

高浓度硫化染色废水处理新工艺研究*

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摘要 采用混凝沉淀-铁屑过滤-碱析组合工艺处理高浓度硫化染色废水。生产性试验结果表明:此工艺对硫化物、COD、BOD₅和色度的去除率分别达97.0%、84.7%、85.7%和98.9%,处理后出水的各项污染指标均符合国家排放标准,具有系统运行稳定,操作管理简便,工程投资少,处理费用低等优点。

关键词 混凝沉淀, 铁屑过滤, 碱析, 硫化染色废水。

近年来,国内外陆续报道了利用铁屑过滤法处理染料、印染、电镀等工业废水的试验研究^[1-3]。对于高浓度硫化染色废水,若直接采用铁屑过滤法处理,废水中高浓度的硫化物将在铁屑过滤塔内同铁屑发生化学反应生成正常处理条件下难以溶解的FeS沉淀,不但堵塞滤料孔隙,且降低滤料活性,严重影响处理量及处理效果。为此,本工作采用混凝沉淀-铁屑过滤-碱析组合工艺处理高浓度硫化染色废水,该新工艺经小试、中试,已在新乡市制线厂投入工业化生产运行。

1 废水水质与工艺流程

新乡市制线厂排放的生产废水主要来源为染色工艺中的轧染、水洗、皂煮等工序,染色使用的主要染料为硫化染料(硫化黑、硫化蓝、硫化草绿等),其次有分散染料(分散黑、分散蓝、分散墨绿等)和直接染料(直接耐晒黑、直接耐晒蓝、直接耐酸枣红等),主要助剂有硫化钠、过硼酸钠、纯碱等。据监测,其主要水质指标为:硫化物10—300 mg/L; COD 300—3600 mg/L; BOD₅ 100—1350 mg/L; 色度500—2000倍; pH值5—12。废水排放量约20 m³/h,属无规则排放的高浓度硫化染色废水。

混凝沉淀-铁屑过滤-碱析组合工艺流程如图1所示。

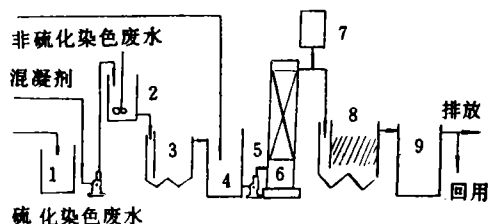


图1 混凝沉淀-铁屑过滤-碱析组合工艺流程

1. 硫化染色废水调节池 2. 反应池 3. 脱硫沉淀池
4. 综合水调节池 5. 耐酸污水泵 6. 铁屑过滤塔
7. 碱液槽 8. 碱析沉淀池 9. 集水池

工艺中的混凝沉淀工序由反应和沉淀2步完成,用以去除高浓度硫化染色废水中的硫化物,同时亦可去除部分有机物。选用FS型混凝剂,其投加量与硫化物含量之比控制在11.50—12.50。该工序的操作程序为:将收集在硫化染色废水调节池内的废水加石灰乳或硫酸调pH值为8.0—8.5,用泵打入反应池中,混凝剂采用泵前加入,起混凝中的混合作用,进入反应池中的加药废水在慢速搅拌下(40 r/min)反应20 min后进入脱硫沉淀池去除沉淀物,出水排入综合水调节池进行下一步处理。

工艺中的铁屑过滤与碱析工序,用以去除

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染色废水的色度和有机物。使用的铁屑经过改性处理，且配有少量的石墨粉等辅助过滤材料。该工序的操作程序为：经脱硫后的废水进入综合水调节池与非含硫染色废水混合，通过耐酸污水泵注入铁屑过滤塔(调 pH 为 5.0—6.0)，过滤塔出水加碱液(调 pH 为 7.5—8.5)，通过静态混合器进入碱析沉淀池沉淀，沉淀池出水经收集池回用或排放。

工艺中脱硫和碱析沉淀池所产生的污泥，不含有毒有害物质，均与厂内的锅炉炉渣混合，做铺路材料或送至垃圾场。

2 结果与讨论

2.1 处理效果

混凝沉淀-铁屑过滤-碱析组合工艺处理新乡市制线厂高浓度硫化染色废水工程于 1994-07-06 投入试运行。试运行期间，定期对各工序的运行情况进行取样测试；运行 2 个月后，新乡市环境保护监测站对其设备进口及出口水质进行了连续 3 d 的验收监测，其结果分别列于表 1—3。取样及分析方法均按国家环境保护局《水和废水监测分析方法》^[4]进行。工程验收、评价执行国家 BG8978-88《污水综合排放标准》和 GB4287-92《纺织染整工业水污染物排放标准》中的二级标准。

表 1 混凝沉淀工序运行情况测试结果

取样日期	污染物	原水浓度 (mg/L)	出水浓度 (mg/L)	去除率 (%)
07-10	S ²⁻	43.2	7.8	81.9
	COD	987.5	532.0	46.1
07-16	S ²⁻	68.8	6.5	90.6
	COD	2352.2	467.6	80.1
07-26	S ²⁻	32.6	2.3	93.3
	COD	1894.8	916.7	51.6
08-06	S ²⁻	17.3	2.5	85.5
	COD	569.6	340.4	40.2
08-16	S ²⁻	93.1	14.8	84.1
	COD	784.9	203.6	74.0
08-26	S ²⁻	136.4	11.4	91.6
	COD	3426.5	753.8	78.0
09-06	S ²⁻	28.7	5.6	80.5
	COD	309.4	108.7	64.8

表 1 表明，混凝沉淀工序对废水中的硫化物具有较好的处理效果，其去除效率达 80%—93%，同时可降低 40%—80% 的 COD，为后续工艺铁屑过滤法的稳定运行创造了有利条件。

表 2 铁屑过滤与碱析工序运行情况测试结果¹⁾

取样日期	污染物	原水浓度 (mg/L)	出水浓度 (mg/L)	去除率 (%)
07-10	COD	485.7	156.4	67.8
	S ²⁻	6.2	0.84	86.5
	色度	636 倍	6 倍	99.0
07-16	COD	453.6	180.1	60.3
	S ²⁻	5.4	0.63	88.4
	色度	1476 倍	11 倍	99.3
07-26	COD	837.2	188.5	77.5
	S ²⁻	2.0	0.29	85.5
	色度	1025 倍	5 倍	99.5
08-06	COD	312.5	61.3	80.4
	S ²⁻	3.8	0.53	86.1
	色度	512 倍	8 倍	98.4
08-16	COD	294.6	64.2	78.2
	S ²⁻	9.4	0.60	93.6
	色度	864 倍	14 倍	98.4
08-26	COD	644.1	128.6	80.0
	S ²⁻	8.5	0.37	95.6
	色度	1850 倍	26 倍	98.6
09-06	COD	158.9	56.4	64.5
	S ²⁻	5.3	0.53	90.0
	色度	820 倍	7 倍	99.1

1) 表中出水硫化物浓度采用对氨基二甲苯胺光度法测定

表 2 表明，铁屑过滤与碱析工序对 COD 的去除率为 60%—80%，对硫化物的去除率为 85%—95%，对色度的去除率高达 99%。过滤塔进水含硫浓度低于 10 mg/L 时，对滤塔的正常运行及 COD、色度等处理效果不会产生大的干扰影响。

分析表 3 数据并与国家排放标准比较可知：

(1) 设备进口(原水)污染物浓度变化幅度大，水质不稳定。水质除 09-08 日的 BOD₅ 不超标外，其余均超标。根据各污染物 3 日平均浓度对纺织染整工业水污染物排放标准的超标倍数(COD4.4 倍、BOD₅5.4 倍、S²⁻19.3 倍、色度 7.0 倍)判断，废水中的主要污染物依次为 S²⁻、色度、BOD₅ 和 COD。

(2) 设备出口(出水)水质除 09-09 日的

COD 和 BOD₅ 由于原水浓度超常的高导致超标外,其余的污染指标及各污染物 3 日平均浓度均符合上述国家排放标准。

(3) 表 3 表明,该工艺对硫化物、色度、COD 和 BOD₅ 均具有很高的去除率、其中 S²⁻ 高达 100%,色度高达 99.2%,COD 高达 90.7%,BOD₅ 高达 87.4%,其平均值分别为 97.0%、98.9%、87.4%和 85.7%。

表 3 新乡市环境保护监测站监测结果

取样日期	污染物	原水浓度 (mg/L)	出水浓度 (mg/L)	去除率 (%)
09-08	COD	324.1	30.19	90.68
	BOD ₅	44.45	29.47	33.70
	S ²⁻	14.0	4.4	68.57
	SS	92	87	5.43
09-09	COD	3046	368.9	87.89
	BOD ₅	1309.22	164.38	87.44
	S ²⁻	84.6	1.6	98.11
	SS	418	90	78.47
09-10	COD	543.8	93.59	82.79
	BOD ₅	189.22	43.28	77.12
	S ²⁻	23.2	未检出	100
	SS	83	75	9.64
3 日平均值	COD	1304.6	164.2	87.41
	BOD ₅	514.3	79.04	84.63
	S ²⁻	40.6	2.0	95.07
	SS	197.7	84	57.51

2.2 处理效益分析

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力有关。 E_{HOMO} 在模式中最后出现,表明有些化合物在藻胞内发生了氧化反应,主要是那些— E_{HOMO} 低的、易给出电子的胺类、酚类化合物。

3 结语

采用量子化学 MNDO 法计算了 18 种硝基芳烃的 5 种描述符 E_{LUMO} 、 E_{HOMO} 、 $\Delta(\Delta H_i)$ 、 μ 及 $Q_{-\text{NO}_2}$ 。应用 5 参数对斜生栅列藻的急性毒性值进行了 QSAR 研究,得到有意义的方程,应用方程计算了所研究系列化合物的毒性。从对量化数据的分析和 QSAR 方程的研究,推测本系列化合物中,二硝基苯、二硝基甲苯的反应

采用本工艺处理 1 t 废水需电费 0.05 元、药剂费 0.30 元,人工费 0.08 元,总处理费用为 0.43 元/t。按设计 500 t/d 计,则年处理费用需 6.45 万元。

经处理后的废水,通过集水池可回用于设备冲洗、锅炉除尘和卫生用水,年回收水量 10 万 t,价值 4 万元,且可免交排污 15 万元/a,消除了高浓度硫化染色废水对环境的污染。

3 结论

混凝沉淀-铁屑过滤-碱析处理高浓度硫化染色废水组合工艺,集混凝、吸附、物化、电化、絮凝等综合作用于一体。其工艺流程合理、运行高效稳定、操作管理简便、工程投资和处理费用低廉。对硫化物、色度、COD 和 BOD₅ 的总平均去除率分别高达 97.0%、98.9%、87.4%和 85.7%;处理后的水质各污染指标可以达到国家《污水综合排放标准》和《纺织染整工业水污染物排放标准》中的二级标准。适用于印染行业高浓度硫化染色废水的处理。

参 考 文 献

- 1 杨凤林等.化工环保,1988,8(6):330
- 2 金燮,杨凤林.工业水处理,1989,9(6):7
- 3 祁梦兰.环境工程,1993,11(3):3
- 4 国家环保局《水和废水监测分析方法》编委会.水和废水监测分析方法.第三版.北京:中国环境科学出版社,1989

活性较高,在体内容易发生还原反应,产生毒性;硝基苯胺、二硝基苯胺及硝基苯酚类化合物在体内易于氧化;硝基苯、硝基甲苯、硝基苯甲醚等反应活性相对较弱。

参 考 文 献

- 1 波普尔,江元生译.分子轨道近似方法理论.北京:科学出版社,1976:117
- 2 斯塔克 J G,华莱士 H G,杨厚昌译.化学数据手册.北京:烃加工出版社,1986:35
- 3 刘次全.量子生物学及其应用.北京:高等教育出版社,1990:16
- 4 Loew G H, Spangler D and Spanggord R J. Computer-Assisted Risk Assessment: Mechanistic Structure Activity Studies of Mutagenic Nitroaromatic Compounds. Elsevier Sci. Pub. B. V., 1985:111
- 5 永田亲义等,徐景达等译.药物结构与活性关系.人民卫生出版社,1978:191
- 6 郎佩珍等.东北师大学报,1994.(增刊):1

tor. Zhou Lu et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 54–56

This paper indicated a new way to speed up granulation in UASB reactor by adding GAC. The results of experiment on UASB reactor with and without GAC treating effluence from petrochemical plant showed that the time of sludge granulation in the reactors with and without GAC were 39 days and 63 days respectively. The sludge pellet in the reactor with GAC had larger diameter than one in the reactor without GAC, and maximum COD removal rate was above 86%. Organic load of reactor with GAC was 2 times larger than the reactor without GAC. The reactor with GAC became more steady in process.

Key words: UASB reactor, granular active carbon, sludge pellet, granulation.

A Study on New Purification of High Concentration Sulphur Dyeing Sewage. Sun Jianhui et al. (Research Institute of Environ. Sci., Henan Normal Univ., Xinxiang 453002); *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 57–59

The combined technology of coagulative precipitation-iron chippings filtering-alkaline separation was used to purify the high concentration sulphur dyeing sewage. The results in the mode of production showed that the removal rates of sulphide, COD, BOD₅ and colority were 97.0%, 87.4%, 85.7% and 98.9% respectively. Every pollution index is up to the National Water Emission Standard. This technology system has the advantage in run stable, operation and management easy, engineering invest low, and treatment cost cheap.

Key words: coagulative precipitation, iron chippings filtering, alkaline separation, sulphur dyeing sewage.

Ecological Restoration of Coal Mining field in Loess Plain. Xue Ling et al. (Inner Mongolia Environmental Research Institute, Huhhot 010010); *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 60–63

This paper reports the results of an ecological restoration project in the Zhunger open-cut coal mining field in Inner Mongolia. The design, technique and effectiveness of the project are described. The results showed that the key points for ecological restoration in the Loess Plain condition include: selection of suitable plant species, proper soil treatments plus necessary construction work, adapt suitable ecological planting patterns based on site conditions. More than sixty plant species and eight ecological planting patterns were evaluated. Over 70% plant coverage and high yields of the crops (compared with the same crops in the nearby area) were obtained. A good ecological and economical return was achieved from the project.

Key words: ecological restoration, demonstrative project, Zhunger, open-cut coal mine in inner mongolia, land reclaim.

Determination of Atmospheric Methyl Bromide by Photoionization Detector. Zhong Jinxian and Liu Ye (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 64–65

Atmospheric CH₃Br was trapped by Tenax adsorbent and was determined by gas chromatography with photoionization detector. The CH₃Br concentrations in indoor and

outdoor are 24×10^{-12} (V/V) and 77.4×10^{-12} (V/V). The standard deviation and detection limit for the method are 0.0521, 10 pg respectively. The level of CH₃Br pollutions is 10^{-11} (V/V).

Key words: methyl bromide, GC, photoionization detector.

Indirect Spectrophotometric Determination of Trace Cyanide by Means of the Colour Reaction of Silver with Cation in Presence of Triton X-100. Gong Churu et al. (Dept. of Chemistry, Hubei Normal University, Huangshi 435002); *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 66–67

Silver gives a colour reaction with Cation in the presence of Triton X-100, and suppression of the colour competitive complex ion of the silver can be used for the indirect spectrophotometric determination of trace cyanide. Cyanide in waste water can be separated by distillation from other ions that also interfere, and then determined. The determination range of this method is 0–10 µg/25 ml. The recoveries of standard cyanide added to waste water samples are in the range of 91.0–100%, and its relative standard deviation is less than 9%.

Key words: cyanide, cation, indirect spectrophotometry.

The Liquid-Solid Extraction of Methomyl in Environmental Water and Gas Chromatographic Analysis. Chen Yanjun et al. (Dept. of Chemistry, Jining Medical College, 272113); *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 68–70

A solid-phase extraction procedure of methomyl from environmental water with active carbon cartridge for gas chromatographic analysis is presented. The detection limit and the minimum detectable concentration of methomyl in water were 0.2 ng and 0.2 µg/L, respectively. The average recoveries of methomyl as added to water were in the range of 95.8–100.7%. The relative standard deviations were lower than 5%.

Key words: methomyl, solid-phase extraction, active carbon, gas chromatography.

Determination of Trace Levels of Nitrophenols in Water by Polyvinylpyrrolidone Modified Carbon Paste Electrode. Wang Kaixiong et al. (Dept. of Environ. Protection, Zhejiang Agricultural University, Hangzhou 310029); *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 71–73

In this paper, a method to determine simultaneously p-nitrophenol and 2,4-dinitrophenol in water by differential pulse voltammetry (DPV) with a carbon paste electrode modified with 10% (W/W) polyvinylpyrrolidone (PVPr) was described. The electrode showed a strong response to the nitrophenols, and the sensitivity and selectivity were much higher than ordinary carbon paste electrode. The nitrophenols were preconcentrated in 0.1 mg/L KCl solution during open circuit period, then the preconcentrated nitrophenols at the electrode were determined in phosphate buffer solution (pH7.0). The oxidation peak potentials were +0.88 V and +1.23 V (VS Ag-AgCl) respectively and two current peaks were completely separated. The detection limits were 0.50 µg/L (p-nitrophenol) and 1.80 µg/L (2,4-dinitrophenol). This method had been applied to the determination of nitrophenols in pol-