高浓度 J 酸废液资源化技术研究*

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摘要 探讨了 N_{235}-煤油-H_2SO_4-NaOH 化学萃取-反萃取体系提取浓缩 J 酸废母液中染料中间体的工艺特性. 试验结果表明, 通过萃取工艺, J 酸废液中的 COD_{Cr} 去除率可达 95%, 萃余液 COD_{Cr} 在 500- 2000 mg/L 之间, 色度去除率可达 95%; 该工艺可使废母液中的回收物浓缩 5- 10 倍. 萃取剂可以循环使用而不改变性质, 损失较少.

关键词 染料中间体, J 酸废母液, 萃取, 资源化.

J 酸是萘系染料中间体典型产品之一, 生产过程中投加的 90% 的无机盐和 10% 以上的有机原料转移到工艺废水当中[1], 使得废母液中有机物浓度含量高、酸度大、色度深、含盐量高、对生物有毒性, 属于极难治理的有机工业废水之一[2,3]. 废液中的有机质为带磺酸基(-SO_3^-)、胺基(-NH_2)与羟基(-OH)的萘系染料中间体, 利用这些特定基团与废液的酸性, 通过离子缔合-离子交换过程, 将废液中的染料中间体一步提取浓缩后回用到染料中间体生产工艺中, 实现废母液中有用物质的资源化, 并且大大降低出水有机物的浓度. 本试验以三烷基胺为萃取剂、煤油作稀释剂、氢氧化钠溶液作反萃剂, 系统地研究了该萃取-反萃取体系对 J 酸废母液的萃取和反萃取过程特性; 并根据对回收物的成分分析, 进行了回收物回用于生产中间工段的试验, 显著地提高了有用资源的利用率而不影响产品质量.

1 材料和方法

1.1 材料

J 酸废母液: 采用天津某化工厂酸析工段外排的废母液, 其物理化学性质如表 1.

表 1 J 酸废母液的主要物理化学性质

颜色	pH	COD_{Cr} /mg·L^{-1}	含盐量 /g·L^{-1}	氨基 J 酸含量/%	J 酸含量 /%	γ酸含量 /%	双 J 酸含量/%
深棕色	0.1- 1.5	20000- 60000	50- 150	50 以上	17	0.22	未测到

萃取剂采用三烷基胺(N_{235}), 稀释剂采用磺化煤油, 反萃取剂采用氢氧化钠水溶液, 酸采用浓硫酸.

1.2 仪器

HP1090 高压液相色谱分析仪; TA-LA 型污水 COD 速测仪; 721 分光光度计; pHS-3B 型数字式酸度计.

1.3 试验设备

静态萃取-反萃取试验采用如图 1 所示的装置.

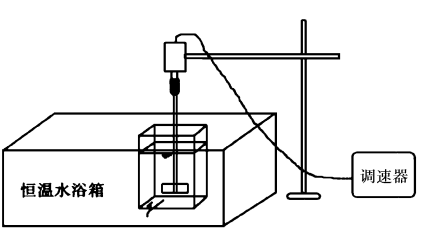

图 1 试验装置

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2 结果与讨论

2.1 萃取与反萃的最佳工艺参数

控制萃取-反萃取过程的 2 个基本指标是萃取和反萃取过程的萃取效率与反萃取回收液的浓缩倍数. 萃取效率高低决定了废液中染料中间体的回收率, 实验表明它的主要影响因素有萃取体系两相体积比 O/A (萃取剂体积 O 与废水体积 A 之比)、废液 pH 值、萃取反应温度、反应时间、分离时间; 浓缩倍数决定着浓缩液返回工艺的可行性, 实验表明它的主要影响因素为反萃取剂(NaOH) 浓度与反萃取相比 O/B (萃合物体积 O 与反萃剂体积 B 之比).

(1) 萃取反应相比 O/A 试验结果如图 2 所示. 在图 2 中横坐标用相比 O/A 的倒数 A/O 表示. 图 2 可见, 相比对萃取效率有较显著的影响, 有机物的萃取效率随相比 O/A 值的降低而下降. 在 $A/O<3$ 之前, 其效率均高于 95%; 当 $A/O>3$ 之后, 其效率迅速下降. 综合分析上述结果, 最佳相比 O/A 确定为 1/2.5- 1/3.5.

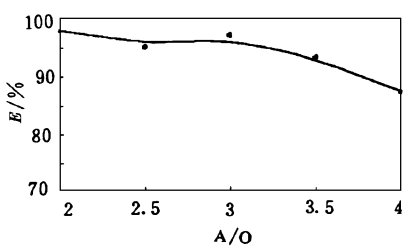

图 2 相比对萃取效率的影响

(2) 废液 pH 值 试验前, 向废母液中预先投加不等量的 H_2SO_4 和 NaOH 调节废水 pH, 通过试验得出不同 pH 下的萃取效率, 从而求得萃取反应的最佳 pH 范围. 反应结果见图 3.

在试验的 pH 范围内, J 酸废液的萃取效率有一个缓慢升高, 然后迅速下降的过程. 这是由于 N_{235} 必须先与酸发生如下离子缔合反应后才有萃取活性:

$$2R_3N_{(O)} + H_2SO_4 \rightleftharpoons (R_3NH^+)_2 \cdot SO_{4(O)}^{2-}$$

然后该缔合物与染料中间体分子发生如下阴离子交换反应:

$$(R_3NH^+)_2 \cdot SO_{4(O)}^{2-} + 2R' - SO_3^- \rightleftharpoons 2R_3NH^+ \cdot SO_{3-R(O)}^- + SO_4^{2-}$$

因此如果 pH 过高、含酸量过低, $R_3N_{(O)}$ 仅有一部分生成胺盐, 还有部分空载的有机相存在. 当 pH 过低、含酸量过多, 有一部分胺盐还会发生如下的胺盐加合反应:

$$(R_3NH^+)_2 \cdot SO_{4(O)}^{2-} + H_2SO_4 \rightleftharpoons 2R_3NH^+ \cdot HSO_{4(O)}^-$$

同样使 N_{235} 丧失萃取活性, 降低了 N_{235} 的利用效率. 因此, 在萃取前用酸碱将废母液的 pH 值调节至 1.0- 1.5 作为萃取过程的基本条件之一.

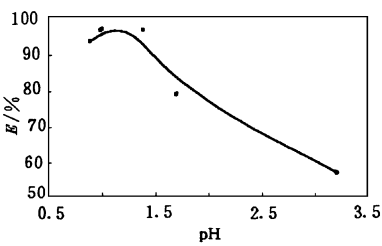

图 3 pH 对萃取效率的影响

(3) 萃取反应时间、分离时间 萃取反应在 3min 内基本达到平衡, 两相分离时间也很短, 静置 10min 后即达到完全分层.

(4) 萃取反应温度 由图 4 可见, 在 12- 56℃这一很宽的温度范围内, 都可以达到较高的萃取效率. 萃取效率随温度先稍有升高, 然后稍有下降. 这是由于升温能降低有机相粘度, 改善萃取剂分散特性, 加快反应速率; 同时过高的温度也会增加萃取剂在水中的溶解度, 导致萃余液 COD_{Cr} 的升高.

此外, 适宜的反应温度还能防止反应过程中盐的结晶. 综上分析, 最佳反应温度应在 20- 50℃为宜.

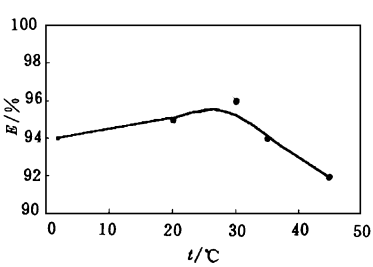

图 4 萃取反应温度

(5) 反萃剂(NaOH) 浓度 反萃剂的浓度主要影响反萃取是否完全以及染料中间体的浓

缩程度. 对同一萃取条件下制得的萃合物, 通过改变反萃剂的浓度(NaOH 溶液的浓度) , 得出完全反萃时, 提取浓缩物总浓缩倍数与反萃剂浓度的关系(图 5) .

图 5 表明, 反萃剂浓度在 16% – 40% 之间的前段, 浓缩倍数随反萃剂的浓度增大而增加的幅度较快, 之后增长趋于平缓. 但当反萃取剂的浓度大于 32% 后, 提取浓缩液有固体盐分析出, 导致两相分离困难, 极易发生乳化现象. 因此, 确定 NaOH 最佳浓度范围为 24% – 32% .

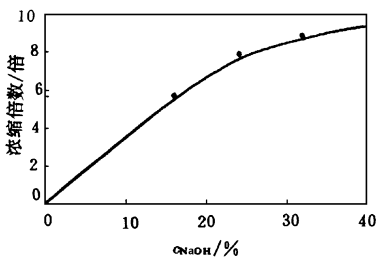

图 5 反萃剂浓度与浓缩倍数的关系

(6) 反萃相比(*O*/*B*) 反萃取相比寻优试验是要找到不同反萃剂浓度下完全反萃时的最大反萃相比 *O*/*B*(最小反萃取需要量) . 表 2 列出了实验得出的不同反萃剂浓度下完全反萃时的最大反萃相比 *O*/*B*. 从表 2 可以得出在最佳 NaOH 浓度范围下(24% – 32%) 的最佳反萃相比约为 2– 3.

表 **2** 最大反萃相比与反萃剂浓度的关系

反萃剂浓度/ g · L^{-1}	160	200	240	320	400
最大相比 O/ B	1. 50	1. 89	2. 10	2. 83	3. 77(易乳化)

2. 2 提取浓缩液回用试验

为了进一步验证提取浓缩液直接回用于染料生产中间工段的可行性, 将浓缩液按不同比率加入特定生产工段, 经过几个中间体生产工段后, 对滤液及产物进行分析, 实验结果如表 3. 表 3 表明, 滤液的氨基值未发生显著变化, 表明浓缩液中的有用染料中间体已转移到过滤物中; 从对产物的分析看出, 回用实验并未因投加浓缩液量的增大而使产物百分含量减少, 表明浓缩液中的中间体得到有效的利用.

表 **3** J 酸提取物回用到生产中间工段可行性试验[1)]

生产料液与萃取浓缩液体积比	滤液氨基值/ g · L^{-1}	滤液 Na_2SO_4 含量/ g · L^{-1}	中间工段产物/ %
1∶0	11. 04	69. 19	82
15∶1	12. 42	104. 2	65
7∶1	11. 04	93. 89	78
4. 6∶1	11. 04	106. 28	98
3. 2∶1	9. 66	95. 17	98

1) 浓缩液的氨基值为 56 g/ L

3 结论

(1) 以 N_{235}–煤油–H_2SO_4 组成的萃取体系可以高效率地提取 J 酸废母液中的染料中间体. 主要参数为: 稀释比为 20% – 50% , 萃取相比为 1/ 2. 5– 1/ 3. 5, 反应 pH= 1. 0– 1. 5, 反应时间 3– 10min, 分离时间 10– 30min, 反应温度 20– 50℃.

(2) 采用 NaOH 浓溶液作反萃取剂, 反萃取分相速度快、萃取剂回收率高、浓缩液有机物含量大. 从优化试验中得到反萃取过程的主要参数为: 反萃剂浓度为 24% – 32% , 反萃取相比约为 2– 3, 反应时间 5– 10min, 分离时间 10 – 30min, 反应温度 20– 50℃, 浓缩倍数 5– 10 倍.

(3) 在优化条件下, J 酸废液中的染料中间体萃取率常高达 90% – 95% , 提取浓缩液浓缩倍数达到 5– 10 倍, 残液中 COD_{Cr} 浓度降低到 500– 2000 mg/ L.

(4) 通过回用试验表明, J 酸废母液的反萃取浓缩液可以直接返回到生产工艺中的中间工段, 以回收其中大部分染料中间体, 产生显著的环境与经济效益.

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The Effect of 2-Nitrofluorene Exposure on Gill Structure of the Grass Carp. Yu Gang and Xu Xiaobai (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 1-3

Nitrated polycyclic aromatic hydrocarbons are a class of important pollutants with direct-acting mutagenicities and carcinogenicities. 2-nitrofluorene is a representative compound of nitro-PAHs. This paper reported the effect of 2-nitrofluorene exposure on gill structure of the grass carp. After 2, 4, 10 days of exposure, gill of fish was examined under electron microscope. The most severe gill lisions included the hypertrophy and increased number of chloride cells. This type of structure damage shows a close similarity to those caused by other pollutants, such as lindan.

Key words: 2-nitrofluorene, grass carp, gill, toxical effect.

The Blown Sand Disaster Along Tarim Desert Oil-Transportation Highway. Dong Zhibao, Chen Guangting et al. (Institute of Desert Research, Chinese Academy of Sciences, Lanzhou 730000): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 4-9

By means of field observation and laboratory experiment, the generation of the blown sand disaster along Tarim desert oil-transportation highway was analysed, the extent assessment model was established. Finally the conclusions reached are: (1) In the temporal distribution, the disaster is mainly concentrated on spring and summer (April-September), the most severe is in April. (2) In the spatial distribution, the disaster is more intensive into the desert. (3) Extent zones are outlined accorting to the theoretically estimated values of blown sand disaster extent, which fit well in the blown sand disaster phenomena observed and recorded.

Key words: blown sand disaster, tempo-spatial distrubution, Tarim desert oil-transportation highway.

Study on Degradation of Phenolic Compounds by *Candida maltosa*. Yin Ping, Yang Yanxi and Yang Huifang (Institute of Microbiology, Chinese Academy of Sciences, Beijing 100080): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 10-13

Degradation of 15 kinds of phenolic compounds by *Candida maltosa* 10-4 was studied. This yeast can utilize dihydric phenol and trihydric phenol as sole carbon source for growth. Three kinds of dihydric phenol (300 mg/L) can be degraded 97%-99% in 48 hours. Nitrophenol, aminophenol and cresol can not be used as sole carbon source, but nitrophenol and aminophenol can be used as nitrogen source for growth. With glucose as carbon source and $(NH_3)_2SO_4$ as nitrogen source, the growth and degradation activity can be promoted obviously. Removal of mononitrophenol (300 mg/L) can reach 93%-100%, 2-or 4-cresol 86% and monoaminophenol 68%-84%. With substituting groups increase, degradation of phenolic compounds become slower. Cells adapted by 1200 mg/L of phenol can oxidate high concentration (2800 mg/L) of phenol and 15 kinds of phenolic compounds (300 mg/L) to different degree.

Key words: phenolic compound, *Candida maltosa*, degradation.

Nitrogen Content Dynamic Variation Analysis in the Second Songhua River. Liu Jingshuang, Yu Junbao et al. (Changchun Institute of Geography, Chinese Academy of Sciences, Changchun 130021): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 14-16

Space-time variation law of nitrogen content in different river sections, water periods and years in the second Songhua River were described in detail. The results showed that there are direct relation between nitrogen content variation in water and nitrogen in waste water to come from cities and runoff water of both banks of the river. Nitrate and nitrite contents in water in flood period are higher than that of mid and low water periods. In flood period, nitrate content in water increases gradually with extension of river section, ammonia content in polluted river section is higher than that of unpolluted river section. Nitrate and nitrite contents in water in three water periods from 1985 to 1989 are slightly higher than that from 1980 to 1984 and from 1990 to 1994, ammonia content in water increased annually.

Key words: nitrogen content, space-time variation law, the Second Songhua River.

A Research on Technology for Recovery Resource from High Concentration J-Acid Waste Liquors. Li Zhonghe, Zhu Wanpeng et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 17-19

J-acid waste liquors is a high concentration organic waste water. In this research N_{235} was used as extratant to extract useful substance from the J-acid waste liquors. The tests indicated that more than 95% of COD_{Cr} in J-acid waste liquor can be removed and COD_{Cr} in the remained liquors can be dropped to 500-2000 mg/L. 95% of colourity can be removed from the waste liqours. By back-extraction tests, extracted organic from waste liquors can be concentrated 5 to 10 times. In the process the extractant could be recycled for that its properties don't vary and it's lost is little. By recovery tests, the concentrated solution could be back to the appropriate section of the producing process directly to recovery useful substance, which will have no detrimental effects on the comprehensive in-

dexes controlled in producing.

Key words: dye intermediates, J-acid, wasteliquor, extraction, resource recovery.

Study On Full-scale Test of Biological Contact Oxidation Pretreatment in Drinking Water Treatment from Huaihe River Source Water (Bengbu Reach). Liu Wenjiun, He Beiping et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084), Lu jianhong et al. (Bengbu Water Company, Bengbu, 233000): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 20- 22

In this study, the test of full-scale biological contact oxidation pretreatment in drinking water treatment was discussed, which is first in domestic. The results demonstrated that biological pretreat process can remove organic compounds and ammonia of source water by 13. 6%- 20. 5% and 70%- 90% respectively when the ratio of water to air is 1 ∶ 1; the key factor to affect the biological pretreat process performance is dissolved oxygen and temperature.

Key words: drinking water, biological pretreatment, pilot scale test, Huaihe River.

Degradation of Black Liquor Lignin Produced from Kraft Pulping Process of Pine by White-Rot Fungi. Lin Lu, Yang Gao et al. (State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510641): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 23- 25

Black liquor lignin is the main pollutant in the black liquor produced from kraft pulping process of paper-making raw materials. In this paper, effect of white-rot fungi on degradation of black liquor lignin produced from pine kraft cook was studied. Results showed that white-rot fungus could degrade more than 74. 5% of black liquor lignin in the medium after 10 days of culture, the main part of black liquor lignin degraded was in the range of 1500- 3000kD of molecular weight. Culture factors such as cabon and nitrogen source, pH value in the medium and temperature exerted during the culture had an important role respectively on the effect of degrading black liquor lignin by white-rot fungus.

Key words: white-rot fungus, black liquor from kraft pulping process, sulfonate lignin, biodegradation.

Pilot Scale Petrochemical Wastewater Treatment Using Inner Loop Fluidized Bed Bioreactor. Zou Ping, Wang Chengwen and Qie Yi (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 26- 29

A Pilot scale experiment on petrochemical wastewater treatment using inner loop fluidised bed bioreactor and floatation process was conducted. The effluent COD from the process is about 200 and 100 mg/L when influent COD is 800 and 500mg/L, respectively. The loading rate of the bioreactor can be achieved above 15kgCOD/(m^3.d).

Key words: inner loop fluidised bed bioreactor, petrochemical wastewater, floatation process.

Investigation of the Landfill Gas Composition and Its Yield in South China. L. Y. Chan and S. C. Lee (Dept. of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hong Kong), Y. Qin (Institute of Environmental Science, Zhongshan University, Guangzhou, 510275): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 30- 34

Five landfill gas monitoring wells were installed and the composition of landfill gases were monitored in Wufengshan landfill in Foshan, south China. For the wells located in the late landfilled region, CH_4 and CO_2concentrations of landfill gases are high and stable. For the wells located in the early landfilled region, CH_4 and CO_2 concentrations of landfill gases are low and variable. In the last field measurement, the gases in the well located in early landfilled region has lost the characters or landfill gas. It's implication is that the biological decomposition process of the refuse underground has completed or the anaerobic environment has been destroyed. It just lasted for about 4 years and is much shorter than the expected time of 10- 20 years. The differences of landfill gas between Foshan Wufengshan landfill and Hong Kong Shuen Wan landfill were compared and discussed. The yield of landfill gas in Wufengshan landfill was estimated according to the original carbon component of the refuse.

Key words: landfill, waste gas, biological decomposition, monitoring well, CH_4, CO_2, gas yield, Foshan.

Photolysis of α-Naphthaleneacetic Acid in Aqueous Solution. Zufei Zhou, Weichuan Jiang and Weiping Liu (Dept. of Chemistry, Zhejiang University, Hangzhou 310027): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 35- 37

Photolysis of α-naphthaleneacetic acid(NAA) has been investigated at 25℃ in aqueous solutions by irradiation at different wavelengths. The shorter wavelength of 254nm is considerably more effective in promoting degradation than wavelength of 365nm. The primary degradation of NAA follows a pseudo-first-order kinetics. The photolysis half-life and rate constant were determined to be 60min and $1.15\times10^{-2}min^{-1}$ respectively. The optimum photolysis rate has been observed using TiO_2 powder as photocatalyst. Several reaction intermediates were identified using GC/MS technique. The photolysis of NAA involves decarboxylation and oxidation on aromatic ring. On the basis of the analytical data, a mechanism of the process has been proposed.

Key words: photolysis, α-naphthaleneacetic acid, ultraviolet light.

Mn^{2+}-Oxidizing Bacteria and the Mn^{2+}-Removing Activity of the Filter Sand Used in Water Plants. Bao Zhirong et al (Dept. Molecular Biology, Jilin Univ,