非活性黑根霉菌对废水中重金属离子的吸附*

屠 娟 张 利 赵 力 俞耀庭

(南开大学分子生物学研究所,天津 300071)

摘要 为探讨发酵工业中废弃的菌丝体黑根霉菌(*Rhizopus nigricans*)对水中重金属离子的吸附特性,考察pH、浓度、共存离子等因素对吸附能力的影响,进行了实验室吸附试验,绘制出吸附等温线,并由Langmuir曲线和Freundlich曲线求出相应参数。对化学改性前后的黑根霉进行了吸附对比。初步分析了吸附机理。结果表明,黑根霉在pH=3—6.5范围内,对Pb^{2+}、Cu^{2+}、Mn^{2+}、Cr(VI)几种主要重金属离子都有吸附作用,其中吸附Pb^{2+}能力最高,饱和吸附量可达88mg/g。经化学改性的黑根霉可不同程度地提高吸附能力。用0.5mol/L HCl和NaoH可以洗脱和再生。

关键词 黑根霉,吸附,重金属,废水处理。

目前工业上普遍应用的几种处理含重金属废水的方法,如活性污泥法,生物膜法,化学沉淀法,活性炭吸附法和离子交换树脂法,以及最近报道的微生物法等,虽效果较好,但因过程繁琐,成本较高,而不够理想。另一方面我国的发酵工业比较发达,大量的废弃菌丝体无法处置,已成为一个新的污染源。近几年来国外有利用废弃菌丝体吸附废水中重金属离子的报道[1—6],这样既解决了工业废水污染问题,又解决了发酵废渣处置问题,而且回收大量贵重金属,成本低廉,是环保领域以废治废,变废为宝的新举措。但目前我国还未见这方面的报道。本文做了这方面的探讨,对废水中几种主要的重金属离子的吸附进行了研究,取得了一些有参考价值的参数,为以后进一步开发利用奠定了基础。

1 材料与方法

1.1 试剂与溶液配制

HCl,HNO_3,H_2SO_4,NaOH,$FeCl_3$,$ZnCl_2$均为分析纯试剂,水为去离子水。

原始溶液:将分析纯的$Pb(NO_3)_2$,$CuSO_4$,$MnSO_4$,$K_2Cr_2O_7$,配制成1000mg/L的原始溶液,根据需要进行稀释。

1.2 仪器

日立180-80型原子吸收分光光度计。

THZ-82型恒温振荡器。

pH S-3C型酸度计。

1.3 吸附剂的处理

由天津药业公司提供的废弃黑根霉菌经去离子水洗3遍,洗去可溶性成分,过滤,在室温下干燥至恒重,粉碎成40-80目。

1.4 吸附操作

取20ml一定浓度的工作液,加入一定量的黑根霉,于25°C摇床中振摇2h,过滤,收集滤液,用原子吸收分光光度计测其中剩余金属离子浓度。

1.5 吸附量的计算

$$q = (c_i - c_f) \times V/W$$

式中,q为吸附量(mg/g),c_i为吸附前金属离子浓度(mg/L),c_f为吸附平衡时金属离子浓度(mg/L),V为溶液体积(L),W为吸附剂重量(g)。

2 结果与讨论

2.1 pH值的影响

pH值对Pb^{2+},Cu^{2+},Mn^{2+}和Cr(VI)吸附量的影响见图1。

由图1可见,金属离子溶液pH值是影响黑根霉吸附能力的重要因素。当pH<3时,黑根霉对以上4种离子的吸附能力都很低;在pH=3—6.5范围内,黑根霉的吸附几乎不受pH影响,且最利于吸附作用。当溶液pH值高于7时,由于

* 青年科学基金资助项目

收稿日期:1994-06-15

金属氢氧化物的形成而干扰吸附，故实验中工作液 pH 值为 3—6。

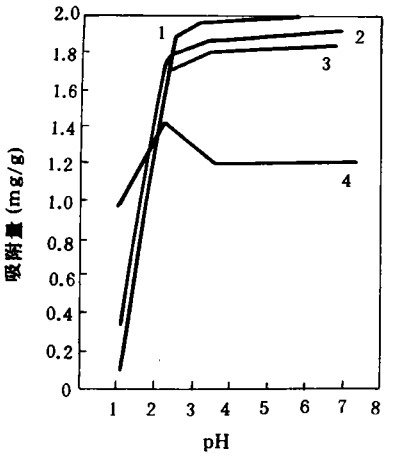

图 1　溶液 pH 对金属离子吸附的影响

(1.0g/20ml　c_i=100mg/L)

1. Pb^{2+}　2. Cu^{2+}　3. Mn^{2+}　4. Cr(Ⅵ)

2.2 吸附等温线

黑根霉对 4 种不同金属离子的吸附等温线见图2。

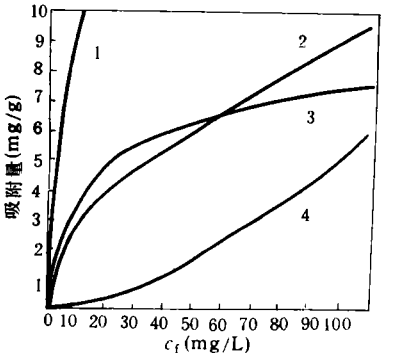

图 2　黑根霉对金属离子的吸附等温线(25℃)。

1. Pb^{2+}　2. Cu 2+　3. Mn^{2+}　4. Cr(Ⅵ)

黑根霉对 4 种离子的吸附能力顺序为 $Pb^{2+}>Cu^{2+}>Mn^{2+}>$Cr(Ⅵ)，其中对 Pb^{2+} 的吸附能力远远大于其他 3 种离子。这可能是由于正电荷离子与细胞壁上负性基团如羧基、酚羟基、巯基等相结合力不同的结果，其机理可能与静电引力及离子或水合离子半径有关[7,8]，同时由于六价铬负离子受到负性基团的排斥作用而影响吸附效果。在 pH=4.2，温度为 25℃时，黑根霉对 Pb^{2+} 的饱和吸附量达 88mg/g。

2.3 吸附参数

Langmuir 式：$c_f/q = c_f/q_\infty + 1/q_\infty \cdot b$

Freundlich 式：$\lg q = \lg K + \frac{1}{n}\lg c_f$

式中，q 为吸附量(mg/g)，b 为吸附平衡常数(L/mg)，q_∞为饱和吸附量(mg/g)，K、$\frac{1}{n}$均为经验常数，c_f为吸附平衡时溶液中重金属离子浓度(mg/L)。

由吸附等温线(图 2)，做出 Langmuir 曲线(图 3)和 Freundlich 曲线(图 4)，求出方程参数(表 1)。

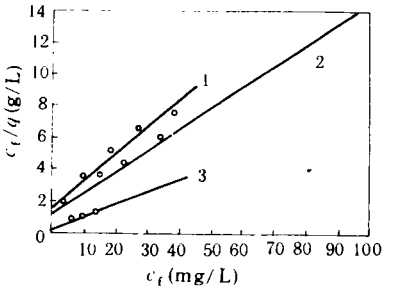

图 3　Langmuir 图

1. Cu^{2+}　2. Mn^{2+}　3. Pb^{2+}

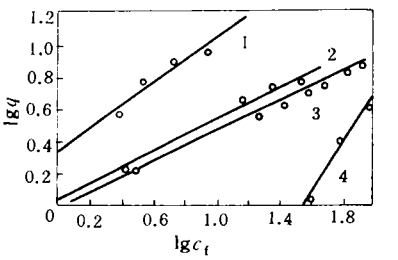

图 4　Freundlich 图

1. Pb^{2+}　2. Mn^{2+}　3. Cu^{2+}　4. Cr(Ⅵ)

表 1　吸附参数

离子	q_∞(mg/g)	b(L/mg)	K	$1/n$
Pb	13.140	0.259	2.685	0.554
Cu	6.536	0.086	0.943	0.477
Mn	8.064	0.080	1.285	0.400
Cr			9.550×10^{-4}	1.870

由图 3、4 可见，黑根霉对 Pb^{2+}、Cu^{2+}、Mn^{2+} 的吸附等温线与 Langmuir 方程和 Freundlich 方程符合得很好，说明以单分子层吸附占优势。对 Cr(Ⅵ)的吸附比较复杂，有待于进一步探索。

2.4 共存离子的影响

本实验分别研究了 Cu^{2+} 存在对 Cr(Ⅵ)吸附的影响和 Zn^{2+} 对 Cu^{2+} 吸附的影响，见图 5、6。

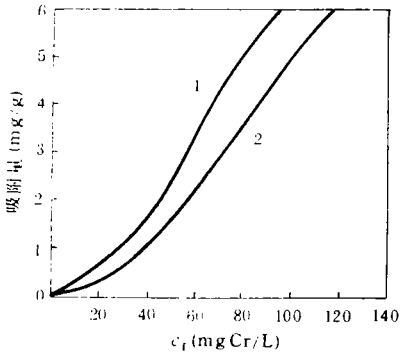

图 5 Cu^{2+} 存在对 Cr(Ⅵ)吸附的影响

(c_0=96mg Cu/L) 1. Cu^{2+} + Cr(Ⅵ) 2. Cr(Ⅵ)

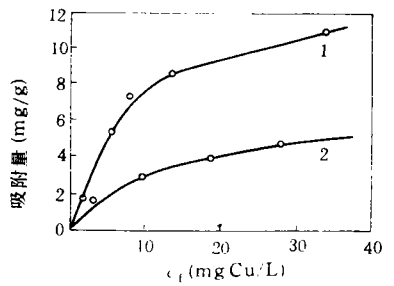

图 6 Zn^{2+} 对 Cu^{2+} 吸附的影响

(c_0=96mg Zn/L) 1. Zn^{2+} + Cu^{2+} 2. Cu^{2+}

由图 5 可见 Cu^{2+} 的存在增加了黑根霉对 Cr(Ⅵ)的吸附，这可能是由于 Cu^{2+} 中和了细胞壁上的负性基团，使得 Cr(Ⅵ)阴离子更易接近细胞壁。

2.5 化学改性前后的比较

发酵工业废弃的菌丝体往往是不纯净的，里面会含有一些杂质或不利于吸附的基团。对黑根霉进行适当的化学处理，将有助于提高吸附能力。

将 5g 黑根霉在 50ml 0.5mol/L 的 NaOH 溶液中加热煮沸 2h，过滤洗涤至中性，40℃烘干，用来吸附 Pb^{2+}，与处理前作对比，见图 7。

黑根霉菌中含有 58%的多糖成分，其中 9%为甲壳素，它们可以在浓碱作用下脱除乙酰基，生成壳聚糖，脱乙酰基后的氨基上的一对孤对电子可以加强作为路易斯碱结合金属阳离子的能力，另外，多糖中的羟基也是作为一种路易斯碱结合金属阳离子。用 NaOH 处理黑根霉，改变了它的化学结构，使其暴露更多的活性位点，从而提高了它的吸附能力。

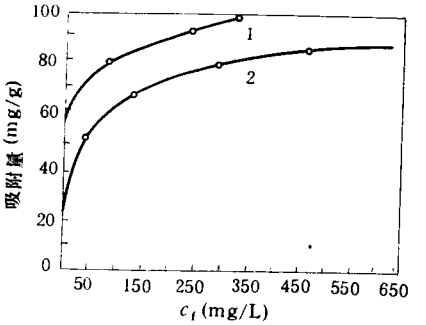

图 7 化学改性前后的黑根霉对 Pb^{2+} 的吸附

1. 处理后 2. 处理前

分别用 $FeCl_3$ 和 $ZnCl_2$ 于室温下浸泡黑根霉 24h，用来吸附 Cr(Ⅵ)，与处理前作对比，见图 8。

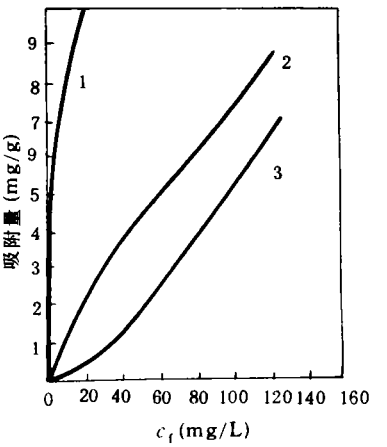

图 8 化学处理前后黑根霉对 Cr(Ⅵ)的吸附

1. Fe^{3+}处理 2. Zn^{2+}处理 3. 未处理

黑根霉菌中含有大量的蛋白质，它的多种氨基酸残基，如羧基，巯基，酚羟基等能强烈结合金属阳离子[9]，当黑根霉结合上金属阳离子，如 Fe^{3+}、Zn^{2+} 等，其负性基团被中和，蛋白质上带有大量正电子，就会显示出对 Cr(Ⅵ)负离子的良好吸附作用。

2.6 洗脱与再生

吸附一定量重金属的黑根霉，经过滤，水洗几遍后，分别加入 0.5mol/L 或 1.0mol/L 的 HC 溶液 50ml，搅拌 30min，过滤，用原子吸收分光光度计测其中金属离子浓度，得洗脱率见表 2。洗

脱后的黑根霉用水洗至中性，分别用 50ml 0.5mol/L 或 1.0mol/L 的 NaOH 溶液浸泡 1h，水洗至中性，烘干再使用。因工厂中产生的废水重金属离子浓度大多在 100mg/L 以下，故再生实验中选择 50mg/L，100mg/L，200mg/L3 个原始浓度。再生黑根霉的吸附性能可以达到甚至超过未经任何处理的黑根霉(见表 3)。

表 2　各种离子洗脱率

吸附剂	HCl 浓度 (mol/L)	洗脱率(%)			
		Pb^{2+}	Cu^{2+}	Mn^{2+}	Cr(Ⅵ)
1#	0.5	88.78	67.29	75.11	59.96
2#	1.0	88.87	56.36	75.43	37.54

黑根霉用 0.5mol/L HCl 和 NaOH 经 4 次洗脱和再生后，吸附性能基本保持不变(表 4)。

表 3　再生与未处理黑根霉吸附量(mg/g)比较

洗脱剂 (mol/L)	c_i (mg/L)	离子			
		Pb^{2+}	Cu^{2+}	Mn^{2+}	Cr(Ⅵ)
0.5	50		4.938	4.508	0.250
(NaOH)	100	15.357	9.929	7.345	2.645
	200	25.422	19.154	12.557	7.780
1.0	50		4.903	4.186	0
(NaOH)	100	15.253	9.900	6.165	2.629
	200	24.971	19.745	9.819	7.602
未处理	50		4.350	2.311	0.544
	100	15.276	8.029	1.359	2.850
	200	25.308	15.330	4.162	8.385

表 4　再生对黑根霉吸附率的影响

次数	0	1	2	3	4	5
吸附率(%)	99.01	99.07	98.50	94.27	98.67	78.56

3　小结

发酵工业中废弃的菌丝体黑根霉对废水中重金属离子，如 Pb、Cu 等具有很好的吸附能力，而且成本低廉，可再生并回收重金属，用后燃烧处理，有一定的实际意义。经加工进一步成型后，有希望作为含铅、铜等工业废水的处理材料。

致谢　天津药业公司为本实验提供了菌丝体，在此表示衷心感谢。

参考文献

1　Galun M et al.. Science. **1983**, **219**:285
2　Sakagachi T et al.. Eur. J. Appl. Microbiol. Biotechnol.. 1979, **8**:207
3　Sid Masri M et al.. J. Appl. Poly. Sci.. 1974, **18**:675
4　Beveridge T J. Koval S F. Appl. Environ. Microbiol.. 1981, **42**:325
5　Beveridge T J et al.. J. Bacteriol.. 1976, **127**:1502
6　Nacajima A T et al.. Eur. J. Appl. Microbiol. Biotecnol.. 1981, **12**:76
7　Kuyucak N, Volesky B. Biotechnol. Bioeng.. 1989, **33**:823
8　Tobin J M , Cooper D G et al.. Appl. Environ. Microbiol.. 1984, **47**:821
9　刘满英，康维钧. 环境科学. 1988, **9**(5): 47

粉煤灰综合利用新途径——粉煤灰浮雕装饰门研制成功

北京思城企业发展策略研究中心开发成功的豪华浮雕装饰门，具有成本低廉，质轻高强，耐酸碱，防水防火、不变形等特点。因表面具有浮雕图案而显得富丽华贵，是现代建筑理想的装饰材料，可广泛用于家庭住宅、宾馆、饭店、写字楼，公寓及花园别墅等高档建筑，市场前景极为广阔。

生产该产品投资 1.5 万元即可，设备仅需搅拌机、模具及操作台，极适合电厂、钢铁厂、化工厂及有条件的单位、个人接产。每扇门综合成本 45 元，参考售价 80 元。为使这一变废为宝的新技术广泛推广，思城中心已面向全国转让，转让费 1 万元，模具制作费 3000 元/套，具体事宜欢迎来人来函洽商。

通讯处：北京 2633 信箱，邮编：100075

联系人：秋野　　电话：9263650

乘车路线：北京站乘地铁到公主坟再乘 901 路公共汽车到西红门立交桥下车，回走 100 米。

Abstracts

Chinese Journal of Environmental Science

Ecophysiological Effect of a Doubly Increased CO_2 Concentration on Some Species of Plant. Lin Shunhua et al. (Institute of Botany, Chinese Academy of Sciences, Beijing 100044): *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 1—4

The research results show that responses of the leaf stoma of *Quercus liaotungensis*, *Ailanthus altissima*, and *Syringa oblata* (woody plant) to a doubly increased CO_2 were not very sensitive; the stomatal resistance did not enlarge; there was no obvious change in transpiration rate, the photosynthesis rate increased by 10%—20% as compared with control or did not increase; the water use efficiency increased from 10% to 100%; and the leaf area increased by a little or was near to the control. It can be considered that a doubly increased CO_2 has a promotion function to different degrees. However, the responses of the leaf stoma of *Oryza sativa*, *Glycine max*, *Setaria italica*, *Echinochloa* sp. (herbaceous plant), especially *Oryza sativa* and *Glycine max* (C_3 plants), to a doubly increased CO_2 were sensitive; the stomatal resistance enlarged; the transpiration rate decreased, and the photosynthesis rate increased in the peak growing period, but decreased in other growing periods. If calculated with the total growing period, it would decrease by about 15%, with a little change in water use efficiency. *Setaria italica* and *Echinochloa* sp. (C_4 plants) had less obvious response to a doubly increased CO_2 as C_3 plants; its stomatal resistance was not much changed, the photosynthesis rate increased in the peak growing period and then had a little decrease, it decreased by 10% in the total growing period and its water use efficiency decreased to some degree.

Key words: doubly increased CO_2 treatment, net photosynthesis rate, stomatal resistance, transpiration rate, water use efficiency.

Residue and Persistence of Pesticide N′-(2, 4-Dimethylphenyl)-N-Methylformamidine Hydrochloride in Cotton Field. Mo Hanhong, An Fengchun et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 5—7

The Residue and persistence of pesticide N′-(2, 4-Dimethylphenyl) - N- methylformamidine Hydrochloride (DMAH) in cotton field were studied in North China during 1992 and 1993. The results showed that the DMAH was a low residual and non-persistent pesticide. The half-life values of DMAH was 4.4—8.1 days in cotton lives and 11.4—12.3 days in soil, respectevely. It was found that the residual level of the pesticide was less than 0.17×10^{-6} in the cotton seeds at an application rate of 10, or 50, 100, 800, 1000 and 1500 fold diluted 25% DMAH sollution and in an application frequency of 7 or 8 times with an interval of 15 days between every two applications.

Key words: pesticide, N′-(2, 4-dimethylphenyl)-N-methylformamidine hydrochloride, residue, persistence, cotton field.

Study on the Bioaccumulation of Chlorobenzenes in Fish and Their Release Behavious. Yu Hongxia et al. (Dept. of Environ. Sci. and Eng., Nanjing Univ., Nanjing 210093): *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 8—11

A fast method was used to determine the bioconcentration factors (BCFs) of seven chlorobenzenes in fish and their release behaviors. The BCF values for the same compounds in various sizes of fish were measured under the same conditions in the laboratory study. The results show that there was a better fitting linear relationship between the logarithmic lipid standardized BCF ($\lg BCF_L$) and the logarithmic octanol/water partition coefficient ($\lg K_{ow}$), expressed by the equation: $\lg BCF_L = 1.918 + 0.044 \lg K_{ow}$, and a better correlationship between each of both the logarithmic uptake rate constant ($\lg K_{12}$) and the logarithmic release rate constant ($\lg K_{21}$) and $\lg K_{ow}$, expressed by the equations: $\lg K_{12} = 0.551 + 0.369 \lg K_{ow} - 1.491 \lg SA$ and $\lg K_{21} = -0.529 - 0.148 \lg K_{ow}$. For those chlorobezanes which are highly soluble in lipid, they may have a huge structure affecting the process of concentration and thus their fitted linear equations were corrected by their molecular surface areas to improve the linear relationship between $\lg K_{12}$ and $\lg K_{ow}$.

Key words: chlorobenzene, bioconcentration, fish, bioacumulation, release behaviors.

Biosorption of Heavy Metals by *Rhizopus Nigricans*. Tu Juan et al. (Institute of Molecular Biology, Nankai Univ., Tianjin 300071): *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 12—15

Adsorption properties of the nonliving *Rhizopus nigricans* for metal ions were studied. The effects of pH, concentration and co-ions on the adsorption efficiency were examined. From the isotherms, the adsorption equilibrium constant (b) and the maximum adsorption capacity (q_∞) in the Langmuir equation and the experimental constant (K) and ($1/n$) in Freundlich equation were determined. Adsorption properties of treated and untreated *R. nigricans* were compared. The results show that the optimum pH value was between 3 and 6.5, the

Abstracts

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($[Fe^{2+}] = 150mg/L$, $[H_2O_2] = 7g/L$) 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 increace 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 evaluting 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 Harpacticoidea 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 harpacticoidea 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 harpacticoidea copepod.

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

Treatment of Spent Tetracycline Liquor by Using an