

## A review on Fenton and improvements to the Fenton process for wastewater treatment

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### ABSTRACT

The increase in the disposal of refractory organics demands for newer technologies for the complete mineralization of these wastewaters. Advanced oxidation processes (AOPs) constitute a promising technology for the treatment of such wastewaters and this study presents a general review on such processes developed to decolorize and/or degrade organic pollutants. Fundamentals and main applications of typical methods such as Fenton, electro-Fenton, photo-Fenton, sono-Fenton, sono-photo-Fenton, sono-electro-Fenton and photo-electro-Fenton are discussed. This review also highlights the application of nano-zero valent iron in treating refractory compounds.

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### Introduction

The presence of many organic contaminants in wastewater, surface water and ground water may result from contaminated

soil, agricultural runoff, industrial wastewater and hazardous compounds storage leakage. The presence of these organic compounds in water poses serious threat to public health since most of them are toxic, endocrine disrupting, mutagenic or potentially carcinogenic to humans, animals and aquatic life in general. Many organic pollutants are considered as toxic and detrimental even when present at very less concentrations. For this reason, their removal from the contaminated water is of high priority. Consequently, the need for efficient treatment of these

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contaminants is imperative. In certain cases, conventional treatment methods such as biological processes are not effective due to the recalcitrant nature of the contaminants present [1,2]. Therefore, oxidation processes are preferred to degrade such organics present.

Direct oxidation processes are widely used to degrade bio-refractory substances. High degradation efficiencies are possible with direct oxidation techniques. However, pollution load, process limitations and operating conditions are the key factors to be considered during the selection of most appropriate oxidation process for a particular compound degradation. Apart from high degradation efficiency, direct oxidation processes demand specified operating conditions to degrade the target compounds and this will increase the operation cost of the process [3–7].

Advanced oxidation processes (AOPs) are alternative wastewater treatment processes, which are able to degrade biorefractory organic compounds. AOPs typically operate with less energy requirement than direct oxidation.

AOPs are near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to affect water purification [8]. The hydroxyl radicals are extraordinarily reactive species, which attack the most part of organic molecules with rate constants usually in the order of  $10^6$ – $10^9$  L mol<sup>-1</sup> s<sup>-1</sup> [9]. The versatility of AOPs is also enhanced by the fact that they offer different possible ways for hydroxyl radical production thus allowing a better compliance with the specific treatment requirements. The reduction potential of various oxidants is presented in Table 1. Hydroxyl radical is the second strongest oxidant preceded by the fluorine, and it reacts  $10^6$ – $10^{12}$  times faster than ozone depending on the substrate to be degraded [11].

AOPs are classified according to the reactive phase (homogeneous and heterogeneous) or hydroxyl radical generation methods (chemical, electro-chemical, sono-chemical and photochemical). The classification of conventional AOPs based on the source used for the generation of hydroxyl radicals is presented in Table 2. The processes involving combined conventional and non-conventional AOPs like photo-electro-Fenton and sono-electro-Fenton are presented. The non-conventional AOPs not presented in the table include ionizing radiation, microwaves and pulsed plasma techniques [12]. In addition, solar-irradiated processes were studied in order to decrease the costs associated with the use of light from non-natural sources [13]. However, the solar energy based processes have restricted applications in countries receiving less solar radiation.

A goal of the wastewater purification by means of AOP methods is the reduction of the chemical contaminants and their toxicity to such an extent that cleaned wastewater may be reintroduced into receiving streams or, at least, into a conventional sewage treatment.

**Table 1**  
Standard reduction potential of common oxidants [10].

| Oxidant  | Oxidation potential (V) |
|--|-------------------------|
| Fluorine (F <sub>2</sub> )                         | 3.03                    |
| Hydroxyl radical ( <sup>•</sup> OH)                | 2.80                    |
| Atomic oxygen (O)                                  | 2.42                    |
| Ozone (O <sub>3</sub> )                            | 2.07                    |
| Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> ) | 1.77                    |
| Potassium permanganate (KMnO <sub>4</sub> )        | 1.67                    |
| Chlorine dioxide (ClO <sub>2</sub> )               | 1.5                     |
| Hypochlorous acid (HClO)                           | 1.49                    |
| Chlorine (Cl <sub>2</sub> )                        | 1.36                    |
| Oxygen (O <sub>2</sub> )                           | 1.23                    |
| Bromine (Br <sub>2</sub> )                         | 1.09                    |

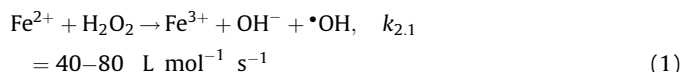
**Table 2**  
Classification of conventional AOPs.

| Type of process                                     | Example  |
|---|--|
| Homogeneous   | <i>Fenton based processes</i>  |
|   | Fenton: H <sub>2</sub> O <sub>2</sub> + Fe <sup>2+</sup>                                   |
|   | Fenton like: H <sub>2</sub> O <sub>2</sub> + Fe <sup>3+</sup> /m <sup>n+</sup>             |
|   | Sono-Fenton: US/H <sub>2</sub> O <sub>2</sub> + Fe <sup>2+</sup>                           |
|   | Photo-Fenton: UV/H <sub>2</sub> O <sub>2</sub> + Fe <sup>2+</sup>                          |
|   | Electro-Fenton   |
|   | Sono-electro-Fenton  |
|   | Photo-electro-Fenton   |
|   | Sono-photo-Fenton  |
|   | <i>O<sub>3</sub> based processes</i>   |
|   | O <sub>3</sub>   |
|   | O <sub>3</sub> + UV  |
|   | O <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>   |
| O <sub>3</sub> + UV + H <sub>2</sub> O <sub>2</sub> |  |
| Heterogeneous                                       | H <sub>2</sub> O <sub>2</sub> + Fe <sup>2+</sup> /Fe <sup>3+</sup> /m <sup>n+</sup> -solid |
|   | TiO <sub>2</sub> /ZnO/CdS + UV   |
|   | H <sub>2</sub> O <sub>2</sub> + Fe <sup>0</sup> /Fe (nano-zero valent iron)                |
|   | H <sub>2</sub> O <sub>2</sub> + immobilized nano-zero valent iron                          |

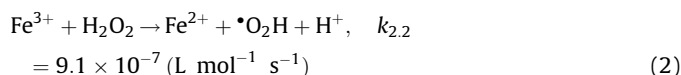
## Fenton process

Fenton (F) and related reactions encompass reactions of peroxides (usually hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)) with iron ions to form active oxygen species that oxidize organic or inorganic compounds. The Fenton reaction was discovered by H.J.H. Fenton in 1894 and he reported that H<sub>2</sub>O<sub>2</sub> could be activated by ferrous (Fe<sup>2+</sup>) salts to oxidize tartaric acid [14]. In the last few decades, the importance of <sup>•</sup>OH reactions has been recognized and over 1700 rate constants for <sup>•</sup>OH reactions with organic and inorganic compounds in aqueous solution have been tabulated [15]. In the recent past, Fenton reaction was efficiently utilized in wastewater treatment process for the removal of many hazardous organics from wastewater [16,17].

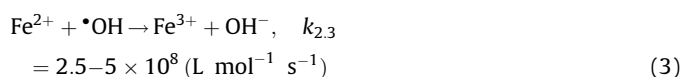
The traditionally accepted Fenton mechanism is represented by Eqs. (1)–(9) and its reaction rates were well reported in the literature [18]. Eq. (1) is recognized as Fenton reaction and implies the oxidation of ferrous to ferric ions to decompose H<sub>2</sub>O<sub>2</sub> into hydroxyl radicals. It is usually considered as the core of the Fenton chemistry. Furthermore, other reactions must be considered to understand the whole process:



The generated ferric ions can be reduced by reaction with excess hydrogen peroxide to form again ferrous ion and more radicals as shown in Eq. (2). This reaction is called Fenton-like reaction and slower than Fenton reaction, and allows Fe<sup>2+</sup> regeneration in an effective cyclic mechanism. In Fenton like reaction, apart from ferrous ion regeneration, hydroperoxyl radicals (<sup>•</sup>O<sub>2</sub>H) are produced. The hydroperoxyl radicals may also attack organic contaminants, but they are less sensitive than hydroxyl radicals. It should be noted that, the iron added in small amount acts as a catalyst while H<sub>2</sub>O<sub>2</sub> is continuously consumed to produce hydroxyl radicals.



The following reactions are involved in Fenton chemistry.



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