Wastewater Treatment by Enhanced H$_2$O$_2$ – Based Advanced Oxidation Process (AOP) Methods: A Review

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Abstract. The development of industries leads to large amount of organic wastewater that contains phenol and dyes. For the treatment of these pollutants, the applications of H$_2$O$_2$ based – AOP have advantages in less pollution, low costs and high efficiency. In order to promote the degradation effect of H$_2$O$_2$, researchers used several methods to strengthen the effect of H$_2$O$_2$ based – AOP. This article mainly reviews the development of catalysts of the strengthened Catalytic Wet Hydrogen Peroxide Oxidation (CWPO), Fenton-like and other assistant-H$_2$O$_2$ systems in the degradation of phenol and dyes recent years. Challenges and development directions concerning catalysts in the future are discussed.

Keywords: H$_2$O$_2$, advanced oxidation process, phenol, dyes.

1. Introduction

The dramatic development of organic synthesis leads to increasing concentration of organic pollutants in wastewater in recent years. These pollutants, especially phenols and dyes, have characteristics of toxicity and water – solubility. Due to these properties, when they are put with wastewater into the water system, the accumulation of toxic compounds in the eco-system will be harmful to not only marine animals but humans’ safety. Therefore, it is necessary to find efficient and commercial methods to degrade the toxic pollutants in wastewater from dyes industries. Typical ways to remove the pollutants includes physical methods, chemical methods and biochemical methods.

Physical methods mainly contain UV light illumination, ultrasonic degradation[1] and absorption[2]. However, using single physical methods cannot easily get high removal of organic pollutants. This is because the pollutants are transformed into another phase, which needs an additional treatment for complete degradation.

Biochemical methods include the using of enzyme[3] and bacteria to assist chemical reactions, but enzyme and microorganisms cannot singly degrade dyes. Biological means have their economic advantages, but the applications are limited by pH, temperature, light, concentration of chemical reagents and other surrounding conditions. Also, the limitation of microorganisms is that the difficulty of decomposition of organisms that have large molecular weight.

Chemical methods contain the use of advanced oxidation process (AOP), which contains the use of peroxide oxidation (H$_2$O$_2$). Fenton and Fenton-like reactions, the Catalytic Wet Hydrogen Peroxide Oxidation (CWPO) and other systems of H$_2$O$_2$ can be included in this kind of ways. Among these methods, CWPO can be defined as the oxidation reaction of organic matters (or inorganic matters) by peroxide oxidation with catalysts which mainly occurs in aqueous solutions[4]. The advanced
oxidation process (AOP) has advantages because it can be widely used in different conditions. The relatively convenient obtaining way and low price of H$_2$O$_2$ result in good development potential that the H$_2$O$_2$-based AOP has. Studies have proved that using H$_2$O$_2$-based AOP to degrade organic pollutants such as dyes and phenols has great experimental results [5].

The studies in recent years about this kind of methods mainly focus on how to increase the effect of the process using H$_2$O$_2$ as oxidant to degrade organic pollutants. Adding chemical Synthetic catalyst, using UV or microwave and agents can significantly rise the efficiency of H$_2$O$_2$. This paper reviews the development of agents that promote the effect of AOP in H$_2$O$_2$ system. It classifies and summarizes the studies about this kind of method, expecting to provide reference for the research in this field.

2. Catalytic Wet Hydrogen Peroxide Oxidation (CWPO) for the degradation of dyes and phenol

To date, CWPO have been used widely the degradation of dyes and phenol. Herein, we have searched through most current researches to summarize the different CWPO methods in degradation dyes and phenol and discussed their degradation efficiency.

Kunjachan et al. used Zr$_x$Ce$_{1-x}$O$_2$ (x: 1, 0.75, 0.5, 0.25, 0) nanocatalysts to assist the oxidation (CWPO) of 4-chlorophenol (4-CP), 2,4- dichlorophenol (2,4-DCP) and 2,4-dichlorophenoxy acetic acid (2,4-D) to abate non-biodegradable organic wastewater pollutants [6]. The stability of structure, reuse and recovery ability of catalysts was studied. This kind of nanocatalysts was prepared from cerium (III) nitrate hexahydrate and zirconium (IV) oxynitrate precursors by the method of

![Figure 1. COD removal of CWPO of (a) 500 mg/L 4-CP with 0.13 mol/L H$_2$O$_2$ (b) 250 mg/L 2,4-DCP with 0.1 mol/L H$_2$O$_2$ (c) 250 mg/L 2,4-D with 0.1 mol/L H$_2$O$_2$ over Zr$_x$Ce$_{1-x}$O$_2$ (x = 1, 0.75, 0.5, 0.25, 0) composite oxides (500 mg/L) at 70 °C.](image)
coprecipitation. The increasing proportion of Zirconium in nanoceria lattice increases activity of catalysts. At 70°C, using Zr0.75Ce0.25O2 catalyst, 4-CP (500mg/L) was removed after 75min with the decrease of 14.9% Total Organic Carbon (TOC) and 45.8% Chemical Oxygen Demand (COD). For Zr0.5Ce0.5O2 catalyst, 2,4-DCP (250mg/L) was removed after 75 min with the decrease of 22.5% TOC and 52.8% COD. At 70°C after 90 min, the catalytic oxidative conversion of 2,4-D (250mg/L) reached 100%, with the increasing removal of TOC and COD. From the observed result, the chemical interaction of zirconium species and ceria in the catalysts improved the reducibility of Ce-Zr mixture. The stability and reusing ability of this kind of catalysts was guaranteed by the result of X-ray diffraction (XRD) and surface area measurements.

Samoila et al. added lanthanum, gadolinium and dysprosium cations into cobalt ferrites to degrade Rhodamine 6G-(Rh6G), making the catalyzing of wet hydrogen peroxide oxidation (CWPO) more effective[7]. After adding cobalt ferrites, the degradation rate of Rh6G had a dramatic rise from 35.7% to 92.8% in 15 min. The adding of lanthanum increased TOC from 17% to 40%. These phenomenon were tested by the experiment of using CoFe2O4 and CoFe1.98RE0.02O4 (RE=La, Gd and Dy). For the sample with all rare-earth containing catalysts, the decolorization of Rh6G got over 90% in 15 min, while the control group using cobalt ferrite as catalyst had only 35.7% degradation rate of Rh6G. The stability of CoFe1.98Gd0.02O4 catalyst was confirmed by its constant 94% efficiency in five runs. Its activity had almost no loss.

He’s team found that the prepared catalysts of Cu-ZSM-5 could be used for the CWPO of phenolic degradation in a fixed bed reactor[8]. This kind of catalysts was formed by loading Cu, which provided the main catalytic ability, on ZSM-5. From the analysis, the preparing method, content of Cu, temperatur and flow rate had effect to degradation rate of phenol. The catalytic ability of Cu-ZAM-5 for the CWPO was promoted with the increase of temperature and the amounts of loaded Cu. For Cu-ZSM-5 with 6 wt% of Cu, the phenol could be completely degraded and the reduction rate of TOC reached 51% at 80°C. The efficiency of Cu-ZSM-5 (6%) changed slightly after 3 runs of CWPO.

CuO/γ-Al2O3 was prepared by impregnation to degrade three kinds of Azo dyes (Reactive Red 2BF, Methyl orange and direct green) in the CWPO process[9]. The molecules of dyes could be adsorbed on the surface or get into the active site of catalysts, and be oxidized by ·OH radicals. For MO among three dyes, both TOC and COD could reach 80%. The result from different dyes indicated that the reactive red had the highest degrading speed. This phenomenon resulted from the different structure of organic dyes.

Hosseini et al. studied for the CWPO of phenol catalyzed by ZnFe2O4 nano spinels[10]. The condition of 0.144 M of H2O2, 0.156g of the catalyst, T=70°C and 300 min of reaction time could lead to the highest degradation rate of phenol, which was 97%. The temperature was the most important among these factors.

3. Fenton - like method for the degradation of dyes and phenol

Another method used for promoted the efficiency of H2O2-based AOP methods in degradation phenol and dyes is the Fenton - like method.

For example, Bai et al. synthesized Fe3O4 magnetic nanoparticles (MNPs) to degrade MO by Fenton-like reaction[11]. When the concentration of MO and H2O2 were 100mg/L and 4.0mL/L, the dosage of Fe3O4 was 0.25g/L, pH=4.0, T=80 °C, the degradation rate of MO was more than 90%. This rate largely went over the process that didn’t have Fe3O4 with same conditions of other reagents (typical Fenton-like reaction). Using microwave could shorten the reaction time, which could let the degradation rate reach the level about 100% in the Fe3O4-H2O2 condition above. This result showed that this catalyst has high activity. The reusing ability was also confirmed by experiments of Fe-H2O2 system. Fe3O4 still had catalytic activity and the degradation rate remained >=99% in 6 runs.

Ge et al. used two-step calcination method to obtain g-C3N4/MgO nanosheets, which could be used to catalyze Fenton-like reaction to degrade organic pollutants from wastewater and dyes[12]. This process could be operated without light, external energy or toxic Fenton-like catalysts. Main reason of the high catalytic activity of this catalyst was the bonds between MgO and g-C3N4 in the catalyst that
could activate the production of hydroxyl radical from H₂O₂. From the result of experiments, it was easy to see that g-C₃N₄/MgO nanosheets performed better than g-C₃N₄/TiO₂ (a normal catalyst for degradation of dyes) in the degradation of MO. When there was 100mL of 20mg/L MO, 20mg of catalysts and 0.3mL of 30% H₂O₂, the degradation rate of MO in the test of g-C₃N₄/MgO could reach 95% after 4h regardless of light, while the degradation rate of MO in the test of g-C₃N₄/TiO₂ could not reach 20% after 4h in sunlight surroundings. In the dark side, g-C₃N₄/TiO₂ could not catalyze the reaction. Therefore, the key characteristic of g-C₃N₄/MgO nanosheets is its light-independent activity. This catalyst can also be used to degrade MB and RhB and have similar degradation effects, but the decolorization of RhB need more time than other tested organic pollutants.

Tian et al. synthesized Fe₃O₄ decorated multi-walled carbon nanotube (Fe₃O₄/MWCNT) to catalyze Fenton reaction of the degradation of phenol[13]. When the wt% of Fe₃O₄ was about 25%, the removal rate of phenol and COD could reach 99.20% and 58.09%. The test result showed that the decomposition rate of H₂O₂ could be improved by the increase of Fe₃O₄ content. This was because Fe₃O₄ NPs in nanocomposite could provide active sites, where H₂O₂ decomposed and produce e OH. The 25 wt% of Fe₃O₄ content was mainly resulted from the efficiency and relative costs.

4. Other assistant-H2O2 system for the degradation of dyes and phenol

Other assistant-H2O2 based AOP methods for the degradation of dyes and phenol mainly include the using of HCO₃- enzymes as assistance.

Xu et al. introduced a method called bicarbonate-activated hydrogen peroxide (BAP) to degrade the organic pollutants[14]. From the observation, the color of methyl blue (MB, a typical pollutant from textile industries) had almost no change with the use of H₂O₂ alone for 300 min. However, after adding both H₂O₂ and NaHCO₃ with the same condition (pH 8.2), the color fading performed fast in 10 min. Pre – preparation for reactants could lead to a better result (less than 10 min). There were 23% removal of TOC and 62% removal of COD. NaHCO₃ was also useful for target organic pollutants such as methyl orange (MO) and rhodamine B (RhB). When NaHCO₃ was used for degrade chlorophenols, the results showed that at 35°C, 4-CP was removed about 88% in 8h, and the chlorine atom in the organic matter were transferred to inorganic ions with low danger. From the study of mechanism, HCO₃⁻ and H₂O₂ can generate HCO₃⁻, which produces free radicals, for example, 'O₂ and O₂'. The strong ability of oxidation of these radicals can decrease the concentration of organic pollutants in waste water.

Li et al. reported the performance and mechanism of decolorization of organic dyes in Co²⁺ - HCO₃⁻ - H₂O₂ system[15]. In HCO₃⁻ atmosphere, Co²⁺ and MB could form complexes, which could catalyze H₂O₂ into ·OH radicals. Researchers set conditions: Co²⁺ 10 μM, NaHCO₃ 10 mM, H₂O₂ 10 mM, MB 17.7 μM. The analysis showed that the removal of TOC and COD were around 19% and 42% after 30 min, confirming that good amount of carbon in MB had been transformed into intermediates with low pollution. Reactive brilliant red (X-3B) had the highest degradation rate among tested pollutants in similar conditions (decoloration time: 3 min). However, this kind of catalysts have little influence toward p-nitrophenol (PNP) and 2,4-dinitrophenol (DNP), which had little or almost no degradation after 60 min. The best pH for Co²⁺ - HCO₃⁻ - H₂O₂ system was 8.2. At 30°C, the stability of this system had unobvious changed after 4 cycles.

Min et al. researched the efficiency and mechanism of using the enzyme from Serratia marcescens AB 90027 as catalyst to degrade 4-aminophenol[16]. The researchers mainly analyzed four effecting factors during degradation process: time, the concentration of H₂O₂, temperature and ph. When adding 3mL H₂O₂, 40-60°C and pH between 9.0 and 10.5, the enzyme performed the best activity and the highest degradation rate could reach above 95% in 6h. From the analysis of the location of active enzyme, the main effective enzyme which could catalyze the degradation was extracellular enzyme.

5. Conclusions

This review summarizes that the strengthened H₂O₂ - based AOP has advantages in various fields. Preparing catalysts is a main method to enhance efficiency of degradation reaction of the CWPO and
Fenton-like methods. The activity of catalysts could be mainly formed by transition elements, such as Cu, Fe and Ce, while g-C3N4/MgO nanosheets catalytic activity has relation with the existence of MgO (and g-C3N4). Other main methods to increase the efficiency of H2O2 are adding HCO3- and using enzyme. Catalysts and enzyme have relatively low activity loss after several runs, which could reduce the cost of treatment. HCO3- has low cost in reactions and does not need to recycle, which reduce the processing cost.

Although these methods appear huge potential with impressive advantages in waste water treatment, more efforts are still needed in a few aspects. This is because the catalysts always perform as small particles to contact with reactants. This phenomenon results in the secondary pollution that needs more steps for treatment. Production process of large scale could be limited by it. So, this problem can be solved in the field of the preparation of catalysts, for example, membrane catalysts can be synthetized can applied in order to avoid the dispersion of particles of catalysts.

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