

造纸漂白废水中多氯联苯的测定*

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摘要 介绍了造纸氯化漂白废水中痕量多氯联苯(PCBs)的测定方法。采用国产 GDX-501 树脂进行富集, 经索氏提取、浓硫酸洗涤和去活化的氧化铝-硝酸银硅胶层析柱净化后, 用毛细管气相色谱法测定。实验结果表明, 造纸氯化漂白废水中产生的 PCBs 为 10^{-9} 级, 且以低氯取代产物为主。方法回收率在 60% 以上。

关键词 氯化漂白, 造纸废水, 多氯联苯, 气相色谱。

多氯联苯(PCBs)具有高稳定性和良好的绝缘性, 曾广泛应用于电加工业、油墨和油漆等生产领域之中。但它又是一类具有致癌、致畸和致突变的有机污染物, 在水中的溶解度极低, 在酸性或碱性环境中也不易分解, 易被水生生物富集而进入食物链的循环, 构成对人类健康的严重威胁。PCBs 主要来源于人工合成。近 10 年来, 人们对饮用水氯化消毒及造纸纸浆氯化漂白进行了研究, 已查明含有 300 多种化合物, 其中 200 多种为氯化有机物, 且 75%—90% 氯化有机物是在漂白的头两段排放的, 多数为有毒物质^[1-3]。但这些工作偏重于挥发性的、低分子量的、易检测的氯代烃和氯酚等有机氯化物^[4,5]。氯化漂白是否也产生 PCBs, 在废水中含量多少, 国内外尚未见文章报道。

测定 PCBs 的方法很多, 笔者曾著文对此作了较详尽的阐述^[6]。本文采用 GDX-501 树脂吸附富集, 索氏提取后经去活化的氧化铝-AgNO₃ 层析柱净化, 气相色谱测定北京某造纸厂的废水, 结果表明, 纸浆氯化漂白过程中有多氯联苯产生。

1 实验部分

1.1 仪器设备

- (1) 全玻璃富集柱, 层析柱, 浓缩器;
- (2) 冷冻干燥仪(日本, Yamato);
- (3) 美国 Varian-3700 气相色谱仪, ⁶³Ni 电子捕获检测器;
- (4) Shimadzu, C-R3A 记录仪。

1.2 试剂

- (1) 正己烷(北京金星化工厂, 分析纯, 精密蒸馏后使用);
- (2) GDX-501 树脂(天津试剂二厂, 60—80 目, 依次用甲醇和正己烷索氏提取 24h 后使用);
- (3) 多氯联苯标准溶液(Aroclor 1242, Supelco Inc.)。

1.3 气相色谱条件

色谱柱: SE-54, 18m × 0.25mm(i.d.) 石英毛细管柱(J&W Scientific Inc. U.S.A.);
进样器温度: 300℃; 检测器温度: 350℃; 程序升温: 柱温 50℃ 保持 2min, 以 10℃/min 升温至 290℃, 保持 10min。

1.4 实验操作

(1) 样品的富集和提取 采集北京某造纸厂次氯酸钙漂白纸浆后的废水 10L, 以 40—50ml/min 的流速流经装有 17g GDX-501 树脂的玻璃柱; 富集完毕的树脂经冷冻干燥除去水分后, 称取 10g 以正己烷为溶剂索氏提取 12h。

(2) 样品的净化 将上述提取液浓缩到 5ml 左右, 加入 10ml 浓硫酸洗涤 3 次, 再用 3% 稀硫酸钠溶液(二次蒸馏水配制)洗至中性, 经无水硫酸钠干燥后, 用 8g 去活化的氧化铝-5g 硅胶(10% 硝酸银)层析柱净化, 以 170ml 正己烷洗脱, 收集后面 130ml 洗脱液用全玻璃 K.D 浓缩

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器浓缩至 1.0ml;

(3)气相色谱分析 将浓缩液进气相色谱分析,采用外标法定性和定量。由于氯化漂白产生的多氯联苯的组成不可能与标准样品完全相同,若简单地以标样与样品的气相色谱中的峰总面积换算,势必造成很大误差。本文参照文献[7],计算出 Aroclor 1242 标准样品中异构体的浓度,并以此为依据求出水样中多氯联苯各种异构体的浓度。

2 结果和讨论

2.1 漂白废水样品的预处理

造纸漂白废水中含有大量的有机物,给测定废水中的多氯联苯带来许多不便。由于多氯联苯在酸性和碱性条件下不易分解,本文采用先经浓硫酸酸化,除去样品中的烷烃及芳香烃等(见图 1,2),再用去活化的氧化铝-硝酸银硅胶层析柱净化,除去大量干扰物质,有效地提高了测定的准确性(见图 3)。

将 200ml 精密蒸馏的正己烷浓缩至 1.0ml,进气相色谱分析。从谱图 4 可以看出,大量正己烷的使用不影响多氯联苯(保留时间为 12-22min)的准确测定。

2.2 样品测定结果

测定结果表明,该造纸厂氯化漂白废水中所含物质极多,尤其是低沸点的物质浓度较高,多

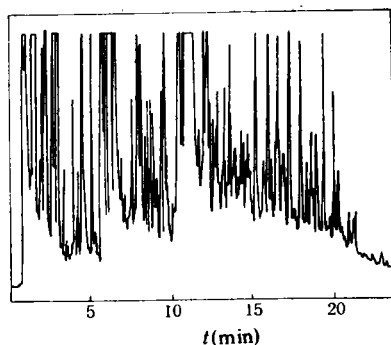


图 2 经浓硫酸洗涤后水样的气相色谱图

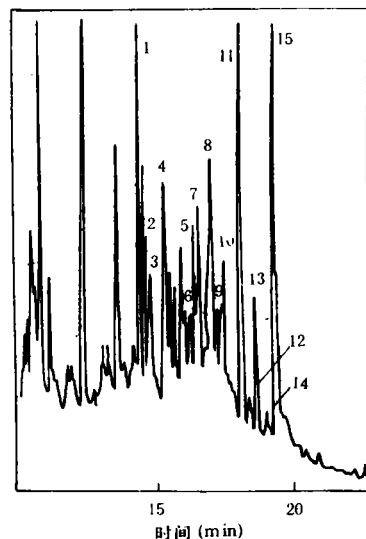


图 3 经层析柱净化后的水样的气相色谱图



图 1 未经酸洗水样的气相色谱图

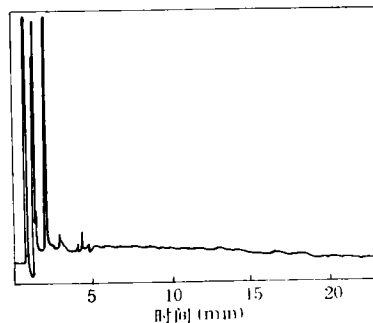


图 4 正己烷溶剂空白气相色谱图

氯联苯浓度为 0.13×10^{-9} 。这可能是在氯化过程中,强氧化性的 Cl_2 (或 ClO^-) 与纸浆中大量木质素或其它成分发生反应生成的。反应机理尚不明瞭,有待进一步探讨。同时从表 1 和图 6 可以看

出,造纸废水中的多氯联苯的含量随着苯环上取代氯原子个数的增多而降低,二氯联苯和三氯联苯总计占总体的 80%左右,这可能与低氯取代的 PCBs 在水中的溶解度比多氯取代者的大,反应进行的程度大有关。

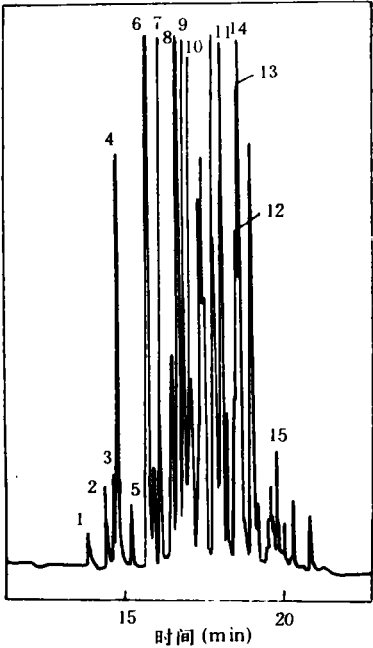


图 5 Aroclor 1212 标准样品的气相色谱图

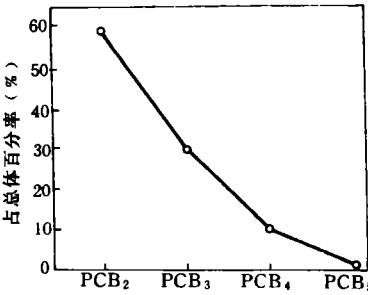


图 6 造纸氯化漂白废水中各种 PCBs 的分布

3 结论

利用本文方法可测定水样中痕量的多氯联苯(10^{-9} 级),平均回收率在 60%以上。测定结果表明,采用原始的氯化漂白方法的造纸废液中,不仅产生大量的低沸点的污染物,而且产生如多氯联苯这样的高沸点的有毒物质。因此,多氯联苯在水环境中的行为、迁移及富集等规律值得深入探讨,也应引起有关部门的重视。

表 1 造纸废水中 PCBs 的各种异构体的浓度

峰号	Aroclor 1242(1.9740×10^{-6})		水样		
	异构体	占总体百分比(%)	浓度(10^{-9})	浓度(10^{-12})	占总体百分比(%)
1	22'	1.37	27.0	42.7	32.1
2	24	0.65	12.8	2.7	2.0
3	23'	1.29	25.5	1.7	1.3
4	24'	11.45	226.0	30.9	23.3
5	22'6	1.03	20.3	11.9	9.0
6	22'4,22'5	13.65	269.5	7.2	5.6
7	22'3	5.77	113.9	11.4	8.6
8	24'5,244'	11.74	231.8	1.6	1.2
9	2'34	7.32	144.5	7.1	5.3
10	234'	1.79	35.3	0.3	0.2
11	22'34,234'6	4.62	91.2	2.2	1.7
12	244'5	1.92	37.9	0.6	0.5
13	23'4'5	3.68	72.6	4.5	3.4
14	23'44'	4.22	83.3	8.0	6.0
15	22'3'45	0.53	10.5	0.1	0.1
总计			132.9		100

表 2 Aroclor 1242 的添加回收率

编号	二次蒸馏水(L)	添加 Aroclor 1242(μ g)	回收率(%)
1	2.0	1.9740	60.4
2	2.0	1.9740	67.1
3	2.0	1.9740	58.8
平均回收率			62.1 ± 4.4

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Abstracts

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residence time (HRT) of 40 h with an influent having a COD_{Cr} concentration of 1101 mg/L, then the second stage of the A/O system and the biological activated carbon unit had their effluents with a COD_{Cr} concentration of 82 mg/L and 55 mg/L respectively, and a corresponding COD_{Cr} removal of 92% and 95%, respectively. When the pilot plant was operated at a HRT of 32 h with an influent having a COD_{Cr} concentration of 1112 mg/L, the second stage of the A/O system and the biological AC unit had their effluents with a COD_{Cr} concentration of 86 mg/L and 64 mg/L respectively, and a corresponding COD_{Cr} removal of 92% and 95%, respectively. Under the above conditions of operation, the second stage of the A/O system had a TA (total acid) removal of 93% for both cases.

Key words: A/O biofilm process, terephthalic acid wastewater, wastewater treatment, pilot plant.

Study on the Acid Hydrolysis- Anaerobic- Aerobic Fixed Biofilm System for the Treatment of Wastewater from Coking Plant. Shao Lin' guang et al. (Dept. of Environ. Eng., Wuhan College of Construction, Wuhan 430070); *Chin. J. Environ. Sci.*, 15(6), 1994, pp. 51—53

An acid hydrolysis- anaerobic- aerobic fixed biofilm system filled with a YDT elasto-steric packing was used to treat wastewater from coking plant. The results show that when the system was operated with an influent in which the concentrations of COD and $\text{NH}_3\text{-N}$ were 1065 mg/L and 253 mg/L respectively, a total hydraulic residence time (HRT) of 33.5 h, and a mixed liquor recirculating ratio of 3.6, then there was an effluent with a COD concentration of about 180 mg/L and a $\text{NH}_3\text{-N}$ concentration of 5 mg/L, namely that the removals of COD and $\text{NH}_3\text{-N}$ were up to 83% and 98%, respectively.

Key words: acid hydrolysis- anaerobic- aerobic treatment system, fixed bed biofilm, wastewater from coking plant.

Study on the Treatment of wastewater from the Production Process of Vitamin C by Using a Complex Reactor of Upflow Anaerobic Sludge Blanket-Filter. Yang Jingliang et al. (Dept. of Environ. Eng., Hebei Institute of Light and Chemical Industries, Shijiazhuang 050018); *Chin. J. Environ. Sci.*, 15(6), 1994, pp. 54—57

A complex reactor of upflow anaerobic sludge blanket-filter (UASB + AF) with an available volume of 6 m³ was used to treat a highly concentrated organic wastewater from the production process of Vitamin C. During the period of its stable operation, it had a volumetric COD loading of up to

10—12 kg COD/(m³ · d), a COD removal of over 80%, and a volumetric biogas yield of over 3.0 Nm³/(m³ · d), as well as a high start-up speed and a stronger resistance to shock loading.

Key words: upflow anaerobic sludge blanket-filter reactor, wastewater, Vitamin C, synthetic fiber filter.

Feasibility Study on the Use of Several Devices for Sampling Natural Hydrocarbons. Bai Yuhua, Li Jinlong et al. (Dept. of Technical physics, Environ. Sci. Center, Peking University, Beijing 100871); *Chin. J. Environ. Sci.*, 15(6), 1994, pp. 58—62

The tests were conducted on the performances of several devices such as polished canister, steel tank, sampling bag and Tenax GC stainless steel tube for sampling HCs emitted from natural sources. It was found that the polished canister is well sealed and has a less wall effect. The Tenax GC tube has excellent performances in absorption and desorption. It is insufficient for steel tank and sampling bag to sample natural HCs over C₆ because of their serious wall absorption. However, the sampling bag is useful for sampling and saving HCs below C₆.

Key words: natural hydrocarbons, sampling devices, feasibility.

Determination of Polychlorinated Biphenyls (PCBs) in the Effluent from a Pulp Bleaching Process. Yang Chun, Yao Weixi (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 15(6), 1994, pp. 63—65

Trace PCBs in the effluent from a pulp bleaching process with liquid chlorine or deactivated chlorinated lime were quantitatively determined with a method in which the samples were enriched by using a resin GDX-501, then extracted, washed with a concentrated sulfuric acid, and cleaned up over a deactivated alumina-silver nitrate-silica gel column before determination using a gas chromatography with a capillary and an electron capture detector. The PCBs in the effluent were found to be at a level in the range of 10⁻¹²—10⁻⁹ and to consist of dominant PCBs substituted with less (2 or 3) chlorines.

Key words: PCBs, pulp bleaching effluents, determination.

Qualitative Determination of Organic Pollutants in Atmospheric Vapor Phase and Particulate Phase in the Urban Area of Huhhot. Feng Shen' ying et al. (Inner Mongolia Center Station of Environ. Monitoring, Huhhot 010010); *Chin. J. Environ. Sci.*, 15(6), 1994, pp. 66—69

Full air samples were collected from the urban area