几种难降解有机废水的光化学处理研究*

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摘 要 采用日光和中压汞灯为光源,分别在充空气、O_3、加入 H_2O_2 或 TiO_2 等半导体催化剂条件下,对几种难降解的有机废水进行了光化学处理研究. 结果表明:石化和焦化废水中挥发酚、油和 COD 的去除率分别为 86.3%–100%, 39.8%–97.8%, 26.4%–60%;几种偶氮染料水溶液的脱色率、COD 去除率分别为 80.0%–100%, 48.0%–75.0%. 还测定了苯酚的降解产物,讨论了影响光解的要素和苯酚的降解历程.

关键词 光化学,光降解,废水处理,石化废水,焦化废水,偶氮染料,苯酚.

利用光化学氧化降解废水中污染物(Advanced Oxidation Process, AOP)是近 20 年来迅速发展的新领域[1,2]. 研究表明,若水样中存在氧化剂或半导体粉末催化剂,经过一定强度的光照射,便能产生多种形式的活性氧和自由基,使溶解或分散于水中的有机物氧化,直到矿化成水、CO_2 和其它无机物[3,4]. AOP 技术特别适合不饱和有机化合物、芳烃和芳香化合物的降解[5],且反应条件温和,无二次污染. 现已开发的人工光源(如汞灯、氙灯系列)或日光均可用于光解.

利用 AOP 技术处理污水的报道还不多. 石化、焦化废水成分复杂,含有大量芳烃、芳香化合物及其衍生物,现有的处理方法都有不足之处. 本工作较系统地研究了 AOP 技术对此类污染物(包括偶氮染料)的降解,为实际应用作了有益的尝试.

1 材料与方法

1.1 仪器和试剂

NDC-3 型光化学反应仪和 300W 中压汞灯(南京大学环科系研制)[6], LCF-5 型 O_3 发生器(北京玉渊潭环保设备仪器厂), HP5840 型 GC 和 ZAB-HS 型 MS 联用仪(英国 VG 公司), H66025T 超声清洗器(无锡超声电子设备厂), JD-3 型数字式照度计(上海嘉定学联仪表厂).

直接耐晒大红 4BS、活性艳红 X-3B、活性黑 KN-B(下简称 4BS、X-3B 和 KN-B)等偶氮染料和半导体粉末 Fe_2O_3, WO_3 为市售,所用 TiO_2 为锐钛型(上海钛白粉厂出品),其颗粒均小于 100 目. 所用分析试剂为 A.R. 或 G.R. 级.

1.2 分析方法

水样 COD、油和挥发酚的分析分别采用重铬酸钾法、重量法和直接光度法[7]. 试样的色度用比色法测定,脱色率计算如下:

$$\text{脱色率}=\frac{\sum A_0-\sum A_i}{\sum A_0}\times 100\%$$

式中, $\sum A_0$、$\sum A_i$ 分别为水样处理前后在 11 处波长(420、440…600、620)测得的吸光度之和.

1.3 石化废水处理

水样为某炼油厂隔油池后的废水,含油、COD 和挥发酚分别为 40–77.5mg/L, 424.6–600mg/L 和 34.9–45.3mg/L.

(1) 中压汞灯光照 取 200ml 水样 5 份,其中 1 份为空白,其余各加入 10mg TiO_2, Fe_2O_3, WO_3 和 20μl H_2O_2. 将此系列溶液分别在光化学反应仪的中压汞灯下光照 20min,同时充空气并搅拌,照毕取样测定. 另取一相同系列作暗对照试验,以扣除非光解因素引起的浓度变化(以下光解都作了暗对照试验).

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(2) 日光光照 取 3 份 200ml 水样分别置于 1L 石英锥形瓶中, 其中 1 份为空白, 其余各加入 10mgFe_2O_3 和 20μl H_2O_2. 充空气并搅拌, 日光照射 30min, 日光强度测定值为 180–190W/m^2.

1.4 偶氮染料水溶液处理

配制 100mg/L 的 4BS、X–3B 和 KN–B 水溶液各 700ml, 按下列方法处理: ①各取 200ml 水样在光化学反应仪的中压汞灯下光照 120min, 同时充空气、搅拌. ②各取 200ml 水样于锥形瓶内, 通 O_3 25min. O_3 发生器的工作条件: 高压 180V, 空气流速 2m^3/h, O_3 产生速率 3.8g/h. ③各取 200ml 水样以充 O_3 代替方法①中充空气. 测定样液的脱色率和 COD 去除率.

1.5 焦化废水处理

水样采自某钢铁厂, 呈浅褐色, 有异味. 过滤后测得的 COD 为 700–900mg/L, 挥发酚为 155–180mg/L. 取 3 份 200ml 水样, 其中 1 份为空白, 其余各加入 10mg TiO_2 和 20μl H_2O_2. 分别置于光化学反应仪的中压汞灯下光照 20min, 充空气并搅拌, 测定 COD 和挥发酚的去除率.

1.6 苯酚水溶液的光解

配制 50mg/L 的苯酚 250ml(溶剂为 30% 的甲醇和 70% 的水, V/V), 置于超声清洗器中 10min 使其溶解. 取 200ml 于光化学反应仪的中压汞灯下光照 30min, 充空气并搅拌. 取光照后水样作 GC–MS 测定, 测定前水样需衍生化处理. 方法是: 取 50mg 样液于分液漏斗中, 加 20ml 10% 的 K_2CO_3 溶液, 摇匀. 加 5ml 乙酸酐, 摇匀放置 20min, 加 18ml 乙醚萃取, 将有机相浓缩后测定. GC–MS 的工作条件: OV–101 石英毛细管柱(ϕ0.25mm×25m), 程序升温 50–200℃(6℃/min), 气化室温度 270℃, 离子室温度 260℃, 加速电压 8kV, 收集电流 200μA, 电子能量 70eV, 分辨率 1000, 质量范围 30–500, 扫描时间 1s, 载气为氦气.

2 试验结果与讨论

实验结果分别列于表 1, 表 2 和表 3, 表明各项指标的去除率是显著的.

表 1 石化废水光解结果

光源	光照时间/min	添加剂(同时充空气)	COD 去除率/%	油去除率/%	挥发酚去除率/%
中压汞灯	20		38.6	73.1	88.3
		TiO_2	53.1	89.2	96.9
		Fe_2O_3	60.0	90.8	100.0
		WO_3	55.1	93.5	99.3
		H_2O_2	57.4	97.8	100.0
日光	30		28.2	39.8	87.0
		Fe_2O_3	52.1	47.3	100.0
		H_2O_2	46.5	48.4	100.0

表 2 焦化废水光解结果

光源	光照时间/min	添加剂(同时充空气)	COD 去除率/%	油去除率/%	挥发酚去除率/%
中压汞灯	20		31.2	64.2	86.3
		Fe_2O_3	48.3	87.4	100.0
		H_2O_2	52.2	95.7	99.6
日光	30		26.4	40.0	100.0
		H_2O_2	44.3	70.2	100.0

表 3 偶氮染料水溶液光解结果

染料	O_3 氧化		中压汞灯光解		中压汞灯+ O_3	
	COD 去除率/%	脱色率/%	COD 去除率/%	脱色率/%	COD 去除率/%	脱色率/%
4BS	51	100	50	80	70	100
X–3B	42	100	48	90	64	100
KN–B	54	100	60	93	75	100

中压汞灯发出紫外光(简称 UV)、可见光和红外光, UV 占总能量的 1/3[8]. 日光中 UV 部分(290–400nm)占总能量的 4%. 光化学第一定律认为, 只有被分子吸收的光才能产生光

化学反应. 实验废水的主要成分为不饱和烃、多环芳烃(简称 PAHs)和多环芳香化合物, 连同3种偶氮染料, 它们在 UV 范围都有较强吸收. 光照后通过 $\pi\rightarrow\pi^*$ 跃迁成为激发单重态, 继又经过系间穿越成为化学性质活泼、参与反应的活化能比基态低30kJ/mol 的激发三重态. 该状态寿命较长(10^{-4} – 10^{2}s), 可进行异构化、加成、聚合、消去、脱氢、氧化-还原和裂解反应.

充氧促进光氧化是由于光照后通过能量转移使基态 O_2 成为激发单重态$^1O_2$, 后者的能量提高了 92kJ/mol, 因此氧的作用是明显的.

H_2O_2 与 UV 结合, 反应为:

$$H_2O_2 \xrightarrow{h\nu} [H_2O_2]^* \longrightarrow 2HO\cdot$$

HO · 属强氧化剂(氧化电位 2.80V), 可参与夺H、亲电加成或电子转移反应. 该法的 HO · 得率高, 表1和表2也显示该法效果比仅通空气好.

O_3 是强氧化剂(氧化电位 2.07V), 在水中可分解为各种形式的活性氧. 表3显示仅用 O_3 处理偶氮染料效果已很明显. 当 O_3 和 UV 联用后, 去除率又提高约1.5倍. 这一方面是联用后生成更多 HO · ($O_3 \xrightarrow{h\nu<310nm} O_2 + O(^1D)$, $O(^1D) + H_2O \longrightarrow 2HO\cdot$); 另一方面, 由于有机物(HRH)和溶解氧存在, 便产生了多种自由基的循环[10].

半导体粉末具有光催化作用, 以 TiO_2 为例:

$$TiO_2 \xrightarrow{h\nu} TiO_2(e^- + h^+)$$

产生的 h^+ 通过电子转移使吸附在 TiO_2 表面的 H_2O 生成 HO · 和 H^+, 或使 RX 形成 RX^+ ·, 实现有机物降解. 表1显示几种半导体催化剂的处理效果为: Fe_2O_3 > WO_3 > TiO_2. 对此, 可认为是禁带宽度不同所致(分别为 2.3, 2.8 和 3.0eV), 禁带宽度小, 激发所利用光的范围大. Fe_2O_3 可被< 560nm 的光所激发, 而 TiO_2 仅可利用< 410nm 的光. 另据半导体价带的能级位置, 可认为 Fe_2O_3 和 WO_3 属强氧化型催化剂[11], 它们更适于光氧化反应.

挥发酚是石化和焦化废水的重要成分, 表1和表2显示它们的去除率最高. 苯酚为常见的挥发酚, 图1和图2为苯酚光氧化后经衍生化测定的 GC 和 MS 图. 图2的 A 和 B 为醋酸苯酯和醋酸苯二酯, 对应图1中的峰1和峰2,

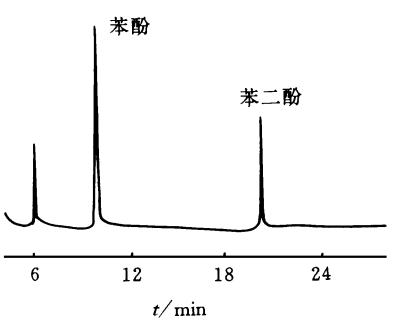

图1　苯酚光解产物衍生化色谱图

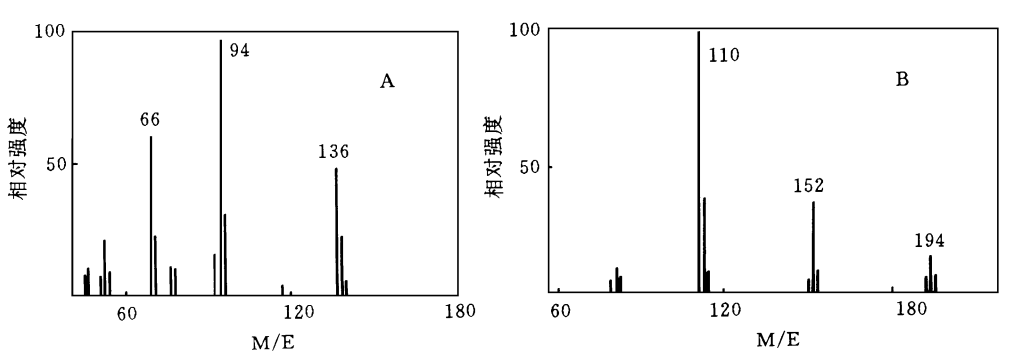

图2　质谱图

A. 醋酸苯酯　B. 醋酸苯二酯

表明苯酚光解产生了苯二酚. 苯酚光氧化反应过程较为复杂, 产生了许多中间体[12]. 表1和

表 2 也说明, 正是这些中间产物使废水的 COD 去除率不像其他指标那样高.

3 小结

AOP 技术处理有机废水的结果为 UV 与充氧气结合, 处理费用低但效果差; UV 与 O_3 结合效果好但费用高, 且 O_3 的溶解度低; UV 与 H_2O_2 结合效果较好, 易操作, 且 H_2O_2 易得到和保存, 可无限溶于水; 半导体粉末作光催化剂的效果适中, 且可重复使用, 但需附着固定.

考虑到挥发酚、油和色度等各项指标的去除率高而 COD 去除率低, 表明该方法将污染物彻底降解有一定难度. 但对目前某些生化法或化学法难降解的高浓度有机废水, 若先用 AOP 技术氧化, 使难降解的大分子变成小分子, 再辅以常规方法处理, 仍不失为一种可供选择的办法.

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要是由于热源的加热作用所致; 山区 C、D 类时比国标值大 0.5—1 级; 平原地区与国标基本相当; 沿海地区, 则低于国标不到 0.5 级左右。

(2) 横风向扩散参数, 山区地形复杂, 风向多变, 在 C、D 类稳定度时高出国标 0.5—1 级; 工业区和平原地区与国标值基本相当; 沿海地区受海陆风和热内边界层的影响, C 类稳定度时稍高于国标值。

(3) 污染物扩散浓度的大小和扩散的快慢, 与扩散参数直接有关。大的扩散参数使污染物迅速扩散, 在较近的距离内达到较大浓度; 小的扩散参数减缓污染物的扩散速度, 而有利于污染物的远距离输送。

(4) 根据分析结果认为, 平原及沿海地区的大气扩散参数, 可以直接从国标中查算。工业和山区的扩散参数, 则可提高 1 个级别后, 再按国标查算.

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Keywords: SO_2, washout, stable isotope, model, Mingnan Area, summer.

Study of Organic Hydroperoxides and H_2O_2 Yields in Isoprene and O_3 Reactions. Li Shuang et al. (The State Key Lab of Environ. Simulation and Pollution Control, Center of Environ. Sci., Peking Univ., Beijing 100871): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 16—18

The atmospheric reaction of isporene with O_3 was simulated under the dark and room temperature in the 28.5L quartz reactor coupled with a Long Path Fourier Transform Infrared Spectrometer, while the Dual Channel H_2O_2 Analytical System was used to determine the production of organic hydroperoxides and H_2O_2. Yields measured respectively in the three repeated experiments are 3.8%, 4.3% and 3.9% for organic hydroperoxides with the average of 4.0%, and 2.2%, 1.6% and 1.8% for H_2O_2 with the average of 1.9%. The formation mechanisms of organic hydroperoxides and H_2O_2 were briefly discussed.

Keywords: isoprene, O_3, Dual Channel H_2O_2 Analytical System, organic hydroperoxides, H_2O_2.

The Atmospheric Diffusion Parameter in Various Terrain in Comparison with Each Other in Shandong Province. Mao Hengqing (National Meteorological Center, Beijing 100081) *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 19—22

Analysing the experimental result in Shandong province, it is found that the atmospheric diffusion parameters vary obviously with terrain. The diffusion parameters are about as big as that of national standard in the plain and half to one class bigger than it in the mountain areas. In industrial park the cross-wind diffusion parameter is about the same as while the vertical one is one more class bigger than that of national standard. In coastal areas the cross-wind parameter is bigger slightly and the vertical one is smaller slightly than that of national standard. The pollutant diffusion density and the air diffusiophoretic velocity are related directly to the diffusion parameter.

Keywords: atmospheric diffusion parameter, national standard, air pollutant, cross-wind diffusion parameter, vertical diffusion parameter.

Cross-flow Membrane Bioreactor for Domestic Wastewater Treatment and Its Biological Behavior. Xing Chuanhong, Qian Yi (State Key Lab of Environ. Simulation and Pollution Control, Dept. of Environ. Eng., Tsinghua Uni., Beijing, 100084), *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 23—26

It is proven that Crossflow Membrane BioReactor (CMBR) applied to domestic wastewater treatment, under conditions of hydraulic retention time 5h, sludge retention time 15d, membrane surface velocity 4m/s and membrane flux 75, 150L/(m^2·h), is technically feasible and reliable during six weeks. Removal rate of COD, NH_3-N, and turbidity of the system are equal to or higher than 97%, 97% and 98%, SS and E. coli., 100%. The effluent quality is always better than the quality standard for reuse issued by the Ministry of Construction in China. An important formula to calculate the sludge concentration for CMBR at steady state is successfully derived from material balance equations. The apparent yield factor Yg is approximately 0.65mgVSS/mg COD and the decay constant, 0.1d^{-1}. Furthermore, the biofacies analysis of CMBR is included.

Keywords: crossflow, membrane, bioreactor, biological behavior, domestic wastewater.

Photochemical Treatment of Selected Organic Wastewater. Zhu Chunmei et al. (State Key Lab. of Pollution Control and Resource Reuse, Dept. of Environ. Sci. and Eng., Nanjing Univ. 210093): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 27—30

The photochemical oxidation treatment for selected organic wastewaters which were hard to degrade and were performed by adding H_2O_2 or some semiconductor powder and bubbling of O_2 or O_3 under sunlight or a middle pressure mercury lamp. The results showed that the removal rates of COD, oil and volatile phonols were 26.4%—60%, 39.8%—97.8% and 86.3%—100% respectively for the wastewaters of oil refinery and coking industry; the removal rates of COD and decoloration rates were 48%—75%, 80%—100% for selected

azo-dye aqueous solutions. The photodegradation products of phenol were also determined.

Keywords: photochemistry, photodegradation, wastewater treatment, oil refinery wastewater, coking industry wastewater, phenol.

The Preliminary Study on The Mechanism of Dyes Waste Water Treatment with ACF Electrode. Jia Jinping et al. (Dept. of Applied Chem., Shanghai Jiao Tong Univ., Shanghai, 200240): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 31—34

In this article, a new type of electrode made of ACF to treat several simulated dye waste water was studied. Under the electrolytic voltage ranged from 15V to 25V, all the wastewater's chromaticity removals are near 100%, with COD removals within 30%- 80%. And the reaction mechanism were figure out preliminarily by various characterization means such as IR、UV、spectrofluorimetry and TOC. Mainly, it may be that the treating processes involve radical reaction and coagulation simultaneously. The radical reaction can combine several organic molecules by radical coupling, so the larger molecule can be coagulated easily.

Keywords: active carbon fiber, electrode, electrochemistry, dyes waste water, reaction mechanism.

Determination and Discussion of Hydraulic Retention Time in Membrane Bioreactor System.

Zhang Shaoyuan, Wang Jusi et al. (Research Center for Eco-Environ. Sci., Chinese Academy of Sci., Beijing 100085): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 35—38

Based on the microorganism kinetic model the formula for computing the hydraulic retention time in the membrane bioreactor system (MBR) is derived, and then influencing factors of MBR are discussed. The results showed that the influencing factors are listed in order from strength to weakness as maximum specific removal rate K, saturation constant K_S, maintenance coefficient m, net bacteria yield coefficient Y_G and maximum specific growth rate μ_m. Finally, the formula is simplified and its simple form is as follows: $T = 1.1 \times (1/\beta - 1)(K_S + L)/KS_0$.

Keywords: membrane bioreactor, wastewater treatment, hydraulic retention time, microbial kinetic model, kinetic constant, operation constant.

The Pilot Test of Electrostatics-cyclone Precipitation Technology. Xu Dexuan and Qu Zhihe (Institute of Electrostatics, Northeast Normal University, Changchun 130024): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 39—41

The mechanism of electrostatics-cyclone precipitation technology has been researched in this paper. The pilot demonstration showed that this technology, using to improve the wet cyclone precipitator of power station, can heighten the precipitation efficiency from 92.55% to 98.4%. The precipitation efficiency for different concentration of flue gas is quite stable. When the gas flow is 10600 Nm^3/h, the resistance is 800- 920 Pa and the consumption per unit flow of high voltage power supply is 0.2 $W \cdot h/(m^3 \cdot h)$.

Keywords: electrostatics-cyclone precipitation technology, wet cyclone precipitation, high voltage power.

A Study of Sulfate Reducing Bacteria in Two Phase Anaerobic Process of UASB Reactors. Zhu Jianrong et al. (Dept. of Environ. Eng. Tsinghua Univ., Beijing 100084): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 42—44

This paper described the properties of numeration and distribution of sulfate reducing bacteria (SRB) in two phase process of UASB reactors. Using Hungate anaerobic technique and MPN determination method, it was showed that SRB of acidogenic phase are 2.0～5.7× 10^6 cells/ml, and the population of SRB in methanogenic phase are 0.93～9.3× 10^7 cells/ml. The difference of SRB between acidogenic and methanogenic phase is about 1 order of magnitude. The numeration of SRB in single UASB reactor is similar to that of methanogenic phase. The distributions of SRB exhibited that the bacterial population of acidogenic and methanogenic phase are 7.5× 10^5 and 4.3× 10^5 in upper layer of suspended mixed liquids, and 2.5× 10^6 and 2.5× 10^7 cells/ml in lower layer of anaerobic sludge, re-