A REVIEW OF FENTON PROCESS FOR ORGANIC WASTEWATER TREATMENT

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Abstract - *Water pollution has become a serious matter worldwide. Due to the environment concern and requirement of pure water for increasing population high efficiency water treatment methods are needed. Advanced Oxidation Process (AOPs) are promising for wastewater treatment. Fenton process is type of AOP which has been studied widely. In this report basics of Fenton process are discussed, its reaction mechanism, pros & cons, it's application in different industries. Different optimization techniques to overcome limitation of Fenton process, their mechanism along with problems related with this techniques. Several experimental results are also listed for each type. Based on that various parameters and there effect on wastewater treatment is also covered. A small comparison is also made for Fenton process with some other AOPs. At end future prospect of Fenton process with some of R&D aspect are discussed to scale-up the process.*

Key Words: **Fenton Process, Advanced Oxidation Process (AOP), Homogeneous Fenton Process, Heterogeneous Fenton Process, Organic Wastewater Treatment, Water Pollution**

1. INTRODUCTION

1.1 Overview of Wastewater Treatment

It is of no doubt that wastewater treatment is essential part of any industry either it be food industry, textile industry, pharmaceutical industry, petrochemical plant or any refinery. To meet new standards of environment effluent emission and requirement of pure water due to increasing population, it is needed to treat wastewater generated at industrial and domestic level. Conventionally wastewater (WW) treatment is done in three ways: **Physical, chemical & biological**. Brief details of these methods are as below:

Physical methods
- Resulting primarily from the formation of low-solubility solids and auxiliary reagent for flocculation and precipitation

- Examples: adsorption, coagulation, sedimentation, distillation, filtration, floatation, membrane treatment, solvent extraction, reverse osmosis

Chemical methods
- Promising, but still undergoing up-scaling as emergent processes
- Examples: neutralization, ion exchange, electrolysis, oxidation (using ozone, chlorine, hypochlorite, H_2O_2), reduction, catalysis

Biological methods
- The most commonly used on industrial scale in terms of versatility and cost
- Examples: activated sludge, aerated lagoons, anaerobic digestion, flocculation, tracking filters, fungal treatment, stabilization

Several methods are available for wastewater treatment as mentioned above or combination of these methods can be used. But this conventional method for water treatment fails when organic compounds present in wastewater have **recalcitrant and refractory characteristic** and are so complex to be break easily. The presence of these organic contaminants in wastewater, surface water and ground water may result from contaminated soil, agricultural runoff, industrial wastewater and hazardous compounds storage leakage. [1]

The different types of organic pollutants present in WW are:
Pesticides, Herbicides, Phenols, Polycyclic aromatics hydrocarbon (PAHs), aliphatic & heterocyclic compounds, Polychlorinated Biphenyls (PCBs), Polybrominated diphenyl ether (PBDE), Surfactants, Carbohydrate, fatty acids, N-S-K based fertilizers, Organics resulting from paper and pulp industry, Textile Dyes which have complex aromatic structures etc.[a]

List of different WW and organic matter present in them is listed below (Table 1.1):

WW type[a]	Type of Organic Pollutants[a]
Farmland WW	Pesticides & Herbicides
Chemical WW	PAH, PCB, Phenols, Formaldehydes, Anilines, petroleum fractions, Surfactants compounds, etc.

Food WW	high concentration of Suspended Solids (SS) & BOD, Oils
Municipal WW	Oil, Food waste, some dissolved organic & Surfactants
Pharmaceutical WW	drugs having complex chemical structures
Textile WW	Complex dyes such as Acid, Basic, Azoic, Nitro, Reactive dyes etc.

Table 1.1 different Waste Water and Organic Pollutants present in them

Some of these organic pollutants are very stable mixtures that are resistance to extreme Temperature & Pressure; which do not easily degrade. These organic compounds in water poses serious threat to public health since most of them are toxic, endocrine disrupting, 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. [3]

For this reason, their removal from the contaminated water is of high priority. Chemical method of which oxidation process have potential to break down this pollutants but this direct oxidation method requires specified operating conditions to degrade the target compounds and this will increase the operation cost of the process.

1.2 Advanced Oxidation Process

Advanced Oxidation Process (AOP) is up-gradation of chemical oxidation process to overcome the shortcoming of oxidation processes. In AOP by use of chemical reactions between different species highly oxidative **hydroxyl radical ($\bullet$OH)** is generated that completely destructs the pollutant into elementary part of carbon dioxide (CO_2) and water (H_2O) and salts depending upon type of pollutant. AOPs are near ambient temperature and pressure water treatment processes. [3]

Examples: UV/O_3, UV/H_2O_2, Fenton, Non thermal plasmas, Sonolysis, catalytic wet oxidation, Photo catalysis, Supercritical Water Oxidation, etc.

In general, the following are positive aspects of AOPs [1]:

- Unlike conventional technologies which use strongly oxidant species, under certain conditions AOPs can provides the complete mineralization of pollutants.
- Used for the destruction of refractory & recalcitrant compounds which are resistant to other treatments, such as biological processes.
- It can be used in combination with other processes for pre-or post-treatment.
- Possess strong oxidizing power with high reaction rates.

- The formation of by-products can be minimized if optimized amounts of reactants are employed.
- In many cases, AOPs consume less energy compared to thermal destruction processes (incineration) of liquid wastewaters.

2. FENTON PROCESS

2.1 Introduction to Fenton Process

Fenton process is such type of AOP that is widely studied & is under research that will find its application in industries in near future. It was first described by H.J.H. Fenton (Fenton, 1894). He reported that Hydrogen Peroxide (H_2O_2) could be activated by ferrous (Fe^{2+}) salts to oxidize tartaric acid. It is **reaction between H_2O_2 & Fe^{2+} in presence of strong acid** that generates Hydroxyl radical. This reaction is called as **"Fenton chemistry"**. Alternatively, the name of **"Fenton Reaction"** or **"Fenton reagent"** is often used. Following reaction takes place in Fenton chemistry [2]:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + \bullet OH$$
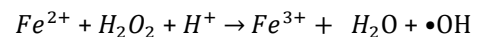
As stated earlier this Hydroxyl radical helps to break down the organic pollutant into elementary parts. The oxidation mechanism for the Fenton process is shown in Fig. 2.1
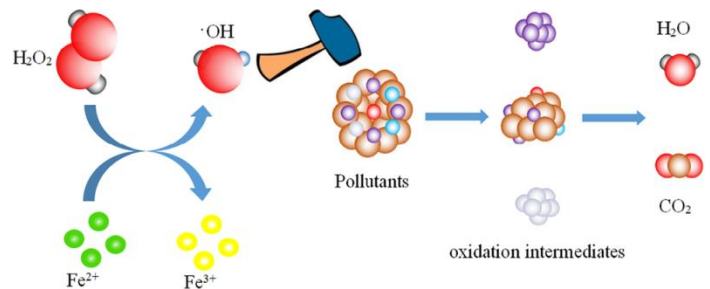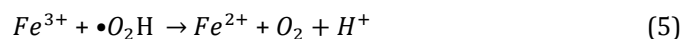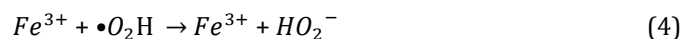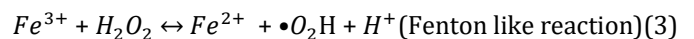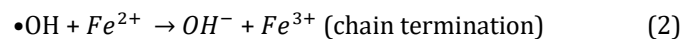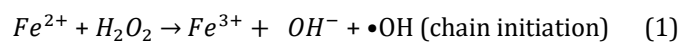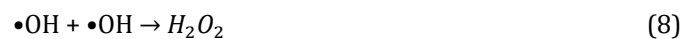

Fig. 2.1 Reaction Mechanism for the Fenton Process [2]

Although it was discovered in 1894 but actual reaction mechanism was understood after 90 years. Research shows that it contains more than 20 reactions of which following are the reactions that plays important role in Fenton chemistry [1]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \text{ (chain initiation)} \quad (1)$$

$$\bullet OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \text{ (chain termination)} \quad (2)$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe^{2+} + \bullet O_2H + H^+ \text{(Fenton like reaction)} \quad (3)$$

$$Fe^{3+} + \bullet O_2H \rightarrow Fe^{3+} + HO_2^- \quad (4)$$

$$Fe^{3+} + \bullet O_2H \rightarrow Fe^{2+} + O_2 + H^+ \quad (5)$$

Reaction (2)-(5) are rate limiting steps

$$\bullet OH + H_2O_2 \rightarrow H_2O + \bullet O_2H \quad (6)$$

$$\bullet OH + \bullet O_2H \rightarrow H_2O + O_2 \quad (7)$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \quad (8)$$

$$\bullet O_2H + \bullet O_2H \rightarrow H_2O_2 + O_2 \quad (9)$$

The ferrous iron (Fe^{2+}) initiates and catalyses the decomposition of Hydrogen Peroxide (H_2O_2), resulting in the generation of hydroxyl radicals (•OH), shown by reaction (1). Rxn (1) is recognized as **"Fenton reaction"**.

The generated ferric ion (Fe^{3+}) can be reduced by reaction (3) with excess hydrogen peroxide to form again ferrous ion and that will take further part in Rxn (1) & more radicals are generated. Rxn (3) is called as **"Fenton-like reaction"**. In Fenton like reaction, apart from ferrous ion regeneration, hydroperoxyl radicals (•O_2H) are produced. The hydroperoxyl radicals may also attack organic contaminants, but they are less reactive 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.

Rxn (2) is considered as chain termination step because newly formed hydroxyl radical is consumed in this reaction thus eliminating process of decomposition of organics.

Rxn (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. Rxn (6)–(9) also reported to occur during the Fenton process and they are radical–radical reactions or hydrogen peroxide–radical reaction.

From this sets reaction we can say that Fenton process follows complex reaction mechanism. Here hydroxyl radical is terminated by many reactions which are not desired. From Rxn (1) & (6) it seen that hydrogen peroxide acts as both •OH producer as well as scavenger. Study of this reaction mechanism is necessary as they affect the performance of Fenton process.

Hydroxyl radicals can oxidize organics (RH) by abstracting proton & producing Organic radicals (R•) (Rxn (10)), which are reactive and can be further oxidized;

RH + OH• → H2O + R• → further oxidation   (10)

Here we can say that ferrous ion (Fe^{2+}) works as a catalyst to oxidize the hydrogen peroxide. This all reaction takes place in presence of H^+ ion suggesting need of Acidic environment. Fenton process work at ambient Temperature and atmospheric pressure, this is biggest advantage of Fenton process.

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} [3]. The reduction potential of various oxidants is presented in Table 2.1:

Oxidant	Oxidation potential (V)
Fluorine (F_2)	3.03
Hydroxyl radical (•OH)	2.80
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.77
Potassium permanganate ($KMnO_4$)	1.67
Chlorine (Cl_2)	1.36
Oxygen (O_2)	1.23

Table 2.1 Comparison Standard reduction potential of common oxidants [3]

Hydroxyl radical is the second strongest oxidant after fluorine and it reacts 10^6-10^{12} times faster than ozone depending on the substance to be degraded. Thus AOPs have got much attention in recent years due to such high reactivity. [3]

2.2 Merits & Demerits of Fenton Process

Merits

- Works on ambient Temperature and Pressure.

- Less energy inputs required.

- Rapid degradation and complete mineralization of organic matter.

- Can be used as Pre or post treatment with other processes.

- This process reduces organic loading in terms of chemical oxygen demand and removal of recalcitrant and toxic pollutants thus allowing ease for further conventional biological treatment.

- Fenton process is a relatively economical method since it requires no additional energy when compared to many other AOPs. Furthermore, both iron and hydrogen peroxide are relatively cheap and safe.

Although this process has greater advantage compare to other process there are some drawbacks of Fenton process which needs to be addressed before commercial use of Fenton process.

Demerits/Shortcoming

There are mainly three shortcoming of Fenton Process, which are as follows:

- pH value

In Fenton process pH is a highly important parameter for effective wastewater treatment; **Optimum pH range** is found to be around **2-4**.

  o pH < 2, results scavenging effect of •OH by H^+ becomes strong (Rxn (11)), resulting in decrease in oxidation capacity of Fenton process.

    H+ + •OH + e- → H_2O (11)
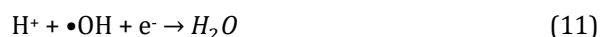
  o pH > 4, results hydrolysis and precipitation of Fe^{3+} called as **'Iron sludge'.**

Also, large amount of chemicals are required to maintain the pH of wastewater as wastewater from different industries have different pH values. [2]

Also MOC for process vessel should be considered accordingly.

- Handling of reactant

As it includes hydrogen peroxide and ferrous-ion chemical as a reactant, storage and handling of them is needed to be addressed. Both these reactants are reactive and unstable in chemical properties thus may detonate in storage, resulting into waste of reagents. Also, H_2O_2 is explosive and toxic thus harmful to humans. [2]

- Formation of iron sludge

Fenton process involves cyclic reaction of Fe^{2+} to Fe^{3+} and Fe^{3+} to Fe^{2+} as shown in Rx^n (1) & (3). However, rate of Rx^n (1) is 6000 times than Rx^n (3) indicating slower conversion of Fe^{3+} to Fe^{2+}. This leads to accumulation of Fe^{3+} in solution that starts to precipitate out above pH 3 in the form of **oxyhydroxide [Fe(OH)$_3$]** which is so-called **iron sludge**. [2]

It is difficult to separate and recover iron sludge, which not only causes serious loss of iron species and reduction of catalytic activity, but also causes secondary pollution to the environment.

2.3 PFD for Fenton Process

Fig. 2.2 represents general flow scheme for Homogeneous Fenton process:
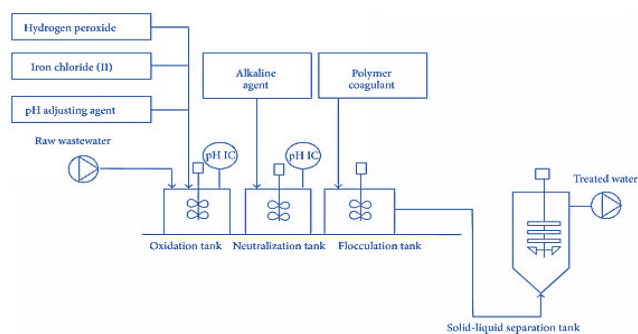

Fig. 2.2 Typical scheme for Fenton Process [1]

Flow diagram is self-explanatory; it does not involve any complex series of equipment. Here after process reactor flocculation tank is provided where polymer coagulants are added so as to accelerate the flocculation process.

2.4 Work done in area of Homogenous Fenton Process

Table 2.2 shows highlights of work done in Homogenous Fenton process.

3. CLASSIFICATION OF FENTON PROCESS

3.1 Classification of Fenton Process

To overcome shortcomings of Homogeneous Fenton process different optimization approaches are used by means of employing some other mechanism in Fenton chemistry. Fig. 3.1 describes tree diagram for Fenton process types.
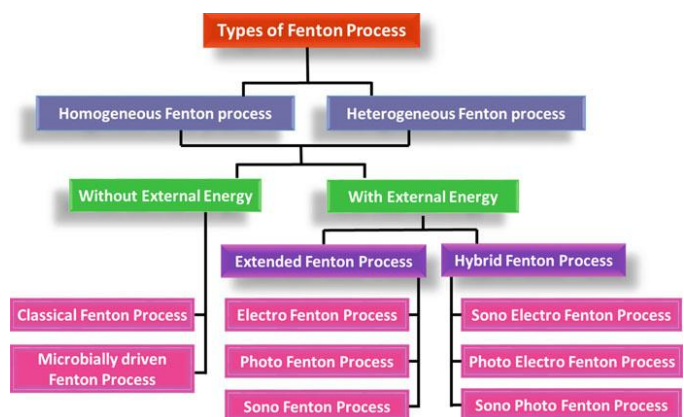

Fig. 3.1 Tree diagram showing Classification of Fenton Process [6]

These optimization techniques are:

Single optimization Fenton Process – such as Heterogeneous Fenton, Photo Fenton, Electro Fenton, Sono Fenton process

Combined optimization Fenton Process – this include combination of one or more single optimization Fenton process, shown as hybrid Fenton process in Fig. 3.1

3.2 Heterogeneous Fenton Process [2]

Heterogeneous Fenton process is **to overcome disadvantage of** homogeneous Fenton process which is **narrow working pH range and production of large amount of iron sludge**. In this process instead of feeding ferrous (Fe^{2+}) ion as Inorganic solution of Fe^{2+} ion, solid catalyst containing catalytic Fe^{2+} active component is used. By doing so Fenton catalytic reactions occur at the active site on the surface of solid catalyst, preventing the iron ions leaching, extending the working pH range, and reducing the iron sludge production.

This is possible because: (1) Iron species with catalytic activity are immobilized on some supports such as zeolite, clay, grapheme and activated carbon. This support gives protection effect that prevents iron immersing in the solution, which reduces the loss of iron species. (2) The structure and composition of the heterogeneous Fenton catalyst itself facilitate the electron transfer from the electron donor to Fe^{3+}, accelerating the reduction of Fe^{3+} to Fe^{2+}, achieving the efficient cycling of Fe^{3+} and Fe^{2+} on the heterogeneous Fenton catalyst.

Fig. 3.2 indicates reaction mechanism of Heterogeneous Fenton Process:

Table 2.2 Overview of work done in Homogeneous Fenton process [3]

| Sr. No.	Wastewater /Organic compound used	Catalyst Dosage	Experiment Conditions				Treatment efficiency	Remarks	Reference
			pH	H_2O_2 Dosage	Rx^n time	Others			
1	Phenol	Fe^{2+} : 10 ppm	3–3.5	300 or 600 ppm	6 hr	glass reactor with a capacity of 100 mL	Complete destruction of phenol in 6 hr. 60% mineralization	Higher temperature will leads faster degradation of phenol	[7]
2	Chlorobenzene	Fe^{2+} at a rate of 5 mL/h	2-7	at a rate of 5 mL/h	2 hr	Reactor capacity was 500 mL	Complete removal of Chlorobenzene and other intermediate	optimum pH was found to be in the range of 2–3	[8]
3	Catechol	$FeSO_4$ range used: 75–600 mg/L	3	75–700 mg/L	30 min.	500 mL Cylindrical vessel was used, [Catechol]=110 mg/L	COD removal of 83% and aromaticity removal of 93% was achieved at 30 min reaction time	Higher concentration of Fe^{2+} and H_2O_2 lowered the COD removal	[9]
4	Methyl tert-butyl ether (MTBE)	Fe^{2+} range: 10–20 mg/L	3–7	10–20 mg/L	1hr	Reactor with 4 L capacity, Fe^{2+}/MTBE molar ratio: 10:1, [MTBE]=1–2 mg/L	90–99% MTBE was degraded, Mineralization of MTBE was low & 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	[10]
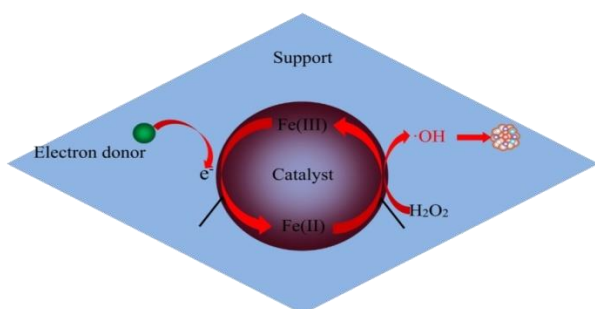
Fig. 3.2 Reaction mechanism for the heterogeneous Fenton process [2]

However, the key concern in Heterogeneous Fenton process is developing the long-term stable heterogeneous Fenton catalysts with high catalytic activity that can be used at a wide pH range and easy separated without the aid of extra energy input.

There are basic **two types of Catalyst** used in Heterogeneous Fenton process which are supported catalyst & non-supported catalyst.

Supported catalysts are prepared by loading Fe^{2+} on high-specific-surface-area solid support that will facilitate Fenton reaction on support surface.

Examples: Fe^{2+} on magnetic porous carbon microspheres, Fe-N-grapheme wrapped on Al_2O_3, Pentlandite composite from microalgae, Schorl

Non-supported catalysts are mainly natural iron containing minerals, which can directly form heterogeneous Fenton system with H_2O_2 to degrade refractory organic pollutants. Examples: α-FeOOH Nano-rods, Pyrite, Iron oxides

In summary, Heterogeneous Fenton process has following advantages over Homogeneous Fenton process;

Merits

- Low iron leaching & iron sludge formation.
- Efficient cycling of Fe^{3+} to Fe^{2+}.
- Wide working pH range.

However, most studies on heterogeneous Fenton process are conducted in lab scale, and its industrialization promotion is limited because of following reasons limitations.

Demerits

- Harsh synthetic conditions.
- Complicated synthesis routes.
- High synthesis costs of heterogeneous Fenton catalysts.
- Design of heterogeneous Fenton reactor.

3.2.1 Work done in Heterogeneous Fenton Process

Table 3.1 highlights some of work done in area of Heterogeneous Fenton Process.

3.3 Photo-Fenton Process [2]

This process is combination of **ultraviolet or visible light** with conventional Fenton process that can enhance the catalytic effect of iron and increase the degradation efficiency of organic pollutants and reduce the iron sludge production.

In this process **reduction of Fe^{3+} to Fe^{2+} is accelerated** by energy provided from light source. Under light irradiation, Fe^{3+} which will be present as an intermediate of $[Fe(OH)]^{2+}$ undergoes metal charge transfer excitation, regenerating Fe^{2+} (according to Rx[n] (12)) that will further take part in Rx[n] (1) and additional •OH will be produced. This will give less iron sludge formation.

In addition to this, **direct photolysis of H_2O_2** also produces •OH (according to Rx[n] (13)) which can be used for the degradation of organic pollutants.

$$[Fe(OH)]^{2+} + hv \rightarrow Fe^{2+} + \bullet OH \qquad (12)$$
$$H_2O_2 + hv \rightarrow 2\ \bullet OH \qquad (13)$$

Thus, combine effect of decomposition of H_2O_2 by Fe^{2+} & by light energy produces more amount of hydroxyl radical which will enhance oxidation efficiency in the photo-Fenton process. (It should be noted that Rx[n] (13) itself alone is a one of the AOPs called as UV/H_2O_2 process, so one can say that photo-Fenton is **combination of two AOP** Fenton and UV/H_2O_2)

Fig. 3.3 indicates reaction mechanism of photo-Fenton Process:

A **light irradiation device** is the **core component** in the photo-Fenton process, which has a significant influence on the destruction rate of organic pollutants. Two common light sources in the photo-Fenton process mainly include ultraviolet light and sunlight.
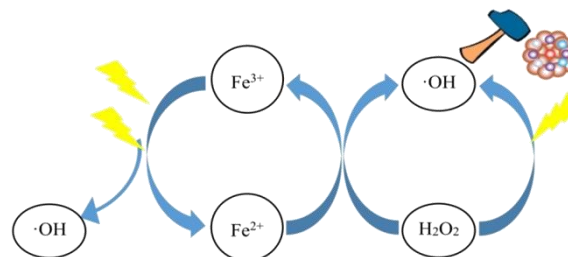

Fig. 3.3 Reaction mechanism for the photo-Fenton process [2]

The application of ultraviolet irradiation devices in the UV-Fenton process faces many challenges such as short working life span, high energy consumption, high environmental pollution risks and high economic costs, so compare to ultraviolet light source alternative use of sunlight as a free and renewable energy source has gained increasingly attention in the photo-Fenton process.

In summary Photo-Fenton has following Merits & Demerits;

Merits

- The efficient cycling of Fe^{3+} to Fe^{2+}.
- The low initial Fe^{2+} concentration input.
- The low iron sludge production.
- The high hydroxyl radical production.

Demerits

- The low utilization rate of light energy.
- Environmental and safety issue from use UV light.
- The excessive economical costs arising from the use of light irradiation devices.
- Design of photo-reactor.

3.3.1 Work done in photo-Fenton Process

Table 3.2 highlights some of work done in area of photo-Fenton Process.
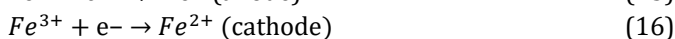
3.4 Electro-Fenton Process [2]

This process is developed to **overcome the limitations of** classical Fenton process which is related to the **high costs and risks associated with handling, transportation and storage of reagents** and also the accumulation of iron sludge. **Combine concept of Electrochemistry and classical Fenton** process is called as Electro-Fenton process.

Table 3.1 Overview of work done in Heterogeneous Fenton process [4]

Sr. No.	Wastewater /Organic compound used	Catalyst Dosage	Experiment Conditions				Treatment efficiency	Remarks	Reference
			pH	H_2O_2 Dosage	Rx^n time	Others			
1	Acid orange II (AOII)	FeOOH-C 1.0 g/L	5	15 mM	120 min.	[AOII]=100 mg/L, WW vol.=100 mL, T=30 °C	98% (AOII)	A membrane module was used in this work to separate the solid catalyst and effluent	[11]
2	Chicago sky blue (CSB)	Fe^{2+}/activated carbon (AC), Iron account for 7% (wt %) W_{cat}/Q = 4.1 (gm*min)/mL	3	2.3 mM	20 min.	[CSB]=0.012 mM; WW flow rate=2.5 mL/min, T=50 °C	88% (CSB) 47% (TOC)	The leaching iron concentration is 0.4 ppm, which is lower than European limits.	[12]
3	Methyl orange (MO)	Fe^{2+}/NdFeB-AC 10.0 gm/L Iron account for 94.4% (Wt %)	3	0.6 mM	1 hr	[MO]=20 mg/L, WW vol.= 200 mL, T=20 °C	97% (MO)	The MO degradation ratio could reach 97.1% after 5 cycles; the catalytic degradation process follows the pseudo first order kinetics model	[13]
4	Aniline	Iron Oxide/SiO_2 = 100.0 g/L	6	50 mM	160 min.	[Aniline] =2*10-4 M, T = 30 °C	73.30% (Aniline)	The decomposition of H_2O_2 decreased with increasing concentrations of H_2O_2	[14]

Here, reactants of Fenton process H_2O_2 & Fe^{2+} are in-situ generated via the electrochemical reaction on cathode and anode. H_2O_2 is generated via reduction of O_2 on the cathode (according to Rx^n (14)), similarly Fe^{2+} is generated via oxidation of Fe ion (according to Rx^n (15)).

By producing Fe^{2+} & H_2O_2 in the reactor itself we can avoid the cost and risks associated with handling, transportation and storage of reactants. Also, Fe^{3+} generated by Fenton reaction can be reduced to Fe^{2+} on the cathode (according to Rx^n (16)), that reduce the iron sludge production.

$$O_2 + 2H^+ + 2e- \rightarrow H_2O_2 \text{ (cathode)} \quad (14)$$
$$Fe \rightarrow Fe^{2+} + 2e- \text{ (anode)} \quad (15)$$
$$Fe^{3+} + e- \rightarrow Fe^{2+} \text{ (cathode)} \quad (16)$$

Electro-Fenton process is classified into **four categories** depending on Fenton reagents addition or formation:

- **Cathode electro-Fenton process (EF- H_2O_2)** - Fe^{2+} is externally added while H_2O_2 is in situ generated, reducing handling problems of hydrogen peroxide.
- **Sacrificial anode electro-Fenton process (EF-Feox)** - H_2O_2 is externally added while Fe^{2+} is electro-generated using a sacrificial anode. However, EF-Feox process has some disadvantages such as **serious consumption of anode** and a **large amount of iron sludge production**.
- **Fe^{2+} cycling electro-Fenton process (EF-Fere)** - H_2O_2 and Fe^{2+} are both externally added, but Fe^{3+} is generated by Fenton reaction is reduced to Fe^{2+} on the cathode (Rx^n (16)), which can **reduce the iron sludge production** and the initial Fe^{2+} concentration input.
- **Cathode and Fe^{2+} cycling electro- Fenton process (EF- H_2O_2-Fere)** - combination of EF- H_2O_2 & EF-Fere.

Fig. 3.4 indicates reaction mechanism for four kinds of Electro-Fenton processes:

Table 3.2 Overview of work done in photo-Fenton process [4]

| Sr. No.	Wastewater /Organic compound used	Catalyst Dosage	Experiment Conditions				Treatment efficiency	Remarks	Reference
			pH	H_2O_2 Dosage	Rxn time	Others			
1	Phenol red (PR)	Fe^{3+} 1.7 mg/L	3.5	0.12 mL 30%	130 min.	Tungsten lamp power=200 W, Light intensity=60 mW/cm, [PR]=$1.34*10^{-4}$ M	94% (PR)	The ferric ions on exposure to light generate a proton and ●OH radicals and it is reduced to ferrous state	[15]
2	Bromocresol green (BCG)	Fe^{3+} 5.6 mg/L	3	0.1 mM	1 hr	Three low P Hg-lamps of power=45 W, [BCG] = $(6*10^{-5})$ M, WW vol. =100 mL	100% (BCG)	Results showed that colour removal followed the increasing order: Fe^{3+}/H_2O_2 < Fe^{2+}/H_2O_2 < Fe^{2+}/H_2O_2/Solar < $Fe^{2+}/H_2O_2/UV\text{-}254_{nm}$ < $Fe^{3+}/H_2O_2/UV\text{-}254_{nm}$	[16]
3	Antibiotic fermentation	Fe^{3+}/oxalic-acid Fe^{3+} comes from the coagulant (poly-ferric Sulphate)	7	4.4 mM	1 hr	UV power=30 W, UV wavelength=254 nm, [Oxalic-acid]=45mg/L, T=20 ∘C	96.70% (decolourization) 93.50% (COD)	Coagulation process was used before the photo-Fenton-like process.	[17]
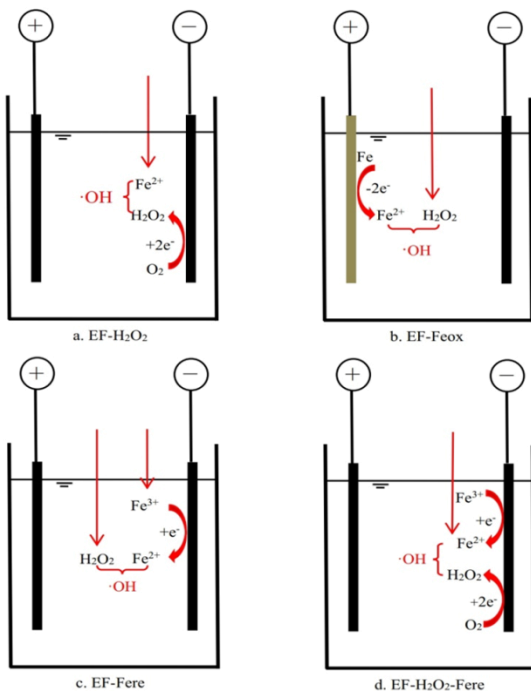
Fig. 3.4 Reaction mechanism for the Electro-Fenton process [2]

Important parameter in Electro-Fenton process is the **cathode** which has a significant influence on the performance of Electro-Fenton process. The types and properties of cathode play a crucial role in production of H_2O_2.

Gas diffusion electrodes are used as cathode owing to its porous structure by which oxygen or air can quickly reach the electrode surface to produce hydrogen peroxide.

Activated carbon fiber is also a commonly used cathode because of its advantages such as no toxicity, low-cost, good stability, conductivity, low catalytic activity for H_2O_2 decomposition.

In summary Electro-Fenton has following Merits & Demerits:

Merits

- The on-site production of reactant, which can avoid the risks related to its transport, storage, and handling.
- The continuous regeneration of Fe^{2+} on the cathode, which can minimize the iron sludge production and improve the degradation efficiency of organic pollutants.

Table 3.3 Overview of work done in Electro-Fenton process [4]

Sr. No.	Wastewater /Organic compound used	Catalyst Dosage /Cathode	Experiment Conditions				Treatment efficiency	Remarks	Reference
			pH	H_2O_2 Dosage	Rxⁿ time	Others			
1	Sulforhodamine B (SRB) 2,4-Dichlorophenol (2,4-DCP)	Co_3O_4-Graphite Cathode	2-10	H_2O_2 was produced on Cathode from pH 2–10	150 min. (SRB) 240 min. (2,4-DCP)	Anode is Pt-net (1.0 cm^2), Electrolyte is Na_2SO_4=10 gm/L, Voltage= 6V(DC), [SRB]= 1.0*10^{-5} M, [2,4-DCP]= 1.0*10^{-3} M, WW vol.=50 mL, T=20 ∘C	100% (SRB) 98.60% (2,4-DCP)	The removal rate of SRB did not decrease obviously after catalyst was used for five times, The Co_3O_4-graphite composite Electrode displays good Electrochemical characteristics & can produce H_2O_2 and ●OH From pH 2–10.	[18]
2	Rhodamine B (RhB)	Fe^0=15.0 mg/L Fe^{3+}=5.0 mg/L	2.5	H_2O_2 was produced in-situ by adding Cathode Bubbling air	180 min.	Cathode & anode are both graphite, Voltage= 8 V, [RhB]=10 mg/L, Room temperature.	>90% (RhB)	The rate of RhB removal at optimum catalysts conc. follows the order of Fe^0 > Mn^{2+} > Fe^{3+} > Fe^{2+} > Cu^{2+}. Ferric ions was the best catalyst for the RhB removal with a less concentration of 5 mg/L.	[19]
3	Metomyl	Fe^{3+} = 5.6 mg/L	3	H_2O_2 was produced from reduction of O_2 dissolved in the solution	200 min.	Cathode is carbon belt, Anode is Pt grid, Current=200 mA, [Metomyl]= 200 gm/L, Electrolyte Vol.=150 mL, [Na_2SO_4]= 0.05 M, Room T, Air was bubbled for 10 min through the Solution at about 1 L/min	100% (Metomyl) 98.20% (COD)	Fe^{3+} was the most efficient catalyst compared with cobalt, silver and copper. Metomyl degradation obeyed apparent first-order reaction kinetics.	[20]
4	Phenol	Nano zero valent iron (NZVI) = 0.5 gm/L	6.2	14.7 mM	30 min.	Electrodes are SS with 50 mm distance, Surface area of electrodes = 25 cm^2, Current density = 12 mA/cm^2, Electrolyte is Na_2SO_4 = 1 gm/L, Low pressure Hg lamp = 8 W, [Phenol] = 200 mg/L; WW vol. = 1 L.	100% (Phenol)	The removal rate constant (K_{obs}) was proportional to the NZVI and H_2O_2 dosage and inversely proportional to the initial phenol concentration and initial pH of the solution.	[21]

Demerits

- The low H_2O_2 yield**.**
- Cathode structure is key parameter on performance.
- The low unit cell body throughput.
- The low current density & low Conductivity of electrode as well as wastewater.

3.4.1 Work done in Electro-Fenton Process

Table 3.3 highlights some of work done in area of Electro-Fenton Process.

3.5 Sono (Cavitation) Fenton Process [3]

Sono Fenton process is combination of Fenton process with use of Ultrasound waves. Though application of ultrasound doesn't overcome any limitation but it enhances the performance of Fenton process by following method.

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 vapour 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. When these cavitation bubbles explosively collapse, the pressure and temperature in the bubbles can reach up to **several hundred atmosphere and several thousand Kelvin** respectively. Under these conditions, organic compounds are decomposed directly by pyrolytic cleavage. Fig. 3.5 shows mechanism for bubble formation & implosion. On the other hand, the hydroxyl radicals formed by pyrolysis also help to degrade the organics. Thus, in Sono-chemistry, 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.
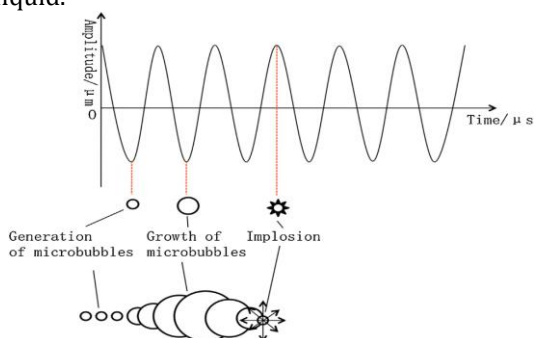

Fig. 3.5 Typical mechanism of Sono Cavitation [4]

The hydroxyl radicals are generated by water pyrolysis as shown in Rx^n (17):

$$H_2O \rightarrow \bullet OH + \bullet H \qquad (17)$$

By this amount of Hydroxyl radical increases which is advantageous as it will help in increase in degradation efficiency. To increase the hydroxyl radical concentration in the bulk solution, Fenton and Sonolysis can be combined together.

3.6 Combined Fenton Process [2]

To further strengthen the advantages of single Fenton optimization processes and improve the degradation efficiency of organic pollutants, a coupling strategy of different single Fenton optimization processes has gained increasingly attention.

Examples of combine Fenton process are:
Photo-electro-Fenton process, Heterogeneous-electro-Fenton process, Heterogeneous-photo-electro-Fenton process, Three Dimensional-electro-Fenton process, Sono-electro-Fenton process, Sono-photo-Fenton process

Table 3.4 highlights some of work done in area of Combined Fenton Process.

4. OPERATION PARAMETER OF FENTON PROCESS

4.1 Operation parameter in Fenton process

pH, Catalyst concentration, H_2O_2 concentration, organic pollutant concentration, Effect of H_2O_2/Fe^{2+} molar ratio, Effect of feeding mode, Reaction time, Temperature, Agitation rate are different parameters that influences the performance of Fenton process. [5]

Based on experiment conducted on Fenton process following important points should be noted for parameter variation in Fenton process:

- **pH**

In Fenton processes pH is a **highly important parameter** for effective WW treatment. However, in the different studies the researchers always reached different conclusions about the pH.

There is an optimum pH range beyond which the degradation efficiency of organic pollutants decreases. However, different types of Fenton optimization processes have different optimum pH ranges for organic pollutants degradation.

For Homogeneous Fenton effect of pH is discussed in section 2.2 (limitation of Fenton process). The optimum pH range for Homogeneous Fenton is between 2 to 4.

For Heterogeneous process some studies revealed that ~3 was still the best pH, while others showed that the neutral-

Table 3.4 Overview of work done in Combined-Fenton process [4]

Sr. No.	Wastewater /Organic compound used	Catalyst Dosage	Experiment Conditions				Treatment efficiency	Remarks	Reference
			pH	H_2O_2 Dosage	Rx^n time	Others			
1	Acid orange 7 (AO7) & Phenol	A-Fe_2O_3/S 0.1 gm/L	6.9	1.9 mM	14 OR 60 min.	High-pressure Hg lamp power = 300 W, OR Halogen lamp power = 1000 W, [AO7] = 35 mg/L, [Phenol] = 40 mg/L, WW vol. = 100 mL.	95% (AO7, 14 min, visible), 100% (AO7, 60 min, UV), 85% (phenol, 60 min, UV or visible)	α-Fe_2O_3/S showed little Fenton reactivity in the dark, but had an excellent heterogeneous Fenton activity under either UV or visible irradiation. Other kinds of α-Fe_2O_3 had no activation.	[22]
2	Petroleum hydrocarbon (PH)	Nano zero-valent iron (NZVI) = 0.02 g/L	3	5 mM	1 hr	UV lamp power= 125 kW, UV wavelength= 247.3 nm, [PH]= 0.7 mg/L, T= 24-26 ∘C	95.8% (PH)	Degree of significance for PH Con., NZVI dosage, H_2O_2 dosage, pH and reaction time are 7.643, 9.33, 13.318, 15.185 and 6.588 %, respectively. Photo-Fenton process using NZVI could be used as a pre-treatment.	[23]
3	Neutral Red (NR) Azure-B (AB)	Copper Pyro-vanadate 0.05 g/L (NR) 0.06 g/L (AB)	8 (NR) 6 (AB)	4.0 (NR) 5.0 (AB)	2 hr	Tungsten lamp power= 200 W, T= 25 ∘C, [NR]= 7*10^{-5} M, [AB] = 1.2*10^{-5} M, WW vol.=1 L	75% (NR, COD) 60% (AB, COD)	Degradation followed pseudo-first-order reaction, The catalyst activity decreases slightly, only around 5% in the 5th run after 30 min reaction.	[24]
4	Aniline	Fe^{2+} concentration was 1 mM	-	H_2O_2 was produced on carbon-PTFE cathode	6 hr	Pt anode, constant current of 0.1A was supplied. 125 W Hg lamp with an emitting wavelength of 360 nm was used as the irradiation.	92% of TOC removal after 6 hr	The aniline mineralization was increased by UV irradiation. The photo-electro-Fenton process allows 92% of TOC removal after 6 hr. Whereas in electro-Fenton, only 68% of mineralization was achieved.	[25]
5	Benzene sulfonic acid	Fe^{2+} concentration was 8 mM	2	166 mM	1 hr	3.5 L cylindrical reactor fitted with titanium net coated RuO_2/IrO_2 was used as anode and SS as cathode was used. Sixteen 3 W UV lamps (λ>320	TOC removal efficiency was 72% at the optimum electrode distance of 3 cm.	Synergistic effect of photo-electron-Fenton method showed a COD removal efficiency of 14% higher than that of electro-Fenton process, The double cathode reactor increases the working area & enhances the removal efficiency by 75% and	[26]

						nm) were used, current density of 71 A/m^2		this would cause greater production of ferrous ion.	

-condition (even alkaline conditions) could achieve a better organic WW treatment efficiency. Yang et al. [13] (See pt. 3 in Table 3.1) observed that the organics in WW could be treated effectively under acidic condition and the treatment efficiency decreased obviously with an increase in pH. However, Huang et al. [14] (See Pt. 4 in Table 3.1) from different research groups, had different study results. Their studies showed that organic WW could be treated effectively under close to neutral (pH 6.0) (even slightly alkaline (pH 9.0)) conditions when iron oxide/SiO$_2$ composite (Fig. 4.1) were applied, respectively.
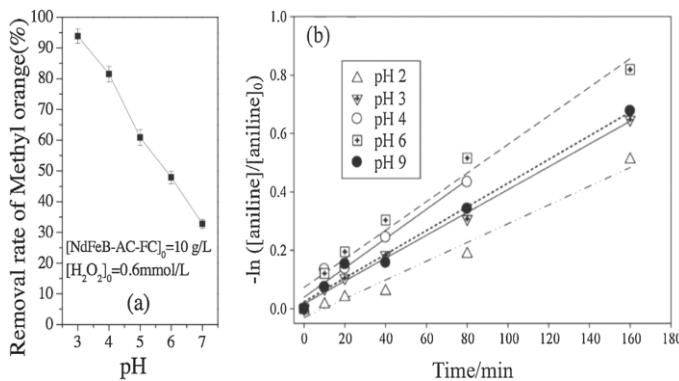

Fig. 4.1 Effect of pH on the removal rate of organics in two different Heterogeneous Fenton processes [13] [14]

This difference in result cloud be because of the different solubilities of a metal ion (such as the Fe ion) on the surface of a catalyst and the different activities of active sites on the catalyst surface could be the primary reason.

Some kinds of catalyst could play a **catalytic role** mainly by means of the dissolution of metal ions from the catalyst surface, while other kinds of catalyst may perform mainly through the active sites on their surface. For the former case, the increase in pH could be able to stop/slow the leaching of metal ions from the solid catalyst surface and inactivate the metal ions in the aqueous phase due to hydrolysis and precipitation. For the latter case, the catalysts could be more resistant to pH because they play the catalytic role through the active sites. [4]

It should be noted that the **same type of Fenton optimization processes also have different optimum pH ranges** for organic pollutants degradation **due to the different experimental conditions such as composition and structure of catalysts, type and concentration of organic pollutants**. [2]

Though the result is different, all of their research results showed that the pH can't be varied without any limitation, there is always an optimum pH value/range for the WW treatment.

- **H$_2$O$_2$ Dosage**

Usually the degradation efficiency of organic pollutants increases with the increasing of H$_2$O$_2$ concentration, however, H$_2$O$_2$ cannot be added without any limitation.

The excessive H$_2$O$_2$ not only increases the operational costs, but also enhances the scavenging effect of •OH by H$_2$O$_2$ (refer Rx^n (6)), which has a negative effect on the degradation of organic pollutants.

In Electro-Fenton process H$_2$O$_2$ is produced by reduction of O$_2$ supplied by pumps. Therefore, the air flow rate affects the H$_2$O$_2$ production, which indirectly affects the degradation of organic pollutants. Researches show that high air flow rate can be beneficial to the degradation of organic pollutants. However, extremely high air flow rate can cause decrease in H$_2$O$_2$ accumulation and disturb mass transfer between electrodes and increase energy consumption of pumps, which has a negative effect on the degradation of organic pollutants. [2]

When Fenton process is used as pre or post treatment with any other biological WW treatment higher amount of H$_2$O$_2$ could have a negative effect on the reactivity of the microorganisms that are used to treat the pre-treated organic WW in the subsequent bio-treatment process. [4]

- **Catalyst/Fe^{2+} Dosage**

As discussed earlier Fe^{2+} acts as a catalyst for degradation of H$_2$O$_2$ to generate hydroxyl radical, so its amount becomes important parameter for Fenton chemistry. Similar to H$_2$O$_2$, with there is an optimum value for catalyst amount.

For homogeneous Fenton process increasing of Fe^{2+} concentration increases the efficiency of process but after some value it has negative effect on efficiency as termination of ●OH by Rx^n (2) becomes more, also high iron sludge is formed.

For homogenous Fenton process despite Fe^{2+} many other metal ions are also used to catalyses the degradation of H$_2$O$_2$, that include **Fe^{3+}, Cu^{2+}, Mn^{2+}, Co^{2+}, and Ag$^+$**. However most research is based on Iron catalyst based. Reaction mechanism for H$_2$O$_2$ degradation based no other metal (except for the Fe) is to some extent similar to that of Fe based, but removal efficiency of organics, COD, TOC is seen higher in Fe based Fenton chemistry. [4]

For Heterogeneous Fenton process the production cost of the solid catalyst could be a limiting parameter in organic WW treatment. Studies are going on for different types of catalyst that can be used in Heterogeneous Fenton process. There are four different types of catalyst source available for Heterogeneous Fenton processes which are under study:

1) Heterogeneous catalyst from natural minerals (Non-supported) [4]

Fenton processes using mineral materials as the catalyst are called mineral catalysed Fenton processes and most of the catalysts used are **natural iron-bearing mineral** materials, such as schorl, goethite (α-FeOOH), pyrite (FeS_2), hematite (α-Fe_2O_3), magnetite (Fe_3O_4), ferrihydrite, and lepidocrocite (γ-FeOOH).

There are four advantages when iron- bearing minerals are applied as the catalyst:

(I) Catalyst can be removed from the treated WW easily by sedimentation and/or Filtration.

(II) Catalyst life can be extended by recycling the catalyst from the treated WW.

(III) Initial pH of the WW could be extended into the neutral range (such as pH 5–9).

(IV) Reaction system is not affected much by inorganic carbonate.

2) Heterogeneous catalyst from composite by artificial synthesis (Supported) [4]

Many composites have been studied for use as heterogeneous catalysts in Fenton-like processes, such as Fe^{2+}/Activated Carbon (AC), α-Fe_2O_3/S, CuO/Al, Fe^{2+}/Magnetic NdFeB-AC, FeOOH–C, Iron oxide/SiO_2, TiO_2/glass sphere and the magnetite-based catalysts. They can be synthesized by the impregnation method.

The application of a composite makes it possible to reuse the active metal element because of the composite's property of being easily separated from treated WW by means of the precipitation method. Clay has been used widely as a catalyst support because it is relatively cheap when compared with other catalyst supports.

While selecting the catalyst support, the effect of the support on the catalytic activity should be considered. Supports with highly porous natures, high stabilities, and large surface areas are preferable. The supports used frequently in recent years include: clay, activated carbon, zeolite, silica, fibers, alumina, fly ash, and magnetite

3) Heterogeneous catalyst from Nano materials [4]

The large surface area makes Nano materials exhibit many advantages in the chemical catalysis field, such as low diffusion resistance, easy accessibility to reactants, and a large number of active sites.

There are many kinds of Nano material such as: **Nano zero-valent iron (nZVI), Nano α-Fe_2O_3, Nano CuO, Nano-Ferro/ferric ions**.

Nano zero-valent iron, as the typical catalyst used in organic WW treatment, can remain in suspension and produce ●OH effectively by corroding its surface in an aqueous solution because of its Nano size and large specific surface area. (Pt. 4 in Table 3.3 & Pt. 2 in Table 3.4)

4) Heterogeneous catalyst from industrial waste [4]

Fly ash is a fine powder-like solid waste that is produced from modern power stations and steel mills. It is usually discarded as an industrial waste and the annual production of coal fly ash is at least 200 million tonnes globally.

Coal fly ash consists totally of the non-combustible matter in coal and a small amount of carbon remaining from incomplete combustion of the combustible matter. The detailed components of coal fly ash include SiO_2, CaO, Al_2O_3, Fe_2O_3, MgO, K_2O, P_2O_5, Na_2O, SrO, ZrO_2, and ZnO. Most coal fly ash is used in the production of cement and concrete in many countries but still there is much amount of fly ash that is unused.

Due to the fact that it possesses a porous surface and active metal elements (such as the iron element), fly ash has been explored for use in the heterogeneous Fenton processes.

- **The influence of the H_2O_2/Fe^{2+} molar ratio**

In Fenton process, hydrogen peroxide and iron are two major chemicals that determine the operation costs as well as efficiency. In order to maximize the effectiveness of the process, it is important to determine the optimal operational H_2O_2/Fe^{2+} molar ratio. Optimal H_2O_2/Fe^{2+} ratio varies highly with type of waste to be oxidized. [5]

- **Effect of feeding modes**

When large amount of H_2O_2 & Fe^{2+} are required for organic WW treatment, feeding the reactants in one time can result into scavenging effect of Hydroxyl radical by both H_2O_2 & Fe^{2+}. Instead feeding reactant one at a time **intermediate feeding mode** of reactant helps in increase in efficiency of WW treatment, increase in COD and colour removal efficiencies. [5]

- **Organic pollutants concentration**

It is obvious that with increase in organic pollutant concentration efficiency of Fenton process was reduced, higher amount of reactants were required for complete degradation.

- **Optimum reaction time**

With increase in reaction time high amount of degradation was obtained till some limit after that removal efficiency becomes constant.

- **Effect of temperature**

Although Fenton reaction works on ambient temperature (T) but variation with temperature is needed to be

considered as it is not always possible to get WW from different industry at room temperature. With increase in reaction T, generation rate of ●OH was increased. This trend can be explained by the influence of temperature in the kinetic constants according to Arrhenius law.

- **Effect of the agitation rate**

High agitation rates leads to more rapid and high efficient process.

5. COMPARISION OF FENTON PROCESS

5.1 Comparison between Fenton and other AOPs processes

Table 5.1 shows comparison between Fenton process and other AOPs such as Ozone oxidation, UV Photo-oxidation & Electrochemical oxidation.

From Table 5.1 comparison it is clear that Fenton process has relative low cost and greater advantage in WW treatment.

5.2 Comparison between Fenton and other Ozone-based AOP processes [27]

It clear that the highly reactive of ●OH is the main driver for all AOPs, and the effectiveness of the method depends on the efficiency by which ●OH is produced. Table 5.2 shows radicals generated into Fenton process and ozone based AOPs, which helps in degradation of organics.

AOP	Reactive Species
O_3	●OH , ●O_2H, ●O_3H, ●O_2^-, ●O_3^-
O_3/ H_2O_2	●OH, ●O_2^-, ●O_3^-
Fenton	●OH , ●O_2H

Table 5.2 reactive species generated into AOPs [27]

Though it seems that Ozone process generates more different radicals but the hydroxyl radical generation amount is less. Also, hydroxyl radical is main radical generated into Fenton process which has higher activity compare to others. That's why Fenton process holds advantage in treatment of WW.

Generally, the rate constant for the reaction of the contaminant with ●OH determines the rate of destruction of a contaminant. Following table 5.3 shows rate constant for different pollutants in Fenton & O_3 AOP. It clearly indicates that the reaction rates are much faster with the Fenton process compared to ozone.

Compound	O_3 ($M^{-1}S^{-1}$)	Fenton($M^{-1}S^{-1}$)
Chlorinated alkenes	10^3-10^4	10^9-10^{11}
Phenols	10^3	10^9-10^{10}
Aromatics	1-10^2	10^8-10^{10}
Ketones	1	10^9-10^{10}
Alcohols	10^{-2}-1	10^8-10^9

Table 5.3 Reaction rate constants of ozone vs. Fenton[27]

Table 5.1 Comparison between Fenton and other AOPs processes [b]

	Non-photochemical Fenton processes	Electrochemical oxidation	Ozone-based AOPs	UV photo-oxidation processes
Effluent treatability	Wide COD range. It is not affected by colour or turbidity presence. pH adjustment is critical.	Optimized to high COD values. Adequate for specific segregated effluent treatment.	Suitable for effluent decolouring. Ozone transfer is difficult because of organic matter presence.	Limited to effluents with very low turbidity. Not applicable to highly coloured effluents nor strong loaded flows
Installation	Conventional. It allows facilities reuse. It can be incorporated in any treatment stage. Flow rate variability is supported.	Electrode selection and design are critical to optimize the process.	Relatively easy. Adapted to Commercial ozonation equipment.	Adapted commercial UV equipment
Sludge production	Yes	No	No	No

Commercial technology availability	Yes. Both homogeneous and heterogeneous treatments available	Yes. Electrode selection is definitive.	Yes	Yes. Limited experience at real scale with textile effluents
Investment costs	Low	High	High	High
Operation costs	Moderate	High	High	High
Operation & Maintenance	Easily acquired reactors equipment and H_2O_2 and pH adjustment chemicals	Chlorine generation in treated effluents can represent a problem. Electricity consumption	It requires oxygen and H_2O_2 supply. Ozonation equipment O&M requires skilled person.	Limited UV lamps lifetime. A commercial catalyst is needed. Biofouling reduces process efficiency.

6. APPLICATION OF FENTON PROCESS

Fenton process is effective in treating various industrial wastewater components including range of aromatic, amines, a wide variety of dyes, pesticides, surfactants, explosives as well as many other substances. Fenton process has found its application in following industries:

- **Chemical Industry**

- **Pharmaceutical Industry**
The substances synthesized by the pharmaceutical industry are in most cases structurally complex organic chemicals that are resistant to biological degradation. For this reason, conventional methods are usually inappropriate for the treatment of pharmaceutical wastewaters and advanced oxidation processes can be considered good candidates for providing feasible technical solutions.

Fenton oxidation is applied as a pre-treatment for the wastewaters generated by a drug manufacturing, leading to an improvement of the wastewater biodegradability and a reduction of the toxicity of these effluents [1]

- **Pulp And Paper Industry**
More than 250 chemicals may present in the effluents resulting from the different stages of papermaking. Whereas some of these pollutants are naturally occurring wood extractives (tannins, resin acids, lignin, etc.), others are xenobiotic compounds that are formed mostly in pulp manufacture (chlorinated lignin, phenols, dioxins and furans, among others).These effluents are highly coloured and contain high organic loads. Fenton oxidation is effective for the treatment of pulp bleaching effluents. [1]

- **Textile Industry**
Textile industry is particularly known for its high water consumption as well as the amount and variety of chemicals used throughout the different operations. The environmental problems associated with textile effluents are in a great part due to colour. The bio-refractory nature of textile wastewaters from the dyeing and finishing stages is mainly attributable to the extensive use of various dyestuffs and chemical additives (such as polyvinyl alcohol, surfactants, etc.). Therefore, the wastewaters are characterized by high organic matter content (COD), colour. Fenton process is effective in removing COD and colour. [1]

- **Landfill Leachates**
Although landfill leachates have been proved to be toxic and recalcitrant, land filling still remains one of the main systems for municipal and industrial solid waste disposal. The composition of landfill leachates varies greatly depending on the type of wastes and the age of the landfill. [1]

- **Dry-Process Industrial Waste**
There is a need for the development of on-site wastewater treatment technologies suitable for "dry process industries," such as the wood-floor sector. Due to the nature of their activities, these industries generate lower volumes of highly polluted wastewaters after cleaning activities. Advanced oxidation processes such as Fenton is potentially feasible options for treatment of these wastewaters. [1]

- **Food Industry**

7. OUTLOOK & SUMMARY

7.1 Outlook

Fenton optimization processes have higher potential in organic wastewater treatment because of its significant advantages over other process. In order to further improve the effect of organic WW treatment, reduce operational costs and environmental risks, the following issues should be given priority for significant developments:

1) **Degradation mechanism of organic pollutant by Fenton process** should be investigated as it provides the theoretical basis for the development of novel Fenton optimization processes.

As discussed in Chapter 4, different trends were observed in Parameter optimization, this could be due to the fact that different types of pollutants and reaction mechanism have impact in parameter optimization.

Further and more detailed studies of Fenton optimization processes should be focused on the degradation kinetics of organic pollutants, development of rate expressions based on established degradation mechanism and identification of reaction intermediates, and so on.

2) **Development of heterogeneous catalysts in Heterogeneous process.** The iron or other metals containing catalysts with low leaching rate, high stability, high catalytic activity and low preparation costs are the main directions for the development of heterogeneous catalyst.

3) **Development of electrode materials.** One of the key factors that limits the development of Electro-Fenton optimization processes on a large scale is the costs and efficiency of electrode materials. High catalytic activity, high corrosion resistance, long working life span and low preparation costs are main characteristic required for electrode

4) **Analysis of economic costs**. Economic costs are the restrictive factors for the large-scale development of Fenton optimization processes. The detailed information of economic costs such as chemicals cost, reactor investment cost, energy consumption cost and etc. should be accurately provided in future work.

5) **Analysis of environmental impact**. Considering the growth in the research of Fenton optimization processes in near future many processes will be scaled up. To avoid unintended consequences caused by the development of large-scale Fenton optimization systems, it is necessary to estimate their environmental performance.

6) **Coupling between processes**. Efficient wastewater treatment performance can be obtained by combining Fenton process with other WW treatment methods.

7.2 Summary

Fenton process to degrade various types of organic pollutants was seen to have high degradation rate and effective removal. The fundamentals, advantages and disadvantages of Fenton optimization processes for organic wastewater treatment were reviewed in detail. The effect of operation parameters on the degradation of organic pollutants was evaluated.

Following points were understood from study:

1) Homogeneous Fenton process is basic Form of Fenton process which has some disadvantages to overcome that different optimization techniques are used in Homogenous Fenton process.
2) Heterogeneous Fenton process overcomes iron sludge formation & pH limitation, Photo-Fenton overcomes iron sludge formation problem & Electro-Fenton overcomes reactant handling issues.
3) Coupled Fenton optimization process shows greater efficiency than single optimization processes.
4) Process parameter for Fenton processes have varying effect in different studies, however there is always optimum value for process parameters.
5) More detail study is required for reaction mechanism of organic pollutant degradation so that parameter evaluation can be done accordingly and scale-up of Fenton process becomes possible.
6) There is need to develop catalyst for Heterogeneous Fenton process, Electrode for Electro-Fenton process so as to scale-up Fenton process to industrial level.
7) Fenton process has wider application in WW treatment and has much potential for WW treatment compare to other conventional WW treatment process & AOPs, thus in near future it will find its place in Industries to meet new strict Environment Emission standards

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