

H-酸废母液的湿式空气氧化处理*

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摘要 研究了用湿式氧化法处理染料中间体 H-酸废母液。在 200—250 ℃, $P_{O_2}=1-3$ MPa 下, H-酸的湿式氧化反应可分为 2 个阶段, 最初 10 min 为快反应段, COD 快速下降, UV/可见光吸光度先急剧升高, 之后快速降低; 慢反应段延续到 30 min, COD 和吸光度缓慢下降, 其后变化不大。经过湿式氧化处理之后, 可生化性大幅度改善, 在 160℃, 充氧 3 MPa, 反应 1 h, 可使 10 g/L 的 H-酸液的 COD 降低 50%, BOD_5/COD 由 3.4% 升高到 33.3%。反应后尾气中不含 SO_2 , NO_x 类有害气体。

关键词 湿式空气氧化, H-酸, 可生化性。

H-酸(1-氨基-8-萘酚-3, 6-二磺酸)是重要的染料中间体。在酸析工序中排出的母液即为 H-酸废母液, H-酸废母液浓度很高(COD = 30—60 g/L), 色度深(2.1—6.3 万倍), 且含盐量高(90—300 g/L), 难以用一般的生物法或物化法处理。对于此类高浓度有毒有害难降解的废水, 湿式空气氧化法(Wet Air Oxidation, 简称 WAO)具有独到的优点, 已在污泥处理, 石油化工废水处理, 活性炭再生等领域获得应用^[1]。在我国, 该技术也引起了广大环保科技工作者的关注与研究^[2-9], 江义等研究了用催化 WAO 处理焦化废水^[10]。本研究以 H-酸废母液中的主要成分 H-酸为对象, 考察了 H-酸在 WAO 处理过程中有关水质指标的变化。

1 材料与方法

1.1 实验装置

选用 GS-0.5 型高压釜(山东威海化工器械厂)。主要指标: 容积 500 ml, 最高工作压力 10 MPa, 最高工作温度 300 ℃, 最大搅拌转速 1500 r/min, 设备材质 1Cr18Ni9Ti 不锈钢。附带温控仪, 以控制高压釜温度。实验装置流程见图 1。

1.2 实验方法

首先用化学纯 H-酸单钠盐配制一定浓度的溶液, 其 pH 值约为 2.5, 加 NaOH 调至适当的

pH 值做为实验用液。在高压釜中加入 300 ml 此试液, 打开加热电炉升温, 升至预定温度时取样, 然后开动搅拌器, 充入氧气至一定压强, 此时计为反应时间的零点。隔一定时间取样, 并记录温度, 压力值。实验初期, 取样间隔时间较短, 实验后期, 取样间隔时间较长。

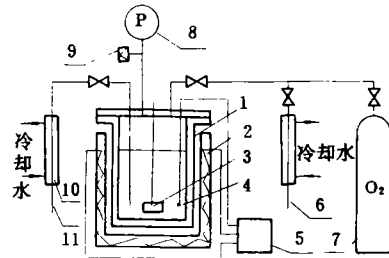


图 1 湿式氧化实验装置示意图

1 高压釜体 2 加热外套 3 搅拌器
4 热电偶 5 温控仪 6 气样管 7 氧气瓶
8 压力表 9 安全阀 10 冷却套管 11 水样管

1.3 指标与方法的分析

各水质指标的测定均参照《水和废水监测分析方法》^[12]。

COD: 污水 COD 速测仪(河北承德华通环保仪器厂)。

pH: 精密 pH 试纸, pH 计。

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UV/可见光吸光度: 日本岛津 UV-250 紫外分光光度计。

BOD₅: 标准接种稀释法(菌种取自北京染料厂污水处理车间污泥)。

SO₄²⁻: 离子色谱法。美国 Dionex 公司 DX100 离子色谱仪。采用 AS4A-SC 分离柱, AMMS-2 阴离子微膜抑制器, CDM-2 电导检测器。淋洗液为 1.80 mmol/L Na₂CO₃/1.70 mmol/L NaHCO₃, 再生液为 12.5 mmol/L H₂SO₄。

反应后期, 取气样测定 NO_x 及 SO₂ 含量。用美国 Thermo Environmental Instruments Inc. 的 Model 40 脉冲荧光二氧化硫分析仪(测量下限 3 mg/Nm³), 和化学发光 NO_x 分析仪(测量下限 0.1 mg/Nm³)。

2 实验结果与分析

2.1 反应过程中各水质指标的变化

(1) COD 的变化 在 200、250℃ 下进行实验的结果见图 2。由图 2 可见, COD 的去除过程可分为 2 个阶段, 快反应段和慢反应段: 在最初的 10 min 内, 由于迅猛的反应, COD 快速下降, 约降低 50% 左右, 此为快反应段; 然后是慢反应段, COD 持续降低, 直至 0.5 h, 之后降低不多, 这说明生成了难于进一步氧化的中间产物。即使反应时间进一步延长, 也不能使它

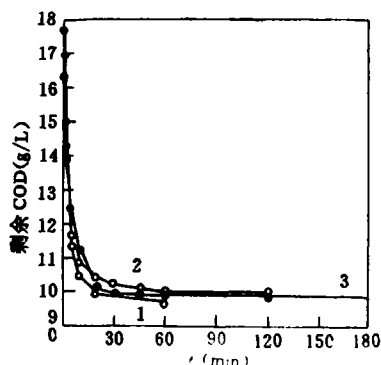


图 2 10000 mg/L 的 H-酸反应过程中 COD 的变化

1. $P_{O_2}=3\text{ MPa}$, 250°C , $\text{pH}=2.5$
2. $P_{O_2}=3\text{ MPa}$, 200°C , $\text{pH}=2.5$
3. $P_{O_2}=1\text{ MPa}$, 250°C , $\text{pH}=7$

们得到氧化。同时可以看出, 200℃ 与 250℃ 下处理效果相差不大, 为节省处理费用, 在 200℃ 下运行即可。

(2) UV/可见光吸光度的变化 反应过程中的 UV/可见光吸光图谱见图 3。由图 3 可见, 在不充氧的升温过程中, 吸光度略有升高; 在充氧后的几分钟内, UV/可见光吸光度快速升高, 然后 UV/可见光吸光度开始下降。随反应时间的延长, UV/可见光吸光度持续降低。这可能在刚充氧后所生成的某种中间体, 导致了 UV/可见光吸光度的升高, 然后进一步的氧化破坏了发色基团使得 UV/可见光吸光度降低。

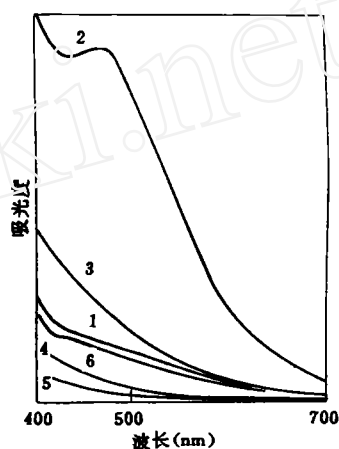


图 3 反应过程中吸光值随时间的变化
(10 g/L H-酸, 250°C , $P_{O_2}=3\text{ MPa}$)

1. 不充氧升至 250°C 时水样
2. 反应时间 2 min
3. 反应时间 5 min
4. 反应时间 10 min
5. 反应时间 20 min
6. 原水样

(3) pH 值与 SO₄²⁻ 浓度的变化 反应过程中 pH 值与 SO₄²⁻ 浓度的变化见图 4。可见充氧前的升温过程中 pH 值略有下降, 而 SO₄²⁻ 有所升高。充氧后最初 10 min 内 pH 快速下降, 大约降低 2 个单位, 之后缓慢降低, 30 min 后基本维持不变。SO₄²⁻ 在反应初期快速升高, 之后缓慢升高, 表明磺酸基脱离苯环, H-酸分子结构被破坏。pH 值的降低一方面由于 H-酸水解生成 H₂SO₄, 另一方面, 氧化生成的羧酸也会导致 pH 值的降低。

2.2 反应尾气中成分的测定

在反应后期, 对反应尾气取样分析, 结果

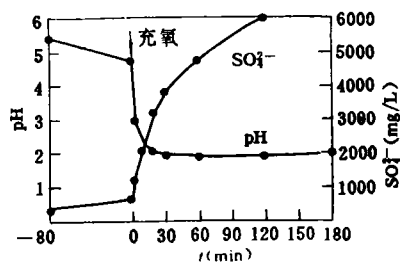


图 4 反应过程中 pH 值与 SO_4^{2-} 随时间的变化

实验条件: H-酸浓度 10 g/L, $P_{\text{O}_2}=3 \text{ MPa}$, 160°C

表明,尾气中 SO_2 、 NO_x 的含量低于检测限。在采用焚烧法处理废液时,由于温度较高,会产生 SO_2 、 NO_x 等气体污染物,需后续的尾气处理,使得工艺复杂化。而采用 WAO 工艺时,氧化反应在液相中进行。避免了这类气体污染物的形成,省去了后续处理的麻烦。

2.3 WAO 对可生化性的改善作用

本研究以 BOD_5 与 COD 之比为指标来衡量水样的可生化性,各不同处理条件下 BOD_5 与 COD 之比见表 1。

表 1 不同处理条件下 WAO 对 H-酸可生化性的改善

H-酸初 始浓度 (mg/L)	$\text{BOD}_5/\text{COD}(\%)$ 原水	$\text{BOD}_5/\text{COD}(\%)$ 反应后	反应 时间 (h)	反应 温度 ($^\circ\text{C}$)	充氧 压强 (MPa)
1000	3.2	34.3	8	160	1.0
1000	3.0	25.7	8	200	1.0
2000	2.9	39.0	8	240	1.0
10000	3.1	50.4	3	250	1.0
10000	3.3	36.0	2	200	1.0
10000	3.9	38.1	2	160	1.0
10000	3.4	33.3	1	160	3.0
10000	2.9		不充氧升温至 160°C 时水样		

由表 1 可见,原 H-酸水样的 BOD_5/COD 低于 4%,难于生物降解。WAO 处理对水样的可生化性具有明显的改善作用,在较低的反应温度 (160°C),较短的反应时间 (1 h) 内,可使 BOD_5/COD 由 3.4% 提高到 33.3%,大大提高

了水样的可生化性。同时注意到仅升高温度到 160°C 而不充氧,不能改善水样的可生化性。很多研究者认为, WAO 处理后的中间产物主要为低级酸、酮等^[12, 13],在 WAO 处理条件下,它们难于被进一步氧化,但它们很容易被生物所降解。因此提高了 BOD_5/COD 值。本试验在水样中也检出了甲酸、乙酸等成分,特别是乙酸含量较高。

3 结论

(1) H-酸在充氧后的反应过程可分为 2 段,快速段与慢速段。快速段约持续 10 min,这时 COD 以很快的速度降低, COD 可降低 50% 左右。其后为慢速段, COD 以较慢的速度降低, 30 min 后 COD 基本维持不变。

(2) 水样 UV/可见光吸光度在充氧之后数分钟内迅速变高,之后随反应进行逐渐降低。

(3) H-酸原水样可生化性很差 (BOD_5/COD 为 3% 左右),经 WAO 处理后,可生化性大幅度提高,在 160°C ,充氧压力 3 MPa 下处理 1 h,可使 BOD_5/COD 提高到 33.3%。若仅升温而不充氧,则可生化性没有获得改善。

(4) H-酸 WAO 处理的尾气中不含有 SO_2 、 NO_x 等有害气体。

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that PCP removal by granular sludge in UAD reactors was due to biodegradation rather than adsorption and volatilization.

Key words: pentachlorophenol, biosorption, de-sorption, biodegradation, anaerobic.

Photocatalytic Oxidation of Benzene Hexachloride and Pentachlorophenol in Aqueous Solution. Li Tian and Qiu Yanling (School of Environ. Eng., Tongji Univ., Shanghai 200092); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 24–26

Photocatalytic oxidation of low concentration of benzene hexachloride (BHC) and pentachlorophenol (PCP) in aqueous solution is studied with a high pressure mercury lamp as radiation resource and TiO_2 as a catalyst. BHC can be oxidized easily, half life periods of the 4 isomers of BHC are all around 20 minutes. Oxidation rate of γ -BHC is higher under neutral condition. Chlorinated medium products formed in the photocatalytic oxidation of BHC can be gradually removed by further reaction. For PCP reaction rate of photocatalytic oxidation is much higher than that of photolysis. Dechlorination of PCP can be completed within 30 minutes. As the reaction process continues, PCP will be oxidized into simple small molecules and finally mineralized completely. It is predictable that photocatalytic oxidation has bright prospect in advanced treatment of drinking water.

Key words: photocatalytic oxidation, benzene hexachloride, pentachlorophenol, aqueous solution.

The Dissipation and Residue of Quinclorac in Rice Field Water, Soil and Rice Plant. Wang Yiru et al. (Institute of Agro-environmental Protection, Tianjin 300191); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 27–30

Quinclorac is a new herbicide with high efficiency and low toxicity. The field experiments were carried out both in Tianjin and Jilin Province in 1993 and 1994, respectively. It has been found that the herbicide dissipated rapidly from water and leaves. Its half life values in the water was 0.8 days in Tianjin and 2 days in Jilin, and the half life in rice leaves was less than 1 day. The residue in sediment remained quite low during 6 days of half life. No metabolite was detected in soil. Applied to rice field as a 50% WP formulation at the recommended rates of 412.5 g–525 g/hm², one application, preharvest interval 96–105 days, the residue remaining in unpolished rice was less than 0.005 mg/kg, far below MRL, and was safe to human being.

Key words: Quinclorac, metabolite, dissipation, final residue, water, rice, soil.

Wet Air Oxidation Treatment of H-acid Production Waste Liqueur. Wang Yongyi et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 31–33

Under the condition of reaction temperatures of 200–250°C, initial oxygen partial pressures of 1–3 MPa, the wet air oxidation (WAO) of H-acid has 2-step process, including rapid reaction step, in which during the first 10 minutes after the beginning of the reaction COD is decreased rapidly, and UV/Vis. absorbance is increased drastically at first and then reduced rapidly, and slow reaction step, in which, both COD and UV/Vis. absorbance are decreased slowly during about 20 minutes.

WAO treatment can improve biodegradability of H-acid significantly. After 1 hour reaction carried out at 160°C and 3 MPa initial oxygen pressure, COD was decreased by 50%, and the BOD₅/COD ratio of 10 g/L H-acid solution was increased from 3.4% to 33.3%. The offgas from the WAO treatment of H-acid contains undetectable amount of SO₂ and nitrogen oxides.

Key words: wet air oxidation, H-acid, biodegradability.

Emission Factors of Trace OCS from Crop Residues Burning and Estimation Its Amount in China. Cao Meiqiu and Zhuang Yahui (Research Center for Eco-Environmental Sciences, CAS, Beijing 100085); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 34–36

A method of sampling and analysis for trace carbonyl sulfide has been described. The sample is trapped and concentrated at temperature of liquid N₂ and liberated directly into a gas chromatographic column. The concentration of OCS in compressed air as determined as 2.94×10^{-3} µg/L. The method accuracy expressed in term of standard deviation coefficient is $\pm 0.72\%$. The emission factors of carbonyl sulfide, which were measured during the combustion of rice straws, maize stalks and wheat stalks in an enclosed combustion system, are 1.80, 2.75 and 2.05 g/t for rice straws, maize stalks, and wheat stalks, individual. Standard deviation coefficient are $\pm 6.67\%$, $\pm 8.36\%$, and 9.27% for rice straws, maize stalks, and wheat stalks, respectively. Distribution of the amount of crop residues burned in China is presented with a resolution 1° latitude \times 1° longitude. The amount of trace OCS could be calculated with their emission factors.

Key words: carbonyl sulfide, biomass burning, emission factor.

The Study of Trace Elements in Human Hair from the Area of Endemic Arsenism. Jiang Ling et al. (Institute of Environ. Medicine, Tongji Medical Univ., Wuhan 430030); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 37–39

217 hair samples and environmental samples from endemic arsenism in Linhe, Inner Mongolia were analyzed. The results showed that the levels of As, Cu and K in hair in studied area were higher than that in control area, but Zn and Se was opposite. The relationship between the typical symptoms of arsenism and the levels of As, Cu, K and Se in hair were found. There were rank correlations between the concentration of Se, Zn, Cu in hair and As in hair (the coefficient = -0.988 , -0.794 , 0.783 , respectively).

Key words: endemic arsenism, trace elements, hair.

Research for the Problem about the Environmental Discount Rate. Wang Yonghang and Fu Guowei (Dept. of Environ. Eng., Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, 17(1), 1996, pp. 40–43

This paper presents a new formula, which describes the relation between private rate or return and social rate of return. The formula includes two environmental parameters, λ , the fraction of national income spent on environmental investment, and η , the elasticity of environmental improvement with respect to environmental spending. From the formula it can be seen that social rate of return or environmental discount rate should decline systematically over time from the point of view of environmental