这给有机污染物生物降解性的研究带来了混乱，而且使测试结果没有通用性和可比性. 因此迫切需要建立一个可靠合理的生物降解性测试方法[5].

用CO_2生成量作为生物降解性的测试指标，不受硝化作用和细胞吸附作用的影响；而且，从对环境污染的角度看问题，有机物转化为CO_2是最为彻底的，因而也是最有意义的. Ludzack[6]等采用了CO_2作为测试指标考察了一些有机污染物在水中的生物氧化作用. Sturm[7]对Ludzack的测试方法进行了改进：采用BOD稀释水作为生物介质代替河水，和采用驯化的生活污水作为接种物. 但由于接种物浓度较低使得测试时间较长. 而且，生物降解性的评价采用CO_2最终生成的百分率，这是不够全面的. 为了克服以上之不足，本文研究并建立了生物降解性合理的测试方法和全面地反映有机物生物降解性的评价标准.

1　实验

1.1　试验装置

试验装置如图1所示. 为了去除进气中的CO_2，采用10 mol/L NaOH和0.05 mol/L $Ba(OH)_2$进行吸收，然后经水洗瓶洗涤以防止碱液进入生物反应瓶，生物降解过程中所生成的CO_2采用0.05 mol/L $Ba(OH)_2$吸收，并用0.1000 mol/L HCl标准溶液滴定以测定CO_2的吸收量.

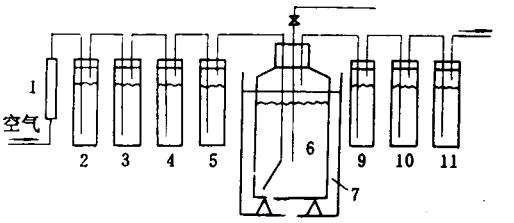

图1　试验装置

1. 气体流量计　2. CO_2一级前吸收瓶　3. CO_2二级前吸收瓶　4. CO_2三级前吸收瓶　5. 水洗瓶　6. 生物反应瓶　7. 恒温水浴　8. 取样与加样管　9. CO_2一级吸收瓶　10. CO_2二级吸收瓶　11. CO_2三级吸收瓶

1.2　生物介质

在生物反应瓶中，加入$CaCl_2$溶液(27.5

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g/L)，$MgSO_4 \cdot 7H_2O$(22.5 g/L)和 $FeCl_3 \cdot 6H_2O$ 溶液(0.25 g/L)各 4 ml，然后加入 10 ml pH=7 的磷酸盐缓冲溶液(每 L 溶液中含 8.5 g K_2HPO_4 和 44.7 g $Na_2HPO_4 \cdot 12H_2O$)以及适量的微量元素. 生物反应瓶中的反应液的总体积为 2000 ml(包括受试物和接种物).

1.3 接种生物

采用城市污水处理厂的活性污泥作为接种物.

1.4 试验条件

在本试验中生物反应瓶可分为内源反应瓶(只加接种物，未加受试物)和生化反应瓶(接种物和受试物都加入). 溶解于反应瓶中的有机物(受试物)浓度均配制成相当于溶解性有机碳(DOC)100 mg/L，反应液中接种物——活性污泥混合液(MLSS)的浓度为 500 mg/L，反应过程中 CO_2 的空白值用空白反应瓶进行扣除. 反应温度为 25℃，气体流量为 20 L/h，反应时间为 14 d. 在不同的时间里测定 CO_2 的生成量.

2 结果与讨论

2.1 试验结果

23 种有机物的生物降解性的测试结果列于表 1 中.

表 1 23 种有机物不同反应时间的二氧化碳生成量/mmol·L^{-1}

反应时间(d)	2	4	6	8	10	12	14
接种物	3.68	6.31	7.05	7.14	7.18	7.20	7.25
生活污水	8.36	12.62	13.71	13.88	14.06	14.14	14.22
乙二胺	3.34	6.31	7.68	8.84	9.26	9.35	9.94
尿素	12.23	14.74	15.31	15.34	15.37	15.38	15.40
乙二胺四乙酸	2.68	4.46	6.03	6.70	6.75	6.78	6.82
葡萄糖	11.81	14.35	15.13	15.18	15.26	15.28	15.31
六次甲基胺	2.01	3.68	4.58	4.81	5.07	5.12	5.14
乙酸	10.93	14.21	15.21	15.28	15.37	15.45	15.47
草酸	10.11	13.87	15.14	15.35	15.41	15.48	15.52
苯酚	8.52	13.80	14.93	15.13	15.16	15.24	15.37
苯甲酸	10.46	15.38	15.21	15.28	15.36	15.38	15.41
苯磺酸	4.42	6.63	8.87	9.21		10.76	11.21
苯甲醛	9.73	14.85	15.03	15.24	15.37	15.39	15.42
苯胺	4.46	6.37	7.65	8.83	9.88	10.22	10.61
硝基苯	4.24	6.13	7.82	8.96	9.78	10.26	10.70
4-甲基苯酚	5.36	11.28	13.63		15.21	15.26	15.34
4-氯代苯酚	4.78	8.98	13.05	14.86	15.15	15.32	15.41
4-溴代苯酚	4.21	8.06	11.92	14.14	14.94	15.20	15.31
4-磺基苯酚	2.81	7.72		14.03	14.20	14.28	14.32
4-硝基苯酚	2.43	6.02	10.14	13.41	14.27		14.29
4-氨基苯酚	2.46	6.13	9.89	13.12	13.98	14.27	14.21
3-羟基苯酚	6.11	12.13	14.12	14.84	15.18	15.33	15.47
3-磺基甲苯	2.73	7.15	10.87	13.59		14.12	14.23
3,4-二甲基苯酚	2.87	6.95	10.08	11.78	12.50	13.24	13.35
1,3-二硝基苯	1.86	3.16	3.27	3.32	3.43	3.45	3.45

2.2 讨论

(1) 有机物生物降解性评价 根据以上的试验结果绘制以二氧化碳生成量(PCD)为纵坐标，反应时间(t)为横坐标的曲线，其中几条典型的二氧化碳生成量曲线如图 2 所示. 生物降解性的评价可以通过这些曲线的分析而进行.

如图 2 所示，受试物(a)不需要驯化过程，生物降解速率和生物降解程度较大，其生物降解性较强，PCD 曲线与横坐标之间的面积也较大；受试物(b)需有一个驯化过程，它的反应速

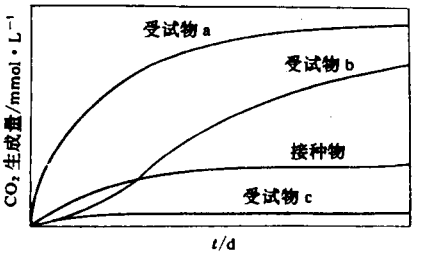

图 2　典型的二氧化碳生成量(PCD)曲线

率和生物降解程度较小，其生物降解性较弱且 PCD 曲线与横坐标之间所组成的面积也较小；受试物(c)不但不发生生物降解作用而且对接种物具有毒性，其 PCD 曲线位于接种物 PCD 曲线之下且 PCD 曲线与横坐标之间所组成的面积最小. 由此可见，PCD 曲线与横坐标之间所组成的面积可以表征有机物生物降解性的大小. 因此，在二氧化碳测试法中有机物的生物降解性能可以采用生物降解性指数表示如下：

$$IB = \frac{A_s}{A_0} \times 100\% \qquad (1)$$

式中，IB 为生物降解性指数；A_s 为受试物生化 PCD 曲线与反应时间组成的面积；A_0 为接种物内源 PCD 曲线与反应时间组成的面积.

二氧化碳生成量与反应时间的关系可以采用以下数学模型进行描述：

$$PCD = PCD_u \frac{1 - e^{-kt}}{1 + B \times e^{-kt}} \qquad (2)$$

式中，PCD 为二氧化碳生成量；PCD_u 为二氧化碳最终生成量；t 为反应时间；k、B 为常数. 对(2)式积分得：

$$A = PCD_u \left\{ t + \left(1 + \frac{1}{B} \right) \times \frac{1}{k} \times \ln \left[\left(e^{-kt} + \frac{1}{B} \right) \times \frac{B}{B+1} \right] \right\} \qquad (3)$$

根据试验结果，采用 FORTRAN 程序在计算机中求出方程式(2)中的 k、B 和 PCD_u，若采用反应时间 10 d，利用式(3)可以求出 PCD 曲线与横坐标之间面积，由式(1)可以求出有机物的生物降解性指数(IB). 计算结果列于表 2 中.

(2) 有机物生物降解性的分类　有机物生物降解性指数越大，生物降解性越强；生物降解性指数越小，生物降解性越弱. 当生物降解性指数小于 100%，从图 2 中可以看出：生化 PCD

表 2　生物降解性指数的计算结果

受试物	k	B	PCD_u	A[1)]	IB/%
接种物	0.675	0.933	7.220	56.00	
生活污水	0.780	1.576	14.263	11.437	205.5
乙二胺	0.337	0.792	10.13	63.45	114.0
尿素	0.792	0.001	15.39	134.47	241.6
乙二胺四乙酸	1.038	9.031	6.821	51.38	92.3
葡萄糖	0.604	0.001	15.41	128.63	231.1
六次甲基四胺	0.525	1.849	5.124	35.46	64.0
乙酸	0.685	0.205	15.42	129.55	232.8
草酸	0.650	0.420	15.49	126.70	227.7
苯酚	0.888	2.825	15.437	122.80	219.3
苯甲酸	1.325	5.062	15.396	128.88	230.1
苯磺酸	0.220	0.001	11.43	68.08	121.6
苯甲醛	1.168	4.279	15.330	126.36	225.6
苯胺	0.211	0.001	11.081	64.64	115.4
硝基苯	0.196	0.001	11.168	62.66	111.9
4-甲基苯酚	0.616	3.196	15.236	106.00	189.3
4-氯代苯酚	0.577	4.814	15.456	98.10	175.2
4-溴代苯酚	0.595	7.450	15.23	90.90	162.3
4-磺基苯酚	0.601	8.158	14.495	85.52	152.7
4-硝基苯酚	0.487	8.069	15.488	78.22	139.7
4-胺基苯酚	0.531	9.945	14.941	76.80	137.1
3-羟基苯酚	0.721	3.717	15.549	113.11	202.0
3-磺基苯酚	0.641	9.894	14.313	82.37	147.1
3,4-二甲基苯酚	0.592	9.094	13.347	76.22	136.1
1,3-二硝基苯	0.921	3.229	3.467	27.56	49.2

1) 表中 A 对接种物为 A_0，对受试物为 A_s

曲线在内源PCD曲线之下，说明受试物对接种物具有毒性作用. 可以认为该有机物为难以生物降解的. 生活污水是容易生物降解的有机物的典型代表，其 IB 值约为200%. 因此，当受试物的生物降解性指数大于200%，此有机物可以认为是易生物降解的；当受试物的生物降解性指数大于100%而小于200%时，可以认为该有机物为可生物降解的.

3 结论

(1) 用二氧化碳生成量作为有机物生物降解性的测试指标，不受硝化作用和细胞吸附作用的影响. 在笔者所建立的方法中，试验条件合理，可以有效地测试有机物的生物降解性能.

(2) 此测试法中，采用生化PCD曲线与横坐标之间所组成的面积对内源PCD曲线与横坐标之间的面积之比值作为生物降解性指数，可以较全面地、准确地反映有机物的生物降解性.

(3) 按有机物的生物降解性指数，可以把有机物的生物降解性划分如下：$IB>200\%$ 易生物降解；$100\%<IB<200\%$ 可生物降解；$IB<100\%$ 难生物降解.

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HUANJING KEXUE

Abstracts

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Study on Electrokinetic Detection Characteristics of Inorganic Cationoid Coagulants in Water. Qu Jiuhui (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 1—4

A new essential factor of electrokinetic characters, streaming current (SC) was introduced into the study of coagulation processes, and the relative law and isoelectronic point between electrokinetic parameters and concentration or efficiency of inorganic cation coagulants were studied. Furtherly, in the paper the characteristics and functions to express coagulants affecting on colloid particles by SC have been investigated and an effective method was presented for studying on the relationship between the coagulation, detecting colloid potential in line and optimum dosage of coagulants.

Key words: ζ potential, streaming current, inorganic cationoid coagulants, electrokinetic detection characteristics.

Function Determination for Biodegradation of Monosodium Glutamate (MSG) Wastewater with Fusants between Photosynthetic Bacteria and Yeast. Cheng Shupei et al. (Dept. of Environ. Sci. and Eng., Nanjing University, Nanjing 210093): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 5—7

The protoplasts of *Rhodopseudomonas sphaeroides* (eukaryote, Nt^rSm^s) and *Saccharomyces cerevisiae* (prokaryote, Nt^sSm^r) were induced with PEG (MW=6000) to fuse for the construction of the fusant cell (Nt^rSm^r). The fusants F13, F15 and F20 screened from the fusion production with high flocculation were used to test the kinetics parameters for degradation of MSG wastewater in the shaking reaction for 7—8 h, while the initial BOD_5 concentration of the wastewater were from 191 to 690 mg/L. The values of maximum specific growth rate μ_{max} and its half velocity constant $K_{s\mu}$, the maximum specific degradation rate q_{max} and its half velocity constant K_{sq}, the true growth yield coefficient Y and the endogenous decay rate coefficient K_d were measured in the reaction. The results of this research suggest that the fusants F13, F15 and F20 have better ability for degradation of the organic waste in MSG wastewater.

Key words: *Rh. sphaeroides*, *S. cerevisiae*, fusant, monosodium glutamate wastewater, biodegradation kinetic.

Study on Purification of Waste Gases Containing Toluene by Using a Biofilter. Huang Ruohua et al. (Dept. of Environ. and Chem. Eng., Kunming Univ. of Sci. and Tech., Kunming 650093): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 8—10

From this study, a fact can be affirmed that in China, it is feasible to purify the waste gas containing organic compounds in low concentration by using the biological trickling filter with biofilm packing-material, inoculated with a mixed culture from a biostation of treating wastewater in a coke-oven plant. The results of preliminary experiment showed that with the increasing of the concentration of toluene in influent gas and gas flow, and decreasing of the flow of circulating liquid simultaneously, the biochemical elimination of toluene in waste gas can be increased, which can reach 157.13 mg per hour per litre packing-material with biofilm in the tower. From the experimental results, it can be inferred that the process of purifying the waste gas containing toluene in low concentration by using the biofilter belongs to mass transfer. By contrast, a good suitability of the kinetic model established in this study for practical process is verified.

Key words: biofilter, toluene, waste gas, biological degradation, kinetics.

A Study on the Determination of Biodegradability of Polluted Organic Substances Using Production of Carbon Dioxide Test. Jiang Zhanpeng et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 11—14

In this paper, a rational PCD test for determining biodegradability of organic substance under aerobic conditions was established. The volume of bioreactor is 2 L, the concentration of organic substance is 100 mg/L (as DOC), the amount of the inoculum is 500 mg/L (as MLSS), the temperature is 25℃, the duration of test time is 14 days. Index of biodegradation (IB) was elaborated through analysis of biodegradability of

organic substances, 23 organic substances were studied with this PCD test, and their indexes of biodegradation were calculated. A classification of biodegradability of the organic substances according to the indexes of biodegradation was suggested.

Key words: organic compounds, biodegradation, production of carbon dioxide.

Comparison of Biodegradability of Aromatic Hydrocarbons by Mixed Bacteria from Different Sources. Zhao Lihui et al. (Research Center for Eco-Environmental Scineces, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 15—18

The biodegradability of benzene, toluene, ethylbenzene, o-, m- and p-xylene by mixed cultures enriched from two activated sludges was studied. The sludges were obtained from two wastewater treatment plants receiving municipal and petrochemical wastewater respectively. The different of biodegradability represented on the lag time, the degraded ratio and the biodegradable degree in both cultures under the same biotest condition with different tested compounds concentration were discussed. The results indicated that the six tested compounds can be biodegraded in different degree in both cultures. The special bacteria for degradation o-, m- and p-xylene were separated from enriched activated sludge of the petrochemical wastewater treatment plant, and the ratio of degradation of three xylenes could reach a hundred percent. The degradable order of the six tested compounds in both culture was ranked according to the rate of degradation.

Key words: biodegradability, aromatic hydrocarbons, active sludge, bacteria.

Adsorption of Organic Pollutants on Particles of Land/Inland Ecotones in Bai Yang Dian Area. Liu Jiang, Wang Yizhong and Tang Hongxiao (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 19—22

The adsorption rule of solvophobic phenol and hydrophobic p-chlorophenol in Bai Yang Dian land/inland ecotones was studied by using batch equilibrium method. For solvophobic organics, the adsorption rules follow the Langmuir type equation, and there is a linear relationship between the logarithm of equilibrium concentration c_e and adsorption coefficient q; but for hydrophobic organics, the relationship between equilibrium concentration c_{e_1} and adsorption coefficient q_1 follows the Linear-type equation, and adsorption amount is higher than that the hydrophobic organic does.

Key words: organic pollutants, particles, adsorption, Bai Yang Dian area, soil of land/inland ecotones.

The Correlation between Selenate Reduction and Nitrate Denitrification in Soil. Piao Hechun et al. (State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 23—26

In order to investigate the correlation between selenate reduction and nitrate denitrification, a series of related experiments were carried out in different soil-water systems, in which a given amounts of KNO_3 and Na_2SeO_4 solution were added, and the transformation processes of chemical speciation of selenate and nitrate were studied. The results indicated that the processes of selenate reduction and nitrate denitrification are identical in temporal and spatial changes, and the transformation of their chemical speciation relates not only to a kind of organic carbon compounds and temperature, but also closely to action of nitrate reductase.

Key words: selenate, nitrate, denitrification, nitrate reductase, organic carbon compounds.

Investigation on the Removal of NO and NO_x from Flue Gas Using a Pulsed Corona Discharge Accounting for Flyash and Humidity Effects. Zhao Zhibin et al. (Institute of Electrostatic and Specific Power Generator, Dalian University of Technology, Dalian 116024): *Chin. J. Environ. Sci.*, **17**(3), 1996, pp. 27—30

The removal of NO and NO_x from flue gas was investigated experimentally using a pulsed corona discharge. The results showed that flyash in flue gas not only removes NO and NO_x about 2%—4% by adsorption, but restrains the pulsed corona discharge and induces a trend of the decreasing removal efficiency of NO and NO_x. Increasing the content of H_2O in flue gas enhances the chemical adsorption of flyash particle surface and when the water vapor content of 15% (V/V) of flue gas and energy consumption of 3 Wh/Nm^3 removal efficiency for NO and NO_x were raised to 5%—