

化学氧化法处理资源回收后的 J-酸和吐氏酸染料中间体废液*

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摘要 萘系磺酸染料中间体 J-酸和吐氏酸废母液经有用资源的回收后, 尚须进行最终出水的达标处理. 通过吐氏酸和 J-酸废母液萃余液的后处理试验, 确定了盐回收-混凝沉淀-化学氧化的达标处理工艺方案, 并确定了相应的工艺参数. 其中化学氧化采用 Fenton 试剂(以双氧水作氧化剂, 绿矾为催化剂), 在经济合理的投量范围内经 2—4h 反应, 萃余液 COD_{Cr} 去除率达 80% 以上, 最终出水 COD_{Cr} 在 200mg/L 以下, 满足有关工业废水排放标准.

关键词 染料中间体, J-酸废母液, 吐氏酸废母液, Fenton 试剂, 化学氧化.

以 2 种典型的萘系磺酸染料中间体吐氏酸(2-氨基-1-萘磺酸)废母液和 J-酸(2-氨基-8-萘酚-6-磺酸)废母液为研究对象, 通过多种方案的试验, 筛选出高效的萃取-反萃取资源回收综合治理体系, 可以回收废液中 95% 左右的染料中间体, 同时使废液的 COD_{Cr} 值由 20000mg/L 左右降低到萃余液中 COD_{Cr} 值 $1,000\text{mg/L}$ 以下, 色度降低 90% 以上^[1,2]. 但是, 根据污水综合排放标准(GB8978-88), 染料工业排水的 COD_{Cr} 值应在 200mg/L 以下. 因此, 萃余液必须作进一步达标处理.

萃余液的 COD_{Cr} 主要由因萃取不完全而残余的染料中间体分子和溶解在萃余液中的萃取剂组成, 不易生物降解, 不能采用常规的生物处理方法, 而主要考虑选择二级萃取法、混凝沉淀法和化学氧化法 3 种方法. 在研究 COD_{Cr} 的去除时, 由于吐氏酸和 J-酸废母液的萃余液性质基本相同, 所以本研究选取吐氏酸废母液的萃余液为研究对象. 通过研究发现, 两级萃取总萃取率可达 98%, 但只能将萃余液 COD_{Cr} 降至 500mg/L 左右. 对于混凝沉淀法, 先后选取了 5 种不同类型的混凝剂及其组合工艺进行研究, 对萃余液 COD_{Cr} 的去除率为 20%—30%, 均满足不了工业废水排放标准.

本研究选取 NaClO 、 H_2O_2 和 Fenton 试剂对吐氏酸萃余液进行化学氧化试验.

1 NaClO 氧化法

由实验结果可知, NaClO 对 COD_{Cr} 的去除效果可达 50% 以上, 虽优于混凝沉淀法, 但仍难以达到排放标准.

2 H_2O_2 氧化法

实验用双氧水 H_2O_2 含量不低于 30%, 反应时间为 24h. 实验结果如图 1 所示. 由图 1 可知, H_2O_2 对萃余液 COD_{Cr} 的去除有明显作用, 去除率随投加量的增加而显著增加, 最高可达 97.4%. 欲满足废水排放标准, COD_{Cr} 去除率只需达到 80% 左右. 为此, 双氧水投量只需要 4— 5ml/L 即可满足. 但使用 H_2O_2 氧化的一个重

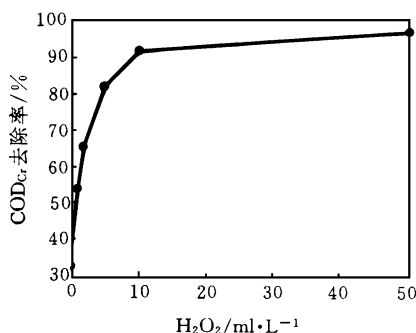


图 1 双氧水投加量与 COD_{Cr} 去除率的关系

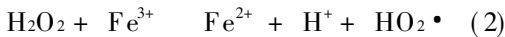
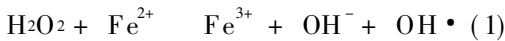
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要问题是反应速度慢,需 24h 左右才能反应较完全.应用在工程实践上,则会使反应池容积过大,增加了基建投资.

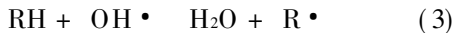
3 Fenton 试剂氧化法

3.1 氧化机理

当在含有 Fe^{2+} 离子的酸性溶液中投加 H_2O_2 时,会发生下列反应^[3,4]:



整个体系的反应十分复杂,其关键是通过 Fe^{2+} 在反应中起激发和传递作用,使链反应能持续进行,直至 H_2O_2 耗尽.该反应被称为 Fenton 型反应, Fe^{2+} 的酸性溶液和 H_2O_2 的混合试剂则称为 Fenton 试剂.反应中激发出的羟基自由基($\text{OH}\cdot$)氧化能力很强,仅次于 F_2 ,因而能有效地分解难生物降解的有机物(RH):



羟基自由基与水中有机物的反应速度很快,速率常数在 $10^8\text{--}10^{10} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ 范围^[5,6].控制适当的反应条件,羟基自由基可使有机物分解无机化.J-酸和吐氏酸废母液中有有机物均为苯和萘的衍生物,分子上带有钝化基团,非常稳定,一般氧化剂较难氧化,而羟基自由基可迅速将其氧化,反应速度比单纯 H_2O_2 氧化将大大加快.而且,J-酸和吐氏酸废母液为酸性废水,Fenton 试剂法在酸性条件下对废水处理效果更好.羟基自由基与其反应时,先脱去磺酸基,生成羟基取代物,使芳香环活化,再进行氧化分解,生成低级有机酸类物质.

3.2 最佳投量

选取价廉易得的绿矾($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$)为催化剂,与 H_2O_2 构成 Fenton 试剂.由于 Fe^{2+} 与 H_2O_2 在不同配比下激发出羟基自由基的程度有所差别,通过正交实验可得出绿矾和 H_2O_2 的最佳投量.在一定的投量范围内,对 COD_{Cr} 去除率的实验结果如图 2 所示.

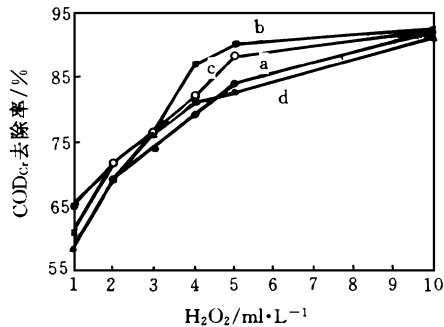


图 2 绿矾和 H_2O_2 投加量与 COD_{Cr} 去除率的关系
 $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ 的摩尔比:a. 12 : 1 b. 8 : 1 c. 6 : 1 d. 4 : 1

在工程实际应用上,应力求降低 H_2O_2 投加量.同时,为控制污泥量也不能投加过多绿矾.鉴于此并综合以上结果,在满足 COD_{Cr} 去除率不低于 80% 的前提下,最佳投量应为每 m^3 废水投加双氧水(含 30% H_2O_2) 4L,绿矾 1.35kg.

3.3 反应速度

使用 Fenton 试剂氧化的初衷乃在于加快反应速度,避免反应池容积过大.实验证明,Fenton 试剂氧化法的反应速度很快,2—4h 反应即可大体完成,速度远远快于单用 H_2O_2 氧化.

为确定 Fenton 试剂氧化的准确反应时间和进一步探讨其反应机理,并为水质和投药量等条件改变时相应改变工程设计的氧化时间提供可靠的理论依据,有必要研究其氧化反应的速率.取一定量水样,投加最佳投量的双氧水和绿矾(每 L 废水投加含 30% H_2O_2 的双氧水 4ml 和绿矾 1.35g),在不同时间依次测定其残余 COD_{Cr} .实验结果如表 1 所示.

由表 1 可看出,反应至 8h 后 COD_{Cr} 的去除率已增加不多,故可近似地认为反应 24h 已基本完成,即最终出水 COD_{Cr} 为 162mg/L.

根据表 1, COD_{Cr} 去除与反应时间的关系可用下述公式表示:

$$\frac{C_i - C_x}{(C_i - C_e)(C_x - C_e)} = kt$$

表 1 Fenton 试剂氧化时间与 COD_{Cr} 的去除

反应时间/h	0.5	1	1.5	2	4	8	24
进水 COD _{Cr} /mg · L ⁻¹	990	990	990	990	990	990	990
出水 COD _{Cr} /mg · L ⁻¹	595	421	328	227	172	166	162
去除 COD _{Cr} /mg · L ⁻¹	395	569	662	763	818	824	828
COD _{Cr} 去除率/%	39.9	57.5	66.9	77.1	82.6	83.2	83.6

式中, c_i : 进水 COD_{Cr} 浓度 (mg/L), c_x : 随时间变化的出水 COD_{Cr} 浓度 (mg/L), c_e : 反应基本完成时间的出水 COD_{Cr} 浓度 (mg/L), k : 反应速率常数 (L · mg⁻¹ · h⁻¹), t : 反应时间 (h) .

以反应时间为横坐标, 出水 COD_{Cr} 为纵坐标, 对表 1 有关数据进行拟合, 可得本试验的反应速率公式为:

$$(990 - c_x) / (828 \cdot (c_x - 162)) = 0.0040 \cdot t$$
该反应速率公式可应用于下列 2 方面:

(1) 在确定了投药量的前提下, 通过试验研究得出反应基本完成时的出水 COD_{Cr} 浓度, 借助于上述公式得出不同反应时间可得到的出水 COD_{Cr} 浓度, 从而根据出水水质要求选取反应时间为工程设计的依据.

(2) 以 c_e 为工业废水排放标准, 可以借助于上述公式得出在满足排放标准的前提下, 所需的最短反应时间.

3.4 铁源的选择

由于 Fenton 反应是由一系列包括 Fe 在不同价态下的物种相互转化的链式反应组成, 因此不同的铁源对于反应可能会有一定影响. 为寻找最有效且经济的铁源催化剂, 分别选取 FeCl₃ 作为 Fe³⁺ 的代表, 绿矾 (FeSO₄ · 7H₂O) 作为 Fe²⁺ 的代表, 还原铁粉作为 0 价铁 Fe⁰ 的代表, 进行实验. 含 30% H₂O₂ 的双氧水投加量为 4ml/L, 铁投加量的基准均为 H₂O₂/Fe= 8 1(摩尔比). 实验结果如表 2.

由表 2 可知, 绿矾和还原铁粉最终处理效果大致相当, 而 FeCl₃ 处理效果较差. 绿矾的反应速度也明显优于 FeCl₃ 和还原铁粉. 因此, 可确定绿矾 (FeSO₄ · 7H₂O) 为 Fenton 试剂的最优铁源. 根据 Fenton 试剂的反应机理, 在一系列链反应中, 公式 (1) 显然是激发羟基自由基的

关键, 而该反应的关键则在于 Fe²⁺. 因此, Fe³⁺ 作为铁源使一部分 Fe 消耗在产生 Fe²⁺ 的链反应中, 效果不如直接采用 Fe²⁺. 实验结果与理论相符.

表 2 不同铁源对 Fenton 试剂去除 COD_{Cr} 效率和速度的影响

项 目	FeCl ₃	FeSO ₄ · 7H ₂ O	还原铁粉
双氧水投加量/ml · L ⁻¹	4.0	4.0	4.0
铁源投加量/ml · L ⁻¹	1350	789	272
原水 COD _{Cr} /ml · L ⁻¹	873	873	873
出水 COD _{Cr} /ml · L ⁻¹	280	155	158
去除 COD _{Cr} /ml · L ⁻¹	593	718	715
COD _{Cr} 去除率/%	67.9	82.2	81.9
反应基本完成所需时间/h	24	4	10

4 结论

对 J-酸和吐氏酸染料中间体废母液经资源回收后萃余液的达标排放处理, 可采用盐回收-阳离子 PAM 混凝沉淀-Fenton 试剂氧化法.

每 m³ 废水吐氏酸废母液投加含 30% H₂O₂ 的双氧水 4L, 绿矾 1.35kg, 可保证最终出水 COD_{Cr} 满足 200mg/L 以下的工业废水排放标准. 若废母液原水浓度过高, 则需适当增加药剂投量.

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at Mt. Emei. Zhu Xiaofan, Lu Hong, Jing Yan (Dept. of Environ. Sci. & Engineering of Sichuan Union. University, Chengdu 610065): *Chin. J. Environ. Sci.*, **18**(4), 1997, pp. 25—28
With simulated acid rain, the experiment on leaching of Al in soil at Mt. Emei was done and the amount of Al leached and Ca/Al ration in soil were examined. The aim is to inquire into the relationship between active Al, Ca/Al ration and the growth of Fir Forest at Mt. Emei. The results showed that the phenomenon of Al activation at Mt. Emei is evident, especially in the decline districts of Fir Forest, the Ca/Al ration in soil is much less than 1. Thus, Al poisoning is one of the important factors which resulted in the decline of Fir Forest at Mt. Emei.

Key words: acid precipitation, Al, soil, fir forest, Mt. Emei.

Kinetics of Reaction of OH Radical with C₂H₂Br and the Residual Lifetime in the Atmosphere. Zhong Jinxian and Zhang Deqiang et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **18**(4), 1997, pp. 29—31

Brominated alkanes are a destructive substances for the ozone layer. The kinetics of reaction of OH radical with C₂H₂Br were studied. The reaction velocity rate constants were measured by the discharge flow-resonance fluorescence technique over the temperature range of 297—369K and the Arrhenius equation was derived. The atmospheric lifetime of C₂H₂Br has been estimated to be 0.168 year due to the Arrhenius equation at condition that the average temperature of atmospheric convection layer is 277K.

Key words: hydroxyl radical, C₂H₂Br, discharge flow resonance fluorescence, atmospheric lifetime.

A Primary Study on the Acid-volatile-sulfide (AVS) in Le An River Sediment and the Effect of Oxygen on the Release of Heavy Metals

in the Sediment. Xianghua Wen (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085), Herbert E. Allen (Civil Engineering Department, University of Delaware, Newark, DE 19716, USA): *Chin. J. Environ. Sci.*, **18**(4), 1997, pp. 32—34

This research did aeration experiments and the measurement of acid-volatile Sulfide (AVS) and simultaneously extracted metals (SEM) for a set of sediment samples in Le An River to determine the metal release potential. It was found that AVS in Le An River sediment is low and there would be the risk of second pollution in the way of mobilization of sediment bound metals to the overlying water. It is most likely that the iron and manganese oxide are important metal binding components in Le An River sediment.

Key words: sediment, metal release, acid-volatile-sulfide, aeration.

Chemical Oxidation of J-Acid and Tobias Acid Dye Intermediate Waste Liquor. Jiang Zhan-peng, Zhu Wanpeng, Yang Zhihua et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **18**(4), 1997, pp. 35—37

After recovering the useful substances from the waste liquor of two kinds of naphthalene series sulfonic acid dye intermediates, J-acid and Tobias acid, it is necessary to have a final treatment of the effluent, remained liquor, according to the National Standard of Industry Wastewater Discharge. The salt recovery-coagulation and sedimentation-chemical oxidation process was carried out for treating the remained liquor (COD_{Cr} 1000mg/L, salt concentration 150—300g/L) in the paper. Fenton reagent (combination of H₂O₂ and Fe²⁺) was used for the chemical oxidation and the optimum parameters of the process had been obtained. The dosages of hydrogen peroxide (containing 30% of H₂O₂) and FeSO₄ · 7H₂O are 4L and 1.35kg per m³ of the remained liquor,

respectively. The COD_{Cr} removal efficiency is more than 80% and COD_{Cr} of the final effluent is decreased to less than 200mg/L which meet the requirement of the National Standard.

Key words: dye intermediate; J-acid waste liquor, Tobias acid waste liquor, chemical oxidation; Fenton reagent.

Projection Pursuit Regressive Model on Concentration Forecast of Pollutant. Li Zuoyong (Dept. of Atmospheric Electronics Eng., Chengdu Institute of Meteorology, Chengdu 610041): *Chin. J. Environ. Sci.*, **18**(4), 1997, pp. 38—40

A projection pursuit regressive model on concentration forecast of pollutant was investigated by analysing environmental monitoring data. Use is being made of the new idea of examination of data-simulation-forecast of projection pursuit regressive techniques. Concentration forecast of water pollutants BOD and DO were carried out, respectively, using this model. The results of the forecasts showed that the qualified rates of fitting and forecasting of the model acquire 100% and 83.3%, respectively.

Key words: environmental pollution, pollutant, forecast, projection pursuit regressive model.

Kinetic Study on the Biodegradation of Organic Pollutants in Coastal Seawater of Dalian.

Tong Zhiyou, Zhou Jiti, Chen Yuchen (Dept. of Environ. Eng., Dalian University of Technology, 116012): *Chin. J. Environ. Sci.*, **18**(4), 1997, pp. 41—44

In this paper, studies were carried out to determine the biological degradation kinetic characteristics of four kinds of organic pollutants in coastal seawater of Dalian. By adding benzene, nitro-benzene, phenol and aniline to natural sea water, respectively, the biochemical oxygen demand (BOD) of the organic compound was tested under different concentration groups of 0.1mg/L, 0.3mg/L, 0.5mg/L, 1mg/L etc. Through data analysis, the kinetic

parameters K and L_0 of the compound were obtained (K represents first-order biodegradation rate constant, L_0 represents ultimate BOD). The mathematic model $y = L_0(1 - 10^{-Kt})$ of the BOD, which was expressed by first-order reaction kinetics, well demonstrated the variation of BOD with time. The results calculated according to the model were similar to the experiment values. Some influence factors on the biodegradation rate of the compound were also analyzed and discussed in this paper. The conclusion was that biodegradation was mainly affected by molecular structure.

Key words biodegradation, benzene, nitro-benzene, aniline, phenol, coastal seawater, biochemical oxygen demand.

Study on Additional Experiment of Chemisorption Catalytic Oxidation for SO₂ from the Smelting Waste Gas. Ning Ping, Sun Peishi, Song Wenbiao (Dept. of Environ. Eng., Kunming University of Science and Technology, Kunming 650093): *Chin. J. Environ. Sci.*, **18**(4), 1997, pp. 45—48

Additional experiments of catalytic oxidation of SO₂ in aqueous solution have been carried out at a smelting plant in a foam tower containing one serve-plate, 16% (wt) H₂SO₄ has been obtained while the absorption efficiency of SO₂ is above 50%. Producing rate of H₂SO₄ is about 1.8% (wt) / h. The best ratio of solution and gases is 5L/Nm³. Addition of Al₂(SO₄)₃ and O₂ in the solution improves the absorption process. The change of SO₂ concentration has small effect on the absorption efficiency.

Key words: sulful dioxide, catalytic oxidation, foam tower, smelting waste gas.

Global Reaction Rate of NO Formation from Fuel Nitrogen. Fan Yaoguo, Xu Minghou et al. (National Laboratory of Coal Combustion, HUST, Wuhan 430074): *Chin. J. Environ. Sci.*, **18**(4), 1997, pp. 49—52

Based on the detailed mechanism of nitrogen chemistry, the reaction characteristics of fuel