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A review on Fenton-like processes for organic wastewater treatment

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ABSTRACT

Fenton-like processes have been studied widely in recent years and are considered promising for organic wastewater treatment. Due to the demand for high efficiency wastewater treatment, a summary of the study status of Fenton-like processes is necessary to develop a novel and high efficiency organic wastewater treatment method. In this review, some important effect parameters (pH, H_2O_2 dosage, catalyst dosage, temperature) in hetero-/homo-geneous Fenton-like processes are discussed, and then the physical field/phenomenon-assisted hetero-/homo-geneous Fenton-like processes are presented. After that, catalyst types and the evaluation of wastewater treatment costs for various Fenton-like processes are summarized and discussed. Finally, possible future research directions and some guidelines for Fenton-like processes are given.

Contents

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1. Introduction

In recent years, advanced oxidation processes (AOPs) have been studied as a promising kind of organic wastewater (WW) treatment method based on the *in situ* generation of hydroxyl radicals ($HO^•$), which have a strong oxidation capacity (standard potential = 2.80 V *versus* standard hydrogen electrode) [1,2]. Under treatment by AOPs complex organic molecules can be either oxidized by $HO^•$ to smaller organics or completely mineralized to carbon dioxide (CO_2) and water (H_2O) [3–6]. Many organic WW treatment methods that are based on $OH^•$ generation can be called AOPs, such as $Fe(II)/H_2O_2$ [7], $Fe(II)/H_2O_2/UV$, ozonation (O_3) [8], O_3/H_2O_2 [9], H_2O_2/UV [10], hetero-/homo-geneous Fenton-like processes, TiO_2/UV [11], ZnO/UV [12], and some other processes involving the photo field, electric field, cavitation effect, microwave field, *etc.* [13].

One of the most frequently used AOPs is the Fenton process where Fe^{2+} is used as the catalyst and hydrogen peroxide (H_2O_2) as the oxidant. The mechanism of the Fenton process has often been described [14,15]. It has many advantages such as its high performance and simplicity (operated at room temperature and atmospheric pressure) for the oxidation of organics [16,17] and its non-toxicity [18] (H_2O_2 can break down into environmentally safe species like H_2O and oxygen (O_2)).

Based on the above advantages, the Fenton process has been applied to treat many kinds of WW such as olive-oil mill WW [19], textile WW [20], laboratory WW [21], pesticide WW [22], cosmetic WW [23], dye WW [24,25], fermentation brine from green olives [26], pharmaceutical WW [27], cork cooking WW [28], pulp mill effluents [29], and phenolic WW [30]. However, although the Fenton process has been studied widely and has performed well in the above WW treatments, it still has some disadvantages such as high operating cost, limited optimum pH range (always works best at around pH 3), large volume of iron sludge produced, and difficulties in recycling of the homogeneous catalyst (Fe^{2+}) [31]. Additionally, the required concentration range of the iron ion is 50–80 ppm for batch processes, which is clearly above the 2 ppm limit imposed by the European Union (EU) directives for direct discharge of wastewater into the environment [32].

In order to overcome these disadvantages, enhancement of the Fenton process has attracted much attention by researchers. Some other kinds of hetero-/homo-geneous catalyst (except for Fe^{2+}) were used to replace Fe^{2+}, including Fe^{3+} [33], Cu^{2+}/Cu^{+} [34], schorl [35], pyrite [36], and nano zero-valent iron [37]. These established systems are called hetero-/homo-geneous Fenton-like processes.

Furthermore, physical field(s)/phenomenon can also be used in both the classic Fenton process and hetero-/homo-geneous Fenton-like processes to enhance the WW treatment efficiency. The typical physical fields/phenomenon include the photo field, electro field, cavitation effect, and microwave field, which correspond to the photo-Fenton/Fenton-like processes [38–40], electro-Fenton-like processes [41–43], cavitation-Fenton-like processes [44–46], and microwave-Fenton-like processes [47,48], respectively, in both hetero- and homo-generous Fenton-like processes.

The basic difference between the homogeneous and heterogeneous Fenton-like processes involves the different positions where the catalytic reactions occur. In the homogeneous system, the catalysis process can occur in the whole liquid phase, while in the heterogeneous system the catalysis process always occurs on the surface of the catalyst. The position at which catalysis occurs in the heterogeneous system determines that the diffusion and adsorption processes of H_2O_2 and other reactants to the surface of catalyst could be significant for the catalysis process [49,50].

For the study of the Fenton-like processes mentioned above, various organics were chosen as target contaminants such as dyes [35,51], drugs [52–54], and pesticides [46]. Most of the above organic compounds present in the WW are refractory to biological treatment and toxic to aquatic organisms, even to human beings. The concentration range studied was always from hundreds of μg/L to hundreds of mg/L [38–56].

In recent years, some typical reviews [43–58] have been published regarding different aspects of the introduction of Fenton/Fenton-like processes. Pliego et al. [58], in their review, presented various methods that can enhance Fenton-like processes, such as radiation, electrochemistry, and heterogeneous catalysts; Bautista et al. [57] provided detailed information on the application of the Fenton process for the treatment of industrial WW. Brillas et al. [43] gave a profound introduction to the electro-Fenton processes and the related electrochemical technologies. In our review, the important effect parameters (pH, H_2O_2 dosage, catalyst dosage, temperature, etc.) are discussed in detail, and then the physical fields/phenomenon-assisted Fenton-like processes are presented. After that, a conclusion about the most suitable catalysts is made in the forth section and the costs of different Fenton-like processes are compared in the fifth section. Finally, recommended research directions for the future and some guidelines are given. The aim of this review is to discuss Fenton-like processes from aspects that are significant in the study of Fenton-like processes and were previously seldom considered but are valuable (such as the types of catalyst). We hope that this paper, based on the systematic introduction below, will provide valuable viewpoints and promote the development of Fenton-like processes.

2. Fenton-like processes

Fenton-like processes consist of heterogeneous and homogeneous Fenton-like processes. Heterogeneous Fenton-like processes can be established by replacing Fe^{2+} in the Fenton reagent with a solid catalyst, while homogeneous Fenton-like processes are due to a combination of other metal ion(s)/metal ion-organic ligand complexes and H_2O_2 [59]. In Fenton-like systems pH, H_2O_2 dosage, catalyst dosage, and reaction temperature have been studied widely because of their significant effect on the oxidation capacity of the Fenton-like reagent. Thus, the systematic introduction and analysis of these parameters is necessary.

2.1. pH

In Fenton-like processes pH is a highly important parameter for effective WW treatment. However, in the previous studies the researchers always reached different conclusions about the pH. In the heterogeneous Fenton-like processes some studies revealed that ~3 was still the best pH, while others showed that the neutral condition (even alkaline conditions) could achieve a better organic WW treatment efficiency. Yang et al. [51] and Xu et al. [35], from different research groups, applied magnetic NdFeB-activated carbon (AC) and schorl, respectively, to treat dye WW. Both of them observed that the organics in WW could be treated effectively under acidic condition (pH 3 (Fig. 1a) and 2–4,