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PACS 絮凝剂的制备及其性能研究

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摘要 以 $Al(OH)_3$, HCl, H_2SO_4 和 Na_2CO_3 为原料制备含 SO_4^{2-} 的聚合氯化铝(简称 PACS)，试验了它的性能及影响因素. 结果表明：SO_4^{2-} 含量、碱化度和 pH 影响 PACS 的絮凝效果，当 Al^{3+}/SO_4^{2-} (摩尔比)=15—17 时絮凝效果最佳. 实验还表明 PACS 较 PAC 的絮凝效果要好.

聚合氯化铝（简称 PAC）自六十年代在日本问世以来，发展迅速，成为国际上公认的一种优良净水剂。它具有净水性能好，用量少，效率高，絮体沉降快，适用范围广等优点. 为了进一步提高 PAC 的净水性能，改进产品质量，我们以文献[1]中提出：含有 SO_4^{2-} 配位基的聚合氯化铝(通常以 PACS 表示)，其稳定性和絮凝效果均优于 PAC 为依据，开展了 PAC 的改性研制并进行影响絮凝效果因素的研究. 此外，还试验了用它处理油田及印染废水的效果。

一、实 验 步 骤

1. 主要试剂和仪器

(1) 主要试剂 $Al(OH)_3$, HCl, H_2SO_4, Na_2CO_3 均为 A.R 纯.

(2) 主要仪器 DBJ-621 定时变速搅拌机，WGZ-II 型光电浊度仪；PHS-2 型酸度计，DXD-I 型微电泳仪，721 型分光光度计.

2. PACS 制备方法

于带有搅拌器，温度计，回流冷凝器的三口瓶中放入一定量的氢氧化铝，盐酸及硫酸. 在 110℃ 左右反应 5—7h. 待反应完全后冷却反应液，然后在搅拌下向反应液中加入一定量的碳酸氢钠溶液，适当搅拌，直至反应完全即得产品.

此法合成的 PACS 含 Al_2O_3 7—9%，pH 为 3.0—3.5，碱化度 60—75%，比重在 1.10 以上，含硫酸根适量.

3. 絮凝实验方法

实验是在人工配制的模拟水样中加入一定量的絮凝剂而进行的，具体方法如下：

硅藻土预先在 105℃ 下干燥 1h，放置在干燥器内备用. 准确称取 1.00g 硅藻土置于 1L 烧杯中，加分散介质(水)到 1000ml，用搅拌器搅拌均匀(此水样的浊度为 221 度)，然后加入一定量的絮凝剂，在速度为 120r/min 下搅拌 1min，在 60r/min 下搅拌 7min，然后静止沉降 10min，取上清液用浊度计测浊度.

4. 电动电位 (ζ) 的测定方法

准确称取 1.00g 硅藻土置于 1L 容量瓶中，加蒸馏水至刻度，摇匀，然后加入一定量的絮凝剂，重新搅均，取出部分溶液，用 DXD-I 型微电泳仪测定电动电位 (ζ)。

$$\zeta = \frac{4\pi\eta v}{\varepsilon E} \times 300^2$$

式中，ζ 为电动电位 (mV)；ε 为液体的介电常数，20℃ 时水为 80；v 为电泳速度 (cm/s)；E 为电位梯度。η 为水的粘度，$\eta^{20°C}$ 为 0.001Pa·s。

二、实验结果与讨论

1. SO_4^{2-} 含量对 PACS 絮凝效果的影响

实验中 PACS 的投加量以有效成份计为 2ppm (以下实验若无指明，絮凝剂的投加均按此量，且以有效成份计)，实验结果示于图 1。可见，SO_4^{2-} 含量对 PACS 的絮凝效果有明显影响，当 Al^{3+}/SO_4^{2-} 的摩尔比为 15—17 时，絮凝效果最佳。

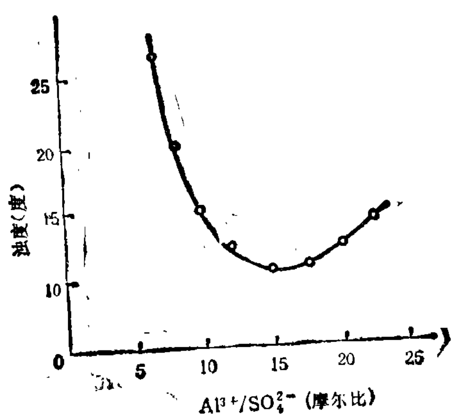

图 1　SO_4^{2-} 含量对 PACS 絮凝效果的影响
(PACS 的碱化度为 60%)

2. 碱化度对 PACS 絮凝效果的影响

维持 Al^{3+}/SO_4^{2-} 的摩尔比为 16 (若无指明，以下实验均维持此摩尔比)，研究碱化度对 PACS 絮凝效果的影响，结果示于图 2 中。开始阶段 PACS 的絮凝效果随碱化度的增高而增加，达75%时，絮凝效果最佳。超过75%，絮凝效果反而下降，这是由于碱化度太高，部分絮凝剂水解造成的。实验过程中明显看到，当碱化度太高(超过 75%)时，产品呈乳白色，并有沉淀产生，这说明 PACS 已部分水解。

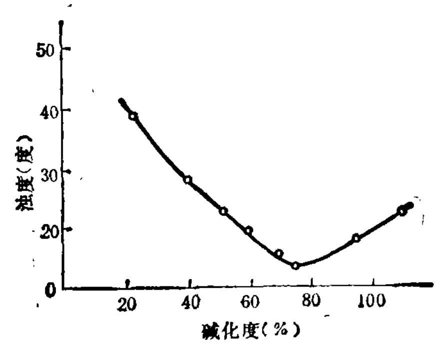

图 2　碱化度对 PACS 絮凝效果的影响

3. PACS 的絮凝特性

评价絮凝剂的絮凝特性的方法一般有两种，一为采用 ζ 电位滴定曲线；二为用模拟水样试验絮凝效果。因此这里评价 PACS 的絮凝特性按上述两法综合考虑。

(1) ζ 电位滴定曲线

为比较方便，PACS 和 PAC 的碱化度均统一用 60% (若无指明，以下实验均用此比例进行)。图 3 是 PACS 和 PAC 的 ζ 电

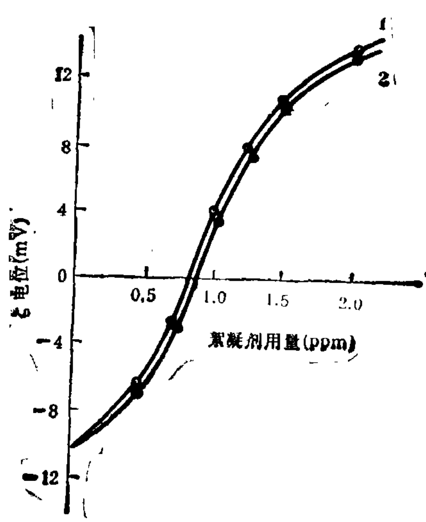

图 3　ζ 电位滴定曲线
1. PAC　2. PACS

位滴定曲线。由图3表明：二者电荷中和能力基本一致，PAC 中和电荷的能力甚至稍大于 PACS 的电荷中和能力。

(2) 用硅藻土模拟水样进行絮凝效果比较

用 PACS 及 PAC 絮凝硅藻土模拟水样的结果示于图4中。可见 PACS 的絮凝效果大大优于 PAC。

综合分析 ζ 电位滴定曲线及模拟水样絮凝实验结果，明显看出 PACS 的絮凝效果优于 PAC。这说明了向聚合氯化铝中加进适量的 SO_4^{2-}，能大大提高聚合氯化铝的絮凝效果。关于适量 SO_4^{2-} 能提高聚合氯化铝的絮凝效果的机制说法不一[1,2,3]，但我们认为，既然 PACS 的电荷中和能力不大于 PAC，而总的絮凝效果却大于 PAC，这意味着 PACS 的"架桥"能力大于 PAC。PACS "架桥"能力的增大可能是由于 SO_4^{2-} 的增聚作用所致，即 SO_4^{2-} 通过氢键把 PAC 分子连接起来增大了 PACS 的分子量。

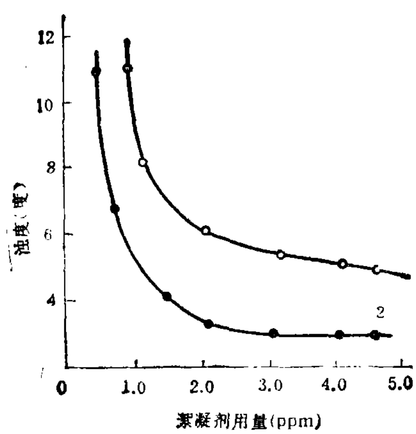

图4 PACS 与 PAC 絮凝效果比较
1. PAC 2. PACS

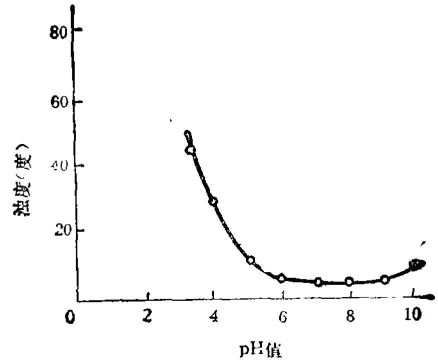

图5 pH 值对 PACS 絮凝效果影响

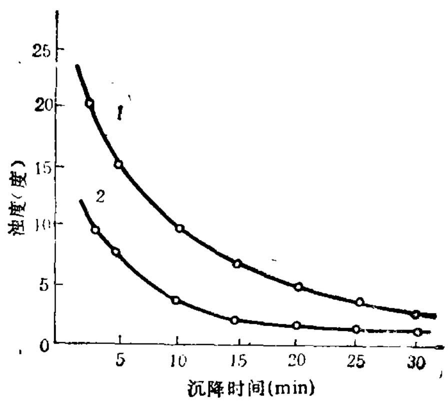

图6 沉降时间与上清液浊度的关系
1. PAC 2. PACS

4. pH 值对 PACS 絮凝效果的影响

调节水样的 pH 值，试验 pH 值对 PACS 絮凝效果的影响。实验结果见图5。由图5可见，PACS 在 pH 值为6—9范围时絮凝效果最佳。

5. PACS 与 PAC 沉降性能比较

实验结果示于图6中。从图6看出，PACS 的沉降性能优于 PAC。另外，实验过程中发现，用 PACS 处理水样时，絮体形成的速度快，且絮体大，故沉降速度快，而用 PAC 时，絮体形成的速度慢，且絮体小，故沉降速度慢。

6. PACS 的应用实例

(1) PACS 在油田污水净化中的应用

中原油田含油污水采用同时投加 PAC 和 CG-A (CG-A 系一种有效成份为12%的改性天然高分子化合物絮凝剂) 来净化油田污水。经多次实验证明，只加 PAC 而不

表 1　PACS 与 (PAC + CG-A)净化油田污水比较

药剂 名称	药剂 浓度* (ppm)	透光率 (%)	含油量 (ppm)	总铁 (ppm)	机杂 (ppm)	pH 值	滤膜系数
	0	70.5	21.75	20.19	80.0	6.83	5.2
PACS	6.0	94.4	1.67	0.40	1.5	6.80	17.2
	8.0	98.1	0.67	0.08	1.2	6.80	22.2
	10.0	98.1	0.67	0.07	1.0	6.80	33.0
PAC + CG-A	6.0+1.2	88.5	6.00	0.26	2.0	6.70	8.3
	8.0+1.2	92.5	2.40	0.25	1.5	6.60	19.5
	10.0+1.2	97.0	2.00	0.23	1.2	6.55	23.5
水质指标		>95	<30	<0.5	<2	6.5—8.5	>17

* 各絮凝剂的浓度是以有效成份计量的.

表 2　PACS 与 PAC 处理印染废水的效果比较

絮凝剂浓度* \ 指标	COD(mg/l) 原水	COD(mg/l) 处理后	COD(mg/l) 去除率(%)	色度(倍) 原水	色度(倍) 处理后	色度(倍) 去除率(%)
PACS(10ppm)	1067	688	35.5	450	180	60.0
PAC(10ppm)	1067	790	26.0	450	180	60.0
PACS(20ppm)	766	305	60.2	250	150	40.0
PAC(20ppm)	766	391	49.0	250	150	40.0

* 絮凝剂的浓度是以有效成份计量的.

加 CG-A，处理后的油田污水达不到回注水质指标。我们试验了只加 PACS 净化中原油田含油污水的效果，并与同时投加 PAC 和 CG-A 的净化效果进行了比较，实验结果列于表 1 中。

表 1 结果表明：投加 8ppm PACS，油田污水经处理后各项指标都达到或优于油田回注水指标，说明 PACS 净化油田含油废水的效果远远大于 PAC。另外，处理油田废水投加 8ppm PACS 处理一吨废水其成本仅为 0.10 元左右，这说明用 PACS 处理油田含油废水不仅效果好，而且处理费用也低。

(2) PACS 在印染废水治理中的应用

我们以济南第二印染厂的废水为代表，探讨了 PACS 处理印染废水的效果，并与 PAC 的处理效果进行了比较。实验时调节水的 pH 至中性。实验结果见表 2。

实验结果表明：PACS 处理印染废水的效果较 PAC 的处理效果好。

三、结　论

1. SO_4^{2-} 对聚合氯化铝的絮凝性能有很大影响，当 Al^{3+}/SO_4^{2-}（摩尔比）在 15—17 之间时其絮凝效果最佳。

2. 碱化度越高，PACS 的絮凝效果就越好，但碱化度过高时产品不稳定，发生水解，生成沉淀。

3. PACS 在 pH 为 6—9 范围时絮凝效果最佳。

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Shanghai): *Chin. J. Environ. Sci.*, **11**(3), 1990, pp. 24—27

It has been proved that there is a root microecosystem in the process of dyeing wastewater treatment by the hyacinth. With four days' retention, the percentage of COD removal in the oxidation tank, where the hyacinth was planted and its root sterilized with chloride, was 13%. However the percentage of COD removal in ordinary biological oxidation pond without the hyacinth was 15%. In comparison with this, a water hyacinth oxidation tank without sterilization showed higher COD removal percentage of 35% due to existence of a root microecosystem. Similar results were obtained when wastewater containing PVC, detergent and some dyes were treated with the three methods mentioned above. Some organic compounds that could scarcely be absorbed by the hyacinth, for example, those easy to be coagulated or floccules, could be sticked and fixed on the root surface, and then degraded by the root microecosystem.

The Toxicological Effect of Cr (VI) on Chlorophyll and Iron Contents and Activities of Some Enzymes in the Leaves of Pepper (*Capsicum annum*). Zhou Yiyong, Liu Tongchou, Deng Boer (Dept. of Soil and Agrochemistry, Huazhong Agricultural University, Wuhan): *Chin. J. Environ. Sci.*, **11**(3), 1990, pp.28—29

The toxicological effect of Cr(VI) on some biochemical parameters in pepper were studied both in soil culture and in nutrient cultural experiments. The treatments of the heavy metals decreased fresh weight and promoted senescence of the pepper plant by decreasing chlorophyll and activities of superoxide dismutase and catalase as well as increasing iron content and peroxidase activity over control values.

Study on the Pretreatment of Coke-Plant Wastewater by Anaerobic Acidification. Zhao Jianfu, Qian yi, Gu Xiasheng(Dept. of Environmental Engineering, Tsinghua University, Beijing): *Chin. J. Environ. Sci.*, **11**(3), 1990, pp.30—34

According to analysis of the constituents and concentrations of organic pollutants in wastewater at Beijing Coke Plant using combined gas chromatography and mass spectrometry (GC/MS), the effect of anaerobic acidification on the bio-treatability of coke-plant wastewater has been studied and the possibility of using anaerobic acidification as pretreatment of aerobic treatment has also been explored. The results described that aerobic biotreatability of coke-plant effluent could obviously increase through 2—6 hours' anaerobic acidification. After 6 hours and 12 hours, anaerobic acidification, COD in the effluent could be removed by 91%, i.e. removal rate increased about 40% more than that without applying anaerobic acidification. As the inffluent COD of the wastewater was 1780 mg/L, the effluent COD removed to 158 mg/L.

Preparation of Polyaluminum Chloride with Sulfate Ion and Study on Its Properties. Gao Baoyu et al. (Environmental Science Center, Shandong University, Jinan): *Chin. J. Environ. Sci.*, **11**(3), 1990, pp. 34—37

Polyaluminum chloride with sulfate ion (PACS) has been prepared by using aluminum hydroxide, hydrochloric acid, sulfuric acid and sodium carbonate as raw materials, and the properties of PACS have also been studied. The factors affecting the flocculating effect of PACS have been investigated. The experimental results show that the flocculating effect of PACS is influenced by the amount of sulfate ion in PACS, basicity of PACS and pH of water solution. When the molar ratio of Al^{3+} to SO_4^{2-} is in the range of 15 to 17, the flocculating effect of PACS is best.

Problems on Yellow-Colouring of the Wastewater Treated with the Coagulant, Ferrous Salt. Guan Xijun, Wang Fei (Dept. of Environmental Engineering, Qingdao Institute of Architectural Engineering): *Chin. J. Environ. Sci.*, **11**(3), 1990, pp.38—40

When ferrous salt is used as a coagulant to treat wastewater, if there exists superfluity in the process of coagulation to sedimentation, purged water will be clear. However, When the purged water is laid aside, it becomes turbid and turns to yellow-colouring. The reason is that oxygen in the air has dissolved in it as time goes on. The authors have proposed a measure to control the phenomenon that a higher pH or an optimal quantity of the mixed coagulant paralleled with tests can avoid color changing.

Application of Inductest in Research of Environmental Mutagens. Ruan Cuicai et al. (Guangxi Cancer Institute, Nannin): *Chin. J. Environ. Sci.*, **11**(3), 1990, pp.41—43

The possible mutagenic activity of 35 different chemicals has been tested with inductest, in which S_9 mixture was used as a metabolizing system. The results showed that 13(37%) chemicals had mutagenic activity, 10 of these chemicals gave positive reaction in inductest in the presence of S_9 mixture, three chemicals gave positive reaction in inductest in the presence of S_9 mixture or without it. Some of the chemicals are known as potent mutagens and carcinogens (aflatoxin B_1) or anticancer drugs (mitomycin C). It is considered that inductest is an effective method in research of environmental mutagens.

A Study on Determination of Formic and Acetic Acids in the Atmosphere. Yu Shaocai,