We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter

Advancements in the Fenton Process for Wastewater Treatment

Min Xu, Changyong Wu and Yuexi Zhou

Abstract

Fenton is considered to be one of the most effective advanced treatment processes in the removal of many hazardous organic pollutants from refractory/toxic wastewater. It has many advantages, but drawbacks are significant such as a strong acid environment, the cost of reagents consumption, and the large production of ferric sludge, which limits Fenton's further application. The development of Fenton applications is mainly achieved by improving oxidation efficiency and reducing sludge production. This chapter presents a review on fundamentals and applications of conventional Fenton, leading advanced technologies in the Fenton process, and reuse methods of iron containing sludge to synthetic and real wastewaters are discussed. Finally, future trends and some guidelines for Fenton processes are given.

Keywords: Fenton, Fenton-like, Fenton sludge, reuse, application

1. Introduction

The presence of many organic pollutants in wastewater, surface water, and groundwater may result from contaminated soil, agricultural runoff, industrial wastewater, and hazardous compounds storage leakage [1]. These organic pollutants, such as volatile phenols, benzene, and benzene derivatives, are considered highly toxic and low biodegradable. In some instances, conventional treatment methods such as biological processes are not sufficient to remove them. In order to improve water quality, advanced treatment is needed to remove the refractory organics.

Fenton is an effective advanced treatment process. The hydroxyl radical ($\cdot$OH) can be generated from the reaction between aqueous ferrous ions and hydrogen peroxide (H_2O_2), and it can destroy refractory and toxic organic pollutants in wastewater [2]. Fenton discovered the Fenton reaction in 1894, and he reported that H_2O_2 could be activated by ferrous (Fe^{2+}) salts to oxidize tartaric acid. However, its application as an oxidizing process for destroying toxic organics was achieved until the late 1960s [3]. Fenton was mainly used to treat wastewater by radical oxidation and flocculation. H_2O_2 is catalyzed by ferrous ions to decompose into HO$\cdot$ and to trigger the production of other radicals, which can fully oxidize organic matters. The hydroxyl radical ($\cdot$OH) has a strong oxidation capacity (standard potential = 2.80 V versus standard hydrogen electrode) [4]. Hydroxyl radicals can effectively oxidize refractory organic pollutants in wastewater and even completely mineralized them into CO_2, water, and inorganic salts [5]. Meanwhile,
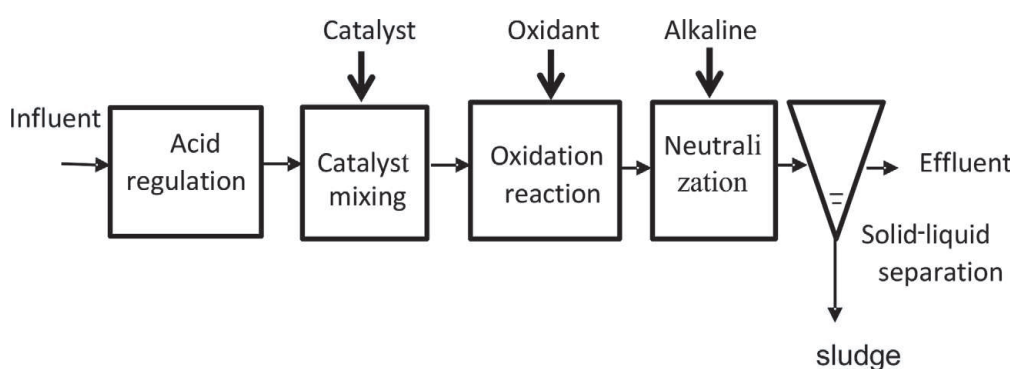
Figure 1.
Schematic diagram of the Fenton process.

the iron complex produced in the treatment of wastewater by Fenton will play the role of flocculant.

The conventional Fenton continuous flow process configuration, as illustrated in **Figure 1**, including acid regulation, catalyst mixing, oxidation reaction, neutralization, and solid–liquid separation. Fenton has many advantages, such as its high performance and simplicity (operated at room temperature and atmospheric pressure) for the oxidation of organics [6] and its non-toxicity [7] (H_2O_2 can break down into environmentally safe species like H_2O and O_2). However, Fenton also has some inherent disadvantages, which limit its application and promotion. For example, strict pH range, high H_2O_2 consumption, and the accumulation of ferric sludge that affects the oxidation efficiency [8, 9]. In order to overcome these disadvantages, the enhancement of the Fenton process has attracted much attention from researchers. Both heterogeneous and homogeneous catalysts were used to replace Fe^{2+}, including ferric oxide [10], iron minerals [11], and nano zero-valent iron [12].
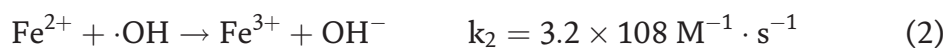
On the one hand, the loss of iron and the consequent sludge generation can be reduced by using reductant or transition metal, giving rise to a heterogeneous Fenton process. On the other hand, some external energy was introduced into the Fenton and Fenton-like processes to form photo-Fenton/Fenton-like processes [13, 14], electro-Fenton-like processes [15, 16], and so on [17, 18]. Hence, this work mainly summarizes the recent advancements in the Fenton process related to improving Fenton oxidation efficiency and minimizing sludge production. It also describes the main drawbacks and potential applications based on recent developments. Some recommendations are also stated in the Conclusions section.

2. Fenton process

Currently, two mechanisms have been proposed to explain the degradation of organic matters by Fenton reaction. One is the Harber-Weiss mechanism [19], which considered that active oxide species ·OH are generated to degrade organics in Fenton reaction. The other is the mechanism of high iron oxide intermediates, which was proposed by Bray and Gorin [20]. They suggested that the strong oxidizing iron substances (FeO^{2+}, FeO^{3+}) were produced in Fenton reaction, rather than ·OH. With the development of spectroscopy and chemical probe method, it is generally accepted that the formation of ·OH initiates the Fenton oxidation.

The traditionally accepted Fenton mechanism is represented by Eqs. (1)–(7) [21].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad k_1 = 63.5\,M^{-1} \cdot s^{-1} \qquad (1)$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^{-} \qquad k_2 = 3.2 \times 108 \ M^{-1} \cdot s^{-1} \qquad (2)$$

$$RH + \cdot OH \rightarrow H_2O + R \rightarrow \text{further oxidation} \qquad (3)$$

$$R \cdot + Fe^{3+} \rightarrow Fe^{2+} + R^{+} \qquad (4)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot OOH + H^{+} \qquad k_2 = 0.001\text{--}0.01 \ M^{-1} \cdot s^{-1} \qquad (5)$$

$$\cdot OH + H_2O_2 \rightarrow \cdot OOH + H_2O \qquad k_2 = 3.3 \times 107 \ M^{-1} \cdot s^{-1} \qquad (6)$$

$$\cdot OH + \cdot OH \rightarrow \cdot OOH + OH^{-} \qquad k_2 = 6.0 \times 109 \ M^{-1} \cdot s^{-1} \qquad (7)$$

According to the above equation, ferrous iron (Fe^{2+}) was rapidly oxidized to ferric ions (Fe^{3+}), while Fe^{2+} is regenerated from the so-called Fenton-like reaction between Fe^{3+} and H_2O_2 at a very slow rate. Equation (1) is usually considered as the core of the Fenton reaction.

The Fenton process is usually operated under the solution pH value of 3. The oxidation activity of $\cdot OH$ is related to the solution pH. The oxidation potential of $\cdot OH$ increases and the oxidation capacity is enhanced with decreasing pH [22, 23]. In addition, the activity of Fenton reagent is reduced with increasing pH due to the lack of active Fe^{2+}, in which the formation of inactive iron oxohydroxides and ferric hydroxide precipitate. Meanwhile, auto-decomposition of H_2O_2 appears at high pH [24].

At very low pH values, iron complex species $[Fe(H_2O)_6]^{2+}$ and stable oxonium ion $[H_3O_2]^{+}$ exist, which reduces the reactivity between Fe^{2+} and H_2O_2 [25, 26]. Therefore, the efficiency of the Fenton process to degrade organic compounds is reduced both at high and low pH. In addition, there are many competitive reactions in the Fenton reaction system. In Fenton oxidation, the reaction rate is dependent on the iron dosage, while the extent of mineralization is directly related to the concentration of oxidant.

It is important to understand the mutual relationships between Fenton reagent in terms of $\cdot OH$ production and consumption. These relationships were investigated and classified them into three categories according to the quantity of the $[Fe^{2+}]_0/[H_2O_2]_0$ ratio (initial concentration of Fe^{2+} versus initial concentration of H_2O_2) [27]. Their results showed that $[Fe^{2+}]_0/[H_2O_2]_0$ ratio and organics can affect the competition in Fenton reaction paths.

The main disadvantages for the application of the Fenton process are the relatively high cost of H_2O_2 and the high amount of ferric sludge produced in the neutralization step of the treated solution before disposal. These drawbacks and the more increasingly stringent water regulations are a challenge to develop solutions addressed to improve the Fenton technology. On one hand, the energy was introduced into Fenton to enhance the $\cdot OH$ generation, such as photo-Fenton, electro-Fenton, and so on. On the other hand, iron-based catalysts and reuse of Fenton sludge were developed as a Fenton-like reaction.

3. Enhanced Fenton process

3.1 Photo-Fenton process

The classic Fenton reaction efficiency was affected by the conversion rate from Fe^{3+} to Fe^{2+}. Recent methods have promoted the in situ circulation from Fe^{3+} to Fe^{2}. A combination of hydrogen peroxide and UV radiation with Fe^{2+} or Fe^{3+} oxalate ion [photo-Fenton (PF) process] produces more $\cdot OH$ compared to the conventional Fenton method [28]. The hydroxy-Fe^{3+} complexes after Fenton reaction mainly exists in the form of $Fe(OH)^{2+}$ at pH 2.8–3.5. The photochemical regeneration of Fe^{2+} by photo-reduction (Eq. (8)) of ferric Fe^{3+} occurs in the photo-Fenton

reaction. The newly generated Fe^{2+} reacts with H_2O_2 and generates $\cdot OH$ and Fe^{3+}, and the cycle continues:

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + \cdot OH \tag{8}$$
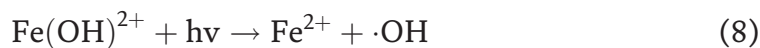
Direct photolysis of H_2O_2 (Eq. (9)) produces $\cdot OH$, which can be used for the degradation of organic compounds, and in turn increases the rate of degradation of organic pollutants [29].

$$H_2O_2 + hv \rightarrow 2 \cdot OH \tag{9}$$

However, photo-Fenton gives a better degradation of low concentration organic pollutants. Because the high concentration organic pollutants could reduce the absorb radiation of iron complex, which needs a longer radiation time and more H_2O_2 dosage.

Excess H_2O_2 can easily capture $\cdot OH$. In order to improve the efficiency of photo-Fenton, several organic ligands such as EDTA, EDDS, oxalate, and other organic carboxylic acid were added and complexed with Fe^{3+} under photocatalysis [29, 30]. The positive effects achieved by these ions can be attributed to the following aspects: (i) iron-ligands having higher ability compete for UV light in a wide wavelength range compared to other Fe^{3+}-complexes, and promoting the reduction of ferric ion to ferrous ion and accordingly, regeneration of higher amounts of $\cdot OH$, (ii) Promoting H_2O_2 activation and $\cdot OH$ radical generation, (iii) improving iron dissolution at pH 7.0, and (iv) operating over the broad range of the solar radiation spectrum [14].

Compared with the classic Fenton, photo-Fenton has many advantages. A photo-induced Fe^{3+}/Fe^{2+} redox cycle could decrease the dosage of catalyst in Fenton, which effectively reduce the formation of iron sludge [31–33]. Meanwhile, solar or UV light can increase the utilization of H_2O_2, and possess photolysis on several small molecule organics. However, photo-Fenton has many disadvantages, such as low utilization of visible light, the required UV energy for a long time, high energy consumption, and cost.

3.2 Electro-Fenton process

Electrochemical processes can be combined with Fenton processes (EF processes) during WW treatment to improve the Fenton processes. Fe^{2+} and H_2O_2 were produced by the electrochemical method as Fenton reagent. The electro-Fenton process follows the reaction shown below [34, 35], where H_2O_2 can be generated in situ via a two-electron reduction of dissolved oxygen on the surface of the cathode in an acidic solution when the electrochemical process is applied (reaction Eq. (10)).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{10}$$

Also, the produced ferric ion from Eq. (1) can be reduced to Fe^{2+} by electrochemical regeneration of Fe^{3+} ions on the cathode surface:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{11}$$

Water was oxidized to oxygen ta the anode (Eq. (12)):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{12}$$
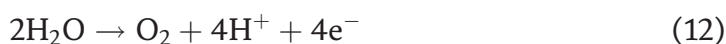
·OH was also generated at the surface of a high-oxygen overvoltage anode from water oxidation:

$$H_2O + H_2O_2 \rightarrow H^- + \cdot OH + e^- \tag{13}$$

Compared with tradition Fenton reaction, electro-Fenton has certain advantages, including (i) the production of H_2O_2 in situ via an electrochemical processes is beneficial for an increase in the organics degradation efficiency, a decrease in the cost, and a reduction in the risks associated with transportation; (ii) ferrous ion is regenerated through the reduction of ferric ions on the cathode, which reduces the production of iron sludge; and (iii) realizing the diversification of organics degradation pathway, such as Fenton oxidation, anodic oxidation, flocculation, and electric adsorption [36].

Electro-Fenton gives a better degradation of alachlor than the tradition Fenton. However, electro-Fenton processes have some problems with respect to H_2O_2 production. The production of H_2O_2 is slow because oxygen has low solubility in water and the current efficiency under reduced pH (pH < 3) is low. In addition, the efficiency of the electro-Fenton process depends on electrode nature, pH, catalyst concentration, electrolytes, dissolved oxygen level, current density, and temperature [37].

3.3 Sono-Fenton process

The combined treatment using ultrasound with Fenton reagent is known as sono-Fenton, which provides a synergistic effect on organic degradation [38, 39]. Ultrasound can enhance the Fenton's oxidation rate due to the generation of more ·OH caused by the cavitation within ultrasonic irradiation.

The physical effect of cavitation is the generation of intense convection in the medium through the phenomena of microturbulence and shock waves, whereas the chemical effect of cavitation is the generation of radical species, such as oxygen (·O), hydroperoxyl (·OOH), and ·OH through the dissociation of solvent vapor during transient collapse of cavitation bubbles [40]. On the other hand, Fe^{3+} continuously reacts with H_2O_2, according to Eq. (5). A part of Fe^{3+} after a Fenton reaction exists in the form of $Fe-OOH^2$. $Fe-OOH^2$ can be quickly decomposed into Fe^{2+} and ·OOH; thereby, the phenomenon promotes the Fe^{3+}/Fe^{2+} redox cycle [41]. In addition, ultrasound provides stirring and mass transfer effects to promote the diffusion of reactants in solution and improve the efficiency of Fenton reaction. However, sono-Fenton has some disadvantages, such as high cost and energy-intensive, so it is limited in practical application.

3.4 Fenton combined with other wastewater treatment technologies

The physical, chemical, and biological technologies have been widely used to treat wastewater. However, most of the real wastewater contains many organic pollutants with high toxicity and low biodegradability [42]. So that biological technologies are not enough. Moreover, the physical and chemical techniques are often effective for color, macromolecular organics, and suspended matter removal.

In order to improve the wastewater quality, advanced treatment needs the removal of refractory organics from the wastewater. In recent years, Fenton has been used to treat refractory wastewater by combining it with other wastewater-treatment technologies. The application of the Fenton oxidation process, as a pre-treatment, oxidizes refractory organics and improves the biodegradability, solubility, and coagulation, which are beneficial to the subsequent treatment.

Fenton was proved to be a feasible technique as the pre-oxidation for polluted pharmaceutical wastewater. Fenton as a pre-treatment process increased the BOD_5/COD value from 0.26 to 0.5, and also removed chloramphenicol, diclofenac, p-aminophenol, benzoic acid, and other toxic organics in the final effluent results from the Fenton-biological treatment processes [43].

Compared with biological treatment alone, Fenton-biological treatment processes improved COD removal [44]. Fenton combined with membrane filtration was also used to treat pharmaceutical wastewater. Although single nanofiltration (NF) and Fenton could effectively remove pharmaceutical active compounds, high organic load favored membrane fouling, and resulting in flux decline. The calcium salts were found to be the main fouling on the NF membrane surface. Fenton as the pre-treatment could ensure higher flux for the NF process. Also, the Fenton-NF system was found to be a promising method for wastewater from the pharmaceutical industry containing etodolac [45].

On the other hand, lime/unhair effluent, which contain highly loaded organic hazardous wastes, have been effectively treated by the Fenton-membrane filtration system at the pilot-scale [46]. Fenton was used also as a post-treatment of other treatment technologies for degrading residual organics, including physico-chemical and biological treatment. Compared with the aerobic sequencing batch reactor (SBR), SBR-Fenton could improve the TOC removal rate of textile wastewater up to 12% [47]. The solar photo-Fenton process was found to be an efficient process in removing phytotoxicity from Olive mill wastewater samples [48]. A COD and phenol removal as high as 94 and 99.8% could be achieved in coagulation/flocculation combined with the solar photo-Fenton system [48]. This combined technology, taking into account its reasonable overall cost, can be applied in somewhere with plenty of sunshine. Based on the technological and economic analysis performed, all combined treatment technologies will provide better performance than single treatment.

The Fenton process, combined with biological technologies, has shown quite low operational cost. The integrated Fenton-membrane processes were found efficient in removing organics from the industry wastewater. The phenolic compounds concentrated in the concentrate flow by membrane filtration could be recovered and further valorized in various industries. Although the combined Fenton and membrane technologies show the relatively higher overall cost of the combined membrane technologies, it is necessary to estimate the accuracy of the potential profit from the sale and valorization of these by-products recovered by this process.

4. The application of modified iron source as heterogeneous catalysts in Fenton reactions

The Fenton reaction in which iron salts are used as a catalyst is defined as a homogeneous Fenton process. Nevertheless, there are some disadvantages, including (i) the formation of ferric hydroxide sludge at pH values above 4.0 and its removal, (ii) difficulty in catalyst recycle and reuse, (iii) high energy consumption, and (iv) limitation of operating pH range. Therefore, the application of modified iron source as heterogeneous catalysts in Fenton reaction to overcome the shortcomings of homogeneous catalysis has been widely studied. Different heterogeneous catalysts have been used in Fenton reactions, including zero valent iron [49], iron pillared clays [50], and iron minerals [51]. **Figure 2** shows various types of heterogeneous Fenton-like catalysts.
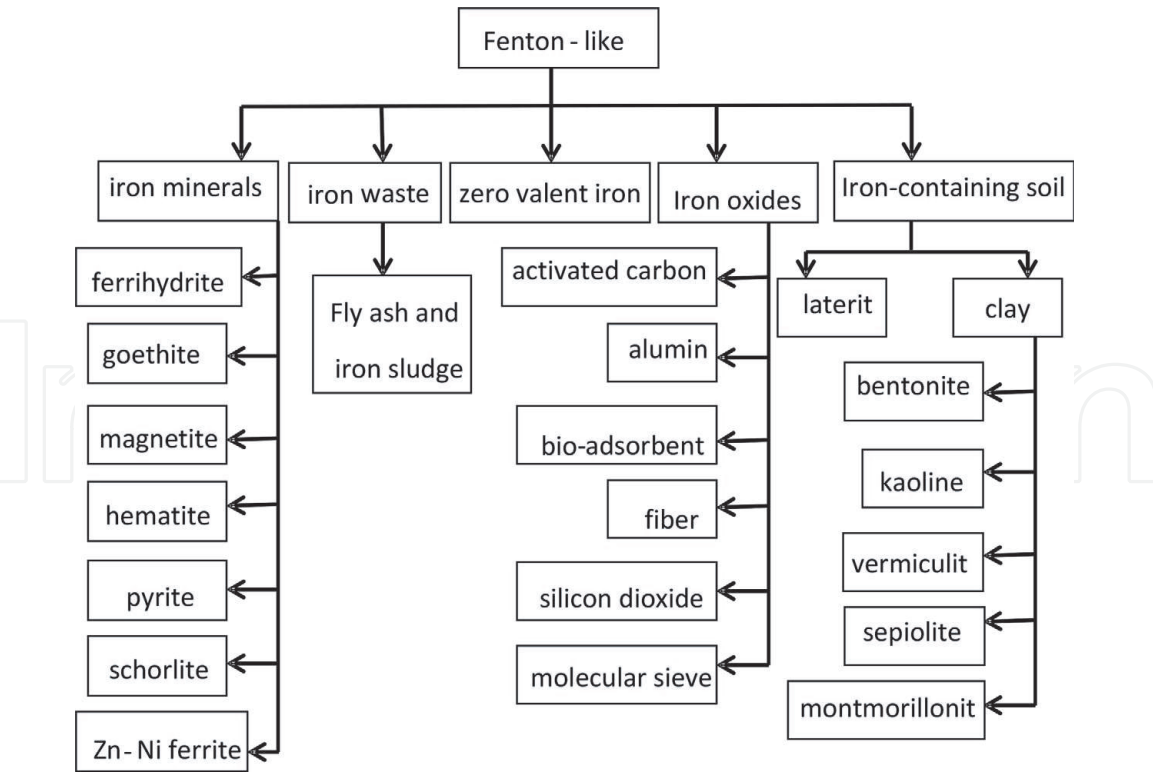
Figure 2.
Iron-containing catalysts.

4.1 Fenton-like reactions using zero-valent iron

Recently, zero-valent iron (Fe^0) has been increasingly used in the heterogeneous Fenton system, due to its large specific surface area and high reactivity. It is reported that the removal of contaminants in the Fe^0 induced heterogeneous Fenton system involves two steps [52–54]: (i) H_2O_2 decomposes on or near the Fe^0 surface to form Fe^{2+} (Eq. (14)); (ii) then, Fenton reaction occurs, Fe^{2+} reacts with H_2O_2 to produce $\cdot OH$ (Eq. (1)), and contaminants are degraded. Meanwhile, the produced Fe^{3+} is further reduced to Fe^{2+} (Eq. (15)).

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \qquad (14)$$

$$Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \qquad (15)$$
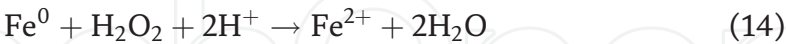
The degradation of trichloroethylene (TCE) in nano-scale zero-valent iron (nZVI) Fenton systems with Cu(II) was investigated [55]. TCE was significantly degraded (95%) in 10 min in the nZVI Fenton system with 20 mM Cu(II) at initial pH 3, while slight degradation (25%) was observed in nZVI Fenton system without Cu(II) at the same experimental condition. Because of the high activity on the Fe^0 surface, Fe^0 could easily coalesce into aggregates, which reduced the reactivity. The particle size of Fe^0 is too small to recycle and separate at the end of the treatment.

4.2 Fenton-like reactions using iron oxides

Different physicochemical characteristics of these oxides make them favorable for oxidative reactions, where the surface area, pore size/volume, and the

crystalline structure have significant effects on their activities. The amorphous Fe_2O with the largest surface area has the lowest catalytic efficiency, while the higher efficiency was achieved with crystalline α-Fe_2O_3, which has a significantly lower surface area [56]. In the Fenton process, magnetite has gained considerable attention than other iron oxides due to its unique characteristic: the magnetically easy separation of magnetite catalysts from the reaction system as a result of its magnetic property.

In many cases, magnetite offered better performance due to the presence of Fe^{2+} cations in its structure [57]. A comparison of the catalytic activity of amorphous iron (III) oxide, maghemite, magnetite, and goethite mixed with quartz was carried out by Hanna et al. [58] for methyl red degradation in presence of H_2O_2. The authors indicated that the oxidation state of iron in the oxides was the critical parameter, considering that Fe^{2+} is superior to Fe^{3+} in Fenton processes. In this study, magnetite exhibited the highest rate constant normalized to surface area per unit mass of oxide (SSA) at neutral pH value.

4.3 Fenton-like reactions using other iron-containing catalysts

The characteristic of iron materials mainly determines the oxidation efficiency in the heterogeneous Fenton reaction. The design of iron-containing catalysts can improve the activity and stability of the heterogeneous Fenton reaction. In recent years, heterogeneous Fenton catalysts have also been developed in the following aspects: (1) iron-loaded material, that is, iron is loaded on the porous materials, such as carbon nanotubes, clay and molecular sieves by a simple method. These materials are considered as potential heterogeneous Fenton catalysts because of low cost, high specific surface area, rich active sites, and easy separation, (2) new iron-containing materials. In the homogeneous Fenton-like processes, the catalysts used in the Fenton-like processes include Fe^{3+}, Cu^{2+}, Mn^{2+}, Co^{2+}, and Ag^+. Sometimes organic or inorganic ligands are also used for complexing and stabilizing the metal ion over a wide pH range. The ligands studied include, but are not limited to, citrate, oxalate, edetic acid (EDTA), humic acids, and ethylenediamine succinic acid (EDDS). The catalysts based on different metal elements and ligands were developed to improve the degradation of organics, promote the Fe^{3+}/Fe^{2+} redox cycle and decrease the sludge production [59, 60].

5. Reuse of the iron-containing sludge after Fenton reaction

A large amount of ferric sludge generated from the Fenton treatment. The practical applications of the Fenton process are limited, mainly because of neutralization after oxidation. The discharge of ferric sludge easily causes secondary pollution because of residual organics adsorbed and accumulated in ferric sludge from treated wastewater. The disadvantage is, therefore, the main obstacle limiting the development and application of the Fenton process [61].

Two approaches have been studied to minimize the production of sludge as a by-product of the Fenton process, including heterogeneous catalysts and the reuse of the iron-containing sludge [61]. However, the catalytic activity is usually weakened after repetitive use due to active iron leaching [62] or the decay of active catalytic sites [63]. Recently, the reuse of iron-containing Fenton sludge has been drawing increasing interest from researchers world-wide.

5.1 Fenton-like reactions using iron-containing sludge

The iron-containing Fenton sludge was used as an iron source for the synthesis of ferrite catalysts that have drawn much more attention due to their potential application in the fields of catalysis in the Fenton process.

Zhang et al. [64] proposed a novel method for the reuse of Fenton sludge in the synthesis of nickel ferrite particles ($NiFe_2O_4$). In phenol degradation with H_2O_2, $NiFe_2O_4$ alone, and $NiFe_2O_4$—H_2O_2, the phenol removal was as high as $95 \pm 3.4\%$. However, the phenol removal efficiencies were as low as $5.9 \pm 0.1\%$ and $13.5 \pm 0.4\%$ in H_2O_2 and $NiFe_2O_4$ alone, respectively. The leaching of iron ion from heterogeneous ferrite catalysts under the acid conditions is a common phenomenon. The leached iron amounted to $6.3 \pm 0.2\%$ of total iron, and the recovery ratio of $NiFe_2O_4$ catalyst in this study was found to be $97.1 \pm 1.7\%$ [64]. Notably, a rapid electron exchange between Ni^{2+} and Fe^{3+} ions in the $NiFe_2O_4$ structure could accelerate the conversion of Fe^{3+} to Fe^{2+}, which was beneficial for the Fenton reaction. In addition, the Fe^{3+} on the surface of $NiFe_2O_4$ particles and the leaching of iron ion from $NiFe_2O_4$ could also react with the H_2O_2 to induce Fenton reaction.

Therefore, phenol could be effectively removed [64]. Roonasi and Nezhad [65] compared the catalytic activity of nano ferrite M-Fenton sludge (M = Cu, Zn, Fe, and Mn), and $CuFe_2O_4$ achieved the best performance. Based on the previous studies, a new catalyst Cu_2O—$CuFeC_2O_4$ was synthesized by co-sedimentation. Compared with $CuFeC_2O_4$, Cu_2O—$CuFeC_2O_4$ improved the phenol removal. The phenol removal as high as $97.3 \pm 0.4\%$, and the leached iron amounted to 4.77% of total iron in Cu_2O—$CuFeC_2O_4$—H_2O_2 reaction. The superior catalytic performance was mainly due to the synergistic effect of both Cu^+ and Cu^{2+} as well as Fe^{2+}/Fe^{3+} redox pairs [66]. An electron bridge was formed between Cu^+ and Fe Fe^{3+}, which accelerates the formation of Fe^{2+} species in order to boost the reaction rate [66].

5.2 Regenerated the iron-containing sludge by the electrochemical process

Fenton process was employed to treat synthetic dye wastewater with a supply of Fe^{2+} electrolytically generated from iron-containing sludge [67]. The concentration of Fe^{2+} increases linearly (r^2 of 0.94) with increasing electrolysis time, but the amount of total iron provided is enough and not the limiting factor for the electrogeneration of Fe^{2+}. In electro-Fenton reaction, Fe^{3+} and O_2 were reduced to Fe^{2+} and H_2O_2 at the same time on the cathode. So, there exists competition between Fe^{2+} and H_2O_2 production. In order to eliminate the competition and decrease the chemical cost of H_2O_2, hypochlorous acid (HOCl) was instead of H_2O_2 [68]. Two iron sludge reuse modes were examined to treat 1,4-dioxane in this study: sequencing batch mode and separation batch mode. The current efficiency (CE) in the electrolytic cell is related to the initial iron concentration, the initial iron species, and operation pH. Fe^{3+} ions were perceived to be more suitable for use as the initial iron species in the electrochemical Fenton-type process, where the CE was found independent of the Fe^{3+} concentration. Compared with the sequencing batch mode, the iron recovery ratio was higher in the separation batch mode. Therefore, the separation batch mode is relatively suitable for iron sludge reuse for both the CE and the iron recovery rate [68].

5.3 Regenerated the iron-containing sludge by the thermal method

In order to remove the residual organics adsorbed in the waste sludge and minimize the sludge production. Baking the sludge was a common method [69, 70]. A higher the baking temperature led to less accumulation of organics in sludge.

The iron-containing sludge catalyst showed more activity (superior TPh, COD, and TOC removals) but higher leaching iron and less adsorption at high baking temperature. Also, the BOD_5/COD ratio was dropped by less than 50% [70]. However, the thermal methods will increase the overall cost and operational difficulty. Fe^{3+}/Fe^{2+} redox cycle cannot be effectively realized in thermal system, thus, decreasing the catalytic ability of the iron-containing sludge catalyst.

5.4 Regenerated the iron-containing sludge by reduction

Some organic ligands (such as EDTA, EDDS) are used for complexing and regenerating iron-containing sludge to promote the Fe^{3+}/Fe^{2+} redox cycle. These organic ligands effectively inhibited the precipitation of Fe^{3+}. However, organic ligands such as EDTA were difficult to b biodegraded, which remained in the water and caused the second pollution. These organic ligands cannot efficiently promote the Fe^{3+}/Fe^{2+} redox cycle, so reductants were required to help the Fe^{3+} reduction.

Organic reductants such as ascorbic acid, glutamic acid, and catechol were usually used in the Fenton-based process to accelerate the Fe^{3+}/Fe^{2+} cycle, enhance the performance of Fenton reaction and expand the range of operation pH. On the other hand, organic reductants can react with ·OH. Because the selectivity of the reaction between reductants and ·OH is different, the degradation efficiency of pollutants is different.

The investigation evaluated the efficacy of the ferric oxy-hydroxide sludge continuous reuse in the Fenton-based treatment of landfill leachate in a sequencing batch reactor with and without the addition of supplementary ferrous iron [71]. The mechanism of the ferric oxy-hydroxide sludge-activated hydrogen peroxide oxidation in the presence of strong complexing and reducing agents was proposed.

Three iron-dissolution mechanisms could be distinguished: protonation, complexation, and reduction. First, in the case of the H_2O_2/sludge system, the probability of iron dissolution by protonation is objectively high at favorable acidic conditions applied. Second, the dissolution of iron by complexation involves the attachment of a complexing ligand onto the ferric oxy-hydroxide surface; humic and fulvic acids, main subclasses in landfill leachate, contain a high density of functional groups, which can conjugate iron ions to form ion-ligand complexes. Third, these complexing ligands were partially dissolved at pH 3, and bound to the protonated OH-group, thus ending in ultimate decomposed of the Fe^{3+}-ligand complex into the bulk solution. Last, both humic and fulvic acids, as effective reductants, reduced Fe^{3+} via electron transfer mechanism [72].

Besides, the addition of a Fe^{2+} activator to the ferric oxy-hydroxide sludge-activated Fenton-based systems increases the total phenols removal rate and reuse cycles. The supplementation of the Fe^{2+} activator could ensure the full utilization of the oxidant.

Organics as quinone- and hydroquinone-structure compounds (such as tannic acid, lignin, phenol, and among others) may assist the Fenton oxidation by reducing Fe^{3+} to Fe^{2+} The loss iron can be used by these organics to form complexes and reduced in the H_2O_2/sludge cycle. Comparing the reducing efficiency of iron-containing sludge by the quinone-structure organics, it is found that H_2O_2/sludge/TN system gave the best performance after adding the quinone-structure organics. Tannins are considered to be strong metal-chelating and reducing agents [73]. They exhibit anti-oxidation (act as ·OH scavengers) and pro-oxidation (promote ·OH generation in the presence of transition metals) properties in biological systems (living organisms).

A comprehensive study of the catalytic performance of Fe^{3+} in the presence of tannic acid during the Fenton-based treatment of 2,4,6-trichlorophenol (TCP) was

performed [74]. The addition of TN significantly promoted the degradation of TCP. H_2O_2 dose and ferric sludge load for water treatment in the presence of TN should be optimized to balance Fe^{3+} reduction to boost the Fenton reaction and ·OH scavenging to remove TN from water. The Fe^{3+} reductive mechanism by tannic acid incorporated tannic acid-Fe^{3+} complex formation and decay through an electron transfer reaction to form Fe^{2+}.

TN availability in wastewater allows for the reuse of non-regenerated ferric sludge for Fenton-based oxidation without any supplementary Fe^{2+}. The positive effect of TN in the Fe^{3+}/H_2O_2 system can be explained by its monomer of gallic acids. Gallic acid complexed with Fe^{3+} to form two complexes that protonated [Fe (LH)]$^{2+}$ and deprotonated [Fe(L)]$^+$ from pH 1.0 to 3.0. These complexes were decomposed into Fe^{2+} and the quinone group by electron transfer, while Fe^{2+} reacted with H_2O_2 to accelerate the TCP removal [74].

The reuse methods of iron-containing sludge have been successfully proved with synthetic aqueous solutions of highly toxic compounds, such as phenols and chlorophenols. However, the decontamination of real wastewater by these enhanced technologies has been so far scarcely performed. The main reason is that real wastewater contains many organic pollutants with high toxicity and low bio-degradability. These pollutants cannot completely mineralize. Organic pollutants will be continuously accumulated in reused iron-containing sludge that produced from treating real wastewater by the Fenton process. The phenomenon causes the low efficiency of the Fenton reaction.

6. Conclusions

During the last few years, many research efforts have been made toward the improvement of the Fenton process. Hybrid methods such as photo-Fenton, electro-Fenton, and sono-Fenton are not economically viable techniques to degrade large volumes of effluent disposed of by the industries. Most experimental studies have been conducted at the laboratory scale; thus, a more detailed investigation is required for the Fenton process to be considered feasible for industrial treatment plants. Further research on the advancement of the Fenton process is needed to demonstrate the economic and commercial feasibility of this process.

Although heterogeneous catalysts demonstrate considerable advances for the elimination of contaminants, there are still drawbacks related to the low oxidation rates, which appeared when pH values above four along with iron leaching, leading to an increase in the H_2O_2 consumption. Future studies should address the stability of the process for broader operational conditions to avoid metal leaching of into the reaction solution and their negative effects on the environment. These combined methods and heterogeneous systems expected to reduce the production of Fenton sludge. However, the high cost of combined methods, the leaching of active iron, and the decay of active catalytic sites should limit the reduction of Fenton sludge.

At present, regenerating the Fenton sludge is crucial for future studies. The use of Fenton sludge as a catalyst for the Fenton process has been tested mainly after thermal regeneration and subsequent re-dissolution of iron-containing solids by acid, chemical regeneration with reducing agent, and electrochemical reduction. The decontamination of real effluents by these enhanced technologies has been so far scarcely performed. The main reason is that real wastewater contains many complex organic pollutants with high toxicity and low biodegradability. These pollutants cannot completely mineralize. Significant attention should be devoted in the future on the development of rate expressions (based on reaction mechanisms),

identification of reaction intermediates, identification of scale-up parameters, and cost-effectiveness analysis.

Acknowledgements

Author details

Min Xu[1,2], Changyong Wu[1*] and Yuexi Zhou[1*]

1 State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environment Sciences, Beijing, China

2 College of Water Science, Beijing Normal University, Beijing, China

*Address all correspondence to: changyongwu@126.com and zhouyuexi@263.net

IntechOpen

References

[1] Babuponnusami A, Muthukumar K. A review on Fenton and improvents to the Fenton process for wastewater treatment. Journal of Environmental Chemical Engineering. 2014;**2**:557-572

[2] Lucas MS, Dias AA, Sampaio A, Amaral C, Peres JA. Degradation of a textile reactive Azo dye by a combined chemical-biological process: Fenton's reagent-yeast. Water Research. 2007;**41**: 1103-1109

[3] Huang CP, Dong C, Tang Z. Advanced chemical oxidation: Its present role and potential future in hazardous waste treatment. Waste Management. 1993;**13**(5-7):361-377

[4] Oturan AA, Aaron JJ. Advanced oxidation processes in water/wastewater treatment: Principles and applications-a review. Critical Reviews in Environmental Science and Technology. 2014;**44**:2577-2641

[5] Gallard H, De Laat J. Kinetic modeling of Fe(III)/H_2O_2 oxidation reactions in dilute aqueous solution using atrazine as a model organic compounds. Water Research. 2000;**34**: 3107-3116

[6] Bigda RJ. Consider Fenton's chemistry for wastewater treatment. Chemical Engineering Progress. 1995;**91**: 62-66

[7] Duarte F, Maldonado-Hódar FJ, Madeira LM. Influence of the characteristics of carbon materials on their behavior as heterogeneous Fenton catalysts for the elimination of the azo dye Orange II from aqueous solutions. Applied Catalysis B: Environmental. 2011;**103**:109-115

[8] Yuan SH, Gou N, Alshawabkeh AN, Gu AZ. Efficient degradation of contaminants of emerging concerns by a new electro-Fenton process with

Ti/MMO cathode. Chemosphere. 2013; **93**:2796-2804

[9] Wang NN, Zheng T, Zhang GS, Wang P. A review on Fenton-like processes for organic wastewater treatment. Journal of Environmental Chemical Engineering. 2016;**4**:762-787

[10] Matta R, Hanna K, Chiron S. Fenton-like oxidation of 2,4,6-trinitrotoluene using different iron minerals. The Science of the Total Environment. 2007;**385**:242-251

[11] Shinya A, Bergwall L. Pyrite oxidation: Review and prevention practices. Journal of Vertebrate Paleontology. 2007;**27**:145A-145A

[12] Babuponnusami A, Muthukumar K. Removal of phenol by heterogeneous photo electro Fenton-like process using nano-zero valent iron. Separation and Purification Technology. 2012;**98**: 130-135

[13] Dehghani M, Shahsavani E, Farzadkia M, Samaei MR. Optimizing photo- Fenton like process for the removal of diesel fuel from the aqueous phase. Journal of Environmental Health Science and Engineering. 2014;**12**:1-17

[14] Pouran SR, Aziz ARA, Daud WMAW. Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters. Journal of Industrial and Engineering Chemistry. 2015;**21**:53-69

[15] Alfaya E, Iglesias O, Pazos M, Sanroman MA. Environmental application of an industrial waste as catalyst for the electro-Fenton-like treatment of organic pollutants. RSC Advances. 2015;**5**:14416-14424

[16] Brillas E, Sires I, Oturan MA. Electro-Fenton process and related electrochemical technologies based on

Fenton's reaction chemistry. Chemical Reviews. 2009;**109**:6570-6631

[17] Wang CK, Shih YH. Degradation and detoxification of diazinon by sono-Fenton and sono-Fenton-like processes. Separation and Purification Technology. 2015;**140**:6-12

[18] Carta R, Desogus F. The enhancing effect of low power microwaves on phenol oxidation by the Fenton process. Journal of Environmental Chemical Engineering. 2013;**1**:1292-1300

[19] Haber F, Weiss J. The catalytic decomposition of hydrogen peroxide by iron salts. Proceedings of the Royal Society of London, Series A. 1934;**147**(861):332-351

[20] Bray WC, Gorin MH. Ferryl ion, a compound of tetravalent iron. Journal of the American Chemical Society. 1932;**54**(5):2124-2125

[21] Neyens E, Baeyens J. A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials. 2003;**B98**(1-3):33-50

[22] Pignatel JJ, Oliveros E, Mackay A. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Critical Reviews in Environmental Science and Technology. 2006;**36**:1-84

[23] Duesterberg CK, Mylon SE, Waite TD. pH effects on iron-catalyzed oxidation using Fenton's reagent. Environmental Science and Technology. 2008;**42**:8522-8527

[24] Szpyrkowicz L, Juzzolino C, Kaul SN. A comparative study on oxidation of disperse dye by electrochemical process, ozone, hypochlorite and Fenton reagent. Water Research. 2001;**35**:2129-2136

[25] Kavitha V, Palanivelu K. Destruction of cresols by Fenton oxidation process. Water Research. 2005;**39**:3062-3072

[26] Xu XR, Li XY, Li XZ, Li HB. Degradation of melatonin by UV, UV/H_2O_2, Fe^{2+}/ H_2O_2 and UV/Fe^{2+}/H_2O_2 processes. Separation and Purification Technology. 2009;**68**:261-266

[27] Yoon J, Lee Y, Kim S. Investigation of the reaction pathway of ·OH radicals produced by Fenton oxidation in the conditions of wastewater treatment. Water Science and Technology. 2000;**44**:15-21

[28] Zepp RG, Faust BC, Hoigné J. Hydroxyl radical formation in aqueous reaction (pH 3-8) of iron(II) with hydrogen peroxide the photo-Fenton reaction. Environmental Science and Technology. 1992;**26**(2):313-319

[29] Zuo Y, Hoigne J. Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III) –oxalato complexes. Environmental Science and Technology. 1992;**26**:1014-1022

[30] Katsumata H, Kaneco S, Suzuki T, Otha K, Yobiko Y. Photo-Fenton degradation of alachlor in the presence of citrate solution. Journal of Photochemistry and Photobiology A. 2006;**180**:38-45

[31] Bandala ER, Brito L, Pelaez M. Degradation of domoic acid toxin by UV-promoted Fenton-like processes in seaeater. Desalination. 2009;**45**:135-145

[32] Giri AS, Golder AK. Chloramphenicol degradation in Fenton and photo-Fenton: Formation of Fe^{2+}-chloramphenicol chelate and reaction pathways. Industrial and Engineering Chemistry Research. 2014;**53**:16196-16203

[33] Xiao D, Guo Y, Lou X, Fang C, Wang Z, Liu J. Distinct effects of oxalate versus malonate on the iron redox chemistry: Implications for the photo-Fenton reaction. Chemosphere. 2014; **103**:354-358

[34] Mohajeri S, Abdul Aziz H, Hasnain Isa M, Ali Zahed M, Adlan MN. Statistical optimization of process parameters for landfill leachate treatment using electro-Fenton technique. Journal of Hazardous Materials. 2009;**176**:749-758

[35] Guinea E, Arias C, Cabot PL, Garrido JA, Rodríguez RM, Centella F, et al. Mineralization of salicylic acid in acidic aqueous medium by electrochemical advanced oxidation processes using platinum and boron-doped diamond as anode and cathodically generated hydrogen peroxide. Water Research. 2008;**42**: 499-511

[36] Panizza M, Cerisola G. Electro-Fenton degradation of synthetic dyes. Water Research. 2009; **43**:339-344

[37] Pipi ARF, De Andrade AR, Brillas E, Sirés I. Total removal of alachlor from water by electrochemical processes. Separation and Purification Technology. 2014;**132**:674-683

[38] Ranjit PJD, Palanivelu K, Lee CS. Degradation of 2,4-dichlorophenol in aqueous solution by sono-Fenon method. Korean Journal of Chemical Engineering. 2008;**25**:112-117

[39] Ioan I, Wilson S, Lundanes E, Neculai A. Comparison of Fenton and sono-Fenton bisphenol A degradation. Journal of Hazardous Materials. 2007; **142**:559-563

[40] Chakma S, Moholkar VS. Physical mechanism of sono-Fenton process. AICHE Journal. 2013;**59**:4303-4313

[41] Neppolian B, Jung H, Choi H, Lee JH, Kang JW. Sonolytic degradation of methyl tert-butyl ether: The role of coupled Fenton process and persulphate ion. Water Research. 2002;**S36**: 4699-4708

[42] Wu CY, Zhou YX, Sun QL, Fu LY, Xi HB, Yu Y, et al. Appling hydrolysis acidification-anoxic-oxic process in the treatment of petrochemical wastewater: Form bench scale reactor to full scale wastewater plant. Journal of Hazardous Materials. 2016;**309**:185-191

[43] Badawy MI, Wahaab RA, EI-Kalliny AS. Fenton-biological treatment processes for the removal of some pharmaceuticals from industrial wastewater. Journal of Hazardous Materials. 2009;**167**:567-574

[44] Martinez NSS, Fernandez JF, Segura XF, Ferrer AS. Pre-oxidation of an extremely polluted industrial wastewater by the Fenton's reagent. Journal of Hazardous Materials. 2003; **B101**:315-322

[45] Vergili I, Gencdal S. Applicability of combined Fenton oxidation and nanofiltration to pharmaceutical wastewater. Desalination and Water Treatment. 2015;**56**:3501-3509

[46] Abdel-Shafy HI, EI-Khateeb MA, Mansour MSM. Treatment of leather industrial wastewater via combined advanced oxidation and membrane filtration. Water Science and Technology. 2016;**23**:26-43

[47] Blanco J, Torrades F, De la Varga M, García-Montano J. Fenton and biological-Fenton coupled processes for textile wastewater treatment and reuse. Desalination. 2011;**286**:394-399

[48] Ioannou-Ttofa L, Michael-Kordatou I, Fattas SC, Eusebio A, Ribeiro B, Rusan M, et al. Treatment efficiency and economic feasibility of biological oxidation membrane filtration and

separation processes, and advanced oxidation for the purification and valorization of olive mill wastewater. Water Research. 2017;**114**: 1-13

[49] Mylon SE, Sun QA, Waite TD. Process optimization in use of zero valent iron nanoparticles for oxidative transformations. Chemosphere. 2010; **81**:127-131

[50] Chen Q, Wu P, Dang Z, Zhu N, Li P, Wu J, et al. Iron pillared vermiculite as a heterogeneous photo-Fenton catalyst for photocatalytic degradation of azo dye reactive brilliant orange X-GN. Separation and Purification Technology. 2010;**71**: 315-323

[51] Lan Q, Li F, Sun CX, Liu CS, Li XZ. Heterogeneous photodegradation of pentachlorophenol and iron cycling with goethite, hematite and oxalate under UVA illumination. Journal of Hazardous Materials. 2010; **174**:64-70

[52] Fu FL, Wang Q, Tang B. Effective degradation of Cl acid red 73 by advanced Fenton process. Journal of Hazardous Materials. 2010;**174**:17-22

[53] Pagano M, Volpe A, Lopez A, Mascolo G, Ciannarella R. Degradation of chlorobenzene by Fenton-like processes using zero-valent iron in the presence of Fe^{3+} and Cu^{2+}. Environmental Technology. 2011;**32**: 155-165

[54] Pecci L, Montefoschi G, Cavallini D. Some new details of the copper-hydrogen peroxide interaction. Biochemical and Biophysical Research Communications. 1997;**235**:264-267

[55] Choi K, Lee W. Enhanced degradation of trichloroethylene in nano-scale zero-valent iron Fenton system with Cu(II). Journal of Hazardous Materials. 2012;**211**:146-153

[56] Hermanek M, Zboril R, Medrik I, Pechousek J, Gregor C. Catalytic efficiency of iron (III) oxides in decomposition of hydrogen peroxide: Competition between the surface area and crystallinity of nanoparticles. Journal of the American Chemical Society. 2007;**129**:10929-10936

[57] Matta R, Hanna K, Kone T, Chiron S. Oxidation of 2,4,6-trinitrotoluene in the presence of different iron-bearing minerals at neutral pH. Chemical Engineering Journal. 2008;**144**:453-458

[58] Hanna K, Kone T, Medjahdi G. Synthesis of the mixed oxides of iron and quartz and their catalytic activities for the Fenton-like oxidation. Catalysis Communications. 2008;**9**: 955-959

[59] Song Z, Wang N, Zhu LH, Huang AZ, Zhao XR, Tang HQ. Efficient oxidative degradation of triclosan by using enhanced Fenton-like process. Chemical Engineering Journal. 2012; **198-199**:379-387

[60] Huang WY, Brigante M, Wu F, Mousty C, Hanna K, Mailhot G. Assessment of the Fe(III)-EDDS complex in Fenton-like processes: From the radical formation to the degradation of bisphenol A. Environmental Science and Technology. 2013;**47**:1952-1959

[61] Bolobajev J, Kattel E, Viisimaa M, Goi A, Trapido M, Tenno T, et al. Reuse of ferric sludge as an iron source for the Fenton-based process in wastewater treatment. Chemical Engineering Journal. 2014;**255**:8-13

[62] Ji F, Li C, Zhang J, Deng L. Efficient decolorization of dye pollutants with $LiFe(WO_4)_2$ as a reusable heterogeneous Fenton-like catalyst. Desalination. 2011;**269**(1-3):284-290

[63] Takbas M, Yatmaz HC, Bektas N. Heterogeneous photo-Fenton oxidation

of reactive azo dye solutions using iron exchanged zeolite as a catalyst. Microporous and Mesoporous Materials. 2008;**115**(3):594-602

[64] Zhang H, Liu JG, Ou CJ, Faheem SJY, Yu HX, Jiao ZH, et al. Reuse of Fenton sludge as an iron source for $NiFe_2O_4$ synthesis and its application in the Fenton-based process. Journal of Environmental Sciences. 2016;**5**:1-8

[65] Roonasi P, Nezhad AY. A comparative study of a series of ferrite nanoparticles as heterogeneous catalysts for phenol removal at neutral pH. Materials Chemistry and Physics. 2016;**172**:143-149

[66] Faheem M, Jiang XB, Wang LJ, Shen JY. Synthesis of Cu_2O-$CuFe_2O_4$ microparticles from Fenton sludge and its application in the Fenton process: The key role of Cu_2O in the catalytic degradation of phenol. RSC Advances. 2018;**8**:5740-5748

[67] Li CW, Chen YM, Chiou YC, Liu CK. Dye wastewater treated by Fenton process with ferrous ions electrolytically generated from iron-containing sludge. Journal of Hazardous Materials. 2007;**144**: 570-576

[68] Kishimoto N, Kitamura T, Kato M, Otsu H. Reusability of iron sludge as an iron source for the electrochemical Fenton-type process using Fe^{2+}/HOCl system. Water Research. 2013;**47**: 1919-1927

[69] Cao GM, Sheng M, Niu WF, Fei YL, Li D. Regeneration and reuse of iron catalyst for Fenton-like reactions. Journal of Hazardous Materials. 2009; **172**:1446-1449

[70] Rossi AF, Martins RC, Quinta-Ferreira RM. Reuse of homogeneous Fenton's sludge from detergent industry as Fenton's catalyst. Journal of

Advanced Oxidation Technologies. 2013;**16**(2):298-305

[71] Kattel E, Trapido M, Dulova N. Treatment of landfill leachate by continuously reused ferric oxyhydroxide sludge-activated hydrogen peroxide. Chemical Engineering Journal. 2016;**304**:646-654

[72] Voelker BM, Sulzberger B. Effects of fulvic acid on Fe(II) oxidation by hudrogen peroxide. Environmental Science and Technology. 1996;**30**: 1106-1114

[73] Bolobajev J, Trapido M, Goi A. Role of organic wastewater constituents in iron redox cycling for ferric sludge reuse in the Fenton-based treatment. International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering. 2016;**10**(4): 352-357

[74] Bolobajev J, Trapido M, Goi A. Interaction of tannic acid with ferric iron to assist 2,4,6-trichlorophenol catalyst decomposition and reuse of ferric sludge as a source of iron catalyst in Fenton-based treatment. Applied Catalysis B: Environmental. 2016;**187**: 75-82