

3. PSAA 在 pH 为 5—10 范围内具有良好的絮凝效果。

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廉价包埋剂聚乙烯醇的研究

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摘要 以洗衣粉废水中的 LAS 为处理对象,研究了 PVA-硼酸化法固定化微生物细胞的物理特性、废水处理特性及相关特性。其多孔结构、高机械稳定性、良好的贮藏性和活性可恢复性、污泥产量少及固定化增殖细胞的性质等说明 PVA 是有开发实用价值的廉价包埋剂。

关键词: 包埋法固定化微生物;聚乙烯醇;直链烷基苯磺酸钠。

用包埋法固定化微生物处理废水是本世纪 70 年代兴起的废水处理新技术。该法在处理包含难于生物降解物质的废水时有其独到的优越性;另外,用它处理生活污水,可以缩短水力停留时间,提高处理效率,减少污泥产量。角野立夫的研究表明,用聚丙烯酰胺固定的活性污泥,其剩余污泥量为一般活性污泥法的 1/4—1/5^[1]。虽然这一技术有许多优点,但目前的研究多处于实验室水平,在实际废水处理中尚未得到应用。笔者认为,除了技术问题外,经济问题是主要原因。由于常用包埋剂一般均较昂贵,包埋法本身又增加了投资,所得包埋体系不一定能长期及反复使用,因而限制了本法在生产中的应用。尽管如此,固定化细胞在其他工业部门不乏成功的例子。例如用聚丙烯酰胺包埋大肠杆菌生产 L-天冬氨酸,可降低 40% 成本^[2,3]。

本研究对廉价包埋剂聚乙烯醇 (Polyvi-

nyl Alcohol, PVA) 包埋体系的物理特性、处理废水特性及其使用中的有关特性进行了研究。PVA 是日本学者开发的一种新型包埋剂^[4,5,6,7],具有强度好,化学稳定性好,有较高的催化活性,以及价格低廉等特点。目前国内对它的研究还不多。本研究结果表明 PVA 是一种在废水处理中具有实际应用可能的包埋剂。

一、材料和方法

包埋采用 PVA-硼酸化法。PVA 为工业品,购自北京有机化工厂。包埋时在 PVA 和菌泥混和液中, PVA 浓度为 12.5%, 菌泥浓度为 5.36%, 将混和液滴加到饱和硼酸液中,在室温下聚合 30h 后,得到粒径为 4—5 mm 的 PVA-细菌固定化小球。再以自来水

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冲洗后备用。

被包埋的细菌是笔者筛选到的专门降解洗衣粉废水中直链烷基苯磺酸钠 (Linear Alkyl benzene Sulphonate, LAS) 的细菌菌系。本试验以洗衣粉废水中的 LAS 为处理对象。洗衣粉废水的配方为: NH_4Cl 3.0g, $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ 1.3g, 酵母膏 0.08g, 5.1% $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 10ml, 0.2% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 1ml, 12.5% KCl 2ml, 熊猫牌高效洗衣粉 0.2g 或 0.35g, 加蒸馏水至 1000ml, 调 pH 至 7.2。

LAS 的测定采用 PVC-AD 电极定值电位滴定法。

降解 LAS 的活性测定是: 取 0.075g 湿菌泥(4000 r/min, 20min 离心所得菌泥)或相当于 0.075g 湿菌泥量的固定化细胞, 置于装有 80 ml 洗衣粉废水(酵母膏含量 0.3g)的 200ml 三角瓶中^[8], 在 30℃ 恒温摇床中, 以 133r/min 的转速培养 30h 后, 测反应液中残余的 LAS 浓度。降解活性可用每小时每克湿菌体分解 1mg LAS 作为一个细菌活力单位来表示, 也可用 LAS 去除百分率来表示。

包埋得到的 PVA 小球, 用扫描电镜观察其结构, 并通过手感判断其相对强度。

试验对包埋菌和未包埋菌降解 LAS 的活性进行了比较。

PVA 小球的保存试验是在干燥室温和在 4℃ 洗衣粉废液(成分见上)中浸泡两种条件下进行的, 在不同的时间取样, 测其降解 LAS 的活性。

另外, 还在 1L 反应瓶中进行间歇式连续运行试验。

二、结果和讨论

PVA 小球的结构见图 1、2。

如图所示, PVA 小球具有多孔结构, 内部孔洞比外表面孔洞大, 这种外密内疏的结构可以有效地防止被包埋细菌的流失, 并为被包埋微生物的生长及物质交换提供了空间和条件。因此从结构上讲, PVA 是一种良好

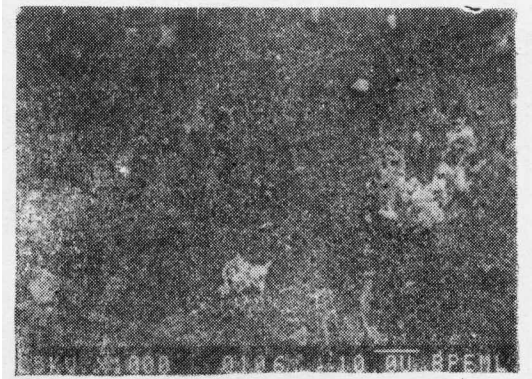


图 1 PVA 小球外表面的多孔结构
孔径为 0.33—0.50μm

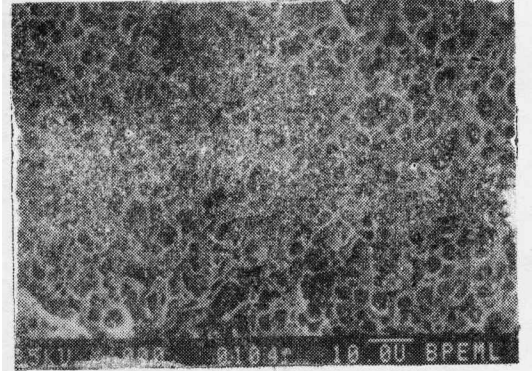


图 2 PVA 小球内部的多孔结构
平均孔径为 3.5μm

的包埋材料。

PVA 小球的强度试验表明, 其强度与浓度有关, 结果见表 1。

表 1 PVA 浓度与凝胶强度的关系

PVA 重量百分比 浓度(%)	2.5	5.0	7.5	10.0	12.5	15.0	20.0
凝胶强度	不成 凝胶	弱	较强	很强	很强	很强	很强

表 1 的结果与桥本奖等人^[4]的试验结果一致。7.5%—20.0% 的 PVA 制得的凝胶, 其强度很好, 但是由于 15.0%—20.0% 的 PVA 不能制成球状凝胶, 而球状固定化细胞体系具有与底物接触面积大, 不易因碰撞或搅拌破碎的特点, 所以 15.0%—20.0% 的 PVA 不适用于制备固定化细胞, 包埋时可选用 7.5%—12.5% 的 PVA。

包埋得到的 PVA 小球降解 LAS 的活力单位是 1.37mg(LAS)/g (湿菌体) · h, 未

包埋的细菌则为 $1.35\text{mg}(\text{LAS})/\text{g}(\text{湿菌体})\cdot\text{h}$ 。可见包埋对菌的降解活力是有益的,不会产生不利的影响。

保存试验表明,用第二种方法保存 PVA 小球效果较好,保存 40d 时,仍可保持 82% 的活力。

在间歇式连续运行试验中,发现 PVA 小球降解 LAS 的活性在运行的前 16d 一直很高,在 3h 内可保持 LAS ($40\text{mg}/\text{L}$, $70\text{mg}/\text{L}$) 的平均去除率在 90% 以上,以后去除率不断下降,到 25d 时已很差。为此,用进水活化培养这些 PVA 小球,每两 d 换一次进水,6d 后发现 PVA 小球的活性可恢复如初。可见 PVA 小球具有活性再生能力,可以反复利用。

在间歇式连续运行中,通过观察 PVA 小球活性和重量的关系(图 3),以及 PVA 小球的扫描电镜观察(图 4-7),证明 PVA 小球降解 LAS 的活性变化和小球的重量变化是一致的,小球重量的增加是被包埋微生物生

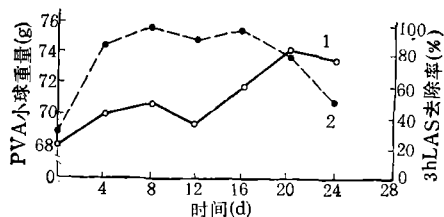


图 3 连续运行中 PVA 小球重量和 LAS 去除率的关系

1. PVA 小球重量 2. LAS 去除率

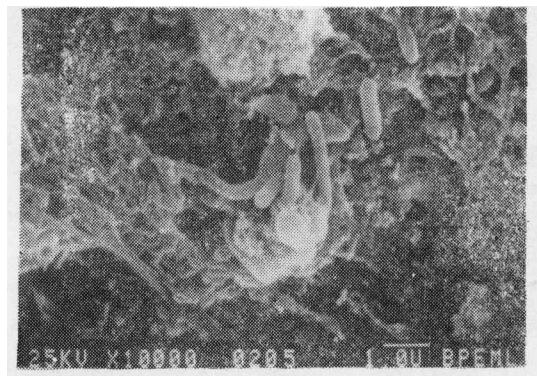


图 4 运行前 PVA 小球外表面生物相观察

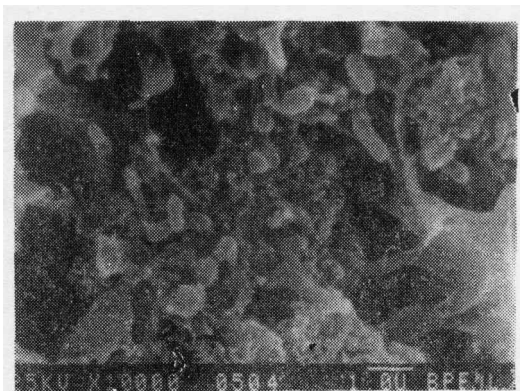


图 5 运行前 PVA 小球内部生物相观察

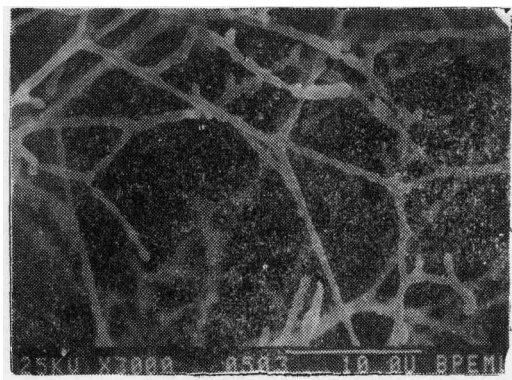


图 6 运行中 PVA 小球外表面生物相观察

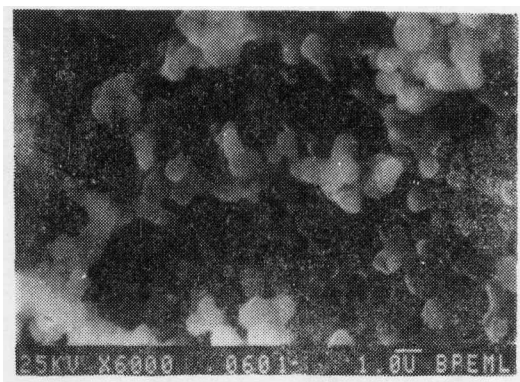


图 7 运行中 PVA 小球内部生物相观察

长繁殖的结果,从而证实了 PVA-硼酸化法可以得到固定化增殖细胞,这对于处理污水这种成分复杂的系统是有利的。

另外,在九十多天的连续运行中,还发现几乎没有污泥产生。

三、结 论

上述试验结果表明,PVA-硼酸化法包埋得到的 PVA 固定化体系,具有外密内疏的多孔结构,这是作为包埋材料理想的结构;具有良好的机械强度;包埋体系的活性比未包埋细菌高;且具有可保存性;丧失活性的可恢复性;具有固定化增殖细胞的性质;以及在运行中几乎没有污泥产生。另外,PVA 的价格比其他常用包埋剂便宜,本实验所用为 5 元/kg。这些特点表明,PVA 是适用于废水处理的价廉物美的良好包埋剂,有实际应用价值。

本研究只是在实验室水平上对 PVA 包埋体系进行的研究,要使其真正用于实际生产,还有两个必须解决的问题,即包埋体系的工业化制备技术及选择适当的反应器形式。包埋体系的制备因包埋方法不同而有所区别,象 PVA-硼酸化法这类包埋方法,其成球的过程一般包括包埋体系液滴的形成和液滴硬化成球。包埋剂与微生物混合液从针头或喷嘴压出,形成液滴或液流,后者需要通过某种方法打断成液滴,如振动喷嘴技术^[9],形成

的液滴滴入硼酸等使包埋体系聚合硬化的反应液中,经适当时间的反应,即可制得大量的固定化小球。反应器的选择与包埋体系特性、废水特性及处理程度等许多因素有关,应针对不同问题通过试验确定。据报道,填充床反应器、连续流罐式反应器、流化床反应器、滴滤床反应器等在固定化细胞中均有应用。我们将在本研究的基础上,对 PVA 包埋固定化细胞体系的实际应用进行研究,在技术上、经济上均使其更具实用性。

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• 环境信息 •

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Nanjing): *Chin. J. Environ. Sci.*, **11**(5), 1990, pp. 20—24

This paper presents a prediction on discharge and utilization of fly-ash in Shanghai area with Grey System, by which a predictable model has been set up. Based on this System, utilization of fly-ash in the area in 1990, 1995 and 2000 has been predicated and its tendency analysed. This work will provide for management of power plants and their development.

Key Words: Grey System, prediction, fly-ash resources, utilization.

A New Decolorizing Flocculant for Dyeing Wastewater. Zhang Xuexin, You Reisheng, Li Zhuomei, He Weiguang (Institute of Polymer Science, Zhongshan University, Guanzhou): *Chin. J. Environ. Sci.*, **11**(5), 1990, pp. 25—29

MG has been prepared by condensation polymerization of dicyanodiamide-HCHO modified with a modifying agent. Its molecular weight and charge density can be adjusted by the reaction condition and the amount of modifying agent. MG is a cationic polyelectrolyte whose characterization has been studied. The factors influencing decoloration have also been studied. The results show that Mg can be used as an effective decolorizing agent in treatment of wastewater containing hydrophilic dyes, particularly for active dyes.

Key Words: decolorizing flocculant, wastewater, ter.

The Steady State Control of Anaerobic Treatment for Monosodium Glutamate Processing Wastewater. Shen Yaoliang, Le Yanran (Dept. of Environmental Protection, Suzhou Institute of Urban Construction and Environmental Protection, Suzhou): *Chin. J. Environ. Sci.*, **11**(5), 1990, pp. 30—34

Anaerobic treatment of high concentrated monosodium glutamate processing wastewater (COD 60000—80000mg/L), which is so far very difficult to be treated biologically, was conducted and the steady state control of the treatment process for the optimal efficiency under different operating parameters (COD loading rate, hydraulic retention time and pH) were demonstrated in this paper. The experimental results showed that COD removal could reach more than 70%, biogas production rate was as high as 10.5 m³/m³·d with more than 58% of methane content under the controlled conditions of hydraulic retention time of 84 hours, COD loading rate of 6—8%, pH of 6.5—7.5 and medium temperature.

Key Words: anaerobic treatment, monosodium glutamate processing wastewater.

Industrial Wastewater Treatment Using the Catalytic Wet Oxidation Process. Jiang Yi, Yu Chunyin, Liu Huiqing et al. (Dalian Institute of Chemical Physics, Academia Sinica, Dalian): *Chin. J. Environ. Sci.*, **11**(5), 1990, pp. 34—37

The aim of this work is to explore application of the catalytic wet oxidation process to wastewater treatment in the coke-oven plants and the coal-gas producers. A series of catalysts, noble metals/semiconductor oxides, were prepared and tested in a high pressure vessel under 250°C liquid phase conditions. It was found that different catalysts demonstrated their own selectivity to different pollutants. The catalyst WT-501 showed high activity toward both ammonia and organic components. Wastewater from the coke-oven plants originally contained COD 9302 mg/L and NH₃ 5230 mg/L, but they were removed into 619 mg/L and 47 mg/L respectively by using the catalyst WT-501 with COD removing rate of 93.2% and NH₃ of 99%.

Key Words: wastewater treatment, catalytic wet oxidation process, noble metals/semiconductor oxides.

Preparation of A New Flocculant, Polysilicate Containing Aluminium Ions. Gao Baoyu, Yue Qinyan, Wang Shuren (Center of Environmental Science, Shandong University, Jinan): *Chin. J. Environ. Sci.*, **11**(5), 1990, pp. 37—41

Polysilicic acid containing aluminium ions (PSAA), a new flocculant, has been prepared by using sodium silicate, sulfuric acid and aluminium sulfate as raw materials. The properties of PSAA and the factors affecting treatment of wastewater were studied experimentally. The flocculating effect of PSAA was compared with that of polyaluminium chloride (PAC). The experimental results showed that the flocculating properties of PSAA was greatly influenced by the content of aluminium ion in PSAA. When the molar ratio of Al to SiO₂ was equal to one, the flocculating effect of PSAA was best. Compared with PAC, PSAA is a low cost, high performance water-treating agent.

Key Words: polysilicic acid containing aluminium ion, inorganic polymer flocculant, wastewater treatment.

A Cheap Entrapping Agent for Wastewater Treatment. Li Tong, Yu Yuxin, Hu Jicun (Dept. of Environmental Engineering, Tsinghua University, Beijing): *Chin. J. Environ. Sci.*, **11**(5), 1990, pp. 41—44

Using the entrapped immobilized cells for treating wastewater is a new technique of biological treatment, but the entrapping agents are so expensive that application of them will be limited. The authors have developed polyvinyl alcohol (PVA) as an entrapping agent with PVA-boric acid method, and have prepared porous PVA-pellets for treating detergent wastewater. The results show that the PVA-pellets have high mechanical stability, good preservative ability, good recovery of activity, nearly no sludge produced, and viability of entrapped cells.

Key Words: entrapped immobilized microbial cells, polyvinyl alcohol.

Determination of Chromium in Wastewater with Nafion Exchange Preconcentration. Flameless Atomic Absorption Spectrometry.

Xu Tongming Shen Huakui Xu Xiaohong Xu Bo xing (Department of Chemistry East China Normal University): *Chin. J. Environ. Sci.*, **11**(5), 1990 pp. 45—48

Nafion is a new type cation exchange polymer. In this experiment coiled tungsten supporter was modified with a thin film of Nafion. Trace amount of Cr (III) in wastewater was exchangeable and could be preconcentrated by the modified supporter. Put it into a graphite cup to take atomic absorption spectrometric measurement. Cr (VI) was reduced to Cr (III) by $\text{NH}_2\text{OH}\cdot\text{HCl}$. A satisfactory result was obtained from the exchangeable preconcentration of chemically modified supporter with high selectivity of AAS. This paper introduces determination of Cr (III) and Cr(VI) in wastewater respectively. A buffer solution of 0.01 mol $\text{NaAc}\cdot\text{HAc}$ ($\text{pH}=4.5$) was well suitable for preconcentration. The linear range for determination of Cr(III) was 5—100 ng/ml Cr(III) and recoveries 92—106%. Ten parallel tests of determining a sample solution containing 25 ng/ml Cr(III) gave a relative standard deviation of 5.9%. The characteristic concentration was 2.4 ng/ml Cr (III). More than 10 foreign ions did not interfere the determination.

Key Words: Nafion cation exchange polymer, Cr (III), flameless atomic absorption spectrometry, wastewater.

Volumetric Method for Silicon Determination in Certified Reference Silicates—Potassium Silicofluoride Volumetry. Zhang Zhigang, Yang Shuzhen, Huang Yongfen (Shanghai Institute of Ceramics, Academia Sinica): *Chin. J. Environ. Sci.*, **11**(5), 1990, pp. 48—52

The optimal experimental conditions for determining silicon by using the volumetric method of potassium silicofluoride were presented in this paper. Different types of silicate materials such as clay, glass, refractories, silicate minerals, domestic certified samples and SRM of USNBS are also determined with this method, for which the authors participated the determination of the certified values of silicon in ERM (environmental reference material of soil and pond sediments. After comparing this method with others, it was found that the analytical results of the former one were accurate as those by the classical methods, and its RSD (relative standard deviation) was 0.09—0.17%. So the volumetric method for potassium silicofluoride can be recommended as an arbitrary method or one for determining the certified value of SRM.

Key Words: silicon determination, potassium silicofluoride volumetry

Determining the Ratio of ^{226}Ra to ^{238}U in Samples and Its Application in Environmental Monitoring. Ma Junjie, Han Shouling (Liaoning Provincial Institute of Labour Hygiene, Shengyang): *Chin. J. Environ. Sci.*, **11**(5), 1990, pp. 53—56

This paper describes the ratio of ^{226}Ra to ^{238}U in 19 kinds of environmental samples in Liaoning Province. The determined results showed that the ratios of ^{226}Ra to ^{238}U in grain and vegetable samples were between 2.6—9.7, mean value was 4.8, those in drinking water between 0.36—0.45, mean value 0.40, and those in soil, ore and phosphate fertilizer were between 0.86—1.10, mean value 0.98. The authors presented a discussion on application of the ratios in environmental monitoring.

Key Words radium-226, uranium-238, environmental monitoring.

Simultaneous Detection of Chlorinated and Organophosphorus Pesticides in Water with GC-ECD. Chen Qinghuo (Henan Provincial General Station of Environmental Hydrogeology, Zhengzhou): *Chin. J. Environ. Sci.*, **11**(5), 1990, pp. 56—60

A highly sensitive analytical system of separation and simultaneous detection for chlorinated and organophosphorus pesticides in water with GC-ECD has been presented. The compounds, α -BHC, β -BHC, γ -BHC, σ -BHC, dimethoate, methylparathion, malathion, parathion, p,p'-DDD, p, p'-DDE, o, p'-DDT, p, p'-DDT were well separated in 1.5% OV-17 + 2% OV-210/Chromosorb-WAW-DMCS-HP (80—100 mesh) column, and their retention time was found to be below 15 minutes. It was