

## 治理技术

## 膜分离技术治理糠醛废水\*

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**摘要** 糠醛生产废水中含 1—2.5% 的乙酸,若废水外排,会造成大量损失且污染环境。通过 30—80 对膜组装的 400×800mm 电渗析器中试操作,回收了浓度为 20% 的乙酸,再经萃取、精馏工艺得到工业一级乙酸。治理后的废水含酸量为 0.02—0.05%,可安全排放及回用。中试技术指标优于小试,重现良好。

**关键词** 糠醛废水,膜分离,电渗析,乙酸。

以玉米芯等秸秆为原料生产糠醛过程中,除得到糠醛外,副产品乙酸约为糠醛量三分之一。糠醛初馏塔底排放废水中,乙酸含量通常为 1—2.5%。年产千吨的糠醛厂,日排含酸废水近百吨,若不经治理任其外排,将严重污染环境,且浪费乙酸资源。欲达到消除污染,回收乙酸,废水再用及安全排放的目的,采用常规萃取、精馏方法<sup>[1-2]</sup>难以实现。应用新型膜分离技术治理糠醛废水,采用电渗析-萃取-精馏工艺,可实现上述目的<sup>[3]</sup>。为进一步了解与掌握电渗析分离过程的性能,在 5 对膜组装的 200×400mm 电渗析器小试基础上,进行了 30—80 对膜组装的 400×800mm 电渗析器中型放大试验,重现良好,为实现工业化提供了必要依据。

本文就影响电渗析过程性能的诸因素做了进一步的探讨,从中得出一般规律,对稳定电渗析操作,提高过程效率及进行放大设计有指导意义。

## 一、试验部分

### 1. 装置

预处理柱:直径 130mm、高 1500mm 聚丙烯柱;

电渗析器:400×800mm;

组装形式:二级二段;

隔板:无回路聚丙烯编织网板;

膜类:均相阴、阳离子交换膜;

膜对:30—80;

电极:石墨板。

### 2. 分析

原料及产品分析:气相色谱;

废水净化度测定:分光光度;

废水中铁离子测定:硫氰化钾比色;

乙酸含量测定:中和滴定。

## 二、工艺过程

### 1. 废水预处理

糠醛废水为土黄色,呈浊状,其中除含乙酸外,还含有少量糠醛及其他微量有机酸、醛等。阴膜对带负电荷的有机物尤为敏感,于脱酸室的一侧形成沉淀,使膜电阻增加;高铁离子与阳膜上的活性基团发生反应,不可逆地固定在膜上,膜被污染或堵塞;悬浮物的沉积结垢,使水流分布不均,电阻增加,导致极化。糠醛废水预处理为:砂粒截留、活性炭吸附、树脂交换等。经预处理后,几乎不含铁离子,呈无色透明液体,透光率达 90% 以上。

\* 参加试验工作的还有赵银、万世义、王秀英、郭爱萍、温元强、王一智等。

## 2. 电渗析分离

电渗析器是由极板、离子交换膜和隔板组成。如图 1 所示,当糠醛含酸废水通入时,在直流电场的作用下,由于膜的选择透过性,

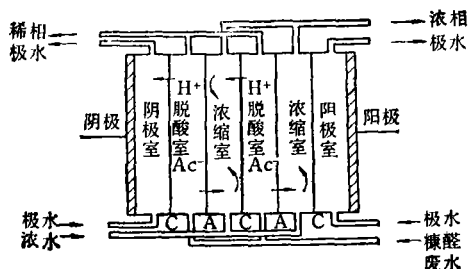


图 1 电渗析过程示意图

A. 阴膜 C. 阳膜

产生离子 ( $H^+$  和  $Ac^-$ ) 的定向迁移。离子迁移的结果,使废水被净化,乙酸被浓缩,达到回收有用物质的目的。

在电渗析分离过程中,随着脱酸室与浓缩室浓差加大,将使过程效率下降。因此,电渗析运行方式采用了分步进行的部分循环式流程。脱酸室流出物为外排水,浓缩室流出物为电渗析浓缩酸。

## 3. 乙酸再浓缩

选用对乙酸选择性较好又具有一定脱水能力,不易积累杂质,低沸点的乙酸乙酯为溶剂。乙酸乙酯于萃取塔内萃取电渗析浓缩酸中的乙酸,其萃取相入脱水塔,由该塔底所得粗乙酸再经精制塔得副产物乙酸。萃余相与

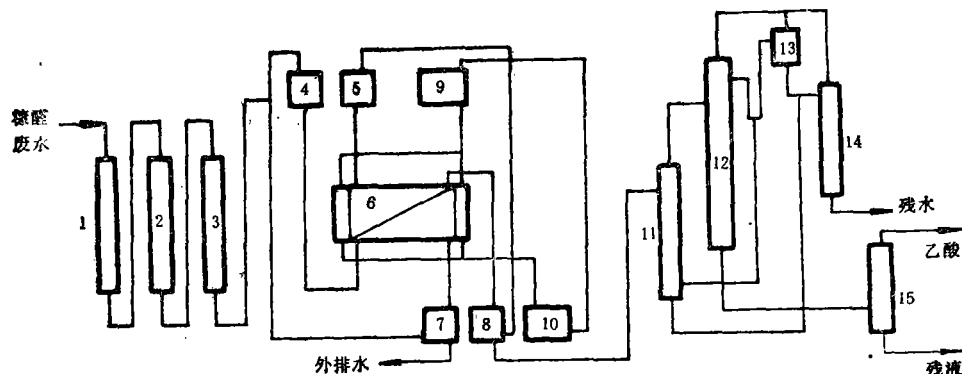


图 2 工艺流程示意图

1、2、3. 预处理柱; 4、5. 稀、浓相高位槽; 6. 电渗析装置; 7、8. 稀、浓相贮槽; 9. 极水高位槽; 10. 极水贮槽; 11. 萃取塔; 12. 脱水塔; 13. 酯水分层器; 14. 回收塔; 15. 精制塔

水层入回收塔,以回收乙酸乙酯。

电渗析-萃取-精馏工艺流程示于图 2。

## 三、结果与讨论

### 1. 极限电流密度

电渗析过程常因发生极化使效率下降,极限电流密度就是发生极化时的电流密度界限。在极限电流密度以下操作,可缓和或避免极化。本试验采用电压-电流曲线法确定极限电流密度。

图 3 示出脱酸室进料乙酸浓度对极限电流密度的影响。极限电流密度随脱酸室进料

乙酸浓度的增大而增大。当浓度大约在 0.6% 以下时,曲线的斜率变大,极限电流密度下降较快;浓度较高时,斜率逐渐变小,极限电流密度上升缓慢。因为物料浓度提高,  $H^+$  和  $Ac^-$  离子浓度增大,浓差扩散推动力加大,增强了传递电荷的能力,致使极限电流密度增高。

图 4 示出物料流量对极限电流的影响。随着物料流量的提高,极限电流增大。因为提高流量,流速增大,电渗析器小室内的物料呈湍流状态,界面层变薄,扩散阻力减小,有利于离子的扩散和迁移,致使极限电流值增

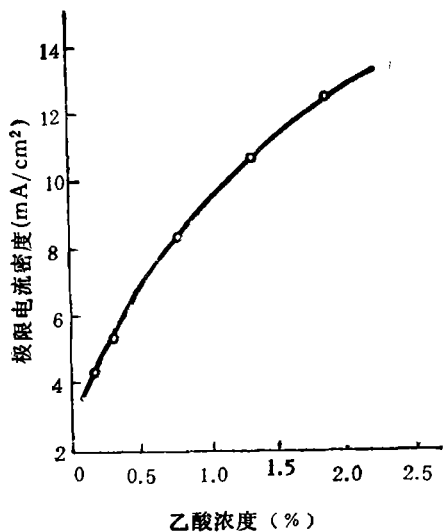


图3 脱酸室进料乙酸浓度对极限电流密度的影响  
物料流量: 210 L/h 浓缩室进料: 5.55—5.85%  
脱酸室进料: 0.21—2.16%

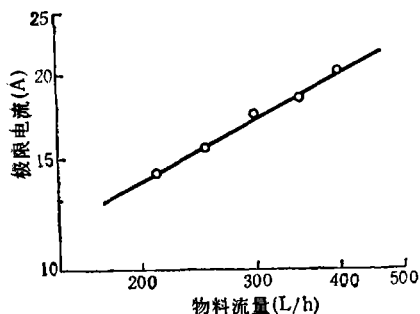


图4 物料流量对极限电流的影响  
脱酸室进料: 0.68—0.38% 浓缩室进料:  
7.35—7.70%

大。

## 2. 操作电流密度

在电渗析过程中,提高操作电流密度,有利于离子迁移,但实际操作电流密度不得高于极限电流密度。

操作电流密度直接影响着电渗析器的性能。图5表明,提高操作电流密度,单程脱酸量、耗电量增加,这是因为提高操作电流密度,必然伴随着推动力(操作电压)的提高,使离子迁移强化。但因接触电阻、膜电阻、水电阻的增加,当电流密度到一定值时,电流效率

却开始下降。可见,电渗析分离存在着适宜的操作电流密度范围。

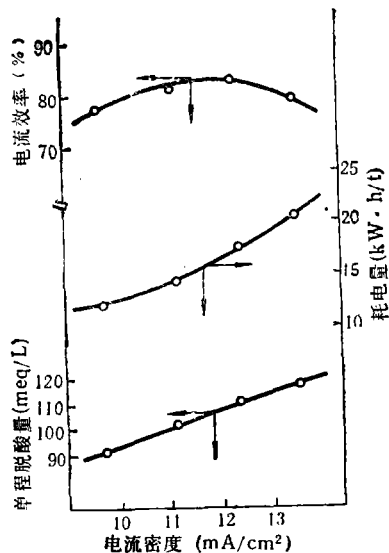


图5 电流密度与单程脱酸量、耗电量、电流效率的关系  
物料流量: 400 L/h 脱酸室进料: 6.79—2.16%  
浓缩室进料: 10.10—15.31%

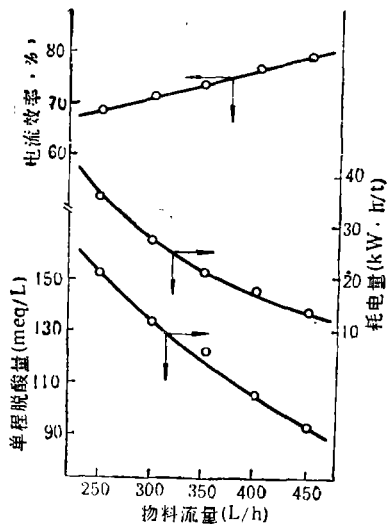


图6 物料流量与单程脱酸量、耗电量、电流效率的关系  
操作电流: 50A 脱酸室进料: 10.10—6.61%  
浓缩室进料: 15.52—20.57%

## 3. 物料流量

加大物料流量可改善电渗析性能,强化操作。图6表明,物料流量增大,膜间物料分

布均匀,使物流呈湍流状态,滞流层变薄,电阻减小,耗电量下降,电流效率增加。但因流量变大,物料在电渗析器中停留时间缩短,使单程脱酸量下降。因此,实际操作中应综合分析,确定最适宜的物料流量。

#### 4. 进料浓度比

进料浓度比的影响示于图7。当脱酸室进料浓度不变,随着进料浓度比(浓缩室进料浓度与脱酸室进料浓度的比值)的增大,浓缩

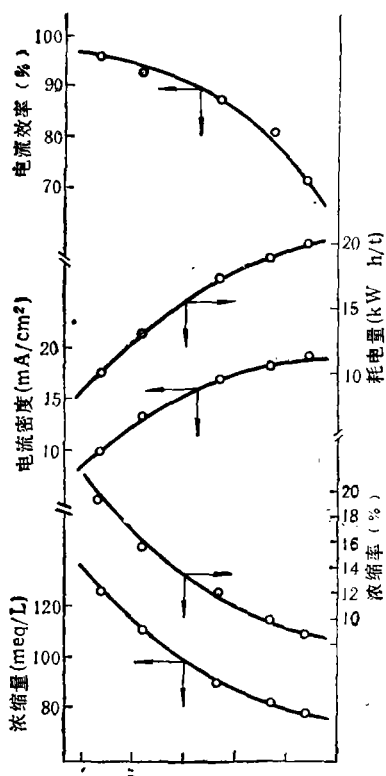


图7 进料浓度比与浓缩量、浓缩率、电流密度、耗电量、电流效率的关系  
电压: 220V 物料流量: 500 l/h 脱酸室进料: -1.52%

量、浓缩率、电流效率相应下降,而电流密度、单位电耗随之上升。因随着进料浓度比的增大,浓缩室与脱酸室的浓度差就增大,溶质由浓缩室向脱酸室的浓差扩散以及水由脱酸室向浓缩室的渗透必然增强,使离子迁移的绝对量减少,浓缩室出料浓度梯度变小,从而导致浓缩率、浓缩量,电流效率下降。但随着浓

缩室进料浓度增大,离子数增多,在恒压操作下电流密度增强,单位电耗也随之上升。

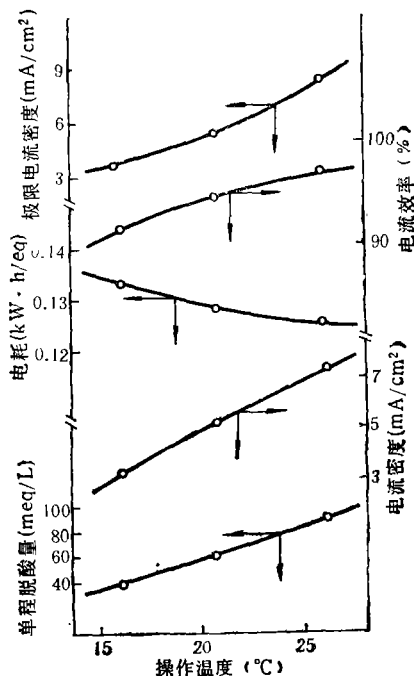


图8 物料温度与单程脱酸量、电流密度、电耗、电流效率、极限电流的关系  
物料流量: 600 l/h 电压: 220V 稀相浓度范围: -0.6% 浓相浓度范围: -5%

#### 5. 操作温度

在电渗析运行中,提高操作温度是有利的。如图8所示,随着操作温度的提高,单程脱酸量、电流密度、电流效率、极限电流密度均提高,而电耗下降。其原因在于提高温度,溶液中离子水合作用减弱,溶液粘度变小,加快离子迁移,使导电性能提高;膜的溶胀度变大,导电性能也随之提高;水电阻减小,降低操作电压,减少电耗。但由于离子交换膜和电渗析装置材质性能所限,操作温度不宜太高。

中型放大试验与小试相比较,重现良好,指标优于小试。应用电渗析技术从糠醛含酸废水中回收乙酸,脱酸率达98%,电流效率在85%左右,流程长度4.8—6m,每处理一吨糠醛废水耗电13.2~16.5kW·h。脱酸室外

排水无色透明,含乙酸量为 0.02~0.05%,接近排放标准,也可供生产回用。浓缩室得到 20% 的乙酸,作为萃取、精馏后浓缩的原料,每吨耗电 175.3~218.1kW·h。

采用较成熟的萃取、精馏工艺,对 20% 的电渗析浓缩酸进行再浓缩。溶剂为乙酸乙酯。来自往复振动筛板萃取塔的萃取相,于填料塔内共沸脱水后,得到 99% 的粗乙酸,再通过间歇塔精制,产出工业一级乙酸(符合 GB1628-79 指标)。萃取、精馏过程中乙酸的回收率为 90% 左右

本方法除具有明显的社会效益、环境效益外,也有一定的经济效益,粗估利润率为 20% 左右。在中型试验基础上,目前已转入工业化实施。

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## 液膜乳化法处理炼油厂精制石蜡废白土\*

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**摘要** 稀碱液在蒸汽搅拌作用下与含蜡废白土接触反应以减弱和破坏废白土的表面能、孔结构及酸性吸附中心的活性,使石蜡充分释出,同时,反应生成物构成的表面活性剂所产生的乳化作用,促使石蜡充分转入水相,形成水包油的不稳定液膜,加水稀释后自然破乳化,石蜡回收率可达 90%。

**关键词** 乳化;液膜;废白土;石蜡回收

炼油厂在石蜡精制生产工艺中,最后一道工序通常是采用活性白土进行精制脱色和纯化,其排出的废白土中吸附了大量的胶质、盐类、色素及 20% 左右的残蜡,成为一种褐色粉状体(有时粘结成块)的工业固体废渣,又称废白土。由于废白土中杂质多而含蜡量少,同时缺少简易有效的手段进行石蜡回收,因此,废白土至今仍为石油化工棘手问题。目前,国内外一般均采用填埋或焚烧法进行废渣处理,既费工又无经济效益。有人曾采用加温、水洗等方法,试行回收残蜡,但回收率只有 25%,无经济效益而作罢。若用溶剂抽提,回收率较高,但工艺设备复杂,成本高,且有防爆等难题。为了较好地解决废白土的处理及石蜡回收,我们于 1986 年着手了该项目

的研究,开发成功了液膜乳化法新工艺,并于 1987 年实现了工业化。

### 一、基本原理

液膜乳化法是采用一种稀碱液,在蒸汽加热搅拌作用下与废白土充分接触反应,以减弱和部分破坏废白土的表面能、孔结构及酸性吸附活性中心,并利用反应生成物构成的表面活性剂所产生的乳化作用,形成水包油的乳液膜,将废白土中吸附的石蜡充分回收。

石蜡精制所用的活性白土,是天然原土经酸化活化处理而得,主要是  $Al_2O_3$  和  $SiO_2$

\* 于 1988 年 12 月通过江苏省科委技术鉴定,并获得中国专利。

leached from red soil were much larger than those from yellow brown soil or black soil. Leaching of Cd was more sensitive than that of Cu.

(2) The effects of simulated acid rain on speciations of Cu or Cd in soils were relatively obvious. With pH values of the precipitation reducing, a partial Cu and Cd in yellow brown soil and black soil were transformed into exchangeable speciation, and those in red soil transformed into water-soluble form.

(3) Acid rain evidently affected biotoxicity of Cu or Cd in soil. The effect of Cu- or Cd-biotoxicity was high in red soil and low in black soil.

In short, the acid resistant capacity of soils in order is black soil > yellow brown soil > red soil.

**Key Words:** acid rain, copper and cadmium, soil, biotoxicity.

**Application of the Theory of Multivariate Statistical Analysis to the Prediction of Air Pollution in Urban Environment.** Huang Guo-he (Xiamen Research Institute of Environmental Protection, Fujian): *Chin. J. Environ. Sci.*, 12(2), 1991, pp. 29—34.

A stepwise cluster analysis method toward a multitude of environmental variables was advanced for the prediction of air pollution in urban environment. The method has improved monovariate AID(Automatic Interaction Detection) algorithm. It can effectively deal with continuous and discrete variables, as well as the nonlinear relations among variables. Compared with classical modelling theories, the method provides a new way for predicting air pollution.

In a case study, the relationship between three air pollutant concentrations and four impact factors in thirty-one grid squares in Xiamen was analyzed. Cluster three concerning quantitative correlation between air quality and the distribution of relevant impact factors were derived from significant test, discriminant analysis and cluster analysis to realize the aim of predicting air quality.

**Key Words:** multivariate statistical analysis, air pollution, stepwise cluster.

**Use of the Residue after Reclamation of Protein and Chrome Salt from Leather Shavings.** Jiang Ting-da, Zhang Chun-ping (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing): *Chin. J. Environ. Sci.*, 12(2), 1991, pp. 35—37.

This paper presents a part of the process which was developed for reclamation of protein and by-products from chrome leather shavings. After protein and chrome(III) are extracted from leather scraps, the remainder is neutralized with quick lime, and then processed into granu-

lated fertilizer. The results of tests showed that the organic fertilizer is available for flowers because of its long-term and high effectiveness.

**Key Words:** reclamation of leather shavings, residue, fertilizer.

**Analysis and Prediction of Traffic Noise in the Mountain City.** Chen Zi-ming, Lin Dong (Department of Physics, Qingdao University of Oceanography): *Chin. J. Environ. Sci.*, 12(2), 1991, pp.38—41.

This paper presents a method for analysis and prediction of traffic noise in the mountain city, emphasizing the characteristics of sloping roads. Taking Qingdao City as an instance, based on road structure, distribution of terraced buildings along both sides of the sloping roads and the conditions of motor vehicles shuttling to and fro on the roads with radiative noise, three different models have been set up for long-term monitoring, and the linear relations among varieties of vehicle noise, speeds and road slopes have been demonstrated. The results summed up correct range of noise levels caused by the road-side buildings and sloping road structure. The authors propose the method for predicting  $L_{eq}$  of traffic noise on the sloping road surface in practice.

**Key Words:** traffic noise, mountain city, prediction, model.

**Influence of Acidic Leaching upon the Contents of Organic Matter and Clay Particle in Soil.** Liu Hong-jie (Department of Geography, South China Normal University, Guangzhou): *Chin. J. Environ. Sci.*, 12(2), 1991, pp. 42—44.

This paper deals with variations of the contents of organic matter and clay particle in soil under influence of acidic precipitation. The results of simulated experiments showed that organic matter contents decreased in varying degree after acidic leaching, but acidity of leaching did not have marked influence upon the clay contents. If the contents of metals in soil solution increased to critical coagulation, efficiency of eluviation would decrease.

**Key Words:** acidic leaching, organic matter, clay particle.

**Treatment of Furfural Wastewater by Membrane Separation Process.** Chen Yu-lian, Zhou Guang-jun, Zhang He (Department of Chemical Engineering, Taiyuan University of Technology, Shanxi): *Chin. J. Environ. Sci.*, 12(2), 1991, pp. 45—49.

A new method for recovering acetic acid from furfural

wastewater containing 1—25%(weight) acetic acid has been developed with electrodialysis. In pilot-plant-scale operation, after the wastewater passed through a 400×800 mm electrodialyzer equipped with 30—80 pairs of membrane modules, the concentration of recovered acetic acid reached 20%(weight), and only 0.02—0.05% of it remained in wastewater, which could be discharged or reused. Furthermore, the recovered acetic acid could be utilized to produce industrial-graded acetic acid by means of extraction and distillation.

**Key Words:** tuffural wastewater, membrane separation, recovery, electrodialysis.

**Reclamation of Wax from the Waste Clay in Oil Refining by the Method of Liquid Membrane Emulsification.** Zhu Xian (Shanghai University of Science and Technology); Zhu Zhi-ping (Taicang Petrochemical Engineering Institute, Shanghai); Zhu Bing-geng (Taicang Pigment Chemical Factory No. 2, Shanghai): *Chin. J. Environ. Sci.*, 12(2), 1991, pp. 49—51.

The process of recovering wax is as follows: The dilute alkaline solution reacts on the waste clay to weaken or destroy its surface energy, pore structure and activation so as to release wax fully. The surfactants produced from the reaction cause spontaneous emulsification to make wax transform water-phase with unstable liquid membrane. When water is diluted to it, the membrane will break and then wax is released. The rate of wax recovery reaches 90%.

**Key Words:** emulsification, liquid membrane, waste clay, wax, recovery.

**Chemiluminescent Method for Determination of Chromium in Natural Water by Reversed Flow Injection Analysis.** Li Guang-hao (Benxi Metallurgy Training School, Liaoning Province); Yu Zan-an (Dept. of Chemistry, Northeast China University of Technology, Shenyang): *Chin. J. Environ. Sci.*, 12(1), 1991, pp. 52—55

The determination of chromium in natural water by reversed flow injection technology combined with ABEI-H<sub>2</sub>O<sub>2</sub>-Cr(III) chemiluminescent system is reported in this paper. The detection limit of this method is  $4.5 \times 10^{-12}$  g/ml for Cr(III), its linear range is in  $1 \times 10^{-10}$ — $8 \times 10^{-6}$  g/ml, and the relative standard deviation is 1.1%. The sample throughput is 100 samples per hour.

**Key Words:** chromium, natural water, chemiluminescence, Reversed Flow Injection Analysis.

**An Investigation on Aerosol Size Distribution around the Area of Xiguan Powerplant, Nan-**

**jing, Liang Bao-ying, Ma Ying (Environmental Protection Institute of Electrical Industry, Ministry of Energy, Nanjing):** *Chin. J. Environ. Sci.*, 12(2), 1991, pp. 55—59.

The main intent of this work is to survey aerosol size distribution around the area of the powerplant with a vehicular instrument PC-2 Typed Aerosol Analyzer. The aerosol sizes downwind and upwind of stack plumes were monitored. The data obtained in comparison with those by other measurements demonstrated the distributive variations of suspended particulate sizes in the air of the said area and the impact of the powerplant to a certain extent.

**Key Words:** powerplant, aerosol size distribution, plumes.

**A Simple Method for Determination of Diluted Muple of Water Samples in Analysis of BOD<sub>5</sub>.** Yang Han (Environmental Monitoring Station of the Dongtinghu Lake, Yuanjiang, Hunan Province): *Chin. J. Environ. Sci.*, 12(2), 1991, pp.60—62.

Presented in this paper is a simple, speedy and reliable method for determining BOD<sub>5</sub> in water samples. After the values of COD<sub>Cr</sub> have been determined, three proper diluted muples are calculated in accordance with the general formula for evaluating the coefficients of dilution:

$$C_n = \text{COD}_{Cr} / 6.5 \times 2^{n-1} \quad (n = 1, 2, 3)$$

**Key Words:** water sample, BOD<sub>5</sub>, determination.

**Application of Photosynthetic Bacteria (PSB) to the Treatment of Organic Wastewater.** Liu Ru-lin (Department of Biology, Nankai University, Tianjin): *Chin. J. Environ. Sci.*, 12(2), 1991, pp. 63—67.

This paper reports the research on PSB in treating organic wastewater. Some heterotrophic bacteria decompose complex organic compounds into low molecular substances such as lower fatty acid, and then PSB utilize them. Some strains of *Rhodospirillaceae* have been found to utilize low the conditions of light or dark, aeration or unaeration. Low molecular compounds and to multiple rapidly under the Conditions of light or dark, aeration or unaeration. By means of the PSB, BOD<sub>5</sub> in sewage massively decreases from more than 10000 mg/L to less than 1000 mg/L. In addition, the bacteria protein can be used as by-product.

**Key Words:** photosynthetic bacteria, sewage, organic compound.

**Photochemical Transformation of Pesticides and Its Environmental Implication.** Wan Yi-