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FOTO-FENTON PROTSESSI KASUTAMINE MIKROSAASTEAINETE LAGUNDAMISEKS NING REOVEE PUHASTAMISEKS

Magistritöö

Katrel Virkus

Juhendaja: Marina Trapido, keskkonnakaitse ja keemiatehnoloogia õppetool, õppetooli juhataja

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Katrel Virkus

TALLINN UNIVERSITY OF TECHNOLOGY

FACULTY OF CHEMICAL AND MATERIALS TECHNOLOGY
DEPARTMENT OF CHEMICAL ENGINEERING
CHAIR OF ENVIRONMENTAL AND CHEMICAL TECHNOLOGY

THE APPLICATION OF PHOTO-FENTON FOR DEGRADATION OF MICROPOLLUTANTS AND PURIFICATION OF WASTEWATER

Master's Thesis

Katrel Virkus

Supervisor: Marina Trapido, Chair of Environmental and Chemical Technology, Head of Chair

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CONTENTS

ABBREVIATIONS

AOP - advanced oxidation process

APS - ammonium persulfate

BOD - biochemical oxygen demand

BOD$_5$ - 5-day biochemical oxygen demand

COD - chemical oxygen demand

DOC - dissolved organic carbon

ORP - oxidation-reduction potential

TOC - total organic carbon

TS - total solids

TSS - total suspended solids

ZVI - zero valent iron

INTRODUCTION

Economic and social development in many countries is limited due to increasing pollution and deficiency of fresh water. In recent decades, population growth, opening of new territories and the development of agriculture and different industries have a great impact on the fresh water resources [1].

Because of the problems concerning fresh water have arised, a lot of attention have been paid to cleaner and sustainable production and wastewater treatment to avoid harmful effects on health and environment [2].

Strict quality standards have been claimed for substances that have toxic effect on biological sphere. So, non biological technologies must be used for the destruction of recalcitrant compounds. Conventional phase separation techniques, like adsorption and stripping, and contaminant destruction methods, such as chemical oxidation or reduction, are often used [3].

The purpose of exploiting chemical oxidation is the mineralization of pollutants to water, carbon dioxide and inorganics or transforming them into harmless products. Chemical destruction methods give solution to the problem of pollutant degradation comparing to phase separation, which partly solves the problem [3].

Several studies have shown that advanced oxidation processes, which operate at ambient temperature and pressure, are most effective methods for the degradation of contaminants [4].

„Advanced oxidation processes are defined as those which involve the generation of hydroxyl radicals in sufficient quantity to affect water purification.“ [4]

AOPs are characterized by production of ·OH radicals. Hydroxyl radicals are very reactive species which attack the most part of organic molecules. These radicals are not very selective regarding the attack of contaminant. Also, there is a number of different processes which offer several ways for creating ·OH radicals and thanks to that, they qualify the specific treatment requirements [3].

Different possibilities offered by advanced oxidation processes are photocatalysis, O_3/H_2O_2, O_3/UV, H_2O_2/UV, Fenton, Fenton-like and photo-Fenton processes [3].

The aim of this Master's Thesis is to evaluate the possibilities using photo-Fenton process for the degradation of different pollutants, since it is one of the cheapest, fastest and most effective methods among advanced oxidation processes. What is more, photo-Fenton system is environmentally friendly, generating no new pollutants and that is why it should be preferred for the treatment of wastewaters.

The following work focuses on photo-Fenton process. In the first chapter, Fenton's oxidation chemistry and it's modifications are introduced. It is followed by second part, where photo-Fenton process, it's modifications and radiation sources are discussed.

Degradation of different micropollutants and the treatment of wastewaters through photo-Fenton process is investigated and compared in third and fourth chapter. Scientific databases, like Scopus and Sciencedirect, are used as sources of information. Also, the effect of operating parameters have been pointed out in fourth section. In the last part, benefits and drawbacks and cost evaluation of the photo-Fenton oxidation are shown.

1. THE FENTON PROCESS

Fenton and Fenton-like reactions are reactions of hydrogen peroxide and iron ions to form hydroxyl radicals to oxidize organic or inorganic compounds [5].
Fenton reaction was discovered in 1894 by H.J.H. Fenton and he found that ferrous salts activate hydrogen peroxide to oxidize tartaric acid [6].

Usually, the name of "*Fenton reaction*" or "*Fenton reagent*" is used and it is a mixture of ferrous iron and hydrogen peroxide. Fenton reaction is determined to be one of the most efficient methods for the removal of organic pollutants in different wastewaters. The Fenton reagent has been known since 1894 but it was applied as an oxidizing process for destroying hazardous organics in the late 1960s [7]. Fenton reagent has been successfully used for treating various industrial wastewater components like aromatic amines [8], different types of dyes [9], pesticides [10], pharmaceuticals [11], surfactants [12], explosives [13] and many other substances.

1.1. Chemistry of the Fenton process

The traditional Fenton mechanism is illustrated by Equations 1.1-1.9 and its reaction rates are found in the literature. Equation 1.1 is called as a Fenton reaction and it means the oxidation of ferrous to ferric ions to decompose H_2O_2 into hydroxyl radicals. It is the basic of the Fenton chemistry [5].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^{-},\ k_{1.1} = 40 - 80\ (L\ mol^{-1}s^{-1}) \qquad (1.1)$$

Excessive hydrogen peroxide is used, to reduce the generated ferric ions to form ferrous ion and more radicals, as seen in Equation 1.2. This reaction is called Fenton-like reaction and it is slower than ordinary Fenton reaction. It allows Fe^{2+} regeneration in an effective cyclic mechanism. Besides the regeneration of ferrous ion, hydroperoxyl (${}^{\bullet}O_2H$) radicals are produced in Fenton-like system. The hydroperoxyl radicals are less potential than hydroxyl radicals, although they can also attack organic pollutants. It should be noted that the iron added in small amount acts as a catalyst while H_2O_2 is continuously consumed to produce hydroxyl radicals [5].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \ {}^{\cdot}O_2H + H^+, \qquad k_{1.2} = 9{,}1 * 10^{-7}\ (L\,mol^{-1}s^{-1}) \qquad (1.2)$$

The following reactions are involved in Fenton chemistry [5].

$$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^-, \qquad k_{1.3} = 2{,}5 - 5 * 10^8\ (L\,mol^{-1}s^{-1}) \qquad (1.3)$$

$$Fe^{2+} + {}^{\cdot}O_2H \rightarrow Fe^{3+} + HO_2{}^-, \qquad k_{1.4} = 0{,}72 - 1{,}5 * 10^6\ (L\,mol^{-1}s^{-1}) \qquad (1.4)$$

$$Fe^{3+} + {}^{\cdot}H \rightarrow Fe^{2+} + O_2 + H^+, \qquad k_{1.5} = 0{,}33 - 2{,}1 * 10^6\ (L\,mol^{-1}s^{-1}) \qquad (1.5)$$

Equations 1.2 - 1.5 stand for the rate limiting steps in the Fenton chemistry while H_2O_2 is consumed and Fe^{2+} is regenerated from Fe^{3+} according to these reactions [5].

Equations 1.6–1.9 also take place during the Fenton process and they are radical–radical reactions or hydrogen peroxide–radical reaction [5]:

$${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2, \qquad k_{1.6} = 5 - 8 * 10^9\ (L\,mol^{-1}s^{-1}) \qquad (1.6)$$

$${}^{\cdot}OH + H_2O_2 \rightarrow {}^{\cdot}O_2H + H_2O, \qquad k_{1.7} = 1{,}7 - 4{,}5 * 10^7\ (L\,mol^{-1}s^{-1}) \qquad (1.7)$$

$${}^{\cdot}O_2H + {}^{\cdot}O_2H \rightarrow H_2O_2 + O_2, \qquad k_{1.8} = 0{,}8 - 2{,}2 * 10^6\ (L\,mol^{-1}s^{-1}) \qquad (1.8)$$

$${}^{\cdot}OH + {}^{\cdot}O_2H \rightarrow H_2O + O_2, \qquad k_{1.9} = 1{,}4 * 10^{10}\ (L\,mol^{-1}s^{-1}) \qquad (1.9)$$

Mostly, Fenton's oxidation process is composed of four stages, which are [14]:

- pH adjustment,
- oxidation reaction,
- neutralization and coagulation,
- precipitation

The organic substances are removed at the oxidation and the coagulation [14].

The highly reactive hydroxyl radicals (oxidation potential 2.8 V) attack and destroy the organic pollutants in wastewater and improve the biodegradability of refractory wastewater [15].

For controlling, monitoring and optimizing biological treatment systems, oxidation-reduction potential (ORP) has been used since 1980s. This technique is effective and economical in many wastewater treatment processes, like extended aeration treatment, alternating aerobic-anoxic system and sequencing batch reactor. Hydroxyl radical is the major oxidizing species for Fenton process but monitoring the hydroxyl radical is difficult. If the ORP value is used as a controlling parameter for the Fenton process, it should be high in the oxidation stage [15].

There are many parameters that affect the efficiency of the Fenton process, such as pH, temperature, concentrations of hydrogen peroxide and catalyst, Fe^{3+} reduction to Fe^{2+}. Reduction of Fe^{3+} and regeneration of the catalyst is possible with the presence of reaction intermediates. Although, there are this kind of reaction intermediates that remove Fe^{3+} from the Fe^{2+}/Fe^{3+} cycle because of the generation of iron complexes [16].

Maximum catalytic activity of Fenton reaction is at pH 2.8–3.0. With a reduction or an increase of pH, maximum activity decreases drastically. If the pH is higher than 3, Fe^{3+} starts precipitating as $Fe(OH)_3$ and breaks down the H_2O_2 into O_2 and H_2O. Besides, concentration of Fe^{2+} decreases due to the formation of Fe(II) complexes at high pH. On the other hand, Fe^{2+} regeneration by the reaction of Fe^{3+} with H_2O_2 is inhibited at more acidic pH values [16].

The reaction temperature is also an important parameter in the Fenton process. On the one hand, increasing the temperature should enhance the kinetics of the process, but on the other hand, it favours the decomposition of hydrogen peroxide towards O_2 and H_2O, whose rate increases around 2.2 times each 10°C in the range 20–100°C [16].

The doses of hydrogen peroxide and iron are closely related factors that affect the Fenton process. The H_2O_2 dose must be chosen according to the pollutant concentration. It is important to use an amount of H_2O_2 corresponding to the theoretical stoichiometric H_2O_2 to chemical oxygen demand (COD) ratio. However, the optimal dose depends on the resistance of the specific contaminants to oxidation and on the objective targeted reduction of the pollutant [16].

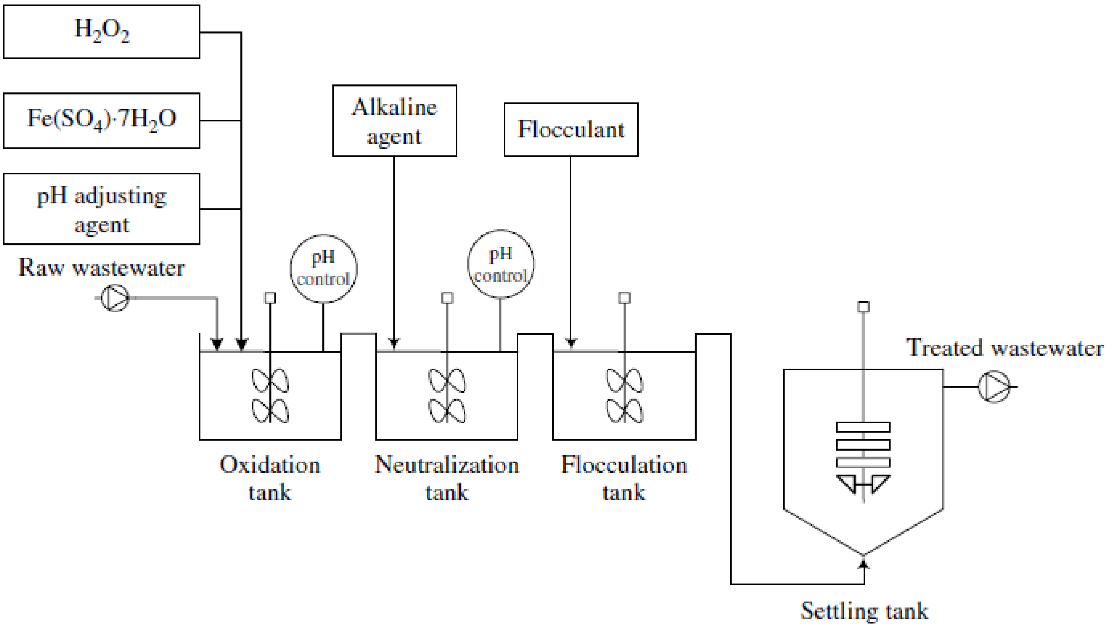

Figure 1. Typical scheme for Fenton treatment [16]

1.2. Application of the Fenton process

Fenton system has been tested with a number of synthetic wastewaters containing different target compounds, like phenols [17], chlorophenols, formaldehyde, 2,4-dinitrophenol, 2,4,6-trinitrotoluene, 2,4-dinitrotoluene, halomethanes, amines, hexahydro- 1,3,5-trinitro-1,3,5-triazine (RDX) [13]. But there are many chemicals which cannot be degraded by Fenton oxidation, for example acetone, acetic acid, carbon tetrachloride, maleic acid, methylene chloride, oxalic acid, etc. It has been demonstrated that these compounds are resistant under the usual mild operating conditions of Fenton oxidation [16].

This process has been applied to several industrial wastewaters (such as pharmaceutical, textile, paper and pulp industry, cosmetic, beverage, cork processing wastewaters, etc.), sludge and contaminated soils. As a result, reductions of toxicity, colour, odour and improvement of biodegradability are achieved [16, 17, 18].

The chemical industry is number one polluter of industrial wastewaters because of the hazardous compounds found in the effluents. The strict regulations have caused the application of advanced technologies to fulfill the discharge limits and allow water recycling.

Among advanced oxidation processes, Fenton oxidation has been gaining interest in recent years [16].

As mentioned before, Fenton system has been used for the treatment of different wastewaters, like textile, pharmaceutical, pulp and paper industry effluents. Pharmaceutical wastewaters contain a number of chemicals used in drug production and due to that treatment of this effluent is often troublesome. Pharmaceutical substances are complex organic chemicals which are often resistant to biological degradation. Because of that, traditional methods are not efficient for the treatment of pharmaceutical wastewaters and advanced oxidation processes are mostly used [16].

Large amount of wastewater is generated by the pulp and paper industry and more than 250 different chemicals have been identified in the effluent. Some of the pollutants are natural wood extractives (tannins, lignin, etc.) while others are xenobiotic compounds from the pulp manufacture (phenols, dioxins and furans). Most frequently used treatment for this type of wastewaters is primary clarification, sometimes secondary or biological treatment is used. Fenton and photo-Fenton oxidation has been tested for this kind of wastewaters and they have proven to be very effective for the treatment of pulp bleaching effluents [16].

Textile industries consume large amounts of water and use a number of chemicals in different operations. Main environmental problems associated with textile effluents are caused by the colour. Extensive use of various dyestuffs and chemicals affect the nature of textile wastewaters from the dyeing and finishing stages. Several studies have shown good results while using the Fenton process for this kind of industrial effluents [18, 19].

The Fenton technology has also investigated for the treatment of wastewaters generated by the food industry, such as olive mill, beverage industry and winery effluents. Olive mill wastewaters are generated in extraction plants and by table olive production. This kind of wastewater has high contaminant load and specifically high concentration of polyphenols [16].

There are more examples of successful application of the Fenton technology for the treatment of different kind of industrial wastewaters.

1.3. Modifications of the Fenton process

In the classic Fenton's reagent, ferrous iron is used as a catalyst, but some other materials have successfully exploited to catalyse degradation of H_2O_2. In recent studies, three categories of catalysts have been tested: soluble ferric iron, iron-chelate complexes and iron minerals. What is more, the efficiency of Fenton process with light irradiation and electrochemical assistance has been evaluated [20].

1.3.1. Fenton catalysts - ferric iron and transition metals

Ferric iron has the ability to catalyse hydrogen peroxide decomposition. Term "Fenton-like reactions" are used when describing reactions of Fe^{3+} or other transition metals with H_2O_2 [21].

Several transition metal ions, such as Cr^{2+}, Co^{2+}, Cu^{+}, Mn^{2+} with hydrogen peroxide have the oxidative features of the Fenton reaction. Transition metals are usually applied in the form of their complexes in their lower oxidation states, and at near neutral pH values they can act as catalyst. Unfortunately, many of those potentially suitable metallic catalysts are toxic [22].

1.3.2. Using iron complexes as Fenton catalysts

As an alternative oxidative process, chelate-mediated Fenton process with ferric iron chelate and hydrogen peroxide has been suggested in the last few years. This way it is possible to overcome the limitations of the classic Fenton reaction [23].

Using organic compounds that can complex ferric iron is very important Fenton process modification due to the fact that the addition of large amounts of acid makes the process unsuitable for different applications mainly because of the increase of salinity. During the studies, it has been found some organic chelates that can complex Fe^{3+} make it possible to carry out the process at higher pH [24].

The main advantage of using chelates as catalysts is that wastewater treatment can be conducted at near neutral pH. Furthermore, iron chelates may infiltrate further in surface than soluble iron improving transport of the catalyst [23].

1.3.3. Heterogeneous catalysts for the Fenton process

The Fenton reaction can be carried out as a heterogeneous process, where the catalyst is used as solid phase, for example iron-containing minerals or iron-coated silica particles. Additionally, the iron can be adsorbed onto zeolites or iron exchangeable membranes [25].

For the mechanism of heterogeneous Fenton-like reactions forming hydroxyl radicals, two mechanisms are possible. The hydroxyl radicals may be formed by the reactions with Fe^{2+} dissolved from the mineral surface or the catalysis may occur on the surface itself [26].

The main advantages of applying iron minerals in the Fenton chemistry are [23]:

- extended periods of catalyst life without the need of regeneration or replacement;
- the catalyst may be removed from the treated water by sedimentation or filtration;
- pH of treated media may be in the range 5-9;
- insensitive to the inorganic carbonate concentration

1.3.4. Electro-Fenton process

In recent years, electro-Fenton process has gained a lot of interest due to the effectiveness of removing pollutants from various wastewaters [27].

The electro-Fenton system is one of the electrochemical advanced oxidation processes and the technology is based on the continuous generation of H_2O_2 using suitable cathode fed with O_2 or air; and iron catalyst. Production of hydrogen peroxide can be catalytically converted into powerful hydroxyl radicals with iron catalyst present [27, 28].

$$O_2 + H^+ + 2e \rightarrow H_2O_2 \qquad (1.10)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \qquad (1.11)$$

Reaction rate and removal efficiency are affected by the cathode and catalyst in electro-Fenton process [29].

1.3.5. Photo-Fenton process

There are many photochemical processes using iron compounds and H_2O_2 that provide alternative ways of generating hydroxyl radicals. Photo-Fenton system and its modifications are very efficient regarding the destruction of organic pollutants. The photo-Fenton reaction is based on the applying of the Fe^{2+}/Fe^{3+} and H_2O_2 reagents with near-UV and visible light [30, 31].

When irradiated with light of suitable wavelength (180-400 nm) Fe^{3+} can catalyse the formation of hydroxyl radicals [32]:

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + H^+ + {}^{\cdot}OH \qquad (1.12)$$

One of the advantages of the photo-Fenton process is that UV radiation can enhance reduction of Fe^{3+} complexes to Fe^{2+}, and generate additional $^{\bullet}OH$ through photolysis. As a result, the production of iron sludge can be reduced. What is more, photo-Fenton reaction does not produce new pollutants and only small amount of iron salt is needed [33].

More detailed analysis of the photo-Fenton process, its modifications, advantages, etc. is given in the next chapter.

2. PHOTO-FENTON PROCESS

Photo-Fenton process is the combination of Fenton's reaction with UV light (180-400 nm) and as a result additional $^{\bullet}OH$ is produced [30]. Some decades ago, it was found that the illumination of Fenton reaction systems with UV or visible light accelerated the rate of degradation of a number of pollutants [31].

Fe(III) can catalyse the formation of hydroxyl radicals when irradiated with light (wavelength 180-400 nm), that is, ultraviolet and some visible light [32].

This process can be illustrated with following reactions [32]:

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + H^{+} + {}^{\cdot}OH \qquad (2.1)$$

It is called photo-Fenton reaction and is followed by [32]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^{-} \qquad (2.2)$$

Hydrogen peroxide photolyzes with UV light [33]:

$$H_2O_2 + hv \rightarrow 2\,{}^{\cdot}OH \qquad (2.3)$$

Iron starts to cycle between the 2+ and 3+ oxidation states. As long as H_2O_2 is available, the continuous recycle of ferrous iron reduces the amount of iron salts required for the Fenton's reaction [32].

The production of hydroxyl radicals is determined by the availability of light and H_2O_2. In theory, by combination of these two reactions, one mole of H_2O_2 consumed should produce two moles of $^{\bullet}OH$ [32].

Photo-Fenton process can also be explained with these reactions [10]:

$$Fe^{2+} + H_2O_2 \ \rightarrow \ Fe(OH)^{2+} + {}^{\cdot}OH \qquad (2.4)$$

$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + \ {}^{\cdot}OH \qquad (2.5)$$

Studies have shown that the photo-Fenton reaction is optimum at pH 2.8 [33]. Under such conditions, half of the Fe(III) is present as Fe^{3+} ion and half as $Fe(OH)^{2+}$ ion, the photo-active species. If pH is lower than 2.8, the concentration of $Fe(OH)^{2+}$ decreases and if pH is higher, the Fe(III) precipitates as oxyhydroxides [10].

The $Fe(OH)^{2+}$ ion absorbs light at wavelengths up to 410 nm. Thanks to that, the reaction can be carried out with longer wavelength light than other advanced oxidation processes like O_3/UV or H_2O_2 (wavelengths <300 nm) [10].

The photo-Fenton process has many advantages. It gives higher degree of mineralization and faster reaction rates than Fenton reaction, the photo-Fenton does not produce new pollutants and small amount of iron salt is needed. Remaining hydrogen peroxide that is not used in photo-Fenton process will decompose into water and molecular oxygen [33].

There are also some disadvantages, which are requirement for acidic conditions, reagent mixture is often unstable, waste of a significant fraction of the bulk oxidant by non-productive conversion to oxygen [34].

2.1. The radiation sources of the Photo-Fenton process

Using UV or solar light can increase the mineralization degree and make dark Fenton process more efficient by the photoreduction of $Fe(OH)^{2+}$ which leads to additional $^{\cdot}OH$ production and continuous regeneration of Fe^{2+} [35].

2.1.1. UV-A light

UV-A wavelength is between 315 and 400 nm [36].

Experiments with UV-A light have been made to determine the best conditions for ethylenediaminetetraacetic acid (EDTA) photochemical removal by photo-Fenton and photo-Fenton-like reactions [35]. EDTA is a common chelating agent used in the photographic and metal industry, in textile and paper manufacturing, but it may cause harmful effects on the environment [37].

In this study, influence of UV-A on EDTA degradation was tested, using Fenton and photo-Fenton-like reactions in the presence of Fe^{2+}, Fe^{3+}, Cu^{2+} and mixtures of Fe^{2+}/Cu^{2+} and Fe^{3+}/Cu^{2+} ions. Results show that the removal of TOC and EDTA degradation was efficient under irradiation [37].

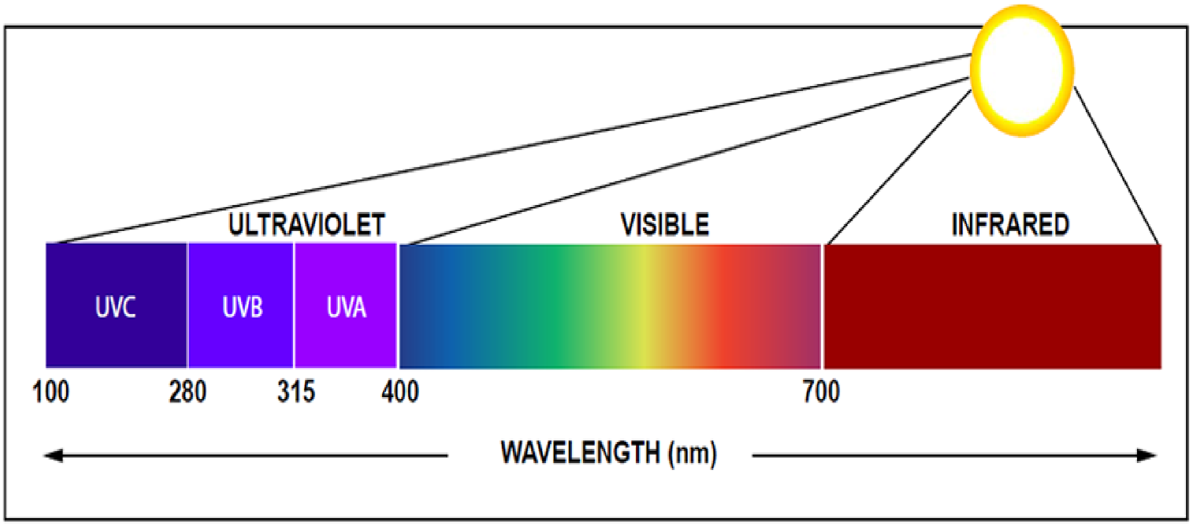

Figure 2. Wavelengths of light [38]

2.1.2. UV-C light

UV-C wavelength is between 100-280 nm [36].

Using UV-C light as a radiation source in the photo-Fenton process has not been tested enough yet, but there are some studies that show very promising results [39,40]. UV-C light has been used in photo-Fenton oxidation of methyl parathion. This is an organophosphorus pesticide, which is used to control insects in crops, contaminated soils and waters. According to the research, methyl parathion was quickly destroyed because of the ·OH generated from Fenton’s reaction and the UV-C irradiation [41].

Presence of UV-C light in photo-Fenton process gives a faster oxidation as a result of the higher quantum yields. In addition, with UV-C, H_2O_2 photolyzes and extra $^{\cdot}OH$ is generated [42].

2.1.3. Sunlight

In the recent years, using radiation of sunlight for the treatment of wastewater has drawn a lot of attention [43].

Experiments with solar photo-Fenton were performed to achieve degradation of alachlor. Solar pilot-plant consisted of a reservoir tank, a recirculation pump, compound parabolic collectors exposed to sunlight and connecting tubing. Experiments were made as follows: alachlor was homogeneously dissolved in the pilot-plant with the parabolic collectors while the pH was adjusted to 2.7 with sulphuric acid [44].

According to the results, alachlor was completely degraded, mineralization of chloride and 85-95% mineralization of dissolved organic carbon (DOC) was achieved [44].

Solar photo-Fenton is also proved to be efficient with winery effluents which have already been treated by membrane bioreactor [45].

2.2. Modifications of the photo-Fenton process

2.2.1. Fe^{3+}/H_2O_2/UV

In this kind of photo-Fenton-like process, Fe^{3+} is used with the UV light and H_2O_2 [46]. H_2O_2 reacts with iron ions as a catalyst. The photo-reduction of Fe^{3+} by UV or visible light produces an $^{\cdot}OH$ radical, which allows to form the photo-Fenton catalytic cycle process where iron is cycled between +2 and +3 oxidation states [47].

This process can be illustrated with simplified reactions [46, 47]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H\dot{O}_2 + H^+ \qquad (2.6)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + H^- \qquad (2.7)$$

$$Fe^{3+} + H_2O \xrightarrow{hv} Fe^{2+} + {}^{\cdot}OH + H^+ \qquad (2.8)$$

$$H_2O_2 \xrightarrow{hv} 2\,{}^{\cdot}OH \qquad (2.9)$$

This modification was used for the degradation of polyacrylic acid in aqueous solution in laboratory-scale batch recirculation photoreactor. The effects of the initial concentration of polyacrylic acid, Fe^{3+} and the H_2O_2 dosage on the percent of TOC removal were studied using response surface methodology. Response surface methodology (RSM) as a reliable statistical tool in multivariate system fits the studied experimental domain in the theoretical design through a response function. According to the experiment, these parameters had significant effect on the percent of TOC removal [48].

Fe^{3+}/H_2O_2/UV process has also been used for the treatment of dye production wastewaters. Acid Blue 193 and Reactive Black 39 production wastewaters were treated with modified photo-Fenton process and real Reactive Black 39 production effluent was investigated [49].

Table 1. Results of synthetic azo dye production wastewater treatment experiments [49]

Color	Color removal, %	COD removal, %	TOC removal, %
Synthetic Acid Blue 193	98	78	59
Synthetic Reactive Black 39	100	84	53

2.2.2. nZVI/UV/H_2O_2

In recent years, a number of studies that employ zero valent iron (ZVI) coming from different sources have appeared. It is possible to use these materials in Fenton technologies or as reductive agents, combined with UV radiation or not [50, 51].

Using ZVI presents higher reaction rates of contaminant decomposition, under certain operating conditions, the possibility of degradation of contaminants by the reductive properties of ZVI and its comparatively low cost [52].

Experiments have been made to find out the influence of operating variables in the degradation of 2-chlorophenol by photo-Fenton reaction using zero valent iron nanoparticles as source of iron. As a result, using ZVI larger conversions of the target compound were achieved with a lower requirement of H_2O_2 and using ZVI nanoparticles, the remaining solution does not present traces of leached iron over the detection limits [52].

2.2.3. $Fe^{3+}/(NH_4)_2S_2O_8$/UV

In one of the photo-Fenton-like processes, ammonium persulfate (APS) is used as a reagent.It has been determined that H_2O_2 is better oxidant than APS. But still, several studies have been made using ammonium persulfate [53, 54].

The degradation on di azo dye Congo Red has been studied by photo-Fenton-like process using Fe^{3+} ions as the catalyst and ammonium persulfate $(NH_4)_2S_2O_8$ as oxidizing agent. Persulfate can be induced to form sulfate radicals, which provides free radical mechanism similar to the hydroxyl radical pathways generated by Fenton's chemistry [53].

Generation of hydroxyl radicals under acidic pH in $Fe^{3+}/(NH_4)_2S_2O_8$ system can be summarized [53]:

1) Fe^{3+} reacts with persulfate anions, producing sulfate radicals, and is reduced to Fe^{2+} [53]:

$$Fe^{3+} + S_2O_8^{2-} \rightarrow 2SO_4^{-\cdot} + Fe^{2+} \qquad (2.10)$$

2) The sulfate radicals react with water forming hydroxyl radicals [53]:

$$SO_4^{-\cdot} + H_2O \rightarrow SO_4^{2-} + {}^{\cdot}OH + H^+ \qquad (2.11)$$

3) Fe^{3+} ions form an intermediate $[Fe(OH)]^{2+}$, which under UV light generates hydroxyl radicals [53]:

$$Fe^{3+} + H_2O \rightarrow [Fe(OH)]^{2+} \qquad (2.12)$$

$$[Fe(OH)]^{2+} \rightarrow Fe^{2+} + {}^{\cdot}OH \qquad (2.13)$$

4) The photo generated Fe^{2+} reacts with persulfate anions generating sulfate radicals, which reacts as a source for the productions of hydroxyl radicals [53]:

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-\cdot} \qquad (2.14)$$

Results show that this process is efficient and complete mineralization of the dye can be achieved particularly at lower iron concentration. To sum up, this process has many advantages and it is simple and cost effective method for the degradation of di azo dye [53].

3. DEGRADATION OF MICROPOLLUTANTS USING PHOTO-FENTON PROCESS

3.1. Pharmaceuticals

Pharmaceuticals are complex molecules with different biological and physicochemical properties. They are usually classified according to their therapeutical purpose (antibiotics, analgesics, lipid regulators, beta blockers, etc.). A lot of pharmaceuticals are biotransformed in the body. That way chemical structure of their active molecules is modified which leads to change in their pharmaceutical or physicochemical properties [55, 56].

Pharmaceutically active compounds in aquatic environment, their occurrence and fate has become one of the main issues in environmental chemistry in recent years [57, 58, 59]. Several studies have shown that more than 80 compounds and pharmaceuticals have been found in aquatic environment [57].

A number of pharmaceuticals applied in human or animal medical care are not completely consumed by the body. They are often excreted, only slightly transformed or unchanged, mostly conjugated to polar molecules. During sewage treatment these conjugates can easily be cleaved and the original pharmaceuticals will be released into the aquatic environment by effluents from municipal sewage treatment plants [57].

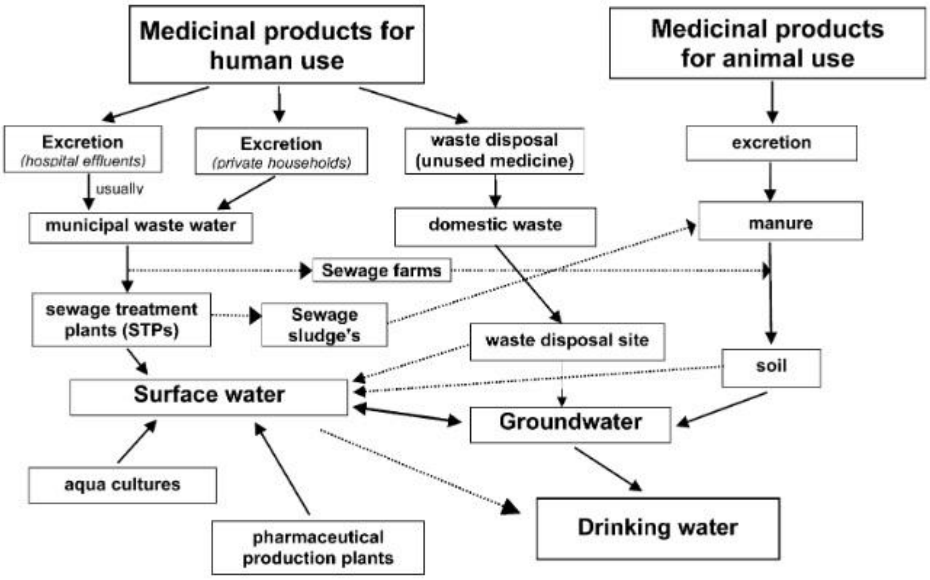

Figure 3. Sources of pharmaceuticals in the aquatic environment [57]

There is little information available on the effects of the active substances on organisms in the aquatic environment. High concentrations of some compounds have been found to have effects in environmental organisms. The active ingredients of medications have been selected because of their activity against organisms. So it is to be expected that following properties, for example effective against bacteria and fungi, will be crucial for their environmental impact [57].

Different procedures, like photo-Fenton process, TiO_2-photocatalysis, electrochemical processes, coagulation and ozonation have been used for the treatment of pharmaceutical wastewater [19, 60, 62, 66, 67].

Table 2. Degradation of pharmaceuticals using photo-Fenton process

Compound	**Irradiation source**	**Initial concentration mgL^{-1}**	**Initial conditions**			**Time min**	**Removal %**	**Ref**
			pH	**H_2O_2 mgL^{-1}**	**Iron mgL^{-1}**			
Metro-nidazole	MP mercury lamp	1	3.5	1	164	1.8	74	[60]
					328	0.8	91	
					656	0.5	94	
Oxacillin	Philips TL-D Actinic BL 350-400 nm	20	5.6	34	5	4	100	[61]
Procaine Penicillin G	UV-A 300-370 nm	COD_0: 600	3	850	83.7	30	COD: 56	[62]
		TOC_0:450					TOC: 42	
Ibuprofen	Xe lamp 290-400 nm	179.5	6.3	10,9	67.0	120	TOC: 40	[63]
Amoxicillin	Solar	50	2.5 - 2.8	120	2.8	5-15	100, $FeSO_4$ and FeO_x	[64]
						240	TOC: 73-81, $FeSO_4$	
Bezafibrate	Black-light fluorescent lamp	20	2.5	170	11.2	5	98 (FeO_x)	[65]
							89 ($Fe(NO_3)_3$)	
Paracetamol		15					98 (FeO_x)	
							53 ($Fe(NO_3)_3$)	
Sulfa-methizole	UV lamp 254 nm	20	3	340	11.2	50	90	[66]
Ampicillin	Solar	100	3	1500	500	120	88	[19]
Diclofenac							94	

Degradation of pharmaceuticals through photo-Fenton process, regarding irradiation sources, initial conditions and removal percentage is given in Table 2.

There have been many studies of degradation of pharmaceuticals (analgesics, antibiotics, lipid regulators) in wastewater via photo-Fenton process [62, 63, 65]. As seen on the table, removal percentage of pharmaceuticals is mostly quite high (> 75%) and it usually takes less than one hour (in few cases two or three hours) to reach more than 90% pharmaceutical degradation.

Metronidazole is an antibiotic which is used against anaerobic microorganisms, including bacteria and protozoa. Metronidazole is very effective against *Bacteroides fragilis*, the most resistant of anaerobic bacteria [68].

Degradation of metronidazole through UV, Fenton and photo-Fenton processes was studied. Photo-Fenton experiment was conducted in room light and under medium-pressure mercury lamp at initial pH of 3.5. Initial concentration of H_2O_2 was 1 mgL^{-1} and ferrous ions were at initial concentrations of 164, 328 and 656 mgL^{-1}. In the beginning, concentration of metronidazole was 1 mgL^{-1}. In less than two minutes, 74, 91 and 94% of metronidazole was removed, respectively [60].

Bezafibrate is a lipid regulator used for the treatment of hyperlipidemia. In recent years, patients with diabetes and hyperlipidemia are increasing and bezafibrate has a large part of oral dosage with about 95% excreted in urine, which will eventually enter to the environment [69].

Degradation of bezafibrate, amoxicillin and paracetamol was carried out using black-light fluorescent lamp. Photo-Fenton degradation efficiency in the presence of $Fe(NO_3)_3$ and FeOx was evaluated. Initial concentration of bezafibrate was 20 mgL^{-1} and pH was 2.5. In five minutes, removal of bezafibrate was 98 and 89%, using FeOx and $Fe(NO_3)_3$, respectively. Results of this experiment show that the degradation of pharmaceuticals was favoured in the presence of FeOx in comparison to $Fe(NO_3)_3$ [65].

Diclofenac is commonly used analgesic which is frequently detected in aquatic environment. It proves that there is a continuous significant output of diclofenac into the environment, mainly associated to the ineffectiveness of traditional wastewater treatment [70, 71].

Diclofenac is usually present at low concentrations, but if it is continuously released into the aquatic environment it may cause potential long-term risk [70].

Experiments with diclofenac were carried out using solar photo-Fenton technology. Initial concentration of diclofenac was 100 mgL^{-1} and pH was adjusted to 3. In 120 minutes, 94% of pharmaceutical was removed [19].

Several studies focus on comparison of the degradation of pharmaceuticals using different processes [60, 66]. One of those includes the degradation of sulfamethizole through UV/H_2O_2, photo-Fenton and photo-Fenton-like processes, as seen in Table 3.

Table 3. Comparison of the degradation of sulfamethizole using UV/H_2O_2, photo-Fenton and photo-Fenton-like processes

Compound	**Process**	**Initial concentration mgL^{-1}**	**Initial conditions**			**Time min**	**Removal %**	**Ref**
			pH	**H_2O_2 mgL^{-1}**	**Iron mgL^{-1}**			
Sulfa-methizole	Photo-F	20	3	340	11.2	60	90	[49]
	UV/H_2O_2				-		16	
	Photo-F-like				11.2		88	

Sulfamethizole is a sulfonamide which is one of the largest classes of antibiotics that is used all over the world. The extensive use of antibiotics may have potential risks to aquatic environment [66].

Degradation of sulfamethizole was investigated using UV/H_2O_2, photo-Fenton and photo-Fenton-like processes. Initial concentration of sulfamethizole was 20 mgL^{-1}. Optimal doses of H_2O_2 in UV/H_2O_2 and iron in photo-Fenton and photo-Fenton-like processes were determined. The optimal dose of H_2O_2 was 340 mgL^{-1} and of iron was 11.2 mgL^{-1}. Under these conditions, reaction time was 60 minutes and degradation percentages were 16, 90 and 88%, in UV/H_2O_2, photo-Fenton and photo-Fenton-like systems, respectively [49].

All the studies show that photo-Fenton and photo-Fenton-like processes are very effective in the degradation of different pharmaceuticals. In most cases, more than 75% of pollutant was mineralized in less than one hour. Removal of oxacillin and amoxicillin was 100% and it took only 4 and 5 to 15 minutes, accordingly.

3.2. Dyes in textile industry

Textile dyes are classified [72]:

1. Based on their application characteristics (Color Index Generic Name such as acid, azo insoluble, basic, direct, disperse, reactive, pigment)
2. Based on their chemical structure (Color Index Constitution Number such as azo, carotenoid, indigoid, inorganic pigment, nitro, sulphur, etc.)

The major textile dyes are divided into two classes: azo and anthraquinone, which include about 65-75% of textile dyes [72].

Many harmful health effects and potential adverse effects have been found for textile dyes. Wastewaters generated in textile industry are complex mixtures of many polluting substances. Large amount of dyestuffs is released because of the inefficiencies in dyeing process and it eventually finds its way into the environment [72].

The textile dyeing industry is one of the biggest polluters of clean water. Effluent from textile industry is hazardous toxic waste which is full of colour and organic chemicals from dyeing. Colour removal is one of the biggest challenges for the treatment of textile industry wastewaters. Chemicals that make the effluent very toxic are acetic acid, chromium compounds, nitrates, soaps, sulphur and heavy metals, like arsenic, cadmium, copper, mercury and nickel [73].

Textile effluents have negative effects on human's health and environment. Organically bound chlorine is a known carcinogen which is a component of 40% of globally used colorants. Organic materials present in the textile industry wastewater react with many disinfectants, for example chlorine. Chemicals evaporate in the air we breathe and this may lead to allergic reactions and have negative effects on unborn children [73].

All of the dyes I have compared in Table 4 are azo dyes. Azo dyes are aromatic compounds with one or more -N=N- groups and they are the largest class of synthetic dyes. Azo dyes are categorized by the affinity with fibres or by the application methods [74].

Different systems have been used for the degradation of azo dyes, for example UV/H_2O_2, UV/O_3/H_2O_2, Fenton and photo-Fenton and electrochemical process [73, 74, 82, 83]. In my comparison (Table 4), regarding the degradation of dyes, photo-Fenton process was used.

Table 4. Degradation of dyes using photo-Fenton process

Compound	**Irradiation source**	**Initial concentration mgL^{-1}**	**Initial conditions**			**Time min**	**Removal %**	**Ref**
			pH	**H_2O_2 mgL^{-1}**	**Ferrous ions mgL^{-1}**			
Reactive Black 5	Solar	50	4	100	0,05 g Fe-films	45	99.29 COD: 90 (artificial)	[75]
							86 COD: 70 (sunlight)	
Disperse Red 1	Black light lamp	20	2.5	170	11.2	45	98	[76]
Reactive Orange 4	MP mercury vapor lamp	385	3	340	27.9	40	95.5	[77]
Reactive Blue 19	UV lamp 254 nm	20	3	50	4	360	97.5	[78]
Remazol Red F3B	LP mercury UV lamp 254 nm	180	3	600	5.6	15	99.4	[79]
		COD_0: 62					COD: 94	
		TOC_0:48					TOC:81.5	
Mordant Red 73	LP mercury lamp	24	3	85	110	180	85	[80]
Reactive Yellow 86	Solar (Xe lamp)	40	3	1700	27.9	20	96	[18]
Acid Violet 90	200 W Tungsten lamp	117.7	3	60000	1.9	180	29	[81]

Disperse Red 1 is an azo dye which is widely used for dyeing polyester, acrylic, polyamide fabrics and vinegar fibre, it can also be applied on wool, plastic and fur [84]. DR1 is extensively used in industrial plants in Brazil [85]. According to some of the studies, Disperse Red 1 has high ecotoxicity [85, 86].

Photo-Fenton experiments with Disperse Red 1 were made in photoreactor with blacklight lamp. Initial concentration of DR1 was 20 mgL^{-1} and pH was adjusted to 2.5. In 45 minutes 98% of initial concentration of Disperse Red 1 was degraded.

Furthermore, acute toxicity test to *Daphnia similis* were made and they showed that after 10 minutes of the degradation of DR1 toxicity decreased. At first, the EC_{50} of untreated dye was stated to be 1.0%, containing 23 mgL^{-1} of dye and after 10 minutes, EC_{50} = 4.4% was achieved and the dye concentration decreased to 15 mgL^{-1} [76].

Reactive Yellow 86 in a reactive azo dye and it is mainly used for cotton and viscose fiber yarn dyeing. It can also be used for cotton and rayon fiber direct printing [87].

Solar photo-Fenton process was used to decolorize Reactive Yellow 86. Initial concentrations of Fe(II) and H_2O_2 and pH were evaluated, as they affect decolorization. Initial concentration of RY 86 was 40 mgL^{-1}. Optimal conditions were obtained: pH 3, Fe(II)=27.9 mgL^{-1} and H_2O_2=1700 mgL^{-1}. Under these conditions, removal of Reactive Yellow 86 was 96% in 20 minutes [18].

Reactive Blue 19 is used for printing and dyeing of cotton fabrics. In one of the experiments, 97.5% of RA 19 was removed in 6 hours using photo-Fenton system. Degradation of Reactive Blue 19 was also made with Fenton process and in this case, removal percentage was 93.3 [78].

In the following table (Table 5), I have compared the mineralization of Reactive Orange 4 using Fenton and photo-Fenton systems.

According to that (Table 5), it can be concluded, that under the same operating conditions, photo-Fenton process is more efficient in the degradation of RO 4 than Fenton process, 95.5 and 79.89%, respectively. There have also been experiments where both these systems are used and photo-Fenton system is always more effective than Fenton system [77, 88].

Table 5. Comparison of Fenton and photo-Fenton processes for the degradation of Reactive Orange 4

Compound	**Process**	**Initial concentration mgL^{-1}**	**Initial conditions**			**Time min**	**Removal %**	**Ref**
			pH	**H_2O_2 mgL^{-1}**	**Iron mgL^{-1}**			
Reactive Orange 4	Photo-F	385	3	340	27.9	40	95.5	[77]
	Fenton						79.89	

To summarize, it can be said that using photo-Fenton process for the degradation of textile dyes is an effective system. In most cases, more than 85% of the dye is removed. Degradation time is longer, comparing to degradation of pharmaceuticals. With textile dyes, time for mineralization is between 15 minutes to 6 hours but with pharmaceuticals, it was between 0.5 minutes to 4 hours.

3.3. Agrochemicals

Pesticides are chemicals used in agriculture to kill, repel or control certain plants or animal life which are considered as pests. Pesticides are herbicides for destroying unwanted vegetation, insecticides for controlling insects and fungicides for preventing the growth of molds and mildew and disinfectants for preventing the spread of bacteria [80].

Use of pesticides has grown in recent decades because of the fast growing population and export of food and crops to other countries. Pesticides are used to avoid the attack from insects, weeds and other organisms to crops. But there are some drawbacks using pesticides, they have harmful effects on environment and people's health [81].

In time, pests have adapted and developed resistance to chemicals and because of that new and higher amounts of chemicals are used to protect crops [82]. Pesticides residue, for example organochlorine and organophosphorous compounds are found in high concentrations in atmosphere, soils and aquatic environment [83].

Different studies have found negative effects on human's health from using pesticides. They have indicated direct exposure of workers to different chemicals and effects on reproduction and central nervous system because of the acute poisoning [84]. Farmers who work with pesticides have higher risk of accidental mortality from poisoning with chemicals than other workers. Furthermore, prostate cancer was increased for the pesticide applicators and the use of phenoxy herbicides increases the risk of soft tissue sarcoma. There is also a possibility of nerve, lymphatic and hematopoietic cancers [85].

In the literature there are mostly articles about the negative effects of pesticides but there are also benefits of using these chemicals. If yields and quality of the production are increasing, that way farm revenues will also increase. Possibility of producing more food allows better nutrition and healthier lives. Healthy people are happier, they are more productive and socially active. Pesticides are reliable because they reduce the risk of huge loss of crop to pests and diseases [86].

There are different ways for the removal of pesticides from water, for example, photocatalysis, ozonation, high frequency ultrasound wave, electrochemical method, Fenton and photo-Fenton process have been used [77, 96, 101-104].

In the following table (Table 6), I have compared degradation of different agrochemicals via photo-Fenton process.

Table 6. Degradation of agrochemicals using photo-Fenton process

Compound	**Irradiation source**	**Initial concentration mgL^{-1}**	**Initial conditions**			**Time min**	**Removal %**	**Ref**
			pH	**H_2O_2 mgL^{-1}**	**Ferrous ions mgL^{-1}**			
Lindane (γ-HCH)	MP mercury lamp	1.01	3	1000	125	120	TOC: 95	[96]
Lambda-cyhalothrin	Sunlight	45	4	1000	3000	180	80.65	[97]
Chlor-pyrifos		200					78.05	
Diazinon		11					50.9	
Diuron	LP mercury lamp	25	4.2	267	36	15	100	[98]
Linuron	Xe lamp	10	4	13.6	2.2	20	100	[99]
Abamectin	UV lamp 365 nm	9	2.5	204	27.9	60	70	[100]

Lindane is the gamma isomer of hexachlorocyclohaxane and it is mainly used for seed treatment and to control wood-inhabiting beetles. Lindane is also used for termite control and for scabies and lice infestation [105]. In one study, the health effects in people who ate food contamined with lindane were investigated. In few hours, they experienced nausea, vomiting, diarrea, headache and/or dizziness [106].

Lindane degradation experiments were carried out in UV reactor, using medium-pressure mercury lamp. Optimal conditions at initial concentration of lindane (1.01 mgL^{-1}) were determined: pH=3, H_2O_2=1000 mgL^{-1} and Fe^{2+}=125 mgL^{-1}. Removal of total organic carbon was investigated. In 2 hours, removal of TOC was 95% [96].

As seen above (Table 6), photo-Fenton process is effective method for the degradation of agrochemicals. Removal percentage of compounds is quite high, mostly over 70%.

4. APPLICATION OF PHOTO-FENTON PROCESS FOR THE TREATMENT OF DIFFERENT TYPES OF WASTEWATER

In the following chapter, treatment of variety of wastewaters through photo-Fenton is discussed. Initial parameters and conditions are found in the literature from scientific databases, such as Sciencedirect and Scopus.

4.1. Examples of the treatment of different wastewaters using photo-Fenton process

Photo-Fenton process has been used for the treatment of different wastewaters. For example, this system is effective for landfill leachate, winery, hospital, coffee effluents, etc. Conditions and results are shown in Table 7.

Table 7. Treatment of different wastewaters using photo-Fenton process

Wastewater	**Irradiation source**	**Initial wastewater parameters mgL^{-1}**	**Initial conditions**			**Time min**	**Removal %**	**Ref**
			pH	**H_2O_2 mgL^{-1}**	**Ferrous ions mgL^{-1}**			
Winery	Solar	TS = 2010 TSS = 8 COD = 120 DOC = 30 TN = 4 TP = 0.3 $BOD_5 < 5$ pH = 8.2	3	250	3	120	COD: 70 ± 3.3 DOC: 53 ± 3.7 Colour: 75± 2.2	[107]
Landfill leachate	MP mercury lamp	Cl^- = 2951 N_{NH4} = 339 TKN = 797 COD = 5678 BOD_5 = 1315 pH=7.8 - 8.7	3	3500	150	360	COD:92.7	[108]
Beverage industry	Solar	TSS = 1300 TOC = 1987 COD = 6500 BOD_5 = 4400 Acetate = 660 Formate = 110 pH=5.35	2.79	1000	150	55	TOC:70.6	[109]
						125	TOC:98.6 COD:100 BOD_5:99.8 Toxicity:100	

Textile industry	Solar	Acrylic: TSS = 16 COD = 828.1 BOD = <1.0 DOC = 334.1 pH=6.8	3.5	6500	113.8	60	Colour: >98-99 COD: 72.0 Mineralization: 71.5	[110]
		Cotton: TSS = 67 COD = 350 BOD = 77.5 DOC = 117.5 pH=11.4		3750	112.5		Colour:>98-99 COD: 30.1 Mineralization: 46.2	
		Polyester: TSS = 21.7 COD = 517.9 BOD = 130.7 DOC = 143.1 pH=8.3		938	131.2		Colour:>98-99 COD: 55.4 Mineralization: 49.6	
Hospital	Solar	TSS = 590±30 BOD_3=200±50 COD= 1200±100 pH=6.4±3	3	1700	279	90	COD:98	[111]
Olive oil mill	UV lamp 245-365 nm	COD = 33600±600 Total phenolic content = 243±14 pH=4.0±0.1	4	$3*10^5$	27900	6 days	Phenols: 100	[17]
Coffee effluent	Black light fluorescent lamps 352 nm	C_0 = 250 TOC = 2000-3000 COD = 3000-8000 pH = 4-7	3	700	15.6	200	90	[112]
Cork boiling wastewater	Solar	DOC=763-892 COD=1786-2403 BOD_5=320-456 pH=5.0-6.5	2.8 - 2.9	2587.4	60	28 days	COD: 95 Mineralization: 91	[113]
Apple-juice wastewater	Hg lamp 190-280 nm	TOC = 700 COD = 1260 BOD_5 = 801	4.2	5800	40	40	TOC: 91	[114]
						120	TOC: 98 COD: 59	

							BOD_5: 68	
Petroleum extraction wastewater	Solar	COD = 220 Fe = 0.93 Cu = 0.04 Cd = 0.05 Pb = 0.76 pH = 7.9	3	16500	-	420	PAH: 92 COD: 53 Aromaticity:96 Phytotoxicity: 50	[115]

4.1.1. Winery wastewater

Winery wastewater is a huge waste stream because of the several cleaning operations that take place during different production phases. Winery wastewater has a high organic content, low pH and unstable nutrient level, so the wastewater might have a potential threat to environment [116].

Winery effluent contains chemicals, fertilizer and pesticide residues, like phosphorus, nitrogen and phenols [117]. Furthermore, a lot of water is used to clean and sterilize winery tanks and barrels. Wine production is seasonal, so the parameters of winery wastewater vary depending on the production period [116, 118].

For the treatment of winery wastewater, solar photo-Fenton process was used. The effluent had been previously treated in membrane bioreactor operating at a winery in Limassol, Cyprus. Main parameters of winery effluent: pH = 8.2, total solids (TS) = 2010 mgL^{-1}, total suspended solids (TSS) = 8 mgL^{-1}, chemical oxygen demand (COD) = 120 mgL^{-1}, dissolved organic carbon (DOC) = 30 mgL^{-1}, total nitrogen (TN) = 4 mgL^{-1}, total phosphorous (TP) = 0.3 mgL^{-1} and soluble biochemical oxygen demand (BOD) < 5 mgL^{-1} [107].

In this study, optimal Fe^{2+} concentration was investigated at pH 3, while the initial concentration of H_2O_2 was kept at 500 mgL^{-1}. It was found that optimal concentrations of Fe^{2+} and H_2O_2 were 3 and 250 mgL^{-1}, respectively [107].

What is more, chemical oxygen demand, dissolved organic carbon, colour, toxicity and phytotoxicity were examined. Solar photo-Fenton system proved to be very effective for winery wastewaters, after 120 minutes of treatment, removal of COD, DOC and colour were 70 ± 3.3%, 53 ± 3.7% and 75 ± 2.2%, accordingly [107]. After the biological treatment, some toxic and phytotoxic components were still present in the winery effluent, but they were reduced or eliminated through solar photo-Fenton process [107].

4.1.2. Landfill leachate

Landfills are the main solution of disposing municipal solid waste in many countries all over the world because high quantities of municipal solid waste can be dumped at reasonable cost. Landfill leachate consists of complex wastewaters and is heavily contaminated, as a result, it is difficult to reach required purification degree for this kind or wastewater [119, 120].

Landfill leachate is acidic, anoxic, rich in organic acid groups and sulphate ions and with high concentrations of metal ions, like iron. Also, leachate has a very peculiar smell [120].

The parameters of the leachate produced are variable, depending on the composition of the solid waste, waste age, landfill design and operation, site hydrology and interaction of leachate with the environment [121].

Main characteristics of landfill leachate are: pH = 7.8 - 8.7, COD = 5678 mgL^{-1}, BOD_5 = 1315 mgL^{-1}, chlorides = 2951 mgL^{-1}, ammonia = 339 mgL^{-1} and BOD_5/COD = 0.23 [108].

Different advanced oxidation processes, like H_2O_2/UV, O_3/H_2O_2, modified Fenton and modified photo-Fenton processes were investigated for the treatment of landfill leachate. Modified photo-Fenton process was conducted in photoreactor where UV radiation was provided by a medium-pressure mercury lamp [108].

As seen in Table 7, optimal dose of H_2O_2 and Fe^{2+} was determined and it was 3500 and 150 mgL^{-1}, accordingly.

To summarize, modified photo-Fenton process for the treatment of landfill leachate is effective procedure because of the high COD removal. In 120 minutes, 83% of COD was removed and in 360 minutes, COD removal was 92.7%.

Comparing different systems for the treatment of landfill leachate, modified photo-Fenton process was also the most efficient. As seen in Table 8, H_2O_2/UV, O_3/H_2O_2, modified Fenton and modified photo-Fenton processes were compared.

Table 8. Landfill leachate treatments by H_2O_2/UV, O_3/H_2O_2, modified Fenton and modified photo-Fenton processes

Wastewater	**Process**	**Initial wastewater parameters mgL^{-1}**	**Initial conditions**			**Time min**	**COD removal %**	**Ref**
			pH	**H_2O_2 mgL^{-1}**	**Ferrous ions mgL^{-1}**			
Landfill leachate	H_2O_2/UV	Cl^- = 2951 N_{NH4} = 339 TKN = 797 COD = 5678 BOD_5 = 1315 pH=7.8 - 8.7	-	5000	-	120	68.9	[108]
						360	89.2	
	O_3/H_2O_2		-	2000	-	120	67.1	
						360	89.9	
	modified Fenton		3	3500	500	120	77.9	
						360	87.5	
	modified photo-Fenton		3	3500	150	120	83.0	
						360	92.7	

Optimal dose of H_2O_2 in H_2O_2/UV system was 5000 mgL^{-1} and in 120 and 360 minutes COD removal was 68.9 and 89.2%, respectively. For O_3/H_2O_2 system, optimal dosage of hydrogen peroxide was 2000 mgL^{-1}, 67.1 and 89.9% of COD was removed in 2 and 6 hours, accordingly.

Modified Fenton process was conducted at pH = 3, H_2O_2 = 3500 mgL^{-1} and Fe^{2+} = 500 mgL^{-1}. COD removal was 77.9 and 87.5% in 120 and 360 minutes, respectively. Initial conditions for modified photo-Fenton process were: pH = 3, H_2O_2 = 3500 mgL^{-1} and Fe^{2+} = 150 mgL^{-1}. Removal of COD was 83% in 120 minutes and 92.7% in 360 minutes.

Oxidation efficiency of these processes in 120 minutes can be ordered as follows: modified photo-Fenton > modified Fenton > H_2O_2/UV ~ O_3/H_2O_2.

4.1.3. Beverage industry

The beverage industry generates large amounts of wastewater effluent. Water is used as an ingredient, a cleaning source, carrier of the raw material and a principal agent for sanitizing plant work areas and machinery. Beverage industry effluents contain high concentration of organics because of the use of raw materials, like apples, grapes, sugar or oranges [122].

Biological processes are often most effective procedures for treating beverage industry effluents, but usually high concentrations of toxic or non-biodegradable compounds prevent mineralization. That is why advanced oxidation processes are used as an alternative [123]. Solar photo-Fenton system induced with/by ferrioxalates are considered as clean technology and it is environmentally friendly [124].

For the mineralization of beverage industry effluent, solar photo-Fenton process mediated by ferrioxalate complexes was used. Under selected conditions ($Fe_0 = 150$ mgL^{-1}, $H_2O_2 = 1000$ mgL^{-1} and pH=2.79) and continuous operation, removal of TOC, COD, BOD_5 and toxicity was investigated [109].

Main characteristics of the beverage industry wastewater are: pH = 5.35, TOC = 1987 mgL^{-1}, COD = 6500 mgL^{-1}, BOD_5 = 4400 mgL^{-1}, acetate = 660 mgL^{-1} and formate = 110 mgL^{-1} [109].

Experiments were conducted in a compound parabolic collector pilot plant using solar radiation. Under optimal conditions, 70.6% of TOC was removed in 55 minutes. In 125 minutes, removal of TOC was 96.6% and removal of toxicity and COD was 100%, removal of BOD_5 99.8%.

Using solar photo-Fenton system for the treatment of beverage industry wastewater is proven to be very effective, because in 2 hours almost all of TOC and BOD_5 was removed and COD and toxicity was removed completely.

4.1.4. Textile industry

Highly coloured effluents with large amounts of organic compounds are mostly created in textile industries [125]. Different pigments have changing chemical characteristics and are selected corresponding to the textile material to be dyed. That is why the composition of dyeing effluent depends on the textile produced [126].

Dyes are being upgraded all the time and replaced by even better compounds. Dye manufacturers are pressured to develop dyes that can be effectively applied using less additional chemicals, especially salt, to reduce environmental problems involving textile industry wastewaters [126]. Dyes reveal low toxicity to mammals and aquatic environment, because of that colour consents are usually applied for aesthetic and industrial reasons [127].

Textile industry is often influenced by fashion as it affects the colours and fabrics used and also the dye types. Black-dyed jeans became very trendy recently and because of that highly coloured effluent which was difficult to treat emerged in a Belgian factory [127].

The degradation of dyes and organic compounds present in acrylic, cotton and polyester dyeing wastewaters through solar photo-Fenton process was investigated in one of the studies [110]. Initial wastewater parameters are seen on Table 7.

In solar photo-Fenton process pH was adjusted to 3.5, COD, DOC and colour removal was determined. Optimal conditions for solar photo-Fenton process were: H_2O_2 = 6500 mgL^{-1}, Fe^{2+} = 113.8 mgL^{-1} for acrylic; H_2O_2 = 3750 mgL^{-1}, Fe^{2+} = 112.5 mgL^{-1} for cotton; and H_2O_2 = 938 mgL^{-1}, Fe^{2+} = 131.2 mgL^{-1} for polyester effluent.

Photo-Fenton system provided high colour removal (more than 98-99%), COD reduction was for acrylic 72%, for cotton 30.1% and for polyester 55.4%. Mineralization degree for acrylic, cotton and polyester was 71.5, 46.2 and 49.6%, respectively.

4.1.5. Hospital effluent

Hospital effluent contains a number of toxic organic substances like pharmaceuticals, solvents, radionuclides and disinfectants for medical purposes in different concentrations [128-130]. If the hospital pollutants get into aquatic ecosystem then it leads to a risk related to the existence of hazardous substances that could have harmful effects on natural environments [130].

Pollution from hospital effluent can have negative effects even at low concentrations. For example, aquatic organisms respond negatively to low concentrations of formaldehyde. Some studies have suggested that formaldehyde may be a carcinogen, so the concern over this pollutant has increased [131].

Hospital wastewater containing organochlorine mixtures in high concentrations has been reported as toxic to aquatic environment. In addition, the halogenated organic compounds adsorbable on activated carbon were found in hospital effluent [132].

In one of the studies, fluidized bed solar photo-Fenton process was used for the treatment of hospital wastewater. Experiments were carried out with silica carriers supplemented in the reactor. Chemical oxygen demand and biodegradability was investigated [111].

As seen on Table 7, characteristics of primary treated hospital wastewater are: pH = 6.4 ± 3, TSS = 590 ± 30 mgL^{-1}, BOD_3 = 200 ± 50 mgL^{-1}, COD = 1200 ± 100 mgL^{-1} and BOD_3/COD = 0.16. Initial conditions were: pH = 3, Fe^{2+} = 279 mgL^{-1} and H_2O_2 = 1700 mgL^{-1}. Under these conditions, COD removal was 98% in 90 minutes. Regarding the biodegradability, BOD_5/COD ratio increased to 0.7.

It was also observed, that COD removal efficiency was 92% in fluidized bed solar photo-Fenton system whereas COD removal in solar photo-Fenton process was 67% in 60 minutes [111].

4.1.6. Olive oil mills

Olive oil is mainly produced in Mediterranean countries like Portugal, Spain, Italy and Greece. The extraction of olive oil is achieved through pressing in traditional mills or centrifuging processes in modern units. During the extraction, the olives are grinded and pressed for separating the residual solids from emulsion of oil and vegetation waters. After that, by centrifugation the oil is separated from the vegetation waters [133].

Production of olive oil generates two by-products: a solid residue and brownish black coloured effluent from olives plus the wash water, which is called olive mill wastewater. Effluent from olive mills has high chemical and biochemical oxygen demands and it contains monomeric and polymeric phenols [133].

Different systems have been used for the treatment of olive mill wastewater. For example, incineration and distillation have been tested but they are expensive methods. Activated sludge and methanization processes are quite effective but olive mill wastewater has to be diluted or biologically or physically pre-treated. Usually, olive mill effluent needs to be treated with several biological or physical steps [133].

Photo-Fenton process has been successfully tested for the treatment of olive mill wastewater [17, 134]. Parameters of non-diluted olive oil mill wastewater are: pH = 4.0 ± 0.2, COD = 33600 ± 600 mgL^{-1} and total phenolic content = 243 ± 14 mgL^{-1}.

Iron sulfate heptahydrate and hydrogen peroxide were used as reagents with concentrations of 27900 and 300000 mgL^{-1}, respectively. pH was adjusted to 4.0. Wastewater contained following phenols: p-coumaric acid, vanillin, guaiacol, caffeic acid, vanillic acid and tyrosol. After 6 days, all the phenols were removed by 100% through photo-Fenton process [17].

Photo-Fenton process is very effective for the removal of phenols from olive oil mill wastewater. Using biological treatment by fungal species *Trametes versicolor* and *Pleurotus sajor caju* or enzymatic treatment by laccase, removal percentage between 7 and 76, while photo-Fenton process removed all the phenols in effluent.

4.1.7. Coffee effluent

Coffee effluent consists of many dark brown persistent pigments, like melanoidins, which are dark brown complex with high value of chemical oxygen demand and biochemical oxygen demand [135]. Coffee melanoidins consist of groups of ligands like polysaccharides, tannins, peptides and their mixtures [136].

Coloured coffee effluent can cause several harmful effects on the environment, for example toxicity, non-biodegradability and colour [100]. Possible negative impact on aquatic life can be caused by even very low concentrations of pigments [137].

If coffee effluent is released in aquatic environment, it cuts off the light because of the intense dark brown colour and has an impact on photosynthesis. What is more, high organic load of coffee wastewater causes eutrophication [112].

Biological treatments have been mostly used for the treatment of coffee effluents [135]. Some studies have been made in order to test photo-Fenton process for the treatment of coffee wastewater [112, 138].

Experiments with photo-Fenton system were made using black light fluorescent lamps as UV light irradiation source. According to Table 7, parameters of coffee effluent are: TOC = 2000-3000 mgL^{-1}, COD = 3000-8000 mgL^{-1} and pH = 4-7 and operation conditions were: c_0 = 240 mgL^{-1}, Fe^{2+} = 14 mgL^{-1}, H_2O_2 = 800 mgL^{-1} and pH = 3 [112].

Results of this study show that photo-Fenton system is quite efficient for the treatment of coffee effluent. After 200 minutes of UV irradiation 90% of coffee effluent was mineralized. In 210 minutes, color removal by the photo-Fenton process was 100%.

4.1.8. Cork boiling industry

More than half of the world's cork is produced in Portugal and their cork oak forest represent 32% of the world total. There are more than 800 industrial facilities employing 12,000 people in 2009 [139].

The industrial treatment of cork involves a number of steps, like: preparation of the cork barks - stabilization, boiling and flattening, production of the cork stoppers - cutting into strips, punching out the stoppers and final treatment - disinfection, drying, sorting and packing. Two types of wastewaters are created by these processes: the cork boiling and the cork bleaching wastewaters [140].

During the treatments, dark liquor in generated, containing some corkwood extracts, like pentachlorophenol, phenolic acids, tannic fraction and 2, 4, 6-trichloroanisol [141]. To remove the flavour and odour, bleaching with different chemicals, like hydrogen peroxide, sodium hydroxide and sodium peroxide, is used. As a result, chlorophenols are formed [140].

Because of the fact that cork industry effluents are toxic, partial inhibition of the biodegration is caused by some microorganisms which are very sensitive to organics, especially the polyphenolic compounds [142].

Solar photo-Fenton process was used for the treatment of cork wastewaters where cork bleaching wastewater was a source of hydrogen peroxide, as it contains significant concentration of H_2O_2. Characteristics of cork boiling wastewater: pH = 5.0 - 6.5, DOC = 763-892 mgL^{-1}, COD = 1786-2403 mgL^{-1} and BOD_5 = 320-456 mgL^{-1} (Table 7).

Optimum dose of iron was investigated and it was 60 mgL^{-1}. High concentration of iron resulted in lower energy consumption; mineralization was 91% and COD removal 98% in 28 days.

To summarize, it can be said that solar photo-Fenton system for the treatment of cork boiling wastewater is efficient method resulting in 91% mineralization and 98% COD removal.

4.1.9. Apple-juice wastewater

Food processing industry produces large amounts of wastewaters containing high concentrations of organic materials, which are often discharged into the municipal wastewater collection system [143]. This effluent contains grease, dissolved solids, oil and suspended solids [144]. Treating of this kind of wastewater can be problematic because of the low pH, imbalanced nutrients and fluctuations in the amount of effluent produced [145].

For the treatment of industrial wastewater with high organic matter content the aerobic digestion technology is often applied [146]. The anaerobic-sludge reactor was believed to be great technology for the treatment of industrial effluent but some problems have aroused due to washout biomass that leads to degradation of effluent quality [147].

Efficiency of the photo-Fenton process for treating apple-juice wastewater was investigated in one of the studies. Industrial wastewater from processing apples for juice was used in experiments [114].

Characteristics of apple-juice wastewater: TOC = 700 mgL^{-1}, COD = 1260 mgL^{-1}, BOD_5 = 801 mgL^{-1} [114].

Initial conditions of the process were: pH = 4.2, H_2O_2 = 5800 mgL^{-1} and Fe^{2+} = 40 mgL^{-1}. In 40 minutes, 91% of TOC was removed and in 120 minutes, 98% of TOC was removed and COD decreased 59% and BOD_5 decreased 68%.

4.1.10. Petroleum extraction wastewater

Large volume of aqueous waste with high salinity is produced during the offshore oil production. Effluent from oil production contains ammonium, metals, organic compounds and sulphite and it is generated on the platform when water is separated from oil [148].

Usual treatment for oil wastewater includes filtration, flotation, ionic change and adsorption in activated charcoal. Very often, the efficiency of those treatments decreases because of the high salinity of wastewater [149].

Besides the hydrocarbon classes, aromatics and polycyclic aromatic hydrocarbons (PAH) are also present in petroleum wastewater and they are main pollutants of the environment. Furthermore, they are harmful on people's health due to carcinogenic and mutagenic properties [150].

Solar photo-Fenton system was tested for the treatment of petroleum extraction wastewater. Parameters of this effluent: pH = 7.9, COD = 220 mgL^{-1}, Fe = 0.93 mgL^{-1}, Cu = 0.04 mgL^{-1}, Mn = 0.79 mgL^{-1}, Cd = 0.05 mgL^{-1}, Pb = 0.76 mgL^{-1} and Zn = 0.02 mgL^{-1}[115].

For the experiments, pH was adjusted to 3 and concentration of H_2O_2 was 16 500 mgL^{-1}. In those conditions, PAH and aromaticity removal was 92 and 96%, accordingly. COD reduction of about 53% was not high as well as 50% reduction of phytotoxicity (Table 7); however, the photo-Fenton process was very efficient in removing of carcinogenic compounds from the petroleum wastewater.

To summarize, according to the information found in the literature, photo-Fenton process has proven to be very effective method for the purification of different wastewaters. In most cases, COD, TOC and colour removal was more than 70%. Usage of photo-Fenton has also shown great results in aromaticity, phytotoxicity and toxicity removal.

4.2. Effects of operating parameters

Based on several studies, there are a number of indicators that affect the efficiency of photo-Fenton process and they must be considered when doing experiments or using it for the clarification of wastewaters.

4.2.1. Effect of pH

Fenton and photo-Fenton processes are dependent of the solution pH because of iron and hydrogen peroxide is used in this systems. Optimal pH for photo-Fenton process is considered to be around 3. If the pH is higher than 3, Fe (III) catalyst starts to precipitate [33]. pH also affects the decomposition of H_2O_2 [151]. Sulphuric acid and hydrogen peroxide are used to control the pH in photo-Fenton process [152].

Usually, neutral pH causes decomposition of hydrogen peroxide, which leads to extension of the degradation reaction. That is why acidic pH is more favourable for the decomposition of H_2O_2 and reaction between H_2O_2 and Fe^{2+}, resulting in the generation of hydroxyl radicals [153].

For the hospital wastewater, optimal pH was investigated and it was 3 according to COD and BOD_5 removal efficiencies which were 43 and 33%, respectively. Photo-Fenton process was efficient when pH was between 2 and 4 [132].

According to Table 7, for the treatment of different wastewaters pH was between 2.79 to 4.2.

4.2.2. Influence of iron and hydrogen peroxide concentration

Dosage of iron and hydrogen peroxide is important because they affect cost and removal efficiency of the photo-Fenton process [152].

When H_2O_2 or Fe^{2+} is overdosed for making enough hydroxyl radicals available for the oxidation, then the best efficiency is achieved. Mineralization is not complete if the hydrogen peroxide dosage is decreased [154].
If the H_2O_2 dosage is higher, then the degradation percentage increases [155]. Extra amount of hydrogen peroxide can cause iron sludge flotation or sedimentation [152].

Sufficient amount of Fe^{2+} is also very important because of the proper reaction initiation. Removal of COD increases when the Fe^{2+} dosage increases but this increase is marginal with certain concentrations of Fe^{2+} [155].

Higher amount of Fe^{2+} can inhibit UV radiation penetration because of the production of brown turbidity in the photo-Fenton system [156]. Through photolysis, Fe^{2+} is regenerated and due to that, the amount of Fe^{2+} can be reduced. If there is not enough H_2O_2, concentration of Fe^{2+} can increase 30% because of the photolytic regeneration [157].

It is important to determine an optimal ratio of hydrogen peroxide and iron to increase COD removal [145]. The ratio of H_2O_2 and Fe^{2+} should be as low as possible to reduce the amount of final sludge and to avoid recombination of hydroxyl radicals [156].

As the optimal ratio of hydrogen peroxide and iron depends not only on the concentration of organic contaminants, but is influenced by other constituents present in the wastewater, the hydrogen peroxide and iron dosages and the optimal ratio should be determined experimentally for every specific case.

4.2.3. Effect of temperature

Temperature has a small positive effect on the treatment efficiency in photo-Fenton process compared to the other factors. Effects of temperature have been investigated and it is been found out that temperature under 8.3°C slows down initial kinetics and affects the reaction rate. If the temperature is higher than 50°C, COD removal increases. Too low and too high temperatures usually decrease the process efficiency, so the suitable temperature is between 20 and 30°C [158].

I have not shown the temperature in Table 7 for different wastewater treatment using photo-Fenton system because in some cases the information was not available. For some wastewaters, the temperature was reported between 17 to 38°C [107, 113].

4.2.4. Contaminant concentration

Several studies have shown that if the initial contaminant concentration is higher, then the degradation of pollutant decreases. It can be said, that lower concentrations are preferred [159, 160].

Based on one article, the effect of initial chlorpyrifos concentration on the degradation efficiency was investigated. Different initial concentrations were used (COD_0: 465, 825 and 1330 mgL^{-1}). It was determined that in less than an hour COD_0 removal was 90% for 465 and 825 mgL^{-1}. Furthermore, it was found that higher concentrations take more time and need higher amount of hydrogen peroxide for the removal of COD_0 [160].

4.2.5. Reaction mixture (matrix)

Composition of the treated water is also a factor affecting the photo-Fenton process. It is known that some inorganic ions inhibit the kinetics of pollutant degradation by photo-Fenton system. Ions, such as bromide, chloride, fluoride, phosphate, etc. are either generated during the degradation of harmful compounds or part of waters [161].

Drawbacks with these ions it that less-active iron complexes are created and the reaction with ·OH radicals might generate some other less active radicals or cause precipitation of iron ions. Concentration of ions affects the kinetics of the reaction [161].

In one study, the effect of inorganic ions, for example Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, Mg^{2+}, Cu^{2+}, etc., on the photo-Fenton degradation of pesticides were investigated. It was determined that chloride and phosphate slow down the reaction, while Cu^{2+} accelerates the process [162].

5. Evaluation of the photo-Fenton process

5.1. Advantages and disadvantages of the photo-Fenton

Photo-Fenton process has proven to be very efficient for the treatment of different types of wastewaters, so the main advantages of this system are [18, 20, 33, 65, 98, 163, 164]:

- Illumination causes the cyclic regeneration of the consumed Fe^{2+} ions
- Presence of light results in generation of more hydroxyl radicals
- Generations of additional hydroxyl radicals reduce the production of iron sludge
- Small amount of ferrous salt is required
- After wastewater treatment, separation of the ferric ions is not required because of the small amount of ferrous salts
- Faster rates and a higher degree of mineralization
- No new pollutants are produced
- Remaining hydrogen peroxide that is not used in photo-Fenton process will decompose into water and molecular oxygen
- Degradation of pollutants is fast
- Effective in the degradation of different pollutants - in many cases, removal percentage is more than 75%.
- Comparing the photo-Fenton process with other AOPs, photo-Fenton is one of the cheapest

There are also some disadvantages of this process, like [165]:

- High concentration of anions in the treated wastewater

Advantages of photo-Fenton process outweigh the disadvantages, so if all things are considered, photo-Fenton system is definitely very efficient, fast and quite cheap method for treating different types of wastewater.

5.2. Cost evaluation

When selecting a wastewater treatment technology, a number of factors must be considered, for example operation, economics, regulations, effluent quality goals and economy of scale. Although they are all important things, economics is generally a priority. Economic analysis of the net present cost is often problematic and time-consuming due to number of treatment technologies that need to be evaluated [166].

One article focuses on figure-of-merit based on electrical-energy consumption because advanced oxidation processes consume a lot of electrical energy and expenses on electrical energy are often a majority of operational costs. What is more, requirements of electrical energy dosage determine the size of the capital equipment needed to generate necessary dosage of energy [166].

In this study, two figures-of-merit were presented:

- Electrical Energy per Unit Mass
- Electrical Energy per Order

Electrical Energy per Mass Unit is useful when concentration of particular organic contaminant is high. In that case, rate removal of the contaminant is proportional to electrical energy use. Electrical Energy per Order is used when concentration of organic contaminant is low [166].

Photo-Fenton process was compared to O_3, UV/O_3 and UV/H_2O_2 processes to estimate relative costs and to determine the most cost-efficient system. For the calculation, landfill leachate was used for experiments, cost per mass was used and costs for additional operations were not included. At first, cost per order was thought to be used for the calculation, but to simplify, cost per mass was used. As it was tested on laboratory scale, energy consumption of the laboratory equipment per unit wastewater used is higher than in a large scale plant [163].

Prices used for calculation are shown in Table 9. All the prices are in Austrian schillings.

Table 9. Prices of chemicals used for calculation [163]

Chemical	Price
H_2O_2 (35%)	11.60 ATS/kg
H_2SO_4	6.55 ATS/kg
$FeSO_4 \cdot 7\ H_2O$	4.50 ATS/kg
O_2	3.0 ATS/Nm^3
Electrical energy	1.56 ATS/kWh

Table 10. Cost evaluation of different AOPs for the degradation of landfill leachate (TOC_0=545 ppm) [138]

Process	Degradation time, h	TOC removal, %	Chemical costs, ATS/m^3	Energy demand, kWh/m^3	Energy costs, ATS/m^3	Total costs, ATS/m^3	Total costs, ATS/kg TOC
O_3	6	59	1440	2400	3744	5184	16122
O_3/UV	4	61	960	2400	3744	4704	14149
UV/H_2O_2	6	13	82	1200	1872	1954	27579
Photo-Fenton	2.5	60	84	500	780	864	2642

As seen from Table 10, TOC removal is about 60% for O_3, O_3/UV and photo-Fenton processes, although degradation time is 6, 4 and 2.5 hours, respectively. Chemical costs are the lowest for UV/H_2O_2 process but total costs are the cheapest for photo-Fenton process - 864 ATS/m^3 and 2642 ATS/kg TOC.

Total costs of the photo-Fenton process are about 10 times lower than costs of UV/H_2O_2 system and about 7 times lower than O_3 and O_3/UV processes. Furthermore, photo-Fenton process has the shortest degradation time, which is 2.5 hours.

ABSTRACT

As the problems concerning the lack of fresh water and water pollution have aroused, efforts for cleaner production and wastewater treatment must be made. Main water pollutants are industries producing pharmaceuticals, clothes, food, beverages, petroleum, etc. Harmful chemicals found in wastewater have negative effects on environment and on people's health.

Advanced oxidation processes are most suitable methods for the degradation of hazardous contaminants. Main characteristic of AOPs is the production of hydroxyl radicals which attack pollutants in wastewater. Variety of AOPs allows finding the best possible solution for the removal of different dangerous substances. Processes available are photocatalysis, O_3/H_2O_2, O_3/UV, H_2O_2/UV, Fenton, Fenton-like and photo-Fenton processes.

Of these processes, photo-Fenton is considered to be the most effective method, because it is one of the cheapest and fastest in degrading various chemicals found in wastewaters.

In the current thesis, photo-Fenton process for the degradation of micropollutants and purification of water was investigated. In the first chapter, Fenton oxidation chemistry, modifications and applications of the process were introduced. Photo-Fenton system, it's variations and radiation sources were expressed in the second part.

Third and fourth chapter are based on scientific articles found mostly from Sciencedirect and Scopus regarding the decomposition of different pollutants, such as pharmaceuticals and agrochemicals, and purification of wastewaters, like winery, apple-juice and petroleum extraction effluents. Furthermore, effects of operating parameters are discussed in this part of the thesis.

Photo-Fenton process has proven to be very effective for the removing pharmaceuticals, dyes and agrochemicals from wastewater. In most cases, removal percentage was over 70% and it was achieved in less than one hour.

For the purification of wastewater, photo-Fenton process is suitable for winery, landfill leachate, hospital, textile, food and cork-boiling industry and petroleum extraction effluents.

Studies show mostly high removal percentage of COD, TOC, colour, phenols, toxicity and aromaticity (>70%). Purification usually takes time 2-3 hours.

In the final part of this thesis, advantages, disadvantages and cost of this process were determined. There are a lot of benefits when applying photo-Fenton process for water purification and degradation of hazardous contaminants.

For example, more hydroxyl radicals are created with presence of light, small amount of ferrous salt is needed, higher degree of mineralization is achieved, new pollutants is not generated, degradation is fast and this process is one of the cheapest.

So, all things considered, photo-Fenton system is definitely a method that must be used for the purification of wastewaters. It is environmentally friendly, very effective and rather cheap method for the degradation of contaminants.

KOKKUVÕTE

Tänapäeval on süvenenud probleemid seoses puhta vee kättesaadavuse ja vee saastatusega. Ajal, mil inimkonna populatsioon kasvab ning maailma veevarud vähenevad, on selge, et inimeste juurdepääs puhtale veele on aina vähenemas. Veesaastet põhjustavad põllumajandus ning tööstus- ja tootmisettevõtted, kes tegelevad peamiselt ravimite, rõivaste, toiduainete, jookide ja vedelkütuste tootmise ja töötlemisega. Nendel põhjustel on hakatud mõtlema säästlikule ja keskkonnasõbralikumale tootmisele ning reovete töötlemisele ja puhastamisele.

Käesolev magistritöö käsitleb süvaoksüdatsiooniprotsesse, täpsemalt foto-Fenton protsessi kasutamist mikrosaasteainete eemaldamiseks veest ning reovee puhastamiseks.

Töö esimeses osas on lähemalt selgitatud Fenton protsessi omapära, selle modifikatsioonid ning kasutusalad. Järgmine peatükk keskendub täpsemalt foto-Fenton protsessile, sh toimuvatele reaktsioonidele, antud protsessi erikujudele ja kasutatavatele valgusallikatele. Magistritöö kolmandas osas on teadusandmebaaside põhjal toodud erinevad mikrosaasteained, mida leidub vees ning mille eemaldamiseks on kasutatud foto-Fenton protsessi.

Vaadeldud on ravimite koostisosade, tekstiilitööstuses kasutatavate värvide ja põllumajanduskemikaalide lagundamise efektiivsust, saasteaine algkontsentratsiooni, Fenton reagentide doosi ning saasteaine eemaldamiseks kulunud aega.

Eelviimases peatükis on vaadeldud erinevate reovete, nagu näiteks prügila nõrgvee, veini- ja oliiviõli tootmise reovete, puhastamist saasteainetest. Lisaks on selles osas toodud välja ka erinevad tööparameetrid, mis avaldavad mõju veetöötlemise efektiivsusele.

Foto-Fenton protsessi kasutamise eelised ja puudused ning maksumuse hinnang on välja toodud viimases peatükis, millest järeldub, et foto-Fenton protsess on erinevate saasteainete lagundamisel ja reovete puhastamisel väga efektiivne, keskkonnasõbralik ja üks odavamatest süvaoksüdatsiooniprotsessidest.

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