染料中间体废水的催化臭氧化预处理*

张彭义 祝万鹏 余 刚 蒋展鹏

(清华大学环境工程系,北京 100084)

摘要 自制了 2 种高活性的催化剂 Mn-02 和 Fe-Ni-Urea,并对典型染料中间体废水——吐氏酸废水进行金属催化臭氧化预处理. 对初始 COD 浓度约为 1500 mg/L 的废水,当臭氧投加量为 0.82 g/L 时,COD 去除率大于50%;其臭氧化指数(OI)分别为 1.44 和 1.07,而相应的空白则为 1.90. 色质联用和离子色谱分析表明吐氏酸的金属催化臭氧化产物为,邻苯二甲酸、乙二酸、硝酸根、硫酸根,提出了吐氏酸的臭氧化途径;理论分析表明,吐氏酸经金属催化臭氧化后,可生化性大大改善.

关键词 吐氏酸废水,催化剂,金属催化臭氧化.

近年来,对染料废水的治理已进行了较多的研究,尝试了多种处理方法,如混凝沉淀法、吸附法、化学氧化法、还原法等[1]. 臭氧氧化技术在原来 O₃、O₃/H₂O₂、O₃/H₂O₂/UV(O₃/UV)等形式的基础上又发展出 O₃/固体催化剂形式(本文称为金属催化臭氧化),它以固体状的金属(金属盐及其氧化物)为催化剂,加强臭氧化反应. 曾有文献对此进行报道[2-4]. 笔者用浸渍法和附着沉淀法制备过渡金属氧化物催化剂,对染料中间体废水进行金属催化臭氧化预处理研究. 本文报告部分研究结果.

1 催化剂制备

1.1 催化剂材料

载体: γ -Al₂O₃, 其主要性质为: 直径 2.5—4.5 mm, 煅烧温度 500℃, 比表面积 250 m²/g, 真密度 3.17 g/m³. 催化剂活性组分前驱物: 分析纯 Mn(NO₃)₂, Ni(NO₃)₂, Fe(NO₃)₃. 沉淀剂 母体: 分析纯尿素[CO(NH₂)₂].

1.2 浸渍法制备 Mn-02 催化剂

(1) 配制浓度为 6%—7%(以 Mn 元素含量计)的 Mn(NO₃)₂ 溶液; (2) 称取 150 g γ -Al₂O₃载体,浸入溶液中(250 ml),浸渍 4 h; (3) 滤去浸余液,将负载后的载体置于瓷盘中,室温下凉干,大约 12 h; (4) 将瓷盘放入烘箱,在 85 ℃

下干燥 12 h; (5) 从烘箱中取出载体,然后放入马福炉,在 450 个下焙烧 4 h; (6) 重复步骤 (2)—(4) 1次,得到催化剂成品.

1.3 附着沉淀法制备 Fe-Ni-Urea 催化剂[5]

(1) 分别配制 6%-7%(以金属元素含量计)的 $Ni(NO_3)_2$ 、 $Fe(NO_3)_3$ 溶液,并以 4:1 的体积比混合;(2) 称取尿素 80 g 溶于以上混合溶液中;(3) 称取 γ - Al_2O_3 150 g,浸渍 4 h;(4) 将浸有 γ - Al_2O_3 的溶液水浴加热升温,同时慢慢搅拌直至 55 °C,保持恒温放置约 5 h;(5) 滤去浸余液,负载后的载体在 85 °C 下干燥 12 h,然后在 450 °C 焙烧 4 h,得到催化剂成品.

1.4 催化剂的表征[6]

对所制的 2 种催化剂进行了分析表征:(1)原子吸收光谱法(AAS)进行组分含量测定;(2)扫描电子显微镜(SEM)进行催化剂表面和体相晶粒分析;(3)电子能谱(ESCA)进行表面化学态分析;(4) BET 氮吸附容量法进行比表面积测定.

2 吐氏酸废水金属催化臭氧化试验

2.1 试验材料

* 国家"八五"科技攻关项目 收稿日期: 1995-10-20 催化剂: 为前述制得的 2 种催化剂.

吐氏酸废水:天津某化工厂的吐氏酸废母 液经资源回收后的出水,初始 COD 约 1500 mg/L, 色度 300 度(稀释倍数法), 并用氨水调 节 pH 到 9.0.

臭氧气:由 XFZ-5 型臭氧发生器产生.

2.2 试验装置和试验方法

试验装置如图 1 所示, 试验用反应器为 Carberry 无梯度反应器[7].

试验时, 先将一定量(105 g)催化剂装入催 化剂筐内,然后加入4L吐氏酸废水,将催化剂 筐与搅拌器相连,开启搅拌器. 通入臭氧气,其 流量为 0.05 m³/h, 其中臭氧浓度为 21-27 mg/L. 每隔 20 min 取水样和气样分析,分别测 COD、色度、pH 和臭氧浓度.

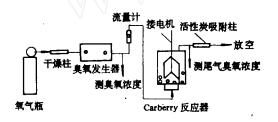


图 1 反应装置

2.3 催化剂活性评价指标

- (1) COD 去除率 在试验条件完全相同 时,可用 COD 去除率衡量催化剂活性;
- (2) 臭氧化指数(OI) 其意义为每去除单 位数量 COD 所消耗的臭氧量(g/g),即 OI=臭 氧纯消耗量/COD 绝对去除量,这是一个无量 纲指数,其理论值为1.0.

3 吐氏酸臭氧化产物分析[6]

3.1 分析水样制备

用高纯水配制吐氏酸(瑞士进口分析纯,纯 度>98%)溶液,分别以 γ-Al₂O₃、Mn-02、Fe-Ni-Urea 为催化剂进行催化臭氧化,条件同废水 臭氧化试验. 反应 2 h 后, 取水样分析, 水样号 依次为1、2、3号.

3.2 产物鉴定

用色质联用和离子色谱对水样中物质进行 4.2 催化剂的催化作用

分析. 预处理及分析步骤如图 2 所示.



图 2 臭氧化产物鉴定步骤

结果与讨论

4.1 臭氧化过程中废水色度和 pH 的变化

臭氧化过程中废水色度和 pH 的变化如图 3 所示. 由图 3 可见, 无论在空白 γ-Al₂O₃ 载体还 是在 Mn-02 和 Fe-Ni-Urea 催化下, 反应过程中 废水的 pH 和色度的变化趋势是相同的. 即① pH 随反应进行而逐渐下降. 这是由于在反应过 程中产生了有机酸类物质(这在反应产物分析中 可得到证实). ② 在反应起初的 20-40 min, 色 度急剧上升,这是由于在反应开始时生成了高 色度的醌类物质所致; 之后又迅速下降.

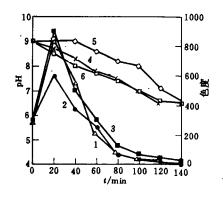


图 3 pH 值和色度随反应时间的变化 1. γ-Al₂O₃-Color 2. Mn-02-Color 3. Fe-Ni-Urea-Color 4. 7-Al₂O₃-pH 2. Mn-02-pH 3. Fe-Ni-UreapΗ

废水在不同条件下的 COD 去除率与 OI 指数随臭氧投加量的变化如图 4 所示. 对 COD 初始浓度为 1500 mg/L 的吐氏酸废水,当臭氧投加量为 0.82 g/L 时,在 Mn-02 和 Fe-Ni-Urea 催化下,COD 去除率分别为 43%和51.8%. OI 指数分别为 1.44 和 1.07,而空白的 COD 去除率和 OI 指数分别为 33%、1.90. 可见与空白的 γ -Al₂O₃ 相比,2 种催化剂都有明显的催化作用,每去除 1 kg COD 臭氧消耗量分别降低 24.2%和 43.6%.

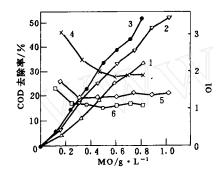


图 4 COD 去除率和 OI 指数随臭氧投加量 MO 的变化 1. 7-Al₂O₃-COD 2. Mn-02-COD 3. Fe-Ni-Urea-COD 4. 7-Al₂O₃-OI 5. Mn-02-OI 6. Fe-Ni-Urea-OI

催化剂的表征结果列于表 1. 催化剂的 X 光电子能谱分析表明,催化活性组分分别为 MnO₂ 和 Ni₂O₃、Fe₂O₃. 催化剂的活性组分之间并没有发生化学结合,活性组分之间与载体之间也没有发生化学结合.

表 1 催化剂表征结果

NH (I. b. l	金属含量	/L 24 /A *	化学结	比表面积
催化剂	/%	化学价态	合形式	$/m^2 \cdot g^{-1}$
γ-Al ₂ O ₃				250
Mn-02	9.68	Mn^{4+}	MnO_2	131.6
Fe-Ni-Urea	Fe 6.04	Fe ³⁺	$\mathrm{Fe_2O_3}$	269.5
	Ni 0.56	Ni ³⁺	Ni ₂ O ₃	

4.3 影响催化剂活性的因素

及其配比. 因为 γ -Al₂O₃ 的比表面积比 Mn-02 的大得多,但活性则差得多. ② 从组分相同但制备方法不同的催化剂的活性比较实验(本文略)可以清楚地看到附着沉淀法较浸渍法更有效.

所以影响催化剂活性的因素主要是活性组 分及其配比,另外制备方法、条件也是重要的 因素.

另外从臭氧化产物离子色谱分析结果(见表 2,3)看,2种催化剂与 γ -Al₂O₃在臭氧化过程中 还有以下差别: ① 分析水样中乙二酸浓度的差 别可以很好地说明吐氏酸被臭氧氧化的程度, 虽然 1、2、3 号水样中乙二酸的浓度相差不大, 但是从转化百分率看,则 2、3 号明显地比1号 氧化程度深, 也说明催化剂活性的差别. ② 吐 氏酸分子上-NH₂、-SO₃H 基团在臭氧化过程 中的受攻击情况是不一样的. 在 Mn-02 和 γ -Al₂O₃ 作催化剂情况下, -SO₃H 比-NH₂ 更易 从环上脱落;在 Fe-Ni-Urea 情形下则反之. ③ 碱催化(1号)与金属催化氧化(2、3号)相比, 吐氏酸分子上的-NH2氧化成-NO2后从环上 脱落的速度和程度不同,金属催化能强化 -NH₂的氧化脱落;在2种金属催化剂中,Fe-Ni-Urea 的作用更强.

表 2 有机酸柱分析结果/mg·L-1

水样编号	1	2	3
乙二酸根浓度	433.65	425.86	437.53
一个环打破生成的乙二酸根浓度	301.50	271.14	231.72
二个环打破生成的乙二酸根浓度	603.00	542.78	463.44
二个环打破的百分率/%	71.92	78.46	94.41

表 3 阴离子柱分析结果/mg·L-1

水样编号	1	2	3
-NH₂ 全部转化为 NO₃ 的浓度	207. 71	186. 79	159.63
-SO₃H 全部转化为 SO⊱ 的浓度	321.61	289. 22	247. 17
NO₃ 浓度	6.53	21.79	158.75
SOf- 浓度	181.84	180.36	123. 39
-NH₂ 转化为 NO₃ 的百分率/%	3. 14	11. 67	99. 45
-SO₃H 转化为 SOℓ- 百分率/%	56.54	62. 36	49. 92

4.4 臭氧化产物

气相色谱-质谱联用分析 1、2、3 号水样, 均检测到邻苯二甲酸,另外对反应 20 min 后的 水样同样进行色质分析,检测到 2-胺基-1,4 苯 醌和 2-硝基-1,4 苯酯(限于篇幅,所有分析条 件、样品检测谱图略).

离子色谱分析结果如表 2、3 所示.

从色质联用和离子色谱检则的结果看,金属催化与空白 γ -Al₂O₃条件下臭氧化的最终产物是相同的,即为 NO_3^- 、 SO_4^+ 、乙二酸、邻苯二甲酸,臭氧化中间产物有 2-胺基-1,4 苯醌、2-硝基-1,4 苯醌.

5 结论

- (1) 与空白的 γ-Al₂O₃ 相比, Mn-02、Fe-Ni-Urea 2 种催化剂有明显的催化作用, 其中 Fe-Ni-Urea 的催化效果尤其突出, 其 OI 指数 (1.07)已非常接近理论值(1.0).
 - (2) 用金属催化臭氧处理吐氏酸废水,当

COD 去除率达 50%左右时,可以推测此时废水 已适合生物处理.

(3) 吐氏酸臭氧化的产物为: NO₃⁻、SO₄²、乙二酸、邻苯二甲酸,臭氧化初始阶段有 2-胺基-1,4 苯醌、2-硝基-1,4 苯醌产生.

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电话: 62545511—2138 **联系人:** 万维纲 Degradation of CF₂ClBr by Spark Plasma. Liu Zhengchao et al. (Environ. Sci. Institute, Fudan University, Shanghai 200433), Pan Xunxi et al. (The Second Dept. of Physics, Fudan University, Shanghai 200433); Chin. J. Environ Sci., 17(4), 1996, pp. 1-3

In this investigation a preliminary study of spark plasma for the degradation of CF₂ClBr was studied. The products were analysed mainly by gas chromatography. At the pressure of 2. 67 × 10³ Pa the degradation rate of CF₂ClBr is about 90%. The main products of degradation are CF₃Cl, Br₂, CF₄, CF₂Cl₂. In addition, the products were discussed on the ther ther modynamic view-point. The conclusion showed that the production process can always make the system more stable.

Key words: CF₂ClBr, spark plasma, degradation.

Study on Purification of Smelting-Gases Containing SO₂ in Low Concentration by Liquid-Phase Catalytic Oxidation Method. Sun Peishi et al. (Dept. of Environ. & Chem. Eng., Kunming University of Science and Technology, Kunming 650093); Chin. J. Environ. Sci., 17 (4), 1996, pp. 4-6

In order to approach an applicable method of purifying smelting-gases containing SO₂ in low concentration for China, the experimental research of catalytic oxidizing SO₂ in smelting-gas by Mn²⁺, Fe²⁺ and Zn²⁺ in liquid-phase was performed in a copper smelter. The optimum proportion of metal ions in the absorption solution was obtained by the orthogonal experiment. The solution with mixed metal ions offered a better purification ability to smelting-gases, when the concentration of H₂SO₄ in the solution rose to 20%, the purification efficiency of SO₂ still could be maintained above 85%. The method is applicable for the waste gas treatment in the smelter of nonferrous metals.

Key words: liquid-phase catalytic oxidation, smelting-gases containing SO₂ in low concentration, purification of waste gases.

Photocatalytic Oxidation of H-acid in Aqueous Solution. Zhu Wanpeng et al. (Dept. of Envi-

ron. Eng., Tsinghua Univ., Beijing 100084): Chin. J. Environ. Sci., 17(4), 1996, pp. 7-10

Photocatalytic oxidation of H-acid in aqueous solution was investigated by irradiating with a 30 watts low pressure mercury lamp and using TiO₂, ZnO, CdS, Fe₂O₃ as catalysts. The results indicated that TiO2 and CdS have higher catalytic activity than ZnO and Fe₂O₃. H-acid in aqueous solution can be degraded more than 90% during a period of 5 hours irradiation when TiO₂ is used as catalyst. The rate of photocatalytic oxidation can be expressed by Langmuir-Hinshelwood Equation, the constants K and k were found by experiment to be K = 12.3 L/mmol and $k = 25.2 \times$ 10⁻⁶ mol/h respectively. The reaction time can be shortened 2-3 hours when 10 mg/L Fe3+ or Ag+ is added in H-acid solution. The effects of dosage of catalyst, pH and concentration of Hacid in the solution on photocatalytic oxidation of H-acid were also studied.

Key words: titanium dioxide, photocatalytic oxidation, H-acid.

Emission of N₂O from Burning Coal in China. Zhao Ruilan et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): Chin. J. Environ, Sci., 17(4), 1996, pp. 11-13

In this paper the actual emission of N₂O from power station boilers, other industrial boilers, industrial kilns and civil coal fired furnace was measured. The concentration of N₂O in flue gases was in range of 1.5—57. 4 mg/m³. After analyzing coal to be burned and determining carbon content of the slags and ashes, the efficiencies of coal combustion in different boilers were estimated and the flux of the flue gases were calculated. From these data the N₂O emission factor was obtained. According to the coal consume profile of our country, the total emission of N₂O from burning coal in China was 35. 69 Gg/a (N₂O-N).

Key words: nitrous oxide, emission source, emission factor.

Dye Intermediate Wastewater Pretreatment by Metal Oxide Catalyzed Ozonation. Zhang Pengyi et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084): Chin. J. Environ. Sci., 17(4), 1996, pp. 14-17

Two catalysts were prepared and used for pretreatment of typical dye intermediate wastewater tobias acid wastewater by metal oxide catalyzed ozonation. For wastewater with initial COD concentration of 1500 mg/L, when ozonation dose is 0.82 g/L, COD removal efficiency is above 50%. And Ozonation Index (OI) of the two catalysts are 1.44 and 0.7 respectively, while the blank γ-Al₂O₃ is 1. 90. The ozonation products of tobias acid identified by gas chromatography-mass spectrography are o-benzendicarboxylic acid, oxalic acid, sulphate ion and nitrate ion, and then the ozonation pathway is proposed. After tobias acid is treated by metal oxide catalyzed ozonation, the biodegradability is improved apparently.

Key words: tobias acid wastewater, catalyst, metal oxide catalyzed ozonation.

Removal of 9 Kinds of Trace Element in Burning Coal in the Layer-Burning Boilers. Wang Qichao et al. (Changchun Institute of Geography, Chinese Academy of Sciences, Changchun 130021), Wang Zhigang et al. (Environmental protection Institute of Northeast Coal Industry): Chin. J. Environ, Sci., 17(4), 1996, pp. 18—20

An empirical formula on the content of trace elements as Be, Co, Cr, Cu, Mn, Ni, Pb, V, Zr in fly ash and bottom ash of burning coal in layerburning boilers was developed, by which the distribution and transfer quantity of trace elements from coal into fly ash, bottom ash and atmosphere was calculated. The grain size distribution of content and mass of trace elements in fly ashes was also studied, and the laws of enrichment or dispersion of trace elements in burning process were approached. The content of most of trace elements in bottom ashes is higher than that in fly ashes, most quantity of 9 trace elements in coal is removed into bottom ash after burning, but the enrichment factor of element in fly ashes is higher than that in bottom ashes. The enrichment extent of trace elements in fly ashes increases as grain size decreases. About 90 percent of total quantity of trace elements in fly ashes are distributed in the particles with the diameter less than 0.125 mm.

Key words: layer-burning boiler, burning coal,

trace element, removal.

The Application of Surfactants on Treatment of Petroleum-contaminated in Unsaturated Zone. Zhu Mei and Xu Jialin (Institute of Environ. Sci., Beijing Normal University, 100875), Tian Honghai (Center of Environ. Sci., Peking University, Beijing 100871): Chin. J. Environ. Sci., 17(4), 1996, pp. 21-24 The paper focused on the application of aqueous surfactant washing for cleaning up petroleum contamination in unsaturated zone. Regional geographical features and contamination characteristics have been investigated. Nine commercial nonionic surfactants were analyzed and tested. Their critical micelle concentrations were measured and their effects on emulsification and solubilization of oil and benzene as well as on soil dispersion were compared. The results showed that the best surfactants are AEO-9 and SA-20, i. e., alcohol polyethoxylated ethers. Their optimum concentrations were also determined. In batch-washing tests the highest removal efficiency can be as high as 94%. Results of leaching tests for soil columns and lime stone columns were satisfactory as well. From this study, it is clear that the application of surfactants can be included in field experimental research for the treatment of contaminated unsaturated zone of groundwater.

Key words: groundwater, petroleum contamination, surfactant, unsaturated zone.

Studies on Removing Uranium from Digested Solutions of Uranium Bearing Ascharite-Magnetite Syngenetic Mineral by Sulfuric Acid in Wengquegou Liaoning Province. Cao Jiling et al. (School of Chemical Engineering, Dalian University of Technology, Dalian 116012): Chin. J. Environ. Sci., 17(4), 1966, pp. 25-27 The digested solution of uranium bearing ascharite-magnetite syngenetic mineral in Wengquegou by sulfuric acid contains a large amount of H₃BO₃ and MgSO₄ and a little Fe³⁺ (after oxidation with NaClO₃) and UO₂²⁺. The experiments of removing uranium from solutions containing Fe³⁺ and without Fe3+, after adjusting their pH with MgO, were carried out. After precipitation of UO₂²⁺ from solution without Fe³⁺, the U content is still higher than that in digested solution, whereby it is impossible to remove U. When Fe(OH)₃ exists, which can act as coprecipitant, the U content after purification can be depressed,