粉煤灰基混凝剂的制备及应用研究*

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摘要　在粉煤灰中加入少量黄铁矿烧渣和适量固体NaCl，在90℃温度下用稀H_2SO_4搅拌浸提3 h，即制得集物理吸附和化学混凝为一体的粉煤灰基混凝剂。这种混凝剂用于不同工业废水处理，COD去除率在50%－83%之间，色度去除率在89%－98%之间，混凝沉淀速度快，污泥体积小，处理废水费用低。

关键词　粉煤灰，混凝剂，黄铁矿渣，制备，废水处理。

我国每年约有6000万t粉煤灰产生，目前的利用率仅为30%左右，主要用于烧砖，筑路，作水泥、砂浆和混凝土的掺合料，选取漂珠，在农业上用于改良土壤等[1]。化工利用主要是从粉煤灰中提取精炭，铁精矿，三氧化二铝等[2]。近年来环保科技工作者正在致力开发研究粉煤灰的环保利用[4-6]。本文报道在粉煤灰中加入另一种固体废弃物——黄铁矿烧渣，再加入助溶剂NaCl，然后在90℃温度下用稀H_2SO_4浸提而制备粉煤灰基混凝剂的方法。这种集物理吸附与化学混凝为一体的混凝剂，用于各种工业废水处理，效果良好，COD的去除率在50%－83%，色度去除率在89%－98%之间，与常用混凝剂相比，其突出优点是混凝沉淀快，沉淀体积小，污泥含水率低，脱色效果好，处理废水费用低，是值得重视的一种无机复合混凝剂。

1　粉煤灰基混凝剂的制备

1.1　原料及化学组成

粉煤灰取自西安霸桥电厂除尘器排干灰，主要化学组成列于表1。

黄铁矿烧渣取自西安硫酸厂沸腾炉排渣(粉状)，主要化学组成列于表2。

表1　粉煤灰主要化学组成

组分	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	挥发份
含量(%)	5.1	25.7	48.9	1.5	1.5	3.1

表2　黄铁矿烧渣主要化学组成

组分	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO
含量(%)	68.70	3.15	17.50	1.40	0.70

1.2　制备方法

粉煤灰中除硅外，铝的含量最高，且以复杂的复盐形式存在[7]，酸溶性较差。粉煤灰中铁主要以氧化物形式存在，且较易溶于酸，但含量相对较低，故加入以含铁的氧化物为主的黄铁矿烧渣，以增加铁含量。

实验发现，盐酸比硫酸能显著提高粉煤灰中铁和铝(尤其是铁)的浸出率，但在硫酸中加入适量NaCl后，其对铁、铝的浸出率与同浓度

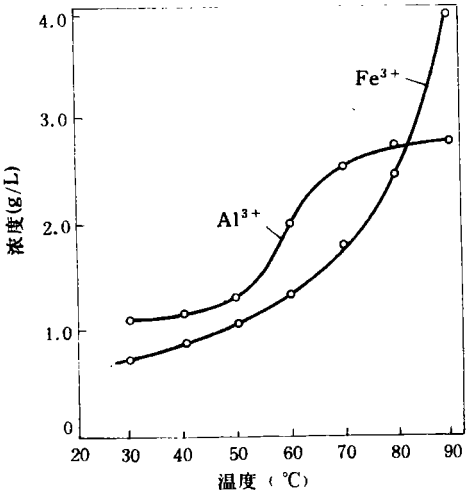

图1　温度对粉煤灰中Fe、Al浸提的影响

条件：50 g粉煤灰加入150 ml 6.32 mol/L H_2SO_4($\frac{1}{2}$分子量)，100 r/min搅拌2 h；50 g粉煤灰，10 g黄铁矿烧渣，3 gNaCl于200 ml玻璃容器中，加入150 ml 4.0 mol/L H_2SO_4($\frac{1}{2}$分子量)，在90℃恒温水浴中，以100 r/min的速度连续电动搅拌3 h，即得产品。

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的盐酸接近。实验证明，温度能显著提高灰、渣中铁，铝的浸提率，对铁的浸出更为显著，如图1。所以浸提需在较高温度下进行。除上述外，还详细试验了 H_2SO_4 浓度，搅拌时间，灰，酸比，黄铁矿烧渣以及 NaCl 加入量对 Fe，Al 浸出率的影响，最后确定实验室制备工艺。

1.3 物理性状及组成

粉煤灰基混凝剂为粘稠、灰色液体，比重为1.4－1.6 g/cm³，久置固液分层，用时搅匀，pH≒1.0，硫酸铁含量为44 g/L，硫酸铝含量为38 g/L。

2 粉煤灰基混凝剂的应用及比较

2.1 废水水质

选择4种废水进行对比处理，原废水水质列于表3。

表3 实验用原废水水质

废 水	造纸	制革	印染	制药
COD(mg/L)	1268.7	914.9	435.4	364.9
SS(mg/L)	681.4	1142.0	140.0	420.0
透光率(T_{400nm}/%)	0.05	0.8	38.0	30.8
pH	9.50	8.92	10.85	7.25

2.2 废水混凝处理方法

取500 ml 废水于800 ml 烧杯中，必要时，先用石灰或稀 H_2SO_4 将废水 pH 调整到8，加入计量混凝剂，先以300 r/min 速度搅拌3 min，再以150 r/min 速度搅拌2 min，转入500 ml 量筒中，静置30 min 并作必要的观测，取上清液分析有关项目。

2.3 对比实验

在对比实验中，各混凝剂均配成25%水溶液，准确测定起混凝作用的主成分(Al，Fe)含量。处理同一废水，各主成分的投加量彼此相当，pH 控制在6－9之间。

表4 不同混凝剂对4种废水处理效果对比

混凝剂	造纸废水				制革废水				印染废水				制药废水			
	剩余COD (mg/L)	COD去除率 (%)	T[2] (%)	色度[1]去除率 (%)	剩余COD (mg/L)	COD去除率 (%)	T[2] (%)	色度[1]去除率 (%)	剩余COD (mg/L)	COD去除率 (%)	T[2] (%)	色度[1]去除率 (%)	剩余COD (mg/L)	COD去除率 (%)	T[2] (%)	色度[1]去除率 (%)
自制	419.6	67.0	88.7	98.4	306.5	66.5	90.1	98.8	215.4	50.5	90.4	89.5	60.9	83.5	97.6	98.3
$Al_2(SO_4)_3$	464.1	63.4	71.8	95.6	323.9	64.6	88.1	97.4	215.4	50.5	86.3	84.8	66.8	81.7	93.5	94.3
碱式氯化铝	436.7	65.6	68.2	95.0	314.7	65.6	68.1	92.1	337.3	22.5	83.0	80.7	66.8	81.7	94.2	94.9
$FeCl_3$	477.9	62.3	65.0	94.3	323.9	64.6	75.9	94.3	259.3	40.4	82.8	80.5	78.2	78.6	93.1	92.0

1) 色度去除率(%)$=\frac{A(原水)-A(处理)}{A(原水)}\times 100$；$A=\lg\frac{1}{T_{400\,nm}}$；$A$ 为400 nm 处吸光度；2) T 为4000 nm 处透光率

(1) 去除率对比　不同混凝剂对同一废水污染物去除率对比结果列于表4。

由表4看出，粉煤灰基混凝剂对废水中COD和色度的去除率明显地比用其它混凝剂的去除率高，由此可见，粉煤灰基混凝剂有较高的混凝效果和脱色能力。

(2) 混凝沉淀速度和污泥体积对比　将废水分别用不同混凝剂处理后，倒入500 ml 量筒中，观察测量不同沉淀时间的上清液高度，结果绘于图2－5。30 min 后量取的清液和沉淀高度(cm)列于表5。

图2－5可见，所有废水用不同混凝剂处理后的污泥沉淀速度，粉煤灰基混凝剂最快，10 min 之内可沉淀完全，这是粉煤灰中未溶固体起了加重作用的原因。30 min 后，用粉煤灰基混凝剂处理的废水的清液高度最高，污泥体积最小，这是该混凝剂的最突出优点之一。

(3) 处理废水费用对比　对比结果列于表

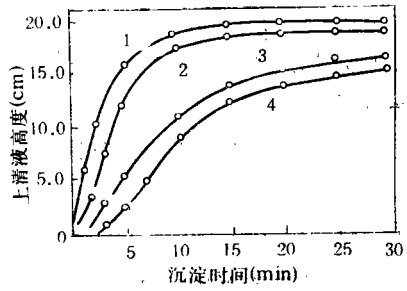

图2　不同混凝剂处理造纸废水的沉淀速度对比
1. 自制　2. $FeCl_3$　3. $Al_2(SO_4)_3$　4. 碱式氯化铝

6。由表6可见，粉煤灰基混凝剂的处理费用最低。

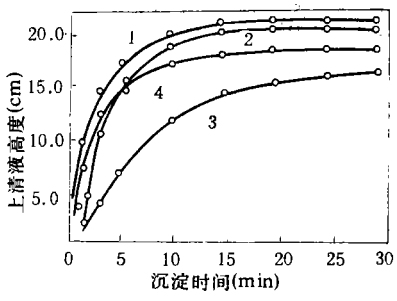

图3　不同混凝剂处理制革废水的沉淀速度对比

1，2，3，4含义同图2

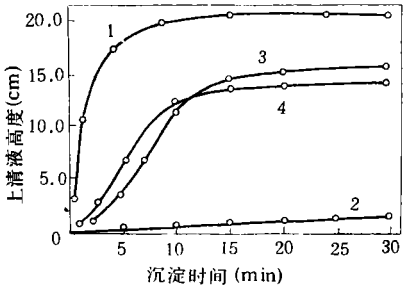

图4　不同混凝剂处理印染废水的沉淀速度对比

1，2，3，4含义同图2

表5　废水用不同混凝剂处理后的液/固比

混凝剂	液/固比			
	造纸	制革	印染	制药
自制	19.5/2.5	19.4/2.6	20.5/1.5	20.8/1.2
$Al_2(SO_4)_3$	16.4/5.9	16.1/6.2	15.8/6.5	19.7/2.6
碱式氯化铝	15.2/7.1	18.0/4.3	15.2/7.1	19.1/3.2
$FeCl_3$	18.3/4.0	18.1/4.2	1.0/21.3	19.7/2.6

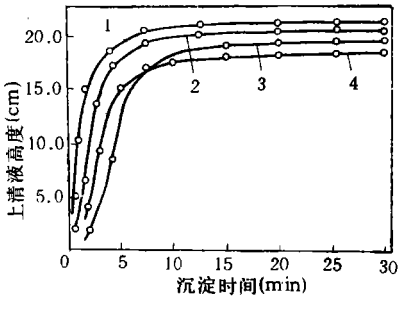

图5　不同混凝剂处理制药废水的沉淀速度对比

1，2，3，4含义同图2

表6　不同混凝剂处理废水需混凝剂费用对比

混凝剂	单价	造纸		制革		印染		制药	
	(元/t)	用量[1]	费用[2]	用量	费用	用量	费用	用量	费用
自制	150	10.0	1.5	7.0	1.1	7.0	1.1	4.0	0.6
$Al_2(SO_4)_3$	810	3.0	2.43	2.1	1.7	2.1	1.7	1.2	0.97
$FeCl_3$	2310	1.1	2.54	0.74	1.7	0.74	1.7	0.42	0.97
碱式氯化铝	2000	1.34	2.68	0.94	1.88	0.94	1.88	0.54	1.08

1) 单位为 kg/m^3废水　2) 单位为元/m^3废水

3　粉煤灰基混凝剂高效机理概说

粉煤灰本身具有多孔性，对废水中的有机物和颜色有吸附作用[8,9]，用酸在较高温度下浸提后，其表面或微孔内变得更加粗糙，比表面会显著增加，如图6所示。所以粉煤灰经酸浸

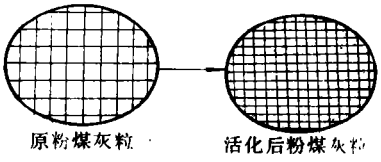

图6　酸浸提粉煤灰表面活化示意图

后，相当于表面被活化，活化后的粉煤灰对有机物和颜色吸附能力更强，所以粉煤灰基混凝剂具有混凝(Al、Fe 等起作用)和高效吸附的双重作用。

4　小结

(1) 粉煤灰配以适量的 NaCl 和黄铁矿烧渣在较高温度下用酸浸提，即得粉煤灰基混凝剂，这种固、液共存的混凝剂具有化学混凝和物理吸附的双重作用。

(2) 粉煤灰基混凝剂能广泛用于各种废水处理，对 COD、色度等的去除率高于其它常用的无机混凝剂，更突出的优点是沉淀体积小，含水率低。

(3) 该混凝剂生产原料来源广泛，利用工业废渣，废酸，生产成本低，处理废水费用低，是一种值得重视的无机复合混凝剂。

(4) 粉煤灰基混凝剂用于废水处理，虽沉淀体积比用其它混凝剂小，但沉淀的绝对重量比用其它混凝剂大，这是一个缺点，有待进一步研究。

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光强度的影响。结果表明，在 25%醋酸铵缓冲介质中(pH=7.0)，苯胺的荧光发射强度最强。另外，一些表面活性剂对荧光发射有显著增敏作用。其中 Triton X-100 效果最佳，其适宜浓度范围为 0.1%—0.4%(V/V)。

2.3 工作曲线、精密度和检出限

在最佳实验条件下，苯胺的浓度在 2.0×10^{-7}—5.0×10^{-6} mol/L 范围内，与相对荧光强度呈良好的线性关系(见图 2)。对 1.0×10^{-6} mol/L 苯胺的 10 次测定，相对标准偏差为 2.5%。根据计算公式 $X=X_b+kS_b$[1]，选定置信水平为 90%，即 $k=3$。对空白值 20 次测定，经处理得到检出限为 1.0×10^{-7} mol/L。

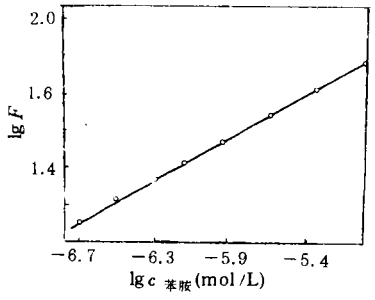

图 2 工作曲线

2.4 共存物质的影响

在最佳实验条件下，苯胺浓度为 1.0×10^{-6} mol/L，相对误差小于 5%。共存物质对苯胺化合物测定的干扰结果为(摩尔倍数)：苯(250)，甲苯(230)，乙苯(230)，硝基苯(240)，二苯胺(100)，N-甲基苯胺(75)，蒽(70)，萘(20)，芘(40)，菲(25)，酚(270)，对甲基苯酚(320)，苏(4)，苯乙烯(170)，水杨酸(150)，一氯苯(300)，三氯苯(300)，α-666(200)，β-666(250)，甲醛(500)，乙醛(500)，乙醇(100)，Na^+、K^+、NH_4^+(>10000)，Mg^{2+}、Ca^{2+}、Ba^{2+}(>5000)、Al^{3+}、Fe^{3+}、Cr^{3+}(>1000)。

2.5 样品分析及回收率试验

对 2 种工业废水(制药厂排放废水和染料厂排放废水)中苯胺含量的分析结果见表 1。该法与萘乙二胺偶氮光度法所测结果一致。在废水样品中进行加标回收试验，获得较为满意的结果(见表 1)。

表 1 样品分析结果

样 品	测定值[1)] (mg/L)	相对标准偏差 (%)	萘乙二胺偶氮光度法(mg/L)	回收率 (%)
制药厂废水	14.3	2.4	14.0	97
染料厂废水	50.3	2.6	50.9	99

1) 4 次测定的平均值

3 结束语

三维荧光光谱法测定苯胺的方法有灵敏度高、重现性好、选择性高、有一定的线性范围、取样少、节约试剂、干扰少等优点。是一种较好的监测苯胺的分析方法。

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Analysis of the Current Structure of Beijing Municipal Water Use and a Study on the Response strategy for Water Conservation. Wang Hongrui et al. (Insitute of Environ. Sci., Beijing Normal Univ., Beijing 100875); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 31—34

In Beijing, a particularly big metropolis which has been experiencing a bad shortage of water and where water resources have been seriously wasted due to an unreasonable structure of water uses in various industrial sectors, the current conditions of the municipal water use structure and its change in the industrial sectors were overally analyzed and discussed in terms of indicators, such as direct water use coefficient, complete water use coefficient, water multiplier, and water reuse rate, by taking the year 1991 as a base year. Some response strategies for water conservation to change this situation were studied and the corresponding recommendations were made. All of these provided a basis for coordinating the relationship between aquatic environment and economic development in this city, establishing a system of rational utilization of water resources, and promoting the implementation of a strategy for sustainable development.

Key words: direct water use coefficient, complete water use coefficient, water use multiplier, water reuse rate.

Chemical complexation-based Technique for the Treatment of phenolic Industrial Effluents. Yang Yiyan et al. (Dept. of chemical Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 35—38

Following the idea of reversible chemical complexation, a study on thermodynamic equilibrium and cross-current flow extaction of various industrial phenolic effluents has been carried out. The new mixed solvents (QH) for this purpose have been developed. The results show that by using this treatment technique the raffinates of phenolic effluents can comply with the required disposal standard through only 2—3 stages of cross-current flow extraction. This treatment technique has been used successfully.

Key words: extraction by chemical complexation, phenols, industrial effluent, COD.

Study on the Treatment of Gaseous Sulfur-bearing Wastes from a Rayon Manufacturing Plant. Xu Guodong and Huang Wenyi (Dept. of Chem. Eng., Fuzhou Univ., 350002); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 39—42

A TF-TA process was developed for the treatment of gaseous sulfur compounds-containing wastes from a rayon production process. The gaseous wastes were first contacted with a TF desulfurizing liquor to remove H_2S and then passed through a TA liquid to further remove CS_2 from them. The removal of H_2S and the regeneration of TF desulfurizing liquor could be carried out in a step. H_2S was removed at a rate of over 98%, and CS_2 was removed at a rate of up to 80%—90% if there was a gas/liquid ratio of 200—300. The overall pollution abatement of waste gases emitted from a rayon manufactoring plant was also discussed.

Key words: treatment of waste gases, H_2S, CS_2, rayon, removal.

Pilot Study on an Enclosed Circulation System for Treating the Wastewater from Phosphoric Acid Production Process. Fang Weimao, Chen Wenmei et al. (Chengdu Univ. of Sci. and Technology, Chengdu 610065); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 43—46

An enclosed circulation system comprising four operation units, i. e., spiral flow centrifuge separation, flocculation, gravity settling, and mixed thick sludge filtration, has been developed for the treatment of wastewater from a wet process of phosphoric acid production. The results from a pilot study on this system show that the spiral flow centrifuge separation in stage 1 had an efficiency of over 80%. The overflow containing fine solid particles from the spiral flow process in stage 1 was subject to a flocculation pretreatment in stage 2, allowing the settling rate to be increased by near 30 times and the supernatant to contain less than 200 ppm of solid. The thick sludge from stage 1 and that from stage 2 were mixed at a ratio of 1.5, resulting in a good performance of filtration.

Key words: phosphoric acid, wastewater treatment, enclosed-circulation.

Studies on the Preparation and Application of a Fly Ash-based Coagulant. Huang Caihai et al. (Shaanxi Institute of Science for Environ. Protection, Xi'an 710061); *Chim. J. Environ. Sci.*, **16**(2), 1995, pp. 47—49

A fly ash-based coagulant combining the capabilities of both physical adsorption and chemical coagulation has been prepared by adding a small amount of pyrite slag and an appropriate amount of NaCl to fly ash, and then the resulting mixture being stirred and extracted with a dilute H_2SO_4

for 3 hours at a temperature of 90℃. The coagulant thus prepared was used to treat various kinds of industrial wastewaters, giving a COD removal of 53%—83%, a colourness removal of 89%—98%, a higher rate of settlement, a smaller volume of sludge, and a lower cost of treatment.

Key words: fly ash, coagulant, pyrite slag, wastewater treatment.

Concentration Levels, Change Records and Enrichment Patterns of Heavy Metals in Waters and Sediments in Both Lake Dianchi and Lake Erhai, Yunnan Province. Li Bingmin et al. (National Laboratory of Environ. Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002): *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 50—52

The heavy metals in waters of Lake Erhai, Yunnan Province, were found not at higher levels, with the following mean values calculated in ppb: Cu 1.6, Pb 0.59, Zn 9.8, Cd 0.009, and Cr 0.24, so that the water quality was assessed as a better one. The same elements in each sample of the sediments form Lake Erhai generally had a value approximate to their respective average levels as calculated in ppm as follows: Cu 111, Pb 60, Zn 127, Cd 0.591 and Cr 130, so that so far Lake Erhai has been still a cleaner lake. Lake Dianchi in the Yunnan Province was found to have a rather worse water quality, particularly in its section of Inner Caohai where there were significantly increased levels of heavy metals in water as calculated in ppb as follows: Cu 5.8, Pb 0.55, Zn 32, Cd 1.611 and Cr 0.24, which are well below the national standards for drinking water. The sediments in different sections of the lake have been found to be polluted with some heavy metals, to a more significant extent in the section of Outer Caohai and to a more serious extent in the section of Inner Caohai. The heavy metals in the top layer of sediment were calculated in ppm at the following levels: Cu 920, Pb 647, Zn 2208, Cd 164.85 and Cr 55.

Key words: Dianchi, Erhai, Sediment, heavy metals.

Effects of Environmental Change on the Corrosion of Historical Bronze Relics. Cheng Derun et al. (College of Culture and Museuology, Northwest Univ. Xi'an 710069): *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 53—55

Affected by the change in environmental factors, the ancient bronze relics in several famous cultural relics sites in Shaanxi Province were found being subject to a serious rusting corrosion, especially by forming a powdery copper rust, the development of which may lead the historical relics to being destroyed in a moment. Based the environmental monitoring carried out in the above relics sites, the reports on the environmental monitoring in Xi'an area, and the analysis for the chemical compositions of the main body and surface rust of the ancient bronze relics, a corrosion mechanism of cultural bronze relics was suggested, which was a combination of chemical and electrochemical corrosions. The conditions under which the historical bronze relics were being rustingly corroded were identified as a chloride ion contained, humid and acidic environment. Thus, it was pointed out that the environmental control would be a key to the protection of the historical bronze relics. In order to maximize the life time of the historical bronze relics, it was necessary to improve the environmental conditions that were a radical measure for conserving the relics.

Key words: historical bronze relics, chemical corrosion, electrochemical corrosion, environmental factors.

Environmental Impact Assessment of Electromagnetic Radiation by a Doppler Very High Frequency Omnirange/Distance Measuring Equipment (DVOR/DME). Yao Gengdong et al. (School of Public Health, Zhejiang Medical Univ., Hangzhou 310006): *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 56—58

Based on an analogic survey and a theoretical calculation, an environmental assessment impact of the electromagnetic fields (EMF) of a Doppler very high frequence omnirange/distance measuring equipment (DVOR/DME) to be extensively applied in China has been conducted. The results show that the field intensities were below 8.5×10^{-2} V/m at an altitude of 1.7—20 m above the ground within an area of a 1000 m radius centred on the antenna of a DVOR/DME, indicating that the low level of EMF from a DVOR/DME used in the guide station of civil aviation would not cause a health hazard among the local residents.

Key words: DVOR/DME, electromagnetic radiation, environmental impact assessment.

Determination of Anionic Surfactants in Water. Liu Weiguo, Zhu Herong (Environ. Protection Research Institute, Shanghai Petrochemical Company Ltd., Shanghai 200540): *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 59—62

The molar concentration of various kinds of