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

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A B S T R A C T

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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Contents

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 speci-fied 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 wastewa-ter 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^{-1} s^{-1} [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 (homoge-neous 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_2)	3.03
Hydroxyl radical ($^\bullet OH$)	2.80
Atomic oxygen (O)	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.77
Potassium permanganate ($KMnO_4$)	1.67
Chlorine dioxide (ClO_2)	1.5
Hypochlorous acid (HClO)	1.49
Chlorine (Cl_2)	1.36
Oxygen (O_2)	1.23
Bromine (Br_2)	1.09

Table 2
Classification of conventional AOPs.

| Type of process	Example
Homogeneous	*Fenton based processes*
	Fenton: $H_2O_2 + Fe^{2+}$
	Fenton like: $H_2O_2 + Fe^{3+}/m^{n+}$
	Sono-Fenton: $US/H_2O_2 + Fe^{2+}$
	Photo-Fenton: $UV/H_2O_2 + Fe^{2+}$
	Electro-Fenton
	Sono-electro-Fenton
	Photo-electro-Fenton
	Sono-photo-Fenton
	O_3 based processes
	O_3
	$O_3 + UV$
	$O_3 + H_2O_2$
	$O_3 + UV + H_2O_2$
Heterogeneous	$H_2O_2 + Fe^{2+}/Fe^{3+}/m^{n+}$-solid
	$TiO_2/ZnO/CdS + UV$
	$H_2O_2 + Fe^0/Fe$ (nano-zero valent iron)
	$H_2O_2 +$ immobilized nano-zero valent iron

Fenton process

Fenton (F) and related reactions encompass reactions of peroxides (usually hydrogen peroxide (H_2O_2)) 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_2O_2 could be activated by ferrous (Fe^{2+}) salts to oxidize tartaric acid [14]. In the last few decades, the importance of $^\bullet OH$ reactions has been recognized and over 1700 rate constants for $^\bullet OH$ 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].
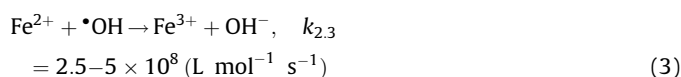
The traditionally accepted Fenton mechanism is represented by Eqs. (1)–(9) and its reaction rates were well reported in the literature [18]. Eq. (1) is recognized as Fenton reaction and implies the oxidation of ferrous to ferric ions to decompose H_2O_2 into hydroxyl radicals. It is usually considered as the core of the Fenton chemistry. Furthermore, other reactions must be considered to understand the whole process:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH, \quad k_{2.1}$$
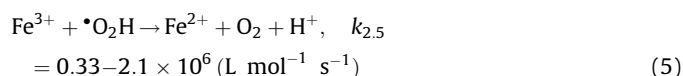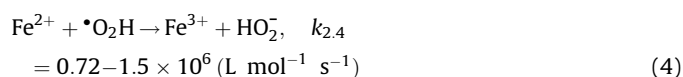$$= 40\text{–}80 \quad L \; mol^{-1} \; s^{-1} \tag{1}$$
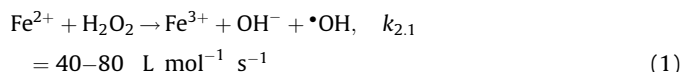
The generated ferric ions can be reduced by reaction with excess hydrogen peroxide to form again ferrous ion and more radicals as shown in Eq. (2). This reaction is called Fenton-like reaction and slower than Fenton reaction, and allows Fe^{2+} regeneration in an effective cyclic mechanism. In Fenton like reaction, apart from ferrous ion regeneration, hydroperoxyl radicals ($^\bullet O_2 H$) 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_2O_2 is continuously consumed to produce hydroxyl radicals.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^\bullet O_2 H + H^+, \quad k_{2.2}$$
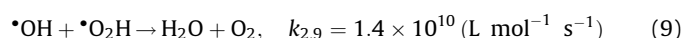$$= 9.1 \times 10^{-7} \; (L \; mol^{-1} \; s^{-1}) \tag{2}$$
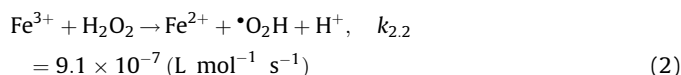
The following reactions are involved in Fenton chemistry.

$$Fe^{2+} + {}^\bullet OH \rightarrow Fe^{3+} + OH^-, \quad k_{2.3}$$
$$= 2.5\text{–}5 \times 10^8 \; (L \; mol^{-1} \; s^{-1}) \tag{3}$$

$$Fe^{2+} + {}^\bullet O_2H \to Fe^{3+} + HO_2^-, \quad k_{2.4}$$
$$= 0.72-1.5 \times 10^6 \,(\text{L mol}^{-1}\,\text{s}^{-1}) \tag{4}$$

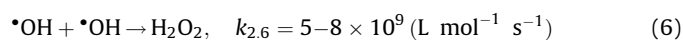$$Fe^{3+} + {}^\bullet O_2H \to Fe^{2+} + O_2 + H^+, \quad k_{2.5}$$
$$= 0.33-2.1 \times 10^6 \,(\text{L mol}^{-1}\,\text{s}^{-1}) \tag{5}$$

Eqs. (2)–(5) represent the rate limiting steps in the Fenton chemistry since hydrogen peroxide is consumed and ferrous iron is regenerated from ferric ion through these reactions. Eqs. (6)–(9) also reported to occur during the Fenton process and they are radical–radical reactions or hydrogen peroxide–radical reaction:

$${}^\bullet OH + {}^\bullet OH \to H_2O_2, \quad k_{2.6} = 5-8 \times 10^9 \,(\text{L mol}^{-1}\,\text{s}^{-1}) \tag{6}$$

$${}^\bullet OH + H_2O_2 \to {}^\bullet O_2H + H_2O, \quad k_{2.7}$$
$$= 1.7-4.5 \times 10^7 \,(\text{L mol}^{-1}\,\text{s}^{-1}) \tag{7}$$

$${}^\bullet O_2H + {}^\bullet O_2H \to H_2O_2 + O_2, \quad k_{2.8}$$
$$= 0.8-2.2 \times 10^6 \,(\text{L mol}^{-1}\,\text{s}^{-1}) \tag{8}$$

$${}^\bullet OH + {}^\bullet O_2H \to H_2O + O_2, \quad k_{2.9} = 1.4 \times 10^{10} \,(\text{L mol}^{-1}\,\text{s}^{-1}) \tag{9}$$
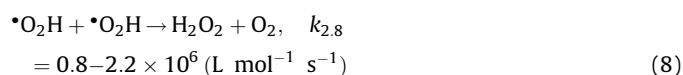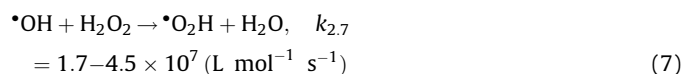
In the absence or presence of any organic molecule to be oxidized, the decomposition of hydrogen peroxide to molecular oxygen and water occurs according to Eq. (10). This reaction leads to exploitation of bulk oxidant and thus an unnecessary increase on treatment cost [19]:

$$2H_2O_2 \to O_2 + 2H_2O \tag{10}$$

Eqs. (1)–(9) demonstrate that the Fenton process follows a complex mechanism. The production of desired hydroxyl radical occurs through the chain initiation reaction (Eq. (1)). However hydroxyl radicals can be scavenged by ferrous ions (Eq. (3)), hydrogen peroxide (Eq. (7)), hydroperoxyl radicals (Eq. (9), and/or even may be auto scavenged (Eq. (6)). The foregoing analysis indicates that hydrogen peroxide may act both as radical generator (Eq. (1)) and as scavenger (Eq. (7)). Hydroxyl radicals may attack organic radicals produced by organics present in the wastewater. Those radicals form dimmers or react with ferrous and ferric ions, as shown in Eqs. (11)–(13) [16,19]:

$$2R^\bullet \to RR \tag{11}$$

$$R^\bullet + Fe^{2+} \to R^- + Fe^{3+} \tag{12}$$

$$R + Fe^{3+} \to R^+ + Fe^{2+} \tag{13}$$

Fenton process can be carried out at room temperature and atmospheric pressure. In addition, required reagents are readily available, easy to store and handle, safe and they do not cause environmental damages [19]. However, two main drawbacks were identified. The first is related to the wastage of oxidants due to the radical scavenging effect of hydrogen peroxide (Eq. (7)) and its self-decomposition (Eq. (10)). The second refers to the continuous loss of iron ions and the formation of solid sludge. Several economic and environmental drawbacks have been reported to occur with Fenton sludge [20]. Thus, technologies allowing an efficient use of H_2O_2 have to be studied. Furthermore, an attempt has to be made for the recovery of iron ions and their subsequent recycle and reuse. Table 3 depicts some of the illustrative work done in recent years with discussion about the type of the equipment used along with the experimental conditions and important findings observed in the work. Based on the exhaustive analysis of the existing literature on the application of Fenton oxidation to wastewater treatment, following optimum conditions is outlined.

Operating pH

Fenton process is strongly dependent on the solution pH mainly due to iron and hydrogen peroxide speciation factors. The optimum pH for the Fenton reaction was found to be around 3, regardless of the target substrate [32–35].

The activity of Fenton reagent is reduced at higher pH due to the presence of relatively inactive iron oxohydroxides and formation of ferric hydroxide precipitate [36]. In this situation, less hydroxyl radicals are generated due to the presence of less free iron ions. The oxidation potential of hydroxyl radicals decreases with increasing pH. The oxidation potential for the redox couple ${}^\bullet OH/H_2O$ has been reported to be 2.59 V vs. NHE at pH 0 and 1.64 V vs. NHE at pH 14 [37]. In addition, auto-decomposition of hydrogen peroxide is accelerated (Eq. (10)) at high pH [38]. At pH below 3, decrease in degradation efficiency was observed [39]. At very low pH values, iron complex species $[Fe(H_2O)_6]^{2+}$ exist, which reacts more slowly with hydrogen peroxide than other species [40]. This phenomenon was also influenced by the concentration of ferrous ion present. In addition, the peroxide gets solvated in the presence of high concentration of H^+ ions to form stable oxonium ion $[H_3O_2]^+$. Oxonium ions make hydrogen peroxide more stable and reduce its reactivity with ferrous ions [39,41]. Therefore, the efficiency of the Fenton process to degrade organic compounds is reduced both at high and low pH. Thus an adequate control of pH would increase process efficiency. It should be noted that the type of buffer solution used also has effect on the degradation process [42]. The acetic acid/acetate buffer gives maximum oxidation efficiency whereas least is observed with phosphate and sulfate buffers [42]. This can be attributed to the formation of stable Fe^{3+} complexes that are formed under those conditions [43]. However, reaction buffering will increase the operating costs and hence, final decision of utilization of buffers varies with situation.

Ferrous ion concentration

Usually the rate of degradation increases with an increase in the concentration of ferrous ion [27]. However, the extent of increase is sometimes observed to be marginal above a certain concentration of ferrous ion as reported by Lin et al. [28], Kang and Hwang [31] and Rivas et al. [32]. Also, an enormous increase in the ferrous ions will lead to an increase in the unutilized quantity of iron salts, which will contribute to an increase in the total dissolved solids content of the effluent stream and this is not permitted. Thus, laboratory scale studies are required to establish the optimum loading of ferrous ions to mineralize the organics.

Hydrogen peroxide concentration

Concentration of hydrogen peroxide plays a crucial role in deciding the overall efficiency of the degradation process. Usually it has been observed that the % degradation of the pollutant increases with an increase in the dosage of hydrogen peroxide [27,28,31,33]. However, care should be taken while selecting the operating oxidant dosage. The unused portion of hydrogen peroxide during the Fenton process contributes to COD [27] and hence excess amount is not recommended. Also, the presence of hydrogen peroxide is harmful to many of the organisms [44] and will affect the overall degradation efficiency significantly, where Fenton oxidation is used as a pretreatment to biological oxidation. Another negative effect of hydrogen peroxide is the scavenging of generated hydroxyl radicals, which occurs at large quantities of hydrogen peroxide. Thus, the dosage of hydrogen peroxide should be adjusted in such a way that the entire amount is utilized and this can be decided based on the laboratory scale studies.

Table 3
Overview of work done in the area of Fenton oxidation in recent years.

S. no.	Wastewater/organic compounds used	Experimental conditions	Remarks	Reference
1	Formic acid, phenol, 4-chlorophenol, 2,4-dichlorophenol and nitrobenzene	Fenton reactor of 1.5 L capacity was maintained at isothermal conditions. Fe^{2+}/compound ratio equal to 1, 0.1 and 0.01 was used. Corresponding H_2O_2 dosages were 0.1–50 mol H_2O_2/mol organics	The peroxide dosage and iron concentration influences the degradation efficiency reaction kinetics. Biodegradability (BOD_5/COD) of the organic compounds was increased	[21]
2	Phenol, 2-chlorophenol (2-CP) and 2-nitrophenol (2-NP)	Batch reactor (2 L) open to atmosphere was used. Initial concentration of phenol, 2-chlorophenol and 2-nitrophenol were 2.66 mM, 1.95 mM and 1.8 mM, respectively. H_2O_2 concentration: 0.2–3.5 mM/mM of phenolic compounds. Fe^{2+}/phenol compounds: 0.01/1, treatment time: 24 h	Presence of chloride and sulfate anions influenced the phenol, 2-CP and 2-NP degradation. Higher resistance of formed intermediates was observed. Biodegradability of phenol was enhanced by the presence of chlorides	[22]
3	2,4-Dichlorophenol (2,4-DCP)	Batch reactor (600 mL) was used to degrade 200 mg/L at ambient conditions. The contents were mixed thoroughly using magnetic stirrer. pH range studied: 2.5–7, time: 2 h, H_2O_2 used: 300–580 mg/L, Fe^{2+} used: 10–20 mg/L	Optimum concentration of Fenton reagents was found to be 20 mg/L of Fe^{2+} and 580 mg/L of H_2O_2 at pH 2.5. About 70% of 2,4-DCP degradation was observed. Kinetics studies showed that the degradation of 2,4-DCP follows pseudo first order kinetics	[23]
4	Phenol	Magnetically stirred three-necked glass reactor with a capacity of 100 mL was used at room temperature. pH range studied: 3–3.5, Fe^{2+}: 10 ppm, H_2O_2: 300 or 600 ppm. Reaction time: 6 h. An alumina supported Pd catalyst was used to replace Fe^{2+}	Complete destruction of phenol was obtained within 6 h and at which 60% mineralization was attained. Higher temperature will leads faster degradation of phenol	[24]
5	Methyl tert butyl ether (MTBE)	Batch reactor of capacity 4 L purged with high purity N_2 was used. Fe^{2+}/H_2O_2 used: 1:1 and Fe^{2+}/MTBE molar ratio: 10:1, pH range studied: 3–7 and initial MTBE concentration: 1–2 mg/L	About 90–99% MTBE was degraded after 1 h reaction time. Mineralization of MTBE was low and reached only 31.7% at best conditions. MTBE degradation follows pseudo first order kinetics. Degradation of MTBE was found to be high at acidic pH, while at neutral pH the degradation rates dropped significantly	[25]
6	Phenol	1000 mL glass reactor in the presence of O_2 at room temperature was used. H_2O_2 range studied: 0–5 mM, pH range studied: 1–7, Fe^{2+} range studied: 0–1 mM (Fenton), Fe^{3+} range studied: 0–1 mM (Fenton-like)	At low level of iron concentration, Fenton reaction appeared to be more efficient than the Fenton-like reaction in terms of phenol degradation and hydrogen peroxide decomposition. For Fenton process, effective pH range was found to be 2.5–6.0, while Fenton-like reaction was limited to a narrow pH range of 2.8–3.8	[26]
7	Poly vinyl alcohol (PVA)/Blue G and PVA/Black B	Reactor with a capacity of 2 L equipped with variable mixer and cooling jacket for temperature control was used. Initial pollution concentration of 1500 mg/L, pH of 2.5 was maintained and treatment time is 1 h	The extent of degradation was decreased at above pH 3. Increase in $FeSO_4$ concentration increases the extent of COD removal. Optimum operating temperature was observed to be 30 °C, above which COD removal was marginal. Coagulation after Fenton oxidation helps in keeping the concentration of soluble iron within the limit	[27]
8	Surfactant wastewater containing alkyl benzene sulfonate and linear alkyl sulfonate	Reactor with 2 L capacity was used. Fe^{2+} range: 30–180 mg/L, H_2O_2 concentration range: 20–80 mg/L, treatment time: 3 h	Optimum pH was observed as 3 and optimum $FeSO_4$ and H_2O_2 concentrations were found to be 90 and 60 mg/L respectively. Subsequent treatment with coagulation is recommended to improve settling. Reaction followed first order with respect to reactants and rate constants depend on concentration of Fe^{2+} and H_2O_2	[28]
9	Catechol	All experiments were carried out at room temperature in 500 mL cylindrical vessel. Initial concentration of Catechol was maintained as 110 mg/L. pH was lowered to 3 using H_2SO_4. $FeSO_4$ range used: 75–600 mg/L, H_2O_2 range used: 75–700 mg/L, treatment time: 30 min	COD removal of 83% and aromaticity removal of 93% was achieved at 30 min reaction time with H_2O_2/$FeSO_4$ ratio of 600/500 w/w. Higher concentration of Fe^{2+} and H_2O_2 lowered the COD removal. GC/MS analysis showed that complete removal of Catechol obtained at a ratio of H_2O_2/$FeSO_4$: 2000/500 w/w with 30 min	[29]
10	Chlorobenzene	Reactor capacity was 500 mL and temperature maintained at 25 °C. Operating pH range: 2–7; Fe^{2+} and H_2O_2 addition at a rate of 5 mL/h and the reaction time was 2 h	Complete removal of chlorobenzene and other intermediate was observed within 2 h. Intermediates were identified using GC/MS analysis. Reaction pathway was proposed and the optimum pH was found to be in the range of 2–3	[30]
11	Real effluent with COD: 1500 mg/L	Reaction was carried out in a 2 L Fenton reactor at a constant temperature of 25 °C and the contents were mixed with magnetic stirrer. Fe^{2+} range used: 250–2250 mg/L; H_2O_2 range used: 0–1600 mg/L; pH range studied: 2–9	The maximum COD removal efficiency was observed at a pH of 3.5 and it was drastically reduced when pH increased above 6. COD removal efficiency increased when Fe^{2+} dosage increased up to 500 mg/L, beyond which removal efficiency becomes constant. Similar trend was observed in H_2O_2 dosage	[31]
12	Poly hydroxyl benzoic acid	1 L capacity Fenton reactor was used. Fe^{2+} concentration range used: 0–0.01 M, H_2O_2 operating range used: 0–4 M, temperature: 20 °C and pH 3.2	Increase in Fe^{2+} and H_2O_2 concentration increases the pollutant removal and optimum Fe^{2+} dosage was found to be 5 mM. H_2O_2 was completely utilized and found to be a limiting reactant. Increase in pH from 3 to 7 decreased the rate appreciably. Increase in temperature from 0 to 40 °C showed a variation in extent of degradation	[32]

Initial concentration of pollutant

Usually lower initial concentration of the pollutants are favored [41,42], but the negative effects of treating large quantity of effluent needs to be analyzed before the dilution ratio is fixed. For real industrial wastewater, dilution is essential before any degradation is effected by Fenton oxidation.

Operating temperature

Limited studies are available depicting the effect of temperature on the degradation rate. Moreover, ambient conditions can safely be used with good efficiency. In fact, Lin and Lo [27] reported an optimum temperature of 30 °C, whereas Rivas et al. [32] reported that the degradation efficiency is unaffected even when the temperature is increased from 10 to 40 °C. If the reaction temperature is expected to rise beyond 40 °C due to exothermic nature, cooling is recommended. The efficient utilization of hydrogen peroxide decreases due to accelerated decomposition of hydrogen peroxide into water and oxygen [45].

Chemical coagulation

Chemical coagulation step is recommended after Fenton oxidation to keep the concentration of the soluble iron with the specified limits [27]. Lin et al. [28] have demonstrated the efficacy of chemical coagulation in controlling the concentration of total dissolved solids below the specified limits.

Sono-Fenton process

The oxidation of organics by ultrasound has received considerable attention because of its rapid degradation of chemical contaminants [46]. Ultrasound is a sound wave with a frequency greater than the upper limit of human hearing (approximately 20 kHz). In practice, three frequency ranges of ultrasound are reported for three different uses [47]: (1) the relatively low frequency range, which is applied for conventional power ultrasound (20–100 kHz), (2) the medium frequency range, which is used for sonochemical effects (300–1000 kHz), (3) and the high frequency range, which is typically used for diagnostic imaging (2–10 MHz).

The application of ultrasound wave creates expansion and compression cycles. The expansion cycle causes reduction of pressure in the liquid, and, if the amplitude of ultrasound pressure is sufficiently large, it can result in acoustic cavitation, a process of formation, growth, and implosion of bubbles filled with vapor and/or gas. The growth and implosion of bubbles are affected by physical properties of gas and liquid, initial size of gaseous nuclei present in liquid, and ultrasound frequency and intensity. Before implosion, the cavities oscillate in size, following the expansion and compression cycles of the ultrasound wave. When these cavitations bubbles explosively collapse, the pressure and temperature in the bubbles can reach up to several hundred atmosphere and several thousand Kelvin, respectively [48–50]. Under these conditions, organic compounds are decomposed directly by pyrolytic cleavage. On the other hand, the hydroxyl radicals formed by pyrolysis also help to degrade the organics. Thus, in sonochemistry, there are three potential reaction sites: (1) inside of cavitation bubbles, (2) interfacial region between the cavitation bubble and liquid phase, and (3) bulk liquid [50].

The hydroxyl radicals are generated by water pyrolysis as shown in Eq. (14). After that, the radicals can enter into a variety of chemical reactions in a gas bubble and/or in the bulk solution. Some typical reactions involved are shown in Eqs. (15)–(18)

[51,52]:

$$H_2O +))) \rightarrow {}^{\bullet}OH + {}^{\bullet}H \tag{14}$$

$${}^{\bullet}OH \rightarrow {}^{\bullet}H + {}^{\bullet}H_2O \tag{15}$$

$$2{}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}O \tag{16}$$

$$2{}^{\bullet}OH \rightarrow H_2O_2 \tag{17}$$

$$2{}^{\bullet}H \rightarrow H_2 \tag{18}$$

Hydrophobic chemicals with high vapor pressure have been proved to undergo mainly thermal decomposition inside the cavitation bubbles [53,54]. Whereas, hydrophilic compounds with low vapor pressures tends to remain in the bulk solution. Therefore, the major reaction site for these compounds is bulk liquid region, where they can be easily destroyed by an oxidative degradation. But, sufficient quantities of hydroxyl radicals are ejected into the liquid phase during the collapse of cavities.

To increase the hydroxyl radical concentration in the bulk solution, Fenton and sonolysis can be combined together. These methods utilize the advantages of ultrasound and Fenton's reagent, allowing improved degradation of organic pollutants [50]. The studies reported in the literature related to sono-Fenton (SF) process on organic compounds degradation are summarized in Table 4.

Electro-Fenton process

There is a greater interest in the development of effective electrochemical treatments for the destruction of toxic and biorefractory organics [64]. Anodic oxidation and indirect electro-oxidation are the most usual techniques utilized to achieve the mineralization of such pollutants. In anodic oxidation, pollutants are mineralized by direct electron transfer reactions or action of radical species (hydroxyl radicals) formed on the electrode surface as shown in Eq. (19):

$$H_2O \rightarrow {}^{\bullet}OH_{ads} + H^+ + e^- \tag{19}$$

This radical, as discussed previously, is a powerful oxidizing agent, with an ability to react with organics giving dehydrogenated or hydroxylated derivatives. Anodic oxidation [65–68] is usually performed in the anodic compartment of the divided cell, where the contaminated solution is treated using an anode of Pt, undoped and doped PbO_2 and SnO_2. Under these conditions, however, most aromatic solutions are poorly mineralized, because of the generation of hardly oxidizable carboxylic acids.

In electro-Fenton (EF) process, pollutants are destroyed by the action of Fenton's reagent in the bulk together with anodic oxidation at the anode surface. Electro-Fenton process is classified into four categories depending on Fenton's reagent addition or formation. In type 1, hydrogen peroxide and ferrous ion are electro-generated using a sacrificial anode and an oxygen sparging cathode respectively [69]. In type 2, hydrogen peroxide is externally added while ferrous ion is produced from sacrificial anode as shown in Eq. (20) [70]:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{20}$$

In type 3, ferrous ion is externally added and hydrogen peroxide is generated using an oxygen sparging cathodes [71,72]. In type 4, hydroxyl radical is produced using Fenton reagent in an electrolytic cell and ferrous ion is regenerated through the reduction of ferric ions on the cathode [73,74]. 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

Table 4
Overview of work done in the area of sono-Fenton oxidation in recent years.

S. no.	Wastewater/organic compounds used	Experimental conditions	Remarks	Reference
1	2,4-Dichlorophenol	Fenton process carried out in 600 mL beaker with reactants volume of 500 mL. The reactor was immersed in ultrasonic bath to carryout sono-Fenton process. Ultrasonic frequency: 35 kHz pH range studied: 2.5–7 H_2O_2 range used: 300–580 mg/L and Fe^{2+} range used: 10–20 mg/L	Sono-Fenton process showed a promising result with lower initial concentration of H_2O_2 and ferrous ion. The optimal concentrations were found to be 10 mg/L of Fe^{2+}, 400 mg/L of H_2O_2 and pH 2.5. Sono-Fenton process could be applicable even at pH 5. Kinetic studies shows that, degradation of DCP follows pseudo first order kinetics	[23]
2	Phenol	Cylindrical glass reactor of 300 mL volume filled with 200 mL of aqueous phenol was used. Ultrasonic probe having intensity of 22.9 W/cm was immersed into the reactor. The temperature was kept constant using external cooling bath. Fe-SBA-15 was used as iron source for the Fenton process (0.2–1.0 g/L). H_2O_2 concentration used: 1.19–4.76 g/L and pH range: 3 and 6.5	Catalyst loading of 0.6 g/L and a concentration of H_2O_2 close to twice the stoichiometric amount showed a remarkable organic mineralization and excellent catalyst stability (<4 ppm loss). Initial pH adjustment was not required due to the use of Fe-SBA-15 catalyst	[55]
3	2,4-Dinitrophenol	Cylindrical glass vessel (75 mL) with water jacket and fitted with ultrasonic horn (6 mm in dia) was used. The reaction was carried out at 15 °C, 60 mg/L $FeSO_4$ and 300 mg/L H_2O_2 concentration	Sono-Fenton system removed 98% DNP after 60 min of reaction. Regeneration of Fe^{2+} was achieved by combining ultrasound with Fenton system. Degradation of DNP follows pseudo first order kinetics	[56]
4	p-Nitrophenol	Stainless steel ultrasonic bath equipped with transducer operating at a frequency of 25 kHz and rated power output of 1 kW was used. The operating temperature was maintained at 28 ± 2 °C. For Fenton system, $FeSO_4$:H_2O_2 ratios of 1:5, 1:7.5 and 1:10 were maintained at pH of 3.7	The enhancement in extend of degradation of p-nitrophenol was observed due to the combination of ultrasound and Fenton system	[57]
5	Phenolic compounds like phenol, 2-CP and 3,4-dichlorophenol	Horn type ultrasonic sonicator with 20 kHz and a maximum power output of 250 kW was used. Glass reactor of 0.12 L provided with water jacket was used. Fe^{2+} concentration was maintained at 0.8 mg/L	The addition of Fe^{2+} increased the degradation of phenolic compounds. The degradation was followed first order kinetics with respect to substrate concentration	[58]
6	2,3 and 4 Chlorophenol and penta chlorophenol	Cylindrical glass vessel of 150 mL volume with an operating volume of 65 mL was used. A horn type ultrasound wave generator of 65 mm dia was used at 200 kHz with an input intensity of 200 W. Fe^{2+} concentrations used were 1 mM and 2 mM	Addition of Fe^{2+} ions enhanced the percentage degradation. Ferrous ions are reacting with H_2O_2 to regenerate hydroxyl radicals thereby increasing the efficiency of ultrasonic degradation. The enhancement in rate observed with 1 mM of Fe^{2+} was 140%, whereas further increase in Fe^{2+} up to of 2 mM showed only 50%. This is due to the scavenging of hydroxyl radicals by Fe^{2+} ions	[59]
7	p-Chlorobenzoic acid	Borosilicate jacketed glass reactor of 150 mL volume and an ultrasonic probe frequency of 20 kHz was used. The temperature was maintained at 20 °C. H_2O_2 concentration used: 2–20 mM. Goethite (FeOOH) concentration range of 0.0375–0.6 g and pH range of 3–9 was used	The addition of $FeOOH$–H_2O_2 enhanced the degradation rate of p-CBA degradation in the presence of ultrasound due to continuous cleaning and chemical activation by acoustic cavitation. First order rate constant obtained for sono-Fenton like system was 1.54×10^{-2} min^{-1}. The rate enhancement was due to the continuous cleaning and chemical activation of FeOOH surfaces by acoustic cavitation	[60]
8	Non-volatile organic compounds	A cylindrical reactor equipped with titanium probe (dia: 1.3 cm, 20 kHz) was used. The temperature was maintained at 25 ± 2 °C using water bath. Power intensity of 14.3 W/cm^2 was used. Fe^{2+} ions added in the range from 0–20 μM. The pH was adjusted to 3.5 using phosphate buffer	The coupled Fe^{2+}/ultrasound process enhanced the hydroxyl radical production rate by 70% compared to the ultrasound process. Degradation rate was increased by 2.8- and 3.6-fold at 10 and 20 μM Fe^{2+}, respectively	[61]
9	Carbofuran	A cylindrical reactor (1 L) with an ultrasound horn of 20 kHz was used. Reaction temperature was maintained at 25 °C using cooling jacket. The Initial concentration range of 0–200 mg/L, Fe^{2+} concentration range of 0–50 mg/L, H_2O_2 concentration range of 0–500 mg/L was used. The solution pH was maintained at 3	More than 40% carbofuron was oxidized by ultrasonic process alone in 120 min. Combined ultrasonic/Fenton process increased the carbofuran degradation by more than 99% and mineralization by 40% within 30 min. Possible degradation pathway for carbofuran is proposed	[62]
10	Rhodamine B	Bath type ultrasonic reactor (25 kHz) with cooling jacket was used for sono Fenton process. The initial pH was adjusted to 2 and in few cases neutral pH also used. Initial concentration of iron was maintained at 0.018 mol/L	The degradation of 50 mL of 5 mg/L Rhodamine B solution using sono-Fe^{2+}, sono-Fe^{3+} and sono-Fe^0 processes showed 46%, 52% and 51% degradation, respectively in 30 min reaction time	[63]

Table 5
Overview of work done in the area of electro-Fenton oxidation in recent years.

S. no.	Wastewater/organic compounds used	Experimental conditions	Remarks	Reference
1	Leather tanning industry wastewater	A glass reactor (0.5 L) equipped with cathode and anode, both made of iron and installed in parallel to each other at a distance of 6 cm. Effective working area of electrodes was 45 cm². The contents were stirred using magnetic stirrer and pH was maintained at 3, 5 and 7.2. H_2O_2 range used: 840–5010 mg/L and current used: 0.35–1.5 A	The COD removal obtained at pH 3 and at neutral pH was 70% and 60%, respectively. During this process energy demand was 3.8 kWh/g COD removal. The results showed 100% sulfide removal in 10 min	[71]
2	Azo benzene	Cylindrical reactor with three electrodes was used. Cathode material: carbon felt (60 cm²); reference electrode: calomel electrode; and anode used: Pt sheet (5.5 cm²). Solution pH was maintained at 2. Oxygen was bubbled prior to electrolysis and about 0.5 mmol/L of ferrous ion was added as iron source. H_2O_2 was produced electrolytically and 60 mA current was maintained throughout the experiment	Over 80% COD removal was observed. The reaction pathway was identified and intermediate compounds were determined by HPLC. Degradation of azobenzene follows pseudo first-order kinetics	[75]
3	Clofibric acid	Electrolysis reactions were conducted in an open, undivided and thermostatic cylindrical cell containing 100 mL of solution stirred using magnetic stirrer. Anode is Pt sheet and cathode is carbon PTFE with 3 cm² area. pH was maintained at 3 and Fe^{2+} concentration of 1 mM was used. All experiments were conducted at 35 °C. H_2O_2 was electrolytically produced and current density of 33, 100 and 150 mA/cm² were used	Percentage mineralization of 80% was achieved and it was due to the efficient production of hydroxyl radicals from Fenton reagent. However, stable Fe^{3+}–oxalato complexes were formed. The degradation kinetics follows pseudo-first order and rate increased with an increase in current density	[76]
4	Phenol	Open and undivided cylindrical glass cell (0.4 L) of internal diameter equal to 60 mm was used as reactor and was operated at room temperature. Cathode is press of carbon felt and cylindrical Pt anode was placed at the center of the reactor. Compressed air was bubbled for 10 min before the experiment. Initial pH was maintained at 3. Catalyst used: Fe^{2+} in the range of 0.05–1 mM and current density studied: 5.29–2.56 mA/cm²	The optimum catalytic condition was observed with 0.1 mM Fe^{2+} and 100% TOC removal of aqueous phenol solution was observed at this condition. Intermediate compounds identified are hydroquinone, p-benzoquinone and catachol. Maleic acid, fumaric acid and oxalic acid were observed as the end products. Phenol degradation was followed pseudo first order kinetics	[77]
6	Indigo carmine	Open undivided thermostatic cylindrical glass cell of capacity 100 mL was used as a reactor. The contents were stirred magnetically. The anode was either a 3 cm² Pt foil or a 3 cm² BDD thin film deposited on a conductive silicon sheet. Cathode was a 3 cm² carbon-PTFE fed with O_2 at 12 mL/min for continuous H_2O_2 production. pH range of 2–6, current density of 33, 100, 150 mA/cm² was used. Ferrous ion concentration of 0.2 mM and 5 mM was used. All experiments were carried out at 35 °C	Complete mineralization was feasible with BDD anode and 1 mM Fe^{2+}. Mineralization was enhanced with an increase in current density. Indigo carmine decay kinetics followed pseudo zero order reaction. Isatin 5-sulfonic acid, indigo and isatin were detected as aromatic byproducts, which are degraded to oxalic acid and oxamic acids. The Fe^{3+}-oxalate complexes were completely destructed at BDD anode surface	[78]
7	Land fill leachate	A rectangular glass reactor containing 200 mL solution was used for batch experiments. Constant current supply of 1–3 A using DC power supply was used. A pair of anode (Ti/RuO_2–IrO_2) and cathode at different distances such as 0.7, 1.3, 2.1 and 2.8 cm were dipped into leachate solution. pH was adjusted to 3 using sulfuric acid. H_2O_2 range of 0.1–0.44 mol/L and Fe^{2+} range of 0.1–0.12 mol/L was studied	The COD removal of 65% was obtained when H_2O_2 alone used in the reactor. Presence of Fe^{2+} greatly improved the COD removal up to 83.4% at a dosage of 0.038 mol/L Fe^{2+}. Further increase in Fe^{2+} concentration decreased the COD removal. The optimum electrode distance obtained was 2.1 cm. The step wise or continuous addition of H_2O_2 was more efficient than addition of H_2O_2 in a single step	[73]
8	PVC-stabilizer processing wastewater	Batch electrolysis was performed in a rectangular reactor operated at constant current mode. Titanium rod coated with IrO_2/RuO_2 was used as anode. Cylindrical cathode was located outside the anode and the distributor. Ratio of working area of the anode to cathode was 1:8. The solution pH was maintained at 2. Required amount of H_2O_2 and Fe^{2+} was added externally.	About 89% COD removal was observed with 2000 mg/L Fe^{2+} and 28,000 mg/L H_2O_2. Electro-Fenton process was found to be superior to direct anodic and Fenton's method. The intermediate complex like acetate, oxalate and formate were identified.	[79]
9	Municipal wastewater	Glass vessel (2 L) containing a cylindrical iron anode (289.4 cm²) and a graphite cylindrical cathode placed at the center (35.8 cm²) was used. Air was supplied at the bottom of the vessel. Contents were stirred continuously using magnetic stirrer. Current range used: 0.2–1 A. Fenton reagent was produced electrolytically and used for the treatment	Complete removal of color was observed at a current input of 1 A and at 30 min of reaction time. Chemical oxygen demand removal of 74.8% and turbidity removal of 92.3% were obtained	[80]
10	Nitro phenols	Undivided glass cell of 250 mL capacity containing graphite cathode and platinum black anode was used. The pH was maintained at 3 using H_2SO_4 and Na_2SO_4 was used to maintain the conductivity. All experiments were carried out at room temperature. Constant current of 50 mA was maintained and 0.5 mmol/L of Fe^{2+} was used	Degradation of 4-nitrophenol was significantly enhanced by the introduction of aeration and Fe^{2+}. The results showed 98% removal of 4-NP and 13% removal of TOC. Electro-Fenton process eliminates the toxicity and improved the biodegradability of 4-Nitrophenols. Intermediates such as hydroquinone and benzoquinone were detected by GC/MS analysis	[81]

reduced pH (pH < 3) is low [69]. This is due to the formation of $Fe(OH)_3$ that is slightly reduced to Fe^{2+}. Stoichiometric quantity of Fe^{2+} can be used at near neutral pH, thus overcoming the need for acidic conditions, which is a fundamental disadvantage of Fenton reaction. In principle, the most promising electro-Fenton method is type 4, in which ferric ion is reduced to ferrous ion at the cathode; however, Fe^{2+} regeneration is slow even at an optimal current density [69]. The efficiency of electro-Fenton process depends on electrode nature, pH, catalyst concentration, electrolytes, dissolved oxygen level, current density and temperature. The studies related to electro-Fenton process reported in the literature are summarized in Table 5.

Photo-Fenton processes

A combination of hydrogen peroxide and UV radiation with Fe^{2+} or Fe^{3+} oxalate ion (photo-Fenton (PF) process) produces more hydroxyl radicals compared to conventional Fenton method or photolysis and in turn increases the rate of degradation of organic pollutants [82–84]. Fenton reaction accumulates Fe^{3+} ions in the system and the reaction does not proceed once all Fe^{2+} ions are consumed. The photochemical regeneration of ferrous ions (Fe^{2+}) by photo-reduction (Eq. (21)) of ferric ions (Fe^{3+}) occurs in photo-Fenton reaction [85]. The newly generated ferrous ions react with H_2O_2 and generate hydroxyl radical and ferric ion, and the cycle continues:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^\bullet OH \qquad (21)$$

The studies reported in the literature showed that the combination of Fenton reaction with conventional radiation zone of the visible and near ultraviolet gives a better degradation of organic pollutants. Pollutants such as 4-chlorophenol [86], nitrobenzene and anisole [87], herbicides [83] and ethyleneglycol [88] were degraded effectively by photo-Fenton process.

Direct photolysis of H_2O_2 (Eq. (22)) produces hydroxyl radicals which can be used for the degradation of organic compounds. However, in the presence of iron complexes, which strongly absorb radiation, this reaction will contribute only to a lesser extent for the photo-degradation of organic contaminants [89,90]:

$$H_2O_2 + h\nu \rightarrow 2{}^\bullet OH \qquad (22)$$

The photo-Fenton process offers better performance at pH 3.0, when the hydroxy–Fe^{3+} complexes are more soluble and $Fe(OH)^{2+}$ are more photoactive [91].

The photo-Fenton process was reported as more efficient than Fenton treatment [84]. In some cases, use of sunlight instead of UV irradiation reduced the costs. However, this offers a lower degradation rate of pollutants. Acidic conditions (about pH 3) were also reported to be favorable and this may be mainly due to the conversion of carbonate and bicarbonate species into carbonic acid, which has a low reactivity with hydroxylradicals [92].

De Oliveira et al. [90] compared the performance of Fenton and photo-Fenton processes for the treatment of painting industry effluent (COD = 80.75 mg/L) and reported higher COD and TOC removal with solar-assisted photo-Fenton process compared to Fenton treatment or when an artificial radiation source was used. The performance comparison study made with three iron sources such as $FeSO_4$, $Fe(NO_3)_3$ and potassium ferrioxalate ($K_3[Fe(C_2O_4)_3]$, obtained by mixing $Fe(NO_3)_3$ with $K_2C_2O_4$ solutions). The formation of Fe^{3+} complex when $Fe(NO_3)_3$ was used resulted in poor performance, whereas the addition of $K_3[Fe(C_2O_4)_3]$ increased the carbon loading of the wastewater. In the presence of 15 mM of Fe^{2+} and 300 mM of H_2O_2, 99.5% COD reduction was reported when the wastewater was irradiated with solar radiation for 6 h.

Amat et al. [93] compared the degradation of two commercial anionic surfactants such as sodium dodecyl sulfate and dodecylbenzenesulfonate, using Fenton reagents (Fe^{2+} or Fe^{3+} with H_2O_2 in the presence or absence of solar radiation), photo-catalysis (TiO_2 with solar irradiation) and photo-degradation using solar sensitizer (pyrylium salt). They demonstrated that the addition of the solar sensitizer did not efficiently degrade the surfactants and their further studies concluded that the photo-Fenton processes using solar radiation (0.1 mM of Fe^{2+} or Fe^{3+}, and 1 mM H_2O_2) had a higher rate of surfactant degradation than that of solar-TiO_2 treatment. The illustrative works related to photo-Fenton process reported in the literature are presented in Table 6.

Sono-photo-Fenton process

The combined treatment using ultrasound and ultraviolet along with Fenton reagent is known as sono-photo-Fenton (SPF) process, which enhanced the production of hydroxyl radicals in an aqueous system significantly. Sonolysis of water produces hydroxyl radicals and hydrogen atoms. However, significant loss of ${}^\bullet H$ and ${}^\bullet OH$ species occurs due to the recombination. On the other hand, the application of UV light, converted the hydrogen peroxide produced by recombination of hydroxyl radicals, and in turn increased the amount ${}^\bullet OH$ [100]. The intermediate complex formed due to the reaction of Fe^{3+} with H_2O_2 during the Fenton reaction could be reduced to Fe^{2+} by sonolysis [57] and photolysis [69].

The direct photolysis ($\lambda < 400$ nm) of H_2O_2 also generates hydroxyl radicals (Eq. (22)) and the process is cyclic one with respect to Fe^{2+} ions. The amount of ferrous salt required under SPF condition is very small compared to Fenton condition, where ferrous ions need to be added at regular intervals to continue the reaction. Otherwise, reaction will stop after the complete conversion of ferrous ions into ferric ions. SPF process reduces the amount of ferrous ions present in the treated water, and this is very important in an industrial point of view [101].

Segura et al. [102] investigated the application of SPF process for the degradation of phenol using Fe_2O_3/SBA-15 as a heterogeneous catalyst. The initial pH was maintained at 3. TOC degradation of 45% was observed with sono-photo-Fenton process whereas 30% and 40% TOC degradation was observed with sono-Fenton and photo-Fenton processes, respectively.

Mendez-Arriaga et al. [103] investigated the degradation of recalcitrant pharmaceutical micro-pollutant ibuprofen (IBP) by means of sono-photo-Fenton, sono-photo-catalysis and $TiO_2/Fe^{2+}/$ sonolysis processes. The presence of ultrasound irradiation in photo-Fenton process improved the iron catalytic activity and ibuprofen degradation and mineralization to 95% and 60%, respectively. On the other hand, total removal of ibuprofen and elimination of more than 50% of dissolved organic carbon were observed by photocatalysis with TiO_2 in the presence of ultrasound irradiation. The results showed that, the hybrid system is a promising method for complete elimination/mineralization of the recalcitrant micro-contaminant ibuprofen.

Vaishnave et al. [101] conducted a study on degradation of azure-B by sono-photo-Fenton and photo-Fenton processes. The degradation rate was found to be strongly dependent on initial pH, initial concentration of azure-B, Fe^{2+} concentration, H_2O_2 concentration and UV light intensity. The effects of these parameters were studied and the optimum operational conditions of these processes were found. The optimum conditions obtained for 1.33×10^{-4} mol/L of azure-B was: pH 2.1; H_2O_2 0.5 mL; Fe^{3+} 5.0×10^{-4} mol/L; ultrasonic frequency 40 kHz; and light intensity 75.5 mW/cm². The results showed that the dye was completely oxidized and degraded into CO_2 and H_2O.

Zhong et al. [104] studied the degradation of C.I. Acid Orange 7 (AO7) by the integrated heterogeneous sono-photo-Fenton process

Table 6
Summary of the works reported in the literature related to photo-Fenton oxidation.

S. no.	Wastewater/organic compounds used	Experimental conditions	Remarks	Reference
1	Landfill leachate containing biorefractory organic compounds	Lab scale glass reactor of capacity 1.6 L was used and the contents were irradiated with mercury high pressure lamp (energy input 500 W/1000 W) was used.	Maximum COD reduction of 80% at pH 2.5 was obtained and the extent of degradation decreased with an increase in pH. Increase in Fe^{2+} concentration from 0.4 to 1.2 mM/L increased the rate of degradation. Photo-Fenton process is more economical with a 32% energy reduction as compared to UV/H_2O_2 system	[94]
2	Mono-di-and-tri-nitrotoluene	Glass tubes of 18 mL capacity (18 in total) was used as reactor and was irradiated with UV light having an incident intensity of 21 W/cm² and at 30 °C	The order of degradation was UV Fenton (pH = 3) > dark Fenton > UV-Fenton (pH = 6.1) > UV/H_2O_2 > H_2O_2. The degradation of nitro toluene follows pseudo first order and rate constants have been given for different techniques. Humic acid showed a little inhibiting effect on degradation process	[95]
3	Pesticide industry effluents containing mixture of components	Cylindrical (30 mL) borosilicate reactor irradiated with 16 fluorescent black lamps of 14 W each was used. Temperature of reaction was maintained at 25 °C	Complete removal of pesticide was observed within 30 min of reaction time except for methoxychlor for which, the removal was approximately 80%. Optimum pH was obtained as 2.8. Thermal pretreatment increased the rates of reaction by photo-Fenton mechanism	[96]
4	Dichloroacetic acid and 2,4-dichlorophenol	Cylindrical upflow reactor with annular irradiation by 15 W black light lamp with a capacity of 280 mL was used. 700 mL of effluent can be treated with recirculated mode operation	Optimum pH for degradation was observed in the range of 2.5–2.8 and hydrogen peroxide consumption is high at this operating pH range. Removal efficiency reaches steady state at concentration of H_2O_2 of 6 mM and 1.5 mM of ferroxalate ions. Complete degradation was observed at 30 W/m² and linear variation with light intensity was observed	[97]
5	Reactive Black 5 and Reactive Black Blue 21 dyes	Annular borosilicate glass reactor equipped with 20 W black light fluorescent lamps was used. Operating temperature of 20 °C was maintained throughout the reaction. 1000 mL of effluent was used and pH was maintained at 4. TiO_2 (1 g/L) was used as photo-catalyst to compare with photo-Fenton process	Partial chemical oxygen demand removal was observed by adsorption with the photo-catalyst where as <10% chemical oxygen demand removal was observed with Fenton chemistry alone. First order kinetics was observed for all the systems studied and rate constant for the decolorization process was in the order of $Fe^{2+}/UV/H_2O_2$ > $Fe^{3+}/UV/H_2O_2$ > UV/TiO_2. Use of advanced oxidation processes resulted in lowering the toxicity toward bacterial treatment	[98]
6	Catechol	Cylindrical pyrex vessel of 300 mL volume was filled with 100 mL catechol solution and was degraded using photo-catalysis and photo-Fenton experiments. All experiments were carried out at room temperature. A 125 W black light fluorescent lamp (350 nm) was used as the light source. pH of the solution was maintained at 3 for all the experiments	The optimum $H_2O_2/FeSO_4$ ratio at pH 3, 30 rpm and 30 min reaction time was determined as 600/500 (W/W). Under these conditions, 83% and 98% of chemical oxygen demand removal was obtained for Fenton and photo-Fenton processes, respectively. Although a good removal was achieved by photo-catalysis process, a significant higher irradiation time was required compared to Fenton and photo-Fenton processes, which may result in an increased energy cost	[29]
7	Phenol	A cylindrical pyrex glass reactor containing 1 L of aqueous solution of pollutant and catalyst was used. A 150 W medium pressure mercury lamp was used as the irradiation source. The reaction temperature was maintained at 25 °C throughout the reaction and pH was maintained at 5.5	Iron containing SBA-15 catalyst consisting of crystalline hematite particle was reported as a promising catalyst for the treatment of phenolic solution. The stability of the catalyst toward iron leaching is strongly dependent on oxidant to catalyst ratio. Catalyst loading of 0.5 g/L and hydrogen peroxide concentration of 2450 mg/L showed a total abatement of phenol and remarkable organic mineralization	[99]

using mesostructured silica (Fe_2O_3/SBA-15) as heterogeneous catalyst. The effect of hydrogen peroxide concentration, initial pH, Fe_2O_3/SBA-15 loading, ultrasonic power and initial solution concentration on the decolorization was investigated. The results showed that the degradation efficiency increased with an increase in hydrogen peroxide concentration, ultrasonic power, Fe_2O_3/SBA-15 loading, but decreased with an increase in initial pH and initial dye concentration. The particle size distribution of spent catalyst evidenced a remarkable size reduction during reaction, leading to more reaction surface and higher mass transfer rate. The reaction intermediates were identified using GC–MS and degradation pathway was proposed.

Sono-electro-Fenton process

Many researchers have reported the coupling strategy between sonochemistry and different AOPs such as the Fenton process giving rise to the concept of advanced sonochemical hybrid techniques that possess significantly greater efficacy for water remediation [105–107]. Hydroxyl radicals produced by water decomposition (Eq. (14)) are used for the degradation of organics [107].

Abdesalam and Birkin [108] studied the sono-electro-chemical degradation of Meldola Blue using a recirculation type three electrode flow cell with Pt gauze as the anode and RVC as the

cathode (15 mm × 10 mm × 5 mm). The reactor was coupled to a piezoelectric transducer of 124 kHz and 100 V for treating 100 mL of 0.1 mM dye solution with different Fe^{2+} concentration at pH 2 and 25 °C. An apparent rate constant of 2.4×10^{-2} min^{-1} was reported for the decolorization with 0.5 mM Fe^{2+} (optimum catalyst content) at $E_{cat} = -0.7$ V/Ag, which is twice the value obtained for electro-Fenton process. Under these conditions, the COD was reduced by 61% after 100 min of sono-electro-Fenton (SEF) treatment.

Yasman et al. [109] studied the degradation of common herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D) and its derivative 2,4-dichlorophenol (2,4-DCP) using SEF process. A cylindrical glass reactor containing ultrasonic generator (75 W and 20 kHz) was immersed from the top of the reactor. Both cathode and anode were made up of nickel foil (0.125 mm thin) in the form of cylindrical segment of 11 mm radius and 20 mm height. Temperature of the solution was maintained at 25 °C by circulating water in a double jacket cooling array. Complete degradation of 2,4-D (1.2 mM) was found using 3 mM Fe^{2+} and H_2O_2 at a reaction time of 60 s. Thus, the time required for the degradation was considerably shorter for SEF scheme when compared to F and SF scheme. This result indicates that the SEF process is an effective method for the detoxification of wastewater.

Oturan et al. [110] investigated the effect of EF and SEF process for the degradation of herbicides namely 2,4-dichlorophenoxyacetic acid (2,4-D) (1 mM)), 4,6-dinitro-o-cresol (0.5 mM) and azobenzene (0.1 mM). The process was carried out using 0.1 mM Fe^{3+} in O_2 saturated solution with 0.05 M Na_2SO_4 at pH 3 and at 200 mA of current intensity. For SEF process, either a low frequency of 28 kHz or high frequency of 460 kHz was applied with in an output power range from 20 to 80 kW. Complete degradation of 2,4-D was achieved in 80 min using 20 W output. The results showed that the nature of the organic structure of compounds plays an important role in SEF. The improvement yielded by SEF at 20 W was ascribed to (i) the enhancement of the transfer of reactants Fe^{3+} and O_2 toward the cathode for the electro generation of Fe^{2+} and H_2O_2; (ii) the additional generation of hydroxyl radicals by sonolysis of water and (iii) the pyrolysis of organics due to the cavitaion promoted by ultrasound irradiation.

Li et al. [111] evaluated the effect of low frequency ultrasonic irradiation on the sono-electro-Fenton oxidation of cationic red X-GRL. Ultrasonic irradiation significantly increased the hydrogen peroxide production rate and reduced the time needed to reach the maximum hydrogen peroxide concentration. In addition, ultrasonic irradiation has a considerable effect on the degradation of cationic red X-GRL. The results showed that the degradation rate followed pseudo-first order kinetics and also decolorization rate increased with ultrasonic power. Furthermore, total organic carbon removal efficiency and mineralization current efficiency were greatly promoted in sono-electro-Fenton process compared to electro-Fenton process. These results proved that sono-electro-Fenton process is a promising technology in terms of colored wastewater treatment.

Martinez and Uribe [112] investigated the degradation of Azure B dye by Fenton, sonolysis and sono-electro-Fenton process employing ultrasound at 23 kHz and the electrolytic generation of hydrogen peroxide at the reticulated vitreous carbon electrode. The dye degradation followed apparent first-order kinetics in all the degradation processes. The rate constant was affected by pH and initial concentration of ferrous ion, with the highest degradation obtained at pH between 2.6 and 3. The rate constant for Azure B degradation by sono-electro-Fenton is 10 times higher than that of sonolysis and 2 times larger than that of Fenton process. The COD removal of 68% and 85% was obtained by Fenton and sono-electro-Fenton process, respectively and 90% removal of Azure B was observed with both the processes.

Photo-electro-Fenton process

The catalytic effect of Fe^{2+} in the electro-Fenton process can be enhanced by irradiating the contents with UV light. Thus, the combination of electrochemical and photochemical process with Fenton process is called photo-electro-Fenton (PEF) process generates greater quantity of free radicals due to the combination effect [113,114]. The direct photolysis of acid solution containing peroxide generates hydroxyl radicals through the hemolytic breakdown of the peroxide molecule according to Eq. (22). This reaction increased the oxidative capability of the process due to the additional production of hydroxyl radicals. Thus, the degradation of target organic substrate can be enhanced when the solution is irradiated with UV light in addition to the application of electro-Fenton process. Photochemical regeneration of Fe^{2+} by the photo-reduction of Fe^{3+} ions and photo-activation of complexes renders the photo-electro-Fenton systems more efficient [115,116]. At acidic pH, oxalic acids behave as the photo-active complexes in the presence of ferric ions which undergo photo-decarboxylation reaction [19] as shown in Eq. (23):

$$R(CO_2) - Fe(III) + h\nu \rightarrow R(CO_2^{\bullet}) + Fe(II) + R^{\bullet} + CO_2 \qquad (23)$$
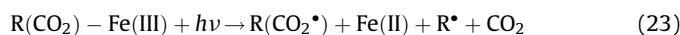
The studies pertaining to the application of PEF process are very limited and most of the studies are related to the treatment of herbicide [113,115–117], 4-chloro-2-methylphenol [118] and dyes [78]. Flox et al. [119] recently used solar photo-energy as photon source and reduced the operating costs of the process substantially. The various studies carried out using photo-electro-Fenton process are summarized in Table 7. Some of the illustrative works in recent years have been discussed in detail so as to establish the optimum operating parameters and other critical considerations for attaining maximum efficiency of this hybrid oxidation technique.

Nano-zero valent iron mediated degradation

In homogeneous Fenton and combined processes, the main disadvantage is the requirement of 50–80 ppm ferrous ion and this value is much above standards. In addition, the application of homogeneous AOPs to treat large quantity of water may produce large amount of sludge in the final neutralization step [123]. In order to avoid these disadvantages, nano-zero valent iron (NZVI) could be used as an alternative way to induce Fenton oxidation.

Zero valent state metals (such as Fe^0, Zn^0, Sn^0 and Al^0) are surprisingly effective agents for the remediation of contaminated ground water [124,125]. In particular, it has been the subject of numerous studies over the last 10 years and this is an interestingly popular choice for treatment of hazardous and toxic wastes, and for remediation of contaminated sites.

Fenton like reactions using nano-zero valent iron

In heterogeneous Fenton reaction, oxidation of NZVI provides an alternative means of inducing Fenton oxidation [126,127] as shown in Eq. (24):

$$O_2 + Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \qquad (24)$$

Use of NZVI to induce Fenton oxidation has two advantages beyond addition of Fe^{2+}/H_2O_2 [128]:

- NZVI is able to attach or coat on large particle, therefore NZVI absorbed media could treat contaminated water passing through a sand filter or other type of filtration system.
- NZVI injected through wells could be immobilized in/on soil grains in contaminated aquifers.

Table 7
Summary of the studies reported in the literature related to photo-electro-Fenton oxidation.

S. no.	Wastewater/organic compounds used	Experimental conditions	Remarks	Reference
1	Aniline	Glass reactor provided with Pt anode and carbon PTFE cathode was used for the mineralization experiments. A constant current of 0.1 A was supplied. A 125 W mercury lamp with an emitting wavelength of 360 nm was used as the irradiation source. Fe^{2+} concentration was maintained at 1 mM	The aniline mineralization was increased by UV irradiation. The photo-electro-Fenton process allows 92% of TOC removal after 6 h. Whereas in electro-Fenton, only 68% of mineralization was achieved. Reaction pathway for aniline mineralization to CO_2 involving intermediates was proposed	[120]
2	2,4,5-Trichlorophenoxy acetic acid	An undivided, open cylindrical cell stirred with magnetic bar was used for electrolysis reaction. The anode and cathode was Pt sheet and carbon-PTFE respectively. O_2 flow rate of 20 mL/min was sent to the cathode for continuous production of H_2O_2. The pH range of 2–6 and current range of 100–450 mA was used. All experiments were conducted at 35 °C. Fe^{2+} concentration range studied was 0.5–2 mM. The solution were irradiated with a Philips 6 W fluorescent bulb ($\lambda = 360$ nm)	PEF process showed a fast and complete removal of herbicides in the pH range of 2–4, operating at low current and 1 mM Fe^{2+}. Whereas only 60–65% of mineralization was achieved by electro-Fenton process. The herbicide degradation follows pseudo first order kinetics. All oxalate complexes produced at the end of the treatment are rapidly photo-decarboxylated by UV light in the photo-electro-Fenton treatment	[116]
3	3,6-Dichloro-2-methaxy benzoic acid	Undivided cylindrical stirred electrochemical cell was used for all electrolysis process. Platinum sheet and carbon-PTFE fed with an O_2 flow rate of 20 mL/min was used as anode and cathode respectively. A 6 W Philips fluorescent light ($\lambda = 360$ nm) placed at the top was used as the irradiation source. Fe^{2+} concentration of 1 mM was used and the temperature was maintained at 25 °C. The initial pH of solution was maintained at 3	Electro-Fenton process showed 60–70% mineralization, whereas photo-electro-Fenton process showed a fast and complete degradation of herbicide solution at low current by the action of UV irradiation. The degradation of herbicide follows pseudo-first order kinetics. The fast photo-decarboxylation of stable complexes explained the highest oxidation ability of photo-electro-Fenton process	[115]
4	Indigo carmine dye	Experiments were conducted in an open, one compartment and thermo static cylindrical glass cell. The anode was either Pt foil or BDD thin film and the cathode was carbon-PTFE. The reactor was fed with pure O_2 for the continuous production of H_2O_2. A 6 W fluorescent bulb ($\lambda = 360$ nm) was used as the irradiation source. The Fe^{2+} and Cu^{2+} concentrations used were in the range of 0.25 and 1.0 mM. All experiments were carried out at 35 °C. The mineralization of indigo carmine solutions was monitored by the removal of their total organic carbon and the intermediates were identified by HPLC	Complete mineralization was achieved using photo-electro-Fenton method with BDD anode and 1.0 mM Fe^{2+} and 0.25 mM Cu^{2+} as the catalyst. The corresponding optimum pH value obtained was 3. Mineralization was enhanced with increasing current density. The Fe^{3+}–oxalate complexes are destructed under the action of ultraviolet light. The degradation followed pseudo-zero order kinetics	[78]
5	Clofibric acid	Open, undivided thermostatic cylindrical cell stirred with magnetic bar was used for the electrolysis. A 3 cm^2 Pt sheet and 3 cm^2 carbon-PTFE was used as the anode and the cathode respectively. The O_2 flow rate of 12 mL/min was used to generate H_2O_2 electrolytically. A low pressure Philips fluorescent bulb ($\lambda = 360$ nm) was used as the irradiation source. Fe^{2+} concentration of 1 mM and a current of 0.1 A was used	TOC removal of 86% was obtained in EF process whereas 96% TOC decay and complete dechlorination were observed in PEF process. Decay of clofibric acid followed pseudo first order kinetics for EF and PEF processes. The Fe^{3+}–oxalate complexes formed were efficiently photodecarboxylated in PEF under the action of UV light	[76]
6	Benzene sulfonic acid	A 3.5 L cylindrical reactor fitted with titanium net coated RuO_2/IrO_2 (DSA) was used as anode and stainless steel as cathode was used. Sixteen 3 W UV lamps ($\lambda > 320$ nm) were used as the irradiation source. All experiments were carried out at room temperature. Fe^{2+} concentration of 8 mM and H_2O_2 concentration of 166 mM at pH 2 with a current density of 71 A/m^2 was used for mineralization	The double cathode reactor increases the working area and enhances the current efficiency by 75% and this would cause greater production of ferrous ion. The maximum TOC removal efficiency of 72% was achieved at the optimum electrode distance of 3 cm. Synergistic effect of photoelectron-Fenton method showed a COD removal efficiency of 14% higher than that of electro-Fenton process	[69]
7	Real wastewater (COD: 24,000 mg/L)	A 4 L capacity reactor with a UV light source ($\lambda = 365$ nm) fixed inside the cylindrical pyrex tube was used. The reaction solutions were mixed using a circulation pump with 200 mg/L ferric sulfate and different H_2O_2 dosage supplied continuously at room temperature. The anode was Ti rod coated with IrO_2/RuO_2 (DSA) and cathode was a cylindrical Ti-DSA grid. The pH of the solution was adjusted and maintained at 2	The TOC removal of 98% and 99% was achieved by semi batch electro-Fenton and semi batch photo-electro-Fenton method, respectively. The optimum Fe^{2+} and H_2O_2 concentrations were found to be 200 mg/L and 6 mL/min, respectively. The other optimum conditions were pH 2, current intensity 20 A and 420 min of reaction time. The electro-generated Fe^{2+} ions were efficiently used to produce hydroxyl radicals and prevented H_2O_2 from overflow	[121]
8	Sulfomethaxazole	Undivided two electrode quartz cell stirred by using a magnetic stirrer was used. The anode was a RuO_2/Ti mesh and a cathode was ACF felt. O_2 was fed into the solution at a rate of 100 mL/min prior to electrolysis for 30 min. The UV lamp (254/365 nm) was placed parallel to the side of the cell at a distance of 5 cm from the solution. Solution pH was maintained at 3. Fe^{2+} of 1 mM and current of 0.36 A were maintained throughout the experiments	The applied current of 0.3 A showed a faster and more complete degradation. TOC removal of 80% was observed after 6 h electrolysis. In electrolysis process only 63% mineralization was achieved due to carboxylic acids production as intermediates. But those complexes were rapidly removed by PEF because of quicker photo-degradation by the UV light	[122]

Tang and Chen [129] investigated the effect of iron powder and H_2O_2 on degradation of azo dyes and phenolic compounds. At pH below 2.5, dye removal was found to be mainly by adsorption whereas, at higher pH, the adsorption was less important. The addition of H_2O_2 doubled the dye removal and was greater than 90%.

Takemura et al. [130] investigated the influence of steel wool, steel foil, and reticulated iron in the presence of hydrogen peroxide on the oxidation of perchloroethylene (PCE). The solids mentioned above reduced the PCE concentration from 100 mg/L to <0.1 mg/L in 24 h. The reaction with reticulated iron could be conducted at pH 5–9 with no apparent iron-oxide by product.

Joo et al. [131] have observed the oxidation of organic compounds in aqueous solution when mixed with nano scale zero valent iron particles in the presence of air and no added H_2O_2. Evidently, H_2O_2 and Fe^{2+} are generated by dioxygen corrosion of the metal and released into solution, or react on the surface. This represents a novel use of zero-valent iron, normally a reducing agent, for the oxidation reaction that has potential application for soil treatment.

Joo et al. [126] studied about the ability of NZVI to induce oxidative degradation of contaminants. This study demonstrated that NZVI was capable of degrading the herbicide molinate in the presence of oxygen. In this study, it was shown that NZVI-induced Fenton oxidation could degrade over 60% of molinate at pH 8.1 and 65% at pH 4. Subsequent to this investigation, Feitz et al. [132] reported that NZVI under the optimal column configuration showed more than 90% removal of 100 ppb molinate in 3 h. While NZVI appears to induce oxidation effectively at low pH, the accumulation of ferric oxyhydroxides on the surface of Fe^0 in neutral to slightly alkaline environments is expected to reduce the reactive surface area for the formation of hydroxyl radical and hence, reduce the efficiency of NZVI remediation.

Bergendahl and Thies [128] have investigated the feasibility of oxidative removal of methyl-tert-butyl ether (MTBE) using ZVI. The results showed that over 99% of MTBE in water was degraded within 10 min and the major oxidation product was acetone. The addition of H_2O_2 greatly enhanced the degradation efficiency. The rate of degradation of MTBE increases with an increase in H_2O_2:MTBE ratio.

Simultaneous use of NZVI and complexes such as ethylene-diamine tetraacetic acid (EDTA) showed complete destruction of refractory compounds [133]. The use of ultrasound with this ZVI–EDTA system could improve the degradation of organic compounds due to the synergistic effect [134–137]. Zhou et al. [134] studied the simultaneous degradation of 4CP and EDTA in a heterogeneous ultrasound/Fenton like system at ambient conditions. The results showed weak relationship between 4-chlorophenol and EDTA.

Besides wastewater treatment, the contaminated soil remediation comprises one of the important domains of environmental engineering. Supported and catalyzed iron nanoparticles have been utilized for the remediation of contaminated soil and ground water [138,139]. Xu and Zhou [140] conducted batch and column experiments to investigate the feasibility of NZVI particles for in situ reductive immobilization of Cr(VI) in water and in a sandy loam soil. Batch kinetic tests showed that 0.08 g/L of NZVI could able to rapidly reduce 34 mg/L of Cr(VI) in water at an initial pseudo first order rate constant of 0.08 h^{-1}. Column experiments indicated that the stabilized NZVI particles are highly deliverable in the soil column and reduce the TCLP leachability of Cr in the soil by 90%.

The iron minerals in combination with H_2O_2 were used to study the natural attenuation of organic compounds in the environment, or to serve as an alternative to Fenton type treatment [141]. Although oxidation is generally much slower than the corresponding solution reaction at the same mole per liter reagent concentrations, the heterogeneous reactions are sometimes more efficient; that is, they consume less peroxide per mole of contaminant degraded. Oxidation at the surface is often speculated but there is little compelling evidence and further study is clearly warranted.

Fenton like reactions using immobilized nano-zero valent iron

NZVI was successfully used for the generation of hydroxyl radicals in AOP system [142–144]. Due to their larger specific surface area and reactive sites, NZVI has gained prominence in environmental remediation [143]. Although NZVI particles were successfully used in wastewater treatment, there are still some drawbacks associated with the process and needs to be addressed. For example, NZVI could coalesce into aggregates, which reduced the reactivity [145] and filtration is required to remove NZVI particles at the end of the treatment. To overcome these problems, NZVI particles were immobilized in or on suitable solid supports, and also to expand the effective pH range of the Fenton reaction. Some success in this regard was achieved with PVA microsphere [146,147]. The others include calcium alginate beads [148], iron exchanged with Nafion membranes [149], iron modified clays [150,151]. The modified supporting materials such as silica fabric [152], Al_2O_3 [153], zeolites [154], resins [155], and cotton [156] which are used for immobilization of iron ions could be used for immobilizing NZVI. The main advantage of the heterogeneous catalyst is its separation from the waste stream. The fundamental disadvantage is that the dissolved target molecules must diffuse to the surface to reach active sites before they are degraded.

PVA-alginate beads were used for immobilization of NZVI. The PVA-alginate beads showed improved durability and strength [157]. PVA consists of many hydroxyl groups, which generally form complexes with metal ions [158]. Thus, the usage of these beads avoids or alleviates the problems associated with the release of iron into wastewater [146].

Nafion is a perfluorinated oxyalkyl polymer with sulfonate groups capable of binding cations. Ferric exchanged Nafion membrane is claimed to be an effective photo-Fenton catalyst [149,159]. Fe-Nafion membranes appear to be effective up to an operational pH of 5. Although it was possible to achieve mineralization of 2,4-dichlorophenol at higher initial pH (up to 11), the pH(unbuffered) always drifted quickly to a value below 5 [160]. The detailed mechanism covering the role of surface reaction and of adsorption/desorption of iron ions and reactants in Fe-Nafion systems is unclear. Fernandez et al. [161] showed that Nafion bound Fe(III) could be photo-reduced to Fe(II), which subsequently undergoes the Fenton reaction. Some disadvantages of Nafion membrane for practical application is their higher cost and these membranes are not totally inert. Fluorinated radicals were found in solutions exposed to Nafion, which are produced by photo-Fenton reaction [162].

The use of novel structured inorganic silica fabrics loaded with Fe ions (Fe-EGF) by exchange–impregnation as a heterogeneous photo-catalyst was an alternative approach proposed to degrade organic compounds [152]. It was proved that the degradation of oxalates on the Fe-silica fabric was due to Fe ions leaching into solution that were re-adsorbed onto the silica fabric when compounds were mineralized.

Ferric species were also immobilized on different types of ion exchange resins and used as a heterogeneous catalyst for the degradation of cationic and anionic dye pollutants under visible light ($\lambda > 450$ nm) irradiation in the presence of H_2O_2. The cationic dyes are effectively photo-degraded on a cationic resin exchanged Fe(III) catalyst and the anionic dye is photo-degraded on an anionic resin supported catalyst [155].

Ramirez et al. [163] studied the removal of orange II dye solution using heterogeneous photo-electro-Fenton process using different iron supporting materials. Spectroscopic analysis and TOC results indicate that the process can be carried out with any of the iron supporting material used in this study. Amberlite and Purolite resins can be incorporated with 59 and 65 mg Fe/g of substrate, but a Nafion membrane can fix 45 mg/g of supporting material. Iron desorption analysis indicates that more than 90% of iron was retained by nafion membrane.

The performance of a Fe^{3+}-exchanged zeolite Y [154,164] and Fe-Zm5 zeolite [165] as a heterogeneous photo-Fenton catalyst was tested for the degradation of organic compounds. Although some leaching of Fe^{3+} was observed, it amounted to only few percent of the total iron present in the zeolites (0.3–2 mg/L in solution) which did not play a major role in the reaction.

A common characteristic of designed heterogeneous catalyst for photo-electro-Fenton reaction is that the optimal pH is generally 3. These materials are, however, efficient at higher pH values and leaching is minimized under these conditions. The contribution of heterogeneous photo-electro-Fenton process depends on the kind of catalyst, experimental conditions and target contaminants. In fact, the dissolved iron concentration in the solution is time dependent and the change in optical properties of photo-reactor. An interesting phenomenon was observed for most of the proposed catalyst, that, the leached iron ions are found to re-adsorb on catalyst surface allowing to maintain good catalyst stability.

An ideal supporting material for iron species is expected to have the following attributes: (a) to favor strong surface chemical–physical binding with the iron particles without affecting their reactivity; (b) to have high specific surface area; (c) to have good adsorption capacity for the organic compounds to be degraded; (d) to be in a physical configuration which favors the ultimate liquid-solid phase separation; (e) to allow a reactor design that facilitates the mass transfer processes; and (f) to be chemically inert. From the immobilization point of view, a good adherence catalyst/support, and no degradation of the catalyst activity by the attachment process are important. The first condition is essential, since the support/catalyst junction should resist to the stress derived from particle to particle and pesticide-fluid mechanical interactions in the reactor environment, in order to avoid detachment of catalyst particles from the support [166].

Thus, the overall efficiency of the degradation can be significantly enhanced when hybrid processes are used. Especially, use of immobilized NZVI as Fenton catalyst in hybrid treatment processes showed better performance in treating refractory compounds.

Conclusions and recommendations

Advanced oxidation processes are found to be an environmental friendly process for the degradation of refractory compounds. Different AOPs have been reported to select the most appropriate technique for the specific treatment. Major attention should be devoted in the future on the identification of reaction intermediates, development of rate expressions based on established reaction mechanisms, identification of scale-up parameters and criteria for cost effectiveness.

Hybrid methods are not economically viable techniques to degrade large quantum of effluent disposed by the industries. Hence it is advisable to use these methods as pretreatment to reduce the toxicity to a certain level beyond which biological treatment can be employed. These combined methods expected to reduce the reactor size and decrease the operating cost. However, the oxidants added during the pretreatment should be completely eliminated before subjecting to the biological treatment as they may act as inhibitors to the microorganism. On the other hand, the different AOPs were found to follow similar mechanism and hence, the may be combined in various manners to obtain maximum efficiency.

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