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Photo-Fenton Reaction: How to Remediation Waste-Water Using (Fe⁺²/ UV)

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ABSTRACT

In recent years, pollution of soil and groundwater caused by fuel leakage from old underground storage tank, refineries, fuel distribution terminals, improper disposal and also spills during transferring, has been reported [1-3]. The accidental spills of more than 2 million tons of refined oil products per year into the environment are a worldwide problem [4]. Large amounts of benzene, toluene, ethyl benzene, and xylenes (BTEX) have been detected in polluted water resources [5]. The leaching of petroleum hydrocarbons such as diesel fuel into water resources causes many serious environmental problems [6]. Diesel fuel consists of a complex compound including paraffin, olefins, aliphatic hydrocarbons, as well as a lesser amount of aromatic compounds and includes molecules containing sulfur, nitrogen and metal oxides [2]. The toxicity of diesel fuel is mostly due to BTEX aromatic hydrocarbons. The carcinogen property of diesel fuel is due to C10 and C20 alkenes and alkylated benzene. Therefore, developing an efficient method for the removal of diesel fuel from contaminated water resources is very crucial [4]. Different physical, chemical, and biological techniques have been used to degrade the contaminated soils and water [6-10]. Advanced oxidation processes (AOPs) is an efficient environment-friendly method in which hydroxyl radicals (OH•) are used to oxidize recalcitrant organic pollutants and convert them to harmless end-products such as H₂O and CO₂ [11-12]. One of AOPs is photo-Fenton reaction which will discuss in this review. In photo-Fenton process, the formation of ferrous ion reduces the process effectiveness and eventually it will halt the reaction [13].

Keywords: photo-Fenton, UV-light, OH•

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INTRODUCTION

The principle of advance oxidation processes (AOP)

Advanced Oxidation Processes typically employ chemical oxidizing agents in the presence of an appropriate catalyst and/or ultraviolet light [14-15] to oxidize or degrade the pollutant of interest [16]. AOPs are suited for destroying dissolved organic contaminants such as halogenated hydrocarbons (trichloroethane, trichloroethylene), aromatic compounds (benzene, toluene, ethylbenzene, xylene – BTEX), pentachlorophenol (PCP), nitrophenols, detergents, pesticides, etc. AOPs can also be used to oxidize inorganic contaminants such as cyanide, sulphide, and nitrite [17]. The AOP have in common the involvement of hydroxyl radicals ($\cdot\text{OH}$) as shown in Fig. 1.

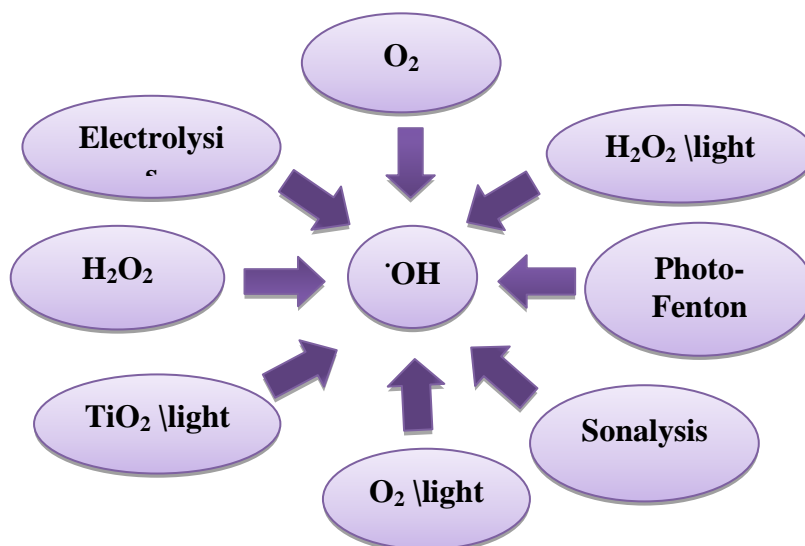
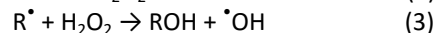
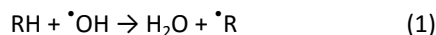


Fig. 1: AOPs recently studied implying the central role of the OH-radical

In 1987, Glaze et al. [18]. defined AOPs as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification”. The hydroxyl radical ($\cdot\text{OH}$) is a powerful, non-selective chemical oxidant, which acts very rapidly with most organic compounds. Once generated, the hydroxyl radicals aggressively attack virtually all organic compounds.

Depending upon the nature of the organic species, two types of initial attack are possible: the hydroxyl radical can abstract a hydrogen atom from water, as with alkanes or alcohols, or it can add itself to the contaminant, as in the case of olefins or aromatic compounds [19].

A common reaction is the abstraction of hydrogen atom to initiate a radical chain oxidation:



The attack by the $\cdot\text{OH}$ radical, in the presence of oxygen, initiates a complex cascade of oxidative reactions leading to mineralization of the organic compound [19].

Photochemical and photocatalytic processes have enormous potential for becoming viable alternatives to conventional chemical AOP for the treatment of polluted waters and effluents. Currently available photochemical technology permits the conversion of organic pollutants having a wide range of chemical structures into substances that are less toxic and/or more readily biodegradable. In favorable cases, they can cause total decomposition of the organic constituents of the pollutant, generally referred to as “total mineralization” (complete oxidation to carbon dioxide and water, plus inorganic salts of all heteroatoms other

than oxygen). Light of wavelengths in the range of 250-400 nm, corresponding to the ultraviolet (UV) region of the spectrum, is most commonly used in photochemical degradation processes [20]. Since ultraviolet light is a natural component of solar radiation, the sun provides a low-cost, environmentally friendly, renewable source of ultraviolet photons in photochemical processes. Thus, the use of solar photochemical reactors is an extremely interesting, cost-effective option for treatment of effluents in many of the tropical and sub-tropical regions of the planet. In areas with marginal or inadequate solar radiation intensity, conventional photochemical reactors fitted with ultraviolet lamps or hybrid UV lamp/solar photoreactors can be employed.

Of the AOPs that have been proposed thus far, the Fenton reaction and the light-accelerated Fenton reaction, commonly known as the photo-Fenton reaction, appear to be the most promising for practical industrial applications [21]. In the remainder of this review, we shall focus our attention on fundamental mechanistic details of the Fenton and photo-Fenton reactions, information that is essential for the adequate design and control of photo-Fenton processes for the degradation of organic pollutants [16].

Aquatic iron chemistry

Behind oxygen, silicon and aluminium, iron is the fourth most abundant element in the earth's crust. It occurs in oxidation states from -II to +VI with coordination numbers of 3 to 8 [22]. Desert sands, dust and ash make iron omnipresent in the environment and practically all natural water contains iron at least in traces. In clouds, fog, lakes and rivers the iron concentration is around 10^{-5} M [23]. Iron is as well a vital element for life present in the whole biosphere. In aqueous solution the most abundant iron species have an oxidation number of +II (ferrous iron) and +III (ferric iron). Other iron species are highly unstable. Dissolved ferrous and ferric iron species are present in octahedral complexes with six ligands in water. Iron is complexed by water and hydroxyl ligands provided that no other complexing substances are present. How many of these ligands are hydroxyl ions, depends on the solution's pH, which influences directly the acid/base equilibrium of the aqua-complex. Ferric iron is the more critical iron species in the photo-Fenton process, because its hydroxides precipitate at lower pH than those of ferrous iron. Consequently, only the acid/base equilibrium for the ferric iron aqua-complex is discussed here. Fig. 2 shows the equilibrium concentrations of the most important ferric iron aqua-complexes in the absence of further complexing substances at different pH for a ferric iron concentration of 20 mg/L. It is clear that between pH 2.5 and 3 $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ is the dominant species.

Because of the low solubility product of ferric iron hydroxide ($K_S(\text{Fe}(\text{OH})_3) \approx 10^{-37}$), precipitation starts at pH 2.5-3.5 depending on the iron concentration and the temperature. The precipitation process starts with the formation of dimers and oligomeres, which at continuation gradually polymerize further and lose water until forming finally insoluble iron hydroxides (e.g. goethite or hematite). This aging process is slow and can take up to a hundred days [24]. The resulting precipitate is of red brown colour and with no defined stoichiometry. It contains water and has a strong cationic character, thus co-precipitating anions but also organic substances. The precipitate is difficult to re-dissolve through acidification (insoluble above pH $\approx 1-1.5$), but it can be re-dissolved by complexing substances (e.g. oxalic acid) [25] or photobleaching processes [26]. Photo-leaching refers to photo-reduction of ferric to ferrous iron and subsequent leaching of the ferrous iron from the precipitate.

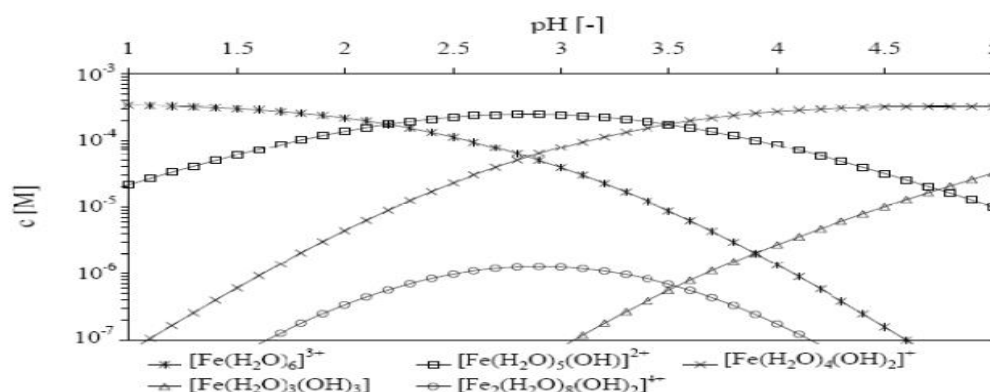
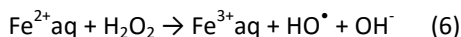


Fig. 2: Ferric ion species present in aqueous solution at different pH at a concentration of 20 mg/L, calculated with equilibrium constants [24], $T = 20^\circ\text{C}$.

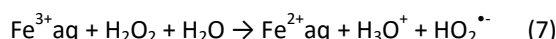
Fenton Chemistry

Over a century ago, Fenton [27] demonstrated that a mixture of H_2O_2 and Fe(II) in acidic medium had very powerful oxidizing properties. Although the precise mechanism of this reaction, now known as the Fenton reaction, is still the subject of some discussion [21], it is generally assumed to be an important chemical source of hydroxyl radicals. The classical mechanism is a simple redox reaction in which Fe(II) is oxidized to Fe(III) and H_2O_2 is reduced to hydroxide ion and the hydroxyl radical:



For the degradation of organic molecules, the optimum pH for the Fenton reaction is typically in the range of pH 3-4 and the optimum mass ratio of catalyst (as iron) to hydrogen peroxide is 1.5 [28].

In the conventional Fenton reaction, carried out in the absence of light, the ferric ion produced in reaction (6) can be reduced back to ferrous ion by a second molecule of hydrogen peroxide:

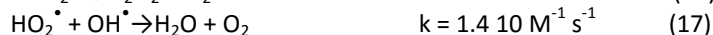


However, this thermal reduction (reaction 7) is much slower than the initial step (reaction 2). Thus, although chemically very efficient for the removal of organic pollutants, the Fenton reaction slows down appreciably after the initial conversion of Fe(II) to Fe(III) and may require the addition of relatively large amounts of Fe(II) in order to degrade the pollutant of interest [16].

Eq. 8-14 show reactions of ferrous iron, ferric iron and hydrogen peroxide in the absence of other interfering ions and organic substances. The regeneration of ferrous iron from ferric iron by Eq. 11-13, is the rate limiting step in the catalytic iron cycle, if iron is added in small amounts. The listed rate and equilibrium constants for Eq. 1.15-1.24 were reported by Sychev et al., [29].



Furthermore, radical-radical reactions have to be taken into account.



Finally, the following acid/base equilibria have to be regarded [30]:

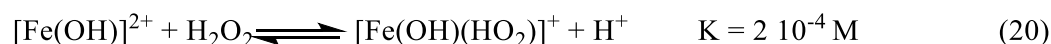


Photo-Fenton reaction

Fenton process has been well studied recently for its prospective applications in unmanageable wastewater treatment [31-33]. The high efficiency of this process is traditionally thought to be due to the generation of hydroxyl radical (HO^\bullet), which is of a high oxidation potential ($E_0 = 2.80 \text{ V}$) and can mineralize the organic compounds completely to water and carbon dioxide (Eq 6,7).

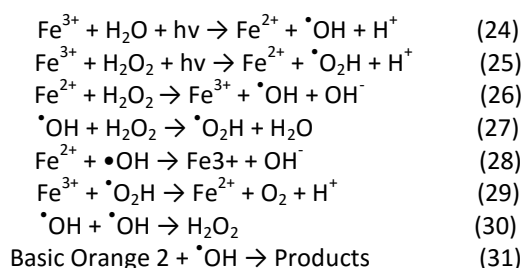
The combination of Fenton reaction in UV (Ultraviolet) light, the so called photo-Fenton reaction, had been shown to enhance the efficiency of the Fenton process. Some researchers also attributed this to the decomposition of the photo-active $\text{Fe}(\text{OH})^{2+}$ which lead to the addition of the HO^\bullet radicals [34]. However, the free radical mechanism had been questioned at times [35]. The alternative mechanisms maintained that complexes and compounds between $\text{Fe}(\text{III})$ and H_2O_2 are the actual intermediates in the reaction. Optical absorption measurements during the reaction also proved the presence of these complexes [36].

Some applications of Photo-Fenton reaction

A wide variety of Fenton's reagent applications have been reported, such as treatment of textile wastewaters [37,41], reduction of Polynuclear Aromatic Hydrocarbons (PAH) in water [42], removal of Adsorbable Organic Halogens (AOX) from pharmaceutical wastewater [43], or treatment of paper pulp manufacturing effluents [44].

Among them, application of the Photo-Fenton reaction is degradation of phenol wherein HO^\bullet reaction pathway or some other complex pathway are involved in the photo-Fenton process; one way is through the inner-sphere electron transfer where phenol directly oxidized to CO_2 and H_2O ; in the other way, phenol is first converted to organic acid under the attack of HO^\bullet , then oxidized to CO_2 and H_2O . Operating parameters such as H_2O_2 variation, Fe^{2+} variation, initial pH, purge-gas were studied to investigate the validity and feasibility of the proposed model.

Also Photo-Fenton reaction used to degradation of Basic orange 2. a tentative mechanism has been proposed for photodegradation of this type of azo dyes with the photo-Fenton reagent.



The aqueous solution of ferric ions on exposure to light dissociates water into a proton and $\bullet\text{OH}$ radical and ferric ions are reduced to ferrous ions (Eq. 24). These ferrous ions will decompose H_2O_2 into a hydroxyl ion and a hydroxyl radical, while ferrous ions undergo oxidation to ferric ions (Eq. 26). Ferric ions generate $\bullet\text{OOH}$ radicals due to dissociation of H_2O_2 in the presence of light (Eq. 25). The incorporation of $\bullet\text{OH}$ with H_2O_2 also produces $\bullet\text{OOH}$ radicals (Eq. 27). Ferrous ions will undergo oxidation to ferric ions by the addition of $\bullet\text{OH}$ radicals, while ferric ions are reduced to ferrous ions by the incorporation of $\bullet\text{OOH}$ radicals, producing H^+ ions (Eq. 28,29). $\bullet\text{OOH}$ radicals are highly unstable in water and undergo facile disproportionation rather than reacting slowly with the dye molecules.

The two possibilities for the consumption of $\bullet\text{OH}$ radicals include, firstly, the dissociation of H_2O_2 into $\bullet\text{OOH}$ and water or combining to form H_2O_2 molecules (Eq. 30), and, secondly, a reaction with Basic Orange 2 to give the colorless degradation products (Eq. 31) [45] The whole process is pictured in Fig. 3.

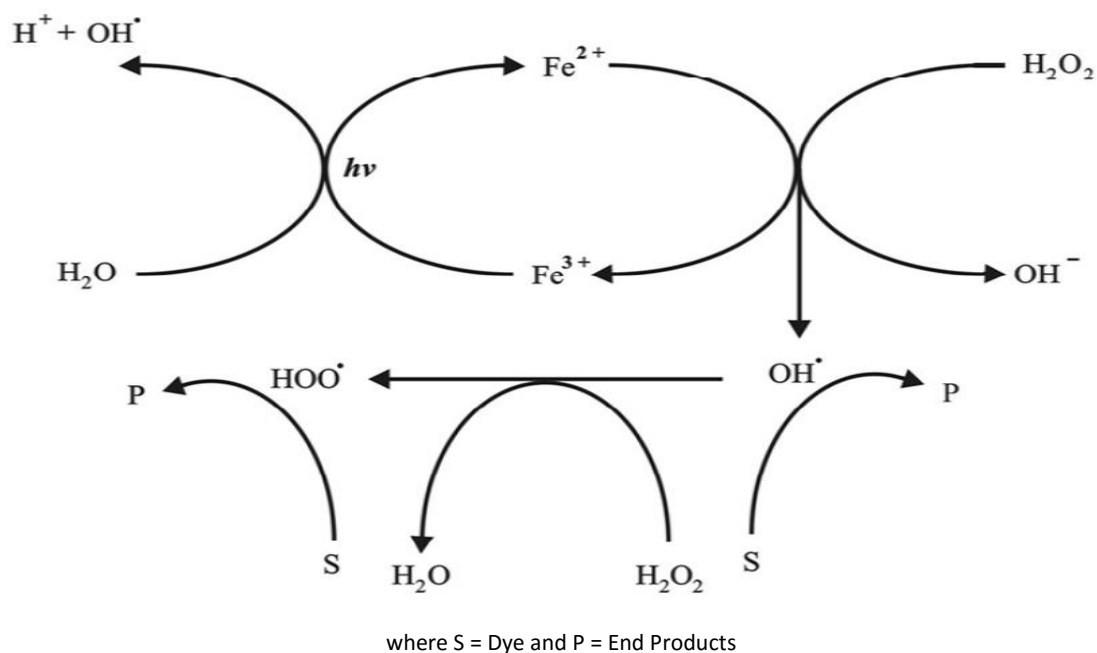
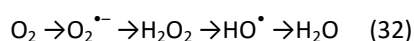


Fig. 3: A Schematic representation of Photo-Fenton Chemistry

Also Iron is an essential constituent of a number of proteins involved in oxygen transport or metabolism. It must also be transported around the body, stored, and made available for synthesis of iron proteins. The ability of iron to undergo redox-cycling is an important aspect of its function. An average adult human male contains some 4.5 g of iron. Iron is stored in cells within two major proteins: ferritin and hemosiderin. In bacteria, it is mainly contained in enzymes involved in electron transfer. The iron content of *Escherichia coli* is, for example, around 106 ions per cell. A second salient feature of metal ions with respect to their ability to mediate biological oxidations is the availability of multiple redox states. In the case of iron, the biologically relevant oxidation states are most often +2 and +3.

On the other hand, oxygen is essential for living organisms, and the mechanism by which oxygen expresses its toxicity is linked with the availability to form different ROS. The step-wise one-electron reduction of molecular oxygen can be summarized as follows:



The final compound of oxygen reduction is water. Some reactive ROS, such as hydroxyl radical, are possible to damage different biological target molecules such as DNA, proteins, or lipids. Fenton chemistry plays an important role in these reactions. Due to its strong reactivity with biomolecules, hydroxyl radical is probably capable of doing more damage to biological systems than any other ROS [46].

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