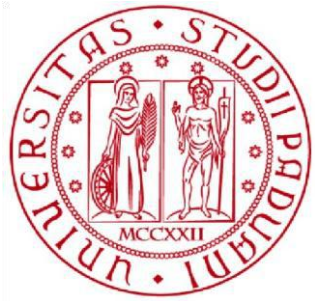
UNIVERSITÀ DEGLI STUDI DI PADOVA

University of Padova

DIPARTIMENTO DI INGEGNERIA CIVILE, EDILE AMBIENTALE
Department of Civil, Environmental and Architectural Engineering

Corso di Laurea Magistrale in Ingegnere Ambientale
Master's degree in environmental engineering



Tesi di Laurea Magistrale
Master Thesis

Leachate Treatment Using Atmospheric Plasma

Supervisor
Prof. Valentina Grossule

Student
Muhammad Owais Khokher
ID 2071524

ACADEMIC YEAR 2025/2026

ACKNOWLEDGEMENTS

First and foremost, I express my heartfelt gratitude to **Professor Valentina Grossule**, my research supervisor, for her invaluable guidance, encouragement, and constructive feedback throughout this thesis. Her support has been instrumental in shaping the direction and quality of this work.

I would also like to thank **Dr. Mubashir** for his technical insights and assistance during the research process. His input helped clarify key concepts and improve the overall depth of the study.

I am deeply thankful to my **parents**, whose unwavering love, sacrifices, and constant support have been the foundation of all my academic and personal achievements. I am especially grateful to my **brother, Hassan**, for his continuous motivation, belief in my potential, and the encouragement he has always provided.

To all these wonderful people, thank you for your understanding, patience, and for being a source of strength during this journey.

This thesis is a reflection of the collective support, care, and guidance I have received from all of you. I remain sincerely appreciative.

ABSTRACT

The treatment of MSW landfill leachate remains a pressing global environmental challenge, largely due to its complex and variable composition that includes high concentrations of organic matter, ammonia, heavy metals, and emerging contaminants. While conventional treatment methods such as biological processes, physicochemical techniques, and membrane systems have been widely applied, they often struggle with issues like incomplete pollutant removal, high operational costs, and the production of secondary waste streams. In response to these challenges, researchers have been exploring a range of novel treatment approaches that offer more sustainable and effective solutions.

This thesis presents a comprehensive review of emerging technologies for landfill leachate treatment, with a particular focus on plasma-based processes. Plasma treatment is gaining attention as an innovative and promising technique, primarily due to its ability to generate highly reactive species capable of breaking down even the most persistent pollutants. Unlike many traditional methods, plasma processes do not require the addition of chemicals and can potentially operate at lower energy costs, making them attractive from both an environmental and economic perspective.

Throughout this work, the principles behind plasma technology, different system configurations, mechanisms of pollutant degradation, and current advancements are critically analyzed. Furthermore, the thesis discusses how plasma treatment compares to other advanced oxidation and conventional methods, highlighting its advantages, limitations, and potential pathways for future development. In doing so, this study aims to provide a clearer understanding of where plasma technology stands today and what role it could play in advancing sustainable leachate management in the years to come.

Table of contents

1. INTRODUCTION

1.1 Background and context

One of the most important environmental concerns of our time is the MSW (Municipal Solid Waste). Even though MSW only makes up around one-third of all trash produced, policy making places a lot of attention on reducing its consequences because of its complicated makeup (Blumenthal K., 2009). According to Eurostat, an average EU citizen produced 5.0 tons of garbage in 2022, of which 30.2 percent was landfilled and 40.8 percent was recycled. With the growth of consumerism, MSW production has increased dramatically because of readily available and reasonably priced goods.

Leachate is the liquid produced due to water coming into contact with different waste fractions and dissolving the components on its way. Landfilling the waste comes with a multitude of challenges including but not limited to-space, leachate handling and air pollution. Leachate is therefore one of the major challenges that comes after the waste has been disposed of. It is of high importance to handle the leachate in a safe and sustainable way so that it does not contaminate soil or groundwater.

1.2 Problem statement

Landfill leachate is one of the most challenging wastewater to treat because of the complexity of the composition. Landfill leachate is a high-strength wastewater, exhibiting acute and chronic toxicity, with a variety of organic wastes and inorganic species. Dissolved organic matters, ammonia, heavy metals, and xenobiotic organic compounds are major contaminants in landfill leachate (Deng Y., Zhao, 2015).

As this liquid percolates through layers of garbage, it becomes contaminated with substances that cannot easily be removed through normal treatment techniques, CECs (Contaminants of Emerging Concern), for example are found to be extremely resilient and have proved to be difficult to remove through conventional treatment facilities. Existing solutions like biological treatments or chemical processes tend to come up short — especially when it comes to older or more concentrated leachate. These techniques can be costly, energy-consuming, or not competitive enough.

Landfill leachate has become an increasingly important component in sustainable solid waste management due to the tightening regulations and an increasing awareness about the potential of contamination of soil and groundwater caused by the leachate. In the solid waste industry, leachate management is hence the single most cost intensive component taking up about 20-33 percent of operating costs (Walker T., 2015)

AOPs (Advanced Oxidation Processes) have gained traction in the recent years to treat wastewater sometimes as an alternative and sometimes as an augmentation to the conventional processes such as biological treatment. AOPs are being studied and implemented for their energy efficiency, sludge production and a relatively smaller usage of chemicals compared to the available alternatives. This research aims to delve into the details of atmospheric plasma and how it compares to other treatment processes.

1.3 Leachate Characteristics and Challenges

As has been already discussed in the sections prior, the leachate has a variable composition-both qualitatively and quantitatively. This is a consequence of not only of the quality of the waste but also a function of environmental factors such as temperature and humidity as well as the type of landfill. These factors combine to give rise to a number of challenges. This section goes on to describe briefly how each factor comes into play.

1.3.1 Leachate Composition

The composition of landfill leachate is influenced by waste composition, landfill age, climate and operational conditions. Constituents in landfill leachate can be broadly classified into four categories; **Dissolved Organic Matter (DOM), Inorganic macro components, heavy metals and Xenobiotic Organic Compounds (XOCs).**

Kumar and Alappat (2005) have proposed an indicator using all these components called the Leachate Pollution Index (LPI). The LPI is basically a weighted average of 18 parameters such as BOD, COD, TDS etc after assigning them an impact weight based upon their pollution potential. LPI can take up values between 0 and 100, a higher value means higher concern. An LPI of 7.5 or higher is generally considered an indicative of poor environmental conditions.

According to the degradation phase, landfill leachate is predominantly characterized into the two groups; acetogenic leachate and methanogenic leachate (Lee et. al., 2010). Acetogenic leachate is typically characterized by high BOD/COD ratio, ammonia, acidic pH (Kjeldsen et al., 2002) and high organic fraction.

The second type is stable methanogenic leachate from an old landfill, which has passed through its methane producing anaerobic stage (Christensen et al., 2001). Methanogenic leachate can be generally characterized by low BOD value, BOD/COD and high methane production (Lee et al., 2010). Methanogenic leachate comprises with non-biodegradable humic like substances that show high molecular weights (Bashir et al., 2011; Lei and Aoyama, 2010)

1.3.1.1 Dissolved Organic Matter

Organic matter is a principal and reactive constituent of leachate in landfills, various organic compounds, including amino acids, volatile fatty acids, humic-like materials and fulvic-like materials. DOM exists in different molecular weights and functionality and often consists of carboxylic, phenolic, and carbonyl groups. The composition of individual organic compounds in leachate is hard to determine experimentally. Therefore, DOM is generally determined as a bulk property such as biological BOD, COD, TOC, VFA and individual compounds, i.e., methane The molecular composition of DOM changes with landfill age with younger leachate with more volatile and readily degradable products and older leachate with high molecular weight humic products.

DOM plays a prominent role in mobility, and speciation of heavy metals in leachate due to complexation.

1.3.1.2 Inorganic Macro Components

NH4 +, NO3 - , NO2 - , SO4 2-, Cl- , PO4 3-, sodium (Na+), potassium (K+), calcium (Ca2+), magnesium (Mg2+), iron (Fe2+) and hydrogen carbonate (HCO3 -) are among the most predominant inorganic compounds (Robinson, 2007). Inorganic macrocompounds exist in a significant concentration in landfill leachate and the concentration may vary based upon landfill age, type etc.

The high pH during methanogenation phase can cause sorption of cations (Such as calcium, magnesium and iron) into organic materials to form precipitates with anions. Therefore, a lower concentration of cations remains in the leachate. While other macrocomponents such as chloride, sodium an potassium barely undergo sorption due to washing out by the leachate (Asadi, 2008).

1.3.1.3 Heavy metals

Some of the common heavy metals found in leachate are Zinc, Nickel, Lead, Copper, Chromium, and Cadmium. Whereas, metalloids such as Arsenic, Selemìnium are present in very low concentrations. The non-biodegradable and soluble nature of the heavy metals often result in a persistence in leachate for long periods of time. As a consequence, heavy metals can undergo biomagnification in food chains (Wijesekar et. al., 2014). The source of the heavy metals is often batteries, automobile parts, wires and electronic components.

The concentration of heavy metals during different phases and from different regions of the world is noted to be different. In the earlier degradation stages, organic acids lower the pH giving rise to a higher solubility for metals and hence the metal concentration in the leachate is higher in the earlier stages of degradation (Naveen et. al., 2014)

All of the heavy metals cause different issues in living systems such as anemia, brain damage, anorexia, mental deficiency, vomiting in human beings. They are able to disrupt normal functions of cells in living bodies by attaching with macromolecules sometimes forming clumps.

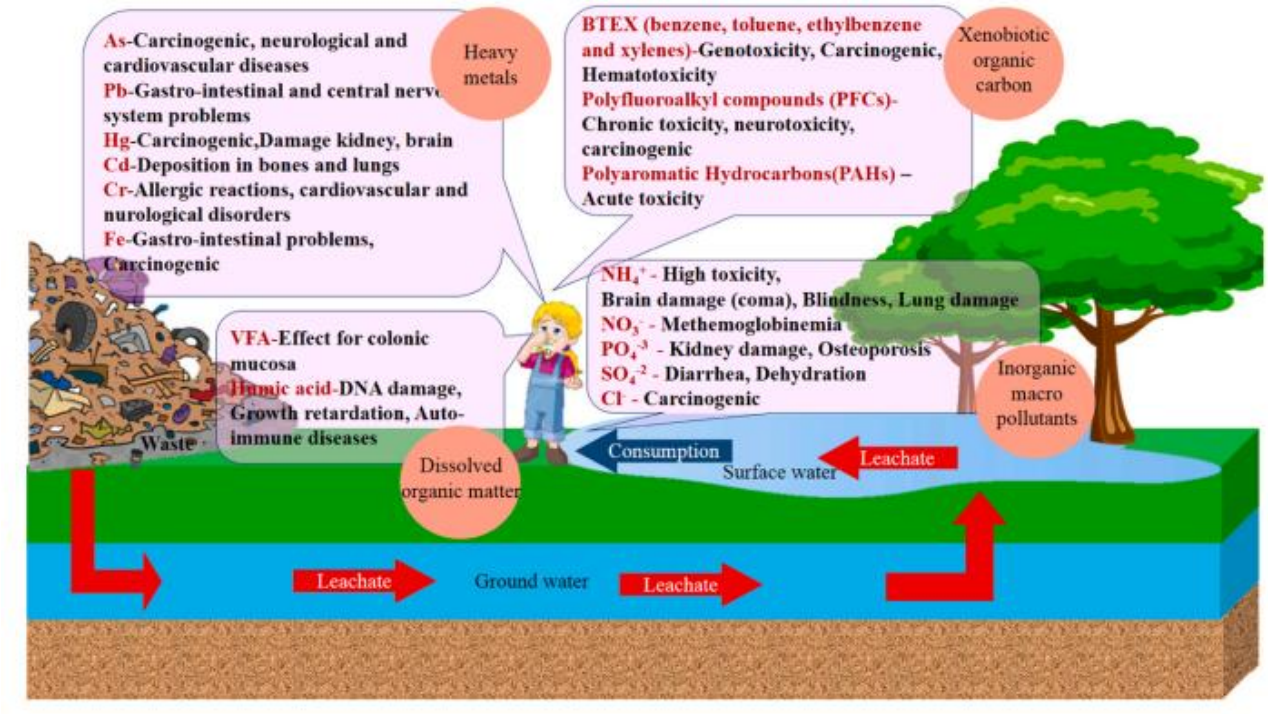


Figure 1.1 effects of contaminants within leachate

1.3.1.4 Xenobiotic Organic Compounds

Xenobiotic organic compounds (XOCs) are usually present in small concentrations usually less than 1 mg/l. Typical examples for XOCs are benzene, toluene, phenols, chlorinated aliphatics, phthalates and halogenated hydrocarbons (PCE and TCE). They usually come from fertilizers, pesticides, and household chemicals such as cosmetics. Waste composition, age and landfill technology largely define the type and quantities of XOCs. Table 1 summarizes some of the commonly detected XOCs and CECs from various sources.

The so-called “contaminants of emerging concern” are chemical substances for which no maximum levels have been laid down in EU legislation, or substances for which maximum levels have been provided but which require revision (Vandermeersch et. al., 2015). CECs are a broad category of chemicals and the list is ever increasing. Some common CECs are

These chemicals are found to be extremely persistent as they usually are pretty stable and do not degrade easily. Because of this the health concerns especially for the marine life are rising. Some of these compounds are formed to be ‘Endocrine Disruptors’ or EDs. By interfering with the body's endocrine system, endocrine disruptors produce adverse developmental, reproductive, neurological, and immune

effects in humans, abnormal growth patterns and neurodevelopmental delays in children (Monneret C., 2017)

Table 1.1 Effects and concentrations of XOCs and CECs

Contaminant	Concentration recorded (µg/L)	Effect	Country	Toxicity levels	References
BTEX (benzene, toluene, ethylbenzene and xylenes)	21.5–354.9	Genotoxic, Carcinogenic, Hematotoxic	Denmark, Sri Lanka	2.5, 14, and 250 mg/L for soil; 10.70 µg/L for benzene/toluene in water	Baun et al., 2004; Paustenbach et al., 1992; Kumarathilaka et al., 2016
Benzene	1.78–21.7 (Benzene), 1.73–20.2 (Toluene), 0.16–7.48	Carcinogenic	Poland		Matejczyk et al., 2011
Polyfluoroalkyl compounds (PFCs)	0.031–12.819	Chronic toxicity, carcinogenesis, reproductive and developmental toxicity, immunotoxicity	Germany	HAL: 70 ng/L	Busch et al., 2010
Phthalate acid esters (various)	0.001–0.340 (2-ethylhexyl) phthalate 39	Mutagenicity, reproductive toxicity	Denmark	MCL: 0.006 mg/L	Baun et al., 2004; Lee and Lee, 2011; Öman and Junestedt, 2008
Bisphenol A	0.0013–17.200, median 0.269	Weak acute toxicity to aquatic biota; Exceeded EC50	Japan	TDI: 0.05 mg/kg bw/day	Yamamoto et al., 2001; Schug et al., 2012
PAHs (Polyaromatic Hydrocarbons)	0.057–77.2, 228	Plant growth reduction; human health concerns	Japan, Southern Poland	30 to > 2000 mg/kg (plant); 1.5 mg/kg (soil)	Baun et al., 2000; Matejczyk et al., 2011; Öman and Junestedt, 2008
Brominated fire retardants,	<dl–39	Acute exposure risks; chronic neurological	Sweden		Öman and Junestedt, 2008; Tzoraki

PBDEs, HBCDD		and reproductive effects			and Lasithiotakis, 2018

1.3.2 Factors Influencing Leachate Quality

Leachate quality is affected by a number of factors which dictate its composition and pollution potential. They depend on the nature of the waste, the age of the landfill, the climate, the way the site is managed and the surrounding environment.

1.3.2.1 Waste Composition

Leachate characteristics are influenced by waste composition. The waste that is rich in organics makes the higher values of the biodegradables, such as BOD and COD, while industrial wastes also add the heavy metals and synthetic compounds.

1.3.2.2 The Age of the Landfill

It is known that leachate from young landfill have high BOD and CODs, which is in good agreement because the microbial activities degrading it are active. Values of these parameters decrease as the landfill gets older and the more stable, less biodegradable species become dominant.

1.3.2.3 Climate

Rainfall contributes volume to the leachate and dilutes contaminants; however, leachate is more concentrated in dry climates. Microbes are more active at higher temperatures, accelerating the decomposition of waste.

1.3.2.4 Landfill Operation and Management

Compaction, cover, and leachate recirculation all affect microbial and moisture conditions. Recycling will speed up stabilisation but could concentrate salt and ammonia.

1.3.2.5 Design and Engineering of the Landfill

Lined landfills prevent leakage, but can collect more concentrated leachate. Unlined landfills would permit some dilution through seepage, but would be more potentially environmentally degrading.

1.3.2.6 Biodegradation and Chemical Reactions

Biological and chemical reactions occur as waste degrades that change the composition of leachate. The first phase with low pH minimizes fermentation producing acid and switches to remediation phase with higher pH and more action of methane; gradually, pH decrease and organic load reduce in time.

Table 1.2 Variation in the physico-chemical characteristics of the leachate generated at the Central Landfill of Asturias.(Castrillon et. al., 2010)

Year	1988	1989	1990	1991	1994	1999	2003	2006
Parameter	Mean values							
pH	7.6	8.0	8	8.3	8.3	8.2	8.4	8.5
COD (mgO_2/L)	15,425	13,478	10,789	5132	3893	2838	3757	3650
BOD_5 (mgO_2/L)	–	8275	–	2414	800	700	858	670
BOD_5/COD	–	0.62	–	0.45	0.2	0.24	0.23	0.14
NH_4^+ "–"N (mg/L)	1862	1478	2142	1485	2156	2300	2132	1880
Cu (mg/L)	–	0.16	0.22	0.04	0.10	<0.1	0.15	–
Zn (mg/L)	–	0.79	2.96	0.49	1.06	0.26	0.42	–
Pb (mg/L)	–	1.18	0.82	0.23	0.65	0.04	<0.05	–
Cd (mg/L)	–	0.07	0.10	0.02	0.04	<0.1	0.02	–
Cr (mg/L)	–	0.59	0.72	0.27	0.54	0.41	–	–

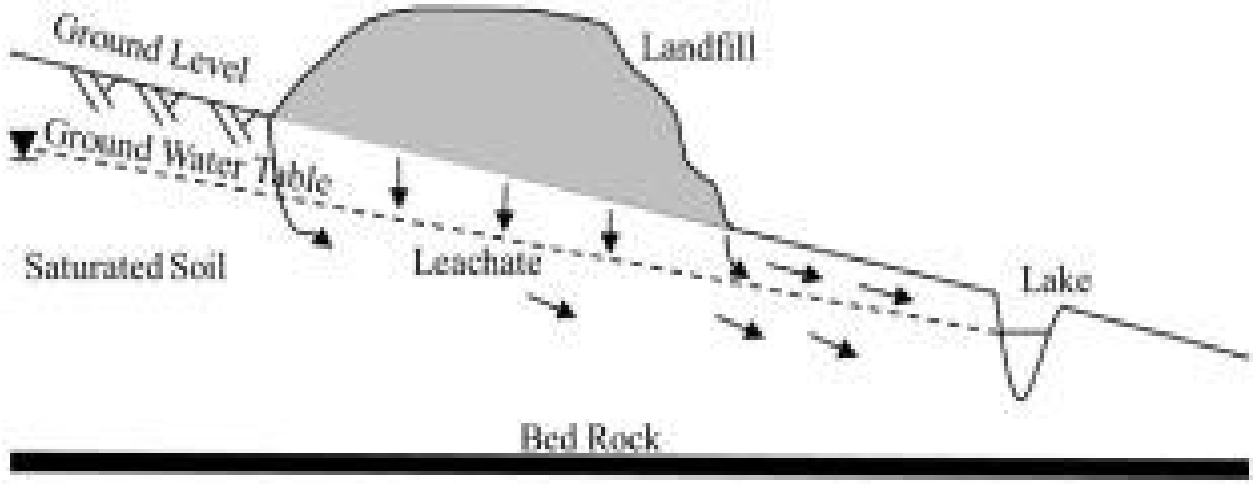
1.4 Environmental and regulatory concerns regarding leachate

Leachate poses several health and environmental risks due to high organic pollutants, pathogenic microorganisms and the nitrogenous compounds such as ammonia. Generally, most landfills produce methane due to anaerobic conditions in presence of organic load.

The methane gas could be released to the atmosphere in poorly ventilated areas in treatment plants. This poses an explosion risk in case of presence of sparks due to electrical or mechanical components. It is therefore essential to prevent discharge of methane from leachate. The permissible limit for methane in leachate is 0.14 mg/l (Abdel-Shafy et. al., 2024).

On the other hand, direct leaching into aquatic compartments and water ways impose vigorous long lasting environmental impact, which necessarily lead to acute diminishment in the biodiversity and reduction in the populations of several sensitive species. In addition, local and far distant dwelling locations may badly suffer from chronic intoxication with cumulative harmful organics and metals.

Figure 1.2 Infiltration of leachate into waterbodies



2. Conventional leachate treatment methods

Given the complexity and variability of landfill leachate, thoughtful and customised management is warranted. The primary factors for choosing a leachate treatment method, according to Luo et al., include the legal requirement for effluent concentration for discharge as well as the flexibility and reliability of the treatment plant. Various traditional treatment techniques have been evolved over time to treat the different pollutants found in leachate. They can be separated into biological and physicochemical techniques which have different advantages, limitations and are applicable only to specific conditions of the leachate. In reality, a combination of the two is usually used to reach the required discharges standards. These methods will be further explained in the next sections.

2.1 Biological treatment process

Biological treatment is often employed for leachate with a high BOD/COD ratio corresponding to a young leachate (Ilmasari et. al., 2022). As biodegradable matter decreases and concentration of refractory compounds (fulvic and humic acids) increases biological treatment may not remain adequate for treatment of leachate up to an acceptable level prescribed by the law. Biological treatment as the name suggests employs microorganisms which require very precise conditions for maintenance and growth viz. temperature, pH, alkalinity, oxygen (in the case of aerobic treatment) etc. The mode of operation for the bacteria is usually either aerobic or anaerobic (anoxic processes exist too) and hence, in principle, biological processes can be fundamentally subdivided into aerobic and anaerobic processes.

2.1.1 Aerobic Treatment

Aerobic biological treatment takes place in the presence of molecular oxygen, which permits aerobic microorganisms to metabolize organic substances. This technology is being increasingly adopted because of its operational ease and its capability of effectively perform the organic matter removal and nitrogen conversion through nitrification and denitrification. Aerobic methods applied for leachate decontamination: Commonly used aerobic treatment systems for leachate treatment are the activated sludge process, sequencing batch reactor (SBR), membrane bioreactor (MBR), rotating biological contactor (RBC), and trickling filter (TF).

In such systems, organics are oxidized by aerobic bacteria in suspension or attached growth. The degradation causes production of surplus biomass, which should be removed regularly. Young and medium-age leachate with a high biodegradability (as shown by high BOD/COD ratio) can be degraded effectively by aerobic treatment. These systems can provide reduction of organics and greatly reduced levels of ammoniacal nitrogen by use of biological nitrification (often adding a process of denitrification for total nitrogen removal).

Nevertheless, aerobic reactors are not very efficient for mature leachates where it is common to have high proportions of non-biodegradable or resistant organic compounds, such as humic and fulvic acids. Additionally, they produce large amounts of sludge and need continuous aeration to operate, which makes their operation energy intensive. The presence of inhibitors such as high concentration of ammonia, heavy metals can also cause the inhibition of microbial activity and reduction of

treatment effectiveness. Table 2.1 provides a summary of performance of some common aerobic reactors for leachate treatment. (Ilmasari et al, 2022)

Table 2.1 comparison of aerobic processes for leachate treatment

System	Leachate type	Operational conditions	Influent (mg/L)	Removal efficiency (%)
AS	Mature	HRT:22,38,53 h	COD:2860 NH_4^+-N:1400	COD:46 NH_4^+-N:78 Color:50
AS	Mature	HRT:3.6 d SRT:30 d	COD:1905 NH_4^+-N:306 TP:0.4	COD:54 TN:41 TP:58
AS	Mature	–	COD:3388 NH_3-N:14	COD:82 NH_3:22 TP:92
AS	Mature	HRT:0.48 d	COD:522–614	COD:87 BOD:82
AS	Intermediate	HRT:1 d	COD:3900 NH_3-N:39 TP:110	COD:91 BOD:94 NH_3-N:100 TP:75
SBR	Mature	Cycle:24 h	COD:3489 TN:1102 BOD:665	BOD:48 COD:48 NH_4^+-N:42
SBR	Mature	Cycle:48 h	Phenolic compounds:173	Phenolic compounds:96
SBR	Synthetic	Cycle:6 h HRT:2.9 d	NH_4^+-N:300–900 DO:0.05–0.7	TN:81
Twin SBRs	Mature	Cycle:24 h SRT:11.67d HRT:11.67 d	COD:727 BOD:183 NH_4^+-N:365 TN:417	COD:41 BOD:86 TKN:93 TN:71 NH_4^+-N:97
SBR	Intermediate	Cycle:12 h SRT:60–80 d	COD:6914 NH_4^+-N:1863 TN:2024	COD:55 TN:60
SBR	Synthetic	Cycle:8 h SRT:20 d HRT:16 h	COD:300–1000 NH_4^+-N:50–330 PO_4^{3-}:8.5–37.6	Heavy metals:99
MBR	Mature	HRT:10 d	BOD:230 TKN:1780 NH_4^+-N:1770	TN: 90 NH_4^+-N:98
MBR	Mixture from several landfills	SRT:144 d HRT:10 d	COD:8050 BOD:2280 TN:1730 NH_4^+-N:1325 TP:57	COD:75 BOD:98 NH_4^+-N:96 TSS:99
MBR	Mature	SRT:20 d	COD:6088 BOD:724 NH_3:2200–3035 TN:2300–3350 TP:14.5–36.5	COD:51 BOD:92 NH_3:37 TN:35 TP:71
MBR	Young, mand partially mature	HRT:2.5 d	COD:2889 BOD:21915 NH_3-N:130 TKN:383 SS:3520 VFA:6728	COD:96 BOD:99 NH_3-N:97 TKN:97 SS:100 VFA:95
MBR	Young	SRT:150–300 d	COD:2109 BOD:143 TKN:402 NH_3-N:292 SS:297 TP:13.3	COD:79 BOD:99 TKN:99 NH_3-N:99 SS:99 TP:69
MBR	Young	HRT:15 d	COD:68250 BOD:44500 NH_4^+-N:1470 Fe:36 Cu:2 Cd:0.5	Fe:96 Cu:23 Cd:84
TF	Mature	–	COD:3365 BOD:217 NH_4^+-N:610 SS:197	COD:48 BOD:76 NH4-N:59 SS:73
TF	Young and mature	–	COD:131–5315 BOD:22–639 NH_4^+-N:39–1150	BOD:80–96 TOC:50–68 NH_4^+-N:68–88
TF	Mature and synthetic	HRT:7–21d	–	COD:76–90 BOD:81–96 NH_4^+-N:15–86
RBC	Young	4 stages acetate discs HRT:24 h	COD:2500–9000	COD:52
RBC	Nitrate-rich leachate	1 stage poly-methylmethacrylate discs HRT:10 h	COD:866 NO_3-N:1103 NO_2-N:0.19 NH_4^+-N:470	NO_3.N:95
RBC	Mature	1 stage poly-methylmethacrylate discs HRT:10 h	COD:743 BOD:10 TOC:284 NO_3-N:1824 NH_4^+-N:714 PO_4^{3-}:0.88	NO_3.N:99 TOC:19
RBC	Mature	2 stages HRT:24 h	COD:1154 BOD:92 NH_4^+-N:834 TN:879	NH_4^+-N:99

2.1.2 Anaerobic Treatment

Unlike the aerobic system, anaerobic biological treatment is performed in absence of oxygen and operated in series steps including Hydrolysis, Acidogenesis, Acetogenesis and Methanogenesis. This treatment method has many advantages for leachate with a high organic content, as it permits effective degradation of complex organic materials and generation of biogas, consisting mainly of methane and CO2.

The most common anaerobic systems for leachate treatment among others are anaerobic digesters (AD), anaerobic sequencing batch reactors (AnSBR), upflow anaerobic sludge blanket (UASB) reactors, expanded granular sludge bed (EGSB) reactors, as well as anaerobic membrane bioreactors (AnMBR). The three systems have different hydrodynamic characteristics, sludge retention properties and loading rate capacities.

Anaerobic treatment is particularly applicable for leachates of young and intermediated age with high COD and moderate BOD/COD. It has some advantages such as low sludge production, heavy metal resistance and possibility of energy recovery through methane. But it is normally unsatisfactory with respect to nitrogen compounds, in particular ammoniacal nitrogen which escapes into the treated

effluent. Moreover, it is a costly system which may fail under the influence of temperature and pH variations, and may have to be shut down due to accumulation of inhibiting compounds, such as ammonia or high salinity. Therefore, anaerobic treatment is frequently followed by post-treatment to meet discharge criteria.

Table 2.2 summarises and compares some common anaerobic treatment processes in regards to the age of leachate, operating parameters and process results in terms of removal percentage and biogas production. It's quite clear that the anaerobic processes mainly operate in the mesophilic range 35-50 degress Celsius and hence the heating cost and temperature control becomes a crucial factor in the decision of whether to employ anaerobic processes or not.

Table 2.2 Comparison of different anaerobic processes for leachate treatment

Treatment	Leachate type	Operational Condition			Biogas production	Removal (%)
		°C	HRT	Organic load (COD) (mg/L)		
AD	Intermediate	37	–	48,000	0.2–0.32 L/g $COD_{removed}$	COD:71–92
AD	Mature	35 and 55	–	5625	22 mL/h	COD:81
AD	Mature	35	–	13,257	139.3 mg C	COD:85
AD	Composting leachate	37	7.7–20 d	213,400	387 m_3/ton COD influent	COD:60
AnSBR	Intermediate	35	72 h	2518–7695	0.35 L/g $COD_{removed}$	COD:42 sCOD:48
AnSBR	Young	25	6 d	16000	–	COD:90 NH_4^+-N:16
AnSBR	Intermediate	35	–	5890–6800	12 L	COD:80
AnSBR	Intermediate	35	24 h	30,540	330 mL/d	sCOD:82
AnSBR	Young	35	2 d	7341–10448	–	COD:83
UASB	Mature	35	72 h	11,907	10.27 L	–
UASB	Hazardous landfill leachate	25	23 h	4358	–	COD:10 TSS:15 VSS:42
UASB	Hazardous landfill leachate	–	23, 11.3, 5.7 h	3421	–	COD:23 TSS:45 VSS:37
UASB	Young	35	32–72 h	800–1300	–	COD:85
UASB	Young and mature	37	24 h	45,000	–	COD:93
UASB	Mature	37	96 h	2500	40% of COD influent	COD:79
UASB	Intermediate	25	–	19,000	–	COD:84 TN:34
AnMBR	Intermediate	35	48 h	7014	60% of COD influent	COD:63 Color:60 Micropollutants:100
AnMBR	Young	35	10 d	1000–10000	0.42–6.18 L/d	COD:80
AnMBR	Synthetic	35	24 h	3790	6.18 L/d	COD:82 BOD:90
AnMBR	Young	55	24 h	113,000	–	COD:61 NH_4^+-N:7 SS:99 PO_4^{3-}:97 Ca^{2+}:92 Mg^{2+}:60
Two-stage AnMBR	Young	37 & 55	40 & 25 h	12,000	–	COD:61 TOC:55 Humic acids:50 Hydrophilic substance:60
AnMBR	Intermediate	35	5 d	7300	–	COD:90
AnMBR	Young	37	10 d	52,700	38 L/d	COD:90
AnMBR	Mixture of young and mature	37	2.5 d	13,000	0.34 L/g COD removed	COD:62
EGSB	Young	33	2.5 d	18,000	–	COD:86 Sulfate:80
EGSB	Young	33	2.5 d	17,000	–	COD:98
EGSB	Young	33	2 d	17,000	5.69 L/d	COD:96 Fulvic acids:86
EGSB	Young	35	68 h	66,000–68,000	6 L/d	COD:96 SS:85
EGSB	Young	35	12 h	12,000	2.2 L/d	COD:66
EGSB	Young	35–37	17 h	25,000	0.34 L/g COD influent	COD:93

2.2 Physicochemical Treatment

Physicochemical treatment methods augment the use of chemicals which usually aid in enhancing biological processes when they are not adequate on their own especially due to persistent, non biodegradable pollutants. These methods are useful especially in the cases when the fraction of biodegradable material is low i.e mature leachates or leachates that are rich in heavy metals or refractory organic compounds. Such processes are not employed as stand alones but rather used in conjunction with other biological processes (Renou et. al, 2008). Some of the most common physicochemical methods are; Precipitation, adsorption and coagulation-flocculation.

2.2.1 Air Stripping

The most common application of air stripping is the recovery of ammonia from leachate, especially from older and highly ammonia concentrated leachates which are difficult to treat by biological means. This is accomplished by raising the pH of the leachate (usually by the addition of lime - $Ca(OH)_2$)) so that the ammonium ion (NH_4^+) is converted to free ammonia (NH_3) gas. This transformation is equilibrium controlled and occurs at pH above 10.5. The freed ammonia gas is then vented from the liquid phase by bubbling air through the leachate in a stripping column or aeration basin.

In very favourable condition ammonia removal efficiency > 90% can be achieved by air stripping. Nevertheless, the method has significant disadvantages such as generation of alkaline sludge, the necessity of using acid scrubbing or absorption apparatuses to treat the off-gas rich in ammonia, heavy consumption of chemicals. Nevertheless, it is one of the few available methods for ammonia stripping from mature leachates at present time, particularly as a pre-treatment to biological or membrane techniques.

2.2.2 Coagulation flocculation

Coagulation–flocculation is a traditional process used for treatment of suspended solids, colloids, and some part of dissolved organic matter. This can then be treated with coagulants including aluminum sulfate or ferric chloride, which destabilize colloidal particles, and with flocculants, which facilitate their aggregation to form larger particles (flocs) that can be removed by sedimentation or filtration.

This is a very effective process for turbidity, color, and particulate-bound COD reduction, but COD removals usually range up to 60%. In general, it is ineffective against dissolved high molecular weight organics or ammoniacal nitrogen. Therefore, it is predominantly applied as a pre-treatment, in particular in order to reduce the burden to more sensible following processes like membrane filtration or biological purification. Optimization of pH, type and dose of coagulant are important for the systems to perform effectively.

2.2.3 Chemical precipitation

Chemical precipitation can be used as a pretreatment for removing ammonium based Nitrogen using salts such as $MgCl_2 \cdot 6H_2O$ or $Na_2HPO_4 \cdot 12H_2O$. It has been observed that presence of ammonia can result in a significant decrease in COD removal rate. Selective precipitation is a relatively costly procedure as the salts are difficult to regenerate/recycle. Hence, the augmentation in the process must be justified by the offset of increased COD removal.

2.2.4 Adsorption

Adsorption is a surface phenomenon by which a multi-component fluid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and forms attachments via physical or chemical bonds. Since our early history, Activated Carbon (AC) was the first widely used adsorbent. However, adsorbents dealing with new porous materials are recommended for ecologically friendly processes, important methods of sustainable development and development of appropriate technologies suited for each specific area.

Indeed, it has been extensively proved that any cheap material with a high carbon content and low levels of inorganic compounds can be used as a raw material for the production of activated carbons: various carbonaceous materials such as coal, lignite, nutshells, wood, tobacco stems and peat are used in the production of commercial activated carbon. Adsorption of pollutants into columns of AC or in powder form, in general, provides a better COD reduction compared to other alternatives such as calcium carbonate and and peat. However, adsorption is relatively less useful at COD removal for lower COD (Renou et. al., 2008).

Table 2.3 summarizes the relative merits and demerits of different conventional processes.

Table 2.3 comparison of conventional treatment methods

Treatment	Merits	Demerits
Biological Aerobic	•Cost-efficient • Satisfying in treating young and intermediate leachate •Aids nitrification/denitrification • Less start-up time (3–4 weeks) • Causes less odor	• Lower efficiency when a high organic loading rate (OLR) is applied • Generates excessive amount of sludge • Inadequate for standalone old leachate treatment
Biological Anaerobic	• Generates less amount of sludge • Captures valuable biogas (CH_4) • Uninfluenced by heavy metals present in leachate • Satisfactory performance in treating young and intermediate leachate	• Some organic compounds cannot be degraded by anaerobic bacteria • COD and ammonia remain in the effluent and require supplementary treatment • Longer start-up period (2–4 months) • Possibility of odor
Physicochemical	• Effective for old leachate • Shows satisfactory performance in removing ammoniacal nitrogen and refractory compounds • Applicable for non-biodegradable substances and heavy metals	• Relatively more expensive than biological treatment • Inadequate for standalone young and intermediate leachate treatment

3. Emerging and novel treatment technologies

3.0 Overview of novel technologies

The conventional technologies discussed in the previous chapter such as CAS and AD may still be widely used but they have their shortcomings every now and then. The requirement of space, energy usage or sometimes the inadequacy of the treatment system to remove certain pollutants are one of the few challenges being faced by the landfill management industry. This issue is only going to become worse as the legal limits around contaminants, especially CECs, become more stringent.

It is however of paramount importance to not only augment existing systems wherever necessary with novel treatment methods (Such as MBBR and MBR) or to replace existing technologies with new ones where the gamification is either infeasible or just too complex. In this section we will discuss some of the emerging technologies used for wastewater and leachate treatment.

The use of these technologies isn't one size fits all and hence the application of one may be considered considering the cost, composition of leachate and very importantly the required composition of effluent set by the legal limits.

3.1 Membrane Filtration

For advanced leachate treatment, membrane technologies, such as (in the decreasing order of sieve size) MF, UF, NF and RO, are used. These are pressure-driven processes in which semi-permeable membranes are used to filter contaminants from water by size exclusion and charge interactions.

Specifically, RO could be used to eliminate various pollutants dissolved organic matter, salt, heavy metal, residual ammonia. The reported separation removal efficiency is generally higher than 95% for most solute compounds. Membrane-based systems, however, are high capital cost, and often operate in conditions that are prone to fouling, scaling as well as the production of a concentrated brine or reject stream which must be further managed.

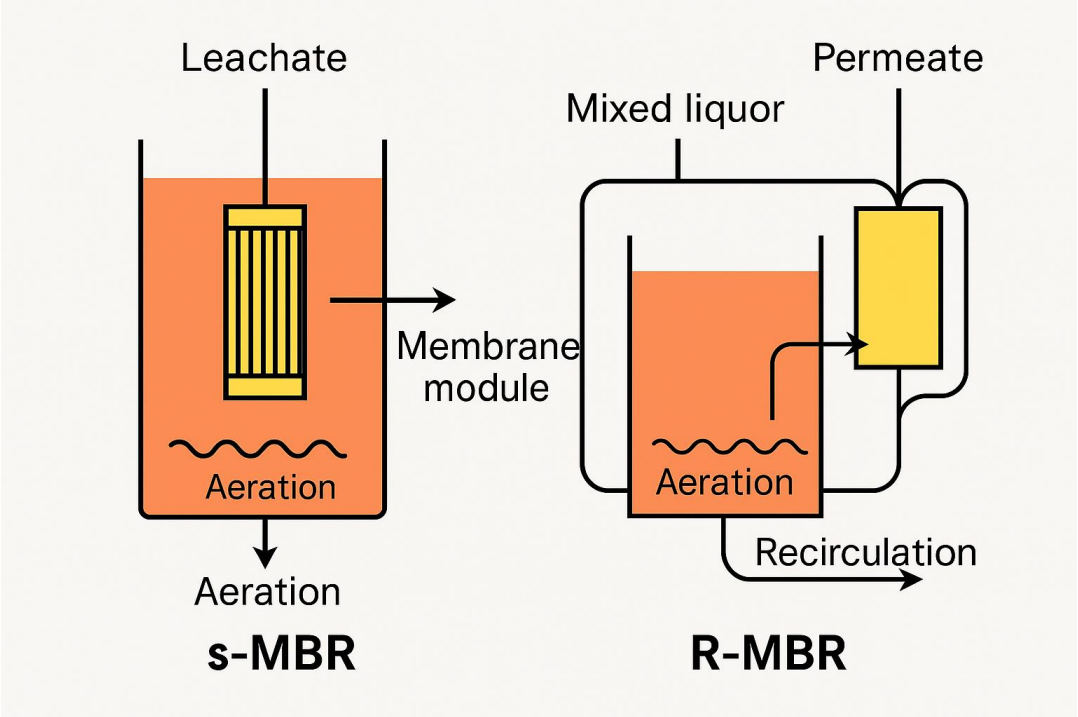
Although the membrane technology has limitations, it is frequently applied as a polishing step at the end of treatment trains, after biological or physicochemical pretreatment. And when it comes to discharging leachate to sensitive environments or recycling leachate for industrial purposes you need this to be of high quality.

3.1.1 Membrane Bio Reactors (MBRs)

The MBRs are an advanced biological treatment technology that combines CAS process with membrane based solid-liquid separation. The membranes are placed in two modes; s-MBR (Submerged MBR) and R-MBR (Recirculating-MBR).

In the first case the membranes are immersed within wastewater, in the oxidation tank. Through a pump, a slight depression is created inside the filter module, allowing the treated effluent to pass through the membranes, thus obtaining an efficient solids separation without the need to proceed with further sedimentation treatments. In the second case, membranes are positioned external to the aeration tank: the effluent from the oxidation tank is pumped into the membrane filtration module, while the sludge is recirculated into the bioreactor. This is elaborated using figure 3.1.

Figure 2.1 S-MBR and R-MBR layout



Toretta et. al. (2016) discusses how the removal efficiency of specific contaminants usin eg MBRs is affected by different factors such as type of membrane (flat sheet or hollow fiber), temperature etc.

Table 3.1 factors affecting contaminant removal efficiency of MBRs

Contaminant	Removal Efficiency	Influencing Factors
BOD	92–93% (standard), up to 97–99% (at ≥45 °C)	Temperature (improves BOD removal at higher temperature); membrane type
COD	68–71% (standard), up to 79% (at ≥45 °C)	Temperature (improves COD removal at higher temperature); membrane type
Phosphate (PO_4^{3-})	81–87%	Membrane type (no significant difference noted)

Total Nitrogen (TN)	61.2% (flat-sheet), 49.4% (hollow-fiber)	Membrane type (flat-sheet superior); temperature less effective
Ammonium (NH_4^+)	63.4% (flat-sheet), 47.8% (hollow-fiber); drops to 60% at ↑T	Temperature (high temperature reduces NH_4^+ removal); membrane type

Removal efficiency is also subject to SRT and HRT (not discussed above). Fouling is another important aspect to consider in this type of systems which is usually the lowest around neutral pH range 6.5-7.5 and is the most severe at slightly acidic levels (5.5). It is due to this reason that MBRs can be expensive to maintain and that the pressure buildups can be extremely high contributing to rapid deterioration of membrane material.

Despite that, MBR produces significantly less sludge than CAS, has comparatively lower SRT and is versatile in the applications (for old and young leachate) and is effective in removing micropollutants such as BPA nonylphenol. According to Wintgens et al., a BPA removal rate of 95.3% and a NP removal of 85% were achieved in the MBR. The overall BPA removal was 96.8% and 97.8% in the MBR + GAC and MBR + NF + PAC systems, respectively, a clear indication that most of the initial BPA load was reduced in the MBR alone.

3.1.2 Membrane Aerated Biofilm Reactors

The gas-permeable membrane Biofilm Reactor (MfBR), more accurately known as the membrane-aerated biofilm reactor (MABR) is a novel aerobic treatment process providing oxygen directly into a biofilm of microorganisms via membranes. In sharp contrast to conventional membrane/assemblies for filtration, the membrane of MfBR is employed just as a bubbleless oxygen transfer interface. Oxygen passes through from the interior of the membrane lumen to the exterior surface of the biofilm on the surface of the membrane outer surface, and contaminants in the leachate pass through from the bulk liquid, and results in the simultaneous aerobic and anoxic reactions in the profiled biofilm.

This is in strong contrast to standard type Membrane Bioreactor (MBR) systems, where membranes are used for the solid–liquid separation (football side) and oxygen is provided by aeration of the entire bulk liquid (library side). MfBRs are complete agersion-off systems and are much more efficient in terms of oxygen transfer and energy requirement. Moreover, the counter-diffusion operation provides enough redox stratification to nitrification at the vicinity of the membrane interface and denitrification in the outer biofilm layers without the need for separate reactor zones or external carbon source.

Performance-wise, MfBRs have shown high removal rates for the priority pollutants present in landfill leachate. When COD/N is over 5, reported degrees of COD of 83.7%, NH of 93.1% and T-N of 84.6% of removal are obtained with 80–99% nitrification (Torretta et. al).

However, several limitations remain. The performance of the process is affected by COD/N ratios and influent composition. The membrane in long-term application may be blocked, peeled off or clogged by the biofilm, thus failing for long-term use and maintenance frequently. Fine control of the oxygen is also required to be able to maintain redox gradients, as well as to avoid over-oxygenation. Moreover, the technology has so far largely been applied at pilot scale, based on a few full-scale implementations, because of its process complexity and cost.

3.2 Advanced Oxidation Processes (AOPs)

AOPs utilize highly reactive oxidizing species such as hydroxyl or sulfate radicals that can react and decompose contaminants present in wastewater. AOPs were first proposed in 1980s for treating potable water but later caught on to be applied for the treatment of various types of wastewaters because oxidants can degrade recalcitrant organic pollutants and certain inorganic pollutants.

Advanced oxidation processes (AOPs) which are defined as the oxidation processes involving the generation of hydroxyl radicals (OH·) in sufficient quantity to effect water purification. Later, the AOP concept has been extended to the oxidative processes with sulfate radicals (SO4 ·−). Different from common oxidants such as chlorine and ozone that have a dual role of decontamination and disinfection, AOPs are applied primarily for destruction of organic or inorganic contaminants in water and wastewater.

The mechanism for contaminant removal using AOPs is more or less the same, i.e producing a highly oxidizing specie. Hence, based on the nature of the specie and the way this specie is produced, AOPs can be classified into several types which are to be discussed as follows.

3.2.1 Hydroxyl based AOPs

Hydroxyl is the most reactive oxidizing agent in water treatment with an oxidation potential ranging between 1.95-2.8 volts, depending upon pH (Tchobanoglous et al., 2003). Hydroxyl radicals attack organic pollutants through four basic pathways: **radical addition, hydrogen abstraction, electron transfer, and radical combination.**

Their reactions with organic compounds produce carbon-centered radicals (R· or R·–OH). With O2, these carbon-center radicals maybe transformed to organic peroxyl radicals (ROO·). All of the radicals further react accompanied with the formation of more reactive species such as H2O2 and super oxide (O2 •−), leading to chemical degradation and even mineralization of these organic compounds (Deng, Zhao, 2015). Hydroxyl radicals have a very short time and hence must be produced in situ during application using one of the several methods described further

3.2.1.1 Ozone-Based AOPs

Ozone (O_3) is a powerful oxidizing agent (E^0 = 2.07 V), and it can cause both direct and indirect oxidation. In the AOPs, ozone is utilized for the formation of hydroxyl radical (•OH) which are used along with other radicals released for scope of oxidation. On-line ozonation is selective and dependent on pH and causes primary attack on unsaturated and ionized organics. Nevertheless, in an alkaline environment or in presence of other compounds, ozone dissociates to produce •OH radicals. For

example, in O_3/H_2O_2 (peroxone), H_2O_2 decomposes to HO_2^-, which reacts with O_3 to generate •OH. In addition, with O_3/UV technology, UV radiation can enhance the decomposition of O_3 and result in the production of H_2O_2 to provide •OH by secondary photolysis. These dual processes enhance the •OH generation, further broadening the scope of organic pollutants treatment.

3.2.1.2 UV-Based AOPs

UV light is applied to activate oxidants or catalysts, which would start •OH production. TiO2 in the UV/TiO2 system absorbs the photons, and results in the production of the electron e− and hole h+ pairs. The valence band hole (h^+) oxidize water or hydroxide ions to •OH and the conduction band electrons reduced O_2 to O_2^-•. In UV/H_2O_2 processes, H_2O_2 is photolytic decomposed in UV and followed by the formation of two •OH radicals. In addition, water at wavelengths <242 nm can be photolyzed to produce •OH and H• radicals. These UV approaches are successfully employed because they are versatile, particularly for the refractory materials.

3.2.1.3 Fenton and Fenton-Like AOPs

In the Fenton process, Fe^{2+} reacts with H2O2 to generate •OH through the electron transfer:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$$

Theoretically catalytic, but not a real catalyst, since the regeneration of Fe^{2+} to Fe^{3+} is too slow Therefore at normal conditions, Fe^{3+} precipitates as sludge, which need to be separated and the operation cost will be increased. In Fenton-like systems, Fe^{3+} substitutes Fe^{2+}. Derivatives like photo-Fenton employ UV-light to photoreduce Fe^{3+} to Fe^{2+} and thus increase •OH production, whereas electro-Fenton electrochemically generates so with reagents.

3.2.1.4 Other Hydroxyl-Based AOPs

Other AOPs such as US (Ultrasound) and electron-beam irradiation exist but are not widely used. Ultrasound causes cavitation—microbubble collapse—generating very high local temperatures (∼5000 K) and pressures (∼500 atm), which break water into •OH and H• radicals. When water is irradiated with electron beam it will undergo direct water splittings to give a number of hemospecies * OH, H_3O^+, H_2O_2, e, and H•. These techniques are not as widely used, however they can be useful for some high-strength or difficult-to-treat wastewaters.

4. Leachate treatment using Plasma

4.1 Principle of plasma technology

Similar to other AOPs, plasma generates a variety of reactive oxidative species (e.g., •OH, O, HO_2•, O_2^-• , O_3 , H_2O_2) however it also produces reductive species (e.g., free and aqueous electrons e_{aq}- , H + , Ar , Ar*) along with local heating. Reductive species have been shown to play an important role in the degradation of PFAAs molecules (Thagard et al., 2016; Stratton et al., 2017).

The obvious difference between plasma and other AOPs is the ability of plasma to generate the reactive species in-situ i.e chemical additives are not required for the process to proceed. Similar to AOPs, the plasma generates reactive species (both oxidizing and reducing) that go on to degrade the various types of contaminants present in the wastewater or leachate.

4.2 Classification of plasma systems for water treatment

Cold plasma applications have been studied as powerful instruments for wastewater treatment due to the generation of extremely reactive species such as hydroxyl radicals (•OH), ozone (O_3), hydrogen peroxide (H_2O_2), aqueous electrons etc. These species are produced by various reactor types; so far, they utilize different principles and process conditions. The following summary provides an overview of the most common plasma reactor types used in different applications.

4.2.1 Dielectric Barrier Discharge (DBD) Reactors

DBD reactors are more commonly used for gas phase segregation. DBD reactors apply a high voltage (typically high-voltage AC) across two electrodes, separated by a dielectric barrier (for example glass or ceramic), resulting in non-thermal plasma. This arrangement suppresses arc generation and creates micro-discharges, both of which serve to release electrons and reactive species at atmospheric pressure.

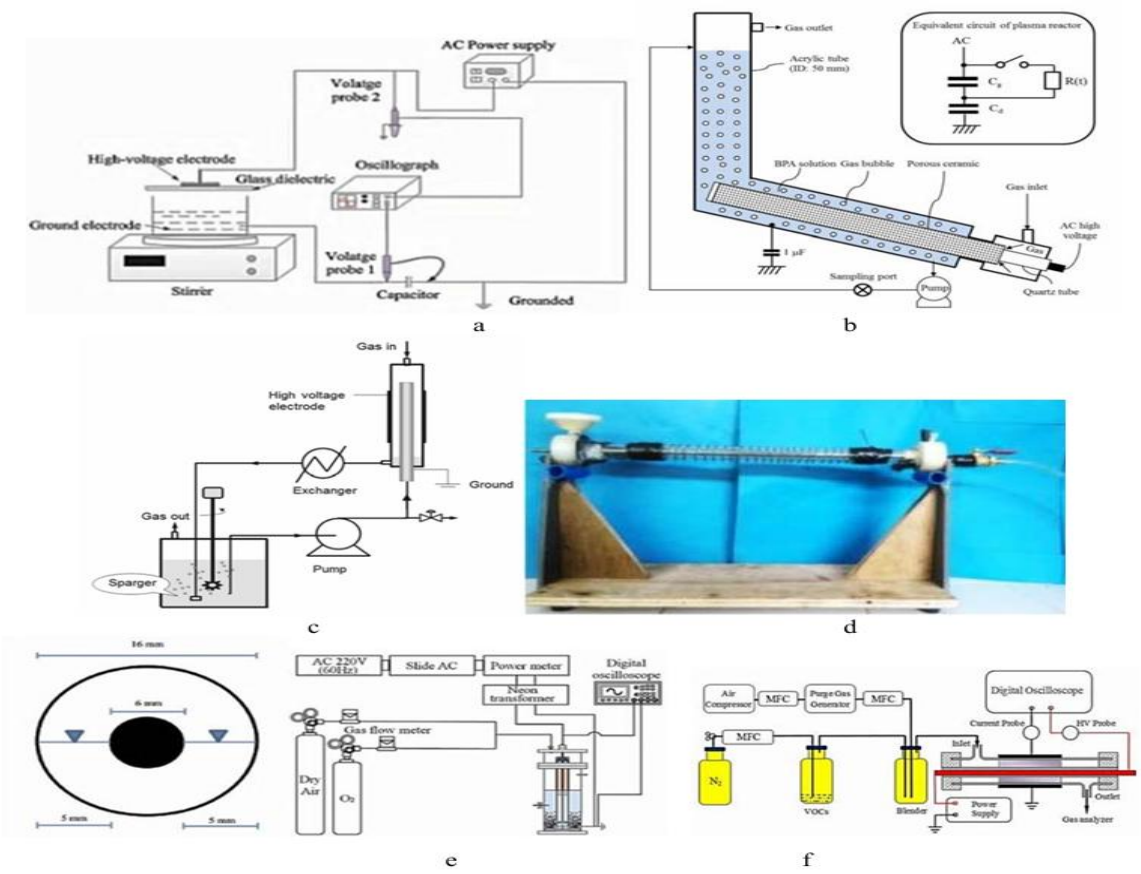


Figure 4.1 different plasma reactor configurations

Variations are the plate-to-plate (fig. 3.1a), loop (figure 3.1c), porous ceramic tube (figure 3.1b) and double-dielectric (figure 3.1f) configurations (Cui et al., 2018). Such systems are capable of successfully decomposing dyes, antibiotics and other organic compounds in general, particularly when used with additive agents of the type which cause radical formation, such as persulfate which generates further other radicals, such as sulfate radicals ($\bullet SO_4^-$). DBD systems are attractive due to their robustness and scalability for applications, however they suffer from relatively high energy consumption, and are especially suitable for the gas-liquid interface reaction types (Xu, 2001; Shang et al., 2017).

4.2.2 Reactors Using Pulsed Corona Discharge (PCD)

PCD reactors use high-voltage pulses to generate transient plasma discharges (also known as streamers) in a gaseous phase. These streamers produce energetic electrons, UV, and ROS. They can also degrade water pollutants including pharmaceuticals and endocrine-disruptors in cooperation with water treatment via bubbling or surface interaction (Ajo et al., 2015; Cui et al., 2018). e.g., less than 30 min with over 90% removal for decomposition of carbamazepine, and Acid Blue 25. Reactor configuration and solution conductivity, however, influence performance.

4.2.3 Gliding Arc Discharge Reactors

GADR reactors generate a thermal–non-thermal hybrid plasma by striking an arc between diverging electrodes in the flow of a gas. The arc “hovers” on the lowest potential energy path and generates

powerful oxidants such as •OH, NO, and H2O2 (Gharagozalian et al., 2017; Du & Yan, 2015). They are very efficient for the degradation of recalcitrant organic compounds (e.g, dyes; pharmaceuticals), showing > 90% degradation. Because of relatively high temperatures and larger plasma zones, gliding arcs can be applicable to concentrated and high-strength wastewaters, at the expense of more energy consumption compared to non-thermal ones.

4.2.4 Contact Glow Discharge Electrolysis (CGDE)

In CGDE systems, plasma is generated directly at the surface of the electrolyte in contact with an anode to yield dense glow discharges. This system creates both •OH and H_2O_2 on-site and has been widely reported for the decomposition of various kinds of organics including dyes, antibiotics, phenols, and persistent organic pollutants (Sen Gupta et al., 2015; Cui et al., 2018). For example, near-complete mineralisation of dyes such as Remazol Red and alkyl benzene sulfonates has been reported in other studies using CGDE. But the CGDE systems could have the potential drawback of electrode erosion and loss of excessive energy if not well designed.

4.2.5 Atmospheric Pressure Glow Discharge (APGD)

The APGD reactors produce aerosols by means of the glow discharge produced at atmospheric pressure by means of a direct current between the pin electrode and liquid surface. This technique generates a multitude of radicals (•OH, NO, NH), UV light, and heat (Motyka et al., 2019; Jamroz et al., 2018). These systems may be used for antibacterial activities and de-coloration of dye-contaminated effluents. Operating at atmospheric pressure and small size are advantages of APGD reactors for decentralized water treatment, though treatment volume and electrode lifetime are still restrictive.

4.2.6 Enhanced Contact Plasma Reactors (ECo-PRe).

The ECo-PRe process is a system designed for PFAS treatment; it injects argon gas into PFAS-contaminated water for the concentration of PFASs at the gas–liquid interface. The plasma is ignited above the liquid surface using a rotating spark-gap, to obtain oxidative (•OH, O_3, H_2O_2) and reductive (e_aq^-, H•, Ar^+) species (Singh et al., 2021). Such combination increases the degradation of both long-chain and short-chain PFAS in LL. Long-chain PFAS are removed >99.9% and short-chain PFAS are removed 10–99.9% by the system, which is more energy-efficient compared to UV, sonolysis, and electrochemical methods. The status of the technology is bench-scale and the mechanism of the surfactant-assistance had to be optimized yet, but it is a promising and still experimental answer.

Type of Discharge Reactor	Conditions	Removal Efficiency (%)
DBD	sulfonamide antibiotics	90
PCD	RCW, BTCW	93

Pulsed-streamer corona discharge	CBZ	94
Pulsed spark plasma	Staphylococcus aureus	90
DC pulseless corona discharge	Acid Blue 25	99.03
G Arc	RB19	98.19
CGDE	Remazol Red	99.97
APGD	organic dyes	92–100

Table 4.1 removal efficiency of plasma reactors (cui. et. al., 2018)

4.3 Degradation Mechanism of Plasma Assisted Waste Water Treatment

The efficacy of plasma-assisted wastewater treatment is due to the fact that, plasma technology generates a composite mix of various reactive species which act on the contaminants through different chemical and physical channels. These mechanisms depend on the type of the reactor and the plasma parameters.

4.3.1 Hydroxyl Radical Pathway

•OH species are one of the strongest oxidants, which are produced in non-thermal plasma systems. They are nonselective in attacking organic compounds by hydrogen abstraction, radical addition, and electron transfer.

Formation of •OH due to electron impact on water:

$$H2O + e^- \rightarrow \cdot OH + \cdot H + e^-$$

4.3.2 Ozone Pathway

Ozone (O_3) is generated during plasma discharge in an oxygen environment, serving as a direct oxidizer and being a precursor of hydroxyl radicals.

Ozone production from atomic and molecular oxygen proceeds as follows:

$$\cdot O + O_2 + \rightarrow O_3$$

Production of hydroxyl radical:

$$\cdot O + H_2O \rightarrow 2OH\cdot$$

Unsaturated compounds and aromatic rings are particularly well reacting with ozone. It can also be dissolved in water with strong base, which results in more •OH generation.

4.3.3 Hydrogen Peroxide Pathway

Hydrogen peroxide (H_2O_2) is an important oxidant generated in plasma sources. It is formed by the recombination of OH radicals. Hydrogen peroxide can then be excited by an electron, hydrogen radical or ozone to produce hydroxyl radicals again.

Recombination of radicals:

$$\cdot OH + \cdot OH \rightarrow H_2O_2$$

UV photolysis of H_2O_2:

$$H_2O_2 + h\nu \rightarrow 2OH\cdot$$

4.3.4 Reductive species pathway

Reductive species such as solvated electrons (e_{aq}−), Ar+ and hydrogen radicals (•H) play important roles in plasma processes, especially in the defluorination of halogenated compounds, such as PFAS (per- and polyfluoroalkyl substances).

In plasma-based degradation of perfluoroalkyl substances (PFAS), the mechanism involves a sequence of reductive and oxidative reactions that progressively shorten the perfluorinated carbon chain.

Initially, PFAS molecules such as $C_nF_{2n+1}X$ (where X is a functional group like $–COO^-$ or $–SO_3^-$) are exposed to plasma-generated reactive species including argon ions (Ar^+), electrons (e^-), and solvated electrons (e_{aq}^-).

These species induce the cleavage of the terminal group, generating a perfluoroalkyl radical (C_nF_{2n+1}•). This radical then reacts with hydroxyl radicals (•OH) to form a perfluoroalcohol ($C_nF_{2n+1}OH$), which subsequently undergoes elimination of hydrogen fluoride (HF), yielding a perfluoroacyl fluoride intermediate ($C_{n-1}F_{2n-1}COF$). This COF group is hydrolyzed in the presence of water and hydroxide ions to produce a shorter-chain perfluorinated carboxylate ($C_{n-1}F_{2n-1}COO^-$). The entire process repeats, breaking down the PFAS molecule carbon by carbon (Singh et. al., 2021).

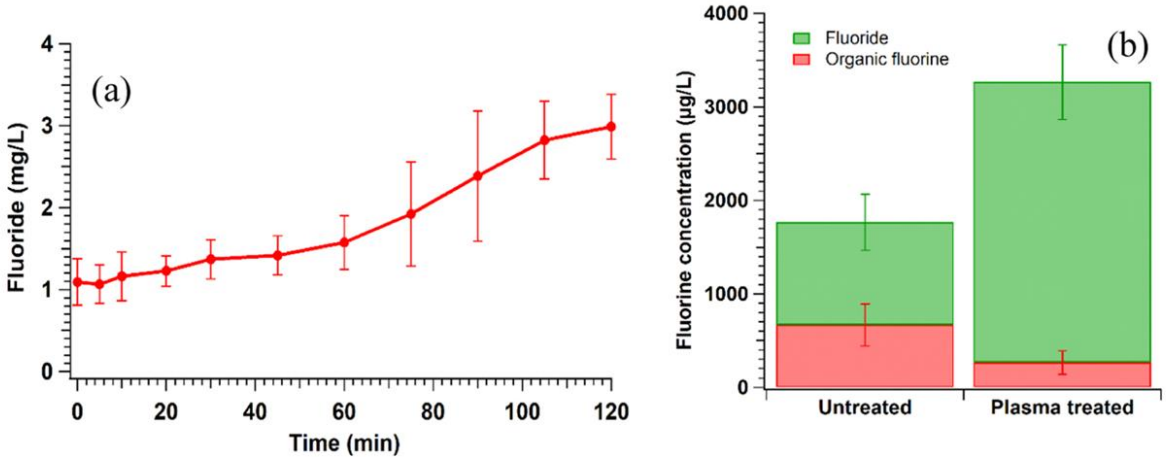


Figure 4.2 transformation and evolution of organic fluorine into inorganic fluorine (fluoride) Singh et. al., 2021

4.4 Comparative advantages of plasma

Plasma treatment demonstrates several advantageous aspects over other available treatment methods such as biological or chemical treatment. A brief description of these comparative advantages are listed below.

4.4.1 Generation of Multiple Reactive Species

Plasma generates multiple oxidizing and reducing species in-situ that are able to degrade extremely persistent contaminants such as PFAS (Singh et. al., 2021). These species include hydroxyl, ozone, peroxide, solvated electrons and Ar+. This multi-pronged cocktail of reactive species helps degrade a wide array of organic contaminants and industrial dyes (cui et. al., 2018).

4.4.2 No chemical additives required

Plasma processes are largely self-sustaining in terms of oxidant generation. Reactive species are produced in situ from air, water, or added carrier gases (e.g., argon), reducing the need for external chemicals such as chlorine, ozone, or Fenton's reagents (Torretta et al., 2017). This gives plasma a great competitive advantage over other AOPs and obviously the biological treatment processes.

4.4.3 Removal of Emerging Contaminants and Refractory materials

Plasma has shown high removal efficiencies for CECs and refractory materials. Ajo et. al., demonstrated a more than 90% reduction in refractory materials using a PCD reactor whereas Singh et. al. obtained a nearly 99% reduction in PFAS. These discoveries make plasma a suitable method at least for targeted pollutants.

4.4.4 Faster reaction kinetics

The reaction kinetics for plasma based reactions are of much higher order compared to biological treatment. Singh et. al. tabulated the decay constant for combined PFAS and PFOS removal to be between 0.2 /min and 0.34 /min. The removal rates required to obtain concentrations under **HAL** are achieved between 10 and 90 mins.

4.4.5 Operation at ambient conditions

Most cold plasma systems (e.g., DBD, APGD) operate at or near room temperature and atmospheric pressure, avoiding the high thermal (unlike anaerobic processes) or pressure demands (Torretta et al., 2017). Nevertheless, energy demands arise mainly due to electricity requirement for plasma generation.

4.4.6 Adaptability with other technologies

Plasma is well suited to give synergistic effects to work with other technologies in order to remove targeted contaminants such as PFAS or other CECs. Plasma can be effectively combined with photocatalysis, Fenton-like reactions, or persulfate activation to enhance performance through synergistic generation of radicals.

4.4.7 Electrical Energy per order EE/O

Energy efficiency of plasma reactors is calculated by the equation suggested by Nzeribe et. al., 2019.

$$EE\ /\ O = \frac{P * t * 1000}{V * 60 * \log(\frac{Ci}{Cf})}$$

Where, P= power (kW), t= time required for 90 percent degradation (=2.303/k), V= volume of reactor, Ci, Cf= initial and final concentration.

EE/O for the treatment of PFOA and PFOS ranged between 20-36 kWh/m^3 for leachate. These values are in the same range or a little higher compared to EE/O required for treatment of groundwater samples 1.7-56 kWh/m^3.

4.5 Limitations and challenges of plasma treatment

Although plasma treatment has shown great promise to remove some contaminants, the shortcomings of the process still hinder the process to be applied beyond lab-scale/pilot plants. Understanding these drawbacks is essential for optimizing and integrating plasma into real world wastewater treatment system. This section includes a non-exhaustive list of potential challenges the technology needs to address.

4.5.1 Non-standardization of reactors

Numerous configurations (DBD, PCD, EcoPre etc) have their unique advantages and limitations. This lack of standardization makes it difficult to implement technology on an industrial scale.

4.5.2 Limited treatment volume

Most of the plasma reactors are bench or pilot scale and optimized for small flowrates. Scaling up to industrial or municipal wastewater treatment presents engineering challenges related to mass transfer, electrode design etc.

4.5.3 Poor energy efficiency for some pollutants

Although, the energy efficiency for plasma reactors is high for long chain PFAS the short chain PFAS may require significant amounts of energy since the degradation is much slower. In order to enhance the removal rate, certain additives such as surfactants (e.g CTAB) may be employed (Singh et. al., 2021)

4.5.4 Generation of Byproducts

Formation of byproducts such as chlorite, chlorate and perchlorate are investigated by some studies. Particularly, perchlorate is a major concern since it is an EDC (Singh et. al.). It is also a major byproduct in electrochemical processes (Yang et. al., 2019). Singh et al observed an increase in chlorite and chlorate in treated water whereas perchlorate was below the detection limit (0.2 mg/l).

Other than these, breakdown of PFAS may yield short chain fluorinated carboxylates which are persistent.

4.5.5 Lifespan of electrodes

Many plasma systems, especially the contact based, suffer from electrode erosion or fouling which reduces their operational life and requires frequent maintenance.

4.5.6 Capital and operational costs

Although plasma may not require reactive species in the amounts comparable to other AOPs, the capital, maintenance and operational costs much higher compared to other processes. This will probably be a less of an issue when the technology matures and scalability eventually flattens out the steep costs at present.

5. Comparative analysis and future perspectives

Plasma-based technologies have emerged as a promising method for treating persistent and emerging contaminants in leachate from the landfills. However, the technology has shown limitations in several areas discussed in the last chapter. This chapter gauges how plasma treatment compares with other contemporary and conventional technologies and how it can be improved to be implemented on a larger scale.

5.1 Performance summary

This section presents a comparative evaluation of conventional, novel (MBRs, AOPs), and plasma-based leachate treatment technologies based on key performance metrics. The comparison highlights differences in pollutant removal efficiencies, energy consumption, sludge generation, and technological readiness.

Technology Type	Target Pollutants	Removal Efficiency	Energy Consumption	Sludge Generation	Scalability/Readiness
Conventional (e.g., Biological treatment)	BOD, COD, NH_4^+	Moderate to High	Low	High	Widely implemented
Novel (e.g., MBR, AOPs)	NH_4^+, COD, micropollutants	High	Moderate to High	Moderate	Pilot to commercial
Plasma-based (e.g., ECo-PRe, DBD)	PFAS, COD, dyes, CECs	Very High (up to >99%)	Moderate to High	Minimal	Pilot-scale, emerging industrial

Table 5.1 comparison of treatment technologies

5.2 Technological suitability and application scenarios

While performance metrics provide a useful tool for the comparison of treatment technologies, the utility of these metrics in practice will ultimately be determined by site-specific conditions, treatment objectives and operational limitations. This section describes when conventional, innovative and advanced technology are most appropriate for leachate treatment.

Conventional treatment techniques; Biological and physicochemical processes are most effective on young leachate with high biodegradable organic matter and ammoniacal nitrogen. These systems are mature, economically competitive and can be easily implemented at large scale. However, their removal is still not satisfactory for refractory organics, color, salinity, and emerging organic contaminants, in particular, from aged leachate.

In fact, MBRs, nanofiltration, electrochemical oxidation and other new technologies are more suitable for aged leachate or leachate which contains recalcitrant or low- biodegradability compounds. They provide good selectivity and pollutant rejection at the expense of higher energy requirements, membrane fouling and more complexity in operation. Where regulatory demands are strict, however, these systems are frequently part of a modular or hybrid setup.

Although plasma based treatment processes are still relatively new, they are particularly suitable for the degradation of recalcitrant micropollutants including PFAS, pharmaceuticals, synthetic dyes, and colour compounds. These systems are excellent for discrete polishing or finishing operations where traditional methods prove incapable. Their low-sludge production, capacity to produce both oxidizing and reducing active species, and potential to be combined with other AOPs set them as suitable candidates for decentralized or high resilience-based applications. However, existing applications are mostly limited to pilot plant and specialty industry, waiting for developments in terms of scalability and cost-effective production.

5.3 Future directions

While individual treatment technologies offer distinct advantages, their limitations often become evident when applied to complex and variable leachate matrices. In this context, hybrid systems—which combine two or more treatment technologies—are gaining traction as a means to enhance overall treatment efficiency, reliability, and cost-effectiveness. Plasma-based technologies, in particular, exhibit strong potential for integration with both conventional and novel approaches.

One promising avenue is the integration of plasma with membrane systems, such as Membrane Bioreactors (MBRs) or nanofiltration (NF) units. Plasma treatment can serve as a post-treatment polishing step, removing residual color, pharmaceuticals e.g antibiotics, and persistent contaminants like PFAS that membranes alone may not eliminate. Additionally, pre-treating leachate with plasma may reduce membrane fouling by breaking down high-molecular-weight organics.

Another viable hybrid configuration is plasma combined with Fenton-like advanced oxidation processes (AOPs). The generation of reactive radicals (e.g., •OH, O_3) in plasma can be further enhanced by the addition of hydrogen peroxide or persulfate, creating a synergistic radical pool that improves the degradation of refractory compounds. Such configurations may also allow for lower energy requirements, as radical formation can be chemically assisted rather than entirely plasma-driven.

Recent studies have also explored the use of surfactants or catalysts (e.g., CTAB by Singh et. al, TiO_2 by Zhang et. al., 2016) to enhance plasma-liquid interactions and radical generation. These adjustments can improve the contact efficiency between plasma and nonpolar contaminants, thereby expanding the range of pollutants that can be effectively treated.

Moreover, hybridization may be critical for addressing some of the current limitations of plasma systems, such as limited throughput and high energy demand. By using plasma reactors in a targeted, modular manner, alongside biological or physicochemical treatment units, the overall system can achieve higher removal performance without disproportionately increasing operational costs.

In summary, hybrid systems that incorporate plasma technology offer a flexible and effective approach to leachate treatment, particularly when designed to exploit complementary strengths of each component. Future research should focus on optimizing these configurations, understanding synergistic mechanisms, and validating long-term performance at pilot and full scales.

5.5 Conclusion

A comparative analysis was presented in this chapter between traditional, emerging and plasma based technologies for leachate treatment and their level of appropriateness, potential integration, and future developments. It is evident that conventional technology is the cornerstone of the current treatment landscape there is an increasing need to cope with refractory pollutants, especially in response to more stringent effluent regulations.

Although plasma-based methods are at the initial or pilot phase of development, they have a number of unique opportunities for the destruction of refractory and emerging contaminants including PFAS, pharmaceuticals and synthetic dyes. The fact that they can work with a minimum number of reagents, to generate a broad range of reactive species, and that they produce low amounts of sludge, make them very attractive for polishing applications or specific treatment needs. Nevertheless, issues with energy requirements, reactor volume, and standardization have prevented widespread commercial applications.

By the process of hybridization with established technologies and the optimization of reactor design, plasma systems can progress from the experiment stage to practical industrial use. In short, the future of leachate treatment could perhaps not be about singling out technologies, but instead about combining them in a smart manner to tap into the best of both worlds.

With increasing severity of the environmental and regulatory issues and the increasingly complex challenges to be addressed, it is absolutely necessary for treatment systems to not only be effective but also for treatment technology to be able to operate in a wide range of conditions. In this context, plasma technology could be considered as a futuristic, versatile and promising tool in the growing toolbox for sustainable leachate treatment.

REFERENCES

Eurostat. (2022). Generation of waste by waste category, hazardousness and NACE Rev. 2 activity [Dataset]. Eurostat. https://doi.org/10.2908/ENV_WASGEN

Blumenthal, K. (1995). Generation and treatment of municipal waste. *Notes*, *2002*, 2009.

Deng, Y., Zhao, R. Advanced Oxidation Processes (AOPs) in Wastewater Treatment. *Curr Pollution Rep* **1**, 167–176 (2015). https://doi.org/10.1007/s40726-015-0015-z

Walker, T. (2013). Managing leachate at different landfills across the US: perspectives from an owner. *EREF Regional Summit on Leachate Management, Philadelphia, PA*.

Lee, A., Nikraz, H., Hung, Y., 2010. Characterization of Acetogenic and Methanogenic Leachates Generated from a Sanitary Landfill Site Proc. Int. Conf. Environ. Eng. Technol., World Acad. Sci., Eng. Technol. 2010 24 29.

Kjeldsen, P., Barlaz, M. A., Rooker, A. P., Baun, A., Ledin, A., & Christensen, T. H. (2002). Present and long-term composition of MSW landfill leachate: a review. *Critical reviews in environmental science and technology*

Lei, L., & Aoyama, I. (2010). Effect-directed investigation and interactive effect of organic toxicants in landfill leachates combining Microtox test with RP-HPLC fractionation and GC/MS analysis. *Ecotoxicology*

Asadi, M., 2008. Investigation of heavy metals concentration in landfill leachate and reduction by different coagulants, in: Proceedings of the 7th International Conference on Environmental Engineering Fac. Environ. Eng. Vilnius Gedim. Tech. Univ., pp. 484–488

Vandermeersch, G., Lourenço, H. M., Alvarez-Muñoz, D., Cunha, S., Diogène, J., Cano-Sancho, G., Sloth, J. J., Kwadijk, C., Barcelo, D., Allegaert, W., Bekaert, K., Fernandes, J. O., Marques, A., & Robbens, J. (2015). Environmental contaminants of emerging concern in seafood – European database on contaminant levels. Environmental Research, 143, 29–45. https://doi.org/10.1016/j.envres.2015.06.011

Monneret, C. (2017). What is an endocrine disruptor? Comptes Rendus. Biologies, 340(9–10), 403–405. https://doi.org/10.1016/j.crvi.2017.07.004

Naveen, B. P., Mahapatra, D. M., Sitharam, T. G., Sivapullaiah, P. V., & Ramachandra, T. V. (2017). Physico-chemical and biological characterization of urban municipal landfill leachate. Environmental Pollution, 220, 1–12. https://doi.org/10.1016/j.envpol.2016.09.002

Adhikari, B., Dahal, K. R., & Khanal, S. N. (2014). A review of factors affecting the composition of municipal solid waste landfill leachate. *International journal of engineering science and innovative technology*, *3*(5), 273-281.

Abdel-Shafy, H. I., Ibrahim, A. M., Al-Sulaiman, A. M., & Okasha, R. A. (2024). Landfill leachate: Sources, nature, organic composition, and treatment: An environmental overview. Ain Shams Engineering Journal, 15(1), 102293. https://doi.org/10.1016/j.asej.2023.102293

Ilmasari, D., Kamyab, H., Yuzir, A., Riyadi, F. A., Khademi, T., Al-Qaim, F. F., Kirpichnikova, I., & Krishnan, S. (2022). A review of the biological treatment of leachate: Available technologies and future requirements for the circular economy implementation. Biochemical Engineering Journal, 187, 108605. https://doi.org/10.1016/j.bej.2022.108605

Castrillón, L., Fernández-Nava, Y., Ulmanu, M., Anger, I., & Marañón, E. (2010). Physico-chemical and biological treatment of MSW landfill leachate. Waste Management, 30(2), 228–235. https://doi.org/10.1016/j.wasman.2009.09.013

Sanguanpak, S.; Chiemchaisri, C.; Chiemchaisri, W.; Yamamoto, K. Influence of operating pH on biodegradation performance and fouling propensity in membrane bioreactors for landfill leachate treatment. *Int. Biodeterior. Biodegrad.* **2015**, *102*, 64–72

Torretta, V., Ferronato, N., Katsoyiannis, I., Tolkou, A., & Airoldi, M. (2016). Novel and Conventional Technologies for Landfill Leachates Treatment: A Review. Sustainability, 9(1), 9. https://doi.org/10.3390/su9010009

Renou, S., Givaudan, J. G., Poulain, S., Dirassouyan, F., & Moulin, P. (2008). Landfill leachate treatment: Review and opportunity. Journal of Hazardous Materials, 150(3), 468–493. https://doi.org/10.1016/j.jhazmat.2007.09.077

Tchobanoglous G, Burton F, Stensel H. Wastewater engineering. New York: Metcalf & Eddy Inc; 2003

Deng, Y., & Zhao, R. (2015). Advanced Oxidation Processes (AOPs) in Wastewater Treatment. Current Pollution Reports, 1(3), 167–176. https://doi.org/10.1007/s40726-015-0015-z

Ajo, P., Kornev, I., & Preis, S. (2015). Pulsed corona discharge in water treatment: The effect of hydrodynamic conditions on oxidation energy efficiency. Industrial & Engineering Chemistry Research, 54(30), 7452–7458. DOI: 10.1021/acs.iecr.5b01915

Singh, R. K., Brown, E., Mededovic Thagard, S., & Holsen, T. M. (2021). Treatment of PFAS-containing landfill leachate using an enhanced contact plasma reactor. Journal of Hazardous Materials, 408, 124452. https://doi.org/10.1016/j.jhazmat.2020.124452

Nzeribe, B. N., Crimi, M., Mededovic Thagard, S., & Holsen, T. M. (2019). Physico-Chemical Processes for the Treatment of Per- And Polyfluoroalkyl Substances (PFAS): A review. Critical Reviews in Environmental Science and Technology, 49(10), 866–915. https://doi.org/10.1080/10643389.2018.1542916

Yang, S., Fernando, S., Holsen, T. M., & Yang, Y. (2019). Inhibition of Perchlorate Formation during the Electrochemical Oxidation of Perfluoroalkyl Acid in Groundwater. Environmental Science & Technology Letters, 6(12), 775–780. https://doi.org/10.1021/acs.estlett.9b00653

Zhang, C., Liu, J., Yang, X., Cao, W., & Qian, G. (2017). Degradation of refractory organics in biotreated landfill leachate using high voltage pulsed discharge combined with TiO 2. Journal of Hazardous Materials, 326, 221–228. https://doi.org/10.1016/j.jhazmat.2016.12.034

Abbreviations

MSW Municipal Solid Waste

CEC Contaminants of Emerging Concern

DOM Dissolved Organic Matter

XOC Xenobiotic Organic Compounds

LPI Leachate Pollution Index

XOC Xenobiotic Organic Compound

CEC Contaminant of Emerging Concern

EDC Endocrine Disrupting Chemical

RO Reverse Osmosis

NF NanoFiltration

AOP Advanced Oxidation Processes

MBR Membrane Bio Reactor

DBD Dielectric Barrier Discharge

GADR Gliding Arc Discharge Reactors

HAL Health Advisory Limit

TOP Total Oxidizable Precursor assay

Eco-Pre Enhanced Contact Plasma Reactors