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].

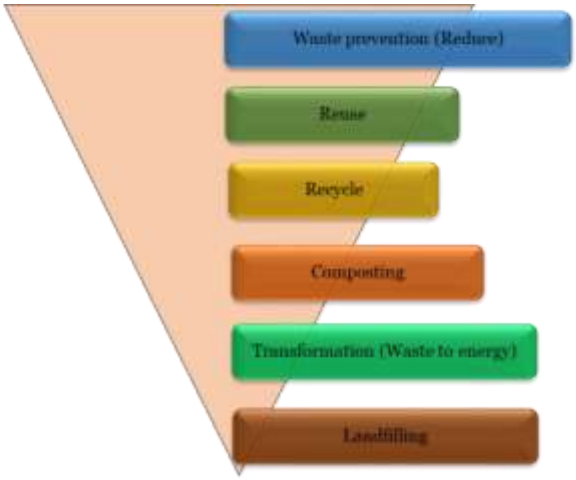

Figure 1: Solid waste management paradigm

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 (·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	3.03
2	Hydroxyl Radicals	2.8
3	Atomic oxygen	2.42
4	Ozone	2.07
5	Hydrogen Peroxide	1.77
6	Potassium permanganate	1.67
7	Chlorine dioxide	1.5
8	Hypochlorous acid	1.49
9	Chlorine	1.36
10	Oxygen	1.23
11	Bromine	1.09

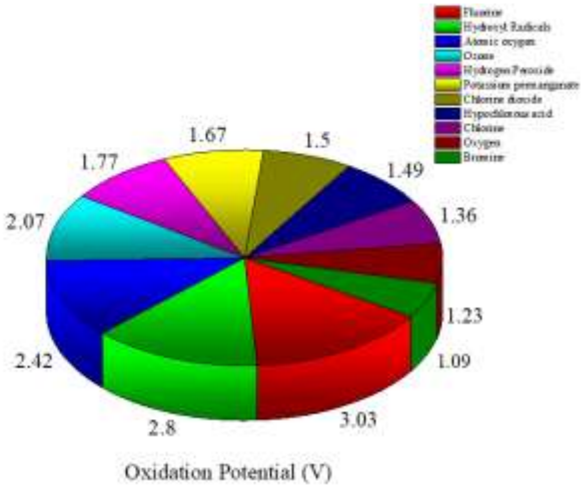

Figure 2: Graphical representation of oxidation potential of various common oxidizing agents

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^-
Heterogenous	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 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.

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

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 selective mechanism with rate constants of $1.0\times10^{0}–10^{3} M^{-1}\ s^{-1}$ in which ozone reacts with ionized and disintegrated form of organic compounds rather than in their neutral form [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:

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

In the presence of other radicals, the degradation 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].

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

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

In UV irradiation, hydrogen peroxide is generated as an additional 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), also known as anodic oxidation or electrochemical oxidation, is a technique used for wastewater treatment, mainly for industrial effluents, and is a type of advanced oxidation process (AOP) [17].

The most general layout comprises two electrodes, operating as anode and cathode, connected to a power source. When an energy input and sufficient supporting electrolyte are provided to the system, strong oxidizing species are formed, which interact with the contaminants and degrade them [18]. The refractory compounds are thus converted into reaction intermediates and, ultimately, into water and CO_2 by complete mineralization [19]. To assure a reasonable rate of generation of radicals, voltage is adjusted. While the cathodes materials are mostly the same in all cases, the anodes can vary greatly according to the application, as the reaction mechanism is strongly influenced by the material selection. Cathodes are mostly made up by stainless steel plates, Platinum mesh or carbon felt electrodes [20].

Electro-oxidation has recently grown in popularity thanks to its ease of set-up and effectiveness intreating harmful and recalcitrant organic pollutants, which are typically difficult to degrade with conventional wastewater remediation processes [11]. Also, it does not require any external addition of chemicals, as the required reactive species are generated at the anode surface [22]. Depending on the effluent nature, an increase of the conductivity of the solution may be required. Salts like sodium chloride or sodium sulphate can be added to the solution, acting as electrolytes, thus raising the conductivity.

Electro-oxidation has been applied to treat a wide variety of harmful and non-biodegradable contaminants, including aromatics, pesticides, drugs and dyes. Due to its relatively high operating costs, it is often combined with other technologies, such as biological remediation [16]. It can additionally be paired with other electrochemical technologies suchas electrocoagulation, consecutively or simultaneously, to further reduce operational costs while achieving high degradation standards [23].

Direct oxidation

When voltage is applied to the electrodes, intermediates of oxygen evolution are formed near the anode, notably hydroxyl radicals. Hydroxyl radicals are known to have one of the highest redox potentials, allowing the degrading many refractory organic compounds [24]. A reaction mechanism has been proposed for the formation of the hydroxyl radical at the anodethrough oxidation of water. The radical species can interact with the contaminants through two different reaction mechanisms,according to the anode material, Where R is the generic organic compound, while RO is the partially oxidized product [25].

Mediate Oxidation

When appropriate oxidizing agents are dissolved into the solution, the electro-oxidationprocess not only leads to organics oxidation at the electrode surface, but it also promotes the formation of other oxidant species within the solution [26]. Such oxidizing chemicals are not bound to the anode surface and can extend the oxidation process to the entire bulk of the system. Chlorides are the most widespread species for the mediated oxidation. This is due to the chlorides being very common in most landfill leachate and being easily converted into hypochlorite, according to global reaction [17,27,28]

$MO_x + H_2 \rightarrow MO_x(OH) + H^+ + e^-$ (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)

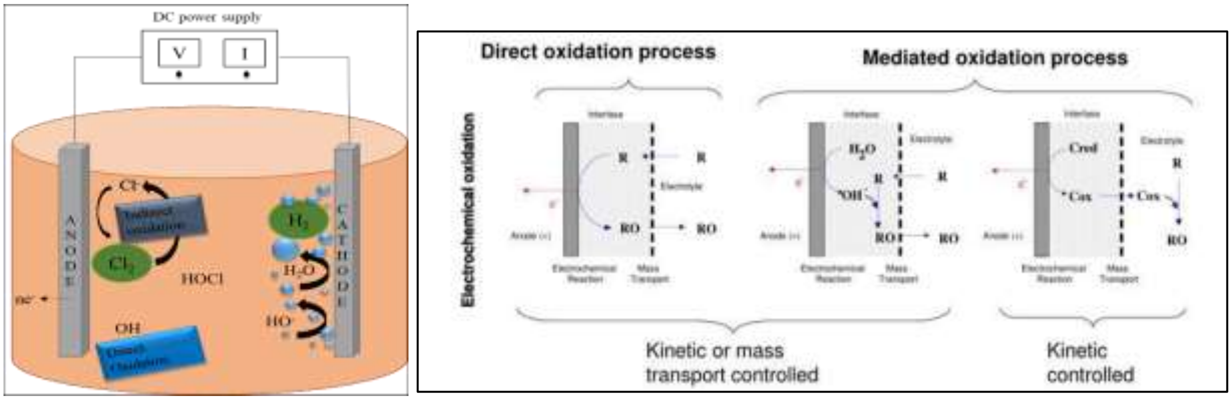

Figure 4a. Electrooxidation mechanism representation; 4b.Mechanism of hydroxyl radicals

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 [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 technique used for landfill leachate treatment. Electrocoagulation has become a rapidly growing area of wastewater treatment due to its ability to remove contaminants that are generally more difficult to remove by filtration or chemical treatment systems, such as emulsified oil, total petroleum hydrocarbons, refractory organics, suspended solids, and heavy metals [30]. There are many brands of electrocoagulation devices available and they can range in complexity from a simple anode and cathode to much more complex devices with control over electrode potentials, passivation, anode consumption, cell REDOX potentials as well as the introduction of ultrasonic sound, ultraviolet light and a range of gases and reactants to achieve so-called Advanced Oxidation Processes for refractory or recalcitrant organic substances [31]. Coagulation is one of the most important physio-chemical reactions used in water treatment. Ions and colloids (organic and inorganic) are mostly held in solution by electrical charges. The addition of ions with opposite charges destabilizes the colloids, allowing them to coagulate.

Aluminum or iron are usually used as electrodes and their cations are generated by dissolution of sacrificial anodes upon the application of a direct current. The process works by applying electrical current to the water, which causes metal ions to be released from the electrodes and interact with impurities in the water, resulting in the formation of coagulated particles that are then removed from the water [32-33]

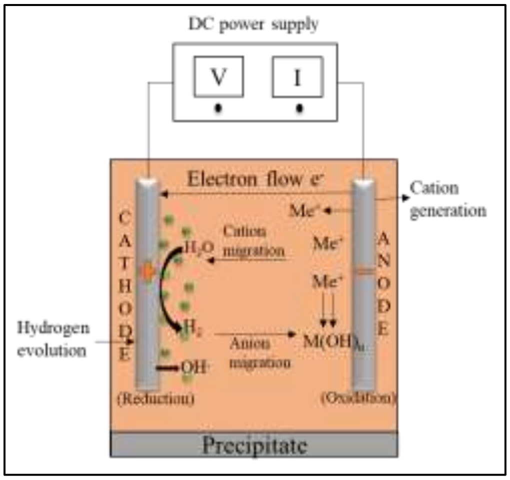

Figure 5: Mechanism of Electro coagulation

At anode:

$M_{\text{(solid)}} \rightarrow M^{n+}_{\text{(aqueous)}} + ne^-$ (23)
$2H_2O_{\text{(liquid)}} \rightarrow 4H^+_{\text{(aqueous)}} + O_2(g) + 4e^-$ (24)
At cathode:
$M^{n+}_{\text{(aqueous)}} + n\,e^- \rightarrow M_{\text{(solid)}}$ (25)
$2H_2O_{\text{(liquid)}} + 2e^- \rightarrow 2OH^- + H_{2\,\text{(gas)}}$ (26)

In solution:
$M^{n+}_{\text{(aqueous)}} + n\,OH^- \rightarrow M(OH)_{n\,\text{(solid)}}$ (27)

Electrocoagulation is electrochemical process based on application of sacrificial electrodes such as aluminum, iron, and zinc which undergo oxidation to form metal ions, which eventually act as coagulant and attract oppositely charged contaminants [32-34]. When the current is applied, metallic ions further react with hydroxides to form primary hydroxides to form polyhydroxides and polyhydroxy metallic flocs [26]. However, the efficiency of electrocoagulation process depends upon pH, current density, distance between electrodes, electrode arrangement, and cell geometry. With the latest technologies, reduction of electricity requirements, and miniaturization of the needed power supplies, EC systems have now become affordable for water treatment plants and industrial processes worldwide [29].

E. Photocatalysis

Photocatalysis water splitting in general is based on the generation of photo- excited charge carriers [34-36] Photocatalytic process are very efficient methods for destruction and mineralization of recalcitrant organic compounds and simultaneous hydrogen production in wastewater [35,36]. Such an ideal process couples the wastewater treatment with energy recovery (Hydrogen energy) together, which meets the desires of sustainable water 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 effluents, presents normally recalcitrant organic compounds, such as humic and fulvic acids, pesticides, xenobiotic organic compounds (benzene, phenols, phthalates) and inorganic compounds including heavy metal [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. In summary, photocatalysis is a promising technology to convert clean and inexhaustible UV energy into storable chemical energy. It has the advantages of low cost, environmentally friendly, safety, and renewable, and the development of highly efficient photocatalytic systems is highly desirable in dealing with energy crisis and environmental governance. Photocatalysis with mild environments, a simple process and sustainable technology, can removal of organic pollutants contained in wastewater into water, carbon dioxide or other small molecules, and reduce or oxidize inorganic pollutants to harmless substances and then to producing sustainable hydrogen production from wastewater [39-40].

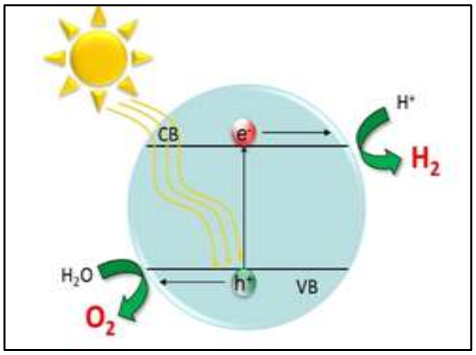

Figure 6: Mechanism of Photocatalysis

F. Sonication

Sonochemistry is principally based on acoustic cavitation which includes the formation, growth, and implosive collapse of bubbles in a liquid. The diffuse energy of sound is enhanced through cavitation [42]. Positive and negative pressures are exerted on a liquid by compression and expansion cycles respectively of ultrasound waves [15]. When a sufficiently large negative pressure is applied to the liquid, the average distance between the molecules would exceed the critical molecular distance necessary to hold the liquid intact, and the liquid will break down and voids or cavities will be created; cavitation bubbles will then be formed [18]. The negative pressure works against the tensile strength of the liquid and thus it depends on the type and purity of the liquid. In pure water more than 1000 atm of negative pressure would be required for cavitation whereas in tap water, negative pressure of only a few atmospheres will form bubbles [5]. Once produced, these cavities, voids, or bubbles may grow in size until the maximum of the negative pressure has been reached [43].

The formation and growth of the cavitation bubble is shown in Figure 7a. Gas and vapors are compressed inside the cavity and this generates heat, which finally produces a short-lived localized hot spot figure 7b. In brief the cavitational collapse creates an unusual environment for a chemical reaction in terms of enormous local temperatures and pressures [44]. The most sophisticated models predict temperatures of thousands of degrees Celsius, pressures of from hundreds to thousands of atmospheres and heating times of less than a microsecond [19].

The physical phenomena leading to sonochemical effects in water are complex and not yet fully elucidated. Whether the origins of the molecular activation be thermal, electrical, or a combination of the two, the location where water molecules are brought to an excited state and dissociate is the gas and vapor-filled interior of the cavitation bubble [18]. In the case of water saturated with air, the initial reactions include the cleavage of water and dioxygen molecules:

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

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

The radicals generated from the above reactions combine in various ways or react with gases such as nitrogen and vapor present within the cavitation bubble or in the liquid shell surrounding the cavity. This leads to the generation of HNO_3, HNO_2, and H_2O_2 in solution according to the following reactions:

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

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

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

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

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

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

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

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

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

A major sink of the hydroxyl radical generated during sonication of aqueous solutions is its recombination with a hydrogen atom to form water (reaction 30). Such recombination reactions are very likely since the two species are in close proximity of each other after their initial formation. This recombination process represents a major impediment to the efficient production of hydroxyl radicals. Once produced, the hydroxyl radicals recombine (reaction (36)), react with other gaseous species (reaction (38)), or diffuse into the bulk solution [44].

${}^\bullet OH$ + other species → oxidized products (39)

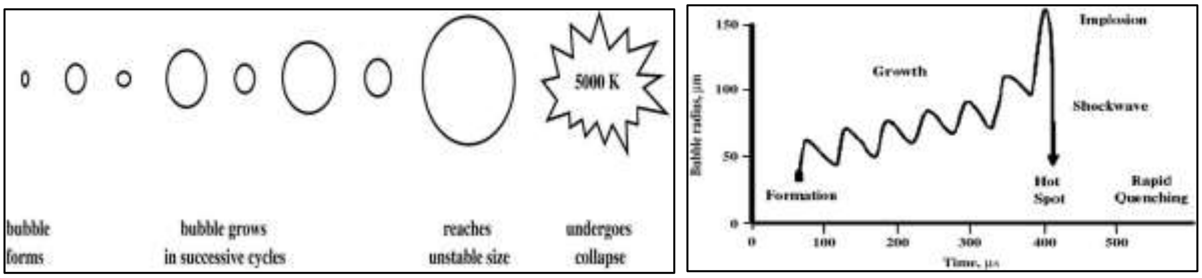

Figure 7a. Mechanism of cavitation bubble formation and collapse; 7b. Graphical representation of bubble growth and implosion

Ultrasonic irradiation has received considerable interest as an advanced oxidation process (AOP) because it leads to rapid degradation of chemical contaminants in water. Sonolysis has a distinct advantage over ultraviolet light mediated AOPs since ultrasound is readily transmitted even through opaque systems. The highly oxidizing $^{\bullet}OH$ radicals generated during sonication are identical to those produced in other AOPs. Ultrasonic irradiation of liquid reaction mixtures induces cavitations, a process during which the radii of preexisting gas cavities in the liquid oscillate in a periodically changing pressure field created by the ultrasonic waves. Ultrasonic waves in water provoke the collapse of cavitation bubbles and induce the formation of reactive chemical species such as $H^{\bullet}$, $^{\bullet}OH$, $O^{\bullet}$, and H_2O_2. These reactive species are responsible for the destruction of the chemical contaminants in solution.

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

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