Chemical Method For Wastewater Management: Developments Of Fenton Process

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Abstract: Fenton process represents a promising technology for the treatment of recalcitrant wastewaters. In recent years, many studies have been conducted on the applications of Fenton process for the removal of organic pollutants in wastewater. This study presents Fenton and improvements of Fenton process such as photo-Fenton, electro-Fenton and sono-Fenton processes. Previous studies on catalysts and their efficiencies in Fenton and improvements of Fenton process were also analyzed. The effects of many important operational parameters such as pH, Fenton reagents, initial concentration of the pollutants, concentration of inorganic ions and energy input in Fenton process have been discussed and their roles are highlighted. It has been concluded that further investigations are needed to evaluate the cost of Fenton process, especially when it is combined with other energy input processes. Integration of Fenton process with other conventional methods as pre-treatment or post-treatment stage is a strategy that could enhance efficiency and reduce cost of Fenton process, hence, it should be one of the research focus of Fenton process.

Keywords: Fenton, wastewater, catalyst, photo-Fenton, sono-Fenton, electro-Fenton

1. Introduction

Industrial revolution has brought rapid development in provision of goods and services for human needs. However, this development comes with responsibilities. During industrial processes, a significant quantity of water is consumed at various stages of the process, which are released as wastes. The effluents from industries contain a varying amount of organic and inorganic pollutants that are toxic to human and environment. Hence, there is a need for efficient treatment of industrial effluents. Current techniques that are employed in the treatment of recalcitrant industrial wastewaters have some challenges. Some of these challenges are inefficient and incomplete degradation, transfer of contaminants from one medium to another, generation of high amount of sludge, low efficiencies, and slow reaction rates [1], [2]. In this category of wastewaters are petroleum refinery wastewaters, tannery wastewaters, textile wastewaters, metal working fluids, pollutants from pharmaceutical industry such as ibuprofen, aromatic, among others [3]. Advanced oxidation processes (AOPs) have been identified as effective techniques for the treatment of recalcitrant wastewaters. Among them, Fenton process (FP) is gaining more attention due to its high performance, operational at room temperature and ambient pressure [4] and is also non-toxic [5]. The process is based on generation of powerful oxidizing species (hydroxyl radical) that is capable of degrading most of the pollutants in wastewaters. FP can be classified based on reaction phase (homogeneous or heterogeneous system) or based on methods for generation of hydroxyl radicals (OH.) (photo-Fenton, electro-Fenton, and sono-Fenton). Over the years, several studies have been reported in the literature on the potential application of the FP for treatment of recalcitrant industrial wastewaters [3], [6], [7]. However, these studies focus on some special cases of Fenton process, such as treatment of textile effluents, thus a comprehensive analytical study on Fenton and improvements on Fenton process in a broad perspective is of demand at present. Therefore, this present study has been undertaken to fill the existing vacuum. Fundamentals of Fenton process and their efficiencies for degradation of pollutants in wastewater have been presented in this paper. It also investigates the factors that affect Fenton process.
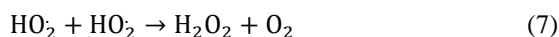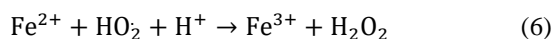
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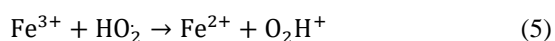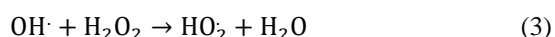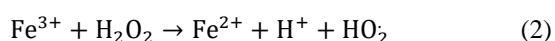
2.1 Fenton-Based AOPs

Fenton process is principally a reaction between iron ions and hydrogen peroxide to form hydroxyl (OH) radical that degrade organic or inorganic compounds. The name 'Fenton' was originated from H.J.H. Fenton who in 1894 reported that hydrogen peroxide (H_2O_2) can be activated by ferrous salts to oxidize tartaric acid [8]. However, not until 1934, it was

proposed that Fe^{2+} or Fe^{3+} can promote the activation of H_2O_2 to generated powerful $OH^·$ that is highly reactive with organic pollutants [9]. Over the last decades, there was resurgence interest in the Fenton process by researchers' due to its potential applications for treatment recalcitrant wastewaters. The efficiency of the Fenton process is highly dependent on several factors such as pH, concentration of H_2O_2 and types of iron ions. In classical Fenton process, several studies in literature have reported acidic conditions to be effective in generation of OH radicals [10], [11], which promotes the quick degradation of pollutants. At lower pH, the reaction between the Fenton reagents is inhibited [12]. The process has been successfully applied for the depuration of recalcitrant industrial wastewaters that cannot be adequately treated by conventional biological process. In these categories are textile wastewaters [7], [13], [14], petroleum refinery wastewaters [15], [16] and effluents from the production of olive oil [17]–[19] among others. H_2O_2 is generally reactive at ambient temperature and pressure thus the Fenton process does not require energy input [20]. In addition to that, Fenton reagents can be easily handled and the reaction occurs within a short period [21]. In conventional Fenton process, the mechanisms involve reaction between Fe ions that act as a catalyst and hydrogen peroxide to generate short-lived OH radicals under mild conditions either in dark (Fenton) or in the presence of light (Photo-Fenton). The overall reaction mechanisms of Fenton process are represented by Eqs. 1-7 as proposed by [22], [23].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^· \qquad (1)$$
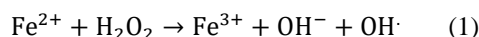
Fe^{3+} generated in Eq. 1 can further react with excess hydrogen peroxide to form more OH radicals and Fe^{2+} in Fenton-like reaction as shown is Eq. 2. However, this reaction is slower that Fenton reaction and in addition to the regeneration of Fe^{2+}, hydroperoxyl radicals ($HO_2^·$) are produced (Eq. 3), which also oxidizes organic pollutants, although are less sensitive than the Fenton reaction [24].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^· \qquad (2)$$

$$OH^· + H_2O_2 \rightarrow HO_2^· + H_2O \qquad (3)$$

$$OH^· + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad (4)$$

$$Fe^{3+} + HO_2^· \rightarrow Fe^{2+} + O_2H^+ \qquad (5)$$

$$Fe^{2+} + HO_2^· + H^+ \rightarrow Fe^{3+} + H_2O_2 \qquad (6)$$

$$HO_2^· + HO_2^· \rightarrow H_2O_2 + O_2 \qquad (7)$$

In these reactions, there was continuous cycling between Fe^{2+} and Fe^{3+} oxidation states with OH^- and H_2O as the only coordinating ligands. The reaction can be terminated in the absence of any excess oxidizing agent (Eq. 8).

$$2H_2O_2 \rightarrow 2HO_2^· + O_2 \qquad (8)$$

It is noteworthy that the above reaction occurs even when the targeted pollutants are not completely degraded, thus leading to a waste of oxidants [12]. A typical process flowsheet for the Fenton process is depicted in Fig, 1. The process is usually conducted in a batch reactor for easy control of pH, which is often in the range of 3-3.5. The reaction occurs in an oxidation tank, in which wastewater is initially allowed to flow into the tank, followed by addition of dilute H_2SO_4 to ensure acidic conditions. Further to that, catalyst and acid or base to adjust pH are added in sequence, and then finally, hydrogen peroxide is added for the reaction to proceed. The discharges from oxidation tank passes through a neutralization tank where it is alkalinized, then undergoes flocculation stage before separation of settled solids in settling tank [25].

2.2 Homogeneous and Heterogeneous Fenton systems

Fenton process can be performed in a homogeneous or heterogeneous system. In the homogeneous Fenton process, both the iron species and reactant exists in the same phase, hence there is no mass transfer limitation. Several studies have been conducted using the homogeneous Fenton system for the depuration of both synthetic and real recalcitrant wastewaters. Earlier studies have reported the application of homogeneous Fenton system for degradation of model compounds such as dye [26], [27], phenol [28]–[30], and also in the treatment of actual wastewaters such as textile wastewaters [31], [32], petroleum refinery wastewaters [15], [33], olive oil wastewaters [17], [34], [35] and pulp and paper mill wastewaters [36]–[38]. Some of the previous works done on homogeneous Fenton process are shown in Table 1.
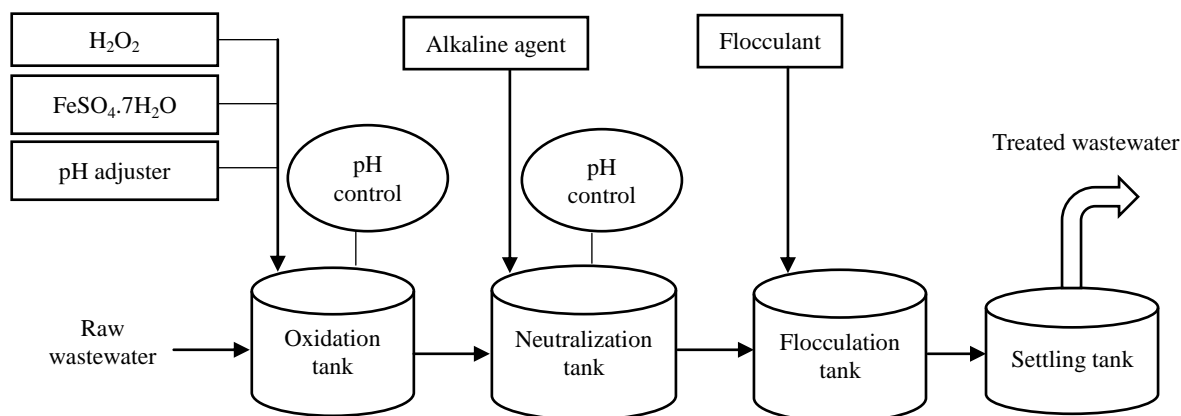
Fig 1. *Schematic Fenton process flowsheet [25].*

Besides the formation of OH radicals, intermediates are formed due to non-radical reaction pathways. For instance, Lucas and Peres [34] performed a kinetic study for the removal of COD from olive mill wastewater in a lab-scale batch reactor. They achieved a 70% conversion of COD at initial pH of 3.5, and molar ratio of H_2O_2/Fe^{2+} of 15. The incomplete conversion of the effluent's COD could be attributed to smaller fraction of intermediates that were formed due to non-radical pathways. Moreover, the integration of Fenton and other conventional physicochemical or biological process has proven to be effective in high degradation of pollutants compared Fenton process alone. Blanco and co-workers [31] performed a comparative study on Fenton and biological-Fenton coupled processes for the treatment of real textile wastewater with initial COD and TOC of 2100 mgL^{-1} and 465 mgL^{-1}C respectively. The study on the effect of Fe^{2+}/H_2O_2 ratio revealed that an increase in the catalyst concentration can promote the reduction of TOC within short reaction time. However, the Biological-Fenton coupled process has exhibited high efficiency compared to the Fenton process alone. Blanco and co-workers concluded that the treated olive effluents from this coupled process could be adequately recycled. Despite the numerous advantages of homogeneous Fenton process for the treatment of recalcitrant wastewaters, the process is associated with drawbacks as well. Some of these drawbacks are pH dependence, consumption of high amount of Fe (50-80 ppm) [39], and generation of large amount of Fe sludge leading to loss of catalyst [40]. Treatment and disposal of the sludge could increase the overall operational cost thus, limits the application of homogeneous Fenton process. A great deal of work has been done to overcome these challenges associated with homogeneous Fenton process by using heterogeneous catalysts. The major difference between homogeneous and heterogeneous system is that homogeneous reaction occurs in liquid phase, while in heterogeneous, the reaction occurs on the surface of the catalyst. In heterogeneous Fenton process, the apparent diffusion and adsorption processes of H_2O_2 and other reactants on the surface of catalyst could enhances catalytic reaction [41]. Other advantages of heterogeneous Fenton oxidation are applicability in wider range of pH, high catalyst activity, and stability, less formation of $(Fe(OH)_3)$ precipitate, easy separation of catalyst and is cost-effective compared to homogeneous system [42]–[45]. Additionally, Fe ions consumption in heterogeneous system can be controlled and high surface areas of heterogeneous catalysts can enhance the process efficiency. However, the reaction rate of heterogeneous system is slower than that of homogeneous system [46], which could be a result of small fraction of iron deposited on the surface of the catalyst.

2.2.1 FeO minerals-based Heterogeneous Fenton catalysts
FeO minerals such as ferrihydrite (Huang et al., 2001), goethite (α-FeOOH) [48], magnetite (Fe_2O_4) [49], hematite (α-Fe_2O_3) [50], lepidocrocite (γ-FeOOH) [51], pyrite (FeS_2) [52] have been investigated as heterogeneous catalysts for recalcitrant wastewater treatment (Table 2). Researchers interest in Fe-based minerals can be attributed to easy separation of catalyst by sedimentation or filtration, recycling of the catalyst, possibility to operate at near neutral pH and resistant to radical scavengers such as inorganic carbonate [53]. In general, the factors that influence FeO-based heterogeneous Fenton process are concentration of the Fenton reagents, solution pH, initial concentration of the pollutants and surface area of the catalyst. Goethite is named after German poet J.W. von Goethe. It is one of the most abundant Fe-bearing minerals that can be found in soil and low-temperature environments. It is thermodynamically stable and can be found from many iron ores, soils, and sediments [54]. Goethite exhibits nanometer size particles and it has high surface area in the range of 10-132 m^2g^{-1} [55]. Moreover, goethite can act as a semiconductor with significant amount of iron, thus, it poses high photoactivity [56]. For its ubiquity and high catalytic activity, goethite has found application as naturally occurring catalyst in Fenton-like process for the depuration of contaminants in the environment. The applications of goethite in the adsorption of heavy metals from aqueous solution have been documented. α-FeOOH has been synthesis from ferric oxide for the uptake of Ar in aqueous solution [57] and also from ferric nitrate for adsorption of Cu^{2+}, [58], and Cr^{2+} [59]. In a α-FeOOH Fenton-like process, the formation of OH radicals is greatly influenced by the concentration of α-FeOOH and H_2O_2 dosages. However, high concentration of the reactants could also inhibits OH radicals generation by possible anions formed that poses varying effects on the whole process [60]. Anions on the surface of goethite can deactivate the catalyst leading to formation of non-radical pathways. Hence, careful selection of reactants dose is essential for successful application of α-FeOOH Fenton-like process. Further to that, the photoactivity of α-FeOOH Fenton-like process in the degradation of contaminants has also been reported [48],

[61]–[63]). FeS_2 is Fe-bearing minerals that can be obtained from coal and metal ore mines. The most interesting properties of FeS_2 for application in environmental remediation is its high surface area [65], which is suitable for oxidation reaction. However, FeS_2 oxidation rate is quite faster when operated under acidic condition. In addition to that, excessive amount of oxidant might be required for improved degradation efficiency in Fenton process [66], which could limit its application due to additional cost. Hematite, on the other hand, exhibits high stability under ambient conditions and can also be obtained from many natural rocks. Due to high content of Fe in hematite, it is considered as one of the most important iron ore. It is abundant, low-cost, non-toxic and environmentally friendly iron-bearing mineral [67]. Moreover, in the event of surface activity lost, it can be sustainably discarded to produce pig iron in a blast furnace. Earlier study has reported almost complete color removal can be achieved under optimum conditions in hematite heterogeneous Fenton-like process (No 2 in Table 1). Fe_2O_4 is another kind of Fe-bearing minerals that is naturally abundant. Specifically, due to its essential peroxide-like activity that promotes the decomposition of H_2O_2 as well as easy regeneration from reaction medium, α-Fe_2O_3 has found application as a heterogeneous catalyst in Fenton process. However, slow reaction rate is the major drawback in using Fe-bearing minerals for Fenton process. Researchers efforts to overcome this challenge have been substituting the ionic iron with metals or chelating agent such as organic acids (Nos 3, 7 and 8 in Table 2). This formed of modification could improves the crystallinity, solubility and adsorptive surface properties of Fe-based catalysts [68]. Mesquita et al [4] found that α-FeOOH modified with boronic acid can increase the catalytic activity towards degradation of phenol compared to α-FeOOH alone. Characterization analysis revealed that the mechanism for improved degradation efficiency was a result of increase in surface area of the catalyst, which was promoted by boron in the transfer of electron from Fe to H_2O_2. Similarly, niobium (Nb) substituted magnetite catalyst was prepared for the degradation of methylene blue (MB) in aqueous solution [69]. In this study, Pouran and co-workers observed an improved catalyst activity towards removal of MB, which was attributed to oxygen vacancies that are generated on the surface of the catalyst, Fe^{2+} regeneration cycles promoted by Nb, as well as increase in surface area of the catalyst.

2.2.2 Composites-based heterogeneous catalysts

Composites such as Fe/alginate beads [70], Fe^{3+}/collagen fiber, Fe/clay [71], CuFe/zeolites [72], Fe/AC [73] have finds applications as catalysts and catalyst support in the heterogeneous Fenton-like process. Reusability of active metal element and easy separation of the composite from the treated wastewater by precipitation method are some of the major benefits composite-based catalysts. Among these materials, activated carbons (ACs) are the most widely used in wastewater [74]. ACs is relatively cheap, poses high surface area, due to their high porosity and amphoteric properties. Additionally, ACs poses high chemical stability and the surface and texture of ACs can be easily controlled. AC can be used as adsorbent, catalyst or catalyst support in wastewater treatment. In Fenton process, Fe/AC catalyst was found to maintain its activity after several cycles with improved efficiency and selectivity towards contaminants

[73]. Despite its potential applications as adsorbent, catalyst and catalyst support for wastewater treatment, ACs has some drawbacks. Some of these drawbacks are difficulty in regeneration of catalyst, adsorption of secondary molecules, and low efficiency on some pollutants [43]. Nevertheless, for its numerous advantages for application in wastewater treatment, more studies on the improvement in performance of ACs as support materials for Fenton process can be envisaged.

2.2.3. Industrial waste-based heterogeneous Fenton catalysts

Every year large amount of industrial wastes are generated whose disposal is of great environmental concerns. However, increase awareness and strict environmental regulations especially in developed countries has influenced the utilization of industrial wastes for application in various industrial processes aimed at the so-called 'zero-waste strategy'. This could be beneficial in terms of resource conservation and recovery as well as reduced costs. Fly ash [75]–[77], acid mine drainage (AMD) [78] and rice husk ash [79] are some of the waste materials that have been studied as heterogeneous Fenton- like catalysts due to their active iron species content. Fly ash is a waste product from coal-power plants and steel mill industries, which contain various chemical components such as SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, and SO_3^-. Globally, more than 300 billion tonnes of coal fly ash are generated annually [80]. It is, therefore, evident that the disposal of fly ash is of major concern. However, sustainable utilization of this abundant resource either in situ or in other industrial applications could be beneficial to the environment. In addition to its iron content, fly ash poses a large surface area and a porous surface, which are of great interest in adsorption and catalytic activity for wastewater treatment processes. Fly ash based heterogeneous Fenton-like catalyst has shown to be effective in the removal of organic pollutants under optimum conditions [76], [77], [79]. On the other hand, iron oxide in the form α-FeOOH has been recovered from AMD by precipitation method and was successfully used in the removal of dye in aqueous solution [78]. Despite the potential application of these industrial wastes in the Fenton process, optimum performances were observed under acidic pH (Nos 12, 20 and 21 in Table 2). Therefore, further development of industrial waste-based heterogeneous Fenton catalysts for wastewater treatment should be on its application in wider range of pH, since they can be obtained at low-cost.

2.2.4 Nanomaterials-based heterogeneous catalysts

In recent times, the application of nanomaterial for wastewater treatment is gaining momentum among researchers. Nanomaterials poses high porosity, a large surface area with extremely small particle sizes, low toxicity, as well as reduced cost in terms of raw materials usage. With size less than 100 nm, nanomaterials have opened a new route for manufacturing new materials and devices at relatively low cost for applications in several industrial processes compared to micro- and macro sized materials [81]. For its large surface area, nanomaterials can exhibit low diffusion resistance, accessibility to reactants as well as large number of active sites. Nanomaterials-based heterogeneous catalysts for Fenton process have been reported in the literature. Some of these materials are nano zero valent iron (nZVI) [82], [83], nano γ-FeOOH [51], nano Fe_3O_4 [84]

nano α-Fe_2O_3 [85], and Fe-titrate/TiO_2 [86]. nZVI poses a large surface area and can remain in suspension, thus generating $OH^.$ through corroding its surface in an aqueous solution [87]. nZVI in recalcitrant wastewater treatment could limit the formation of Fe sludge and the residual particles can be used safely in a magnetic field [88]. In addition to degradation efficiency towards organic pollutants, nZVI is also capable of removing possible intermediates that are formed during the Fenton reactions [89]. Generally, nanomaterials hold more promise as future alternative material for wastewater treatment. Previous studies have demonstrated high degradation efficiencies of organic pollutants using nanomaterial-based heterogeneous Fenton process (Table 2). To overcome the limitations of Fe sludge and intermediates formations in Fenton process, more studies are expected on the optimization and development of nano-scale heterogeneous Fenton catalysts for industrial applications.

2.3 Photo-Fenton

In Photo-Fenton process, ultraviolet or visible light provide the necessary energy that could enhances catalytic activity in both homogeneous and heterogeneous Fenton-like processes. The reaction mechanisms are based on photo-reduction of Fe^{3+} that exist as $Fe(OH)^{2+}$ to generates Fe^{2+} ions under UV-irradiation (Eq. 9), and then subsequent photolysis process of H_2O_2 to generates OH radicals under short wavelength radiation (Eq. 10) [24], [90]. Hence, the degradation of pollutants in wastewaters can be improved. As noted earlier, conventional Fenton process can be terminated once all the Fe^{2+} ions are consumed during the reactions. However, in photo-Fenton process, more OH radicals and ferric ions are generated and the cycles continuous.

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + OH^. \qquad (9)$$

$$H_2O_2 + hv \rightarrow 2^.OH \qquad (10)$$
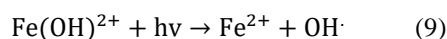
Iron oxides [62], [91], other transition metals [92], [93] and soluble bio-organic substances (SBO) [94], [95] are some of the catalysts and catalyst supports that have been investigated as photo-Fenton-like processes (Table 2.). For instance, Demarchis and colleagues [91] studied the photoactivity of different particle sizes of hematite for degradation of phenol in aqueous solution. They found that hematite as an iron source catalyst poses high photocatalytic activity towards degradation of phenol under optimal pH in the range of 3-4. However, Demarchis and co-workers observed Fe leaching with the most photoactive sample. This could be attributed to partial dissolution of hematite during the photo-Fenton reaction. Although the Fe leaching was found to be lower than the EU standards, further studies to improve the dissolution of Fe might be needed. Similarly, Ref. [93] prepared Fe^{2+} supported on Al_2O_3 catalysts for degradation of dye in heterogeneous photo-Fenton process. They found that the increased in dye degradation was a result of increased in the power of UV radiation, but also the degradation efficiency decrease with increased concentration of dye. However, long catalyst activity and negligible Fe leaching are some important features of Muthukumari and co-workers study. Another aspect of their study was the efficiency of the catalyst for degradation of dye at optimum pH in the range of 2-7. This is a significant improvement compared to pH dependent of the classical Fenton process. In

has also been demonstrated that the removal efficiency of pollutants using nZVI catalyst can be improved by UV-irradiation compared to dark- Fenton process [96]. SBO as catalysts and catalyst supports exhibits macromolecular structure with average molecular weight in the range of 67-463 kg/mol, poses long aliphatic chains, aromatic rings, and O- and N- functional groups, which are essential in photochemical processes for environmental remediation [97], [98]. Gomis and co-workers [95] found that photo-Fenton process with SBO catalyst is suitable for the degradation of organic pollutants in wastewater at optimum pH of 5. The efficiency of the process was attributed to the capacity of SBO to complex iron, which in turn limit the formation of Fe precipitate. However, the authors do not give an insight into mechanistic behavior of the pollutants as results of other species formed during the process. Nevertheless, further investigation on mechanistic study could be necessary for further development of photo-Fenton process using renewable bio-based catalysts. Although the application of photo-Fenton process in the degradation of pollutants holds more promises, one major drawback is the presence of inorganic ions in wastewaters. The inorganic ions could affect the kinetic and reaction mechanisms. Yet still, like in conventional Fenton process, high efficiencies in the photo-Fenton processes were mostly reported under acidic conditions (Table 3). As noted earlier, under acidic conditions, Fe complexes could be formed, which could hinder the process through undesirable reaction paths. Solar assisted photo-Fenton has shown to be effective in the degradation of pollutants in wastewater. However, the cost associated with solar collectors and weather variations could also limit the development of solar of photo-Fenton process. Further to that, as recalcitrant wastewaters is characterized by high content in terms solid substances, hence, the apparent distribution of UV irradiations to certain pollutants can be affected. Therefore, integration of photo-Fenton with a pretreatment or post-treatment stage using a simple and cost-effective conventional methods that can reduce the solid substance contents prior to or after photo-Fenton reaction could enhance the process efficiency.

Table 1. Previous work done on homogeneous Fenton process

Pollutants	Operating conditions/optimum conditions	Optimum performance	Reference
Olive mill wastewater	pH = 3, [COD] = 4017 mg dm^{-3}, [phenol] = 66.2-129 mg dm^{-3}	X_{COD} = 97%, X_{phenol} = 99.2-99.6%	Hodaifa et al., (2013)
Textile wastewater	pH = 3, [COD] = 8100 mg/L, [H$_2$O$_2$] = 0.88 mM, Fe^{2+} = 40 mg/L	X_{CR} = 71.5%, X_{COD} = 45% (240 min)	Papadopoulos et al., (2007)
Nuclear laundry wastewater	pH = 6, [H$_2$O$_2$]/[Fe^{2+}] = 2, [H$_2$O$_2$] = 1000 mg/L	X_{COD} = 85%, X_{TOC} = 69%	Vilve et al., (2009)
Phenol	[H$_2$O$_2$] = 8250 mg/L, [Fe^{3+}] = 500 mg/L	X_{phenol} = 85% (180 min)	Bach et al., (2010)
Orange G	pH = 4, [H$_2$O$_2$] = 0.01 M, Fe^{2+}:H$_2$O$_2$ =1:286, [OG] = 2.21*10^{-5}-1.11*10^{-4} M	X_{CR} = 94.6% (60 min)	Sun et al., (2009)
Real naphthalene dye	pH = 2.5, [COD] = 7300 mg/L, [H$_2$O$_2$] = 4.5 g/L, Fe^{2+}/H$_2$O$_2$ = 1/20	X_{COD} = 93%, X_{TOC} = 62%	Gu et al., (2012)
Olive-oil mill wastewater	pH = 3.5, [H$_2$O$_2$]/[Fe^{2+}] = 15	X_{COD} = 70%	Lucas and Peres, (2009)
Methyl methacrylate	pH = 2-5.3, [COD] = 651.25 g/L, [TOC] = 227.86/L, Fe^{2+}/ H$_2$O$_2$ = 0.0198M:22.9M	X_{COD} = 73.6% X_{TOC} = 73%, X_{CR} = 94%	Almazán-Sánchez et al., (2014)
Methyl parathion	pH = 3, X_{COD} = 440 mg/L	X_{COD} = 71-79%	Saini et al., (2016)
Nonylphenol ethoxylates (NPEOs)	pH = 3, H$_2$O$_2$ = 9.74*10^{-3}, [H$_2$O$_2$/Fe^{2+}] = 3	X_{NPEOs} = 84%	Cui et al., (2014)
Direct Blue 71 (DRB71)	pH = 3, [Fe^{2+}] = 3 mg/L, [H$_2$O$_2$] = 125 mg/L	X_{COD} = 50.7%, X_{CR} = 94%	Ertugay and Acar, (2013)

COD = Chemical oxygen demand
TOC = Total organic carbon
CR = Color removal

Table 2. Previous work done on heterogeneous Fenton process

No.	Pollutant	Catalyst	Operating conditions/optimum conditions	Optimum performance	Reference
1.	Methyl orange (MO)	α-FeOOH	pH = 3, [MO] = 75 mg/L, [α-FeOOH] = 0.3 g/L, [H$_2$O$_2$] = 3.88 mmol/L	X_{CR} = 98.9% (70 min)	Wang et al., (2015)
2.	Drimane Red X-6BN	α-Fe$_2$O$_3$	pH = 2.5, [H$_2$O$_2$] = 800 mg/L, [α-Fe$_2$O$_3$] = 20 g/L	X_{CR} = 99% (120 min)	Araujo et al., (2011)
3.	Methylene Blue (MB)	Gt-B	pH = 6 [H$_2$O$_2$] = 0.1 mL, [Gt-B] = 10 mg	X_{MB} = 80% (240 min)	Mesquita et al., (2016)
4.	Chloramphenicol (CAP)	FeS$_2$	pH = 2.5, [H$_2$O$_2$] = 5 mM, [α-FeS$_2$] = 1 g/L, [CAP] = 5 mg/L	X_{CAP} = 85.2%	Wu et al., (2015)
5.	Methyl pyridinium (MP)	Fe/AC	pH = 3.0, [H$_2$O$_2$] = 30 mM, T = 30°C	X_{TOC} = 54.1%, X_{MP} = 93.2%	Duarte et al., (2013)
6.	Orange G (OG)	Fe$_3$O$_4$ /CeO$_2$	pH = 2.5, [H$_2$O$_2$] = 30 mM, [Fe$_2$O$_3$/CeO$_2$] = 20 g/L	X_{OG} = 98.2% (120 min)	Gan et al., (2017)
7.	Methylene Blue (MB)	Fe$_{2.9}$Nb$_{0.19}$O$_4$	pH = 10, [MB] = 25-100 mg/L, [catalyst] = 1 g/L	X_{MB} = 47.7%	Pouran et al., (2015)
8.	Ofloxacin antibiotic (OA)	Fe/Alg	[OA] = 10 mg/L, [H$_2$O$_2$] = 10 mmol/L, [Fe/Alg] = 0.05 g	X_{OA} = 94%	Titouhi and Belgaied, (2015)
9.	C.I. Reactive Orange 29 (RO29)	FeS$_2$	pH = 2, [H$_2$O$_2$] = 3 mM, [FeS$_2$] = 3 g/L, [RO29] = 10 mg/L	X_{RO29} = 94% (120 min)	Khataee et al., (2016)

| 10.	Azo dye	nZVI	pH = 2.1-2.3, $[H_2O_2]$ = 300-400 mg/L, [nZVI] = 60-80 mg/L	X_{CR} = 80-90%, X_{COD} = 10-15%	Yu et al., (2013)
11.	Basic Blue 3 (BB3)	nano-Fe_2O_4	pH = 5	X_{BB3} = 96%	Khataee et al., (2015)
12.	Reactive Black 5 (RB5)	Electric arc furnace slag (EAFS)	pH = 2-7, $[H_2O_2]$ = 2-12 mM, [EAFS] = 0.01-0.06 g, [RB5] = 25-150 mg/L	X_{RB5} = 94% (60 min)	Nasuha et al., (2016)
13.	Malachite Green (MG)	$GOx/Fe_3O_4/TiO_4$	pH = 5.5, $[GOx/Fe_2O_4/TiO_4]$ = 2 g, [MG] = 20 mg/L	X_{CR} = 99% (120 min)	Elhami et al., (2015)
14.	Rhodamine 6G (R6G)	CuFeZSM-5	pH = 3.4, [CuFeZSM-5] = 1 g/dm^{-3}, [R6G] = 1 g/dm^{-3}	X_{CR} = 100% (45 min, X_{COD} = 51.8% (120 min)	Dükkanci et al., (2010)
15.	Chlorpheniramine	nZVI	pH = 3, $[H_2O_2]$ = 0.1 mM, [nZVI] = 22.4 mg/L	X_{CR} = 100% (60 min)	Wang et al.,, (2016)
16.	Reactive Black 5 (RB5)	Fe-RHA	pH = 3, $[H_2O_2]$ = 4 mM, [Fe-RHA] = 0.5 g/L, [RB5] = 100 mg/L	X_{CR} = 89.18%, X_{RB5} = 59.7%	Ersöz, (2014)
17.	Methylene Blue (MB)	PMC	[MB] = 40 g/L	X_{MB} = 90%	Zhou et al., (2015)
18.	Orange II (OII)	Fe/ZSM-5	pH = 3, $[H_2O_2]$ = 6 mM,	X_{CR} = 91%, X_{OII} = 36% (90 min)	Queirós et al., (2015)
19.	2,4-dicholorphenol (DCP)	nZVI	pH = 3, [nZVI] = 1-2 mg/L, [DCP] = 100 mg/L,	X_{DCP} = 98% (180 min)	Li et al., (2015)
20.	Methyl orange dye	Fly ash	pH = 2, $[H_2O_2]$ = 34 mM, [fly ash] = 200 mg/L, [dye] = 20 mg/L	X_{CR} = 98% (90 min)	Ali et al., (2013)
21.	n-butyl xanthate (n-BX)	Fly ash	pH = 3, $[H_2O_2]$ = 1.176 mmol/L, [fly ash] = 1 g/L, [dye] = 20 mg/L	X_{n-BX} = 96.9%, X_{COD} =96.7% (120 min)	Chen and Du, (2014)
22.	Chemical wastewater	FeS_2	pH = 1.8-7, $[H_2O_2]$ = 50 mmol/L, $[FeS_2]$ = 10 g/L	X_{COD} = 30%	Sun et al., (2015)
23.	Petroleum refinery wastewater	Fe^0	pH = 2.5, $[H_2O_2]/[COD]$ =6, $[H_2O_2]/[Fe^0]$ = 10	X_{COD} = 76.5%, X_{TOC} = 45%, X_{phenol} =96%	Hasan et al., (2015)
24.	Tannery wastewater	Immobilized TiO_2	pH = 4, $[TiO_2]$/[Immobilized sand] = 2.1 g/100 mL sand, [dye] = 10-50 mg/L	X_{CR} = 100%	Valeria et al., (2015)

COD = Chemical oxygen demand
TOC = Total organic carbon
CR = Color removal

2.4 Electro-Fenton Process

Fenton process can be improved by combining it with electrochemical processes termed "electro Fenton-like" (EF-like) process. For both homogeneous and heterogeneous processes, the mechanism is based on in-situ generation of H_2O_2 at cathode via two-electrochemical reduction of dissolved oxygen (Eq. 11) [99], [100].

$$O_2(g) + 2H^+ + 2e \rightarrow H_2O_2 \qquad (11)$$
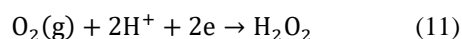
Other mechanism is where anode of homogeneous metal catalyst such as Fe^{2+}, Mn^{2+}, Cu^{2+}, and Co^{2+} [45], [101]–[103] are sacrificed directly or regenerated on the surface of cathode after external addition of metal ion as shown in Eq. 12.

$$M^{(n+1)+} + e^- \rightarrow M^{n+} \qquad (12)$$
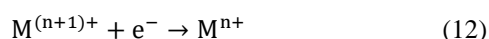
The in-situ production of H_2O_2 plays a vital role on degradation of organic pollutants into H_2O, CO_2 and inorganic ions [104]. Anodic oxidation or electrochemical oxidation (EO) are simplest types of electrochemical advanced oxidation processes (EAOPs), which are capable of oxidizing organic pollutants at high current via the formation of physisorbed M(OH) during anodic water discharge to O_2 (Eq. 13) [105], [106].

$$M + H_2O \rightarrow M(OH^.) + H^+ + e^- \qquad (13)$$
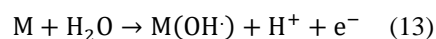
Addition of small amount of Fe^{2+} to the solution under acidic condition can enhance the electro-Fenton process by generating OH radical and Fe^{3+} as result of Fenton reaction with H_2O_2 (Eq. 14) [99].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^. + OH^- \qquad (14)$$
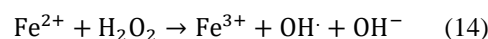
The process can also be enhanced by UV irradiation with artificial UV light or by solar (Se Nos. 8-11 in Table 4). By combination of photochemical and electrochemical processes, more OH radicals are generated, hence the process efficiency can be improved. For instance, Peng et al [107] fabricated a 3D ordered macroporous Fe_2O_3/CA cathode via sol-gel and hard template method, which was used to remove imidacloprid (IMP) in aqueous solution. The fabricated

cathode has shown high removal efficiency of IMP (95%) compared to reference cathode Fe_2O_3/CA (74%). However, IMP removal efficiency was improved to 97% when irradiated with UV. This was attributed to enhance photocatalytic activity by UV irradiation that favors the formation of more OH radicals. EAOPs have attracted attention over the years since it is simple, versatile, cost-effective, energy efficient and environmentally friendly. EAOPs have been used effectively in the degradation of pharmaceutical compounds [108], [109], phenol [41], [110], herbicides [104] and dye [111], [112]. The process is greatly influenced by factors such as pH, temperature, reactants concentrations, applied current density, oxygen sparging rate, distance between the electrodes and nature of the supporting electrolyte [113]. Therefore, optimization of process parameters is essential in achieving high process efficiency.

2.5 Sono-Fenton Process

Sonochemistry is a chemical process in which the degradation of organic pollutants is promoted by ultrasound (US) irradiation. Researchers interest in this process for environmental remediation is attributed to its ability for rapid degradation of chemical contaminants. Ultrasound is a sound wave whose frequency is higher than the normal audible of human hearing. The three frequencies of ultrasound are 20-100kHz for conventional power ultrasound, 300-1000kHz for sonochemical effects, and 2-10MHz for diagnostic imaging. In sono-Fenton (SF) process, OH radicals are formed by water pyrolysis (Eq. 15) when an aqueous solution is exposed to US waves. The generated OH radicals then attack and destroy organic pollutants.

$$H_2O \rightarrow +OH^\cdot + H^\cdot \qquad (15)$$

Although US are effective method in the degradation of organic pollutants, however, achieving a complete degradation has been a major challenge with this process. Therefore, the degradation efficiency of organic pollutants can be improved by utilizing the benefits of ultrasound and Fenton reactants to increase the OH concentrations in SF process. Further to that, the process can also be improved by combining ultrasound with ultraviolet and Fenton (SPF) process. In this process, $OH^\cdot$ and H_2 atoms are generated by sonolysis of water. During the recombination, the produced species from the sonolysis of water are lost. Hence, UV light is applied to increase the generation of $OH^\cdot$ by converting H_2O_2 generated from the recombination. This process is beneficial in reducing the intermediates formation due to Fenton reaction of Fe^{2+} by photolysis [114] and sonolysis [115]. SPF process has been demonstrated to be effective in the degradation of various organic pollutants (Nos 6-9 in Table 5). However, the synergic effects of these combinations are not fully understood. In addition to that, the costs associated with these combinations are not comprehensively reported. Therefore, for further development of this process, more studies on the optimization of process parameters and kinetic studies that would exploit the effect or variation of experimental conditions from one system to another is necessary.

2.6 Factors Affecting Fenton Process

As pointed earlier, the efficiency of Fenton and related process is strongly affected by factors such as pH, H_2O_2 dosage, catalyst concentration and initial concentration of pollutants in wastewaters. The role plays by these factors in Fenton process is crucial in generation of $OH^\cdot$, which in turn aided the degradation of pollutants in wastewaters. Hence, comprehension studies of the relationship between these factors and $OH^\cdot$ generation and consumption in Fenton process is very crucial. Several studies have been conducted on the effects of these factors in Fenton and related process (Table 1-5).

2.6.1 pH Value

pH as a parameter in Fenton process have great influence in the process efficiency due to Fe and H_2O_2 speciation factors. Researchers have reported different conclusion on the optimum pH for Fenton processes. However, many studies have reported 3 as the optimum pH in homogeneous Fenton systems (Table 1). At higher pH, inactive Fe oxyhydroxides and iron hydroxide $(Fe(OH)_3)$ precipitate are formed, which can affect the activity of Fenton's reagents. On the other hand, at pH less than 3, OH radical scavenging effects predominates in Fenton process [89]. For heterogeneous systems, researchers have reported contradictory results on the optimum pH of Fenton process (Table 2-5). Some studies have observed high efficiencies under near neutral pH (Nos. 3, 13 in Table 2; Nos. 3, 5, 12, 13 in Table 3; Nos 7, 10 in Table 4 and Nos. 1, 2, 3 in Table 5) and even under alkaline conditions (No 7. in Table 2). In addition to that, pH is the most predominate factor that control the photocatalytic activity due to its effects on catalyst's surface charge, flat band potential, and dissolution of compounds in aqueous solution [116]. Nevertheless, the optimum pH of Fenton process is complicated but essential factor that can only be determined through experiment. Existing literature, especially on heterogeneous system, have attempted to widen the pH dependency of Fenton process, and more studies can be foreseen in coming years.

2.6.2 Fenton reagents

Fenton reagents (Fe^{2+} or catalyst and H_2O_2) have profound effects on the overall process efficiency with regards to rate of degradation of pollutants in wastewater. The optimum dosage of H_2O_2 for Fenton process depends upon the concentration of contaminants in a solution. Although it is quite higher than the theoretical value needed for complete mineralization of contaminants. Specifically, non-radical pathways could promote the decomposition of H_2O_2 into O_2 and H_2O [117]. An increase in H_2O_2 concentration can enhance the degradation of pollutants in wastewater. However, excessive amount of H_2O_2 could also contribute to high content of COD as well as increase in operation cost especially when the volume of wastewater is very high [89]. Besides, excessive amount of H_2O_2 is harmful to certain organisms. Therefore, careful selection of H_2O_2 concentration for Fenton process is necessary. On the other hand, an increase in Fe^{2+} or catalyst dosage can enhance the generation of more OH radicals available to remove pollutants in wastewaters. However, excessive catalyst loading could also lead to OH radical scavenging effects. Further to that, the cost associated with solid catalysts in a heterogeneous system can also be a limiting factor for its large-scale application. The efficiency of Fenton process depends on the rate at which OH radical is formed to attack organic pollutants in wastewater. Generally, the initial reaction in Fenton process is characterized by quick

degradation of pollutants and then follow by slow reaction [118]. Therefore, optimization of Fenton reagents is essential to avoid radical scavenging effect as well as reduce cost.

2.6.3 Initial concentration of pollutants

One major aim of any Fenton process is to degrade pollutants in wastewaters, hence, initial concentration of pollutants has a significant effect on degradation efficiency. Lower concentration of pollutants is favorable in Fenton process (Benitez et al., 2001), but also has adverse effect when treating a large amount of effluents. In a heterogeneous system, an increase in initial concentration of pollutants can lead to a decrease in the overall process efficiency [120], probably due to absorption of more pollutants on the surface of the catalyst. Similarly, in a photo-Fenton process, high concentration of pollutants can have a negative effect by reducing the path length of photons entering the wastewater, As such the number photons that are absorbed on the surface of catalysts are reduced, which ultimately affect the process efficiency [121]. Specifically, longer UV irradiation time and further magnification in Fenton reagents are required to generate the necessary OH radicals for the reaction [122]. Therefore, dilution of wastewater to reduce its concentration prior to Fenton process could be necessary for large-scale industrial applications.

2.6.4 Effects of inorganic ions

Inorganic ions are usually found in industrial wastewaters due to application of chemicals during manufacturing processes. Industrial wastewaters may contain high concentrations of nitrates, chlorides, carbonates and sulfides ions. These background impurities when present in wastewaters may affect the oxidation process via OH radical scavenging effects [123], [124]. Although, the inorganic ions pose varying effects in Fenton process, however, it is essential to consider matrix compositions of theses ions due to their inhibitory effects.

2.6.5 Energy input

Transmittance and solid catalyst loading are two parameters that have significant effect on photo-Fenton process. Poor transmittance and excessive catalyst loading could decrease the light intensity thereby leading to low degradation efficiency as well as additional cost in terms of energy input [89]. In a clear term, the apparent rate reaction is strongly dependent on light intensity, however, the process can be terminated at certain extent of light intensity. This has further necessitated the need for optimization of process parameters. Generally, low transmittance is usually favorable to high efficiency in photo-Fenton process [125]. In E-Fenton process, energy consumption is proportional to distance between the electrodes. Longer distance between the electrodes could lead to increase in energy consumption and vice versa. Mass transfer limitations of Fe^{3+} for the regeneration of Fe^{2+} in E-Fenton process is also influenced by longer distance between the electrodes [126], [127]. For US process, power intensity and irradiation time have direct effect on energy consumption and overall total cost of the process. Weng et al. [128] found that high power density is required for improved degradation efficiency of pollutants. Therefore, energy consumption is a major issue in US process, which needs to be addressed for further development of the process.

3. CONCLUSION

Industrial wastewaters are difficult to be treated by conventional methods due to their recalcitrant nature and low biodegradability. AOPs have been identifies as viable techniques for the treatment of suck kind of wastewaters. Among them Fenton process is gaining more attention since it can be operated at room temperature and ambient pressure, it is simple and non-toxic. The process can be operated in a homogeneous or heterogeneous system. Many studies have reported the efficiency of homogeneous system in the treatment of different kind of recalcitrant wastewaters. However, pH dependency and generation of large amount of sludge are the major challenges associated with homogeneous system. To improve the process, several studies have been conducted using heterogeneous catalysts such as iron minerals, composites, nanomaterials and industrial wastes catalysts. Although some studies have reported 3 as the optimum pH for heterogeneous system, however, other studies have demonstrated the possibility to broaden the optimum pH to near neutral and even alkaline conditions. Therefore, there is need for additional studies on the application of heterogeneous system in wider range of pH values. Nanomaterials hold more promise as future alternative material for wastewater treatment. However, further studies should be exploited to more on novel catalysts using other metals apart from Fe. Photo-Fenton, electro-Fenton, sono-Fenton and even their combinations have shown to improve the Fenton process efficiency. However, energy consumption is a major limiting factor in these processes. Therefore, further studies should focus on energy efficiencies of these processes, since it has direct effect on the overall total cost for large-scale applications. In photo-Fenton-like process, light intensity is crucial in enhancing the process efficiency. Hence, there is need to consider the effect of poor transmittance and excessive catalyst loading, which could reduce light intensity in wastewater and ultimately reduce the process efficiency. Electro-Fenton offers the advantage of in-situ generation of OH radicals, however, more studies are needed to be conducted to exploit the efficiency of the system. The basic operating factors for Fenton process are pH, Fenton reagents (catalyst and H_2O_2), initial concentration of the pollutants and effect of inorganic ions. There are extensive literature studies regarding their effects on the overall process performance. In addition to that, there are also literature studies on the effect of process parameters with regards to photo-Fenton, electro-Fenton, and sono-Fenton. However, more research is needed to enhance their efficiencies in recalcitrant wastewater treatment. Finally, integration of Fenton process either as pre-treatment or post-treatment method with other conventional methods would reduce the operating costs and enhances degradation efficiency, hence it should be one of the main research focus on Fenton process.

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