

## 研究简报

## 河流底泥污染类型标准的制定

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近年来,城市河流的污染采取了一系列的治理措施,河水中污染物的浓度已明显下降。但是经有机物、重金属污染物逐年积累而污染的河床底泥,由于水流作用将释放至水相,再次影响整治后的河流水质。因此制定一个符合我国国情的底泥环境质量标准,已提到议事日程上来。

## 一、制定底泥质量标准的依据

为了尽早填补我国底泥环境质量的空白,首先应该选定危害严重、不易降解、数量较大的污染物作为研究对象,其中应该包括毒性较大的重金属,以及数量较大的有机碳、有机氮污染物指标。作为制定标准的依据,应该对质量基准进行研究,如表1所示。R. A. Baker 曾以浮游动物为研究对象,以控制致死率的生物基准为基础,来制定底泥分类标准<sup>[1]</sup>。本文设想以底泥中污染物释放至水

相的边界环境为研究对象,控制我国地面水水质标准的环境基准为基础,来拟定符合我国国情的底泥标准。其分类标准的依据见表2。

## 二、底泥与流动水相的边界环境

底泥与流动水相之间的物理化学平衡如图1所示。由于水流作用,使底泥中污染物通过悬浮和溶解释放进入水中污染物的量,我们曾做过研究<sup>[2]</sup>。当底泥与悬浮物的物理、化学组成及水质参数等恒定时,底泥中污染物的释放速率  $N_r(\text{mg}/\text{m}^2 \cdot \text{d})$  与水流流速  $u(\text{m}/\text{s})$ 、底泥中污染物含量  $C_s(\text{mg}/\text{kg})$  有下列关系:

$$N_r = k u^n c_s \quad (1)$$

式中  $k$ 、 $n$  为与底泥物理、化学组成、水质有关的系数。

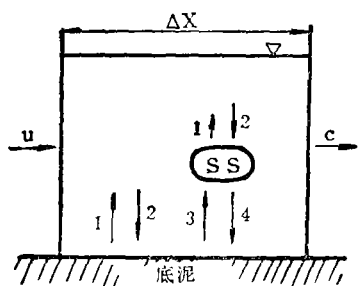


图1 底泥与流动水相的平衡

1. 溶解 2. 吸附 3. 悬浮 4. 沉降

表1 底泥基准研究内容

研究对象	研究学科	剂量-效应类别	基准类别
浮游动物	环境生物学	生物效应	生物基准
底泥、水边界环境	污染生态学	次生污染效应	环境基准

表2 底泥分类标准的依据

类 型	未污染底泥	污染底泥	重污染底泥
基 准			
生物基准 (致死率)	<10%	10~50%	>50%
环境基准 (我国地面水标准)	<二级标准	>二级, <三级	>三级标准

将采集的苏州河上海市区段污染底泥样品置于动态模拟装置(图2)中。该模拟装置的水槽长1m,宽10cm,水深3cm;底泥厚

表 3 底泥中污染物含量与释放速率

D<0.05mm 粒径百分率	94%		96%		97%		相关系数
变量	$c_s$	$\bar{N}_s$	$c_s$	$\bar{N}_s$	$c_s$	$\bar{N}_s$	
参数	(mg/kg)	(mg/m <sup>2</sup> ·d)	(mg/kg)	(mg/m <sup>2</sup> ·d)	(mg/kg)	(mg/m <sup>2</sup> ·d)	
Hg	2.34	0.090	2.10	0.062	1.70	0.045	0.91
Cd	93.0	1.0	24.6	0.74	2.06	0.082	0.86
Pb	214	1.4	210	1.6	43.4	1.2	0.85
Cr	670	10	285	8.6	25.0	0.40	0.87
Mn	612	8.2	726	13	610	11	0.81
Cu	1580	75	670	8.3	25.0	0.7	0.94
Zn	3342	65	1934	17	91.0	1.8	0.93
KTN	2359	285	1745	154	1171	137	0.92
COD <sub>Cr</sub>	69432	2660	38775	1690	20214	1630	0.94
BOD <sub>5</sub>	3828	279	2573	226	1072	154	0.99

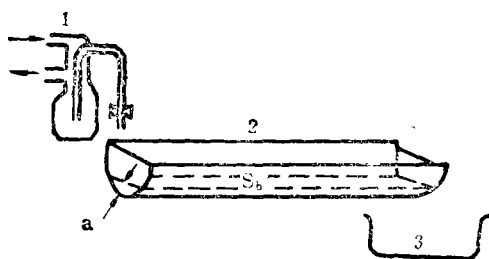


图 2 动态模拟装置

1. 恒流装置 2. 水槽 3. 排水设备

度 1cm, 容重 0.38g/ml; 水流流速为 0.0001、0.0005、0.002、0.01、0.1m/s; 水质符合二级标准的未污染河水。实验时间为 30d。

将实验前与实验后的底泥风干, 分别测出其含量, 应用减量法求得底泥中污染物的释放量  $A(\text{mg/kg})$ 。实测的污染物释放速率  $\bar{N}_t$  可从动态模拟装置中实际测得的参数求得:

$$\begin{aligned}\bar{N}_t &= 10 \times V_t \times r_t \times A/t \times S_b \\ &= 10 \times a \times r_t \times A/t\end{aligned}\quad (2)$$

式 (2) 中  $V_t$  为底泥体积 ( $\text{cm}^3$ ),  $r_t$  为容重 ( $\text{g/ml}$ ),  $t$  为实验时间 ( $\text{d}$ ),  $S_b$  为底泥面积 ( $\text{cm}^2$ ),  $a$  为底泥厚度 ( $\text{cm}$ )。

1. 底泥中污染物含量与释放速率之间的关系

实验选择在底泥颗粒大小组成相近的条件下, 当河流参数固定时, 底泥中污染物释放速率与底泥中含量有密切的相关关系。根据上述实验条件, 取三个断面中颗粒直径小于 0.05mm 的百分率相近的底泥进行动态试验, 结果见表 3。其关系符合  $\bar{N}_t = ac_s + b$  线性方程, 相关系数  $r = 0.8 \sim 0.95$ 。

2. 底泥中不同污染物与释放速率之间的关系

应用上述动态模拟条件, 分别按 0.0001、0.0005、0.002、0.01、0.1m/s 的流速, 将实测参数求得的释放速率代入式 (1) 中, 得出联立方程。根据最小二乘法求出各个污染物的  $k$ 、 $n$  值 (表 4)。从表 4 可见, 由于各个污染

表 4 不同污染物释放时的  $k$ 、 $n$  值

污染物	Hg	Cd	Pb	Cr	Cu	Mn	Zn	KTN	COD <sub>Cr</sub>	BOD <sub>5</sub>
$n$	0.29	0.16	0.24	0.28	0.30	0.29	0.29	0.20	0.11	0.11
$k$	0.061	0.064	0.027	0.11	0.05	0.093	0.05	0.23	0.09	0.18

物在底泥及水中存在的形态不同,其释放速率也不同。

### 3. 水流流速与释放速率之间的关系

用动态模拟装置,改变流速,取得各个污染物的实际释放速率与流速之间关系如图3,它们之间呈指数关系。若与式(1)中按流速、底泥含量及各个污染物的 $k$ 、 $n$ 值计算所得的释放速率相比,其误差不大于35%。因此,可用式(1)来计算底泥中污染物的释放速率。

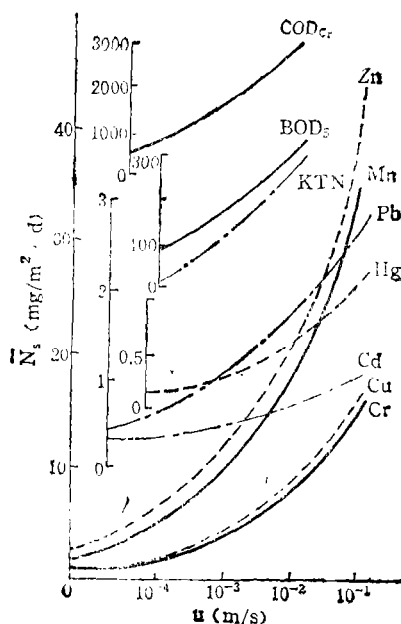


图3 释放速率曲线

### 三、次生污染效应指标

将评价的河段看成一个系统,则系统中由于污染底泥的释放而增加的水质浓度 $\Delta c$ (mg/l)为:

$$\Delta c = \frac{N_s \cdot S}{Q} \\ = 1.16 \times 10^{-3} \times \frac{k u^n \cdot c_s \cdot L_i \cdot W_i}{Q} \quad (3)$$

式(3)中 $L_i$ 为河段长度(m), $W_i$ 为宽度(m), $Q$ 为流量( $m^3/s$ ), $1.16 \times 10^{-3}$ 为单位换算常数。若将系统中的水质浓度 $\Delta c$ 控制在环境基准(表2)基础上,由式(3)得知,系统中的底泥应控制的污染物含量 $c_s$ 为:

$$c_s = 8.64 \times 10^7 \times \frac{\Delta c \times Q}{k u^n \times L_i \times W_i} \quad (4)$$

已知上海苏州河市区段长度为17km,宽度为70m,日平均净流量为 $1.3m^3/s$ ,若以最大水流流速 $u_{max} = 0.5m/s$ 来冲刷底泥,式(4)可简化为:

$$c_s = \frac{94 \times \Delta c}{k \times 0.5^n} \quad (5)$$

若底泥中各个污染物释放速率系数 $k$ 、 $n$ 值应用表4所列;底泥中各个污染物释放至水相的浓度 $\Delta c$ 控制在表5所列的环境基准<sup>[3]</sup>基础上,用式(5)进行计算,可得到限制

表5 环境基准

$\Delta c$ (mg/L) 参数	Hg	Cd	Pb	Cr	Cu	Mn*	Zn*	KTN**	COD <sub>Cr</sub> ***	BOD <sub>5</sub>
类型										
未污染底泥	0.0005	0.005	0.05	0.2	0.01	0.1	0.1	1	20	3
污染底泥	0.0005 —0.001	0.005 —0.01	0.05 —0.1	0.2—0.5	0.01 —0.03	0.1—1	0.1—1	1—4.5	20—30	3—5
重污染底泥	0.001	0.01	0.1	0.5	0.03	1	1	4.5	30	5

\* 未污染底泥项中,Mn为生活饮用水标准,Zn为渔业水标准;重污染底泥项中,Mn、Zn为工业企业设计卫生标准。

\*\* KTN在未污染底泥项中,应用地面水总氮标准;在污染底泥项中,应用上海自来水公司黑臭指数 $1 < 5$ 的指标而定。 $KTN = 1 \times (DO_{\%} + 0.4) = 5 \times (4/8 + 0.4) = 4.5$ 。

\*\*\* 将苏州河底泥释放至水相的水质,同时用COD<sub>Mn</sub>和COD<sub>Cr</sub>法测定,得到换算关系式:  $[COD_{Cr}] = 5 \times [COD_{Mn}]$ 。COD<sub>Cr</sub>项中标准为地面水标准中COD<sub>Mn</sub>指标的换算值。

表 6 底泥分类标准

$c_i(\text{mg/kg})$ / 参数		Hg	Cd	Pb	Cr	Cu	Mn	Zn	KTN	COD <sub>Cr</sub>	BOD <sub>5</sub>
类型											
未污染	本法	<1	<8	<200	<200	<23	<120	<200	<500	<20000	<2000
	[美]	<1	—	<40	<25	<25	<300	<90	<1000	<40000	—
污 染	本法	1—2	8—16	200—400	200—500	23—70	120—1000	200—2000	500—2000	20000—25000	2000—3000
	[美]	—	—	40—60	25—75	25—50	300—500	90—200	1000—2000	40000—80000	—
重污染	本法	>2	>16	>400	>500	>70	>1000	>2000	>2000	>25000	>3000
	[美]	>1	>6	>60	>75	>50	>500	>200	>2000	>80000	—
土壤背景值		0.216	0.134	21.3	64.6	23.5	558	75.5			

底泥中各个污染物的浓度  $c_i$  (见表 6), 定出对底泥污染的分类标准。若与美国应用生物试验分类的结果<sup>[1]</sup>加以比较, Hg、Cd、Cu、Mn、KTN 等结果相近。但 Pb、Cr、Zn 等相差一个数量级, 若以上海地区土壤背景值<sup>[4]</sup>来衡量, 本试验的分类标准较符合我国国情。

#### 四、苏州河市区段底泥的评价

图 4 为 1986 年 5—7 月苏州河市区段实测的底泥中重金属与有机污染物含量分布图。按制定的底泥分类标准评价得知, 市区河段底泥已受到不同程度污染。其中浙江路桥—恒丰路桥区段 NO. 3 采样点表层的 KTN、BOD<sub>5</sub>、COD<sub>Cr</sub>、Cu, 1m 深层的 Hg、Cd; 以及江宁路桥—叶家宅桥区段 NO. 5 采样点 COD<sub>Cr</sub>、Hg、Cu; NO. 6 采样点的 Cu 均超过重污染底泥类型标准, 为苏州河底泥污染严重区段。假如对该二个区段进行整治, 则整个市区段底泥, 由悬浮和溶解释放至水相的浓度, 将不再超过地面水三级标准。

#### 五、小 结

1. 通过动态模拟底泥的释放试验, 建立了底泥中污染物向水相释放的速率方程, 探

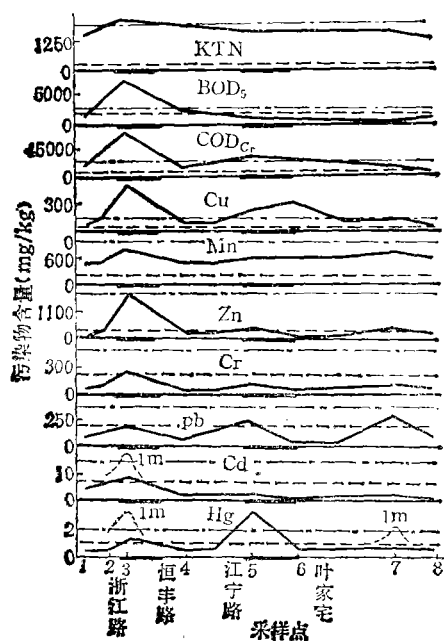


图 4 苏州河市区段底泥污染物含量分布图

— · — · — 重污染底泥类型    - - - - - 污染底泥类型  
—— 严重污染河段

讨了影响释放速率的有关因素, 并以计算值与实测值对比来检验方程, 其误差在 35% 以内。

2. 以底泥释放至流动水相的边界环境为研究对象, 控制地面水水质标准的环境基准

为基础,应用底泥释放模式,拟订出上海地区的底泥分类标准。

3. 应用底泥分类标准,对上海苏州河市区段底泥作了评价,约有四分之一河段为底泥污染严重区段,假如采取整治措施,由底泥释放至水相的浓度,不再超过地面水三级标准。

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## 土壤对酸沉降缓冲机制探讨

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### 一、前 言

土壤对酸沉降具有一定的缓冲作用,不同土壤的缓冲能力也各不相同。那么,土壤缓冲作用的本质是什么,不同土壤为什么具有不同的缓冲能力,要解决这些问题,就必须了解土壤的缓冲机制,了解土壤内部的化学过程。

Tabatabai<sup>[1]</sup> 分析了不同酸度下土壤所发生的中和反应。pH6.2—8.6, 大气中  $\text{CO}_2$  与土壤中  $\text{H}_2\text{CO}_3$  平衡; pH5.0—6.2, 硅酸盐矿物风化产生  $\text{H}_4\text{SiO}_4$ ; pH4.2—5.0, 可交换态阳离子  $\text{K}^+$ 、 $\text{Na}^+$ 、 $\text{Ca}^{2+}$ 、 $\text{Mg}^{2+}$  等与  $\text{H}^+$  交换; pH3.5—4.2,  $\text{Al}^{3+}$  离子由铝化合物中释放出来; pH3.0—3.5, 土壤中  $\text{Fe}_2\text{O}_3$  转换成  $\text{Fe}^{3+}$ 。这些过程都消耗氢离子。显然土壤酸度不同时,中和反应是不同的,缓冲过程也是不同的。Johnson 等<sup>[2]</sup>认为土壤对酸沉降的中和过程分两步进行。第一步最初外来的  $\text{H}^+$  酸度由土壤溶液中溶解的氧化铝中和同时释放出  $\text{Al}^{3+}$ ; 第二步  $\text{H}^+$  和  $\text{Al}^{3+}$  的酸度由土壤中原生矿物的风化解所中和同时释放出碱基阳离子。大多类型的土壤都有通过

阳离子交换来平衡酸沉降带来的过量  $\text{H}^+$  的能力<sup>[3]</sup>, 所以土壤化学组成的变化是缓冲酸侵入的一种机理<sup>[4]</sup>。

本文通过酸性水对中国若干地区森林土壤的模拟淋溶实验,分析了淋出液中 pH 值和  $\text{K}^+$ 、 $\text{Na}^+$ 、 $\text{Ca}^{2+}$ 、 $\text{Mg}^{2+}$ 、 $\text{Al}^{3+}$ 、 $\text{Si}^{4+}$  等的含量和动态变化规律,对土壤缓冲机制进行了初步探讨。

### 二、实 验

#### 1. 样品采集(见表 1)

#### 2. 淋溶实验

用去离子水和稀硫酸配成酸性淋入液。称取定量风干均匀土样装柱,用淋入液淋溶,控制淋出液流速  $80 \pm 5 \text{ ml/h}$  (晚上  $50 \pm 5 \text{ ml/h}$ ),连续淋溶约 70h,淋入液始终浸泡土壤样品。每隔一定时间收集定量淋出液。每个地区各层土壤装柱 4~5 根,用不同淋入液同时淋溶,每根柱分 10 次收集淋出液约 5000ml,共收集淋出液样品 680 个。

#### 3. 淋出液样品测定

(1) pH 值测定: 直接用 pH 计测定。

(2) 金属离子测定: 淋出液经  $0.45 \mu\text{m}$

# Abstracts

Chinese Journal of Environmental Science

## An Experimental Research on Mechanism of Biological Activated Carbon and Theory Concerned

Liao Zhimin, Xu Shusen and Lan Shucheng (Beijing Municipal Research Institute of Environmental Protection, Beijing)

In this experiment, the up-flow columns were used. By controlling different concentrations of dissolved oxygen and phenol in influent and effluent, the quantity of bioregeneration were calculated. Meanwhile the hypothesis of "the outer-cell enzyme" has been discussed. (See pp. 2—7)

## Prediction about the Influence of Hot Water Discharged from the Nuclear Power-Station on Oxygen-Lack in Bottom Water of the Daya Bay Guangdong Province

Lin Hongying and Han Wuying (South China Sea Institute of Oceanology, Academia Sinica, Guangzhou)

In recent years, the investigative data for essential factors of water chemistry in the Daya Bay show that one of the natural eco-environmental characteristics is that water is seasonally divided into layers, and there appears lack of dissolved oxygen in bottom layer during April—October. When hot water from the Nuclear Power Station is discharged to the Daya Bay, temperature of the surface layer water will increase and the phenomenon will be more obvious. According to calculation, if water temperature increases 1—2°C, the affected area will widen 3—5 km<sup>2</sup>, duration of the layer divided will delay 33—67 days, and consumptive rate of dissolved oxygen will increase 14—25%. Finally the authors suggest that if the Power Station draw cooling water from the bottom layer, the primary productivity would increase 2—116% and consumptive rate of dissolved oxygen will decrease 7.7—14%. (See pp. 7—12)

## Nitric Acid and Ammonia in the Air of the Emei Mountain area, Sichuan Province

Sun Qingrui, Wang Meirong and Shao Kesheng (Department of Technological Physics, Peking University, Beijing)

HNO<sub>3</sub>(g) and NH<sub>3</sub>(g) in the air have been measured in four different heights at the Emei Mountain area in October of 1985. The data analysis shows that vertical profiles of the concentrations of HNO<sub>3</sub> and NH<sub>3</sub> increased in a factor of  $e$  as the heights dropped a distance of 780 m

and 1000 m respectively. During that time the equilibrium between NH<sub>4</sub>NO<sub>3</sub>(s) and HNO<sub>3</sub>(g), NH<sub>3</sub>(g) didn't exist. Quite good correlation has been obtained between HNO<sub>3</sub>(g) and O<sub>3</sub> in the air. Calculations suggest that maximum contributions of H<sup>+</sup> and NO<sub>3</sub><sup>-</sup> caused by HNO<sub>3</sub>(g) in fog water at the mountaintop are 11% and 8% respectively. (See pp. 12—16)

## An Experiment of Pathogeny of Kaschin-Beck Disease Caused by Humic Compounds in Water

Wang Weizhe and Feng Lanfei (Liaoning Institute of Fundamental Medicine, Shenyang)

This paper introduces briefly the results of pathogeny of Kaschin-Beck disease (KB) which the authors have researched into for many years. (1) In KB zone, there exists humic substance in drinking water, which causes the damage of chondrocytes *in vitro*. As water quality was improved and the substance lessened, the incidence of KB disease in the residents had dropped and the effects of chondrocyte damage became lower; (2) Selenium can be used to prevent chondrocyte damage caused by humic substance. This result corresponds to the disease that probably occurs in the zone of low selenium nutrition. (3) Cerebral and humic substance in the KB zone has caused GBH-Px activity of rat blood decreasing. (4) The initial results showed that hydroxyl group of the organic compound might affect chondrocyte damage. (See pp. 16—20)

## An Investigation of Air Ions and Radon Hazard in the Underground Installations

Tian Zhigian, Feng Yueduan and Yuan Daiguang (Engineer Unit of Headquarters of the General Staff of PLA)

This paper deals with 3-years investigative results of 37 underground installations in Changsha, Wuhan, Beijing, Shenyang and Dalian cities. The results show that as the installations have been in use, mean concentration of air anions is 201/cm<sup>3</sup>, much lower than that at ordinary rooms, while mono-polarity index are 2.0, much higher. The main factors affecting air anions are radon and its daughter, dust and air humidity, ventilating conditions etc. It has been determined that concentration of radon daughter in the air is 93 Bq/m<sup>3</sup>. In this paper, the method for estimating radon exhalation rate, radon proof ventilation rate and effective way for improving air anions have been discussed. (See pp. 21—25)

## Enactment of the Standard Concerning Polluted Sediment Types in the Rivers

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This work is designed to explore the regularity of organic and heavy metal pollutants released from re-suspended sediment in the Suzhouhe River of Shanghai, and to propose the classification standard of sediment on the basis of surface water quality standard. The proposed standard is classified into nonpollution, pollution and heavy pollution by comparing each of chemical parameters. Pollution assessment was done for the Suzhouhe River according to the standard. It is showed that when the sections of heavily polluted sediment are cleaned up, the sediment would no longer influence on water quality in the Suzhouhe River. (See pp. 26—30.)

### Buffering Mechanism of Soil for Acidic Precipitation

Liao Bohan and Li Changsheng (Research Center for Eco-Environmental Sciences, Academia Sinica)

Buffering mechanism of soil for acidic precipitation is an important topic in studying the effects of acidic precipitation on soil. Based on simulation of leaching experiments of acidic precipitation for some forest soils in China, this paper brings forward a discussion about the buffering mechanism of soil for acidic precipitation. The soil consumes  $H^+$  ion through releasing cations, the total amount of released cations is equal to the total amount of consumed  $H^+$  ion in soil. The buffering mechanism of soil consists of three processes, which are the exchange of cations, hydrolysis of aluminum hydroxide, and weathering of primary minerals. The importance of each process is different in various conditions. (See pp. 30—34.)

### The Structure and Function of Microbial Population ZE-1 for Decolouring Dyeing Wastewater

Qian Bing, Ye Junying and Xu Guanghui (Zhejiang Institute of Microbiology, Hangzhou); Min Yijue and Shen Yuru (Zhejiang Institute of Environmental Protection, Hangzhou)

The principal purpose of this work is to explore the composition and activeness of microbial population ZE-1 which is able to decolour dyeing wastewater of silk goods more effectively. Ten strains of bacteria were isolated from the samples collected from experimental dyeing wastewater and ten strains from pilot plant dyeing wastewater of silk goods. The results showed that the composition of microbial population ZE-1 consisted of genera of *Bacillus*, *Acinetobacter*, *Achromobacter* and *Pseudomonas* essentially. In microbial population ZE-1 conserved in the lab, the dominant bacteria were *Bacillus* and *Acinetobacter*, which occupied 80% of total number of the isolates. The more effective species or strains decolouring dyeing wastewater microbial population ZE-1 were *Bacillus subtilis* and

*Acinetobacter calcoaceticus*, *Aeromonas punctate* and *Pseudomonas* No. 19 isolated from pilot-plant samples were effective too. (See pp. 35—38)

### Interaction of Carbofuran and Activity of Soil Microorganisms in Paddy Fields

Huang Xin, Fan Dejiang and Chen Hexin (Research Team of Pesticide Residues, Zhejiang Agricultural University, Hangzhou)

An attempt was made to understand the biological degradation of Carbofuran in paddy soil and its effect on some microbial activities in soil. The results showed that the degradation of Carbofuran in paddy soil was affected by both biological factors and non-biological factors. Degradation of the pesticide had been retarded by the glucose at concentration of 1% during the early period, though the loss of the pesticide was accelerated during the late period. However, glucose at concentration of 0.1% did not retard degradation of Carbofuran.

Carbofuran at the concentration of 50ppm or more stimulated the degradation of cellulose in four types of soils. The ammonification increased significantly in silty loam while decreased in saline polder soil, when treated with high concentration of Carbofuran (500ppm). (See pp. 38—43)

### Treatment of Brewery Saccharification Waste water with the Anaerobic Attached Film Expanded Bed Reactor

Zheng Ping et al. (Department of Environmental Science, Zhejiang Agricultural University, Hangzhou)

In this paper AAFEB reactor is considered to treat brewery saccharification wastewater. When influent COD concentration was 3808—13770 mg/L, operating temperature 28°C, HRT 6 hours, volumetric COD loading rate 33.76 kg/m<sup>3</sup>·day, the percentage of COD removal attained 86.88% and volumetric biogas production rate 13.90 m<sup>3</sup>/m<sup>3</sup>·day. Per kg COD removed produced 0.34 m<sup>3</sup> of methane. When HRT was shortened to 3.5 hours, volumetric COD loading rate reached 20.35 m<sup>3</sup>/m<sup>3</sup>·day. The critical bed expansion was about 10% and critical ratio of alkalinity to acidity about 3.0 (See pp. 44—48)

### Treatment of Urea-Plant Wastewater by Biological Hydrolysis

Cui Lianqi, Ji Biliang and Li Yaqi (Institute of Environmental Protection, Lanzhou Chemical Industry Co., Lanzhou)

Results of the experiments show that denitrifying bacteria were able to hydrolyze urea in the wastewater into CO<sub>2</sub> and NH<sub>3</sub> which could be recovered under suitable conditions. Sources of NH<sub>3</sub> or organic matters in the waste-