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Enhanced-Fenton Process for Degradation of Wastewater Containing Energetic Compounds

LIU Zuo-hua¹, ZHOU Xiao-xia², DU Jun¹, LIU Ren-long¹, TAO Chang-yuan¹

(1. College of Chemistry & Chemical Engineering, Chongqing University, Chongqing 400030, China;

2. Chemistry Staffroom, Third Military Medical University, Chongqing 400038, China)

Abstract: The integrated Fenton and Fenton-like processes to improve the degradation efficiency were reviewed. Ultrasound and microwave assisted advanced oxidation processes for decontamination of organic wastewater were described. The transition metal ions in the wastewater or oxides in the clay, zero valent iron, fly ash, etc, could be used as the alternative catalysts for Fe^{2+} and generate hydroxyl radical to degrade the energetic compounds. The competitive purification process in cost for energetic material wastewater could be developed by integrated processes and enhanced Fenton processes.

Key words: environmental chemistry; Fenton; ultrasound; microwave; energetic material; Fenton-like

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1 Introduction

The current technologies for removal of the wastewater containing energetic materials, such as TNT, RDX, HMX, include open-air incineration, alkaline hydrolysis, anaerobic process, adsorption on carbon beds and advanced oxidation^[1]. But these methods are often capital and energy intensive, and can produce secondary pollution. In recent research, Desmare Gabriel W et al^[2] studied DMSO/base hydrolysis method for the disposal of high explosives and related energetic materials. Harra-dine D M et al^[3] described the destruction of explosives and rocket fuel components by oxidation in supercritical water. Qadir Lala R. et al^[1] reported that ultrasound can degrade the energetic compounds RDX and ADN in aqueous microheterogeneous media. Research results indicated that the destruction efficiencies were low and the cost for the decontamination was not acceptable. In munitions-manufacturing plants, granular activated carbon (GAC) is used widely, but it is costly for regenerating the spent GAC. While biological processes (e. g. activated sludge) are not effective for energetic material purifica-

tion for nitro group in the molecular inhibit the enzymes. Now, advance oxidation processes (AOPs), which belong to chemical oxidation processes, are regarded as potential treatment alternatives for this wastewater. Up to now, Fenton oxidation process, i. e., oxidation by hydroxyl radical generated by reaction of H_2O_2 and Fe^{2+} , is a common advanced oxidation process for degrading persistent organic pollutants^[4].

2 Degradation of energetic compounds by Fenton reagent

Fenton reagent is a typical advanced oxidation process for mineralization of a wide range of organic compounds. Zoh Kyung-Duk et al^[5] studied oxidation of the high explosives RDX and HMX using Fenton's reagent at 20 - 50 °C and pH 3. At a $\text{H}_2\text{O}_2 : \text{Fe}^{2+} : \text{RDX}$ molar ratio of 5178 : 48 : 1, RDX and HMX were effectively mineralized with Fenton's reagents in 1 - 2 h. Results indicated that the experimental data was fit to a pseudo 1st-order rate equation and the reaction rate was also strongly dependent on Fenton's reagent concentrations. WU Yao-guo et al^[6] analyzed and compared different advanced oxidation processes following hydrogen peroxide, ozone oxidation and Fenton oxidation for treatment of wastewater contaminated by explosives. Although the Fenton process could degrade the pollutants in a short period, disadvantages were formation of new byproducts and low efficiency^[7].

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Biography: LIU Zuo-hua(1973 -), male, PhD, engaged in microwave chemistry and environmental chemistry research. e-mail: liuzuohua@cqu.edu.cn

3 Enhanced Fenton process

3.1 Zero valent iron enhanced Fenton process

For the last decade, zero-valent iron has been used to degrade oxidized pollutants through reductive transformation. Cast iron is often the material of choice for environmental applications because it is inexpensive and readily available commercially. Reductive iron treatment generally has low maintenance cost because of the passive nature of the process. In addition, iron corrosion in water does not generate toxic products. Several studies have shown that zero-valent iron is capable of removing TNT and RDX from solution^[8-9]. And because of the nitro group in the explosive molecules, the reaction by hydroxyl radical will be hindered. To eliminate the hindrance of oxidation, Oh S Y et al^[8-10] studied the transformation of nitro group into in-explosive molecules by elemental iron. Results showed that TNT and RDX were reduced with elemental iron to products that were oxidized more rapidly and completely by Fenton's reagent. Iron pretreatment enhanced the extent of total organic carbon (TOC) removal by approximately 20% and 60% for TNT and RDX, respectively. Complete TOC removal was achieved for TNT and RDX solutions with iron pretreatment under optimal conditions. The bench-scale iron treatment-Fenton oxidation integrated system showed more than 95% TOC removal for TNT and RDX solutions under optimal conditions.

3.2 Photo enhanced Fenton process

Photo catalytic process by ultraviolet or sunlight is to improve the oxidation reaction efficiency. Dillert Ralf et al^[11] investigated light-induced degradation of nitroaromatic compounds in aqueous systems and compared titanium dioxide photocatalysis with photo-Fenton reactions. It showed that reaction rates were always higher in the photo-Fenton reaction than that in TiO₂-mediated photocatalytic reactions in heterogeneous systems. Liou Mingjer et al^[12] used Fenton process to explore the possibility of treating explosives, TNT, RDX and HMX by photo-Fenton process and Fenton process respectively. Results indicated that degradation of the explosives obeyed a pseudo-1st-order behavior. For all explosives, the oxidation rates significantly increased with increasing the concentration of Fe(II), as well as illumination with UV light.

3.3 Fenton-like process

Although H. J. H. Fenton himself used the unformulated Fe²⁺/H₂O₂ mixture in acidic aqueous solution when he first recorded the oxidative potential of this mixture in 1876, many modifications have since been applied in order to alter the reactivity, to enhance the solubility in other solvents, to increase the pH range, and to avoid precipitation of the metal catalyst. This has led to a great variety of coordinated iron(II) complexes in combination with H₂O₂ (or HOCl) or even with different transition metals, such as Mn(II) or Fe(III), which are all often referred to as Fenton-like reagent.

Alexandrova A. et al^[13] studied the effects on ·OH-provoked degradation of deoxyribose in the presence of different metal ions Fe³⁺ and Cu²⁺. The different effects of Fe³⁺, Cu²⁺ and their EDTA complexes were expressed clearer in Fenton (Fe³⁺/ascorbic acid/H₂O₂) and Fenton-like (Cu²⁺/ascorbic acid/H₂O₂) systems generating hydroxyl radicals. Du Yingxun et al^[14] investigated the role of the intermediates in the degradation of phenolic compounds by Fenton-like process. Carrier Marion et al^[15] studied the influence of metal ions like Ni²⁺ and Cu²⁺, which were frequently present in agricultural wastewater, on the photocatalytic efficiency of TiO₂ in the elimination of Imazapyr. Malešic Jasna et al^[16] got the information of influence of halide and pseudo-halide antioxidants in Fenton-like reaction systems containing copper(II) ions.

Yip Alex Chi-Kin et al^[17] synthesized a heterogeneous Cu/clay catalyst by dispersing copper onto the surface of bentonite clay through chemical vapor deposition (CVD). To resolve the copper leaching problem during the catalyst's application in aqueous reaction, a critical pretreatment step, acid activation by H₂SO₄, was applied to the original bentonite clay. Such manufactured Cu/clay catalyst was characterized and evaluated in the photo-Fenton-like degradation of an azo organic dye, Acid Black 1 (AB1). It was found that the acid activation process of clay could significantly reduce the leaching problem by almost 72% and improve the catalytic activity. These improvements came from the active site and the addition of sulfonate functional group on the clay surface. It is also observed that the adsorption and desorption properties of the Cu/acid-activated clay play an important

role in the catalytic reaction and that its catalytic performance is better than Fe/clay at pH 7 and 9. It also has a comparable activity to that of Fe/clay at pH 3. This advantage increases the potential of the catalyst in the treatment of organic contaminated wastewater. The optimum reaction conditions in a 1 L reactor equipped with 8 W UVC light were detected to be 0.1 mM AB1, 6.4 mM H_2O_2 , 0.5 $\text{g} \cdot \text{L}^{-1}$ catalyst loading, pH 3, at ambient temperature of 30 °C. It was also found that splitting the required dosage of H_2O_2 could minimize the H_2O_2 scavenging effect and results in a higher total organic carbon (TOC) removal.

Watts Richard J et al^[18] studied the destruction of a dense nonaqueous phase liquid (DNAPL) by soluble Fe (III)-catalyzed and pyrolusite ($-\text{MnO}_2$)-catalyzed Fenton's reactions (H_2O_2 and transition metal catalysts) using CCl_4 as a model contaminant. In the system amended with 5 mM soluble Fe (III), 24% of the CCl_4 DNAPL was destroyed after 3 h while CCl_4 dissolution in parallel fill-and-draw systems was minimal, indicating that CCl_4 was degraded more rapidly than it dissolved into the aqueous phase. Fenton's reactions catalyzed by the naturally occurring Mn oxide pyrolusite were even more effective in destroying CCl_4 DNAPLs, with 53% degradation after 3 h. Although Fenton's reactions were characterized by hydroxyl radical generation, CCl_4 was unreactive with hydroxyl radicals. Therefore, a transient O species other than hydroxyl radicals formed through Fenton's propagation reactions was likely responsible for CCl_4 destruction. Results demonstrated that Fenton-like reactions in which nonhydroxyl radical species generated might provide an effective method for the in situ treatment of DNAPLs.

During the production of energetic materials, the wastewater may contain some heavy metal ions, which may come from the catalysts or the oxidants. From literature survey, these heavy metal ions, such as Co^{2+} , Cr^{6+} , Ni^{2+} , Mn^{2+} , may form Fenton-like reagent with hydrogen peroxide and generate hydroxyl to degrade POPs. So, the Fenton-like reagent is also capable of oxidizing organic substrates, but it is somewhat less reactive than Fenton's reagent. As iron (III) can be produced in applications of Fenton's reagent, Fenton chemistry and Fenton-like chemistry often occur simultaneously. Interestingly, Fenton and

Fenton-like chemistry are generally believed to proceed via similar mechanisms as oxidation reactions with the aforementioned complex and bulky enzymes^[19-22]. Hur Jung-Wook et al^[23] tested TNT as a representative explosive contaminant of concern in both aqueous and soil samples and its removal was evaluated using 3 different chemical treatment methods: (1) the classical Fenton reaction which utilizes H_2O_2 and solution Fe at pH < 3; (2) a modified Fenton reaction which utilizes chelating agents, H_2O_2 , and solution iron at pH 7; and (3) a Fenton-like process which utilizes iron minerals instead of solution Fe and H_2O_2 , generating a hydroxyl radical. Using classic Fenton reaction, 93% of TNT was removed in 20 h at pH 3 (soil spiked with 300 $\text{mg} \cdot \text{L}^{-1}$ TNT, 3% H_2O_2 and 1 mM Fe (III)), whereas 21% removed at pH 7. The modified Fenton reaction, using nitrilotriacetic acid (NTA), oxalate, EDTA, acetate and citrate as representative chelating agents, was tested with 3% H_2O_2 at pH 7 for 24 h. Results showed the TNT removal in the order of NTA, EDTA, oxalate, citrate and acetate, with the removal efficiency of 87%, 71%, 64%, 46%, and 37%, respectively, suggesting NTA as the most effective chelating agent. The Fenton-like reaction was performed with water contaminated with 100 $\text{mg} \cdot \text{L}^{-1}$ TNT and soil contaminated with 300 $\text{mg} \cdot \text{L}^{-1}$ TNT, respectively, using 3% H_2O_2 and such Fe minerals as goethite, magnetite, and hematite. In the goethite-water system, 33% of TNT was removed at pH 3, whereas 28% removed at pH 7. In the magnetite-water system, 40% of TNT was removed at pH 3, whereas 36% removed at pH 7. In the hematite-water system, 40% of TNT was removed at pH 3, whereas 34% removed at pH 7. For further experiments combining the modified Fenton reaction with the Fenton-like reaction, NTA, EDTA, and oxalate were selected with the natural Fe minerals, magnetite and hematite at pH 7, based on the results from the modified Fenton reaction. As results, in case magnetite was used, 79%, 59%, and 14% of TNT was removed when NTA, oxalate, and EDTA used, respectively, whereas 73%, 25%, and 19% removed in case of hematite, when NTA, oxalate, and EDTA used, respectively. Seo Seung-Won^[19] studied the Fenton-like reaction for 2,4,6-trinitrotoluene removal using three naturally occurring iron oxyhydroxides as the catalysts for the

Fenton's reaction. It was found that the removal of TNT from the artificially contaminated water was dependent on the catalyst and the system pH. Therefore, for overcoming these problems to apply at near neutral pH, the chelating agent was used to solubilize the iron at pH 7. Since the modification of Fenton-like reaction occurs at neutral pH, it would be a more applicable in situ remediation technology.

4 Development trend

Microwave (MW) and high-intensity ultrasound (US) have emerged as powerful techniques for the elimination of persistent organic pollutants (POPs) that constitute a major health hazard, whether by direct exposure or through accumulation in biota. Ultrasound-Fenton and microwave-Fenton processes are two alternatives to completely mineralize the energetic waste into CO_2 , H_2O and smaller amounts of inorganic ions, or at least converted to less harmful chemical species.

4.1 Ultrasound-modified Fenton process

Ultrasound has the cavitation effect on the reactant and contributes to the degradation of organic pollutants. Qadir Lala R. et al^[1] studied the sonochemically induced decomposition of energetic materials in aqueous media and found that sonochemical treatment in the presence of a reduction reagent offered an effective waste remediation option. Sierka Raymond A.^[24] reported TNT and RDX containing munitions manufacturing wastewaters were effectively treated by ultrasound and ozonization. Removal rates increased with reaction temperature and initial solution pH value. Although increased ultrasound power input enhanced system kinetic responses (due to temperature increases), ultrasound at high temperature and pH inhibited reaction kinetics due to the promotion of radical-radical extinguishing reactions. TAO Chang-yuan et al^[4] found that ultrasound can improve the Fenton reagent for the degradation of methyl orange solution by supplying hydroxyl radicals more efficiently. Liang Jun et al^[20] got the improvement performance in sonochemical degradation of 4-chlorophenol by combined use of Fenton-like reagents, i. e., three kinds of solid Fe-containing catalysts, namely iron powder, basic oxygen furnace (BOF) slag and mill scale.

4.2 Microwave-modified Fenton process

Microwave (MW) heating has the thermal and non-thermal effect, which can improve the reaction rate enormously. Research results indicated that microwave of (2450 ± 50) MHz could be used to initialize some secondary explosives such as PETN, RDX, HMX, and TNT without primary explosives^[25-26]. Cartier Jean Pierre et al^[27] studied the disposal of wastes from explosive manufacturing by microwave heating. In the meanwhile, during the last two decades, microwave irradiation has widely been applied in domestic, industrial and medical fields. The applications of microwave energy to enhance chemical reactions are well known. Ai Zhi-hui et al^[28] reported that microwave could enhance the efficiencies of several advanced oxidation processes on the degradation of 4-chlorophenol. TAO Chang-yuan et al^[29] studied microwave assisted wet hydrogen peroxide oxidation method for the decomposition of azo dyes wastewater simulated by dilute methyl orange. Results showed reaction rate for decoloration was improved effectively and good COD removal ratio was obtained. Sanz J. et al^[30] compared Fenton's reagent and microwave irradiation for the treatment of synthetic phenol solutions ($100 \text{ mg} \cdot \text{L}^{-1}$) and of an industrial effluent containing a mixture of ionic and non-ionic surfactants at high load ($20 \text{ g} \cdot \text{L}^{-1}$ of COD) respectively. Results indicated that the oxidation by Fenton's reagent was dependent on the pH, contrary to the microwave system, which is not influenced by this parameter. Han Do-hung et al^[31] found that 2.5 GHz of microwave irradiation could cause a considerable improvement of oxidative decomposition of aqueous phenol in a UV/ H_2O_2 system even under a suppression of thermal effect. JIANG Qi-guang et al^[32] treated fumaric acid wastewater by microwave radiation in the presence of activated C and Fenton agent. Results showed that under the optimal conditions COD of the wastewater was decreased from $300 \text{ mg} \cdot \text{L}^{-1}$ to $96.2 \text{ mg} \cdot \text{L}^{-1}$. LU Min-chun et al^[33] compared the photocatalysis, microwave catalysis, and thermal catalysis during oxidation of 100 mL of $1 \text{ g} \cdot \text{L}^{-1}$ methyl orange solution with 1 mL of 30% H_2O_2 in the presence of 0.7 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Experimental results indicated that the COD removal rate of methyl orange by microwave catalysis for 18 min reached 90.1%, while that by thermal ca-

talysis was only 73.5% , so microwave catalysis was obviously better than thermal catalysis. The color removal rate of methyl orange with low concentration by microwave catalysis for 3 min was nearly 100% while photocatalysis took 30 min to make 100% of removal rate, so microwave catalysis was obviously better than photocatalysis. After being pretreated with Fe-C and microwave catalysis, the COD of the wastewater from dyestuff, coke and refinery plants, and restaurants reached the second grade of National Discharge Standard. Cravotto G et al^[34] found that under US or MW irradiation, rapid degradation of aromatic halides, halogenated phenols and polychlorinated biphenyls in polluted waters was achieved at neutral pH in the presence of a moderate excess of Fenton's reagent. Acidification with acetic acid (pH 2.0 – 2.3) did not affect the process, but sulfuric acid (pH 1.7 – 2.0) facilitated complete degradation. Compared to conventional methods, US and MW combined Fenton processes were faster and much more efficient. TAO Chang-yuan et al^[35–36] studied the degradation of persistent organic pollutants by Fenton-like reagents irradiated by microwave. All the research was carried out experimentally and it is long way to the industrial application^[37].

5 Conclusions

Although Fenton reagent is limited by its instability and production of sludge, etc, Fenton-based reactions are capable of extensively degrading organic wastewater containing energetic compounds and they perform favorably when compared to other hydroxyl radical-generating advanced oxidation processes. The combined Fenton processes and Fenton-like processes enhanced with ultrasound or microwave may overcome the drawbacks of Fenton reagent. To choose cheap catalyst, especially the transition metal ions in the wastewater to form Fenton-like reagent, will improve the cost effectiveness. There is a long way to go for industry application of these integrated processes and enhanced Fenton oxidation processes. Large-scale and long-term evaluation of these modified Fenton processes for decontamination of energetic wastewater will be needed to allow better cost comparison of the other technologies.

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强化 Fenton 法降解含能材料废水的研究

刘作华¹, 周小霞², 杜军¹, 刘仁龙¹, 陶长元¹

(1. 重庆大学化学化工学院, 重庆 400030; 2. 第三军医大学基础部化学教研室, 重庆 400038)

摘要: 综述了能提高废水处理效率的 Fenton 组合工艺和类 Fenton 处理方法, 并对超声波和微波辅助高级氧化技术处理有机废水进行了介绍。在高级氧化技术中, 废水中的过渡金属离子、还原性铁粉、粉煤灰等可以作为 Fenton 试剂中替代亚铁离子的催化剂, 这些催化剂能与过氧化氢形成类 Fenton 试剂, 产生羟基自由基, 以降解含能材料废水中的难生物降解有机物。组合工艺和 Fenton 强化方法的开发将为降低含能材料废水处理成本提供成本优势。

关键词: 环境化学; Fenton; 超声波; 微波; 含能材料

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