Advanced Oxidation Techniques as a future trend in landfill leachate treatment

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Abstract

Owing to its complexity and diversified, landfill leachate is difficult to treat to the dischargeable limits. There are many conventional techniques available and being applied to treat landfill leachate which are not proven efficient. Therefore, implementation of new techniques like advanced oxidation processes (AOP's) can be employed to attain complete degradation. Hydroxyl radicals generated from AOPs degrade the organic compounds which are highly non-biodegradable in the landfill leachate. It is well known that hydroxyl radicals are strong oxidants and highly non selective in nature. Therefore, this chapter attempts to understand the formation of landfill leachate; principle and mechanism of few AOPs like fenton, electrooxidation, electrocoagulation, ozonation, sonication and photocatalysis.

Keywords: Landfill leachate, advanced oxidation processes, fenton, electrooxidation, electrocoagulation, ozonation, sonication and photocatalysis

I. Introduction

Rapid industrialization and urbanization have led to production of huge quantities of solid waste. With the increase in the quantity, solid waste management emerged as one of the major environmental concerns in recent times [1]. Among the solid management practices, the most common methods are incineration, composting, recycling and landfilling as shown in the figure1. Over decades, landfilling has become the most applied option for solid waste management owing to its simplicity and various economic advantages in urban areas. Landfill leachate is generated by the percolation of precipitated water and various physical, chemical and biological reactions occurring in the layers of landfill which is a major drawback [2]. The leachate from the landfill have diversified characteristics which are influenced by the composition of solid waste, rainfall and soil patterns. Landfill leachate is characterized by high organic and inorganic compounds, ammonia, refractory compounds and heavy metals. The presence of these complex compounds in the environment can pose a serious threat to human health [3].

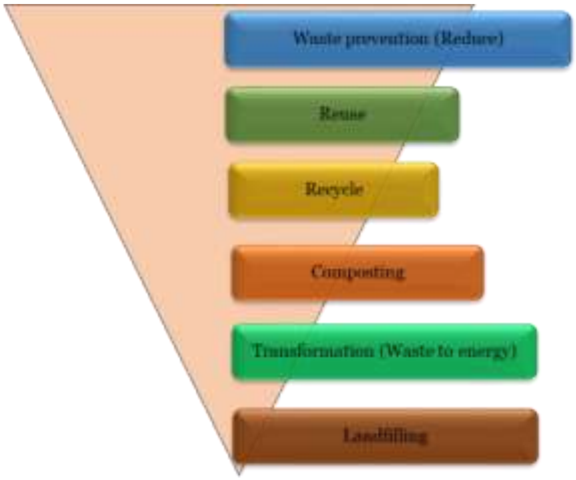

Figure 1: Solid waste management paradigm

The treatment of the landfill leachate prior to its disposal is essential inorder to comply with the stringent dischargeable standards. Therefore various treatment processes have been explored by researchers which include physical, chemical, biological techniques like aerobic and anaerobic oxidation, adsorption, air stripping, membrane filtration, ion exchange, electrochemical methods, Advanced Oxidation Processes (AOPs) and chemical precipitation and a combination of them for mature landfill leachate treatment [3]. Due to their economical simplicity and efficiency in enhancing biodegradability, biological treatment techniques (aerobic and anaerobic oxidation) were widely adopted in landfill leachate treatment [2]. However, presence of recalcitrant compounds like humic and fulvic acids in mature landfill leachate acts as a limitation to achieve desired efficiency in biological treatment. Most common physical treatment methods are adsorption, ion exchange, coagulation-flocculation and membrane filtration. Coagulation-Flocculation can be employed as pretreatment for advanced oxidation techniques and biological techniques. Adsorption and ion exchange cannot remove pollutants as they simply transfer pollutants from one stage to another, thereby causing secondary contamination. Therefore the coagulant formed or adsorbent should be further treated. Membrane techniques like micro filtration (MF), nano filtration (NF), ultra-filtration (UF) and reverse osmosis (RO) are associated with limitations like membrane fouling and cost intensiveness. Poor biodegradability of mature landfill leachate and the presence of refractory compounds may necessitate some pretreatments, advanced treatment methods, or a combination of two or more treatment techniques. Fortunately, in recent years AOPs have gained attention for rapid oxidation, no secondary pollution, generation of oxidants, high mineralization efficiency. AOPs are grounded on oxidation of organic compounds by insitu generation of strong oxidants like hydroxyl, sulfate and chlorine radicals [4]. Hydroxyl radicals ($^{\cdot}OH$) possess high oxidation potential of 2.8V after fluorine and can non-selectively degrade wide range of organic compounds [5]. The oxidation potentials of various oxidizing agents are given below in table 1 as well as figure 2. Free radicals attack the organic compounds in three different ways: (i) electrophilic addition: it refers to the generation of free radicals by the radical chain reaction after the addition of the electron. ; (ii) Dehydrogenation and (iii) electron transfer [1].

Adapting AOPs is enhanced by its radical production possibilities thereby meeting the specific treatment requirements. Hence, the focus of the research has been shifted to Advanced Oxidation Processes (AOP's) which are preferred to treat recalcitrant and complex compounds from different wastewaters.

Table 1: Oxidation potential of various common oxidants

S. No	Oxidant in AOP	Oxidation Potential (V)
1	Fluorine (F_2)	3.03
2	Hydroxyl Radicals ($OH_{\cdot}$)	2.8
3	Atomic oxygen (O)	2.42
4	Ozone (O_3)	2.07
5	Hydrogen Peroxide (H_2O_2)	1.77
6	Potassium permanganate ($KMnO_4$)	1.67
7	Chlorine dioxide (ClO_2)	1.5
8	Hypochlorous acid (ClO^-)	1.49
9	Chlorine (Cl)	1.36
10	Oxygen (O_2)	1.23
11	Bromine (Br)	1.09

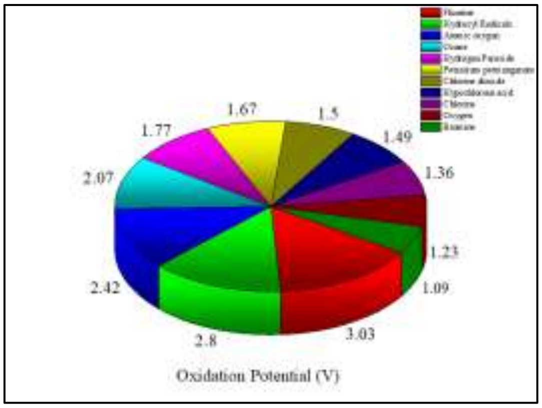

Figure 2: Graphical representation of oxidation potential of various common oxidizing agents

AOPs also provide viable solution of degradation of diversified organic compounds present in mature landfill leachate. Until now few studies have been discussed about the radical mechanism of degradation of landfill leachate in its treatment perspective. Therefore, this paper reviews the research done on application of AOPs in landfill leachate treatment processes and exploring the treatment mechanism, applicability of biological treatment after the treatment processes, application of treatment processes in bioenergy production.

A. Generation and characteristics of landfill leachate

The term “landfill leachate” refers to the liquid effluent produced by the rain water percolating through solid waste in landfill along with the moisture existing in the waste and degradation into organic products [2]. Degradation in waste matrix occurs through various chemical and biological processes in four phases: (i) Stage-I: Aerobic phase begins when the waste enters the landfill, and the aerobic reactions initiate between the microorganisms and the landfill waste with the changes in the environment by producing H_2O and CO_2; (ii) Stage-II: Transition phase begins with depletion of oxygen, resulting in the development of facultative anaerobic conditions that cause the generation of acid and a reduction in pH; (iii) Stage-III: Acidification phase starts by the degradation of waste in landfill by microorganisms which are facultative or anaerobic. The pH value drops drastically with the production of high quantities of acid by the decomposition of organic matter along with generation of H_2 gas; (iv) Stage-IV: Methanogenic phase starts with the production of intermediates in the previous stages are decomposed into CO_2 and methane with the action of methanogenic bacteria. During this process, the biodegradability of landfill decrease and a rise in pH is observed; (v) Stage-V: Mature/Stabilization phase begins with breakdown of easily biodegradable organics and conversion of recalcitrant compounds into humus. In this phase the pH is more likely to be alkaline and biodegradability of landfill remains fairly low [6].

The quantity and quality of landfill leachate is affected by precipitation, surface runoffs, groundwater percolation, evapotranspiration, compaction of layers with landfill, lining layers, water proofing layers, cover layers of landfills and age of landfill. The characteristics landfill leachate is extremely variable and heterogeneous and is entirely dependent on the degradation of waste in stages of its evolution and reactions, environmental conditions. Based on the age of landfill and 5-day Biological oxygen demand/Chemical oxygen demand (BOD_5/COD) of leachate, landfill leachate can be categorized as mature (<0.3), intermediate (0.6) and young (>0.6). Landfill leachate is composed of numerous organic and inorganic pollutants (i) Organic pollutants: humic acid (HA), fulvic acid (FA) and volatile fatty acids (VFAs) which contribute to the dark colour and foul odour of leachate and also makes it challenging to biodegrade; (ii) Inorganic pollutants: Ammonia (NH_4^+-N), chlorides, alkalinity, heavy metals, phosphorous, total nitrogen (TN), sulfates, bicarbonates and heavy metals. Some conventional characteristics of landfill leachate in order to evaluate the efficiency of leachate treatment are chemical oxygen demand (COD), biological oxygen demand (BOD), ammonia, total dissolved salts (TDS), total organic carbon (TOC) and heavy metals [6]. Different characteristics of landfill leachate based on its age are presented in the table 2.

Table 2: Characteristics of landfill leachate based on age

Parameter	Type of landfill leachate		
	Young landfill leachate	Intermediate landfill leachate	Mature landfill leachate
Age (years)	1-5	5-10	>10
pH	<6.5	6.5-8	>8
COD (mg/L)	>60,000	60,000-35,000	<35,000
BOD_5/COD	0.5-1.0	0.1-0.5	<0.1
NH_3-N (mg/L)	<400	NA	>400
TOC/COD	<0.25	0.25-0.5	>0.5
Heavy metals	Medium	Low	Low
VFA/HFA	75% VFA	5-30% VFA+HA+FA	HA+FA
Biodegradability	High	Medium	Low

Note: NA-Not Applicable, HA-Humic Acid, FA- Fulvic Acid VFA-Volatile Fatty acid.

II. Advanced Oxidation Processes (AOPs) in landfill leachate treatment

Although the AOP's are driven by the different radicals produced in the treatment processes, utilization of the radicals is also one of the most common feature [7]. Some of the commonly used AOPs include fenton, photo-catalysis, ozonation, sonication UV irradiation, hydrogen peroxide oxidation, hydrodynamic cavitation, wet air oxidation and electrochemical oxidation.

Figure 3: Representation of different AOPs applied for landfill leachate treatment

According to the reactive phase of the radicals, AOP's can be homogenous and heterogeneous [8]. The below table gives an brief idea about classification of different AOP's with their mechanisms and oxidants responsible for the reactions

Table 3: Classification of the Advanced Oxidation Processes

Classification	Type of AOP	Energy usage	Mechanism	Oxidant responsible for Advanced Oxidation

Homogenous	Classic Fenton (H_2O_2+catalyst)	No energy Usage	Coagulation of Iron	$OH^\cdot$
	Ozonation in alkaline medium		Catalytic Oxidation	$OH^\cdot$
	Ozonation+ H_2O_2		Direct Oxidation	$OH^\cdot$
	Sono-Fenton	Energy Usage	Ultra Sonic, H_2O_2 Oxidation	$OH^\cdot$, SO_4^-
	Electro-Fenton		Electrochemical oxidation, H_2O_2 Oxidation	$OH^\cdot$
	Photo-Fenton		UV photolysis, H_2O_2 Oxidation	$OH^\cdot$
	Hydrodynamic Cavitation		Cavitation	$OH^\cdot$
	Sono-electro-Fenton		Ultra Sonic, Electrochemical oxidation, Oxidation, H_2O_2 Oxidation	$OH^\cdot$, SO_4^-
	Sono-photo Fenton		Ultra Sonic, UV photolysis, H_2O_2 Oxidation	$OH^\cdot$, SO_4^-
	Sono-Photo-Electro Fenton		Ultra Sonic, UV photolysis, H_2O_2 Oxidation, Electrochemical oxidation	$OH^\cdot$, SO_4^-
	Ozonation		Direct Oxidation	$OH^\cdot$
	Ozonation+UV		Direct Oxidation, UV photolysis	$OH^\cdot$
	Ozonation+UV+ H_2O_2		Direct Oxidation, UV photolysis, H_2O_2 Oxidation	$OH^\cdot$
	Sono-Fenton+Ozonation		Ultra Sonic, H_2O_2 Oxidation, Direct Oxidation	$OH^\cdot$, SO_4^-
Heterogeneous	Electro-Fenton+ Pyrite	Energy Usage	H_2O_2 Oxidation, Catalytic Oxidation, Electrochemical oxidation	$OH^\cdot$
	Photo-Fenton+ (TiO_2, ZnO, CdS)		UV photolysis, Catalytic Oxidation	$OH^\cdot$
	Thermal Persulfate		Persulfate Oxidation	SO_4^-
	Catalytic Ozonation		Catalytic Oxidation	$OH^\cdot$
	Photo Catalytic Ozonation		UV photolysis, Direct Oxidation	$OH^\cdot$
	UV+ Persulfate		Persulfate Oxidation, UV Photolysis	SO_4^-
	H_2O_2 + (Immobilized Iron, Zero Valent Iron, Pyrite	No Energy Usage	Direct Oxidation, Coagulation of Iron	$OH^\cdot$
	Persulfate+ Fe^{+2}		Persulfate Oxidation, Coagulation of Iron	SO_4^-
	Persulfate+ $OH^\cdot$		Persulfate Oxidation	

The AOPs which are used are Fenton oxidation, electrooxidation, electrocoagulation, hydrodynamic cavitation, ozonation, plasma technique and sonication.

A. Fenton Oxidation

Fenton method was effectively applied in the treatment of organic compounds in landfill leachate. The classic Fenton mechanism is reported by following equations and along with its reaction rates are represented by Equations (1-9). Equation (1) is the classic and core of Fenton chemistry and indicates the oxidation of ferrous ions to ferric ions to decompose H_2O_2 into hydroxyl radicals [9]. This is called the chain initiation reaction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\cdot \qquad K_1=40\text{-}80\ L\ mol^{-1}\ s^{-1} \qquad (1)$$

The ferric ions produced are reduced on reacting with excess H_2O_2 and form ferrous ions and any other intermediate radicals. This reaction is slower than the first reaction which enables the regeneration of ferrous ions thereby creating a cyclic mechanism [10]. Besides ferrous ions, in the above reaction hydroperoxyl radicals are also produced which may attack the organic compounds although they are less sensitive than hydroxyl radicals. At a lower pH, hydroxyl radicals can abstract a hydrogen atom thereby initiating a radical chain oxidation reaction [11].

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\cdot} + H^+$ $K_1=9*10^{-7}L\ mol^{-1}\ s^{-1}$ (2)

In Fenton chemistry, since all the H_2O_2 is consumed and ferrous ions are regenerated from ferric ions equations (3-5) are considered as rate-limiting. Equations (6-9) depict the radical-radical reactions. The decomposition of H_2O_2 into molecular oxygen and water is shown in equation (10). The hydroxyl radicals produced can be scavenged by ferrous ions, hydrogen peroxide and hydroperoxyl radicals in equation (3), equation (7) and equation (9) [12]. Sometimes hydroxyl radicals can be auto scavenged as in equation (6). Therefore, it can be said that hydroxyl radicals can act as a radical generator as well as a scavenger.

$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^-$ $K_1=2.5\text{-}5*10^{8}L\ mol^{-1}\ s^{-1}$ (3)

$Fe^{+2}+{\cdot}O_2H \rightarrow Fe^{+3}+HO^-_2$ $K_1=0.72\text{-}1.5*10^{6}L\ mol^{-1}\ s^{-1}$ (4)

$Fe^{3+} + {\cdot}O_2H \rightarrow Fe^{2+} + O_2 + H^+$ $K_1=0.33\text{-}2.1*10^{6}L\ mol^{-1}\ s^{-1}$ (5)

$HO^{\cdot} + HO^{\cdot} \rightarrow H_2O_2$ $K_1=5\text{-}8*10^{9}L\ mol^{-1}\ s^{-1}$ (6)

$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HOO^{\cdot}$ $K_1=1.7\text{-}4.5*10^{7}L\ mol^{-1}\ s^{-1}$ (7)

$HOO^{\cdot} + HOO^{\cdot} \rightarrow H_2O+O_2$ $K_1=08\text{-}2.2*10^{6}L\ mol^{-1}\ s^{-1}$ (8)

$HO^{\cdot} + H_2O_2 \rightarrow H_2O+ O_2^{-\cdot}$ $K_1=1.4*10^{10}L\ mol^{-1}\ s^{-1}$ (9)

$2H_2O_2 \rightarrow O_2+2H_2O$ (10)

Based on the conventional fenton oxidation, with slightest of the modifications fenton like systems can be designed like photo-fenton, electro-fenton and sono-fenton [13]. The degradation of organics in fenton process depends upon the iron and peroxide dosage, pH and reaction time.

B. Ozone oxidation

Ozone (O_3) is one of the strongest oxidant with an oxidation potential of 2.07V. Direct ozone oxidation is a highly selective mechanism with the rate constants of 1.0×10^{0}–$10^{3}M^{-1}\ s^{-1}$. Ozone reacts with ionized and disintegrated form of organic compounds rather than in their neutral form in this mechanism [14]. As for the instability of ozone, intermediate radicals like hydroxyl radicals are produced to initiate non- selective degradation. The overall mechanism involves is given below:

$3O_3 + H_2O \rightarrow 4O_2 + 2OH^{\cdot}$ (11)

With the presence of other radicals, degradation of organics by the hydroxyl radical can be improved critically. For instance, if clubbed with peroxide, the hydroxyl radical production in increased hydroperoxide (HO^{2-}) which is produced by the decomposition of hydrogen peroxide [15].

$H_2O_2 \rightarrow H^+ + HO_2^-$ (12)

$HO_2^- + O_3 \rightarrow OH^{\cdot} + O_2 + O_2^-$ (13)

In the process of UV irradiation, hydrogen peroxide is generated as an added oxidizing agent through ozone photolysis [13].

$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2$ (14)

$H_2O_2 + hv \rightarrow 2OH^{\cdot}$ (15)

The ozone related treatment processes for organics degradation depends upon dosage of ozone, reaction time, pH and biodegradability of the landfill leachate [16].

C. Electro-Oxidation

Electro-oxidation (EO) is one of the widely applied AOP technique in treatment of landfill leachate [17]. EO reactor consists of two electrodes namely, cathode and anode which are connected by a DC power supply unit [11]. The oxidation reactions occur by adjusting the voltage, electrode distance, electrolyte concentration and electrode material. EO has two different approaches which are i.) Direct oxidation and ii.) Indirect oxidation. Direct oxidation occurs through mediator and indirect oxidation occurs on the surface of the anode. In indirect oxidation, species like H_2O_2, ozone, hypochlorite ions, chlorine and some metal mediators are generated which are responsible for oxidation in EO [18]. In direct oxidation, the electrochemical reaction involves chemisorption of oxygen in the oxide lattice and active oxygen as hydroxyl radical is physisorbed.

$MO_x + H_2 \rightarrow MO_x(OH) + H^+ + e^-$ (16)
$MO_x(OH) \rightarrow MO_{x+1} + H^+ + e^-$ (17)
$MO_x(OH) \rightarrow \frac{1}{2} O_2 + MO_x + H^+ + e^-$ (18)
$MO_{x+1} \rightarrow \frac{1}{2} O_2 + MO_x$ (19)
$2Cl^- \rightarrow Cl_2 + 2e^-$ (20)
$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$ (21)
$HOCl \rightarrow H^+ + ClO^-$ (22)

The most prevalent reaction in landfill leachate is indirect oxidation which involves chloride and hypochlorite ions from chlorine present in the leachate at the anodic side. Along with this indirect oxidation, some pollutants in the leachate can be oxidized by direct oxidation [18]. Hypochlorite ions are highly oxidant in nature.

The recalcitrant organics are converted into intermediates, water and CO_2 by the process of mineralization [19]. In order to increase the oxidation reactions, voltage shall be adjusted according to the degradation efficiency. Along with voltage, electrode material selection also alters the degradation efficiency [20-22]. Based on the electrical conductivity, electrolyte can be added to enhance the conductivity of the leachate [22]. EO have been applied for degradation of different non-biodegradable pollutants like pesticides, textile dyes, bulk drug, active pharma pollutants and synthetic compounds. [16, 23]. Owing to the high operational costs, EO is often combined with biological and other AOPs to enhance the degradation of the leachate [24, 25]

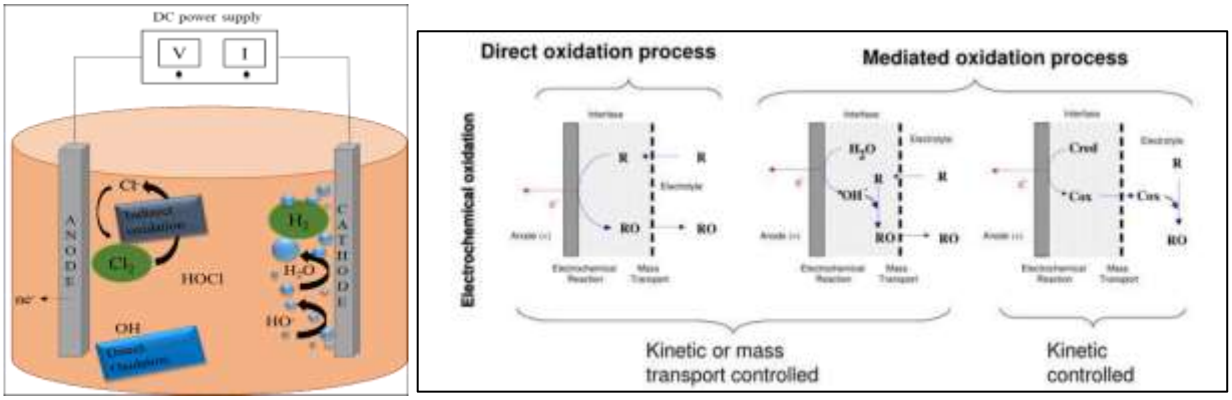

Figure 4a. Electrooxidation mechanism representation; 4b.Mechanism of hydroxyl radicals

Many studies have been carried out to degrade organic compounds from different wastewaters like textile effluent, landfill leachate, pharmaceutical effluents which has shown COD removal efficiency of 86%, 90% and 75% respectively [26-29]. Extensive research is still being carry out the electrochemical treatment process with different electrodes, current density, pH and reaction time [17].

D. Electro Coagulation

Electrocoagulation (EC) is a rapidly growing electrochemical technique which can be used for landfill leachate treatment. It involves the principle of coagulation which is induced by external electric energy along with metal electrodes. Ions or colloidal which are mostly organic and inorganic in nature are retained in the solution by their electric charges [30]. To these charges ions, addition of opposite charge ions will destabilize the colloids and allow them to coagulate [31].

Electrodes used in the EC process usually sacrifice the ions and allow the coagulation process to occur. The most commonly used electrodes are aluminum and iron. On the application of electric current, the cations dissolve from the sacrificial anodes will react with the colloidal and charges ions and form coagulated particles [32-33].

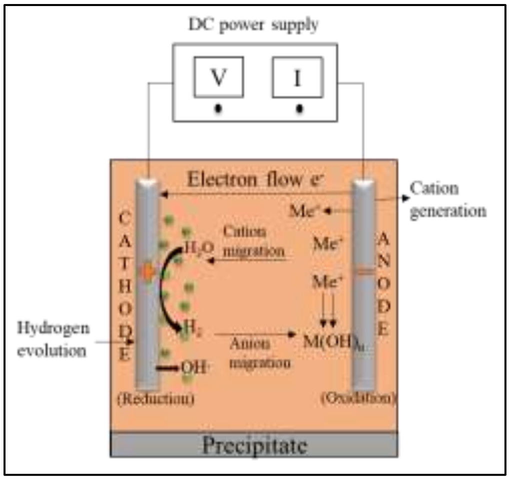

Figure 5: Mechanism of Electro coagulation

At anode:

$$M_{(solid)} \rightarrow M^{n+}_{(aqueous)} + ne^{-} \tag{23}$$
$$2H_2O_{(liquid)} \rightarrow 4H^{+}_{(aqueous)} + O_2(g) + 4e^{-} \tag{24}$$

At cathode:

$$M^{n+}_{(aqueous)} + n\,e^{-} \rightarrow M_{(solid)} \tag{25}$$
$$2H_2O_{(liquid)} + 2e^{-} \rightarrow 2OH^{-} + H_{2\,(gas)} \tag{26}$$

In solution:

$$M^{n+}_{(aqueous)} + n\,OH^{-} \rightarrow M(OH)_{n\,(solid)} \tag{27}$$

Metal ions reacts further with hydroxides and form orimary hydroxides like poly-hydroxides and polyhydroxy metal flocs when electric current is applied [26, 34]. However, various operating parameters like pH, electrical conductivity of the leachate, inner electrode distance, shape of the electrode, cell geometry, reaction time and arrangement of the electrode effect the degradation efficiency [29].

E. Photocatalysis

The main principle of photocatalysis water splitting (PWS) is based on the liberation of photo- excited charge carriers. Photocatalytic process are very efficient methods for destruction and mineralization of recalcitrant organic compounds and simultaneous hydrogen production in wastewater [35, 36]. These ideal processes when coupled with landfill leachate treatment with simultaneous energy recovery such as hydrogen production together can be termed as sustainable wastewater treatment. In the recent years, there is an increasing of urbanization and industrialization to generate wastewater and landfill leachate effluents and scientific community about the recalcitrant compounds in wastewater because of their toxicity and persistent nature to the environment. Landfill leachate usually composes of recalcitrant organic compounds, ammonia content, organic acids, pesticide compounds, high dissolved salts, heavy metals, benzene, phenols and phthalates [37, 38]. Through this photocatalysis process, the toxic compounds can be degraded and the treated effluent also will be free from toxic compounds and energy recovery

In recent years every developmental activity moving towards sustainable environment concern. The present photocatalysis (UV/TiO_2, UVTiO_2 /AC and UV/ZnO) for treating toxic effluents and producing clean energy. Briefly, PWS is a promising and emerging technique to convert UV energy into storable chemical energy. It is advantageous over other AOPs owing to its high efficiency, economic, environmental friendly and high safety. Development of highly efficient and precise photochemical system is desirable in order to meet the rising energy demands [39-40].

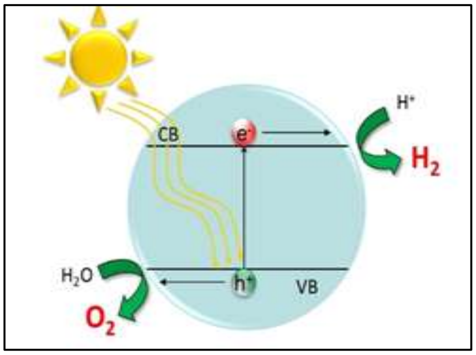

Figure 6: Mechanism of Photocatalysis

F. Sonication

Sonication is principle on the basis of acoustic cavitation in which bubble formation, its growth and collapse of the bubble occurs in the landfill leachate. The energy is diffused and it is enhanced by the cavitation occurring afterwards [42]. Progressive and depressive pressures are exerted on the leachate by expansion and compression cycles by the waves of ultrasound respectively [15]. The high negative pressure when applied on the leachate, the average molecule distance exceed the critical molecule distance which is necessary to uphold the leachate intact. The voids and cavities will be created in the breakdown of the leachate and cavitation bubbles are formed [18]. The so created negative pressure acts against the tensile strength of the leachate which partially depends on the type of the leachate. Pure water requires 1000atm of negative pressure for cavitation whereas tap water and surface water required only a few atmospheres for the bubble formation [5].

Once produced, these cavities, voids, or bubbles may grow in size until the maximum of the negative pressure has been reached [43]. Figure 7a shows the formation and growth of the bubble for cavitation. Heat is generated inside the cavity when gas and vapors are compressed which finally produces a hot spot which is short lived. This mechanism is shown in Figure 7b. The cavitation collapse produces the situation for a chemical reaction which creates enormous temperature and pressure [44].

Sonochemical effects in water are the result of complex physical phenomena that have not yet been fully understood. The gas and vapor-filled interior of the cavitation bubble is the location where water molecules are brought to an excited state and dissociate, regardless of whether the causes of the molecular activation are thermal, electrical, or a mix of the two [18].

When the water saturated with air, the reactions involve the cleavage of oxygen and water molecules:

$$H_2O \rightarrow H^{\bullet} + {}^{\bullet}OH \qquad (28)$$

$$O_2 \rightarrow 2\,O^{\cdot} \qquad (29)$$

The so generated radicals club in different ways and react with vapor and nitrogen present inside the cavitation bubble or inside the outer shell which is surrounded by the cavity. This ultimately lead to production of nitric acid, nitrous acid and hydrogen peroxide with the following reactions:

$$H^{\bullet} + {}^{\bullet}OH \rightarrow H_2O \qquad (30)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow O + H_2O \qquad (31)$$

$$O + H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \qquad (32)$$

$$H^{\bullet} + O_2 \rightarrow HOO^{\bullet} \qquad (33)$$

$${}^{\bullet}OH + N_2 \rightarrow N_2O \rightarrow NO_2^-, NO_3^- \qquad (34)$$

$$O + N_2 \rightarrow N_2O, NO, N \rightarrow NO_2^-, NO_3^- \qquad (35)$$

$$H^{\bullet} + O \rightarrow {}^{\bullet}OH + O \qquad (36)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \qquad (37)$$

$${}^{\bullet}OOH + {}^{\bullet}OOH \rightarrow H_2O_2 + O_2 \qquad (38)$$

A huge cocktail of radicals will be generated during sonication when the hydrogen form water. Once the production of radicals with recombination, they react with gas species or diffuse into an aqueous phase [44].

$$^{\bullet}OH + \text{other species} \rightarrow \text{oxidized products} \tag{39}$$

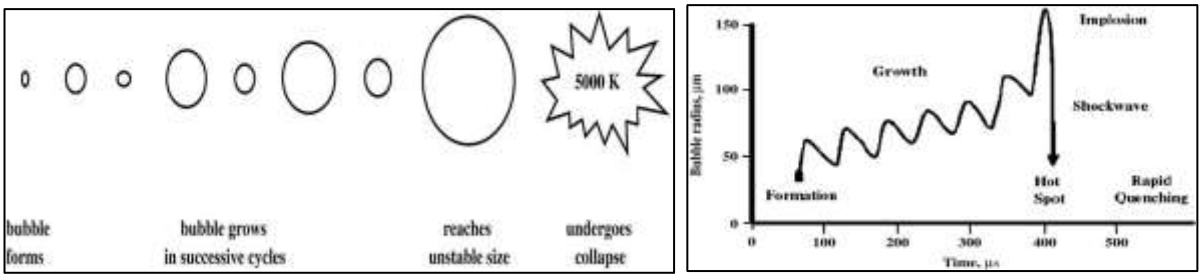

Figure 7a. Mechanism involving the formation and collapse of cavitation bubble; 7b. Schematic representation of implosion after the growth of the bubble

Due to the quick breakdown of chemical pollutants in water, ultrasonic irradiation has attracted a lot of interest as an accelerated oxidation process (AOP). Compared to AOPs mediated by UV light, sonolysis has a clear advantage since ultrasound is easily transferred even through opaque systems. Sonication produces highly oxidising •OH radicals that are identical to those created by other AOPs. Liquid reaction mixes exposed to ultrasonic radiation experience cavitations, a phenomenon in which the radii of pre-existing gas cavities oscillate in a pressure field that is regularly changing due to the ultrasonic waves. In water, ultrasonic vibrations cause cavitation bubbles to burst and cause the synthesis of reactive chemical species such H, $^{\bullet}OH$, O, and H_2O_2. The degradation of chemical pollutants in solution is caused by these reactive species.

G. Plasma based AOPs

Plasma, an extraordinary state of matter characterized by charged particles like ions and electrons displaying collective behavior, plays a vital role in water treatment by generating highly reactive species known as reactive species. These species, identifiable by their unpaired electrons, exhibit remarkable reactivity, making plasma a valuable tool in water purification. The generation of plasma involves applying an electric field to a gas, leading to ionization and plasma formation. This process can take various forms, including dielectric barrier discharge (DBD), corona discharge, gliding arc discharge, and atmospheric pressure plasma jets (APPJs). The nature of these processes varies depending on the discharge type and input energy. These processes encompass the generation of an electric field, the emission of ultraviolet radiation, the creation of overpressure shock waves, and, notably, the formation of diverse reactive chemical species, including radicals (such as $OH^{\bullet}$, $H^{\bullet}$, $O^{\bullet}$) and molecular species (like H_2O_2, H_2, O_3), which play a significant role [45]. The generation of species depends on the type of gas utilized for plasma formation. These reactive species play a pivotal role in oxidizing and breaking down persistent emerging contaminants. Plasma-based water treatment has demonstrated its effectiveness in removing a wide range of contaminants from water, including dyes and antibiotics. The simple schematic of the plasma configuration is given in the Figure 8.

Numerous studies have demonstrated the effectiveness of plasma-based water treatment in removing various contaminants within relatively short exposure times. For example, Aziz et al. investigated the degradation of dichlorophenol using a DBD falling film reactor, achieving a degradation efficiency exceeding 99% in just 15 minutes at an operating power of 150 W [46]. Meropoulis et al. employed double dielectric nano-pulsed plasma to degrade orange II, achieving a removal efficiency of over 99% in 20 minutes at an applied voltage of 31 kV [47]. Similarly, Hafeez et al. studied the degradation of reactive black-5 using a corona-plasma reactor, obtaining a removal efficiency of 98% in 16 minutes with an applied voltage of 5 kV [48].

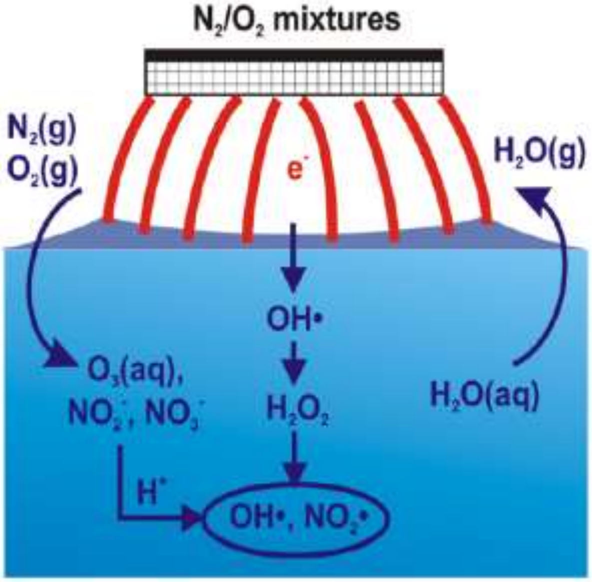

Figure 8: The schematic of plasma and its species generation. The image is reprinted from the literature [49].

Furthermore, Allabakshi et al. explored surface dielectric barrier discharge (SDBD) as an energy-efficient and scalable alternative for treating dye wastewater [50].

These studies collectively underscore the potential of plasma technology in rapidly removing a wide range of pollutants from water, making it a promising approach for efficient water purification. However, it's essential to acknowledge that plasma-based water treatment does have its drawbacks, including high energy consumption, the need for specialized equipment, and the potential for the formation of harmful byproducts. Nevertheless, these challenges do not diminish its promise as a technology for mitigating water pollution. Future research efforts should focus on developing large-scale plasma-based water treatment systems that can adapt to new contaminants, reduce energy consumption, and tailor chemistry to meet site-specific requirements.

III. Conclusion

Landfill leachate which is generated by dumping of municipal solid waste in landfills pose great environmental threat when discharged prior treatment. The type of treatment requires to be applied depends upon the characteristics of landfill leachate and its biodegradability. This chapter mainly summarize on i) the formation and characteristics of landfill leachate ii) the advanced oxidation processes like fenton oxidation, electrooxidation, electrocoagulation, ozonation, sonication and photocatalysis iii) understanding their principles.

IV. References

1. Oturan, M. A., & Aaron, J. J. (2014). Advanced oxidation processes in water/wastewater treatment: principles and applications. A review. *Critical Reviews in Environmental Science and Technology*, *44*(23), 2577-2641.
2. Gautam, P., Kumar, S., & Lokhandwala, S. (2019). Advanced oxidation processes for treatment of leachate from hazardous waste landfill: A critical review. *Journal of Cleaner Production*, *237*, 117639.
3. Vogelpohl, A., & Kim, S. M. (2004). Advanced oxidation processes (AOPs) in wastewater treatment. *Journal of Industrial and Engineering Chemistry*, *10*(1), 33-40.
4. Deng, Y., & Zhao, R. (2015). Advanced oxidation processes (AOPs) in wastewater treatment. *Current Pollution Reports*, *1*, 167-176.
5. Manna, M., & Sen, S. (2023). Advanced oxidation process: a sustainable technology for treating refractory organic compounds present in industrial wastewater. *Environmental Science and Pollution Research*, *30*(10), 25477-25505.
6. Luo, H., Zeng, Y., Cheng, Y., He, D., & Pan, X. (2020). Recent advances in municipal landfill leachate: A review focusing on its characteristics, treatment, and toxicity assessment. *Science of the Total Environment*, *703*, 135468.
7. Ma, D., Yi, H., Lai, C., Liu, X., Huo, X., An, Z., ... & Yang, L. (2021). Critical review of advanced oxidation processes in organic wastewater treatment. *Chemosphere*, *275*, 130104.
8. Golwala, H., Saha, B., Zhang, X., Bolyard, S. C., He, Z., Novak, J. T., ... & Iskander, S. M. (2022). Advancement and challenges in municipal landfill leachate treatment–the path forward!. *ACS ES&T Water*, *2*(8), 1289-1300.

9. Bagal, M. V., & Gogate, P. R. (2014). Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review. *Ultrasonics sonochemistry*, *21*(1), 1-14.
10. Sillanpää, M., Ncibi, M. C., & Matilainen, A. (2018). Advanced oxidation processes for the removal of natural organic matter from drinking water sources: A comprehensive review. *Journal of environmental management*, *208*, 56-76.
11. Chaturvedi, N. K., & Katoch, S. S. (2020). Effect of various parameters during degradation of toxic p-anisidine by Fenton's oxidation. *Applied Water Science*, *10*(1), 1-6.
12. Duan, X., Zhou, X., Wang, R., Wang, S., Ren, N. Q., & Ho, S. H. (2021). Advanced oxidation processes for water disinfection: Features, mechanisms and prospects. *Chemical Engineering Journal*, *409*, 128207.
13. Babuponnusami, A., & Muthukumar, K. (2013). Treatment of phenol-containing wastewater by photoelectro-Fenton method using supported nanoscale zero-valent iron. *Environmental Science and Pollution Research*, *20*, 1596-1605.
14. Ikhlaq, A., Brown, D. R., & Kasprzyk-Hordern, B. (2014). Catalytic ozonation for the removal of organic contaminants in water on ZSM-5 zeolites. *Applied Catalysis B: Environmental*, *154*, 110-122.
15. Bhagawan, D., Poodari, S., Chaitanya, N., Ravi, S., Rani, Y. M., Himabindu, V., & Vidyavathi, S. (2017). Industrial solid waste landfill leachate treatment using electrocoagulation and biological methods. *Desalin Water Treat*, *68*, 137-142.
16. Haapea, P., Korhonen, S., & Tuhkanen, T. (2002). Treatment of industrial landfill leachates by chemical and biological methods: ozonation, ozonation+ hydrogen peroxide, hydrogen peroxide and biological post-treatment for ozonated water. *Ozone: science & engineering*, *24*(5), 369-378.
17. Lavudya, S., Bhagawan, D., Panga, K. K., Golla, S., Saranga, V. K., & Himabindu, V. (2023). Treatment of landfill leachate using advanced oxidation process and struvite precipitation processes. *Materials Today: Proceedings*, *76*, 206-211.
18. Akinapally, S., Dheeravath, B., Panga, K. K., Saranga, V. K., Golla, S., Vurimindi, H., & Sanaga, S. (2021). Treatment of pesticide intermediate industrial wastewater using different advanced treatment processes. *Sustainable Water Resources Management*, *7*(5), 74.
19. Akinapally, S., Dheeravath, B., Panga, K. K., Vurimindi, H., & Sanaga, S. (2021). Treatment of pesticide intermediate industrial wastewater using hybrid methodologies. *Applied Water Science*, *11*, 1-7.
20. Bhagawan, D., Saritha, P., Shankaraiah, G., & Himabindu, V. (2019). Fluoride removal from groundwater using hybrid cylindrical electrocoagulation reactor. *Journal of Water Chemistry and Technology*, *41*, 164-169.
21. Panizza, Marco; Cerisola, Giacomo (2009). "Direct And Mediated Anodic Oxidation of Organic Pollutants". Chemical Reviews.
22. Anglada, Ángela; Urtiaga, Ane; Ortiz, Inmaculada (2009). "Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications". *Journal of Chemical Technology & Biotechnology.*
23. Särkkä, Heikki; Bhatnagar, Amit; Sillanpää, Mika (2015). "Recent developments of electro-oxidation in water treatment — A review". *Journal of Electroanalytical Chemistry.*
24. Sato, Yugo; Zeng, Qian; Meng, Liao; Chen, Guanghao (March2021). "Importance of Combined Electrochemical Process Sequence and Electrode Arrangements: A Lab-scale Trial of Real Reverse Osmosis LandfillLeachate Concentrate"
25. Panizza, Marco; Cerisola, Giacomo (2009). "Direct And Mediated Anodic Oxidation of Organic Pollutants"
26. Tanwi Priya, ... Majeti Narasimha Vara Prasad, in Disinfection By-products in Drinking Water, 2020.
27. Ebba, Million, Perumal Asaithambi, and Esayas Alemayehu. "Investigation on operating parameters and cost using an electrocoagulation process for wastewater treatment." *Applied Water Science* 11 (2021).
28. Karatas, Okan, et al. "Perfluorooctanoic acid (PFOA) removal from real landfill leachate wastewater and simulated soil leachate by electrochemical oxidation process." *Environmental Technology & Innovation* 28 (2022).
29. Pinto, Cláudia, et al. "Reuse of textile dyeing wastewater treated by electrooxidation." *Water* 14.7 (2022).
30. Can, Orhan Taner, Leyla Gazigil, and Ramazan Keyikoglu. "Treatment of intermediate landfill leachate using different anode materials in electrooxidation process." *Environmental progress & sustainable energy* 41.1 (2022).
31. Vicente, Carolina, et al. "Electrocoagulation treatment of furniture industry wastewater." *Chemosphere* 328 (2023)
32. Karimi, Niloufar, et al. "Sequential application of aerated electrocoagulation and γ-Fe2O3 nanoparticle adsorption for COD removal: Consuming the least amount of energy and economic evaluation." *Results in Engineering* 17 (2023).
33. Louhichi, Boulbaba, et al. "Treatment of textile industry effluents by Electro-Coagulation and Electro-Fenton processes using solar energy: A comparative study." *Chemical Engineering Journal* 427 (2022).
34. Shijun Ma, ChuanbinZhou JingjinPan, GuangYang ChuanlianSun YijieLiu, Xinchuang Chen, ZhilanZhao, Leachate from municipal solid waste landfills in a global perspective: Characteristics, influential factors and environmental risks, Journal of Cleaner Production, Volume 333, 20 January 2022, 130234. https://doi.org/10.1016/j.jclepro.2021.130234
35. Lindamulla, L., Nanayakkara, N., Othman, M. Municipal Solid Waste Landfill Leachate Characteristics and Their Treatment Options in Tropical Countries. Curr Pollution Rep 8, 273–287 (2022). https://doi.org/10.1007/s40726-022-00222-x
36. Sankar Sekar, Sejoon Lee, Preethi Vijayarengan , Kaliyappan Mohan Kalirajan ,Thirumavalavan Santhakumar , Saravanan Sekar and Sutha Sadhasivam Upcycling of Wastewater via Effective Photocatalytic Hydrogen Production Using MnO2 Nanoparticles—Decorated Activated Carbon Nanoflakes, Nanomaterials 2020, 10, 1610; doi:10.3390/nano10081610
37. Tao Yan, Qianqian Yang, Rui Feng, Xiang Ren, Yanxia Zhao, Meng Sun, Liangguo Yan, Qin Wei, Highly effective visible-photocatalytic hydrogen evolution and simultaneous organic pollutant degradation over an urchin-like oxygen-doped MoS2/ZnIn2S4 composite, Front. Environ. Sci. Eng. 2022, 16(10): 131 https://doi.org/10.1007/s11783-022-1566-z
38. Yaoyao Wu, Yuqiong Li, Hejing Hu, Guoshen Zeng, and Chuanhao Li, Recovering Hydrogen Energy from Photocatalytic Treatment of Pharmaceutical-Contaminated Water Using Co3O4 Modified {001}/ {101}-TiO2 Nanosheets, ACS EST Engg. 2021, 1, 603−611
39. M. Sumon Reza, Nurnazurah Binti Haji Ahmad, Shammya Afroze, Juntakan Taweekun,* Mohsen Sharifpur, Abul Kalam Azad,Hydrogen Production from Water Splitting through Photocatalytic Activity of Carbon-Based Materials, Chem. Eng. Technol. 2022, 45, No. 00, 1–1.
40. Yunlong Zhou, Dongyao Lin, Xiaoyuan Ye, and Bo Sun,Reuse of Acid-treated Waste Corn Straw for Photocatalytic Hydrogen Production, ChemistrySelect, 2022, 7, e202201596 (1 of 9), doi.org/10.1002/slct.202201596
41. Sankar Sekar, Sejoon Lee, Preethi Vijayarengan , Kaliyappan Mohan Kalirajan ,Thirumavalavan Santhakumar , Saravanan Sekar and Sutha Sadhasivam Upcycling of Wastewater via Effective Photocatalytic Hydrogen Production Using MnO2 Nanoparticles—Decorated Activated Carbon Nanoflakes, Nanomaterials 2020, 10, 1610; doi:10.3390/nano10081610
42. Drijvers, D., Van Langenhove, H., & Herrygers, V. (2000). Sonolysis of fluoro-, chloro-, bromo-and iodobenzene: a comparative study. *Ultrasonics sonochemistry*, *7*(2), 87-95.
43. Fedorov, K., Plata-Gryl, M., Khan, J. A., & Boczkaj, G. (2020). Ultrasound-assisted heterogeneous activation of persulfate and peroxymonosulfate by asphaltenes for the degradation of BTEX in water. *Journal of Hazardous Materials*, *397*, 122804.

44. Gągol, M., Przyjazny, A., & Boczkaj, G. (2018). Wastewater treatment by means of advanced oxidation processes based on cavitation–a review. *Chemical Engineering Journal*, *338*, 599-627.
45. S.M. Allabakshi, P.S.N.S.R. Srikar, R.K. Gangwar, S.M. Maliyekkal, Application of Plasma-Assisted Advanced Oxidation Processes for Removal of Emerging Contaminants in Water, in: S. P. Singh, A.K. Agarwal, T. Gupta, S.M. Maliyekkal (Eds.), New Trends Emerg. Environ. Contam. Energy, Environ. Sustain., Springer, Singapore, 2022: pp. 333–370. https://doi.org/10.1007/978-981-16-8367-1_15
46. K.H. Hama Aziz, H. Miessner, S. Mueller, A. Mahyar, D. Kalass, D. Moeller, I. Khorshid, M.A.M. Rashid, Comparative study on 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenol removal from aqueous solutions via ozonation, photocatalysis and non-thermal plasma using a planar falling film reactor, J. Hazard. Mater. 343 (2018) 107–115. https://doi.org/10.1016/J.JHAZMAT.2017.09.025.
47. S. Meropoulis, G. Rassias, V. Bekiari, C.A. Aggelopoulos, Structure-Degradation efficiency studies in the remediation of aqueous solutions of dyes using nanosecond-pulsed DBD plasma, Sep. Purif. Technol. 274 (2021) 119031. https://doi.org/10.1016/j.seppur.2021.119031
48. A. Hafeez, F. Javed, T. Fazal, N. Shezad, U. e. S. Amjad, M.S. ur Rehman, F. Rehman, Intensification of ozone generation and degradation of azo dye in non-thermal hybrid corona-DBD plasma micro-reactor, Chem. Eng. Process. - Process Intensif. 159 (2021) 108205. https://doi.org/10.1016/j.cep.2020.108205.
49. IPP, Electrical Discharges in Liquids and Gas/Liquid Environment, (2023). https://www.ipp.cas.cz/vedecka_struktura_ufp/Plasma_Chemistry_Materials/impulsni_plazmove_systemy/vyzkumna_temata/vyboje_ve_vode/index.html (accessed September 20, 2023).
50. S.M. Allabakshi, P.S.N.S.R. Srikar, R. Kumar Gangwar, S.M. Maliyekkal, Feasibility of surface dielectric barrier discharge in wastewater treatment: Spectroscopic modeling, diagnostic, and dye mineralization, Sep. Purif. Technol. 296 (2022) 121344. https://doi.org/10.1016/j.seppur.2022.121344.