

亚铁盐混凝处理水的“泛黄”问题

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摘要 通过对亚铁盐混凝处理水的“泛黄”机理探讨,阐明混凝过程中异体凝聚的重要性;同时提出亚铁处理水上清液泛黄原因及其控制措施,得出的结论和有关资料可供混凝法控制亚铁盐投量的参考。

所谓泛黄是指用亚铁盐作混凝剂处理废水时,当混凝剂的投量较多时,被处理水在混合、反应、沉淀后,上清液当时很清,但放置一段时间后,由于空气的溶入水中的溶解氧将亚铁离子氧化成高铁离子,水质产生严重混浊并呈现黄色的现象。

目前,中、小型企业、乡镇企业遍及全国,它们的特点是废水量小,水质变化大。生物法较难适应这种特点。从全国众多废水厂的处理成本看,尽管混凝法药剂费用高(约占处理成本的 50%),但混凝法基建投资省,上马快,设备简单,电耗省,操作管理方便等优点使其在中小企业及乡镇企业的废水处理站中占有优势。国内许多人研究了印染废水混凝处理法的药剂效果,结论是:综合考虑脱色、去除 COD、药剂费用、泥量以及处理后废水的 pH 值等因素,就 FeCl_3 、 FeSO_4 、 $\text{Al}_2(\text{SO}_4)_3$ 及碱铝混凝剂来说,硫酸亚铁比较合适。而目前水厂用铝盐混凝剂较多,原因就是异电胶体共沉后亚铁胶体过剩,悬浮于水中,在氧化成高铁的过程中,造成水体耗氧,降低水体的 pH 值,更为严重的是铁离子有可能与水体中的大量有机酸形成溶解性络合物,其中部分络合物具有明显的颜色,而铝盐不存在此问题。可见,为较好地使用亚铁盐于废水治理,泛黄控制是具有一定现实意义的。

一、实 验

实验中,选用某厂酸洗铁件所产生的含

氯化亚铁的废水对含分散染料的某印染废水进行六联搅拌平行实验,旨在寻找最佳去除分散染料的投药量。首先,根据定投药量变 pH 值的实验方法确定以 FeCl_2 计的合理投药量为 100ppm。并以此为基数,分别以其 1/2、2、4、8 倍的投药量进行实验,绘制 pH、投药量及去除效果的相关图。在实验过程中发现:投药量为 $1/2 \times 100\text{ppm}$ 时,水样几乎没有去除效果;随投药量加大,在 pH6.5—7.5 附近,水样形成絮凝体的速度加快,30 min 静沉后的上清液较清,且具有趋于稳定的去除率。在定 pH 变投药量的平行实验中发现,上述现象只是暂时的。当不同投药量的上清液被放置 6h 后,原来只有 10 倍稀释倍数的上清液将产生有趣变化;对于 100ppm 投药量,水样上清液的色度(包括浊度)比较稳定,一直保持 10 倍的稀释倍数;对于 400ppm 投药量,水样上清液的色度(包括浊度)变化极大,色度可达 200 稀释倍数以上。

图 1 到图 4 是部分实验曲线。其中,图 1 曲线 1、2、3 是投药量分别为 400ppm、200ppm、100ppm 时的定投药量变 pH 值平行试验曲线,它给出了最佳 pH 值在 7 左右的结果;图 2 是选定 pH 值后的变投药量的平行实验曲线,从图中可取得最小投药量值(原水样不同,混凝剂最小投量值不同,相关性较差);图 3 是在 pH6.5—7 的条件下的泛黄实验曲线,曲线 1、2、3 对应投药量分别为 400ppm、200ppm 和 100ppm,实验温

度为 30℃; 图 4 是在 pH6.5—7 和投药量为 400ppm 的条件下, 泛黄与温度关系曲线, 曲线 1 和曲线 2 对应水温分别为 30℃ 和

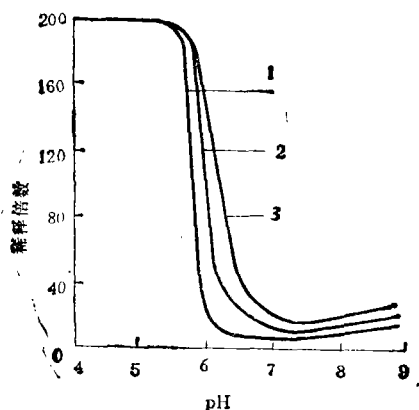


图 1 定投药量变 pH 试验

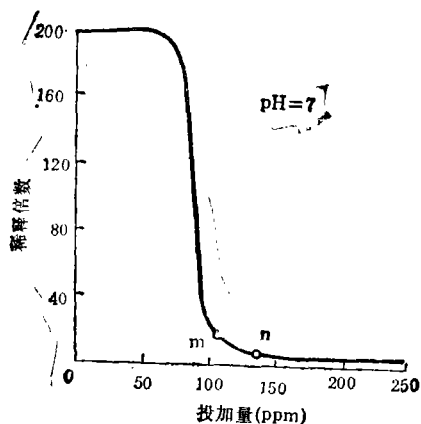


图 2 定 pH 值变投药量实验

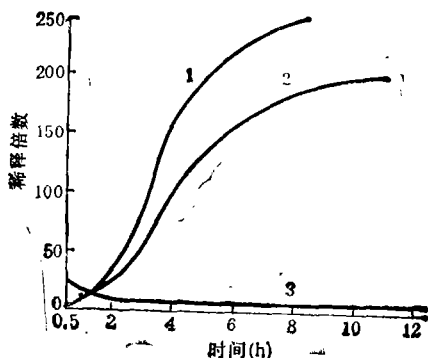


图 3 泛黄与原液加药量关系曲线

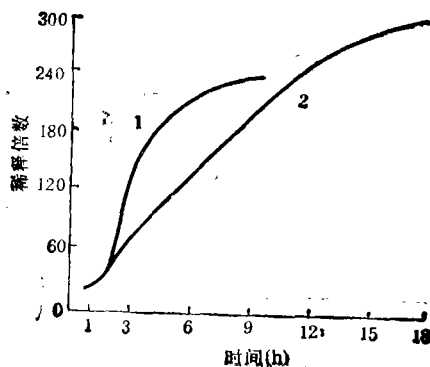


图 4 泛黄与水温的关系曲线

13℃.

二、泛黄机理探讨

众所周知, 胶体的稳定性是由于聚集稳定性和动力学稳定性作用的结果. 聚集稳定性的主要原因是离子双电层作用. 设球型模型, 球周围扩散层中电位分布是第拜·-尤格尔函数:

$$\Phi = \Phi_a \cdot a \cdot \frac{e^{-kH}}{a + H} \quad (1)$$

式中: a 为粒子半径(m); H 为距固定层与扩散层交界面的距离(m); Φ_a 为固定层与扩散层交界处的电位 (V); $1/k$ 为离子云厚度 (m);

$$k = \sqrt{\frac{4\pi e^2 \sum n_i Z_i^2}{DKT}} \quad (2)$$

式(2)中: e 为单位电荷, $e=1.6 \times 10^{-19}C$; n_i 为单位体积中 i 种离子个数(个/ m^3); K 为波尔兹曼常数,

$$K = \frac{R}{N_0} = 1.38 \times 10^{-23} J/K$$

按(1)式, 在无限远处 Φ 才为零, 亦即扩散层是无限的. 按照这个结论, 是不可能产生 ζ 电位为零的现象. 但是实验测得泥土胶体投加大量混凝剂后可使 ζ 电位为零甚至变号. 根据本文所述的泛黄现象及剩余色度-pH 值曲线所反映的问题, 有必要对混凝机理中的“异电胶体共沉”加以强调. 就本实验来说, 当 $pH < 5$ 时, 投药量增加到 800ppm 也未

产生混凝现象。可见,单纯用压缩双电层减小 ζ 电位的混凝机理是无法解释 ζ 电位的变化的现象。当废水中含有大量 NaCl 时,它不能使水中的悬浮物凝聚沉淀,也证明了无机盐混凝机理的“异体凝聚共沉”的正确性。对于本实验呈现的现象,可作如下解释:在合适的 pH 值下,加入的混凝剂的一部分被实验水样中的胶体微粒静电吸附,使胶体微粒间的斥力减小;同时,大部分将产生正电胶体: $\{[m\text{Fe}(\text{OH})_2 \cdot n\text{Fe}^{2+}] \cdot x\text{OH}^-\}^{(2n-x)+}$, 使水样中的负电胶体在此正电胶体的作用下,发生进一步的电位中和,各自降低其稳定性以至发生凝聚。这就是所谓的异电胶体的相互凝聚。如果正负两种电荷总电量相等或相近时,混合后才能达到完全凝聚。如果正负两种胶体的总电量相差较大,则在相互凝聚后仍会留有带电的胶体,其电性和总电量多的一种相同。因此,胶体相互凝聚只有在两种胶体的电量比例较为合适时才能取得良好的效果。应用这个机理来解释实验现象就极合适:当投药量 100ppm 时,水样中的正电胶体总电量可能稍小于负电胶体,在共沉的过程中,矾花进一步吸附了水中的部分溶解态 Fe^{2+} , 使上清液水样中 Fe^{2+} 含量下降到不能使氧化后色度及浊度上升;而投药量为 400ppm 时,存在正电胶体的过剩现象,

水样放置后泛黄现象出现。需要说明的是:对于不同水样及 pH 值,需用的最佳投药量是不同的。以上的分析,说明了最佳投药量的存在及其重要性,要求出其值,只能首先做出图 2 所示的实验曲线,结合定性分析,以图中的 mn 段作为选用范围。

据一些废水厂资料,大量氢氧化铝胶体存在于铝盐作混凝剂处理的水中。另外,无机盐混凝剂在即将达到其完全形成氢氧化物沉淀前的 pH 值处存在最佳 pH 值的事实,都为本文讨论的机理提供了证据。

三、结 束 语

1. 在最佳 pH 值条件下,亚铁泛黄现象可通过降低投加药量来缓解并消除。
2. 最佳投药量可以图 2 所示平行试验曲线下转折点为依据得出。
3. 在比较保守的投药量的情况下,可用较高 pH 值条件来控制泛黄现象。
4. 在无机混凝剂的混凝机理中,应强调异体凝聚理论。避免投药量过多。

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《水科学进展》征稿启事

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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 flocules, could be stuck 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 annuum*). 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 influent 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, Nanning): *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,