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Fenton/UV 氧化法处理高浓度工业酚醛废水的研究

Study on the Treatment of High Concentrated Industrial Wastewater Containing Phenol and Aldehyde with Fenton/UV Oxidation Method

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摘要

酚醛树脂具有优越的综合性能，而且价格低廉，能制成多种产品，是重要的合成树脂之一。然而，在制备酚醛树脂时会产生大量的酚醛废水，废水组成复杂，含有多种难处理的有机物，而且有机物浓度高（即化学需氧量 COD 高），具有很强的毒性，直接排放将对环境产生很大的危害。采用一般的处理方法难以实现好的效果，芬顿试剂（Fenton）是由过氧化氢和亚铁离子组成的试剂，过氧化氢在亚铁离子的催化作用下氧化能力强，可以对多种难处理的有机物进行有效的氧化降解，但国内主要报道了用该试剂处理实验室模拟的含酚或者含醛废水，对实际工业酚醛废水的处理研究较少，对酚醛废水有机物氧化降解途径的探究也不够详细，而且废水处理的操作方法复杂，效果并不显著。本文采用芬顿/紫外法（Fenton/UV）处理了 COD 高达 3 万~5 万 mg/L 的高浓度工业酚醛废水，并与其他方法相结合，研究了联用法的处理效果。具体的工作内容如下：

1. 采用 Fenton/UV 氧化高浓度的工业酚醛废水，通过两次正交试验，确定了各因素的较优水平，即 pH=3、H_2O_2 溶液投量为废水体积的 20%、Fe^{2+}与 H_2O_2 的摩尔比为 1:7、紫外光照射时间为 30min。研究了 H_2O_2 添加量、pH 值、光照时间单因素变量对 Fenton/UV 处理效果的影响，发现提高 H_2O_2 投量能提高 COD 去除率；当 pH=3 时，氧化效果较为理想，COD 去除率为 84.1%；光照 30min 时，去除率可达 90.1%。当 H_2O_2 投量较低时，引入紫外光和超声均能提高 COD 去除率，与这两者同时联用时，COD 去除率可达 93.0%。

2. 首次同时采用紫外-可见分光光度法、红外光谱法（FT-IR）和核磁共振波谱法（^{1}H-NMR）表征反应前后的废水以及沉淀物，提出了 Fenton/UV 氧化酚醛废水有机物的路径。即在充足的·OH 作用下，苯环侧链碳上的 H 被·OH 夺取，形成苄自由基，进而发生羧基化，极性增大导致大部分苯环开环，形成小分子化合物，最后被彻底氧化成 CO_2 和水，COD 大幅度降低。

3. 对酚醛废水进行碱化缩合处理，生成了交联型的 Resole 树脂，COD 降低了 12.2%。以聚丙烯酰胺（PAM）为絮凝剂，发现添加微量的聚丙烯酰胺就能发挥良好的絮凝效果，且阳离子型 PAM 与酚醛树脂产生更牢固的结合。采用碱化-PAM 絮凝-Fenton/UV 处理废水，COD 去除率稳定在 70%左右，在研究的范围

内，PAM 添加量和类型对絮凝效果和 COD 去除率无显著影响。以聚合氯化铝铁（PAFC）为絮凝剂，絮凝沉淀量大，提高 PAFC 添加量能提高 COD 的去除率，当 PAFC 添加量为 1.0%时，COD 去除率为 25%。碱化缩合-PAFC 絮凝-Fenton/UV 处理优于 Fenton/UV 的单独处理效果，COD 去除率可达到 94%左右。PAFC 比 PAM 更适合作为酚醛废水的絮凝剂。

4. 在酸性条件下，用高锰酸钾直接氧化酚醛废水，当 $KMnO_4$ 投量为废水质量的 1.1%时，废水的 COD 去除率可达到 36.5%，但废水依然含有苯环等共轭结构有机物；酚醛废水经过碱催化缩合-PAFC 絮凝-Fenton/UV 处理后，大部分有机物已被降解，$KMnO_4$ 能继续氧化废水中残余的微量有机物，使体系的 COD 进一步降低。

5. 本文的研究表明，碱化缩合-PAFC 絮凝-Fenton/UV 氧化-高锰酸钾酸性氧化的联用是处理酚醛废水的最佳方法，COD 去除率可达到 98.7%，化学需氧量最终降到 391mg/L，水质达到安全排放要求，迄今未见用该法处理高浓度工业酚醛废水并使之达到安全排放的报道。

关键词：酚醛废水；化学需氧量；Fenton/UV 氧化法

Abstract

With the advantages of excellent comprehensive performance and low cost, phenolic resin is widely used with high yield. However, during the process of phenolic resin production, A large amount of high concentrated wastewater is also produced, components of which are very complex, containing both phenols and aldehydes, and the chemical oxygen demand (COD) can reach as high as tens of thousands milligrams per liter. What's worse, the wastewater will do great harm to the environment if directly discharged without any pretreatment. The oxidizing ability of Fenton reagent composed of H_2O_2 and Fe^{2+} is strong enough to degrade most of organic compounds. But the domestic research mainly focuses on treating the stimulated wastewater which contains phenol or aldehyde by Fenton oxidation, less on the treatment of actual industrial wastewater containing both phenols and aldehydes. Most of the water treatment methods are complex and the effects are far away from satisfaction. The oxidation mechanism of Fenton reagent treating phenolic wastewater has not been detailed.

In this paper, high concentrated industrial wastewater containing phenol and aldehyde was treated by Fenton reagent combining with ultraviolet light to reduce the chemical oxygen demand effectively. Not only the influencing factors of oxidation effect but also the degradation mechanism of Fenton/UV treatment was proposed. At the same time, the treatment outcome of Fenton/UV oxidation combined with other methods was also discussed. The specific contents are as follows:

1. The optimal level of each factor in the Fenton/ultraviolet light experiment was determined after twice orthogonal experiments, i.e. the pH value was 3，the amount of H_2O_2 solution was 20 percent, the mole ratio of Fe^{2+} to H_2O_2 was 1 to 7 and the UV exposure time was 30 minutes. It could also be found that the COD removal rate was improved by increasing the dosage of H_2O_2. When the pH value was 3.0, the treatment result was good and the COD removal rate was 84.1%. When the UV exposure time was 30 minutes, the COD removal rate could reach 90.1%. When the

dosage of H_2O_2 was low, the COD removal rate was obviously enhanced by combining Fenton treatment with ultrasound and ultraviolet light irradiation, and the COD removal rate could reach more than 90%.

2. The oxidation pathway of Fenton/UV treatment was studied through analyzing the ultraviolet absorption spectrum of the wastewater as well as the infrared spectrum and ^{1}HNMR of the sediment, i.e. when the hydroxyl free radicals were sufficient, it would firstly capture hydrogen from a side chain of benzene ring with the formation of benzyl radical compound. Then the benzyl radical compound was oxidized and turned into benzoic acid, most of the benzene rings could be opened and degraded into small molecules. At last, those small molecules were completely oxidized into carbon dioxide and water, thus the COD was substantially decreased.

3. A lot of floc named cross-linking resole phenolic resin was generated when the pH value of the wastewater was adjusted to 8~9 and the COD removal rate was 12.2%. Polyacrylamide played an efficient flocculation performance even though the amount was small, and the cationic polyacrylamide could combine with phenolic resin more firmly than that of other types. The COD removal rate was stabilized at 70% when the wastewater was treated with the alkaline condensation-PAM flocculation-Fenton/UV method, the amount and types of PAM had no significant effect on the result. An inorganic flocculant named polyferric aluminum chloride (PAFC) could also promote the precipitation of phenolic resin. The COD removal rate was enhanced by increasing the amount of PAFC. When the amount of PAFC was 1.0%, the COD removal rate was 25%. The effect of condensation - PAFC flocculation - Fenton/UV treatment was better than that of Fenton/UV treatment, and the COD removal rate was 94%.

4. The COD removal rate was 36.5% when the wastewater was treated by the oxidation of potassium permanganate ($KMnO_4$) in acidic condition with a dosage of 1.1%, but the compounds with conjugate structure still existed. After condensation - PAFC flocculation - Fenton/UVtreatment, most of the organic compounds had been wiped out. The wastewater was further treated by $KMnO_4$ under either acidic or alkaline condition. $KMnO_4$ could continue to oxidize the residuals.

5. Overall, the best way to treat the high concentrated industrial wastewater containing phenol and aldehyde was the alkaline condensation-PAFC flocculation - Fenton/UV oxidation-$KMnO_4$ oxidation method under acidic condition, the COD removal rate could reach 98.7%, and eventually the COD of the wastewater was only 391mg/L, meeting the discharging standard, which had not been reported before.

Keywords: phenolic wastewater; chemical oxygen demand; Fenton/UV oxidation method