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Greener and Expedient Approach for the Wastewater Treatment by Fenton and Photo-Fenton Processes: A Review

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Abstract

Advanced Oxidation Processes (AOPs) have emerged as a promising technology for the treatment of wastewaters containing toxic, recalcitrant organic compounds such as dyes, pesticides etc. This review paper focuses on the Fenton and photo-Fenton technique which is one of the most efficient AOPs developed to decolorize and/or degrade organic pollutants. This oxidation method can produce biodegradable intermediates and mineralize complex organic pollutants effectively and efficiently. In this paper Fenton and photo-Fenton methods are categorised into two broad groups as homogeneous and heterogeneous Fenton and photo-Fenton processes. Applications of fundamental and advanced combined Fenton and photo-Fenton processes are also discussed.

Keywords: Advanced Oxidation Processes (AOPs), Dye Decolourization, Fenton, photo-Fenton, Homogeneous and Heterogeneous Fenton Processes

1. Introduction

Since the industrial revolution an expedient world economic growth led to environmental pollution and crisis for clean and safe water. Wastewater can originate from a combination of domestic, industrial, commercial and agricultural activities, surface runoff and from sewer inflow or infiltration. A dramatic increase in recalcitrant compounds in waste water being generated from different industrial activities has been reported[1]. These compounds even present in micro or ppm level are highly toxic as well as persistent and hard to degrade completely by biological or conventional methods. Sometimes their incomplete degradation generates potentially hazardous intermediates. These compounds e.g., dyes, pharmaceuticals, agrochemical waste have higher values of COD and BOD. Waste water containing dyes and other complex organic compounds, generated by many industries like paint, leather, paper, food, plastic industries, are carcinogenic and mutagenic in nature[2,3]. In addition to these adverse effects, these compounds perturb the penetration of sunlight in water and affect photosynthetic activity and thus devastate the water ecosystem[4].

Thus, efficient and effective waste water treatment is a great concern which encompasses degradation as well as mineralization of these complex organic compounds. One of the most promising pathways for degradation of these pollutants is the conversion to their most stable oxidation state i.e., CO_2 and H_2O and oxidized inorganic anions if probe molecules contain any heteroatoms.

In this context, Advanced Oxidation Processes (AOPs) have emerged as a promising technology for waste water treatment[5]. AOPs generally refer to a group of processes which involve generation of hydroxyl radicals, which are the second most reactive oxidizing species which can degrade an array of organic compounds non selectively with a high degree of efficiency. It includes O_3 and H_2O_2 as oxidants with assistance of light, catalyst (iron, TiO_2, ZnO etc). Many combination technologies have come up in this series e.g., – Fenton, photo-Fenton, peroxidation, perozonation, UV light assisted peroxidation, perozonation, O_3/TiO_2/electron beam etc[5–15].

AOPs have a wide range of applications varying

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from laboratory scale to pilot plant scale in the field of overall pollutant degradation to specific organic molecule destruction, degradation of micro pollutants, agrochemicals, pharmaceuticals; decolourization and mineralization of dyes and sludge treatment.

Out of the many AOPs available, Fenton and photo-Fenton processes have been proven to be the most powerful, effective, energetically efficient, cost effective and least tedious method for the treatment of recalcitrant compounds when used exclusively or coupled with conventional and biological methods[16]. These methods do not require sophisticated equipment or costly reagents. These techniques are ecologically viable due to their relatively simpler approach, use of less hazardous chemicals and cyclic in nature so less concentration of these chemicals are needed.

The Fenton reaction was reported in 1894 and is described as the enhanced oxidative potential of H_2O_2 when iron (Fe) is used as a catalyst under acidic conditions[17]. To increase the efficiency, UV or visible light can be used and the process is named as photo-Fenton process[18,19]. The reactions involved in Fenton and photo–Fenton processes are given below -

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$ … (i)
$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH + H^+$ … (ii)
$Fe^{3+} + H_2O_2 + h\nu \rightarrow Fe^{2+} + {}^{\bullet}O_2H + H^+$ … (iii)
${}^{\bullet}OH + H_2O_2 \rightarrow {}^{\bullet}O_2H + H_2O$ … (iv)
$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^-$ … (v)
$Fe^{3+} + \bullet O_2H \rightarrow Fe^{2+} + O_2 + H^+$ … (vii)
${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$ … (viii)
Organic pollutant + ${}^{\bullet}OH \rightarrow$ Degraded products … (ix)

Fenton like reactions are those reactions in which other metals at low oxidation state such as copper and cobalt are used[20,21]. For example,

$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + {}^{\bullet}OH + OH^-$ … (x)

Fenton, photo-Fenton or Fenton like processes can be divided in two board categories namely, homogeneous and heterogeneous processes. In homogeneous Fenton and photo-Fenton processes iron species exist in the same phase as reactants and thus have no mass transfer limitation.

Despite of its high efficiency and broad range of applications, it has associated with some drawbacks like sludge production with high content of iron and deactivation of iron by formation of complex compounds. Additionally, the confining pH range for Fenton reaction is 2.0–4.0 and high efficiency was reported at 2.8–3.0. A large quantity of ferric hydroxide sludge is formed at pH value higher than 4.0 which poses an adverse effect on the environment and terminates the Fenton reaction[22].

To solve these problems and to improve the efficiency of the process, heterogeneous process has been devised by which escape of iron can be prevented. This category has the advantage of maintaining its efficiency over a wider working pH range. This process employs solid iron oxide in which iron is stabilized in catalytic structure without generation of $Fe(OH)_3$ precipitation.

Three possible mechanistic pathways have been proposed to explain the heterogeneous catalysis[23–25].

- Decomposition of H_2O_2 to hydroxyl radicals by binding of H_2O_2 with iron species on the surface of catalyst.
- Chemisorption of probe molecules on the catalyst surface.
- Leaching of iron to the solution and reacting with H_2O_2 by homogeneous mechanism.

The application of heterogeneous phase allows the reuse of catalyst as it can be easily separated. In this process, density, pore size, surface area become the crucial factors which control the efficiency of the process. These processes are found to be slower than homogeneous reaction. To improve the efficiency of this process complexing agents like nafion, zeolite, silica, clay, resin activated carbon have been used as support for Fe ion[26–35].

Moreover, the cost can be further decreased by applying solar energy and integrating biological treatment methods. Fe II/III nanosized iron oxide exhibits improved catalytic activity because of large surface area which have potentially more active sites for OH generation[36].

This present review deals with the application of Fenton and photo Fenton process for the degradation of a plethora of complex hazardous compounds and describes the advancement and development of these techniques in two sections, namely, Homogeneous and heterogeneous Fenton and photo-Fenton processes.

2.1 Homogeneous Fenton and Photo-Fenton Processes

Various applications and advancement of homogeneous Fenton process have been highlighted in this section. The use of different additives has been explored by various group of researchers to improve the efficiency and to widen the spectrum of applications of this process.

For the treatment of acrylic-textile dyeing wastewater, solar photo-Fenton reaction with ferric-organic ligands has been employed by Soares[37]. These ligands have a role in pre-oxidation step to enhance its biodegradability. They observed that the photo-Fenton reaction was negatively affected by two dyeing auxiliary products named as Sera(®) Tard A-AS and Sera(®) Sperse M-IW. The catalytic activity of the organic ligands toward the ferrous-catalysed system followed the order: Fe(III)-Oxalate > Fe(III)-Citrate > Fe(III)-EDDS. A study was made to perform a preliminary in vitro test on the possible use of two different laser wavelengths, 405 and 532 nm to improve the dental bleaching results by Lagori G, Rocca et al[38]. It was concluded that the photo-Fenton degradation of a dye rhodamine B in presence of hydrogen peroxide was reported by all the wavelengths with better results for longer wavelengths. Sharma et al[39] has observed that Iopamidol can be readily degraded in a Fe(III)-oxalate photochemical system under UV (350 nm) and visible light (450 nm) irradiation. It was found that the Fe (III) oxalate/H_2O_2/photochemical system can initiate both reductive and oxidative degradation processes. It was concluded that reductive dehalogenation can dramatically reduce the formation of the problematic disinfection by-products often associated with oxidative treatment processes, thus it can offer an attractive remediation strategy for halogenated organic compounds.

The study was made to evaluate the eco-toxicity of five dyes to freshwater organisms before and during their photo-Fenton degradation[40]. Toxicity tests showed that the partial mineralization may be responsible for the presence of degradation products which can be either more toxic than the original dye or may be further degraded to nontoxic products. The degradation of 2-chloro-4,6-diamino-1,3,5-triazine and of cyanuric acid by photo-Fenton process have been reported by Dbira et al[41]. It was observed that that the degradation of these compounds by photo-Fenton process is faster and effective than Fenton and UV/H_2O_2 processes. By the results of TOC and TKN analyses it was also concluded that no carbon dioxide is formed during the treatment. Rabelo et al[42] employed photo-Fenton process for the treatment of Kraft Pulp Mill effluent. The efficiency of the treatment was measured by COD removal. Various operating parameters were optimized to increase the efficiency of this process. It was reported that during the treatment the organic matter of the effluent was more oxidized than mineralized, showing a higher removal of COD than BOD and TOC, respectively. Therefore, it was concluded that photo-Fenton process increased the BOD/COD ratio but decreased the BOD/TOC ratio.

The decomposition of azure-B by photo-Fenton reagent in the presence of ultrasound in homogeneous aqueous solution has been investigated by Vaishnave et al[43] where a dramatic increase in degradation was reported due to the presence of ultrasound. Kumar D et al[44] studied the degradation of Basic Orange 2 in aqueous medium by use of photo-Fenton reagent. Julian et al[45] observed the cultivability and viability of Salmonella Typhimurium during photo-Fenton process at pH 5.5. It was reported that in *S. typhimurium* cellsugar metabolism was affected rather than amino-acids during photo-Fenton reaction.

A comparative study was made for the removal of 32 selected micro-pollutants by using UV-light (UV_{254}) alone, dark Fenton and photo-Fenton by N. De la Cruz et al[46] where an effective degradation was reported for photo-Fenton treatments employing UV_{254}, 50 mg L^{-1} of H_2O_2, with and without adding iron. Optimization of remazol black B mineralisation by Fenton-like peroxidation has been done by employing D-optimal experimental design[47]. Three reduced empirical models were developed for describing the treatment process. Guimarães et al[48] have evaluated the effectiveness of photolysis (UV), peroxidation, peroxidation combined with UV light, Fenton reagent, and the photo-Fenton process for the degradation of Reactive Blue 19. It was concluded that the photo-Fenton process is the most efficient method. It was also observed that the combination of a biological system and the photo-Fenton process degraded a high level of textile effluent degradation with reduction of BOD, COD and TOC.

The Response Surface Methodology (RSM) using Box-Behnken experimental Design was applied by Gil Pavas et al[49] for the optimization of the photo Fenton degradation process of highly concentrated Diarylide Yellow 12.

The photo degradation of Amaranth (AR) dye in the presence of hydrogen peroxide (H_2O_2) and ammonium persulfate (APS) influenced by various aromatic derivatives was studied by Gomathi Devi et al[50]. The enhancement in the rate of degradation of dye was observed in the following order:hydroquinones > chlorophenol> dichlorobenzene > aromatic carboxylic acids > anilidine > nitrophenol. Jain et al[51-54] studied the photo-Fenton degradation of dyes catalyzed by organic (hydroquinone, resorcinol, catechol) and inorganic additives like sodium thiosulfate and potassium bromate. Maezono et al[55] studied the generation and consumption of hydroxyl radicals as well as effects of operating parameters for the Fenton degradation of azo-dye Orange II. They reported that the generation of hydroxyl radical was found to be maximum at pH 3.0 and it was enhanced with increasing the dosages of H_2O_2 and Fe.

A comparative study was made to evaluate the performance of Fenton and photo-Fenton processes by Jonathan Macias-Sanchez et al[56] using mixture of dyes composed of Acid Yellow 36 (AY36) and Methyl Orange (MO). It was observed that photo-Fenton process is more efficient process which took 70 min for complete decolourization of dyes mixture; whereas 180 min were required for complete mineralization by Fenton reaction. Various AOPs techniques were employed by Santiago et al[57] for the degradation of commercial fungicides like thia- bendazole (Textar 60 T) and imazalil sulphate (Fruitgard IS 7.5) which are used in the post-harvest treatment of bananas. It was observed that Fenton process is the most efficient and low cost method for treatment of this type of water compared to heterogeneous photo catalysis with TiO_2 and TiO_2-activated carbon (TiO_2-CA) and photo-Fenton processes. Degradation of some dyes in presence of some transition metal complexes and hydrogen peroxide has been studied by Lodha et al[58,59].

The effect of oxalate on the photo-Fenton degradation of phenol was investigated by Huang et al[60]. It was observed that the removal efficiency of phenol was highest at a molar concentration ratio of oxalic acid to ferric ions ($[Ox]/[Fe^{3+}]$) of 2.

Ustun et al[61] observed the degradation and mineralization of 3-Indole Butyric Acid (IBA) in aqueous solution by using Fenton and Fenton-like processes. IBA degradation proceeded via two distinctive kinetic regimes where the initial phase of the reaction was directly attributable to the Fenton reaction wherein nearly all of the hydroxyl radicals were generated. This was followed by a slower degradation phase, which can be considered as a series of Fenton-like reactions within a Fenton process. It was concluded that Fenton process may be more useful when only removal of IBA is required but for mineralization of IBA Fenton-like processes are more significant.

Bactericidal properties of the photo-Fenton system were investigated at near neutral pH by Spuhler et al[62]. For this study, *Escherichia coli* K12 suspended in either MilliQ water, water containing mineral ions and in MilliQ water enriched with resorcinol, a model for Natural Organic Matter (NOM) were chosen. It was concluded that this process is very efficient for the acceleration of solar disinfection of river water as well as for the elimination of NOM (precursor for halogenated disinfection by products). It was also observed that inorganic ions present in mineral water inhibit the beneficial effect of Fe^{2+} or $^{3+}$ and H_2O_2 on bacterial inactivation, whereas the systems containing model NOM led to a higher iron-photo-assisted bacterial inactivation.

The degradation performance of the Sulfamethazine (SMT) antibiotic via photo-Fenton treatment was investigated by Perez-Moya et al[63]. The degradation of Reactive Yellow 86 (RY 86) was described by photo-Fenton reaction where during process, the formation of chloride, sulfate, nitrate and ammonium ions was observed. Two kinds of intermediate products were also identified by decomposition of RY 86[64]. The chemical degradation of the fluoroquinolone ofloxacin in secondary treated effluents was carried out by using two different approaches of AOPs i.e., homogeneous photocatalysis by solar Fenton reaction and heterogeneous photocatalysis with titanium dioxide suspension[65]. In this study, the potential toxicity of the parent compound and its photo-oxidation by-products in different stages of oxidation were examined by using a Daphnia magna bioassay. It was reported that photo-Fenton process is more efficient than solar TiO_2 process.

Removal of Natural Organic Matter (NOM) from drinking water by advanced oxidation processes like O_3/H_2O_2, O_3/UV, UV/ H_2O_2, TiO(2)/UV, H_2O_2/catalyst, ultrasound, Fenton and photo-Fenton processes were examined by Matilainen and Sillanpaa[66]. The photo-Fenton degradation of an azo dye Basic Blue 41 (BB41) in aqueous solution was carried out by Bouafia-Chergui et al[67] and the effects of $[H_2O_2]$, $[Fe^{3+}]$ and $[H_2O_2/ Fe^{3+}]$ ratio was examined. The optimal ratio $[H_2O_2]/[Fe(^{3+})]$ was found to be 10 for 0.2 mM $Fe(^{3+})$ concentration. The mechanisms of solar photodegradation of H(2)-receptor antagonist Ranitidine (RNTD) using Titanium-dioxide semiconductor and Fenton reagent were first described by Radjenovic et al[68]. In this study, Fenton reagent in a well-defined system of a pilot plant scale Compound Parabolic Collector (CPC) reactor was used. $UV/H(_2)O(_2)$ and photo-Fenton treatments were studied by Elmorsi et al[69] for the decolourization of the Mordant red 73 (MR73) azo dye and the effect of inorganic salts (NaNO($_3$), NaCl and Na(2)CO(3)) were also examined. Kusic et al[70] developed the mathematical models to describe the kinetics of degradation of two reactive dyes, C.I. Reactive Blue 49 and C.I. Reactive Blue 137 in various system like Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, Fe^0/H_2O_2, UV/Fe^{2+}/H_2O_2, UV/Fe^{3+}/H_2O_2 and UV/Fe^0/H_2O_2.

Oxidation of catechol by various methods such as Fenton, photo-Fenton and photocatalysis processes has been compared by Lofrano et al[72]. It was observed that Fenton and photo-Fenton techniques are highly effective in the mineralization of catechol than others. Bandala et al[73] describe the techniques for the degradation of Domoic acid ([2*S*-[2α, 3β, 4β(1*Z*, 3*E*, 5*S**)]]-2-carboxy-4-(5-carboxy-1-methyl-1, 3-hexadienyl)-3-pyrrolidineacetic acid by four advanced oxidation processes such as Fenton, photo-Fenton, cobalt/peroxymonosulfate and cobalt/peroxymonosulfate/UV. It was found that Cobalt/PMS/UV shows the highest initial reaction rate butlater rate of photo-Fenton reaction decreases due to the formation of chlorine–Fe^{2+} or sulfate–Fe^{2+}complexes.

Photo-Fenton decomposition of chlorfenvinphos was investigated by Klamerth et al[74]. In this study the degradation products and pathway of chlorfenvinphos was determined. HPLC–UV and ionic chromatography, Solid-phase extraction, GC–MS and HPLC–TOF-MS were used for analysis where HPLC–TOF-MS gave more insight of degradation process. On the basis of complete absence of chlorinated aliphatic substances and chlorinated acids, it can be concluded that chlorine is removed very rapidly. Solar photochemical treatment of winery wastewater in a CPC reactor by heterogeneous photocatalysis using TiO_2, TiO_2/H_2O_2 and $TiO_2/S_2O_8^{2-}$ and homogeneous photocatalysis with photo-Fenton was compared where heterogeneous photocatalysis was proven to be inefficient in removing TOC than photo-Fenton process[75]. It was also observed that during the photo-Fenton process, toxicity decreases remarkably from 48% to 28%.

Various advanced oxidation hybrid configurations such as Sono-photo-Fenton (FS), Sono-photocatalysis (TS) and TiO_2/Fe($^{2+}$)/Sonolysis (TFS) were applied for the enhancement of degradation of the biorecalcitrant pharmaceutical micropollutant ibuprofen by Mendez-Arriaga et al[76]. The photo-Fenton reaction was found to be more efficient for the cork boiling and bleaching wastewaters treatment in comparison to TiO($_2$) photocatalysis and TiO($_2$)+S($_2$)O(8)(2-)[77]. Two solar photocatalytic processes, TiO($_2$) and photo-Fenton were examined for the degradation of Flumequine (FLU) and Nalidixic Acid (NXA) by Sirtori et al[78]. The expedient degradation and mineralization of both substances were reported by photo-Fenton process.

Photo-Fenton degradation of Direct Red 28 (DR 28) was analysed by applying Box-Behnken statistical experiment design and the response surface analysis. It was found that decolourization and TOC removal were unfavourably affected at high concentration of H(2)O(2) and Fe(II) which can be attributed to the hydroxyl radical scavenging effects of high oxidant and catalyst concentrations[79]. Sun et al[80] observed that the degradation of p-nitroaniline by photo-Fenton has many advantages such as higher oxidation power, lower ferrous ion usage and wider working pH range in comparison to other techniques. The photo-Fenton process for the degradation of formaldehyde with methanol was reported by Kajitvichyanukul et al[81]. It was observed that the oxidation reaction has three-stages. Formaldehyde and methanol were decomposed rapidly in the first stage whereas slower rate of reaction was observed in second and third stages. It was also observed that the presence of methanol exhibited an adverse effect on the degradation of formaldehyde.

Arslan-Alaton et al[82] studied the effect of untreated and Fenton-treated acid dyes (C.I. Acid Red 183 and C.I. Acid Orange 51) and a reactive dye (C.I. Reactive Blue 4) on aerobic, anoxic and anaerobic processes. After Fenton treatment the inhibitory effect of the blue reactive dye on methane production was found to be 21%. It was also reported that Fenton-treated dyes do not show inhibitory effect on aerobic glucose degradation. Maldonado and Peral[83] investigated the solar-assisted photo-Fenton degradation pathways of the commercial reactive azo dye Procion Red H-E7B. Identification and quantification of the intermediates generated along the reaction time have been done by employing LC-(ESI)-TOF-MS technique. By this technique 18 aromatic compounds of different size and complexity were detected. Generation of heteroatom oxidation products like NH^{4+}, NO^{3-}, Cl^-, and SO_4^{2-} have also been explained and quantified.

Lucas et al[84] developed a method to evaluate the capacity of different AOPs such as Fenton's reagent, ferrioxalate and heterogeneous photocatalysis combined with several radiation sources to degrade the phenolic compound Gallic Acid as a model compound of winery wastewaters. It was concluded that photo-Fenton process is the most efficient process which showed 95.6% degradation of GA in 7.5 minutes and total elimination of toxicity was achieved. A comparative study was done by Gutowska et al[85] to degrade the Reactive Orange 113 dye by H_2O_2/Fe^{2+} and ozone in aqueous solution. Riga et al[86] investigated the degradation of commercial reactive azo dyes such as Procion Navy H-exl, Procion Crimson H-exl and Procion Yellow H-exl by five AOPs like H_2O_2/UV, Fenton, UV/Fenton, TiO_2/UV and TiO_2/UV/H_2O_2. The effect of various inorganic salts such as NaCl, Na_2CO_3, $NaHCO_3$, Na_2SO_4, $NaNO_3$ and Na_3PO_4 were also examined and it was concluded that these salt decrease the rate of degradation.

Fenton/UV-C and Fenton –type process such as ferrioxalate/H_2O_2/solar light for the decolourization and mineralization of an azo dye *Reactive Black 5* have been evaluated by Lucas and Peres[87]. It was observed that decolourization of dye by both the processes is comparable but significant increment in TOC removal was reported by Fenton/UV-C process. Nunez et al[88] employed Fenton's and photo-Fenton's processes for the degradation of two reactive azo dyes, Procion Red H-E7B (CI Reactive Red 141) and Cibacron Red FN-R (CI Reactive Red 238). Effect of various operating parameter as well as the effect of natural or artificial light was evaluated and concluded that solar light is the most effective for this reaction. Sun et al[89] reported the effective degradation of azo dye Amido black 10 B in aqueous solution by Fenton oxidation process at low H_2O_2 and Fe^{2+}concentrations. The effects of different reaction parameters and UV–vis spectral changes of dye during the process were studied. It was found that by Fenton process the destruction of the azo linkage (–N═N–) group is more feasible than destruction of the aromatic rings of dye.

Degradation of Malachite Green by photo-Fenton reagent was investigated by Zheng et al[90] where the effect of various parameters and addition of cation-exchange resin have been assessed. Peternel et al[91] compared the degradation of C.I. Reactive Red 45 (RR45) dye in aqueous solution by various oxidation processes such as UV/TiO_2, UV/ZnO and photo-Fenton and concluded that photo-Fenton process is the most promising technique for the degradation and mineralization of dye. Effect of various parameters and added zeolite was also investigated. Effect of oxalic acid on the degradation of acidic dye Eosin Y by photo-Fenton process has been studied. It was reported that 94.1% of dye was removed in solar-Fenton in 90 min[92]. The expedient degradation of 4-chlorophenol in water by Pulsed discharge plasma induced Fenton-like reactions was investigated by Hao et al[93]. This enhancement can be attributed to ferrous ions generated via plasma induced Fenton-like reactions by UV light irradiation and hydrogen peroxide formed in pulsed electrical discharge, which lead to a larger amount of hydroxyl radicals production from the residual hydrogen peroxide. It was also observed that photo-catalytic reduction of UV light, photo-catalytic reduction on TiO_2 surface and electron transfer of quinone intermediates, i.e., 1,4-hydroquinone and 1,4-benzoquinone facilitate the regeneration of ferric ions to ferrous ions which also lead to increase in the rate of degradation.

The efficiency of various abatement processes like Fenton, Photo-Fenton, TiO_2/UV-A, TiO_2/UV-A/H_2O_2 and ozone were compared for the degradation of a 2,4,4'-trichloro-2'-hydroxydiphenyl ether[94]. To study the UV/Fe^{2+}/H_2O_2 and UV/Fe^0/H_2O_2, Fenton and photo-Fenton type processes, azo dye C.I. Acid Orange 7 (AO7) has chosen as model organic pollutant by Kusic et al [95]. In this study, processes were optimized than combined to enhance the rate of degradation; whereas to study the dark Fenton and photo-assisted Fenton type processes; Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, Fe^0/H_2O_2, UV/Fe^{2+}/H_2O_2, UV/Fe^{3+}/H_2O_2 and UV/Fe^0/H_2O_2 phenol was selected as model compound by them[96]. They developed mathematical models which predict phenol decomposition and formation of primary oxidation by-products. Additional reactions were also suggested which describe removal of iron from catalytic cycle through formation of ferric complexes and its regeneration induced by UV radiation.

The photo-Fenton process has been employed for the degradation of polyvinyl alcohol by Giroto et al[97] and it was reported that under optimum conditions more than 90% of the DOC can be degraded by this process. A model to design of a slurry photoreactor for the treatment of textile effluents was developed by Tokumura et al[98] which is based on the model for the average light intensity in the photoreactor. Design parameters were determined by discoloration of azo-dye Orange II in water by UV or solar light assisted Fenton reaction with iron ion eluted from the natural mineral tourmaline powder. Garcia-Montano et al[99] developed a novel method for the degradation of hetero-bireactive dye, Cibacron Red FN-R by coupling photo-Fenton process with an aerobic Sequencing Batch Reactor (SBR). To assess the chemical stage effectiveness various techniques such as decolourisation, biodegradability enhancement and dye degradation intermediates toxicity were applied. The biodegradability enhancement was determined by BOD_5/COD index and respirometric methods; and dye degradation intermediates toxicity was determined by Biotox® technique The degradation of Reactive Black 5 (RB5) in aqueous solution has been observed by Fenton and photo-Fenton processes[100]. It was found that a ratio $[H_2O_2]_0/[RB5]_0$of 4.9:1, a ratio $[H_2O_2]_0/[Fe^{2+}]_0$ of 9.6:1 at pH = 3.0 showed the maximum degradation. It was also observed that the extent of decolourization with Fenton and photo-Fenton processes has an insignificant difference but photo-Fenton process showed an effective TOC removal (46.4%) compared to Fenton process (21.6%).

The photo-Fenton process has been employed to degrade coffee effluent by Tokumura et al[101] and effects of various operating parameters were assessed. It was found that this process can be divided into three established phases. In phase-I, significant increase in colour of the solution was reported. In phase-II, initially the decolourization rate was high and then decreased. In phase-III, the rate was accelerated again and then complete decolourization was observed. A mechanism of the process was proposed. A comparative study has also been done for TiO_2, ZnO and photo-Fenton oxidation processes and it was concluded that the photo-Fenton process is the most effective technique for decolourization of coffee effluent. Degradation of azo-dye acid orange 24 by solar assisted photo-Fenton process has been examined by Chacon et al[102]. The progress of reaction was monitored by UV/Vis spetrometrometer as well as by determination of COD and TOC concentration; and decrease in toxicity. At optimum conditions using 50 kJ/l of accumulated energy, almost 95% discoloration and a toxicity reduction from 37 to 5 TU were achieved. The degradation of direct fast light black G by photo-Fenton reagent was investigated by Pu et al[103]. Effect of various parameters and the effect of added cationic resin on the photo-Fenton was observed. It was concluded that degradation reaction was enhanced to a greater extent by addition of resin. Muruganandham et al[104] examined the quantum yield and electrical energy per order (E(Eo)) for three advanced oxidative decolourisation of reactive azo dyes Reactive Orange 4 (RO4) and Reactive Yellow 14 (RY14) by UV light. Solar photocatalytic degradation of water-soluble pesticides such as cymoxanil, methomyl, oxamyl, dimethoate, pyrimethanil and telone at pilot-plant scale by heterogeneous photocatalysis with titanium dioxide and homogeneous photocatalysis by photo-Fenton has been investigated by Oller et al[105]. In this study, 75L solar pilot plant with four CPC units was used for photo-Fenton photocatalysis tests. Total disappearance of the parent compounds and almost complete mineralization were reported with all pesticides examined.

The effect of cation-exchange resin on the photo-Fenton degradation of a non-degradable dye great green SF has been investigated by Zheng et al[106.] Due to the introduction of these resins the activation of H_2O_2 was observed which enhanced the rate of degradation. For the electrochemical and photo-electrochemical in situ generation of H_2O_2 an annular tube reactor was designed and constructed by Peralta-Hernandez et al[107] in which H_2O_2 was generated by cathodic reduction of dissolved oxygen and the coupled oxidation of water at a UV-illuminated nanocrystalline-TiO_2 semiconductor anode. This coupled system can degrade the dye Direct Yellow-52 in dilute acidic solution efficiently in the presence of small quantities of dissolved iron (II). Solar/TiO_2 photocatalysis and solar photo-Fenton processes have been investigated by Cho et al[108] for the treatment of ground water sample contaminated with benzene, toluene, ethylbenzene, xylene isomers and TPHs (Total Petroleum Hydrocarbons) at gas station sites. Almost complete degradation of BTEX and TPH was observed within 2 and 4 hrs, respectively. The following order of rate of reaction was observed: $Fe(^{2+})/\ H_2O_2$ system without solar light >TiO_2/solar light>H_2O_2/solar light systems. It was also reported that the degradation rate of n-alkanes with carbon numbers ranging from C10 to C15 was relatively greater than that of n-alknaes with carbon numbers ranging from C16 to C20.

Decolourization of dye C.I. acid red 14 by employing different AOPs was compared by Daneshvar and Khataee[109]. The order of degradation was found to be –
$UV/\ H_2O_2/Fe(III)/oxalate > UV/\ H_2O_2/Fe(III) > UV\ H_2O_2/Fe(II) > UV/\ H_2O_2$.

Ntampegliotis et al[110] studied the kinetics of Fenton and photo-Fenton decolourization of Procion H-exl dyes from textile dyeing. Effect of the addition of different anions like chloride, carbonate and bicarbonate ions on the decolourization was studied, where it was observed that the addition of carbonate and bicarbonate substantially reduces the decolourization rates. It was also reported that the biodegradability increases from Fenton-like and photo-Fenton-like processes. Garcia-Montano et al[111] observed the degradation of Procion Red H-E7B reactive dye by combining photo-Fenton reaction with an aerobic Sequencing Batch Reactor (SBR). In this study, photo-Fenton process was applied as a pre-treatment to achieve a biodegradable water which can be treated by SBR in a second step. Bobu et al[112] investigated the photodegradation of monuron (3-(4-chlorophenyl)-1,1-dimethylurea) by (UV/H_2O_2, $UV/H_2O_2/Fe(2+)$, $UV/H_2O_2/TiO_2$, UV/TiO_2, dark H_2O_2/Fe^{3+} processes. In this research, various intermediary products were identified by using large volume injection micro-liquid chromatography with UV detection (mu-LC-UV), mu-LC-MS and GC-MS techniques. It was concluded that homogeneous photo-Fenton reactions are more efficient than heterogeneous photocatalytic systems.

Organic carbon content of a paper mill effluent was degraded by TiO_2-mediated heterogeneous photocatalysis, TiO_2- H_2O_2, TiO_2-Fenton, photo-Fenton, ozonation and ozonation with UV-A light irradiation[113]. Environmental assessment of different AOPs was done by Life Cycle Assessment (LCA) study. On the basis of this comparative study it was concluded Fenton's reagent proved to have the lowest environmental impact accompanied with a moderate-to-high DOC removal rate. The degradation efficiency of 4-Chlorophenol (4CP), malachite green, formaldehyde, dichloroacetic Acid (DCA) by and the commercial products of the herbicides diuron and tebuthiuron by two different iron sources, $Fe(NO_3)_3$ and complexed ferrioxalate (FeOx) was compared by Nogueira et al[114]. More efficient 4-CP degradation was observed by the use of $Fe(NO_3)_3$, whereas DCA and diuron and tebuthiuron degradation was facilitated by ferrioxalate.

To find out degradation pathway and potential toxicity of the uncoloured species formed during the degradation of E10 Sunset Yellow FCF in a commercial beverage various experiments were performed in different conditions such as thermally induced degradation, visible photo induced degradation, UV-photo induced Fenton reaction and UV-photo induced conditions in reducing environment[115]. A very quick decolourization was observed by Fenton reaction which could not be monitored progressively. For the degradation of dye pollutants accumulated in natural polyelectrolyte microshells a novel and efficient pathway was designed by Tao et al[116] using Fenton reaction. Various organic compounds such as salicylic acid, sodium benzenesulfonate, benzyltrimethylammonium chloride and trichloroacetic acid were employed to accelerate the Fenton degradation of dye such as Alizarin Violet 3B by Ma et al[117]. This dye is having anthraquinone structure unit due to which it act as a co-catalyst for the cycle of Fe^{3+}/Fe^{2+} and an electron transfer from the excited dye molecule to Fe^{3+}. An efficient route was designed for the degradation of some bio-recalcitrant pesticides such as alachlor, atrazine, chlorfenvinfos, diuron, isoproturon and pentachlorophenol by applying photo-Fenton/ozone (PhFO) and TiO_2-photocatalysis/ozone (PhCO) coupled systems[118]. The comparative study showed that expedient mineralization was obtained with photo-Fenton/ozone system expect some cases such as the atrazine and alachlor which showed no detoxification in the experimental conditions. Different methods such as titanium dioxide photocatalysis under aerobic and anaerobic conditions, and photo-Fenton process for the treatment of non-biodegradable chlorinated solvents such as dichloroethane, dichloromethane and trichloromethane were compared[119]. The photo-Fenton process was proven to be more efficient method for the degradation of these compounds.

Muruganandham and Swaminathan[120] studied the degradation of chlorotriazine reactive azo dye Reactive Orange 4 (RO4) by Fenton and photo-Fenton processes. The influence of various operating parameters on the rate of degradation was observed. Various oxidative processes such as $Fe(III)/H_2O_2/UV–Vis$, $Fe(III)/UV–Vis$ and $H_2O_2/UV–V$ were employed and compared for the degradation of fenitrothion[121]. On the basis of data obtained it was concluded the photo-Fenton system is more efficient than other systems in both pure and river waters. Flat-plate solar reactor was developed by Rossetti et al[122] for the degradation of formic acid as model compound by solar light assisted Fenton reaction. It was also reported that the a pollutant conversion by photo-Fenton reaction was 175% greater than the Fenton reaction in dark. Solar light assisted Fenton and photo-Fenton reaction were studied by Torrades et al[123] for the degradation of different commercial reactive dyes such as Procion Red H-E7B, Red Cibacron FN-R and a Standard Trichromatic System. By the use of solar light the reaction efficiencies of removal of color, aromatic compounds (UV_{254}), Total

Organic Carbon (TOC) and the BOD_5/COD ratio were increased. A comparative study was made by Kavitha and Palanivelu[124] to assess the efficiency of Fenton, solar-Fenton and UV-Fenton degradation of phenol in simulated and industrial wastewater. The maximum mineralising efficiency for phenol (97%) was observed for UV-Fenton process. An investigation was also done for iron reusability in these process. Meric et al[125] observed the toxicity of Reactive Black 5 on *Daphnia magna* and reported that toxicity could be completely removed by employing Fenton's oxidation process at optimum removal conditions. For the treatment of wastewater containing rhodamine B photo-Fenton reaction was studied by Zhengand Xiang et al[126]. Bali et al[127] investigated the photodegradation of three dyes named as C.I. Reactive Black 5, C.I. RB5, C.I. Direct Yellow 12, C.I. DY12, and C.I. Direct Red 28, C.I. DR28 by using UV, UV/H_2O_2 and UV/H_2O_2/Fe(II) systems. It was concluded that efficiency of decolourization and mineralization were found to be maximum with photo-Fenton system.

Fenton and photo-Fenton processes along with photocatalysis were examined for their Natural Organic Matter (NOM) removal potential by Murray and Parsons et al[128]. They found that the processes achieved greater than 90% removal of DOC under optimum conditions but an economic assessment of the processes showed that currently such processes are not economic. Various homogeneous (H_2O_2/UV-Vis and H_2O_2/Fe^{2+}/UV-Vis) and heterogeneous (TiO_2/UV-Vis and TiO_2/ H_2O_2/ UV-Vis) systems were assed for the treatment of cork manufacturing wastewater[129]. Expedient mineralization (66%) was achieved in 10 min. with the use of photo-Fenton process, whereas TiO_2 was not found to be suitable for degradation. H_2O_2/UV-V system showed 39% removal of TOC after 4 h of operation. Even combination of TiO_2 and H_2O_2, yields an overall TOC decrease of 46% only. Reactive brilliant red X3B, was decolorized in water by photo-Fenton reactions and TiO_2 photocatalysis[130] [Chemosphere 43 (2001) 1103]. The degradation of two azo reactive dyes, C.I. Reactive Yellow 84 (RY84) and C.I. Reactive Red 120 (RR120) by photo-Fenton and Fenton-like oxidation was examined Montserrat by Neamtu et al[131]. The following order was observed for decolourization of RY84 was solar/Fe(II)/H_2O_2>UV/Fe(II)/H_2O_2>UV/Cu(II)/Fe(III)/ H_2O_2>UV/Fe(III)oxalate/H_2O_2>UV/Fe(III)/H_2O_2>dark/Fe(II)/H_2O_2>solar/Fe(III)oxalat/H_2O_2>UV/H_2O_2>UV/Fe(II)=UV. The order of decolourization of RR120 removal was found to be-solar/Fe(II)/H_2O_2>UV/Fe(II)/H_2O_2>UV/Fe(III)/H_2O_2=UV/Cu(II)/Fe(III)/H_2O_2>UV/Fe(III)oxalate/H_2O_2=UV/H_2O_2>UV. Some fragmental oxidation products of dyes such as formate and oxalate were also identified.

Degradation of some explosive compounds such as 2,4,6-trinitrophenol (PA), ammonium picronitrate (AP), 2,4-Dinitrotoluene (DNT), methyl-2,4,6-trinitrophenylnitramine (Tetryl) and 2,4,6-Trinitrotoluene (TNT), hexahydro 1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) was investigated by employing Fenton and photo-Fenton processes[132]. In this study, the inhibition of hydroxyl radical and theory of CFSE were also introduced. For the treatment of a cellulose conventional bleaching effluent the Fenton reagent under solar light irradiation was examined by Torrades et al[133] and it was reported that 90% TOC reduction could be achieve in only 15 min. For the treatment of various types of agro-industrial wastes photo-Fenton process was applied under artificial light in laboratory experiments in Vienna whereas pilot-plant experiments under sunlight were carried out at the Plataforma Solar de Almeria in Spain by Wolfgang Gernjak et al[134]. Vanillin, protocatechuic acid, syringic acid, *p*-coumaric acid, gallic acid and L-tyrosine were selected as model compounds where complete mineralisation without producing non-degradable intermediates was reported.

Malato et al[135] examined the intermediates formed and their toxicity during the photocatalytic treatment of diuron by employing heterogeneous and homogeneous photocatalysis with titanium dioxide and photo-Fenton, respectivelyat equivalent pilot-scale which was made up of Compound Parabolic Collectors (CPCs) by both phototreatments in 45 min total disappearance of diuron was achieved whereas 90% of mineralization was reported after 200 min of photocatalytic treatment. The amount of transformation products generated was found to be different for both the systems. Montserrat Perez et al[136] investigated the alternate approach for the degradation organic content of a bleaching Kraft mill effluent by Fenton reagent and photo-Fenton reactions. Effects of various operating parameters such as pH, initial concentrations of Fe(II) and H_2O_2, temperature, light intensity and O_2 presence in solution were studied. It was concluded that the combination of Fenton and photo-Fenton reactions is highly efficient and effective process for the treatment of these effluents. Raquel et al[137] examined the photodegradation of Dichloracetic Acid (DCA) and 2,4-Dichlorophenol (DCP) by photo-Fenton process using potassium ferrioxalate and solar light. Completely destruction of the organic carbon of a 1.0 mM DCA solution was reported in 10 min of exposure. It was also observed that photodegradation efficiency increases linearly with the solar light intensity up to15 W m^{-2} beyond this value it showed a square root dependence. The combination of Fenton, Fenton-like and photon-Fenton reactions for the treatment of textile wastewaters generated during a hydrogen peroxide bleaching process was assessed by Montserrat Perez et al[138].

The photo-Fenton process was proven to be most efficient approach for the degradation of AO7 in comparison of photoperoxidation and Fenton processes[139]. Sangkil Nam et al[140] investigated the effect of substituents such as methyl, methoxy and halo substituents on the phenolic ring of 4-(4'-sulfophenylazo)phenol and 2-(4'-sulfophenylazo) phenol in the Fe^{III}–EDTA–H_2O_2 system at neutral pH. Degradation of naphthol dyes Orange I and Orange II by this system were also studied. It was found that halogens substituted dyes were oxidized to a greater extent than the corresponding methyl- or methoxy-substituted dyes. This was explained as the halogen substituents make the phenolic moieties more acidic, which favours the generation of phenolate anion, which in turn more readily attacked by hydroxyl radicals. Combinations of UV/H_2O_2 and the photo-Fenton reaction was investigated for the degradation of *p*-chlorophenol[141]. Five to nine times greater rate of degradation was observed with photo-Fenton process than UV/H_2O_2 process with 73 to 83% less energy consumption. Oxidation positions of five recalcitrant Polycyclic Aromatic Hydrocarbons (PAHs) in ethanol were predicted by Frontier electron density when subjected to Fenton oxidation[142]. Quinone forms of oxidation products were identified in each PAH. It was observed that oxidation positions of quinone forms of products correspond to the predicted positions where Frontier electron density was high.

Araña et al[143] investigated photo-Fenton reaction in highly concentrated phenol solutions where the intermediates were identified by FTIR-ATR device. The formation of dissolved and precipitate tannin was reported which inhibits the complete mineralization of phenol. This inhibition was explained as hydroxyl radicals attack that produce further condensation steps which will increase polymer size. The possibility of formation of Fe^{3+}-Pyrogallol complex before the tannin formation and the global mechanism of photo-Fenton reaction was also reported. Photo-Fenton and TiO_2 photocatalysis at a solar pilot plant was compared for the degradation of aqueous imidacloprid on the basis of technical feasibility, mechanisms, and efficiency[144]. 2.4 times faster TOC disappeared was reported by photo-Fenton faster than with TiO_2. The amount of Transformation Products (TPs) generated was found to be different but detected TPs were same. Low concentration of 2-pyrrolidinone was identified in the dissolution at the end of both processes.

Some AOPs such as H_2O_2/hv, TiO_2/H_2O_2/hv, Fe^{3+}/hv, Fe^{3+}/H_2O_2 and Fe^{3+}/H_2O_2/hv were examined for the degradaion of 5-Amino-6-Methyl-2-Benzimidazolone (AMBI) by Sarria et al[145] and it was observed that photo-Fenton process is the most efficient system. In addition to that for the degradation of AMBI a combined photo-Fenton and biological flow reactor was successfully operated in continuous mode at laboratory scale. Experiments using direct sunlight were carried out at the Plataforma Solar de Almeria, Spain, which revealed that solar catalytic system is an efficient system for the treatment of such effluents. A modified photo-Fenton (UV/Fe oxalate/H_2O_2) process was employed for the degradation of Reactive Red 235[146]. The degradation of oxalate was also investigated in the absence of dye. It was reported that Fe(III)-oxalato complexes forms which could be easily photolysed and relatively unreactive with hydroxyl radicals. Arana et al[147] examined the degradation of highly concentrated solution of phenol by TiO_2 photocatalysis and the photo-Fenton reaction. The formation of polyphenolic polymers was reported in photo-Fenton process which could be the reason of decrease in rate of degradation. A medium concentrating radiation system (Heliomans, HM) and a non-concentrating radiation system (CPC) were compared for the degradation p-nitrotoluene-o-sulfonic acid (p-NTS) by photo-Fenton reactions and by TiO_2 at a pilot-scale under solar irradiation at the Plataforma Solar de Almeria (PSA)[148]. It was concluded that CPC collector are three times more efficient than in the HM collectors.

Degradation of cationic Acridine Orange monohydrochloride (AO) and anionic Alizarin Violet 3B (AV) using photo-Fenton process was investigated by Xie et al[149]. Decolourization of textile wastewater containing reactive dyestuff of R94H by photo-Fenton proves was observed by Shyh-Fang Kang et al[150]. Roberto Andreozzi et al[151] proposed a kinetic model for the degradation of benzothiazole by photo-Fenton process in a completely mixed batch reactor. Consumption of oxygen during the degradation of aniline by Fenton and photo-Fenton reactions was assessed by Berta Utset et al[152]. Effective partial replacement of H_2O_2 by O_2 was also investigated. It was concluded that presence of H_2O_2 is necessary for this process. The potential of the Fenton's reagent for the degradation of Metol [*N*-methyl-*p*-aminophenol] was studied by Loreto Lunar et al[153] in dark as well as in presence of light.

2.2 Heterogeneous Fenton and Photo–Fenton Processes

Despite its high efficiency, the Fenton process is still not considered to be the ultimate treatment technique because it works at very low pH usually at pH 3 to maintain the iron species in solution. The generation of high amount of sludge in neutralization/coagulation step is another major drawback of this process. More recently, research has been directed toward the immobilization of iron species on different solid supports or the use of insoluble iron oxides (goethite, magnetite and hematite) in order to simplify iron separation. This process is named as heterogeneous Fenton reaction. Heterogeneous Fenton process is conceptually attractive and practical because it does not require the sludge separation step thus reduces the cost of operation.

Heterogeneous photo-Fenton decolourization of Orange II over Al-pillared Fe-smectite has been studied by Liet al[154]. It was observed that catalyst loading of 0.5 g/L and hydrogen peroxide concentration of 13.5 mM yielded a remarkable colour removal accompanied by excellent catalyst stability. Tireli et al[155] added a new step to the classic route of iron-pillared clay (Fe-PMAG) obtention which lead to a material with both magnetic and oxidative properties. Fe-PMAG showed an increase of 0.57 nm in basal spacing which contributed to the specific surface area increase from 39.1 to 139.2 m^2/g. This material showed an excellent MB oxidation capacity indicated by complete removal of the colour of the solution within 90 minutes under photo-Fenton conditions. The degradation of Orange II by heterogeneous Fe_3O_4 catalysts in the presence of H_2O_2 was investigated by Kun Chen et al[156]. Fe_3O_4 nanoparticles were successfully prepared *via* oxidation–precipitation method. A significant quadratic model (p-value <0.0001, $R^2 = 0.9369$) was derived using Analysis of Variance (ANOVA).

A novel coupled system for the degradation of Rhodamine B and TOC removal was developed by Chen Q et al[157] using Co-TiO which combined sulfate radical based Fenton-like reaction and visible light photocatalysis. This coupled system exhibited excellent catalytic stability and reusability and almost no dissolution of Co^{2+} was reported. Degradation of aqueous solution of bisphenol A was reported by heterogeneous photo-Fenton using Fe-Y molecular sieve catalyst which was prepared with the ion exchange method[158]. In comparison to photolysis, photo-oxidation with only hydrogen, heterogeneous Fenton, and homogeneous photo-Fenton this method was found to be more efficient. The stability tests indicated that the Fe-Y catalyst can be reused and iron solubility concentration ranged from NA to 0.0062 mg/L. Yao et al[159] developed a magnetic $ZnFe_2O_4$-reduced graphene oxide hybrid act as heterogeneous catalyst for photo-Fenton-like decolourization of various dyes using Peroxymonosulfate (PMS) as an oxidant. The combination of $ZnFe_2O_4$ NPs with graphene sheets leads to a much higher catalytic activity than pure $ZnFe_2O_4$. Graphene acted as a support and stabilizer for $ZnFe_2O_4$ as well as a catalyst for activating PMS to produce sulphate radicals. Degradation of Acid Blue 29 by using iron modified mesoporous silica as heterogeneous photo-Fenton catalyst was studied by Soon and Hameed[160]. The solid catalyst prepared by sol–gel and incipient wetness impregnation method. It was also found that the catalyst is reusable over four consecutive cycles and minimal leaching of iron ions.

The photocatalytic activity of TiO_2/β-FeOOH composite photocatalyst synthesized by hydrothermal method was evaluated in a heterogeneous photo-Fenton-like process where methyl orange was used as model compound. The enhanced photocatalytic activity can be attributed to the formation of TiO_2/β-FeOOH heterostructure, which plays an important role in effectively prolonging the lifetime of photo-induced electrons and holes and in expanding the photo-activity to the visible light region[161]. The amidoximated polyacrylonitrile (PAN) fiber Fe complexes were synthesized and employed as the catalyst for heterogeneous photo-Fenton process to degradation of various anionic water soluble azo dyes. The Quantitative Structure Property Relationship (QSPR) model equations was developed and the predictive ability these equations was assessed by Leave-One-Out (LOO) and Cross-Validation (CV) methods. The effect of Fe content of catalyst and the sodium chloride in water on

QSPR model equations were studied[162]. Degradation of Methyl violet, Rhodamine B and phenol has been reported by heterogeneous photo-Fenton reaction catalysed by $BiFeO_3$. It was observed that the rate of reaction gets accelerated by increasing $BiFeO_3$ load and H_2O_2 concentration. The catalytic activity $BiFeO_3$ can be increased with the addition of surface modifiers like EDTA[163].

A mesoporous iron modified Al_2O_3 nanoparticle pillared montmorillonite nanocomposite, a smart photo-Fenton catalyst, was synthesized by Pradhan et al[164]. This catalyst showed a high photo-Fenton activity towards degradation of organic dyes such as acid blue and reactive blue which can be explained on the basis of small particle sizes of nanocomposite, quick reduction of Fe(III) and mesoporosity. For photo-Fenton oxidation of azo dye Reactive Black B an immobilized iron oxide was used as a heterogeneous catalyst (B1, supported with SiO_2 grain)[165]. A novel reactor consisted of a xenon lamp, a submerged membrane module and $FeVO_4$ was studied by coupling the heterogeneous photo-Fenton-like oxidation with membrane separation to resolve the continuously reuse problem of fine catalysts and it was found that catalyst was left in the reactor[166]. A new coupled photo-electrochemical/electro-Fenton oxidation (PEC/EF) system was developed for the degradation of rhodamine B which showed much higher activity at neutral pH. In this study, Bi_2WO_6 nanoplates deposited on FTO glass used as anode whereas $Fe@Fe_2O_3$ core-shell nanowires supported on activated carbon fibre act as cathode. This high efficiency can be due to the synergetic effect from better separation of photo-generated carriers in the photo-anode and the transfer of photo-electrons to the oxygen diffusion cathode, which generate more electro-generated H_2O_2 and hydroxyl radicals[167]. Zhang et al[168] found that Rhodamine B could be degraded effectively by the Cata/RhB/H_2O_2/vis system where hematite is used as catalyst. The catalyst showed excellent stability with little loss of activity even after 6 recycling experiments.

A bifunctional iron modified rectorite (FeR) was synthesised by Zhao et al[169] also which act as an efficient adsorbent and catalyst for the photo–Fenton degradation of Rhodamine B. It was reported that adsorption capacity of RhB on FeR increased by 11 folds compared to the unmodified one. Chen and Zhu[170] investigated the oxalate enhanced mechanism of hydroxyl-Fe-pillared bentonite (H-Fe-P-B) during the degradation of Orange II by UV-Fenton process. The addition of oxalate increased the Fe leaching of H-Fe-P-B which result in to higher mineralization efficiency and lower energy consumption. The degradation mechanism of microcystin-LR is studied using heterogeneous Fenton system with H_2O_2 and FeY catalyst was investigated by Fang et al[171]. Possible pathways and the three vulnerable oxidation sites were proposed. This catalyst was prepared by loading Fe^{2+} to the molecular sieve NaY which showed good stability, possessing catalytic activity even after repeated use for 5 times.

Soon and Hameed[172] developed the stable heterogeneous catalyst towards minimal leaching, long-term stability and high catalytic activities for Fenton system to degrade dyes. The effect of modified photo Fenton's like method on the degradation of 2,4,6-Trichlorophenol (TCP) was studied by Vinita et al[173] using nano scale iron (III) catalyst bound onto the surface of heterogeneous carbon binder. The degradation and mineralisation efficiencies at the optimised conditions were found to be 100% and 89%, respectively. A novel heterogeneous photo-Fenton catalyst was prepared by iron pillared vermiculite (Fe-VT) and used for photocatalytic degradation of azo dye reactive brilliant orange X-GN[170]. An another catalyst mesoporous SBA-15 doped iron oxide (Fe_2O_3/SBA-15) was prepared by co-condensation and used for photo-Fenton decolourization of azo dye Orange II by Gong et al[175]. In this work, the effect of various operating parameter has been observed by response surface methodology. To catalyse the photo-Fenton degradation of organic contaminants like dye rhodamine B and 4-nitrophenol an efficient Fe(2)O(3)-pillared rectorite (Fe-R) clay was prepared[176]. To study the photoreaction processes Fourier transform infrared spectroscopy and zeta potential were applied. The discoloration and COD removal rate of the two contaminants were reported more than 99.3%, and 87.0%, respectively.

Some researchers examined the photocatalytic activity of prussian blue (iron hexacyanoferrate) colloids for the degradation of dyes by heterogeneous photo-Fenton process. The effects of alkali metal cations on the photo-Fenton process was also investigated. It was found that the degradation of Rhodamine B, Malachite Green and Methyl Orange in the presence of salts such as KCl, KNO_3, and K_2SO_4, respectively were found to be faster than their degradation rates in the presence of the corresponding sodium salts. It was also observed that potassium ions accelerate the degradation rate, whereas sodium, rubidium, and cesium ions decreased the rate of degradation which is consistent with that of the voltammetric oxidation currents of Prussian blue in the corresponding cation solutions. It can be explained on the basis of the molecular recognition of the microstructure in Prussian blue nanoparticles to the alkali cations[177]. Kasiri et al[178] studied the photo-Fenton process for degradation of azo dye Acid Red 14 in presence of Fe-ZSM5 zeolite. The effect of initial pH on the rate of degradation was examined and highest quantum yield was reported at initial pH 5.0. Torres-Palma et al[179] employed AOP that combines sonolysis, $Fe^{2+,}$ and TiO_2 in a photo assisted process for the degradation of bisphenol A. Due the synergistic effect, a complete and rapid elimination of dissolved organic carbon was observed even at low catalyst loadings. Fe-doped TiO_2 catalysts was used for photo-Fenton degradation of 4-nitrophenol by Zhao et al[180]. Zero Valent Metallic Iron (ZVMI) was employed by Gomathi Devi et al[181] in Advanced Fenton Process (AFP) for the degradation of Methyl Orange. The rate of reactions for the Fe^0/UV and Fe^0/Ammonium persulphate (APS)/UV were found to be twice compared to their respective processes carried out in dark. H_2O_2 was found to be better oxidant but more susceptible to deactivation by hydroxyl radical scavengers than APS. It was also reported that recycling efficiency of iron powder retained more in H_2O_2 than APS. Efficiency of various processes showed the following order: $Fe^0/H_2O_2/UV > Fe^0/H_2O_2/dark > Fe^0/APS/UV > Fe^0/UV > Fe^0/APS/dark > H_2O_2/UV \approx Fe^0/dark > APS/UV$. The degradation mechanism of 1,4-dioxane using zero-valent iron (Fe^0) in the presence of UV light was observed by Son et al[182]. The expedient 1,4-dioxane removal can be attributed to increase supply of OH radicals from the Fenton-like reaction induced by the photolysis of Fe^0 and H_2O.

Wang et al[183] selected four types of soil clays from different region of china which contain iron oxides such as magnetite and hematite simulate chemical remediation of soils contaminated with dyes like Rhodamine B by light-assisted Fenton-like process. It was also reported that soil organic matters inhibit the photodecomposition of RhB dye, remarkably.

Fe^{3+}-C_2O_4-loaded resin has been used as a catalyst for the photo-Fenton degradation of malachite green. This Fe^{3+}-C_2O_4/R increased the formation of hydroxyl radicals thus in turn enhance the rate of degradation of MG[184]. A novel catalyst Fe(III)-5-sulfosalicylic acid (ssal) supported on $Al(_2)O(_3)$ was developed by Zhang et al[185] to enhance the photo-Fenton type degradation of 2-sec-butyl-4,6-dinitrophenol (DNBP). This catalyst can be reused for 5 cycles. The degradation of Orange II in a photo-reactor mediated by Fe-Nafion membranes was studied by Manzano et al[186] where the decrease in rate of degradation was observed in presence surfactants such as linear alkylbenzenesulphonates (LAS) and K-perfluoroalkylsulphonate. Heterogeneous photocatalytic degradation of gallic acid under different experimental conditions like UV/TiO_2, H_2O_2, in presence of $Fe^{3+}$and the combination Fe^{3+}/H_2O_2 has been observed by Quici and Litter[187]. Iron vanadate $FeVO_4$ was found to be a highly active heterogeneous Fenton-like catalyst than α-Fe_2O_3, Fe_3O_4 and γ-FeOOH for the degradation of Orange II. High catalytic activity of iron vanadate can be attributed to two-way Fenton-like mechanism i.e., the activation of H_2O_2 by both Fe(III) and V(V) in $FeVO_4$. In addition, this catalyst can be applied to broad pH range[188].

Kasiri et al[189] investigated the estimation capacities of Response Surface Methodology (RSM) and Artificial Neural Network (ANN) in a heterogeneous photo-Fenton process. Degradation of C.I. Acid Red 14 azo dye were carried out in presence of zeolite Fe-ZSM5. Central Composite Design (CCD). In this study, response surface methodology was applied to examine the simple and combined effect of four independent variables such as concentration of the catalyst, molar ratio of initial concentration of H_2O_2 to that of the dye (H value), initial concentration of the dye and initial pH of the solution. Satisfactory prediction second-order regression was derived by RSM. The independent parameters were fed as inputs to an artificial neural network while the output of the network was the degradation efficiency of the process. Comparable results were achieved for data fitting by using ANN and RSM.

A heterogeneous catalyst Ta_3N_5 has been prepared by nitridation of Ta_2O_5 under NH_3 flow at 700°C. A faster Fe^{3+}/Fe^{2+} cycling was achieved by this catalyst because when Ta_3N_5 is added to Fe^{3+}/H_2O_2 solution most Fe^{3+} were adsorbed on the Ta_3N_5 surface. Now in presence of light the adsorbed Fe^{3+} ions were reduced to Fe^{2+} swiftly and Fe^{2+} were oxidized by H_2O_2 on the Ta_3N_5 surface resulting in to faster conversion of Fe^{3+}/Fe^{2+}). By employing this catalyst an expedient degradation of organic molecules such as *N*,*N*-Dimethylaniline (DMA) and 2,4-Dichlorophenol

(DCP) was achieved which can be attributed to efficient and rapid decomposition of H_2O_2 to generate hydroxyl radicals by $Ta_3N_5/Fe^{3+}/H_2O_2$ system[190]. An expedient and efficient degradation of non-biodegradable azodyes ARB, reactive brilliant red X-3B, reactive red K-2G, cationic red X-GRL and cationic blue X-GRL were achieved at neutral pH values by $FeOxH_{2x-3}$/Fe0 catalyst developed by Nie et al[191] in the presence of H2O2 under UVA irradiation. The XRD, FT-IR revealed that the surface layer of the catalyst was composed of alpha-FeOOH and gamma-Fe_2O_3, and the core was Fe^0. The enhanced rate of degradation can be attributed to the synergistic effect of the catalysis of galvanic cells and the oxidation of heterogeneous photo-Fenton process. Arora et al[192] studied the photo-Fenton degradation of the dye rose Bengal over pillared bentonite containing iron

Liu et al[193] developed the heterogeneous iron oxide/bentonite catalyst by a reaction of a solution of OH-Fe salt with bentonite clay dispersion for discoloration and mineralization of dye rhodamine. The effects of various operating parameters as well as comparison between the heterogeneous photo-Fenton process and homogeneous photo-Fenton process was observed. It was observed that heterogeneous photo-Fenton process is much faster than homogeneous photo-Fenton process due to the large surface area. Hydroxyl-Fe-pillared bentonite (H-Fe-P-B) was synthesized by cation exchange reaction which was used as heterogeneous photo-Fenton catalyst for the degradation of Orange II dye. It overcome the drawback of costly pH adjustment of homogeneous photo-Fenton process. Due to the strong surface acidity and the electronegativity of H-Fe-P-B, the pH range of this catalyst could be extended up to 9.5. Total discoloration and more than 60% TOC removal of dye was achieved after 120 min treatment using UVA- H_2O_2 system[194]. In[195] examined the effect of initial pH on the degradation of Orange II by using two clay-based Fe nanocomposites catalysts such as Fe supported on bentonite and laponite clay. It was observed that the catalytic activity as well as the leaching of Fe get affected by initial pH of the solution and best results were obtained at pH 3.0. But these catalysts also showed a good activity at pH 6.6 which is close to neutral pH and thus making this process more viable and eco-friendly where pre adjustment of the pH is not required.

A novel catalyst Fe-C-TiO($_2$) was developed by heating a mixture of TiO_2 and FeC_2O_4 at 673-1173 K in Ar. This catalyst contained the residue carbon (0.2-3.3 mass %), employed for phenol decomposition under UV irradiation via photo-Fenton process. Phenol was degraded by a complex reaction with iron and intermediates of phenol decomposition with higher speed. Thus carbon-coating TiO_2 was found to be advantageous for mounting iron[196]. Degradation of a chlorotriazine Reactive azo dye Reactive Orange 4 (RO4) was investigated by Selvam et al[197] employing ferrous sulphate/ferrioxalate with H_2O_2 and TiO_2-P25 particles. A comparative study of UV/ferrous/H_2O_2/TiO_2-P25 and UV/ferrioxalate/H_2O_2/TiO_2-P25 processes was also done which showed that ferrioxalate is more efficient in solar light whereas ferrous ion is more efficient in UV light. by Tang et al[198] developed a novel and efficient catalyst for the degradation of fenton process for the degradation of dyes by immobilizing Fe(III) onto collagen fiber.

A very promising heterogeneous pillared laponite clay-based Fe nanocomposites catalyst were prepared by pillaring technique for photo-Fenton mineralization of azo-dye acid black[199]. The photocatalytic processes using TiO_2 and the photo-Fenton reaction where Fe^{3+} or ferrioxalate was used as a source of Fe^{2+} were coupled for the degradation of 4-chlorophenol (4CP) and Dichloroacetic Acid (DCA) using solar irradiation to study the effect of combination. Synergistic effects were reported between FeOx and TiO_2 and between H_2O_2 and TiO_2 in the degradation of DCA whereas addition of TiO_2 did not show any significant synergistic effect[200]. By pillaring technique a laponite RD clay-based Fe nanocomposite (Fe-Lap-RD) was prepared whose photo-catalytic activity was examined for the degradation of an azo dye Orange II[201]. It was found that rate of decolourization was much faster than mineralization. Photo-Fenton degradation of salicylic acid by using strongly acidic type of ion exchange resin based catalyst was also studied. Laponite clay-based Fe nanocomposite which consists of Fe_2O_3 (meghemite) and $Fe_2Si_4O_{10}(OH)_2$ (iron silicate hydroxide) was used for the decoloration and mineralization of Reactive Red HE-3B by Feng et al[202]. Due to high specific surface area and a high total pore volume its showed very high reactivity a complete decolourization of dye was achieved in 30 min and the total organic carbon removal ratio of 76% was obtained in 120 min. The degradation of azo dye, Mordant Yellow 10 (MY10) at neutral pH in aqueous dispersions of goethite (α-FeOOH)/H_2O_2 under UV light as well as in dark reaction was examined by He et al[203]. It was attributed that hydroxyl radicals generated by the photolysis of the surface complex of H_2O_2 with the oxide surface metal centers which leads to the faster degradation of MY10. A photocatalyst $TiO_2/SiO_2/\gamma\text{-}Fe_2O_3$ (TSF) was developed whose photocatalytic activity was evaluated by using dyes such as Fluoresein, Orange II and Red acid G[204]. A higher photocatalytic activity was achieved by deducting the UV light absorption of the $\gamma\text{-}Fe_2O_3$ particles. But its photocatalytic activity was much lower than that of the P25 TiO_2 under visible irradiation even deducting the visible light absorption. As it showed good repeatability so it could be recycled.

3. Conclusion

One of the most challenging issues of the last decades is the presence of recalcitrant compounds in wastewater which are damaging the ecosystems drastically due to their highly toxic nature. Fenton and photo Fenton like processes open new avenues for providing greener eco-friendly methods for mineralization of these compounds.

However some limitation have been confronted like working pH and cost of the process. Several strategies have been put in practice to make it more economic and improve photo-Fenton efficiency primarily through application of heterogeneous catalysts and/or chelating agents. In addition, in order to reduce operating costs the use of solar energy and integrating the biological treatment technologies in the Fenton process can be considered.

Although several studies have been done on Fenton and photo-Fenton processes but still there are several points which can be further explored to improve the efficiency and practical applicability of these processes and more lucid mechanism can be developed. It provides platform to new researchers to establish more advanced technologies by combining Fenton process with other wastewater treatment methods.

4. References

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