

彩色显象管发光粉生产废水处理工艺研究

祝万鹏 杨志华

(清华大学环境工程系, 北京 100084)

摘要 为了消除彩色显象管发光粉生产废水中重金属对环境的污染和实现资源回用, 用 P_{204} (皂化)-煤油-硫酸体系分离回收废水中的锌. 研究表明, 以皂化 P_{204} 为萃取剂, 经三级逆流萃取, Zn^{2+} 的萃取率可达 99%, 共存的 Ni^{2+} 几乎不被萃取, Cu^{2+} 的萃取率小于 7%; 用硫酸溶液对负锌萃取剂进行二级逆流反萃取, 反萃取率达 96% 以上, 反萃浓缩液可返回生产过程使用; 萃余液用石灰中和沉淀处理后, 金属离子的浓度可以达到国家的综合排放标准.

关键词 溶剂萃取, 锌, 发光粉, P_{204} .

本研究以某显象管厂发光粉生产废水为对象, 采用溶剂萃取法提取废水中的锌盐, 回用于生产工艺, 并结合化学沉淀法进行达标处理.

1 实验方法

1.1 工艺方案的选择

通过多种途径探索实验, 确定了如图 1 所示方案. 方案分为 3 个部分: ① 料液的调配; ② 溶剂萃取法分离回收有价金属锌, 并返回工艺使用; ③ 达标处理.

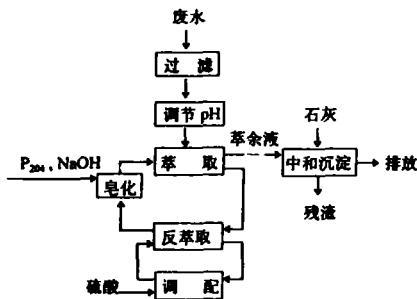


图 1 金属回收和废水达标处理方案示意图

通过筛选, 选用 P_{204} 作为金属的萃取剂, 260[#] 煤油为稀释剂; 以硫酸溶液为反萃取剂.

1.2 实验方法

在分液漏斗中按一定的相比(即有机相对水相的体积比, 以 O/A 表示)分别加入一定体积的经调配的废水和有机相(P_{204} 的煤油溶液), 在摇床上充分振荡, 使之达到萃取平衡, 然后静

止分层, 放出水相, 用原子吸收分光光度计分析金属离子浓度. 以同样的方法, 进行反萃取试验. 用 McCabe-Thiele 图解法求取理论级数, 用串级实验^[1]验证, 为工程设计提供工艺参数.

1.3 主要仪器及设备

康氏电动振荡器, pHs-3B 数字式酸度计, 180-80 偏振塞曼原子吸收分光光度计.

实验用废水主要成分为: Zn^{2+} 500—1000 mg/L, Cu^{2+} 10—20 mg/L, Ni^{2+} 10—20 mg/L, H_2S 5—10 mg/L, pH 1.0—2.0.

2 实验结果与分析

2.1 萃取体系工艺条件研究

实验研究表明, 萃取反应 5 min 即可达到平衡, 实际过程一般在室温条件下进行. 因此, 以下试验均取反应时间 10 min, 环境温度为室温. 实验按正交表 $L_9(3^4)$ 安排试验. 根据单因素条件试验结果, 选择因素水平如表 1 所示, 实验结果见表 2.

表 1 正交试验因素水平表

水平	pH 值	相比 (O/A)	P_{204} 皂化率 /%	有机相浓度 /%
1	1.60	1 : 1.5	10	10
2	1.70	1 : 2	20	15
3	1.80	1 : 2.5	30	20

表 2 正交试验结果

项目	相比 (O/A)	P ₂₀₄ 皂化率 /%	有机 相浓度 /%	pH	锌萃取 效率 /%
1	1:1.5	10	10	1.60	75.9
2	1:1.5	20	15	1.70	98.3
3	1:1.5	30	20	1.80	92.7
4	1:2	10	20	1.70	89.5
5	1:2	20	10	1.80	87.3
6	1:2	30	15	1.60	96.0
7	1:2.5	10	15	1.80	78.7
8	1:2.5	20	20	1.60	91.6
9	1:2.5	30	10	1.70	81.7
I / %	266.9	244.1	244.9	263.5	
II / %	272.8	277.2	273.0	269.5	
III / %	252.0	270.4	273.8	258.7	
I' / %	89.0	81.4	81.6	87.8	
II' / %	90.9	92.4	91.0	89.8	
III' / %	84.0	90.1	91.3	86.2	
极差	6.9	11.0	9.7	3.6	

实验结果经极差分析和综合处理表明:

(1) 在选定的 pH 和相比范围内, 水相 pH 值和相比对萃取效率影响不显著, 萃取剂皂化率和浓度影响较显著。

(2) P₂₀₄-磺化煤油-H₂SO₄ 体系萃取锌的最优工艺条件为: 料液 pH=1.7, 相比(O/A)=1:1.5, 萃取剂组成为 15%P₂₀₄+85%煤油, 皂化率为 20%, 反应时间取 10 min, 温度不小于 20℃。此时, 锌的萃取率可达 98.3%, 但铜的萃取率也偏高(26.8%)。调整相比(O/A)为 1:2 后进行实验, 锌的萃取率仍可达 95%, 镍完全不被萃取, 铜的萃取率小于 7%。此时, 锌、镍的分离系数 $\beta_{Zn^{2+}/Ni^{2+}} > 8 \times 10^3$, 得到很好的分离。锌、铜分离系数 $\beta_{Zn^{2+}/Cu^{2+}} < 20$, 说明分离不好, 但由于原水铜浓度远低于锌, 不会影响反萃取液返回工艺使用。

(3) 在 6 个月的实验中, 萃取剂反复循环使用, 萃取效率不变。

2.2 萃取段理论级数的估算

工程实践中, 金属离子的提取常采用多级逆流萃取过程, 其理论级数可用 McCabe-Thiele 图解法求得。在上述最优工艺条件下(反应时间取 40 min), 萃取平衡等温线实验结果如图 2 中

曲线 1 所示。

萃取过程操作线方程为^[2]:

$$Y_1 = Y_0 + (L/V)(X_f - X_N)$$

式中, Y_1 、 Y_0 分别为负载和空载有机相中被萃组分的浓度(g/L); X_f 、 X_N 分别为原料液和萃余液中被萃组分浓度(g/L); L/V 为水相对有机相的流比, 相当于静态操作的相比(A/O)。

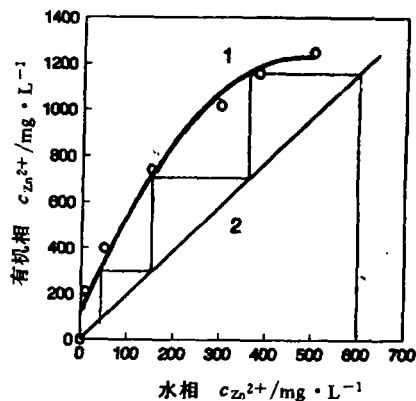


图 2 理论级数的图解法

本实验中, $Y_0 = 0$, $L/V = 2$, 经多级萃取后, 要求 $X_N \leq 20$ mg/L, 可求得操作线(图 2 中直线 2)。从操作线上点 $X_f(600, 1160)$ 为起点, 画阶梯, 求得萃取理论级数为 3 级。

2.3 锌三级逆流萃取单级模拟实验验证

实验采用 4 支分液漏斗, 模拟 3 级逆流萃取分离 Zn^{2+} 过程。实验条件为: 料液 $[Zn^{2+}] = 660$ mg/L, $[Cu^{2+}] = 20$ mg/L, $[Ni^{2+}] = 20$ mg/L。结果表明, 经 3 级逆流萃取, 锌的萃取率可达 99% 以上, Cu^{2+} 和 Ni^{2+} 基本不被萃取。

2.4 负锌有机相反萃取工艺条件研究

根据 P₂₀₄ 与锌的螯合物在酸性条件下不稳定的特性, 采用硫酸溶液作为反萃取剂。

(1) 反萃取工艺条件 有机相中 Zn^{2+} 浓度为 2.05 g/L, 反应时间取 15 min, 在室温条件下反萃取效率随硫酸浓度和相比(有机相与硫酸溶液的体积比)的变化情况如图 3 所示。

从图 3 可以看出, 当相比在 5:1 时, 硫酸浓度为 1.0 mol/L, 反萃取效率最高, 接近 99%, 此时, 反萃液中 Zn^{2+} 浓度达到 9.38 g/L; 而当相比在 10:1 时, 硫酸浓度为 1.5 mol/L, 反萃取效率最高, 达 96.2%, 此时, 反萃液中

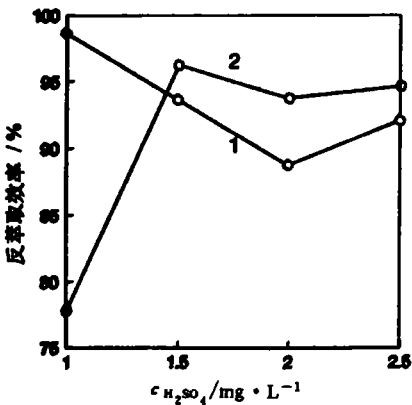


图3 负锌有机相反萃取条件与反萃效率的关系
1. O/A=5:1 2. O/A=10:1

Zn^{2+} 浓度达到 18.28 g/L. 考虑到提取的锌溶液返回工艺过程时, 浓度高较好, 反萃取的较优工艺条件取为: 反萃液硫酸浓度 1.5 mol/L, 相比 O/A=10:1, 反萃时间取 10 min. 在实际中为保证反萃效率, 反萃级数取 2 级.

(2) 反萃液中含锌离子对 Zn^{2+} 反萃过程的影响 实验在上述最佳条件下, 用含不同浓度 Zn^{2+} 的硫酸进行反萃取. 结果如表 3 所示.

表3 硫酸中含锌浓度对反萃取的影响

反萃液 含锌量 /g·L ⁻¹	第一级反萃		第二级反萃	
	锌浓度 /g·L ⁻¹	反萃率 /%	锌浓度 /g·L ⁻¹	反萃率 /%
11.0	31.63	95.7	13.75	100.0
24.1	44.75	96.0	27.13	100.0
30.0	55.50	100.0		

从表 3 可以看出, 当硫酸溶液中的 Zn^{2+} 浓度高达 30 g/L 时, 反萃效率没有显著变化. 此时, 经反萃后的硫酸溶液中 Zn^{2+} 浓度已达 55.50 g/L, 符合工厂回用的要求(40 g/L 以上).

2.5 废水的最终处理

经萃取回收金属锌后, 废水 pH 4—5, 锌浓度约为 10 mg/L, 铜和镍的浓度基本与原水相同, 未达到国家排放标准, 需进一步处理.

实验选用石灰对废水进行中和沉淀处理, 结果列于表 4 中.

从结果可以看出, 废水中金属离子都已达

表4 石灰处理结果

项 目	处理前	处理后
pH	4.26	9.5
Zn/mg·L ⁻¹	19.2	4.5
Cu/mg·L ⁻¹	19.2	<1.0
Ni/mg·L ⁻¹	20	<1.0

到国家排放标准. 原水 COD 浓度极低, 经萃取后, 萃取剂会溶入水中, 但量极少(P_{204} 和煤油溶入水中的量分别为 1.8 mg/L 和 60 mg/L)沉淀处理后出水与全厂废水混合, 不影响全厂的废水后续的达标处理.

3 经济分析

以工厂每日废水排放量 400 m³, 其中锌浓度 600 mg/L, 回收率按 95%计, 经济分析表明, 扣除药剂、电能、人工费后, 每年可有 30—40 万元的净收益.

4 结论

(1) 采用皂化 P_{204} -煤油- H_2SO_4 体系的 3 级逆流萃取工艺能有效地分离提取彩色显象管发光粉生产废水中的 Zn^{2+} , 萃取的最佳工艺条件为: 料液 pH 1.8—2.0, 萃取相组成为 15% P_{204} +85%煤油, 皂化率 20%, 相比(O/A)=1:2, 反应时间取 10 min, 温度不小于 20℃. 此时, 锌的萃取率达 99%以上, 镍完全不被萃取, 铜的萃取率小于 7%.

(2) 负锌有机相反萃取的工艺条件: 反萃液硫酸浓度: 1.5 mol/L, 相比 O/A=10:1, 反萃时间取 10 min, 逆流反萃级数为 2 级, 反萃效率可达 96%以上.

(3) 经萃取回收锌后的废水, 通过石灰中和和沉淀处理, Zn^{2+} 、 Cu^{2+} 、 Ni^{2+} 的浓度可达到国家排放标准.

(4) 初步经济分析表明, 其产值抵消日常运行费用, 还具有一定的经济效益.

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Study on the Residual Dynamics of Cyhalothrin in Soybean and Soil. Li Zhixiang et al. (Institute of Agro-environmental Protection, Tianjin, 300191); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 36—38

In order to make up the standards for safe use of cyhalothrin on soybean, a field experiment was conducted to study the residual dynamics of cyhalothrin in soil and leaves of soybean. The residues of cyhalothrin in green soybean, mature soybean and soil were determined by GLC. Results of two years' study showed that cyhalothrin dissipated rapidly from leaves and soil. Its half lives in leaves and soil were 6.6—7.1 and 6.7—11.6 days, respectively. The soybean field was sprayed twice with cyhalothrin at a rate of 15 g a.i./hm². At harvest, the final residues of cyhalothrin in soil was 0.008 mg/kg, the residues of cyhalothrin in green and mature soybean were all below their detectable limits (0.004 mg/kg). Cyhalothrin is a pesticide of easy dissipation ($T_{1/2} < 30$ d). It is safe if applied twice at a recommended rate (7.5 g a.i./hm²).

Key words: cyhalothrin, soybean, residue, GLC, soil.

Application of Solvent Extraction for Treatment of Wastewater from Luminous Powder (ZnS) Manufacturing Process. Zhu Wapeng and Yang Zhihua (Dept. of Environmental Engineering, Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 39—41

A solvent extraction process for zinc recovery from wastewater from luminous powder (ZnS) manufacturing process was studied. The optimum operation parameters of each unit were determined in laboratory. The zinc ion (I) in wastewater was extracted by D₂EHPA (di-(2-ethyl-hexyl)-phosphoric acid) in the state of saponification-kerosene solution and extracted back by sulfuric acid solution. The zinc recovery rate was more than 95%, nickel in wastewater was not extracted and extraction rate of copper in wastewater was less than 7%. The concentrated zinc solution could be reused in luminous powder (ZnS) manufacturing process. Concentration of zinc, copper and nickel in effluent, after treated by using lime, are lower than the National Wastewater Discharge Standards.

Key words: solvent extraction, zinc, D₂EHPA, di-(2-ethyl-hexyl)-phosphoric acid, luminous powder (ZnS).

pH Value Effect on the Reaction Mechanism of Wet FGD with Lime/Limestone. Chen Zhaoqiong et al. (Dept. of Chemical Eng., Xiangtan University, Xiangtan 411105); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 42—44

The reaction mechanism of wet FGD with Lime/Limestone was studied. The results showed that the species of ions and compounds in the solution effected significantly the reaction mechanism of wet FGD. While pH of the system < 7, main species of sulfur negative ions is HSO₃⁻ and desulphudation are forming Ca(HSO₃)₂ mainly. pH of the system > 7, then main species of sulfur negative ions is SO₃²⁻ and desulphudation are forming CaSO₃ · 1/

2H₂O or CaSO₄ · 2H₂O mainly.

Key words: pH value, FGD with lime/limestone, mechanism.

Designing and Implementation of Acidic Deposition Management Information System in Liuzhou. Guo Jinghai and He Kebin. (Dept. of Environ. Eng. Tsinghua University Beijing, 100084); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 45—47

According to analysis on environmental information regulator regime and combined with the feature of acidic deposition in Liuzhou, the structure and function of management information system of acidic deposition were analyzed systematically, system analysis, requirement analysis and software design were made in detail, on which the overall frame of system were established and five subsystem including database operating, chart, picture, database repairment and model were designed.

Key words: acid rain, acidic deposition, management information system.

Environmental Decision Support System. Peng Zhiliang et al. (South China Institute of Environmental Sciences, NEPA, Nanjing 510655); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 48—52

In this paper a new structure map for decision support systems (DSS) was presented and the concept, content and design guidelines of environmental decision support systems (EDSS) were discussed. An example based on the design guidelines above mentioned was given to illustrate the application of EDSS to regional water quality management.

Key words: environmental management, decision support system, environmental decision support system.

Determination of Nitrite and Nitrate in Water by Capillary Electrophoresis. Ren Hongxing et al. (Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, National Analytical Research Center of Electrochemistry and Spectroscopy, Changchun, 130022); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 53—55

Nitrite and nitrate in mineral water and well water have been determined by capillary electrophoresis with internal standard method at 211 nm in pH 8.2 borate buffer. Cetyltrimethylammonium bromide (CTAB) was used as electroosmotic flow modified (EOF) reagent, and the reproductivity RSDs of migration time for nitrite and nitrate anions were less than 1.5%. Dimethyl sulfoxide (0.05%) was applied as the internal standard in this detection, and the RSDs of peak high ratio of anions to dimethyl sulfoxide were around 20% for the concentration at µg/g level. Detection limits for nitrite were 2.5×10^{-11} mol, and 1.8×10^{-11} mol, respectively. The results were good agree with the results of ion chromatography.

Key words: nitrite, nitrate, internal standard method, capillary electrophoresis.

The petroleum Hydrocarbons in Economical Shellfish along the Coast of Huanghai and Bohai Seas. Shang