STUDIES ON THE TREATMENT OF MUNICIPAL LANDFILL LEACHATE BY ADVANCED OXIDATION PROCESS AND MEMBRANE BIOREACTOR PROCESS

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By

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DECLARATION

I hereby declare that this thesis entitled **“STUDIES ON THE TREATMENT OF MUNICIPAL LANDFILL LEACHATE BY ADVANCED OXIDATION PROCESS AND MEMBRANE BIOREACTOR PROCESS”** submitted to the University of Calicut, for the award of Degree of Doctor of Philosophy under the Faculty of Engineering is an independent work done by me under the supervision and guidance of **Dr. P.A. SOLOMAN**, Professor in Chemical Engineering, Department of Chemical Engineering, Government Engineering College, Thrissur, University of Calicut.

I also declare that this thesis contains no material which has been accepted for the award of any other degree or diploma of any University or Institution and to the best of my knowledge and belief, it contains no material previously published by any other person, except where due references are made in the text of the thesis.

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CERTIFICATE

This is to certify that the work reported in this thesis entitled **STUDIES ON THE TREATMENT OF MUNICIPAL LANDFILL LEACHATE BY ADVANCED OXIDATION PROCESS AND MEMBRANE BIOREACTOR PROCESS,** that is being submitted by **Mrs. MINIMOL PIEUS T.** for the award of the Degree of Doctor of Philosophy, to the University of Calicut, is based on the bonafide research work carried out by her under my supervision and guidance in the Department of Chemical Engineering, Government Engineering College, Thrissur, University of Calicut. The results embodied in this thesis have not been included in any other thesis submitted previously for the award of any degree or diploma of any other University or Institution.

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ABSTRACT

Approximately 90% of municipal solid waste (MSW) in India is disposed off unscientifically in open dumps and landfills, causing public health and environmental problems. The leachate generated from the municipal landfills contains organic and inorganic pollutants which make it unsuitable for a discharge without proper treatment. Due to the high strength of landfill leachate, it is difficult to attain discharge standards using a single biological or physicochemical treatment process.

The present study focuses on the treatment of high strength matured and young landfill leachate by integrating the advanced oxidation processes (AOP) and membrane bioreactor process (MBR) to meet the stringent discharge standards. Due to its simplicity, the Fenton process is most frequently applied for the removal of recalcitrant compounds. Electro-Fenton process(EF) has the advantage of improved process control capabilities and it produces reduced amounts of sludge. Better effluent quality from MBR is a major factor in terms of wastewater management which makes it a prime reason for using MBR in wastewater treatment.

The Electro-Fenton process was compared with the Photo- Electro- Fenton process to select an appropriate AOP for enhancing the biodegradability of the leachate. EF process enhanced the biodegradability index of matured leachate to greater than 0.4, which is required for a greater completion of degradation of organic matter in a subsequent biological treatment system. Optimization of the factors affecting the EF process was performed using response surface methodology.

EF treated landfill leachate was subjected to the MBR process with an ultrafiltration membrane of size 0.1µm for enhancement of pollutant removal efficiency. Despite BOD removal being greater than 90%, matured landfill leachate could not meet the land discharge standards after EF and MBR treatment. Hence the treated leachate was further subjected to the EF process to mineralize the non-degraded pollutants. After EF-MBR integrated treatment system the COD removal efficiency was 98.9%. The kinetic coefficients of the untreated leachate and the EF treated leachate were compared and found that the biological treatability of the leachate has improved considerably due to the EF pretreatment. The toxicity analysis of the EF treated leachate using Poecilia Reticulata fish species showed 100% survival of test organisms after 96 hours of contact. Fouling phenomenon of the membrane showed that 70% membrane fouling occurred for EF treated matured landfill leachate after 150 minutes of flow.

Young leachate having a higher biodegradability index was treated by the MBR process to remove the biodegradable part and was further post-treated with EF process to meet the land disposal standards. MBR-EF integrated treatment system showed excellent performance especially in terms of reduction of COD (98.8%). 73% fouling of the membrane occurred for young leachate after 70 minutes of flow.

Cost estimation of matured and young leachate treatment showed higher treatment cost for matured leachate than that required for young leachate. Chemical cost and electrode cost contributed much towards the operating cost. The findings of the research reveal that EF and MBR processes can be integrated effectively for treating both the matured and young landfill leachate for meeting the strict quality standards for direct use of leachate as irrigation water.

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ABBREVIATIONS

AF	Anaerobic filters
ANOVA	Analysis of Variance
AOP	Advanced Oxidation Process
AOX	Absorbable Organic Halogens
APHA	American Public Health Association
ASBO	Aerobic activated sludge biological pre-oxidation
ASBR	Aerobic Sequencing Batch Reactor
ASP	Activated Sludge Process
BAF	Biological Aerated Filter
BDL	Below Detectable Level
BI	Biodegradability Index
BOD	Biochemical Oxygen Demand
CAS	Conventional Activated Sludge Process
CD	Current Density
COD	Chemical Oxygen Demand
DC	Direct Current
DoE	Design of Experiments
EAOP	Electrochemical Advanced Oxidation Process
EF	Electro Fenton Process
EPA	Environment Protection Agency
HRT	Hydraulic Retention Time

JNNURM	Jawaharlal Nehru National Urban Renewal Mission
LC	Lethal Concentration
LPI	Leachate Pollution Index
MBBR	Moving Bed Biofilm Reactor
MBR	Membrane Bioreactor
MLSS	Mixed Liquor Suspended Solid
MLVSS	Mixed Liquor Volatile Suspended Solids
MSW	Municipal Solid Waste
MSWDF	Municipal Solid Waste Disposal Facility
NEERI	National Environmental Engineering Research Institute
NF	Nano- Filtration
NSWAI	National Solid Waste Association of India
HMW	High Molecular Weight
OLR	Organic Loading Rate
PAC	Powdered Activated Carbon
PAN	Polyacrylonitrile
PCB	Polychlorinated Biphenyl
PE	Polyethylene
PEF	Photo Electro Fenton
PES	Polyethylsulphone
PP	Polypropylene
PVDF	PolyvinylidenumDifluoride

RBC	Rotating Biological Contactor
RNA	Ribosomal Nucleic Acid
RO	Reverse Osmosis
RSM	Response surface methodology
SBR	Sequencing Batch Reactor
SPEF	Solar Photo Electro Fenton process
SRT	Sludge Retention Time
SVI	Sludge Volume Index
TKN	Total Kjeldah Nitrogen
TOC	Total Organic Carbon
TSS	Total Suspended Solid
UASB	Up-flow Anaerobic Sludge Blanket
UF	Ultra-Filtration
UN	United Nations
UNDESA	United Nation Department of Economic and Social Affairs
UNESCO	United Nations
UVA	Ultraviolet long wave
VFA	Volatile Fatty Acid
XOC	Xenobiotic Organic Compound

CHAPTER - 1

INTRODUCTION

1.1 Water: Global perspective

One of the greatest challenges of 21st century is the supply of safe drinking water for people all over the world. Just 2.5 percent of the water available on earth is fresh and two third of it is frozen in polar ice caps and glaciers. World water development 2018 reports that the global demand for water has risen at the rate of 1 percent per year over the past decades as a consequence of economic development, population growth and changing consumption patterns. While agriculture is the greatest consumer of water, industrial and domestic demand is increasing at a faster rate. Considering the ever increasing requirement in the industrial and domestic sectors, world water demand is projected to reach 20 to 30% of the present water consumption level (Wada et al., 2016). By 2050 over half of the world's population and about half of grain production will be at a risk due to water stress. World Bank and UN reports warn that 40 percent of the world is currently affected by water scarcity. Water demand is rising due to expansion of the human population, such that many of the world's major aquifers are becoming exhausted. Water stress including inadequate access to water and sanitation facilities, has been associated with social instability, conflict and even violence, and ultimately with growing trends in human displacement and migration (Miletto et al., 2017). It is now commonly said that future wars are more likely to be fought over water.

Water shortages can result from two methods: Physical water shortages and Economic water shortages. Physical water shortage is a consequence of inadequate natural water resources to meet the water demand. Economic water shortage is due to inadequate process management of the available water resources. Hence it is vital for all countries to have proper and sustainable water management strategies.

Consequently any steps made towards proper water management would have an effect on society's socio-economic well being. Water reuse becomes essential to overcome the growing environmental problems due to water scarcity. It is very important to prevent pollution of available water bodies and remove existing contaminants or reduce concentration of contaminants in water resources. Development of appropriate treatment strategies for wastewater containing toxic, biodegradable and non-biodegradable compounds should be forced to counter balance the growing environmental problems due to pollution of water bodies.

1.2 Indian perspective

UNESCO report predicts an intensified water crisis across India by 2050. More than half of the rivers are heavily polluted. Contamination is no longer a problem with surface water alone but also with groundwater resources. The report found that most of the rivers of Maharashtra, Assam, Madhya Pradesh, Gujarat and Bengal are polluted. In south, quantity of water in the main rivers Godavari, Cauvery and Krishna is much reduced. The Central pollution control board warns that if the situation is not reversed, the demand for fresh water for all uses will be unmanageable.

The state of Kerala is famous for its lakes, backwaters and 44 rivers that run across its terrain. The average rainfall of the state is 3055mm which is 2 times more than that of national average. But due to the climate change, mining, quarrying and pollution, drinking water has become a scarce commodity. As per Kerala Economic Review 2016 a majority of the drinking water supply sources are bacteriologically and chemically contaminated. Use of polluted water causes several water borne diseases.

Hence it is very important to safeguard available water resources and remove existing contaminants or reduce concentration of contaminants entering water bodies.

1.3 Landfills and water pollution

The industrial and economic growth has led to household and industrial waste production on the rise. In the last decade, annual production of garbage in the developed countries is between 300 and 800 kilograms per person per year. Sanitary landfilling is the typical way of disposing urban solid wastes (Abbas et al., 2009). Solid waste can be divided into three categories depending on various sources such as urban waste, biomedical waste and industrial waste. The most typical solid waste is municipal solid waste (MSW) known as garbage which originates primarily from residential and business complexes. A landfill is a place for the disposal of waste materials. This is the oldest and most familiar method of waste treatment approach and it can also be used as a short-term storage, consolidation and transition. Because of their economic benefits, sanitary landfill approach for the final disposal of solid waste remains broadly accepted and used. With many benefits, a major drawback is the production of highly polluted leachate, which poses considerable differences in both chemical composition and volumetric flow. In summary, municipal solid waste management represents today a global environmental, economic and social challenge, mainly because the quantity of waste is growing faster than the world population. In India, the quantity of municipal solid waste produced per day is about 0.15 million tonnes (Rathod et al., 2013). Based on the studies carried out by the National Environmental Engineering Research Institute (NEERI) in Indian cities, the quantum of MSW generation differs between 0.21-0.35 kg/capita/day in the urban areas and goes up to 0.5 kg/capita/day in big cities. Year after year, the identification of the impact of landfill leachate on environment has driven authorities to set ever more stringent specifications for pollution control (Renou et al., 2008). However, when stringent environmental requirements on surface and groundwaters are continuously enforced, the treatment of leachate from landfill becomes a prime environmental concern.

Landfill leachate is an effluent that is created mainly by the rainfalls on the crest of the landfill. The rainwater penetrates into the garbage which causes physical mixing and chemical reactions among the components present in the waste. The leachate commonly comprises high amounts of organic matter, ammonium and toxic compounds. Hence it is categorized as high strength wastewater. The main possible environmental effect of landfill leachate is the contamination of surface water and groundwater. Landfill leachate includes pollutants that can be classified into four catagories including dissolved organic compounds, inorganic macro components, heavy metals and xenobiotic organic compounds. Domestic waste contains little quantity of heavy metals; hence its contribution in leachate is small (Kjeldsen et al., 2002). In tropical weather climate regions leachate generation is comparatively higher due to the greater magnitude of precipitation which penetrates into the landfill cell (Renou et al., 2008).

1.4 Treatment of landfill leachate

The composition of landfill leachate deviates greatly based on the period of the landfilling (Altin, 2008). Depending on the landfill age, it can be classified into three types: young, medium and old (Renou et al., 2008). For example, young leachate is distinguished by high organic fraction such as volatile organic acids, total organic carbon (TOC), high CODs, BOD_5 and a BOD_5 to COD ratio > 0.3 (Umar et al., 2010). Old leachate, in contrast is distinguished by a relatively less biochemical oxygen demand (BOD), slightly basic with $pH > 7.5$ and BOD_5 to COD ratio < 0.1 (Li et al., 2010). Due to anaerobic decomposition, humic and fulvic acid and NH_3–N are also formed at this point (Bashir et al., 2010). Organic portion will be degraded during the stabilization period. The BOD_5/COD ratio reduces with time as the non-biodegradable portion of COD remains unaltered in this process (Ahmed and Lan, 2012).

Leachate needs adequate treatment before final discharge to decrease the high concentration of contaminants to an appropriate level (Hilles et al., 2015). There are a variety of treatment methods available for leachate, including physical, chemical and biological prcesses. Recalcitrant or non biodegradable substances like phenolic compounds, organic halogens and poly chlorinated biphenyls could be removed from leachate using physical and chemical treatment techniques.

Biological treatment has been highly efficient in extracting nitrogenous and organic matter (Abbas et al., 2009) from immature leachate when the BOD_5 is high and the BOD_5/COD ratio is greater than 0.5 (Renou et al., 2008). Biological treatments continue to be one of the suitable means in treating leachate as it provides a low capital and operating cost. Lower ratio of BOD_5/COD indicates that the leachate is in the stable stage and difficult to be decomposed further biologically (Aziz et al., 2010). Biological treatments have low efficiency towards certain substances such as halogenated bio-refractory organic compounds (AOX). Consequently, physical-chemical treatments are proposed for extracting refractory substances from matured leachate, and also as a polishing step for biologically treated leachate.

Landfill effluents need to be treated in the premises in order to attain the disposal standards for its discharge into the sewer / land or into surface water. Large recalcitrant organic molecules are the greater fraction of stabilized or biologically treated leachate which are not easily treatable by biological treatment. Discharge standards are usually unable to attain using a single biological or physico chemical process (Wang et al., 2018; Tarretta et al., 2017; Gotvajn et al., 2009). Development of integrated systems for treatment, i.e. a combination of chemical, physical and biological processes, are required in order to attain the strict quality standards for direct disposal of leachate into the surface water. Coupling an oxidation processes and biological processes will be a good choice for the treatment of leachate from landfill (Lin and Chang, 2000).

New treatment approaches under cleaner production technologies have been developed for landfill leachates. Advanced oxidation processes (AOPs) are employed where the treatment of complicated industrial effluents are not amiable to conventional biological methods. AOPs are utilized as a pretreatment for wastewater to improve the biodegradability of organic components and to assure their mineralization by biological treatment (Carlos Amor, 2019). Among different leachate treatment processes, advanced oxidation process are appropriate due to chemical expulsion of pollutants rather than toxic chemicals phase transfer (Atmaca, 2009; Deng and Ezyske, 2011). Coupling advanced oxidation process with biological treatment is conceptually beneficial as it can drive to increased treatment efficiencies compared with the efficiency of individual treatment units. Advanced oxidation uses radicals usually hydroxyl radical to enhance oxidation in a treatment process (Wei Li et al., 2010; Peralta-Hernández et al., 2009). Fenton process is an agreeable treatment among AOPs for lowering the effect of highly contaminated wastewater (Antonio, 2004). One of the distinct disadvantages of the conventional Fenton process is the excessive use of Fe^{2+} which releases a large quantity of iron sludge (Bui et al., 2019). Several research studies have presented that the Electro-Fenton process (EF) is a promising technique for extracting organic matter more efficiently and environment friendly compared to conventional Fenton processes (Barrera diaz et al., 2014; Ignasi Sires et al., 2014). The key benefit of EF process is in-situ reagent production, anodic dissolution of iron electrode causing lesser sludge production, regeneration of Fe^{3+} to Fe^{2+} at cathode and greater and faster mineralization rate of organic pollutant compounds.

Membrane technologies are used as a major step in the treatment of landfill leachate or as a post-treatment step for achieving water quality standards (Kjeldsen et al., 2002). Membrane bioreactor (MBR) is an integration of conventional biological process and membrane filtration. The segregation of solid from liquid, which is accomplished in a settling tank in conventional biological treatment plant, is replaced by membrane filtration in MBR systems. Hence the benefits of biological process and that of membrane filtration are integrated in MBR process. The foot print savings of the MBR treatment plant by itself can be as much as 50% than the conventional activated sludge process and there are added footprint savings, since the additional tertiary filtration steps are omitted (Galleguillos Torres, 2011). Considering the advantages of MBR system, it is ideally suitable for treatment of strong waste water.

The biodegradability of leachate reduces with growing age and conventional biological treatment by itself may be absolutely ineffective to meet the discharge standards. Combined AOP and MBR process can improve the biodegradability index and curtail pollutants at great extent. The total degradation rate of a combined AOP - MBR process is expected to be much higher than MBR process for treating a slowly biodegradable or biologically recalcitrant effluent like matured landfill leachate. This lower kinetics can end up with the requirement of greater capital investment. The integrated process is interesting in terms of lower capital investment and easiness of operation. Thus the overall treatment series of advanced oxidation process and MBR tend to be an effective method for the treatment of landfill leachate to attain the land disposal standards. The landfill leachate properties, technical applicability and constraints, effluent discharge alternatives, cost adequacy, regulatory prerequisites and ecological effects are essential elements to the choice of the most appropriate treatment procedure for landfill leachate treatment (Mojiri et al., 2013)

1.5 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) have been profitably used as pretreatment methods in order to lower the concentrations of toxic organic compounds that obstruct biological wastewater treatment processes. In AOPs, organic contaminants get oxidized mainly due to the hydroxyl radical reactions. In AOPs, oxidation occurs in two phases (1) strong oxidant (hydroxyl radicals) formation and (2) the reaction of oxidants with organic contaminants in water. AOPs principle mechanism is the production of free radicals which are highly reactive. Hydroxyl radicals (HO•) are efficient in the destruction of organic chemicals as they are reactive electrophiles (electron loving) that non-selectively and rapidly react with nearly every electron-rich organic compounds. Hydroxyl radicals have an oxidation potential of 2.8 V that show greater oxidation reaction rates as opposed to conventional ones. Once formed, the organic chemicals can be attacked by the hydroxyl radicals through hydrogen abstraction, radical addition and electron transfer. These radicals are highly reactive and attack majority of the organic molecules, and they aren’t highly selective. In practice, there are myriads of stubborn pollutants in wastewater, that fall between the potential of hydroxyl radical and other oxidative agents particularly from the challenging chemical or pharmaceutical industries and landfills. Advanced oxidation process is efficient in decomposing many toxic and bio-resistant organic pollutants without the production of additional toxic by-products or sludge that need further handling.

A great number of approaches are classified under the description of AOPs. Most of the AOPs use strong oxidizing agents (such as H_2O_2, O_3) with catalysts like transition metal ions and irradiation (e.g. ultraviolet, visible). Fenton‘s reagent seems to be among the most popular wastewater treatment technologies.

Fenton’s reagent is a combination of hydrogen peroxide (H_2O_2) and ferrous iron ($FeSO_4.7H_2O$). Hydroxyl radicals are generated from oxidizing agent hydrogen peroxide under the presence of catalyst Fe^{2+}. This reagent is considered to be most successful treatment among AOPs for remediation of highly contaminated water. Due to simplicity of the Fenton reaction, it is the most frequently applied method when removing recalcitrant compounds is needed. Fenton process will oxidize and mineralize nearly every organic carbon to CO_2 & H_2O.

However, the advantages of the Fenton reaction in the treatment of waste waters has set forth the development of its modifications such as Photo Fenton process, Electro Fenton (EF) process, Photo Electro Fenton (PEF) process.

1.6 Electro Fenton process and Photo Electro Fenton process

This method is a Fenton reaction aided by electricity. It will create more OH• radicals and accelerate the oxidation of the organics to CO_2 and H_2O. Usually, there are two different versions for Electro Fenton (EF). In the first version the Fe^{2+} and H_2O_2 are applied from outside to the reactor and inert material is used as anode which has high catalytic activity. In the second version, H_2O_2 is applied from outside and the sacrificial anodes of iron produce Fe^{2+}. The benefits of EF method is that it allows good control of hydroxyl radical production. The solvable Fe^{3+} can be cathodically reduced to Fe^{2+} in Electro-Fenton process. The rapid creation of Fe^{2+} promotes the production of OH•.

When an ultraviolet light irradiates the EF process, it can promote the degradation of organic substances (Brillas, 2014). The ferric complexes will be reduced to ferrous ion by photo-reduction or reduction at the cathode; this effectively triggers the Fenton chain reaction. The produced Fe^{3+} ions are photo chemically converted to Fe^{2+} ions. Fe^{2+} ions production is enhanced when the system is irradiated with UVA light of wavelength 320-400 nm.

1.7 Membrane Bioreactor

Membrane bioreactors are one of the efficient treatment options for the young leachate (Vahdani et al., 2015). Membrane bioreactor (MBR) is the most important treatment process out of advanced biological processes. MBR is considered to be a successful integration of conventional activated sludge (CAS) system and membrane separation, allowing for independent control of sludge retention time (SRT) and hydraulic retention time (HRT) and maintaining a high concentration of biomass in the reactors. MBR process has many advantages compared to CAS processes including a smaller footprint, improved effluent quality and less sludge generation. MBR can be worked at lengthy sludge ages and can extend greatly the range of biological processes for strong waste water, like leachate. The integration of bioreactors with membrane separation technology has led to a new focus on treating wastewater. Today, membrane technologies are used both as a significant step and as a post-treatment step in wastewater treatment and have proven to be an important means of attaining necessary standards (Kjeldsen et al., 2002).

1.8 Thesis outline

Thesis mainly intends to find an integrated system of Advanced oxidation process (AOP) and Membrane bioreactor (MBR) for landfill leachate treatment. The major fraction of matured landfill leachate is the presence of the organic recalcitrant molecules which cannot be simply separated by biological process alone. By treating landfill leachate with a single biochemical or physico - chemical process, discharge standards cannot be achieved. Hence integrating Advanced oxidation process with biological process would be a better option for treating high strength landfill leachate.

The landfill leachate samples were obtained from Municipal Solid Waste Disposal Facility at Brahmapuram, Kochi which were analyzed according to the ‘Standard methods for analyzing water and wastewater’. Kinetic coefficients k and Ks of matured and young leachate from the landfill were determined.

Selection of appropriate Electro Fenton based advanced oxidation process for the pretreatment of matured landfill leachate was made. Electro Fenton (EF) treatment of matured landfill leachate was compared with the Photo Electro Fenton process (PEF) using UV light and Solar Photo Electro Fenton process (SPEF) for biodegradability enhancement. The treatment process (EF) that attained maximum BOD/COD ratio was chosen for pretreatment. Specific anode consumption and specific energy consumption were determined. The sludge volume index of the treated leachate was estimated.

Using Response surface methodology optimization of the factors affecting the EF process was achieved. Box Behnken Design was adopted for the experiment design to find the relationship between response function and the variables. RSM was used to obtain an empirical model from the experimental data collected and its significance was checked by using ANOVA.

The biological treatability of the EF treated leachate was found by estimating the kinetic coefficients k and Ks. Toxicity test was performed on raw and treated leachate using test organism Poecilia Reticulata (Fish bioassay test).

The Membrane bioreactor process was integrated with EF process for treating matured landfill leachate. The optimum retention time and biomass concentration were determined. At optimum conditions, other parameters were analyzed. Microbial analysis of the sludge was carried out at microbiology lab. The fouling phenomenon of the membrane was studied and the degree of membrane fouling and its nature were determined.

Young landfill leachate was treated by integrating the MBR process with EF process as post-treatment. The optimum retention time and reduction of pollutants at the optimum condition were estimated. Fouling of the membrane after treating the young leachate was studied. EF process was used as post-treatment for separating the non-degraded pollutants from MBR effluent to meet the irrigation disposal standards. The efficiency of the EF process was studied by analyzing all other parameters at optimum conditions and compared with the discharge standards.

A general strategy was developed that can be used to integrate EF process and MBR process for both matured and young landfill leachate

The annual cost of the EF-MBR integrated system was estimated for treating both matured and young leachate by considering capital cost and operating cost.

CHAPTER - 2

LITERATURE REVIEW

2.1 Introduction

In recent decades, urbanization has increased in speed and scale. Today, fifty five percent of the earth's population lives in urban areas, and is predicted to grow to sixty eight percent by 2050. Forecast indicate that urbanization, the incremental change in human population's residence from rural to city areas, combined with the world population growth, could add another two and half billion people to cities by 2050, according to a recent United Nations report set up by the Population Department of the UN Department of Economic and Social Affairs (UNDESA). By 2050, it is expected that India will have additional four hundred and sixteen million urban dwellers.

The Municipal solid waste (MSW) management is a considerable challenge today. Due to several environmental, economic, social and legislative constraints, the recognition of the most suitable disposal method for MSW is a significant issue in almost all developed countries (Adani et al., 2000). The common forms of solid waste handling include landfill, refuse composting, incineration and hydrogenation. According to the Environment Protection Agency (EPA), landfills are engineered area where waste is deposited in the land. Sanitary landfilling has become the most common way of eliminating MSW in most countries. Yet, in low lying areas MSW is disposed of without taking care or operational controls. While landfilling is viewed as the most cost-effective way of the waste disposal process, defective management operations are the main causes of environmental pollution, particularly in developing countries such as India (Swati et al., 2018).

The amount of MSW produced depends on different elements such as eating habits, living standards, level of commercial activities and seasons. The percentage constitution of solid waste varies between regions because it is affected by various factors such as community attitudes, location, frequency of collection, population characteristics, legal systems, socio-economic and lifestyle as mentioned in Sharholy et al., (2008).

Under Municipal Solid Waste Management & Handling Rule, 2000, Government of India, garbage is classified as municipal solid waste including residential and commercial solid wastes produced in the municipality or in notified regions either in solid or semi-solid state eliminating hazardous wastes from industries but adding treated bio-medical wastes. The MSW includes household waste, sanitation residue, demolition and construction debris and waste from streets.

The large number of urban solid waste landfills and the many hazardous materials which they contain can pose serious environmental hazards to soil and groundwater, as landfills can release a wide variety of chemical compounds due to the waste degradation throughout the whole life cycle. Inside the landfill, the biodegradable portion of household waste is biodegraded to create the liquid leachate and landfill gas. Leachate contamination risk depends on the degree to which the pollutant barrier integrity is maintained and on the management efficiency of leachate.

2.1.1 Municipal Solid Waste Management Practices in India

Majority of the solid waste management practiced in developing countries are either open dumps or control dumps because there is no requirement for equipments and expertise to manage it. These sites pose a significant danger to the human health and environment. Open dumpsites caused a lot of public protest around the site which resulted in the termination of these sites in several developing countries.

Generation of waste is enormously growing and has exceeded 62 million tons per year in India. Around 91.4 percent of the total waste collected in landfills and the remaining 8.6 percent is either composted or incinerated. In India, the municipal solid waste generated capita ranges from 0.17 kg/capita/day in towns to 0.62 kg/capita/day in large cities (Kumar et al., 2009). Indian landfill sites pose threat to the environment, due to their non-engineered nature. The crude landfill sites in Indian scenarios lack baseliners, leachate treatment systems and gas ventilation systems. The heavy rain percolating through the landfills is producing pollutant laden liquid known as leachate. Leachate is the prime cause of the environmental mobilization of pollutants (Christensen and Kjeldsen, 1989).

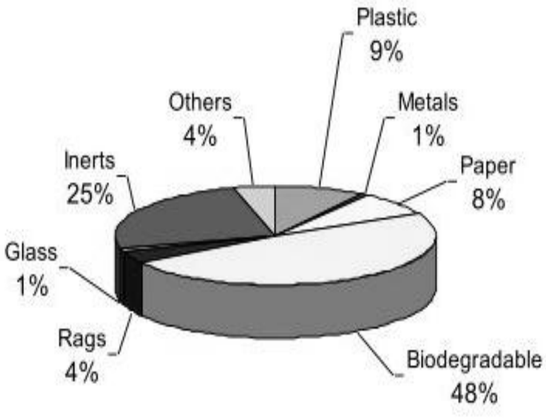

Fig. 2.1 Composition of municipal waste in India

Average waste management system in a middle-income country like India constitutes the following elements:

- Production and storage of waste
- Segregating, reusing and recycling
- Collection and transport of primary waste to a transfer station or community bin
- Street sweeping and cleansing of common spaces

- Management of transfer station or community bin
- Secondary waste collection and transportation to the disposal site

Waste disposal at landfill sites

Table 2.1 Type of litter generated and the approximate period taken to degenerate

Type of litter	**Approximate period taken to degenerate**
Organic waste such as rotten vegetable and peels, leftover food	7-14 days
Paper	10- 30 days
Cotton clothes	8-20 weeks
Wood items	10- 15 years
Woolen items	1 year
Metal items	100- 500 years
Plastic bags	10^6 years
Glass bottles	Not determined

MSW amounts in India are expected to rise remarkably in the near future as the country seeks to achieve astatus of industrialized nation. Figure 2.1 shows the composition of municipal waste in India.

Inferior collection and insufficient transportation are the reason for the accumulation of MSW everywhere. As stated in NSWAI (National Solid Waste Association of India) unscientific disposal creates an adverse impact on everyelement of the environment and human health. The type of litter and the average amount of time it takes for deterioration is shown in Table 2.1 (Rajput et al., 2009).

2.2 Phases of degradation of Landfill

The environment in a landfill depends on different physical, chemical and biological processes. Despite large differences in waste composition, water content and management, it is possible to sort out generalizations and identify a group of particular landfill processes. In a landfill with significant amounts of organic matter, biodegradation of organic substance is the controlling process which governs the landfill biogeochemistry. The characteristics of leachate can be described in terms of various chemicals that can be classified as inorganic maters, organic matters and xenobiotic organic compounds. Within landfill many complex reactions occur sequentially which can be categorized as physical, chemical and biological process. The transformation of organic matter moves through a number of different phases that are relatively same among MSW landfills. They are:

I. Aerobic stage
II. Acidic stage
III. Initial methanogenic stage
IV. Stable methanogenic stage
V. Secondary aerobic stage

When deposited, the waste contains oxygen and the landfill is in stage-I, Microorganisms that thrive in oxygen-rich conditions start to degrade the organic matter. The oxygen is depleted relatively quickly, and when new waste is placed on top or the landfill is covered, no additional oxygen can reach the waste. The aerobic stage typically lasts for only a few hours or days and aerobic degradation of organic matter leads to a high rate of CO_2 formation. When the oxygen is depleted anaerobic microorganisms take over. Initially hydrolytic micro organisms are the most active, degrading large organic molecules into mono-saccharides, alcohols, carboxylic acids, etc. This leads to a build-up of volatile fatty acids causing the pH to decrease, sometimes down towards pH 5, and the landfill enters stage-II, the acid phase. The chemical oxygen demand (COD) and biological oxygen demand (BOD) in the leachate are high and in between 0.7 and close to 1, the BOD/COD ratio is also high at this stage. The acid leachate enhances dissolution and leads to high concentrations of pollutants, such as heavy metals. Stage-II typically lasts for months to years and ends when microorganisms degrading the intermediate products into CO_2, H_2 and acetate become more active and the pH increases. Methanogenic bacteria that are sensitive to low pH thrive and produce methane from these molecules. During stage-III, the initial methanogenic phase, most leachate concentrations decrease. Methane production increases until it reaches a relatively stable value.

During stage-IV the landfill enters a stable state of methanogenesis with only gradual changes in gas and leachate composition. Landfill gas typically consists of 50–70 % methane and 30–50 % carbon dioxide. The pH during this stage is neutral or slightly alkaline. Ammonium is formed due to the degradation of organic matter and typically accumulates in the leachate, as it has no biodegradation mechanism under methanogenic conditions. The rate of ammonium release is relatively low and thus ammonium is expected to be the most significant long-term pollutant at landfills. The BOD/COD ratio is also low; approaching 0.1, because the most degradable dissolved organic matter is consumed by the microbial population. However, concentrations of more stable organic molecules, such as humic and fulvic acids, increase. After years, or even decades or centuries, when the organic matter that is degradable by anaerobic microorganisms has been depleted, the formation of landfill gas will decrease and eventually, the gas pressure within the landfill will equal the atmospheric pressure. At that point oxygen begins to enter the landfill by diffusion and advection, marking the start of stage-V, the second aerobic phase. This phase has rarely been observed but predicted. Initially, the oxygen is consumed by microbes that oxidize the remaining organic matter and produce stable molecules such as humic substances. At this stage, CO_2 is formed by the oxidation, but as degradation ceases, the gas composition approaches that of the atmosphere. Depending on various factors such as the quality of the cover and the water content of the landfill, the time it takes for a landfill to become completely oxidized varies between hundreds and tens of thousands of years (Kjeldsen et al., 2002).

2.3 The generation of landfill leachate

Up to 95 percent of the world's solid waste generated is currently disposed of in landfills (Kurniawan et al., 2006; Bohdziewicz and Kwarciak, 2008). Given the many benefits of landfills, the production of highly contaminated leachates is a major downside, with large variations in both chemical composition and volumetric flows. The leachate from landfills could be generated by two major causes. The first source is external water which goes into the landfill and produces leachate. Due to the biodegradation of organic waste, the second source is leachate generation from the landfill itself.

2.3.1 External Water

Majority of the leachate is generated by direct penetration of water i.e. rainwater and snow melt penetration into the waste. Such liquids can penetrate the landfill for several years and will contact with various substances within the landfill during this period. The water is leaching and dissolving different components until it contains lot of chlorinated organic matter and other substances. The leachate can affect nearby groundwater and surface water. The rainfall intensity, quantity, frequency and duration affect the amount of leachate produced. The humidity in the atmosphere exerts a heavy influence on the production of leachate. The waste is infiltrated by the surface water as well as by the groundwater. The infiltration of surface water is dependent upon the site type. If the landfill is constructed below a sloping field, that has surface water, from the direction of topography it will fall down on the landfill. If the landfill bottom is below the water table, the groundwater can otherwise infiltrate into the waste. The quantity of leachate is dependent on groundwater and waste interface situations.

2.3.2 The wastewater generated within the landfill

Water fractions in the waste contribute to the leachate, too. During the waste placement the waste moisture is created by waste. Untreated solid waste in the landfill will generate leachate which is a major source of organic substances within the waste. By anaerobic decay, this becomes a highly contaminated liquid inside the landfill. The damp waste contains excess moisture from the atmosphere or rainwater which includes the adsorbed moisture andits own moisture. The damp waste gets compacted and organically decomposed in the landfill by biological, physical and chemical processes.

The quantity of leachates depends on the infiltration of rainwater through wastes, the inherent water content of wastes, biochemical processes in the cells of waste and its level of compaction of the landfill as mentioned in Abbas et al., (2009). The leachate generation also depends on other factors such as waste content, landfilling techniques, landfill age and humidity, as mentioned in Adhikari et al., (2014).

2.4 Landfill leachate characteristics

Concentrating on the most usual type of landfill receiving a combination of residential, commercial and blended industrial waste, landfill leachate may be described as a water based solution with four categories of pollutants namely dissolved organic matters, macro inorganic compounds, heavy metals and xenobiotic organic compounds originating from domestic residueand chemical residues present in low concentrations as mentioned in

Christensen et al., (2001). The leachate has an orange brown or dark brown hue. The smell associated with leachate is foul-smell, mainly due to the presence of organic acids, which arises from the high concentration of decomposed organic substances. Depending on the increasing landfillage, the nature of precipitation and the quantity and quality of the waste, the dark colour and malodour will slowly disappear or decrease as mentioned in Li Rong, (2009).

2.4.1 Dissolved organic matters

The component of dissolved organic matter in leachates such as BOD (Biochemical Oxygen Demand), TOC (Total Organic Carbon) and COD (Chemical Oxygen Demand) is defined using various bulk parameters. Acids, alcohols, aldehydes and other dissolved organic matter commonly quantified as BOD, COD, Dissolved Organic Carbon (DOC), other volatile fatty acid and refractory compounds such as humic-like and fulvic-like compounds. A large number of degradation products of organic matter ranging from small volatile acids to refractory humic and fulvic-like compounds are dissolved in leachate as mentioned in Dewalle and Chian, (1977).

Dissolved organic matter may affect the composition of leachate compared to the other constituents by the complex properties of the compounds of high-molecular-weight (HMW) in it. At the most general level, a lower BOD/COD ratio indicates leachate with lesser concentrations of volatile fatty acids and comparatively greater levels of fulvic and humic-like components.

2.4.2 Inorganic macro compounds

These include ammonium (NH_4^+), sulphate (SO_4^{2-}), chloride (Cl-), calcium (Ca^{2+}), sodium (Na^+), magnesium (Mg^{2+}), potassium (K^+), hydrogen carbonate(HCO_3^-), iron (Fe^{2+}) and manganese (Mn^{2+}). The concentration in the leachate of some inorganic macro compounds depends on the landfill stabilization. Due to a lower dissolved organic matter content and higher pH, the cations like magnesium, calcium, iron and manganese are lesser in methanogenic phase of leachate. In the methanogenic phase, sulphate concentrations are also low due to the reduction of sulphate to sulphide by microbes. The effects of complex formation, sorption and precipitation are small for some macro compounds such as chloride, sodium and potassium. Diminishing tendency in concentration of contaminants with time could be due to washing out by the process of leaching as stated in Ehrig, (1989). Many research works report the concentration of ammonia nitrogen in leachate ranges from 500 to 2000 mg/l. Ammonia is extracted from the waste primarily by decomposition of proteins. Leaching is the single mechanism by which ammonia concentration can reduce during waste decomposition.

2.4.3 Heavy metals

The sum of heavy metals is related to how much industrial waste will be present in landfills. Household waste includes only very small quantity of heavy metals. If there is mixed filling in the landfill, then the industrial refuse is the primary source for the content of heavy metals. This include lead (Pb^{2+}), nickel (Ni^{2+}), copper (Cu^{2+}), cadmium (Cd^{2+}), chromium (Cr^{3+}) and zinc (Zn^{2+}). There is a significant variance in the concentration of heavy metals recorded from various landfills. Average concentrations of metal is, however, very small. Several researchers reported low metal concentrations from full-scale landfills, test cells and laboratory tests. The heavy metals in landfill leachate from MSW are therefore not a prime concern as mentioned in Kjeldsen et al., (2002) and Esakku et al., (2005).

2.4.4 Xenobiotic organic compounds

These compounds include hydrocarbon aromatics, chlorinated aliphatics, phenols, pesticides and plasticizers. The mono aromatic hydrocarbons (benzene, ethylbenzene, toluene and xylenes) and halogenated hydrocarbons such as trichloroethylene and tetrachloroethylene are the most frequently occurring Xenobiotic organic compounds (XOCs). Such contaminants are found at the highest levels. In spite of the very complicated structure of landfill leachate, these non-polar organic substances are relatively easy to examine. They have significant negative effects on the aquatic environment. Information on ionic and polar organic contaminants is scarce but many researches are going on as stated by Kjeldsen et al., (2002).

2.5 Factors influencing the leachate characteristics

Leachate consists of both organic and inorganic compounds. The chemical constitutions of leachates vary due to various factors like waste composition, landfill age, seasonal weather/climate variability at the deposited site and landfilling process (Raghab et al., 2013).

2.5.1 Composition of waste

The waste composition has a great impact on landfill leachate water quality. An element that determines the chemical constitution of the landfill leachate is the kind of waste collected on a landfill. Waste from various sources contains different of these organic and inorganic materials, e.g. municipal, industrial etc. Organic waste products in the waste are mainly waste from kitchen while inorganic components are items such as plastics, metals, glass etc. The leachate from landfill includes COD and BOD that are derived from the organic compounds of domestic waste. The proportion of domestic biological waste, which may be high or low in the waste, may directly affect the COD and BOD concentration as mentioned in Madu Jude, (2008).

The residues of dust and soil have the purpose of filtration and adsorption of organic matter present in leachate. Hence the concentration of leachate could also be influenced by the contents of dust and soil within the waste.

2.5.2 Age of landfill

Leachate generation in sanitary landfilling is a complex mix of physical, chemical and biological processes whereby waste age has a major impact on the landfill performance that produces leachate. Leachate quality is significantly influenced by the age or length of time after filling waste. Results show that the content of leachate is well associated with the age of waste. This is largely due to the degradation of both organic and inorganic components in the waste by microbes which experience different exposure of acetogenic and methanogenic phases as mentioned in Lee et al., (2010).

The numerous landfill sites remain with various stages. Leachate can be classified into various forms depending on the landfill age. Leaching from landfills of less than 5 years old is commonly considered as young leachates. It’s said that the young leachates are in the acidogenic stage. In this process, landfills carry large quantities of biodegradable organic matter that is usually considered to undergo fermentation anaerobically facilitated by landfill water content resulting in the genetaion of volatile fatty acids (VFA). As the landfill continues to take place after 5 years, the methanogenic stage begins. Methanogenic microbes grow in the waste, turning the VFAs to CH_4 and CO_2 and the organic portion of the leachate becomes primarily non-biodegradable (refractory) compounds like humic substances. Leachates from landfills between the ages of five and ten are leachates of medium or intermediate age because they may be having both acidogenic and methanogenic characteristics where as those from landfills more than ten years are considered to be stable or old. Table 2.2 reports the leachate composition at various age levels.

Table 2.2 Composition of leachate at different age range

Leachate type	**Young**	**Intermediate**	**Old**
Landfill age (yr)	<5	5-10	>10
pH	<6.5	7	>7.5
BOD/COD	>0.3	0.1- 0.3	<0.1
TOC/COD	0.3	-	0.4
Organic matter	70-90% VFA	20- 30% VFA	High Molecular Wt.
Nitrogen	100-2000 mg/l TKN		
Metals g/l	2	<2	<2

The potential of hydrogen ion (pH) is a measure of a solution's acid or basic content. Table 2.2 reports that the pH of the young leachate is in acid range while the old one is in basic range. COD is a measure of the contaminants concentration in leachatethat can be oxidized by a chemical oxidizing agent. BOD_5/COD is the relationship among BOD and COD which shows the level of biodegradability of the leachate. As mentioned in Renou et al., (2008) if BOD/COD ratio is higher than 0.3, it is young leachate. When the ratio is in the range 0.1 - 0.3, it is medium age leachate and if the ratio is lower than 0.1 then it is old leachate. Volatile fatty acids (VFA) are the results of the degradation of organic matter anaerobically. From table 2.2 it is seen that they account for approximately 80 percent of the content of young leachate while old leachates mainly contain organic content of fulvic and humic substances.

2.5.3 Climate /seasonal weather variation

The variability of climate/seasonal weather affects the leachate production in terms of both quality and quantity. The moisture content of landfills increases during the rainy season. Since the amount of moisture improves the anaerobic degradation of organic matter, in the rainy season biodegradation would be quicker and more compared to the hot season. Thus the humid and hot climate which aids microbial activities produces more leachate and biodegrades more organic compound than the dry climate. Evaporation also adversely affects moisture content in the dry season which decreases the leachate generation and activities of microbes.

2.5.4 Method of landfilling

The landfilling process affects the leachate quantity and quality. The landfill flood control system is useful for aiding the surface water discharge. Additionally, it is better to use the clay layer at the bottom of the landfill to regulate the flowing ground water and surface water into the landfill. Generally, the production is greater when the waste is less compact since compaction reduces the rate of filtration (Bhalla et al., 2012).

2.6 Environmental issues pertaining to landfills

Conventional landfills contain a combination of various types of waste, including residential, industrial, construction and demolition waste, with diverse organic and inorganic substances and a wide variety of physical and chemical characterictics. MSW usually contains a significant fraction of biodegradable material, and thus major conventional landfills contain significant quantity of organic matter. Gas and leachate are the two primary emission pathways for pollutants from landfills. Degradation of organic compounds forms landfill gas. Its main components are CO_2 and CH_4, both of which are greenhouse gases, with CH_4 on a one hundred year time scale being over 20 times more potent than CO_2. A combination of physical, chemical and microbial processes carries contaminants from the waste substance to the leachate, making it a complex liquid.

Waste was disposed off in dumps that did not have liner or pollution control methods. Groundwater and surface water contamination is considered as a serious environmental effect of landfills for several years. Organic substances may cause depletion of oxygen in the reciever. The high levels of nutrients and other leachate and wastewater products, such as xenobiotic organic compounds like phenols and pesticides, pose a risk to the environmentand human health. Inorganic macro components comprise nutrients that induce eutrophication, and many freshwater organisms are toxic to many inorganic compounds mostly seen in landfill leachate, such as ammonia and chloride (Kjeldsen et al., 2002). Leachate released without sufficient treatment will lead to eutrophication of water bodies causing algal blooms, oxygen depletion, habitat loss and increased turbidity and water toxicity. Leachate needs an efficient treatment before final discharge to reduce the higher contaminants concentration to an acceptable range (Hilles et al., 2016).

2.7 Leachate discharge standards

The landfill discharge standards should be reviewed in various aspects: the continuous impact on the environment, the leachate quality, economic abilities and the practical situation of the landfill. Standards aim to furnish executive criteria to be followed. The standard differs in different countries. Table 2.3 shows the limiting concentration of environmental pollutants for discharge in India (Environment Protection Rules, 1986).

Table 2.3 General standards for discharge of environmental pollutants as per The Environment (Protection) Rules, 1986, Govt. of India

Characteristic	**Inland surface**	**Public sewer**	**Land disposal**
SS mg/L	100	600	200
pH	5.5-9	5.5-9	5.5-9
NH_3-N mg/l	50	50	-
BOD mg/L	30	350	100
COD ,mg/L	250	-	-
Chloride mg/L	1000	1000	1000
Sulphate mg/l	1000	1000	1000
Sulphide mg/l	2	-	-
Phosphate mg/l	5	-	-
Bioassay Test	90% survival of fish after 96 hours in 100% effluent	90% survival of fish after 96 hours in 100% effluent	90% survival of fish after 96 hours in 100% Effluent

2.8 Landfill leachate treatment methods

There are numerous techniques for treating landfill leachates. The choice of apt treatment depends on several factors which correspond to the characteristics of each landfill. There are several things to consider such as quality and quantity of leachate, disposal standards, process residuals, geographical and climatic conditions, economic costs etc. Landfill leachate treatment methods can be generally categorized into physico-chemical and biological. Equalization tanks prior to treatment are sometimes needed due to the changes in the amount of leachate produced.

2.8.1 Physico-chemical method

Physico-chemical methods are non-biological methods used for treating leachate. The method accomplishes treatment by oxidizing pollutants with chemicals after which separation processes are applied physically. This method is also coupled along side the biological process to enhance treatment efficiency. It is applied in the removal of recalcitrant substances (humic substances or undesirable compounds) like heavy metals, polychlorinated biphenyls (PCBs) and absorbable organic halogens (AOXs) or non-biodegradable substances from leachate. Before discharge of effluent, an additional refining step using physical-chemical treatments can be carried out on-site. Air stripping, coagulation/precipitation, Electro coagulation, Activated carbon adsorption, Flotation, Advance oxidation technologies and Electro-chemical oxidation are the physico-chemical methods.

- Air stripping

Air stripping is a physico-chemical technique often used along with other technical solutions for ammonia removal (Yuan et al., 2016). It accelerates the biodegradation of organic compounds and inorganic compounds of nitrogen (mainly ammonia-nitrogen). Significant and sustainable reduction of landfill emission occurs, resulting in minimization of environmental risks caused by polluted leachate. It may speed up the decreasing BOD_5 and TOC concentrations, which is an indicator of organic material degradation; while the decrease in ammonium concentration and the similar intermediate presence of nitrate/nitrite are an indicator of nitrification processes. This process is applied for treating stabilized leachates, reaching high efficiencies with higher retention times and temperatures.

- Coagulation/precipitation

It is an effective pretreatment before biological or membrane treatment, or an efficient leachate post- treatment. The method supports the reduction of large organic molecular compounds in leachate. Coagulant Ferric chloride at pH values above 9 is more effective than alum in reducing organic constituent of leachate. Lime can remove heavy metals such as Cd, Fe and Cr by up to 90 percent, but increases hardness and pH, offers low COD removal (20-40%), and produces large amount of sludge at high dosages. Due to its low efficiency for the removal of organic content, it is not suitable for complete treatment of leachate. The efficiencies in COD removal primarily depend on pH, coagulant species, coagulant dose and leachate characteristics, ranging from ten percent to eighty percent.

- Electro coagulation

Electro coagulation involves chemical and physical methods, which use sacrificial electrodes for production of the coagulants. The production of metallic cations occurs at the anode, while H_2 production takes place at the cathode. It has better treatment efficiency than chemical coagulation.

There are many factors able to influence the Electro-coagulation process, such as the reactor design, electrode material and current leachate density and conductivity (the removal of polluting particles increases with the density). Despite higher removal efficiencies achieved with aluminum, iron is considered the best electrode because it is less toxic, requires less energy, and is less sensitive to inhibitor phenomena (Wang et al., 2016). The disadvantage is that Electro coagulation corresponds to high energy consumption and, therefore, it is necessary to find a compromise between the removal efficiency and consumption of power required (Orkun and Kuleyin, 2012).

- Activated carbon adsorption

Adsorption is a surface phenomenon through which a multi-component fluid mixture is attracted to the solid adsorbent surface and gets attached via physical or chemical bonding (Foo and Hameed, 2009). Granular or powdered types of activated carbon accomplished a higher reduction in organic component than that recorded for coagulation or precipitation. It is effective in eliminating non-biodegradable and colour causing organic components that are left after the biological treatment. This method extracts substances that are preferentially low molecular weight. Application is restricted by the need for regular regeneration of carbon particles or, equivalently, high amount of carbon powder.

- Advanced Oxidation technologies

In recent years, there has been a growing interest towards Advanced oxidation processes (AOP) using the combination of strong oxidizing agents such as O_3 and H_2O_2, together .with ultraviolet radiation or ultrasound. Many processes are based on the direct reaction of the oxidant with the contaminants while AOP is characterized by the generation of OH radicals as reactive species able to oxidize halogenated organics and improve the biodegradability of recalcitrant organic pollutants.

Fenton's reagent (H_2O_2/Fe^{2+}) is one of the most efficient method of organic pollutant oxidation among diverse AOPs. The Fenton reaction initiated by Fe^{2+} and H_2O_2 and the Fenton-like reaction initiated by Fe^{3+} and H_2O_2 are used for the treatment of leachates since they can significantly remove recalcitrant and toxic compounds and increase leachate biodegradability low operating cost. O_3, UV, UV + O_3, and O_3 + H_2O_2 have particularly high operating costs for leachate treatment. H_2O_2 used alone has a limited COD reduction capacity, although not all organics are oxidized to carbon dioxide and water at a low operating cost.

- Electrochemical oxidation

The process is theoretically achieved by two distinct mechanisms: indirect oxidation, in which the oxidation is carried out by a mediator, which is electrochemically generated and direct anodic oxidation, in which pollutants are destroyed at the surface of anode. This method will effectively minimize organic content, ammonia, color and metals from leachate of landfill. Current density varies extensively from 5-540 mA/cm^2 for electrochemical oxidation of leachate. However, this technology could be applied to leachates in order to reduce the concentration of refractory organic matter and ammonium. Using this technology alone, it appears that it is not possible to achieve the limits for discharging into sewage, except where local limits for carbonaceous substances and nitrogen are decidedly more permissive. Even though high energy consumption may limit its implementation, Electro Fenton process is an optimistic technology for extracting organic matter more effectively, especially for low BOD_5/COD or high toxic landfill leachate and environmental friendly compared with conventional Fenton process (Rada et al., 2013).

2.8.2 Biological methods

Biological processes include the use of microorganisms to remove the organic and nitrogenous matter from young leachates. It involves modifying the microorganism environment for growth which can eliminate the substances. Biological removals of organic compounds are carried out using anaerobic and aerobic decomposition processes. Under anaerobic conditions (absence of oxygen or nitrate) e.g. Digesters, lagoons, anaerobic filters etc, organic compounds are converted into methane and carbon dioxide (biogas) as well as water and a small fraction of fresh biomass (sludge). Non-injection of oxygen in the anaerobic systems, lowers their cost. Under aerobic conditions (presence of oxygen) organic substances are converted to carbondioxide, water and biomass.

Activated sludge reactors, aerated lagoons and bio rotors are examples of biological processes. Biological processes, however, cannot remove refractory organic compounds. The various biological methods that are used for landfill leachate treatment are Activated sludge process, Rotating biological contactor (RBC), Sequencing batch reactor (SBR), Reed Beds, Biological aerated filters (BAF), Lagoons, Upflow anaerobic sludge blanket (UASB), Anaerobic filters (AF), Moving bed biofilm reactor (MBBR), Membrane bioreactor (MBR).

- Activated sludge process (ASP)

Activated sludge is one of the methods used in leachate treatment. The aeration tank is where oxygen is introduced as the leachate flows along the system. The sludge generated at the clarifier (settling tank), settles at the bottom of the tank while the supernatant is runoff as effluent. Part of the settled material (sludge) is returned to the head of the aeration tank for re-seeding the incoming leachate with microorganisms. The re-seeding portion of the sludge is called return activated sludge while the excess sludge which accumulates is removed. However, the activated sludge process is not adequate for the leachate treatment due to the significant disadvantages of this treatment like high sludge production, which involves considerable costs for disposal; significant energy demand; the presence of inhibitor microorganisms due to the high concentrations of NH_3-N (Renou et al., 2008).

- Rotating biological contactor (RBC)

The rotating biological contactor, an attached growth technology is also known as a bio-rotor. It has plastic circular discs mounted on a shaft which partly submerged in a tank containing the leachate. As the shaft rotates gradually, microorganisms adhere to the disc as biological growth, assimilating and treating organic substances from the leached water as they move over the surface of the disc. When the disc rotates out of the leachate, aerobic conditions are maintained and organic compounds get oxygenated. Thus the disc makes contact between biomass and the leachate, mixing the mixed liquor and aerating the leachate. The performance of RBCs depends upon several design parameters such as rotational speed, organic and hydraulic loading rates, hydraulic retention time (HRT), RBC media, temperature, wastewater and biofilm characteristics, dissolved oxygen level, effluent and solids recirculation, step-feeding and medium submergence. Moreover, RBCs have some operating problems such as difficulty in the maintenance of appropriate biofilm efficiency is generally lower than with that of an activated sludge.thickness under adverse conditions (Cortez et al., 2008).

- Reed beds

Reed beds usually have gentle sloping beds lined with impermeable barriers and planted with emerging hydrophytes such as reeds (phragmites), bulrush (scirpus), or cattails (typha). Reed beds may have a crushed stone inlet zone to distribute wastewater evenly over the bed and an outlet zone of crushed stone for collecting and discharging effluent. Leachate enters at the inlet and flows gradually through the bed following a horizontal flow direction before leaving. The extensive root system of the reed provides a large surface area for attached microorganisms, increasing the potential for the decomposition of organic matter: Nitrogen and phosphorus are removed through plant uptake while ammonia is removed through volatilization and nitrification / denitrification (Kivaisi., 2001). The gravel or soil where the reeds are planted also serve as a filter medium.

- Biologically aerated filter (BAF)

A biological aerated filter is a treatment tank consisting of a submerged aerated fixed film biological filtration system that provides a surface for the biomass and also retains suspended solids which acts both as biological contactor and a filter, eliminating the need for a separate sedimentation step. There are numerous types of filling materials, all of which contribute to the removal of pollutants in different ways which can be ireused materials: plastic, wood or rubber from tyres. In the system, both the influent and the process air flow upward from the bottom. The highest biological activity occurs in the lower half of the filter and the treated leachate stays above the media.

- Lagoons

As in an activated sludge reactor, a lagoon for leachate treatment is normally an artificial pond with microorganisms. Lagoons can be anaerobic or aerobic, artificial or natural. A lagoon is anaerobic because it lacks dissolved oxygen for most of its depth (e.g. lagoons where liquid animal wastes are dumped) whereas an aerobic lagoon is one in which dissolved oxygen exists for most of its depth. Over the years, leachate treatment studies have been performed in anaerobic lagoons as well as in aerated lagoons. If the aerated lagoon method is adopted as a full-scale leachate treatment, hydraulic retention times (HRT) need to be fully evaluated since they can be significant (Mehmood et al., 2009). This treatment is suggested in countries with extensive free areas, with no energy available and low economic funds.

- Up flow anaerobic sludge blanket (UASB)

UASB technology is a form of anaerobic digester used for treatment of leachate and many other forms of waste water. The process involves an upward passage of leachate through an anaerobic sludge bed inside a tank. When the leachate passes through the sludge, microorganisms degrade organic matter in the leachate producing biogas (methane and carbon dioxide). As the gas moves upwards to escape, hydraulic turbulence takes place in the reactor prompting mixing which result to more degradation as a result of more contact of microorganisms with substrate. The gas is collected at the top of the reactor and the liquid phase is separated from the sludge solid. The effluent is collected after the separation of isludge. Retention of active sludge within the UASB reactor enables good treatment performance at high organic loading rates. Natural turbulence caused by the influent flow and the biogas production provides good wastewater-biomass contact in UASB; hence higher organic loads can be applied in UASB systems. Therefore, less reactor volume and space are required while, at the same time, high-grade energy is produced as a biogas that can be exploited. However, the effluent from UASB reactors usually needs further treatment in order to remove remnant organic matter, nutrients and pathogens (Seghezzo et al., 1998).

- Anaerobic filter (AF)

Anaerobic filter is yet another type of anaerobic digester. The digestion tank contains a filter medium (pieces of polyvinyl chloride plastic, etched glass, baked clay, reticulated polyurethane foam, expanded shale, porous stone) on which communities of anaerobic bacteria can grow. The bacteria remain in the filter, providing a long solid retention time, even though the HRT is much shorter. Soluble organic compounds in the influent wastewater pass in close proximity to the biomass and diffuse into the surfaces of the attached or granulated solids. Here they are converted to intermediates and to end products, specifically methane and carbon dioxide (Gourari and Achkari-Begdouri, 1997). AF has several advantages over aerobic and anaerobic processes. It is more suitable for handling high-strength wastewaters as it presents high substrate removal efficiencies at short hydraulic retention times and high organic loading rates. It should be joined with other treatment solutions as its removal yields must be improved for aggressive wastewater treatment.

- Moving bed biofilm reactor (MBBR)

The MBBR process is an attached growth biological leachate treatment process. In a reactor with ithe MBBR process, microorganism attach itself and grow on a plastic biofilm carrier that are suspended and are in continuous imovement within the reactor which maximize growth by protecting the biofilm from abrasion on a specified volume resulting in uniform and highly effective treatment. The media carriers may have different shapes and sizes depending on the application. They can occupy different volumes in the reactor, from 30% to 60%, depending on the amount of required biomass (Hemi et al., 1994). There might be a nitrification tank and denitrification tank. Sludge generated at the settling tank, settles at the bottom of the tank while the supernatant is runoff as effluent. To re-seed incoming leachate with microorganism part of the settled material (sludge) is returned to the head of the aeration tank.

- Sequencing Batch Reactor (SBR)

SBRs are alteration of the Activated sludge process. They vary from activated-sludge plants as they include all of the treatment measures and process wastewater in a single basin or tank where as conventional plants depend on multiple basins. The operation systems used in aerobic conditions comprise four steps: (1) feeding (2) aeration (3) settling and (4) discharge. SBR can be attached growth or suspended growth process. Due to the consumption of carbon sources in the aeration stage, wastewater does not have sufficient carbon source in the following anoxic denitrification stage and it leads to low total nitrogen (TN) removal iefficiency (Wei et al., 2012).

- Membrane Bioreactor (MBR)

Membrane bioreactor technology, which combines the biologically-activated sludge method and membrane filtration, has become more common, abundant, and has been approved for the treatment of landfill leachate in recent years. Membrane bioreactor is a biological waste water treatment process which uses membrane to replace the gravitational settling tank for the solid liquid separation of sludge suspension in the conventional activated sludge process. The MBR produces a clarified and considerably disinfected effluent. In addition, it concentrates the biomass and reduces the necessary tank size, increasing the bio-treatment process efficiency. MBRs thus tend to generate treated waters of higher purity with respect to dissolved constituents such as organic matter and ammonia, both of which are significantly removed by bio-treatment (Santos et al., 2011). MBR's in which biomass is strictly separated by membrane provide many advantages over conventional activated sludge process, including higher concentration of biomass, lower footprint, low output of sludge and improved permeate quality (Naghizadeh et al., 2008).

2.8.3 Coupling physico chemical process and biological process

Taking into account the leachate age, season, climatic conditions, regulation criteria and pollutant concentration, leachate treatment plants are forced to integrate physico-chemical and biological stages which improves the drawbacks and contributes to higher treatment efficiency. Past studies had already highlighted the difficulty of treating landfill leachate by stand-alone conventional chemical/physical or biological treatments due to the high percentage of high-molecular-weight organic materials and biological inhibition suggesting a combination of technologies in order to achieve high pollutant removal rates. Indeed, biological treatments are useful to decrease organic pollutants, but they are not able to reduce heavy metal concentrations or inorganic chemical compounds usually found within landfill leachate; ion the contrary, physical-chemical treatments are not suited to treat young leachates as they are not able to effectively reduce organics fractions. As a result, stand-alone technologies are not useful for leachate pollutant reductions and a combination is suggested in order to achieve regulation limits for the release to water bodies. Many combined treatments (SBR + Electro-oxidatiton, ASP + coagulation + photo fenton, Trickling filter + Electro-coagulation, photo fenton + MBR, Aerobic SBR + Adsorption, constructed wetland + adsorption, MBR + UF + Electro-Oxidation etc.) were studied, which achieved high pollutant removal rates and enhanced treatment efficiencies, thus allowing project developers to implement technological choices suited for specific landfill release management issues.

Advanced oxidation technologies are used in situations where the complex industrial effluents are not suitable for conventional biological treatment methods. The role of oxidation depends on the objectives of the treatment and can range from partial remediation to complete mineralization. In the case of partial treatment, oxidation aims at selectively removing the more bio resistant fractions and converting them to readily intermediates which can then be treated biologically. Coupling advanced oxidation with biological post-treatment is conceptually advantageous because it can lead to improved overall treatment efficiency relative to the efficiency of each individual stage. Membrane technology was noted as a viable treatment technology to comply with strict release concentrations, as reported by Abbas et al., (2009). However, fouling issues and high energy requirements are barriers that need to be overcome, specifically in developing countries.

2.9 Difficulties in treating landfill leachate

At present, the major challenges in handling leachate are as following: (1)Leachate has high organic component and a significant number of toxic and recalcitrant molecules. A single biochemical process or physico-chemical process cannot achieve discharge standards; an integration of physicochemical and biochemical processes is required. The first challenge is to select a fair, economical and efficient integrated process (2) Ammonia nitrogen levels are high, and it is difficult to identify an efficient and full nitrogen removal method for leachate. Improving the performance of nitrogen removal is the second main challange (3) the major variations in water quality and quantity intensify the complexity of finding a reliable discharge method. Leachate water quality and quantity can be varying which challenges both the identification and the operation of an effective treatment process. The third challenge in leachate treatment is the identification of a suitable integration of available technologies and how to apply them for a stable operation (4) the treatment process is highly complex and the cost of treatment are very high. In order to achieve discharge standards, leachate treatment plants often use nano-filtration and reverse osmosis which makes the treatment costs high. Reducing leachate treatment costs is the fourth main difficulty (Wang et al., 2018).

2.10 Advanced Oxidation Process

Advanced oxidation methods are acceptable among different leachate treatment strategies because of chemical expulsion of contaminants instead of toxic chemicals phase transfer (Deng and Ezyske, 2011). Advanced Oxidation Processes (AOPs) are a new and promising technique for the degradation of persistent environmental pollutants. Advanced oxidation processes have proven to be one of the most effective wastewater treatments that are difficult to be handled biologically. They are used successfully to decompose many toxic and bio-resistant organic pollutants in aqueous solution to acceptable levels, without creating additional dangerous by-products or sludge that requires further handling. Such processes are based on the generation of the powerfully oxidizing hydroxyl radicals (OH•), that oxidize a wide variety of organic pollutants that may be present in water and wastewater. Hydroxyl radicals are often distinguished by a little selectivity of attack, attractive attribute for an oxidant to be used in wastewater treatment. Several different organic compounds are susceptible to be removed or degraded by means of hydroxyl radicals. When hydroxyl radicals are generated, almost every organic molecule can be virtually oxidized and mineralized, yielding CO_2 and inorganic ions.

2.10.1 Theory of Advanced Oxidation

These processes are based on generating the highly oxidizing hydroxyl radicals (OH•). Various advanced oxidation processes use several different reaction systems, all of which have the same chemical characteristic: i.e., the development and use of hydroxyl radicals (OH•). Table 2.4 shows oxidation potential of the hydroxyl radical and compares it with other common oxidants used in chemical oxidation.

Table 2.4 Oxidation potential of common oxidants used in chemical oxidation

Oxidizing agent	**Oxidizing potential (Volt)**
Fluorine	3.06
Hydroxyl radical	2.80
Atomic Oxygen	2.42
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Molecular oxygen	1.23

Hydroxyl radical is the strongest oxidant after fluorine; it is capable of initiating multiple oxidation reactions leading to complete mineralization of the original organic compounds and their subsequent degradation products. Hydroxyl radicals are extremely reactive species that can attack and destroy even the most persistent organic molecules which are not oxidized by the oxidants as oxygen, ozone or chlorine. Hydroxyl radical is distinguished by a non-selective attack; this is an extremely useful function for an oxidant to be used for environmental remediation.

Other appropriate and important characteristics are the existence of many possible pathways for hydroxyl radical production and the fact that all reactions occur at normal temperature and pressure as mentioned in Peralta-Hernández et al., (2009).

2.10.2 Technologies used in the production of Hydroxyl Radicals

Advanced oxidation processes include various treatments options: as ozone, hydrogen peroxide, ultraviolet radiation, ultrasound, homogeneous and heterogeneous photocatalysis, photocatalytic disinfection as well as their combination. A common feature of all AOPs as mentioned in Stansinakis (2008) is the use of hydroxyl radicals to promote chemical oxidation. The simplicity makes the Fenton reaction process most frequently applied whenever it is necessary to remove recalcitrant compounds (Li et al., 2010).

2.10.3 Fenton Process

Fenton’s reagent, a mixture of ferrous iron (catalyst) and hydrogen peroxide (oxidizing agent), has been referred to as a potent oxidant for organic contaminants. It was first described in the late 19th century and consists of a homogeneous process, in which an aqueous hydrogen peroxide solution and Fe^{2+} (ferrous) ions generate hydroxyl radicals under acidic conditions (pH

= 2- 4). The Fenton process mechanism is reported using Eq(2.1)–Eq(2.4) as mentioned in Stasinakis, (2008).

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet$ - Eq (2.1)

$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^-$ - Eq (2.2)

$HO\bullet + RH \rightarrow H_2O + R\bullet$ - Eq (2.3)

$R\bullet + Fe^{3+} \rightarrow R+ + Fe^{2+}$ - Eq (2.4)

Fenton oxidation process is one of the most efficient and suitable methods for the abatement of organic pollutants. However, there are three obvious shortcomings in the process: the narrow working pH range, risks associated with the handling, transportation and storage of reagents (H_2O_2 and catalyst) and the significant secondary pollution associated with iron sludge.

2.10.4 Electro Fenton Process

Electro Fenton process (EF) is an electrochemical technique designed to effectively remove organic pollutants from water. EF process is a modification of conventional Fenton reaction (a synergetic action of H_2O_2 and iron catalysts) by means of Fenton’s reagent in situ electro generation. The Electro Fenton process compared to the conventional Fenton process has the advantage of allowing good control of the process. In addition, electricity as a clean energy source is used in the process, so the overall process does not produce secondary contaminants as mentioned in Manivasagan et al., (2012).

Recently there are many implementations of EF process. In general these can be divided into four categories. In the first form, both hydrogen peroxide and ferrous ion are externally supplied. In the second group, hydrogen peroxide is externally applied while a sacrificial iron anode is used as ferrous ion source. Hydrogen peroxide is externally applied in the third category and ferrous ion was electro generated by reducing ferric ion or ferric hydroxide sludge. In the fourth group, both ferrous ion and hydrogen peroxide are electro-generated at sacrificial anode and cathode (Priambodo et al., 2011; Charis M. Galanakis and Evita Agrafioti, 2019).

The mechanism of EF process is represented in Eq (2.5) to Eq (2.8).

At anode:

$Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^-$ -Eq (2.5)

$Fe^{2+}\ (aq) + 2\ OH^-\ (aq) \rightarrow Fe(OH)_2$ -Eq (2.6)

At cathode:

$H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^-\ (aq)$ -Eq (2.7)

Overall:

$Fe\ (s) + 2\ H_2O\ (l) \rightarrow Fe(OH)_2 + H_2(g)$ -Eq (2.8)

The system efficiency depends on many parameters such as pH, applied current, H_2O_2 dosage, distance between electrode and reaction time.

pH is an important operating parameter in EF process. The role of pH is to regulate the hydroxyl radical production and the solution concentration of ferrous ions as mentioned in Pahat, (2013). Fenton process becomes less effective at low pH due to regeneration of Fe^{2+}, through reaction between Fe^{3+} and H_2O_2. At higher pH, the EF process efficiency decreases rapidly, particularly at pH > 5. This is because of the fact that H_2O_2 is unstable in basic solution. At neutral to high pH, H_2O_2 quickly decomposes to oxygen and water as mentioned in Kurt et al., (2007).

Higher electro regeneration of ferrous ion from ferric ion with increasing current improves the efficiency of EF process (Ali Reza Rahmani et al., 2015). But the EF process efficiency will be lower at higher current density after a certain limit which is due to the competitive electrode reactions in the electrolytic cell.

Another factor affecting the efficiency of EF process is the dosage of H_2O_2. An ideal dose will provide better result than a dose of excess oxidant. If H_2O_2 is increased excessively Fenton reaction becomes ineffective due to the undesired reactions. Another important factor that affects efficiency of EF process is the distance between electrodes. For electrode distance between l.3 and 2.5 cm the COD removal efficiency from landfill leachate has remained the same as mentioned in Zhang et al., (2007). The EF system’s removal efficiency was less for the shorter or greater distance. That is because electro-regenerated Fe^{2+} at the anode could be easily oxidized to ferric ion, when the electrodes were placed too close. Long distance causes ferric ion’s limiting mass transfer to the cathode surface that governs ferrous ion regeneration. The use of long electrode distance in EF reactor causes a significant increase in energy consumption as mentioned in Priambodo et al., (2011). The reaction time is another factor affecting EF process efficiency. The downside of EF process is that the oxidation results in the dissolution of sacrificial electrodes into the waste water. Therefore they need to be replaced.

2.10.5 Photo Electro Fenton Process

In Photo Electro Fenton process (PEF), by photo-reduction and by reduction at the cathode the ferric complexes will be reduced to ferrous ion. This would essentially trigger the Fenton chain reaction. This can accelerate the degradation of organic compounds by two principal pathways when the EF process is irradiated by means of UV light,: a) the photolysis of Fe^{3+} - oxidation products complexes, and b) improvement of Fe^{2+} regeneration from the photo reduction of Fe^{3+} ions according to the Eq(2.9), as mentioned in Peralta-Hernandez et al., (2009). By irradiation of electro

Fenton process with UV light (photo electron Fenton process) it may increase the rate of organic pollutant degradation. UV light not only leads to the formation of additional hydroxyl radicals but also to the recycling of ferrous catalyst through Fe^{3+} reduction. This increases the concentration of Fe^{2+} and accelerates the overall reaction. (Sharma et al., 2011)

$Fe(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + HO\bullet$ -Eq(2.9)

2.10.6 Solar Photo Electro Fenton Process

Sunlight can be used as an alternative for artificial UV irradiation in the Solar Photo Electro Fenton (SPEF) process, which is cheap and renewable energy source. The solar photo-electro fenton process is regarded as an environmentally feasible project because it does not cause or increase the ecosystem degradation and does not surpass the basin load capacity where it intends to locate.

2.11 Membrane bioreactor

Membrane bioreactor (MBR) integrates membrane technology with that of bioreactor in leachate treatment. The MBR system is compact; it produces high amount of biomass, and results in good quality effluent. Membrane bioreactors were first constructed for the treatment of waste water at full industrial scale and when they were found to be highly effective, some plants were adapted for with leachatetreatment.

MBR technology, which is a combination of biologically-activated sludge process and membrane filtration, has become more popular and accepted for the treatment of different types of wastewater in recent years, whereas the Activated sludge processes cannot manage with either of wastewater composition or flow rate fluctuations. MBR technology is also used in situations where demand on the effluent quality is greater than the capacity of ASP. Even though capital and operating costs of MBR exceed the costs of conventional processes, it appears that conventional process are upgraded even in cases when conventional treatment works well. It can be due to higher water price, the need for water reuse and also due to more stringent effluent quality regulations. In addition to enhance understanding of new pollutants in wastewater, their biodegradability and their inclusion in new regulations, MBR may become essential to elevate the existing treatment technology in order to meet the legal standards for wastewater treatment (Radjenovic et al., 2007).

2.11.1 Membrane filtration

A membrane is known as a substance that forms a thin wall that can selectively repel the transfer of different fluid constituents and thus effect a separation of the components. Thus, membrane material of acceptable mechanical strength should be produced that can maintain a high output of a desired permeate with a high level of selectivity. The ideal physical structure of the membrane is based on a thin layer of material with smaller pore size range and a higher porosity of surface. This theory is extended to involve the segregation of dissolved solutes from liquid streams and the removal of gases.

Micro -filtration (MF), ultra- filtration (UF), nano- filtration (NF), reverse osmosis (RO) which produce permeate and concentrate, are the most widely applied membrane separation processes.

(i) Micro-filtration

The Micro-filtration membranes have pore size ranging from 0.1 – 5 µm and has the highest pore size of the four major types of membrane. Its pores are wide enough to filter out things such as blood cells, bacteria, flour, talc and many other forms of fine dust present in solution. Since its pores are comparatively larger than that of other membranes, it can be used underlow pressures and hence low energy.

(ii) Ultra-filtration

Ultra-filtration has a range of 0.01 to 0.1µm for pore sizes. UF membranes remove particles like viruses, silica, proteins, endotoxins, plastics and smog/fumes like ZnO. Because of the reduced pore size, the osmotic pressure needed is greater than that of MF.

(iii) Nano-filtration

Nano-filtration has a pore size in the range of 0.001-0.01µm. NF membranes can filter particles up to and including some salts, sugars and synthetic dyes however it is not possible to remove most aqueous salts and metallic ions, as such. NF is usually confined to special uses.

(iv) Reverse Osmosis

Reverse Osmosis has a pore size in the range of 0.0001 – 0.001µm. This is by far the best material available for separation in an industry. It is used for desalination and purification of water on a large scale as it filters out almost everything except water molecules, with pore sizes nearing to the radius of certain atoms in many cases. This membrane pore size means that it can effectively filter salt and metallic ions from water. The smaller pore size of membranes means that a considerable quantity of osmotic pressure is needed to attain filtration.

Micro-filtration and ultra-filtration are low pressure driven processes, in which water to be fed is driven through a micro-porous synthetic membrane and separated into permeate that passes through the membrane and rejects that are non- permeating species. These membrane processes are more effective in removing particles and microorganisms in wastewater treatment applications. Where as Reverse osmosis is a high pressure driven process designed to remove salts, low molecular inorganic and organic pollutants.

Nano-filtration operates between the pressure rangeof RO & UF aiming to remove impurities of the divalent ion.

Membranes are commonly made of various ceramic and plastic materials, but membranes made of metals also exist. Celluloses, polysulphone, polyamides, activated polysulphone and other polymeric materials such as polyvinylidenum difluoride (PVDF), polyacrylonitrile (PAN), polyethylsulphone (PES), polypropylene (PP), and polyethylene (PE) are the most widely used materials. All polymeric materials have a favorable chemical and physical resistance. They are hydrophobic in nature, and it is understood that hydrophobic membranes are more at risk to fouling than hydrophilic ones because of the hydrophobic nature of most of the interactions among the membrane and the pollutants.

Accordingly, every commercially available membranes are improved by organic chemical reaction, chemical oxidation, grafting or by plasma treatment to achieve large hydrophilic surface area. This improvisation process usually varies from one membrane to another along with the manufacturing method of the membrane module (Radjenovic et al., 2007).

2.11.2 Process description

The membrane bioreactor system has two basic configurations: (1) the integrated bioreactor which uses submerged membranes in the bioreactor and (2) the external MBR in which a membrane module is placed outside the bioreactor and the mixed liquor circulates through it.

In the submerged MBR system, the MF membrane is submerged directly into the bioreactor. The membranes are situated in the modules which can be submerged in the bioreactor. The modules consist of membranes, membrane support structure, feed inlet and effluent outlet connection and, an overall support structure. The membranes undergo a vacuum and draws water through the membrane while solid particles retain in the bioreactor.

To hold total suspended solids within the reactor and for membrane surface cleaning, compressed air is introduced at the bottom of membrane module through a distribution manifold. Scouring of membrane surface occurs as the air bubbles rise up to the surface and the air also has oxygen to maintain aerobic conditions.

For external MBR, the bioreactor effluent is fed to a pressure driven tubular membrane where solid particles retain inside the membrane module and water moves outside. The driving force is the pressure through the membrane which is created by higher cross velocity. The solids are recycled to the bioreactor. Membranes are regularly back washed to remove solids and chemically cleaned to control pressure buildup (Metcalf & Eddy, 2013).

2.11.3 Membrane fouling and cleaning

With filtration time the MBR filtration efficiency inevitably decreases. This is because of the accumulation of particulate and soluble materials on and in the membrane, owing to the interactions among activated sludge materials and the membrane. This main disadvantage and process limitation of MBRs has been under investigation, and is one of the major challenging issues in the industry. Membrane fouling occurs due to the contact among the membrane and the materials of the activated sludge liquid, which consists of biological flocs generated by a broad diversity of living or dead microorganisms along with colloidal and soluble compounds. The suspended sludge does not have a fixed formation and differs with the feed water composition as well as with working conditions of MBR utilized. Fouling of membranes in MBRs is due to the physicochemical interactions among the biofluid and membrane. As soon as the surface of the membrane comes in contact with the activated sludge suspension, biosolids are deposited onto it leading to decrease in flux. Since this cake layer is easily removable from the membrane, if a suitable physical washing method is used, it is often categorized as reversible fouling. Fouling is a usual problem in membrane processes but is more tedious to predict and control in MBR because of the high heterogeneous nature of the mixed liquor, and, in particular due to the effect of the active microbes (Radjenovic et al., 2007). Iorhemen et al., (2016) studies indicate that addition of coagulants and adsorbents show significant reduction in membrane fouling. Also Aerobic granulation integration with MBRs demonstrates outstanding filtering efficiency and significant reduction in rate of fouling as well as effective removal of nutrients.

2.12 Previous studies

2.12.1 Fenton based Advanced oxidation process for wastewater treatment

Many authors have reported the usage of Fenton based AOP for treating different types of wastewater such as textile effluent with synthetic dye (J.M Peralta Henandez et al., 2009), effluent containing phenol (Zhang et al., 2007; Jiang and Mao, 2012), landfill leachate (Shabiimam and Dikshit, 2012; Pahat, 2013; Amr et al., 2013; Santin-Gusman et al., 2015) etc.

Brillas, (2014) presented a research study of emerging electrochemical advanced oxidation processes (EAOPs) such as UV Photo Electro Fenton (PEF) and Solar Photo Electro Fenton (SPEF) in which UV light and sunlight irradiation of the effluent. This creates a synergistic effect on the degradation process of organic compounds by the generation of more OH• and/or the photolysis of complexes of Fe(III) with carboxylic acids generated. The fundamentals of these EAOPs are clarified in order to illustrate their effectiveness in eliminating industrial chemicals, pesticides, dyes and pharmaceutical products. Treatments are also examined with a recirculation pre-pilot plant coupled with a solar photo reactor. A combined method is represented that involves PEF and photo catalysis is described. The effect of experimental parameters on the rate of mineralization,

mineralization current efficiency and energy cost of the PEF and SPEF methods is reported. The decay kinetics of pollutants and the evolution of their intermediates and final inorganic ions are discussed. The SPEF process resulted in a lower cost than other EAOPs like anodic oxidation with electro generated H_2O_2, Electro Fenton and PEF.

Sires et al., (2014) studied the characteristics of the Solar Photo Electro Fenton (SPEF) process and the results obtained in the laboratory upon application to degrade organics in waters. In this electrochemical advanced oxidation process (EAOP), organics are removed by OH• formed from water oxidation at the anode and from Fenton's reaction between H_2O_2 generated at the cathode and added Fe^{2+}, along with the synergistic ction of radiation from sunlight that photolyzes generated Fe(III)-carboxylate. The mineralization of several herbicides, pharmaceuticals and dyes in different system were examined, showing that SPEF more efficient and less expensive than other EAOPs like anodic oxidation, EF and PEF with artificial UVA light.

Liu et al., (2013) studied the Photo Electro Fenton oxidation in an electrolysis cell for the degradation of tetracycline with a manufactured Fe_3O^{4-} graphite cathode. Comparisons of tetracycline degradation by Electro Fenton, UV irradiation and Photo Electro Fenton processes were investigated. Efficiency of degradation was in the order: Photo-Electro Fenton > Eectro Fenton > UV irradiation. The effects of current density, pH and UV irradiation on degradation of tetracycline were investigated. High performance liquid chromatography (HPLC), UV–Vis absorption spectra, Fourier transform infrared spectroscopy (FT-IR) and total organic carbon (TOC) were used ito investigate the tetracycline decomposition and results showed that complete mineralization was possible. The Fe_3O^{4-} graphite cathode was stable and could be reused without catalytic decline, indicating its potential use in the tetracycline treatment of wastewater.

Hernandez et al., (2012) performed an environmental evaluation of a pilot plant with photo electro-Fenton technology for the domestic and industrial wastewater treatment. The outcomes showed that the technology can assist to solve the several significant water pollution problems in the basins of the Turbio-Palote and Guanajuato rivers, which are some of México's most prime areas with at least 2.5% of the total population of the country. The problems with water pollution are primarily due to a dense urban population and the development of the local leather and shoe industries. The solar plant was able to reduce organic water pollution by 80 percent. The environmental impact assessment of this alternative indicates a minimum number of major impacts as well as a high viability in terms of economic and environmental implementation.

Jiang and Mao, (2012), investigated the enhanced Electro Fenton (EF-Fere) process using H_2O_2 modifications and electrogenerated ferrous ions to treat wastewater containing phenol. The maximum COD removal efficiency of phenol-containing wastewater is achieved at the condition of 800mg/L initial ferric ions concentration, 1.0A electric current and 1.2mg/l H_2O_2 with continuous H_2O_2 addition mode, for the phenol degradation experiments performed in the EF-Fere electrolytic system.

Salazar et al., (2011) investigated the mineralization of solutions containing azo dyes Acid Violet 7 (AV7) and Reactive Black 5 (RB5) using Electro Fenton (EF) and Photo Electro Fenton (PEF) methods in aqueous solutions. The electrochemical system consists of a glassy carbon mesh electrode (cathode) with a concentric exterior steel mesh as anode. The parameters optimized were: 0.01 mM of Fe^{2+} ions, and 250 mA of current at pH 3. All tests were made at 35°C. The degradation was measured for solutions of 250 mg L^{-1} in both cases by color removal and total organic carbon (TOC) decay. The findings indicate that the system has been observed to achieve high degradation efficiency for both dyes, quick decolorization of the solutions and the complete transformation of organic compounds into carbon dioxide.

Ricky Priambodo et al., (2011) examined the removal of organic compounds from real wastewater from Taiwan’s Sustainable Environment Research Center. In this analysis wastewater was treated by semi batch Electro Fenton method (EF) and semibatch Photo Electro Fenton method (PEF). The wastewater volume in each run was 4L, and total organic carbon (TOC) and chemical oxygen demand (COD) were 16500 and 24000 mgL^{-1}, respectively. Four pairs of electrodes were used in the EF system. The ferrous ions are formed on the cathode by reduction of ferric ions that would react with H_2O_2 to generate hydroxyl radicals ($OH^{\cdot}$). Under EF conditions, the solution was treated and simultaneously irradiated with UVA lights to accelerate the mineralization rate of organics through photo-Fenton process. The optimum conditions ([Fe^{2+}] = 2000 mgL^{-1}, H_2O_2 (50 wt %) dosing rate = 6mL min^{-1}, pH= 2 and current =20A in 420 min of the reaction time) of semi batch EF method and semi batch PEF method could achieve a maximum TOC removal of 98 and 99%, respectively. The cyclically electro-generated Fe(II) may efficiently react with H_2O_2 to prolong the formation of hydroxyl radical. The experimental results showed that an excellent process for treatment of real waste water was the combination of electricity and UV irradiation.

It is found that the Fenton reaction in photo-electro assisted Fenton process can be efficiently enhanced because Fe^{2+} may complex with certain target compounds or byproducts, produced by UVA light and current. The final efficiency of COD removal obtained by the EF process was nearly 17% higher than that of the Fenton’s reagent alone. Meanwhile, as stated in Ting et al., (2008), the PEF process achieved a COD removal efficiency that was 14 percent higher than that of the EF process in the treatment of waste water.

The degradation efficiency for wastewater treatment according to Liu et al., (2013), is in the order: PEF > EF > UV irradiation. The key disadvantage of PEF is the high energy cost of the artificial UVA light utilized.

2.12.2 Advanced Oxidation Process for leachate treatment

Studies performed by Mohajeri et al., (2019) on semi aerobic landfill leachate obtained from Pulau Burung Landfill Site, Malaysia, indicated that Electro-Fenton process is highly effective for the treatment of landfill leachate. The maximum COD and color reductions were 92% and 93%, respectively; at pH=3, applied current=2A, H_2O_2/Fe^{2+} molar ratio=1, treatment duration= 30 min, and distance between electrodes = 3 cm. The current efficiency decreases to 38% from 94% when the current rises to 2A from 0.5A.

Tejera et al., (2019) treated matured leachate by coagulation and Photo Fenton process. $FeCl_3$ + Photo Fenton is much cheaper than Alum+ Photo fenton (7.24$/m^3 vs 32.1$/m^3). Both treatments attained same results with final COD and colour removal > 90%. Discharge limits were not attained with the proposed treatment combination.

Sruthi et al., (2018) conducted research on old landfill leachate treatment by heterogeneous Fenton and Electro Fenton processes. Heterogeneous Fenton process was able to remove 88.6 percent COD from leachate at the optimum conditions, while 87.5 percent COD reduction was observed at optimum conditions for EF treatment. After Fenton treatment, biodegradability of landfill leachate improved from 0.03 to 0.52. Although, both processes are effective for treatment of leachate, the need for low catalyst dosage in EF process justifies it being more suitable than Fenton process.

According to Amor et al., 2015, combining the pre-treatment coagulation/flocculation with Fenton reagent for treating matured leachate, 89% of COD removal could be achieved in 96 hrs. In addition, coagulation/flocculation in combination with solar photo-Fenton resulted in higher DOC (75%) reductions. The leachate under study exhibited non-toxicity after the combined treatment and the biodegradability increased.

In the study conducted by Rabbani et al., (2015), efforts were made to remove the COD and TSS of the leachate collected from Esfahan, Iran using electrochemical, Fenton and Electro Fenton processes. The Electro-Fenton process is the most effective among the studied methods and is able to eliminate up to 73 and 92.4 percent of the COD and TSS, respectively. In addition, the Fenton process is more efficient than the other electrochemical process in extracting COD and Total suspended solids.

The optimum current density, treatment time, pH, hydrogen peroxide dosage and ferrous sulphate heptahydrate ($FeSO_4$ $7H_2O$) dosage for treating landfill leachate samples with aluminium electrode were determined by Zawawi et al., (2013). The best reductions were obtained when current density value was 200 A/m^2, reaction time was 25 min and pH was 4. The optimal dose of H_2O_2 is 800 mg/L obtained 78 percent and 96 percent of COD and colour removal respectively.

Gotvajn et al., (2011) compared Fenton's oxidation with sequencing batch reactor, employed for the treatment of leachate and found that Fenton's process could eliminate organic compounds (80% as COD) as well as other contaminants and could slightly reduce toxicity, but effluent limits were not reached. Therefore Fenton’s oxidation could not replace SBR treatment plant, but it could be a viable option for pretreatment of leachate from landfill.

2.12.3 Membrane bioreactor process for leachate treatment

Hashisho et al., (2016) compared the performance of flat sheet and hollow fiber membranes in membrane bioreactors for treating reasonably matured landfill leachate with the goal of developing regulations for pilot/full scale plants. Both membranes attained comparable removal of total phosphate (79.4% vs. 78.5%) and BOD (92.2% vs. 93.2%). Higher phosphate removal efficiency of percentage (87.3% vs. 81.3%) and marginally higher COD removal efficiency were attained using hollow fiber membrane (71.4% vs. 68.5%). The flat sheet membrane, on the other hand, achieved slightly higher Total Nitrogen and NH_4-N removal efficiencies (61.2% vs. 49.4% and 63.4% vs. 47.8%, respectively).

Ince et al., (2013) examined the treatment efficiency of a jet – loop membrane bioreactor (JLMB) performed at various organic loading rates by observing the variations in COD, Total Kjehldahl Nitrogen and Ammonia nitrogen. The same rate of COD removal (83%) was observed at every loading rates tested and it should be noted that the biodegradable part of the leachate was completely removed. It was also noted that the NH_4– N / TKN ratios was around 0.9, did not shift during the entire study. However, in order to meet related discharge limits more treatment technologies, such as nanofiltration, reverse osmosis or ion - exchange, should be used for the overall removal of COD and NH_3.

Campagna et al., (2013) investigated the arrangement of molecular weight (MW) of a full-scale landfill leachate treatment plant containing MBR and NF membrane. From the equalization tank the leachate was collected, and MBR and NF membrane effluents were taken from the treatment plant. Parameters like COD, TOC, NH_4^+- N, TKN and UV absorbance at wavelength 280, 254 and 320 were analyzed to determine both the removal efficiency and MW distributions in Dalton (Da). Ultrafiltration (UF) (100 kDa, 10 kDa, 5 kDa, 1 kDa and 500 Da) membranes were used to assess MW distribution of samples. The findings showed that one third percent of organic matter is in particulate or colloidal form and almost 50% of the organic fraction has a lesser MW than 500 Da. Therefore, organic matter is of hydrophilic character. Much part of TKN was >500 Da and around 92%

were withdrawn. Further, raw leachate UV absorbance reduced 85% after 500 Da.

Ahmed.and Lan, (2012), reports that MBR with a much shorter HRT and higher organic loading rate (OLR) compared to conventional biological systems are feasible with outstanding BOD and ammonia removals greater than 90%. MBR also offers excellent COD removal (75% or higher). MBRs have also demonstrated to be efficient in eliminating micro pollutants. In addition, recent advances such as anaerobic MBR and powdered activated carbon-amended MBR have showed great potential in treating landfill leachate. MBRs can provide constant output while including broad variations in characteristics of influents and other operating conditions. However, short HRT and high ammonia content have been found to have negative effects. Extremely long residence times for solids have also been found to reduce MBR efficiency.

Liu et al., (2012) studied the fouling mechanism of Polyurethane-based hollow fiber membrane in microfiltration. Three materials (sodium alginate, $CaCO_3$ and humic acid) that might cause fouling were used. Results proved that formation of cake layer by $CaCO_3$ suspension was easily removed through backwashing; the difference in fouling mechanism of sodium alginate and humic acid was that the reduced flux due to humic acid was irreversible by physical backwashing due to its hydrophobicity. For fouling mechanism an empirical formula was supplemented, based on experimental data, to enhance the accuracy of fit of polyurethane membrane microfiltration processes.

Mahmoudkhani et al., (2011) investigated the possibility of biologically treating leachate collected from municipal landfill, Tehran of approximately 0.5 – 1 year age. In aerobic submerged membrane bioreactor the average COD of the leachate is 68000 mg/l. The reactor having working volume of 175 litres and 0.1 μm pore size Hollow fiber membrane module was used.

The concentration of dissolved oxygen (DO) was kept as 3.2 mg/l and SRT and HRT were kept as 55 and 15 days respectively. The mixed liquor suspended solids (MLSS) stabilized at 6.3 g/l afterwards. The average COD of the effluent was 1733 mg/l with average removal efficiency of 97.46 percent under operating condition of COD/N ratio - 46 and COD/PO_4-P ratio - 455 and BOD/COD ratio - 0.65. The average efficiency for NH_4 –N removal was 99% which reached to a maximum of 99.7 percent.

Sang et al., (2007) investigated the composition of leachate from the Go Cat landfill in Vietnam and the performance of a lab-scale bioreactor fitted with a micro filtration unit (MBR) for the treatment of leachate. The COD of leachate in the dry season (Nov. 2003 - Apr. 2004) and the rainy season (May - Aug. 2004), were 39.6-59.8 g/l and 1.1-4.0 g/l respectively, indicating that heavy precipitation of the monsoon climate promotes leachate production and its quality changes due to the increased degradation and dilution. The ratio of BOD/COD above 0.68 throughout the year suggested that biological processes are promising for leachate treatment. The MBR was operated for 90 days. The microfiltration membrane maintained the concentration of sludge high in the MBR. During the experimental period the MBR showed high COD removal of 84-97 percent. These results indicate that the effluent COD standard of 100 mg/l is likely to be achieved in the rainy season, but some post-treatment processes are required, particularly for the dry season.

Bohdziewicz et al., (2007) examined the feasibility of treatment of landfill leachate in anaerobic submerged MBR. The goal of the work was to estimate on the basis of anaerobic digestion efficiency, the optimal strength of leachate in the reactor influent and operating parameters. The treatment efficiency of leachate dilution in the range of 5–75% (v/v) with a wastewater (synthetic) under different feeding condition was studied. A higher COD reduction over 95percent was obtained with leachate addition of 10 percent and 20 percent (v/v). Decrease in organic reductions was observed with leachate percentage. At leachate dosage of 25%, the COD reduction was 80%. Leachate concentration greater than 30 percent (v/v) substantially decreased anaerobic treatment efficiency because of the inhibition of microbiological activity. The effect of various HRT and OLR on pollutant removal efficiency and biogas generation was also analyzed. The highest anaerobic digestion efficiency (COD reduction 90 percent) was noticed for HRT of 2 days.

2.12.4 Integrated physico-chemical and biological treatment methods for landfill leachate

Ai et al., (2019) investigated the implementation of acombination of biological system, which used sequencing batch reactors, and an electro chemical method, using Electro Fenton oxidation process. The COD was reduced by 33.6% and 18.5% of its original value, by the Electro Fenton process alone and combined treatment of sequencing batch reactor- Electro Fenton oxidation, respectively. Based on the Fourier transform infrared (FTIR) spectra absorption intensities, the functional groups in the raw leachate were removed by the biological treatment, but modified due to the Electro Fenton process.

Zhang et al., (2019) developed a pilot scale of combined processes, including coagulation, hydrolysis acidification (HA)–Sequence batch reactors (SBR) and Electro Fenton oxidation in sequence to improve the reduction of contaminants in the landfill leachate, which had high organic and NH_3–N concentrations. The average removal efficiency of the COD was 97.8 percent and removal efficiencies of colour, total phosphorus and turbidity were all higher than 97 percent. The total operating cost for treating leachate was 4.84 US$ per m^3.

Fudala Ksrazek et al., (2018) investigated the landfill leachate treatment efficiency in a MBR/UF system combined with NF, with specific stress on pthalates & bisphenol-A elimination. MBR/UF has been effective in treating landfill leachate. Also the presence of denitrifying bacteria improved nitrogen elimination.

Study done by Silva et al., (2017) on leachate includes an aerobic activated sludge biological pre-oxidation (ASBO), a coagulation and sedimentation step (240 mg Fe^{3+}/L, at pH 4.2) and a photo Fenton (PF) reaction (60 mg Fe^{2+}, at pH 2.8) including solar and artificial light. The ASBO process (pretreated with aerobic lagooning) having high organic and nitrogen content (1.1–1.5 g C/L; 0.8–3.0 g N/L) and lesser biodegradability (BOD_5/COD = 0.07–0.13), was able to oxidize 62–99% of NH_4-N. The coagulation and sedimentation led to the humic acid precipitation, encouraging a pronounced change in leachate colour, from dark-brown to yellowish-brown (due to fulvic acids). A reduction of 60%, 58% and 88% on DOC, COD and Total suspended solids, respectively was achieved. The PF treatment cost was 7.24$/$m^3$to treat 100 m^3/day of leachate.

Amaral et al., (2015) suggested a landfill leachate treatment configuration including air stripping, MBR and Nano filtration membrane that showed best performance especially in the reduction of COD (80-91%), NH_3-N (85-95%), colour (98-99%), phosphate (78-99.8%).

Zolfaghari et al., (2016) suggested coupling of a Membrane bioreactor (MBR) with UF membrane and an electro-oxidation process (EO) using a boron-doped diamond electrode (BDD) for effective treatment of highly polluted, medium-old landfill leachate. The combined MBR and EO at the optimum operating conditions acted as the tertiary treatment which achieved pollutant reduction of COD - 94%, BOD - 97%, NH_4-N - 77%, PO_4 - 53%.

Fleck et al., (2016) conducted bench scale sequential, biological and coagulation-flocculation treatment of mature leachate for the removal of nitrogen and biodegradable and recalcitrant carbonaceous material. Two SBRs were used for biological stage. At different doses and pH adjustments the coagulation-flocculation stage used four coagulants. It produced average removals of BOD_5 - 69.6%, COD - 38.5% and TKN - 51.6%. The ferric coagulants produced removal of turbidity, COD and true colour close to 95%, 78% and 92%, respectively.

The passive aerated immobilized biomass (PAB) reactor was investigated by Ismail and Tawfik, (2016) for the treatment of landfill leachate. Hydraulic retention time (HRT), organic loading rate (OLR), volatile suspended solids to total suspended solids ratio (VSS/TSS) and COD total/NH_4-N ratio have affected reactor performance. COD total and NH_4-N removal efficiency reduced from 55 ± 6 to 33 ± 2% and from 93 ± 8 to 80 ± 11%, when the HRT decreased from 16hrs ito 4hrs, respectively. Ammonia oxidation increased from 69% to 94% when the VSS/TSS ratio decreased from 0.54 to 0.24. Fenton pre-treatment substantially enhanced the removal efficiency of COD total (83 ± 4%) and COD soluble (83 ± 5%).

Anaerobic sequencing batch reactor (ASBR) was proposed by Lim et al., (2016) to treat the locally available real landfill leachate with initial ammonia nitrogen (NH_3-N) and chemical oxygen demand (COD) concentration of 1800 and 3200 mg/L, respectively. During seven days of treatment time, ASBR could remove 65% of ammonia nitrogen and 30% of COD. Thereafter, an efficient adsorbent zeolite was used as a secondary treatment for polishing the ammonia nitrogen and COD content present in the leachate. The findings iobtained are promising where the adsorption of leachate by zeolite further enhanced the removal of ammonia nitrogen and COD iup to 96 and 43%, respectively.

Peyravi et al., (2016) used an integrated bench-scale process on submerged aerobic powdered activated carbon-membrane bioreactor (PAC-MBR) for treating landfill leachate. Results indicated that the submerged PAC-MBR system effectively extracted biodegradable trace organic compounds of 71% at optimum food to microorganism (F/M) ratio of 0.4g COD/g day at 24h HRT. Adding nanofiltration (NF) process improved the treatment efficiency up to 99 percent.

Chemlal et al., (2014) combined Advanced oxidation process (AOP) via heterogeneous photocatalysis (TiO_2/UV) with seeded bioreactors having different inoculums types. The reduction after heterogeneous photocatalysis was between 50% and 84% of the initial COD at pH 5. The AOP–bioreactor coupling allowed a reduction of 90% of the initial BOD_5 and 87% of the initial COD with a final value of 1000 mg O_2/L.

According to Cesaro et al., (2013) Advanced oxidation processes represent one of the most promising choices for eliminating ipersistent compounds in wastewater treatment effluents. A viable alternative could be their combination with conventional biological processes It has been extensively demonstrated that AOPs can improve the biological treatability of wastewaters and thus enhancing the removal of both organic matter and recalcitrant compounds.

Coban et al., (2012) investigated the biological treatability of Komurcuoda landfill leachate in aerobic/anoxic MBR systems followed by a nanofiltration process. Biodegradable organic content of leachate reduces and its nitrogenous content increases with landfill age. The integrated membrane process showed high removal efficiency with high effluent quality.

Moravia et al., (2013) studied leachate treatability using AOP by Fenton’s reagent (AOP/Fenton) combined with microfiltration (MF) and nanofiltration (NF). A high reduction of COD (63%), color (76%) and humic substances (50%) were noticed under optimized operating conditions (1.7 g H_2O_2/g $COD_{rawleachate}$; $FeSO_4 \cdot 7H_2O$:H_2O_2=1:5.3; pH=3.8; reaction conditions =115rpm/28 min) during AOP/Fenton. Membrane separation process presented an efficient complementary treatment according to ithe assessed parameters, in which the integrity of the stages was sufficient to meet regulatory standards in the effluent.

Mahmoudkhani et al., (2012) investigated ithe feasibility of biological and physic chemical treatment of high-strength landfill leachate that was collected from Tehran municipal landfill. In aerobic submerged membrane bioreactor average COD of the leachate is 68000mg/l. The reactor with a working volume of 175L, has a membrane imodule (Hollow fiber) with pore size of 0.1 µm coupled with reverse osmosis with pore size of 0.001 µm. The dissolved oxygen (DO) concentration was maintained at 3.2 mg/l and with solid retention times (SRTs) and hydraulic retention times (HRT) being maintained at 55 and 15 days respectively. The average COD of Membrane bioreactor effluent was 1733 img/l with average removal efficiency of 97.46%. The average removal efficiency of NH_4–N was 99%. On the other hand, near complete nitrification was achieved during ithis time. The effluent concentration iof PO_4–P was low and its average removal efficiency was as high as 90%; particularly during the operating period. Reverse osmosis (RO) effluent COD was 335mg/l with 99.13% average removal efficiency. Concentration of PO_4-P in RO effluent was 0.86 mg/l and its mean removal efficiency was 99.33%.

Wu et al., (2011) developed a series based combination process involving sequence batch reactor (SBR), coagulation, Fenton oxidation and biological aerated filtering (BAF) for the purpose of extracting pollutants from landfill leachate. Out of 70 organic micropollutants thirty-seven organic micro pollutants disappeared completely in Fenton effluent and BAF eliminated low molecular weight fractions. A total removal of COD -98.4%, BOD_5 -99.1%, NH_4-N -99.3%, TP -99.3%, SS-91.8%, turbidity -99.2% and color -99.6% was achieved.

2.13 Response Surface Methodology

Response surface methodology (RSM) is a group of mathematical and statistical methods for empirical model construction. The aim of RSM is to optimize an output variable (response) which is affected by various input variables (independent variables) by carefully designing the experiments. An experiment is a sequence of tests, known as runs, in which the input parameters are changed in order to identify the causes for changes in the output variable. The aim of the RSM is to optimize, find the best set of factor levels to achieve a target. An important feature of RSM is the experiment design, which is usually abbreviated as DoE. The aim of DoE is to select the points where the response should be assessed. Such designs are able to fit a second order equation for predicting the response. Within these equations the quadratic terms model the curvature in the true response function. When within the factor region a maximum or minimum exists, it can be estimated by RSM.

The two most common response surface designs are the central composite design and the Box Behnken design. The central composite design incorporates a fractional factorial of two level and two other kinds of points.

- Points at the centre, where every factor values are at zero or midrange value.
- Axial points, where except one all other factors are set at mid range or zero and that one factor is set at outer axial values.

The substitute to central composite designs is the Box Behnken design. One distinctive aspect of the Box Behnken design is that each component has only three levels. Each independent variable or component is set at one of three values that are equally spaced, normally coded as -1, 0, +1. The design should be capable to suit a quadratic model, including squared terms and products of two variables.

The response can be presented graphically in the 3-dimensional space (Response surface) or in 2-dimensional contour plots that aid in visualizing the response surface form. The graph is useful for showing the shape of a response surface; hills, valleys and ridges. Contours are constant response curves drawn in the xi, xj plane fixing all other variables. Each contour represents a particular value of the response surface. Such graphs help to analyze the interactive relationships between the input variables and output responses.

Variance analysis (ANOVA) is carried out to assess the interactions between the variables and to calibrate the models according to experimental findings (Mahmoud Zaeri et al., 2012). ANOVA uses conventional standardized terminologies. The sample variance is shown using Eq (2.9).

$$S^2 = \frac{1}{n-1} \Sigma (y_i - y)^2 \qquad \text{- Eq (2.9)}$$

Where the divisor is called the degrees of freedom (DF), the summation is known as the sum of squares (SS), the squared terms are deviations from the sample mean and the result is the mean square.

ANOVA confirms the model appropriateness. ANOVA splits the variability among every value into one component that is due to variability among group means (due to the treatment) and another component which is due to variability within the groups (also known as residual variation). Variability within groups is quantified by the sum of squares of the differences between each value and its group mean. It is the residual sum of squares. Variation among groups (due to treatment) is quantified as the sum of the squares of the differences between the group means and the mean of all values in all groups. Adjusted to the size of each group, this becomes the treatment sum of squares. Each sum of squares is correlated with a certain number of degrees of freedom (DF) derived from number of subjects and number of groups, and the mean squares (MS) is determined by dividing the sum of squares by the appropriate number of degrees of freedom. These can be thought of as variances. The square root of the mean square residual can be considered as the standard deviation.

How well the estimated model fits the data can be calculated by the value of R^2. R^2 is the fraction of the total variance attributable to the group mean differences. It matches the variability between group means and the variability within the groups. The R^2 value is determined from the ANOVA and is equal to the group sum of squares divided by the entire sum of squares. It is a descriptive statistic which quantifies the intensity of the relation between group members and the variable calculated. The R^2 lies in the [0, 1] interval. If R^2 is closer to the 1, the better is the regression equation estimate fitting the sample data (Lenth, 2009).

2.14 Research gaps

Many researchers have reported that to meet strict quality standards for direct discharge of leachate, an integrated treatment strategy has to be developed. Hence integrating the physicochemical process and the biological process would be a good alternative for the treatment of landfill leachate. Integrated Electro-Fenton – Membrane bioreactor system for matured and young landfill leachate has not been investigated by any researcher. The annual cost for treating matured and young landfill leachate has not been reported and compared in any of the researches. Advantages of the Electro Fenton process like a lesser sludge production, lesser treatment duration and enhancement of biodegradability can be incorporated for the treatment of the matured landfill leachate thus making it amenable to biological treatment. Membrane bioreactor (MBR) is an advanced technology for the biological treatment of wastewater and has many advantages like lesser footprint, higher effluent quality, less excess sludge production and generally more stable process. Electro Fenton process enhances the biodegradability of the matured leachate and MBR degrades the easily biodegradable organic matter, thus improving overall pollutant removal from matured landfill leachate. Hence in this study, the main aim was to treat municipal landfill leachate by integrating advanced oxidation process and membrane bio reactor to meet the disposal standards.

2.15 Objectives

Current research has been conducted on the leachate from Brahmapuram landfill in Kochi in Kerala, India. The Municipal Solid Waste Disposal Facility at Brahmapuram started operating in 2008 beneath Jawaharlal Nehru National Urban Renewal Mission (JNNURM). The Brahmapuram plant is spread over 104 acres and the land is owned by Cochin Corporation. The plant has an installed capacity of treating 250 tonnes of bio-degradable waste per day. The leachate from the huge heaps of wastes infiltrates through the ground and pollutes the underlying groundwater and also the nearby Kadambrayar River. The impact of discharge from the Brahmapuram landfill on the water quality of Kadambrayar River which is a source of drinking water for many grama panchayaths and Thrikkakkara municipality has been disastrous.

This research investigates the characteristics of the landfill leachate. The main objective of the research is to find an integrated system of the advanced oxidation process and membrane bioreactor for the treatment of landfill leachate. For the treatment of landfill leachate the following objectives are for seen.

- Investigation of the capability of electrically aided Fenton process as a pretreatment for landfill leachate and comparison of its performance with photo aided Electro Fenton process to enhance the biodegradability of matured landfill leachate.

- Optimization of the factors affecting the appropriate advanced oxidation process (AOP) using Response surface methodology.
- Estimation of the biological performance and evaluation of the biocompatibility (toxicity) of the raw landfill leachate and AOP treated landfill leachate.
- Coupling Advanced oxidation process and Membrane bioreactor (MBR) for matured landfill leachate treatment to meet the land disposal standards.
- Integrating Membrane bioreactor with the Advanced oxidation process for the treatment of young leachate to attain the land disposal standards.
- Estimating the annualized capital and operating cost of the AOP-MBR integrated treatment system for treating landfill leachate.

CHAPTER- 3

MATERIALS AND METHODS

3.1 Introduction

Enhancement of biodegradability of matured landfill leachate by Advanced oxidation processes (AOPs) has been investigated in this study. The technical and economical feasibility of an integrated process of coupling appropriate AOP with a Membrane bioreactor for treating of matured and young landfill leachate to meet the disposal standards has been studied.

3.2 Landfill leachate sample collection

The landfill leachate samples were gathered from the Municipal Solid Waste Disposal Facility at Brahmapuram, Kochi, commissioned in the year 2008. It is the first project of Kerala for solid waste disposal under Jawaharlal Nehru Urban Renewal Mission (JnNURM). The landfill site is a non-engineered type open dump. It has no bottom liner or any leachate collection and treatment system. Therefore, all the leachate produced finds its path into the neighboring environment. According to Yang et al., (2015), landfill sites in a region having precipitation >800mm generates leachate around 33.32 litre/ton of waste dumped per year. 21% of the leachate generated is contributed by the water squeezed from the waste and 79% is generated due to the infiltration of the precipitation. However, leachate production amount in different regions vary greatly due to different climate conditions and waste properties. The climate of Kerala, is tropical monsoon with seasonally high rainfall and hot summer. As per Envis centre, Ministry of Environment and Forest, Govt. of India, average rainfall during the southwest monsoon season in Kerala is 2250-2500mm. The average rainfall in Kerala during the northeast monsoon period is 450-500 mm. Brahmapuram municipal solid waste disposal site has a capacity of handling solid waste of 250 tons per day. At present, solid waste collected per day is about 180 tons from Kochi Corporation, Aluva municipality, Thrikkakkara municipality, Thrippunithura municipality and Kalamassery municipality.

According to Samal and Madguni (2018), leachate samples collected during post and pre-monsoon season have a higher leachate pollution index (LPI) than that collected during monsoon season. LPI is a measure of the potential hazards of landfill leachate. Also, an increase in pollutant concentrations in landfill leachate is evident after the monsoon (Esakku et al., 2007). Hence, landfill leachate samples from the landfill site were collected every week during the post-monsoon period (November 2015 – May 2016). The liquid which oozed out from the fresh waste dumps was collected as young leachate. Liquid leached out from old dumps were collected as medium matured leachate. The samples collected in sterile bottles were labeled with the date and time of sampling. The collected samples were stored at 4^{o}C. The characteristics of the collected leachate samples were analyzed as per standard methods (APHA, 2005). The biological performance of the young and matured leachate was determined by measuring the COD variation with time and determining kinetic coefficients. Determining the kinetic coefficients of a wastewater is significant for the rational design of treatment units. Kinetic coefficients are one of the indicators to assess the effluent biodegradability (Haydar and Aziz, 2009). The acclimatized inoculum was added to the matured and young landfill leachate and aerated using aquarium aerator. COD reduction and Mixed liquor volatile suspended solids (MLVSS) were measured each day. Kinetic coefficients, Substrate utilization rate (k) and Half velocity constant (Ks) of matured and young leachate from landfill were determined following Eq (3.1).

$$\frac{x\theta}{(S_0 - S)} = \frac{K_s}{k} \times \frac{1}{S} + \frac{1}{k} \qquad \text{- Eq (3.1)}$$

S_0 and S =initial and final substrate concentration, x = Mixed liquid volatile suspended solids, θ =retention time in days,k = Maximum substrate utilization rate and Ks = Half velocity constant (Metcalf and Eddy,2013).

The slope of the graph sketched with 1/S on x-axis and x θ / (S0-S) on y-axis provided Ks/k value and the y-intercept indicated 1/k.

3.3 Materials

Fig. 3.1(a) Ultra filtration membrane module

Fig. 3.1(b) Hollow fibre membranes inside the module

All the chemicals used in the study were analytically pure. Cast iron electrode plates were fabricated in the mechanical workshop of the institution. Hollow fibre ultra-filtration membrane of 0.1 micrometer pore size, made of polypropylene material was used for the membrane bioreactor process (Fig. 3.1a & Fig. 3.1b).Hollow fibers provide significantly higher membrane surface and higher filtration capacity compared to flat sheet membranes. The Diaphragm pump of capacity 0.7 lpm (Fig 3.2) and an aerator with aeration rate 5 l/min were used.

Fig.3.2 Diaphragm pump

3.4 Analysis of Parameters

The different parameters (pH, TSS, BOD, COD, Ammonia nitrogen, Sulphide, Sulphate, Phosphate, Chloride and Nitrate) were analyzed as per standard procedure (APHA, 2005). The various analytical methods used for analyzing the parameters are recorded in table 3.1.

Table 3.1 Methods and instruments used for analyzing parameters

Sl. No.	**Parameter**	**Method**	**Equipment used**
1	pH	Electrometric	Water quality analyzer
2	TSS	Gravimetric method	N.A.
3	COD	Potassium dichromate reflux method	COD apparatus
4	BOD	Winkler's method	BOD incubator
5	Sulphate	Turbidimetric method	Spectrophotometer
6	Phosphate	Ascorbic acid method	Spectrophotometer
7	Sulphide	Iodometric method	N.A.
8	Chloride	Mohr method	N.A.
9	Ammonia nitrogen	Nessler's method	Spectrophotometer
10	Nitrate	Phenol disulphonic acid method	Spectrophotometer

3.5 Selection of appropriate Electro Fenton based advanced oxidation process for the pretreatment of matured landfill leachate

3.5.1 Electro Fenton treatment for matured landfill leachate

The EF experiment was carried out in 1000ml beaker with a pair of cast iron electrodes. Cast iron sheets (120mm x 65mm x 1 mm) with a maximum surface area that will be fit to the 1 L borosil glass beaker were used as electrodes. The cast iron electrode plates which served as the source of Fe^{2+} ions were vertically positioned in the beaker. The spacing between the two electrodes was set at 2.5 cm based on preliminary studies. For batch studies 800 ml leachate was used which immersed 55.25cm^2 of the surface of the electrode resulting in a specific electrode surface area of 0.069cm^2/cm^3. As the leachate contains chloride content, no separate electrolyte was added for electrochemical reaction. The anode and cathode were attached to the positive and negative terminals of a DC power supply. The reactor mixture was continuously stirred at the rate of 200rpm using a magnetic stirrer. Experiments were conducted at room temperature. Fig.3.3 shows the schematic diagram of the Electro Fenton process.

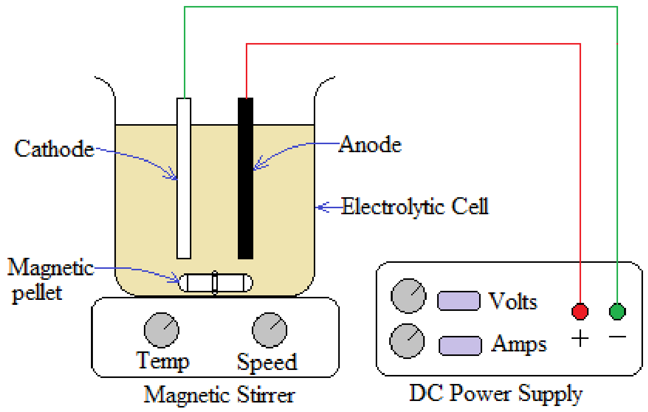

Fig. 3.3 Schematic layout of Electro Fenton Process

The pH of the solution was corrected using H_2SO_4 and Hydrogen peroxide (H_2O_2) 30% (w/w) was added externally.The electrochemical creation of Fe(II) ion takes place through the cathodic reduction of Fe(III) ions or reaction of anodic material dissolution. Factors affecting the Electro Fenton process (pH, current density, H_2O_2 dosage and reaction time) were varied and optimum conditions were found for maximum COD removal.

3.5.2 Photo Electro Fenton Process for matured landfill leachate

The Photo Electro- Fenton (PEF) process was conducted inthe same reactor as that of the Electro Fenton Process. UV light of 6W capacity was irradiated on the reactor at the optimum conditions obtained (Fig. 3.4). In Solar Photo Electro Fenton process (SPEF) sunlight was used for irradiation (average solar intensity - 24 W/m^2). Figure 3.5 shows the digital light meter used to measure solar intensity. The use of solar energy, a renewable energy source reduces the energy cost for irradiation.

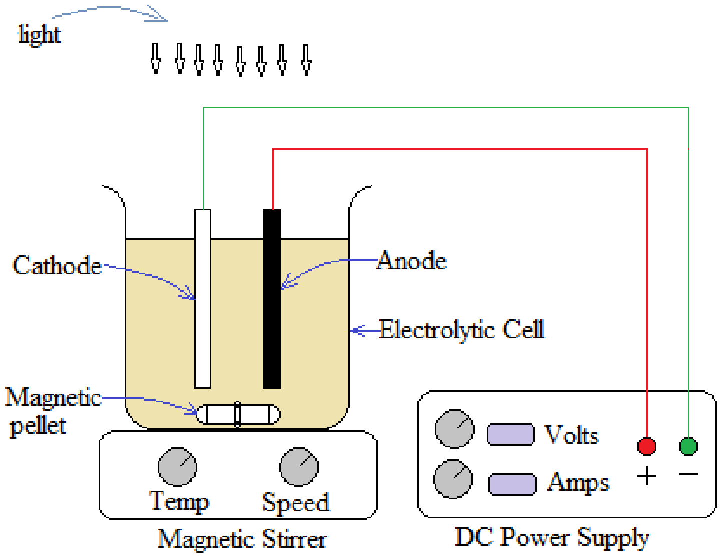

Fig. 3.4 Schematic representation of Photo Electro Fenton process

When the EF process was irradiated withUV/solar light, it accelerated the degradation of organic compounds through two main pathways: a) the photolysis of Fe^{3+} -oxidation products complexes, and b) through the improvement of Fe^{2+} regeneration by the photo-reduction of Fe^{3+} ions. Biodegradability index enhancement and COD reduction were compared for obtaining the appropriate advanced oxidation process for pretreatment before the biological process.

Fig. 3.5 Digital light meter

3.6 Experiment design and optimization of the operating parameters using Response surface methodology

Maximum biodegradability index enhancement was obtained after treating of matured leachate by Electro Fenton process. Response Surface Methodology (RSM) was used for the optimization of variables influencing EF process with the objective response being biodegradability index (BOD/COD). Other responses were COD, Ammonia nitrogen, Phosphate, Chloride, Sulphate and Sulphide. The important variables considered were pH, current density, H_2O_2 dose and reaction time. Variable levels were set in view of both literature reports and preparatory runs to ensure that the design points were within the design area. The estimation of H_2O_2 dosage relied on the stoichiometric ratio with respect to full oxidation. The dose of H_2O_2 was varied from 20% to 80% of the theoretical value. Additionally, the current density was fluctuated from 15 A/m^2 to 150 A/m^2, the reaction time was varied from 15min to 60min and pH was changed from 2 to 4.

Using MINITAB 17, programming the experiment design, optimization and plotting the contours were expertly done. When the number of factors to be studied is three or above, Box-Behnken design is put in application. In the experimental design the input variables were used in uncoded form. Box Benhken experiment design of Response surface methodology (RSM) was accepted to find the relation between the response functions and variables. The domains of all of the variables were determined by conducting preparatory runs and from the literature review. Sequentially, 27 series of experiments with differentoperating conditions as pointed out by the test configuration were carried out to examine the factors (pH, current density, H_2O_2 dosage, and reaction time) needed in the Electro Fenton reaction. The experiment was repeated four times at optimum conditions and validated. The sludge formed was measured to determine the sludge volume index (SVI) using Eq (3.2) which provided the physical state of the sludge. Anode and energy consumption were also determined using given equations 3.3 and 3.4 respectively.

$$\text{Sludge Volume Index(ml/g)} = \frac{\text{settled sludge per sample volume (ml/l)}}{\text{Supended Solid concentration (mg/l)}} \times 1000$$

- Eq (3.2)

Anode consumption = $W_{\text{initial}} - W_{\text{final}}$ - Eq (3.3)

Where W_{initial} is the initial weight of anode and W_{final} is the final weight of the anode after reaction time

Energy consumption (kWh) = VIt /1000 - Eq (3.4)

Where V is the voltage in volts, I is the current consumed in Amperes and t is the reaction time in hours.

3.7 Determination of kinetic coefficients k and Ks of untreated and AOP treated landfill leachate

The biological treatability of the AOP treated matured leachate was compared with that of untreated leachate. Kinetic coefficients maximum substrate utilization rate (k) and half velocity constant (Ks) were determined by inoculating the leachate with acclimatized sludge and measuring COD degradation and volatile suspended solids in mixed liquor (MLVSS) at various detention period (θ).The growth rate of microorganisms is directly related to the rate at which they utilize the waste or metabolize. Under proper environmental conditions the growth rate of microorganisms can ensure waste stabilization effectively. In the system, the bacterial growth rate can be expressed by following Eq.3.1 which is derived using Monod's equation.

3.8 Acute toxicity test

Acute toxicity (LC50) was determined using static 24hr and 96hr fish bioassay. Bioassay test with test organism Poecilia Reticulata fish (Guppy fish) was performed at room temperature on matured landfill leachate and Electro Fenton treated leachate as per IS 6582-1971. LC50 is the lethal concentration that causes the death of 50% of the test organisms. Healthy fishes of lengths 1.0 to 1.3 cm were selected for the experiment. The test fishes were acclimatized for 10 days in dilution water with pH 7 at room temperature and Dissolved oxygen >4mg/l. A preliminary bioassay test was done to determine the approximate range of concentration of leachate samples for full-scale bioassay test. A wide range of concentration of leachate sample was prepared (100, 10, 1, 0.1 percent dilutions).

Five test fishes were placed in each leachate concentration and fish mortality was observed after 24hrs. The range selected was the lowest concentration at which all fish survived after 24 hrs and the highest concentration at which all fish died in 24hrs. For full-scale test fishes were exposed to different leachate concentrations (10 -100%) at pH 7. Group of 10 fishes of similar size were transferred from the acclimatization tank into a suitable vessel with 10 litres of wastewater sample and was aerated. A control group was run exactly under similar condition using dilution water alone. Mortality of the test organisms was measured after 24 hr and 96 hr of contact with different concentration of leachate. LC 50 was estimated for untreated and EF treated matured landfill leachate from the graph plotted with mortality percentage on the y-axis and percentage leachate concentration on the x-axis.

3.9 Integrating Electro Fenton process with Membrane Bioreactor process for treating matured landfill leachate

A reactor of size 15cm x 15cm x 28.5cm and 6L capacity made of acrylic sheet was filled with 3 litre AOP pretreated matured landfill leachate. The reactor was nourished with oxygen at the rate of 5 litre /min by an aerator. The setting consists of a hollow fiber membrane module made of polypropylene with pore size 0.1µm and a pump of 0.7 lpm capacity as shown in Fig.3.6.

Bio-sludge procured from a secondary settling tank of activated sludge process was subjected to 4 weeks acclimatization with leachate. The acclimatized sludge was utilized as inoculum for the bioreactor. The reactor was operated in batch mode with Mixed Liquor Suspended Solid (MLSS) concentration as 20 g/l. The supernatant was moved from the bioreactor by way of hollow fiber membrane module after the reaction period and the effluent was tested. With different Hydraulic Retention Times (HRT) and at pH -7, the process was repeated.

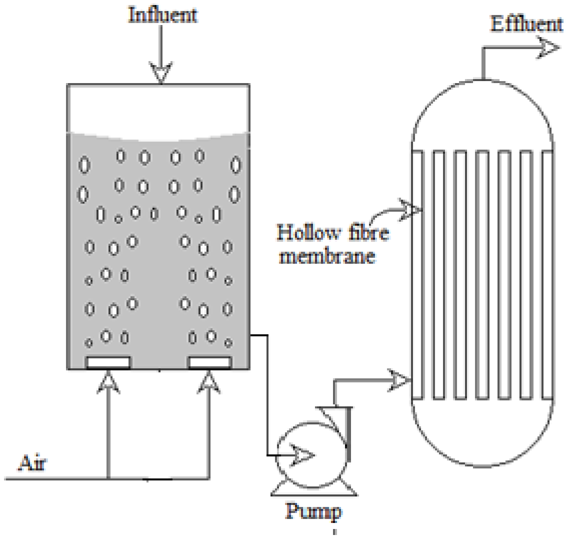

Fig.3.6 Schematic diagram of membrane bioreactor experimental setup

At different HRTs, the COD of the effluent were analyzed and optimum retention time was found. The effect of biomass concentration on pollutant degradation was found by varying biomass concentration from 5g/l to 20g/l and measuring COD and ammonium nitrogen concentrations. The process was run at optimum conditions and the effluent was analyzed for all parameters. Microbial analysis of the membrane bioreactor sludge was done at the Department of Microbiology, Kerala Agriculture University, Vellanikkara. The identification of the microorganism was done by 16 Svedberg unit Ribosomal RNA (16SrRNA) method. Membrane flow rate variation with time was also analyzed to study the fouling of the membrane. The membrane flow rate was measured after 2 minutes of physical backwash. The degree of fouling and its nature was measured by passing deionized water through the membrane after the wastewater filtration. Relative permeability of the membrane and percentage fouling were calculated according to Eq (3.4)–Eq (3.11) (Swierczynska Anna et al., 2016).

Volumetric flux of the waste water

$J_w = V_w/S*t$ $m^3/m^2/sec$ -Eq (3.4)

Volumetric flux of the deionized water prior to waste water filtration

$J_{dp} = V_{dp}/S*t$ $m^3/m^2/sec$ -Eq (3.5)

Volumetric flux of the deionized water after wastewater filtration

$J_{da} = V_{da}/S*t$ $m^3/m^2/sec$ -Eq (3.6)

Where V_w = volume of waste water filtered through membrane in m^3

V_{dp}= volume of deionized water prior to waste water filtration in m^3

V_{da}= volume of deionized water after waste water filtration in m^3

t = time of filtration in seconds

S = membrane surface area in m^2

Relative permeability of the membrane for wastewater flux

$=J_w*100/J_{dp}$ - Eq (3.7)

Relative permeability of the membrane for deionized water flux

$= J_{da}*100/J_{dp}$ - Eq (3.8)

Where J_{da} is the volumetric flux of the deionized water after wastewater filtration in m^3/m^2.sec, J_w is the volumetric flux of wastewater prior to filtration in m^3/m^2.sec andJ_{dp} is the volumetric flux of the deionized water prior to wastewater filtration in m^3/m^2.sec

Based on the equations Eq(3.6)-Eq (3.8) Total, reversible and irriversible fouling were determined.

$R_f = R_{rf} + R_{if}$ - Eq (3.9)

$$R_{rf} = (J_{da}-J_{wp})*100/J_{dp} \qquad \text{- Eq (3.10)}$$

$$R_{if} = (J_{dp}-J_{d})*100/J_{dp} \qquad \text{- Eq (3.11)}$$

Where R_f is the total fouling, R_{rf} is the reversible fouling and R_{if} is the irriversible fouling.

3.10 Treatment of young landfill leachate by Membrane Bioreactor process integrated with Electro Fenton process

3.10.1 Membrane bioreactor process for young landfill leachate treatment

A reactor of size was 28.5cm x 15cm x 15cm and 6L capacity made of acrylic sheet was used. landfill leachate of quanity 3 litres was filled in the reactor and aerated at the rate of 5litre/min using an aerator. The setting consists of a hollow fiber membrane module made of polypropylene having pore size 0.1µm and 0.7 lpm capacity pump as shown in fig. 3.4.

Bio-sludge obtained from a secondary settling tank of activated sludge process and was acclimatized with leachate for one month. This acclimatized sludge was taken as inoculum for the bioreactor. The reactor was operated in batch mode with Mixed Liquor Suspended Solid (MLSS) concentration maintained at 10 g/l. The supernatant from the reactor was passed through the membrane module after the reaction time and the treated effluent was analyzed. The process was repeated with different HRTs at pH 7. The effluent COD at different HRTs were determined. Other parameters were analyzed at optimum HRT. Membrane flow rate variation with time was also analyzed to study the fouling of the membrane. The degree of fouling and its nature was measured by passing deionized water through the membrane after the wastewater filtration. Relative permeability of the membrane and percentage fouling were calculated as per Eq(3.4)–Eq(3.11).

3.10.2 Integrating Membrane bioreactor process with Electro Fenton process to meet discharge standards

Landfill leachate is an intricate liquid that contains an extreme amount of non- biodegradable and biodegradable products that cannot be easily isolated by the biological process alone. Hence appropriate AOP was used as post- treatment for separating the non-degraded pollutants to reach the irrigation disposal standards. The factors affecting the treatment were varied one at a time and optimum conditions were determined by measuring COD reduction. The efficiency of the AOP was studied by analyzing all other parameters at optimum conditions and compared with the discharge standards.

3.11 Cost comparison of the integrated system for the treatment of matured and young landfill leachate

Cost of the EF-MBR integrated system was evaluated for treating both matured and young leachate by considering capital cost and operating cost. Initial capital cost of each unit for treating 100m^3 leachate was determined. Annualized capital cost of each unit was determined by multiplying the unit capital cost with annual ratewith the assumption of 10% interest rate for the design period,. Annualisation factor is obtained as per Eq (3.12).

$$\text{Annualisation factor (r)} =.\frac{i(1+i)^n}{[(1+i)^n-1]} \qquad \text{- Eq (3.12)}$$

where i is the interest rate and n is the life expectancy of the equipment (Gautam et al., 2016).

Electricity cost, electrode cost, chemical cost and cost for sludge management contributed to the operation cost of the integrated treatment system. By defining specific energy consumption (SEC) in kWh/m^3 and specific anode consumption (SAC) in kg of anode consumed/m^3 as shown in Eq (3.13) and Eq (3.14), the electricity utilization and anode utilization were quantified.

Energy utilized (kWh) = VIt x 10^{-3} - Eq (3.13)

Where V is the voltage, I is the current in Ampere, t is the reaction time in hour

Anode utilized (kg) = $W_{initial}$- W_{final} - Eq (3.14)

where $W_{initial}$ and W_{final} are the initial and final weight of the electrode in kg.

According to Robinson, (2005) for treating landfill leachate using MBR process,the specific energy consumption is 3kWh/m^3. Unit cost of different items contributing to operating cost,furnished based on the existing price is shown in table 3.2.

Table 3.2. Unit cost of items contributing to operating cost

Item	Rate	Unit
Electricity	5.5	Rs /kWh
Electrode(cast iron)	80	Rs /kg
Hydrogen peroxide (30%w/w)	24.3	Rs /kg
Sludge management	10	Rs /kg

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The landfill leachate samples were gathered from the Brahmapuram Municipal Solid Waste Disposal site at Kochi during the post-monsoon season. According to Esakku et al. 2007, after the monsoon, an increase in pollutant concentrations in landfill leachate is evident.The landfill site spreads around 110 Acres of land having a capacity to handle 250 tons/day. The average collection rate of solid wastes from Kochi Corporation, Aluva municipality, Thrikkakkara municipality, Thrippunithura municipality and Kalamassery municipality was about 180 tons/day, of which the biodegradable waste is being composted by Windrow process. Non biodegradable waste materials are dumped in open. At present, the site is not equipped with a collection or treatment system for leachate generated.Leachate was collected for 7 months every week from November 2015- May 2016 and was analyzed according to APHA 2005.

4.2 Characteristics of the leachate samples

The leachate samples gathered from the site were analyzed and the characteristics of the samples are shown in Appendix -I and Appendix -II. The average characteristics of the gathered matured and young leachate samples are reported in Table 4.1 and Table 4.2 respectively. Leachate collected from Brahmapuram waste disposal plant was characterized and the average biodegradability index (BI) of matured leachate was 0.21 and that of young leachate was 0.49. Biodegradability index is interpreted as the ratio of BOD to COD.As the landfill matures, the organic portion in the leachate winds upplainly overwhelmed by refractory compounds (Lee et al., 2010). In the later stable methanogenic stage, the pH increases and the BOD/COD ratio diminishes, thus reduction in the biodegradability.

Table 4.1 Average characteristics of matured landfill leachate

Parameters	**Mean ± Std. Deviation**
pH	8.1 ± 0.5
TSS(mg/l)	498 ±53
COD(mg/l)	23200 ± 2054
BOD(mg/l)	4872 ± 820
Sulphate(mg/l)	587 ± 65
Phosphate(mg/l)	185 ± 12
Sulphide(mg/l)	20.1 ± 3
Chloride(mg/l)	2670 ± 114
Ammonia nitrogen(mg/l)	2196 ± 106
Nitrate (mg/l)	1.4 ± 0.3
BOD/COD	0.21 ± 0.03

The presence of ammonia nitrogen is mainly due to their generation from the decomposition of organic matter which are stable in anaerobic condition thus explained the presence of a high percentage of soluble nitrogen compound found in leachate. Ammonia nitrogen concentration was higher in matured leachate which is due to the slow leaching of wastes producing nitrogen with no significant mechanism for the transformation of ammonia nitrogen in leachate over a long period of time. It is also believed that ammonia is mainly released from the decomposition of organic matter such as protein. There is an observed difference in the concentration of other parameters between acidogenic phase and methanogenic phase likely due to the effects of sorption, complex formation and precipitation. Variation in the trend may be due to the slow leaching of wastes or washouts (Lee et al., 2010).

Table 4.2 Average characteristics of young landfill leachate

Parameters	**Mean ± Std. Deviation**
pH	7.2 ± 0.5
TSS (mg/l)	568 ± 148
COD (mg/l)	20180 ± 2852
BOD (mg/l)	9850 ± 923
Sulphate (mg/l)	392 ± 68
Phosphate (mg/l)	98 ± 11
Sulphide (mg/l)	122 ± 21
Chloride (mg/l)	2640 ± 125
Ammonia nitrogen (mg/l)	153 ±56
Nitrate (mg/l)	1.7 ± 0.5
BOD/COD	0.49 ± 0.04

Leachate samples contain high level of organic and inorganic constituents beyond the permissible limits. Heavy metals concentration was in trace amount as the waste is domestic in nature (Kjeldsen et al. 2002).

4.3 Biological treatability of matured and young leachate

The acclimatized inoculum was added to the matured and young landfill leachate under aerobic conditions. COD reduction and MLVSS were measured each day. The kinetic coefficients of landfill leachate were determined by plotting a graph based on Eq. (3.1).

The rate of COD reduction of matured and young leachate in an aerated biological system showed that the degradationrate of organic matter in young leachate is faster than the matured leachate (Fig. 4.1). Young leachate contains higher organic fraction having low molecular weight in comparison with old leachate. In older leachate, organic content prevailingare humic and fulvic substances of high molecular weight with persisting character, which results in low biodegradability (Sivan and Latha, 2013). Kinetic coefficients of the raw leachates are estimated from Fig.4.2 & Fig.4.3. It was found that the Substrate utilization rate (k) was higher and half velocity constant (Ks) was lower for young landfill leachate than matured leachate indicating faster degradation of young landfill leachate (Table- 4.3).

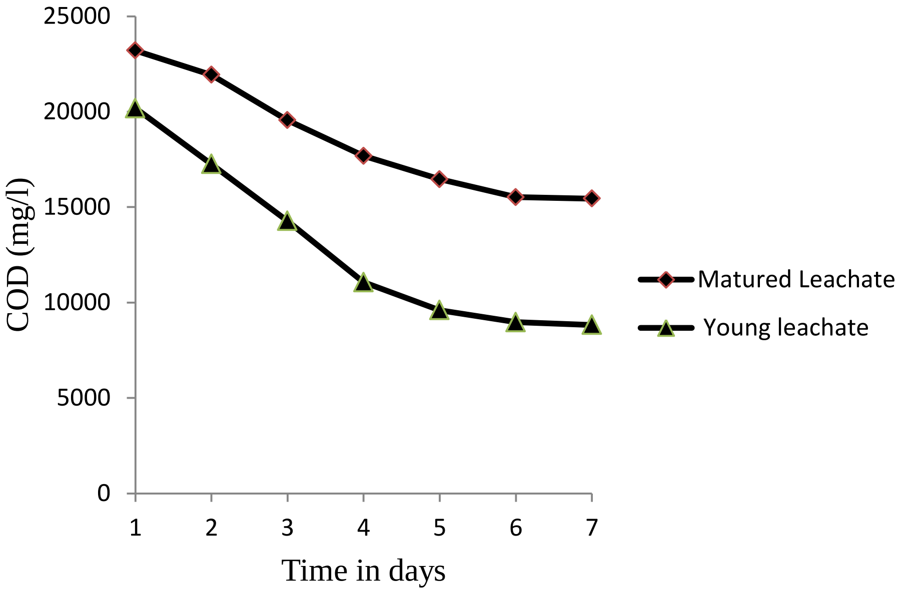

Fig. 4.1 COD reduction of matured and young leachate with time

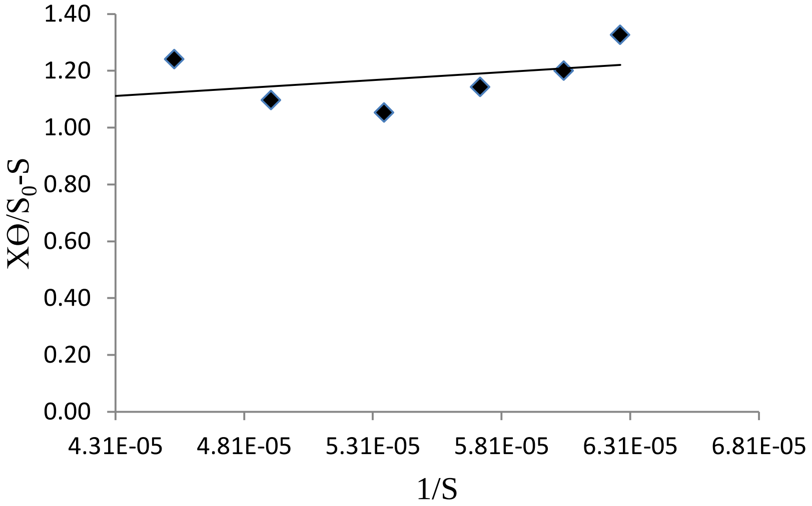

Fig.4.2 Graph for determining kinetic coefficients k and Ks for untreated matured leachate

The presence of degradable organic matter in young leachate caused faster degradation rate whereas the presence of recalcitrant components in matured leachate inhibited the microbial degradation causing slow rate of degradation (Lee et al., 2010).

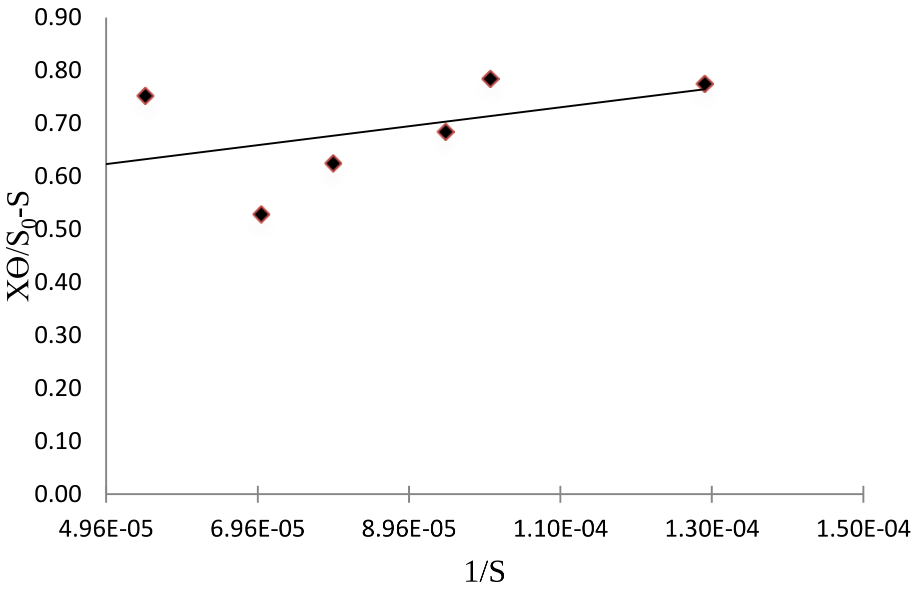

Fig.4.3 Graph for determining kinetic coefficients k and Ks for untreated young leachate

Table 4.3 Kinetic coefficients of matured and young leachate

Kinetic coefficients	**Matured landfill leachate**	**Young landfill leachate**
k day^{-1}	1.146	1.639
Ks g/l	6.366	1.284

4.4 Comparison of Electro Fenton, Photo Electro Fenton(UV) and Solar Photo Electro Fenton processes for treatment efficiency and biodegradability enhancement

Preliminary experiments were performed to select the electrodes. Cast iron electrodes showed better efficiency in comparison with mild steel and stainless steel electrodes. Electrochemical dissolution behavior was dominated by the matrix structure and the geometry of the included graphite particle (Zapp et al., 2015). Cast iron plates were used as electrodes as efficiency improved with the surface area of the electrodes (Kurt et al., 2007). The spacing between the electrodes was kept as 2.5 cm based on preliminary studies and specific electrode surface was $0.069 cm^2/cm^3$. The source of Fe^{2+} ions was the cast-iron plates.

Effect of pH value, H_2O_2 dosage, current density (CD) and reaction time on COD removal was analyzed by varying single parameter at a time and fixing the other parameters. Initially, the percentage reduction of COD increased with time keeping other parameters constant which was due to the formation of hydroxyl radical. After 45 minutes of treatment there was no significant variation in COD removal (Fig.4.4). This may be due to the fact that reaction between H_2O_2 and Fe^{2+} was completed within this time interval as mentioned in Tengrui et al. (2007) and Saleem et al., (2011). In the present study maximum COD removal was obtained at pH-3 (Fig.4.5). When the pH increased there was a decrease in the removal efficiency of COD, this may be due to the precipitation of iron species and formation of a stable compound with H_2O_2. H_2O_2 is unstable at higher pH, it decomposes rapidly to O_2 and H_2O at neutral to high pH as mentioned in Nideesh and Gandhimathi, (2012). At lower pH, H_2O_2 would remain steady due to the formation of oxonium ion as mentioned in Tengrui et al. (2007).

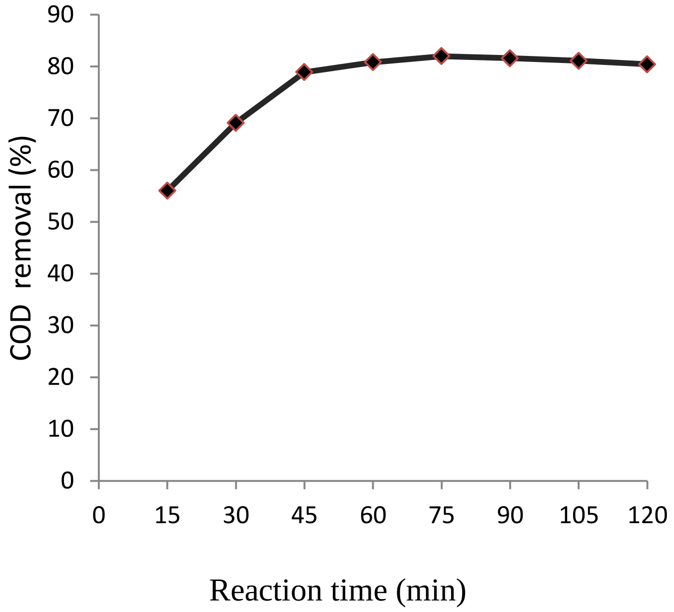

Fig. 4.4 Percentage reduction in COD with reaction time

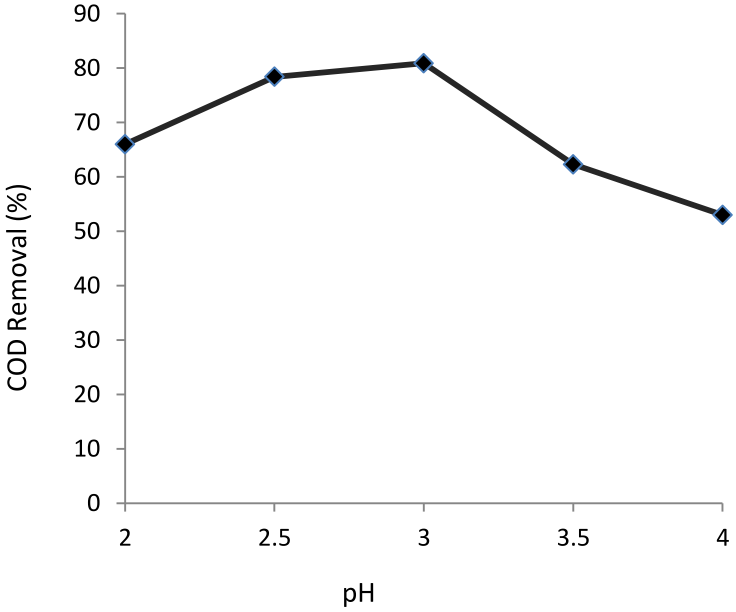

Fig. 4.5 Variation in percentage COD reduction with pH

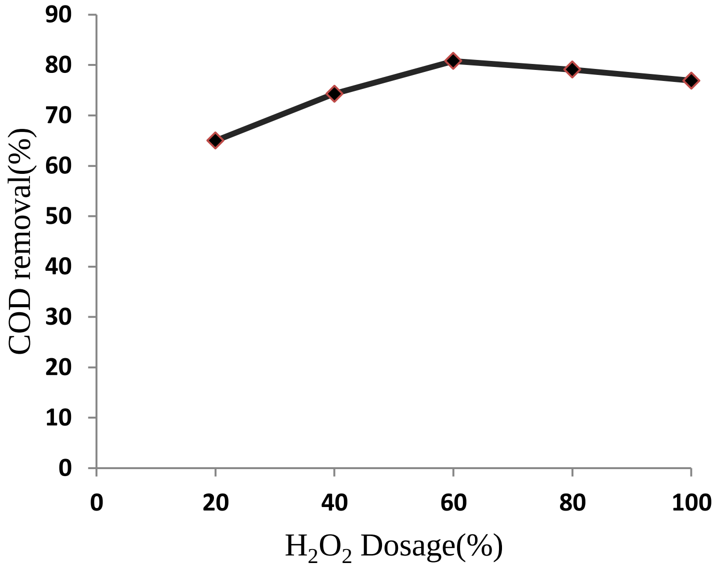

Fig. 4.6 Variation in COD reduction with H_2O_2 dosage

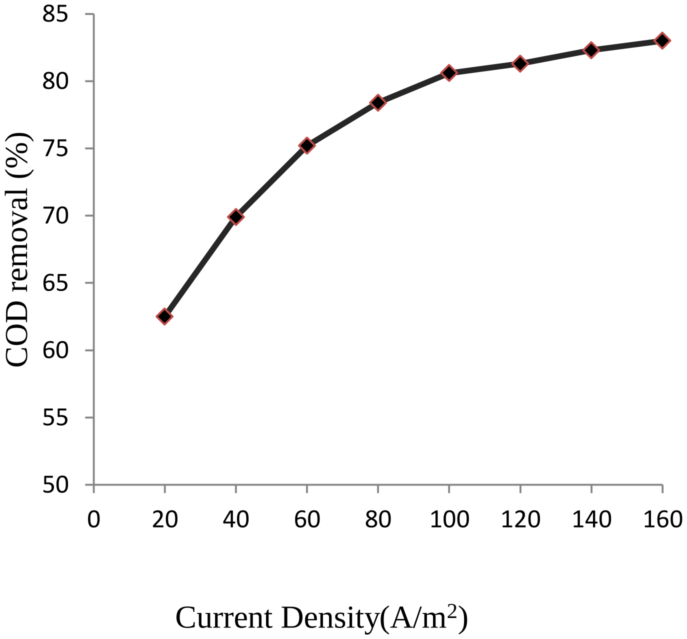

Fig. 4.7 Variation in percentage COD reduction withH_2O_2 dosage

The amount of H_2O_2 added to the reactor is based on the COD value of the wastewater to be treated. But in previous studies, it was found that when the complete quantity of H_2O_2 was supplied, removal efficiencydid not increase (Lin et al., 2000; Kurt et al. 2007; Priambodo et al. 2011). Also, the presence of chloride leads to the formation of active chlorine species and can affect the oxidation efficiency of the process. Electro coagulation also plays a role in removing the organic matter. So the study was conducted using different percentages of the theoretical amount of H_2O_2 required by the leachate sample. COD removal increased up to 60% of the theoretical value of H_2O_2 concentration (Fig.4.6). This is due to the reason that as concentration increases, hydroxyl radical production also increases, which is the main element taking part in the oxidation of pollutants. But when the concentration increases further, the oxidation reaction may become slower because H_2O_2 is consumed for the oxidation of Fe^{2+} ions and the production of $HO_2\bullet$ (Hydro peroxyl radical). Hydro peroxyl radical has lesser oxidation capacity than that of $OH\bullet$.

Electric current plays the most significant part in the Electro Fenton Treatment of wastewater. In the study, it was found that as the current applied increases the efficiency also increases. About 82.3% COD removal was obtained at CD of 140 A/m^2 (Fig.4.7). Thereafter there was no prominant increase in COD removal. Higher removal efficiency may be due to higher hydroxyl radical production. The optimum current density giving efficient treatment and with minimum cost was selected as per Tengrui et al. 2007.

COD removal and biodegradability index of the Electro Fenton, Photo Electro Fenton using UV light and Solar Photo Electro Fenton processes were compared. In the PEF method, the presence of Fe^{2+} and UV illumination of the wastewater, H_2O_2 mineralize the contaminants. The action of UV light and visible light is complicated and can be explained by (a) the increase in the generation of hydroxyl radical due to the photo-reduction of predominant Fe^{3+} species in acidic medium and (b) the photolysis of Fe(III) complexes with produced carboxylic acids. Under the irradiation of UV light and solar light, ferric species can be reduced and hydroxyl radicals are produced for the oxidation process (Jiang and Mao, 2012). Biodegradability index in terms of BOD/COD ratio of leachate enhanced to 0.36 after the PEF process. The treatment efficiency of SPEF is less than PEF, this may be due to the climatic conditions and the lesser amount of UV radiation (Fig.4.8).

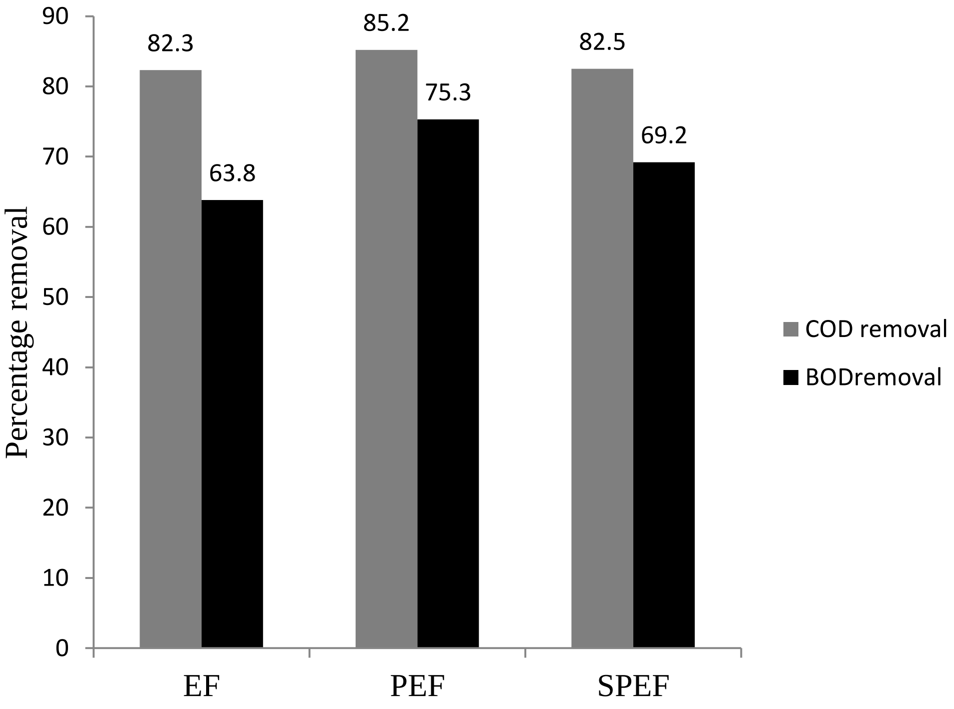

Fig.4.8 COD and BOD percentage reduction after EF, PEF and SPEF processes

SPEF enhanced the biodegradability index (BI) of leachate to 0.38. Irradiation of leachate with UV light increased the degradation of degradable organic matter (Brillas, 2014). The biodegradability of matured landfill leachate after 30 minutes of EF treatment was greater than 0.4 where as BI after PEF and SPEF processes were below 0.4 (Fig.4.9). For complete biodegradation of the organic matter, the biodegradability index should be greater than 0.4 (Soloman et al., 2009; Alessandra Cesaro et al., 2013). Hence EF process was selected as an appropriate pretreatment method for treating matured landfill leachate.

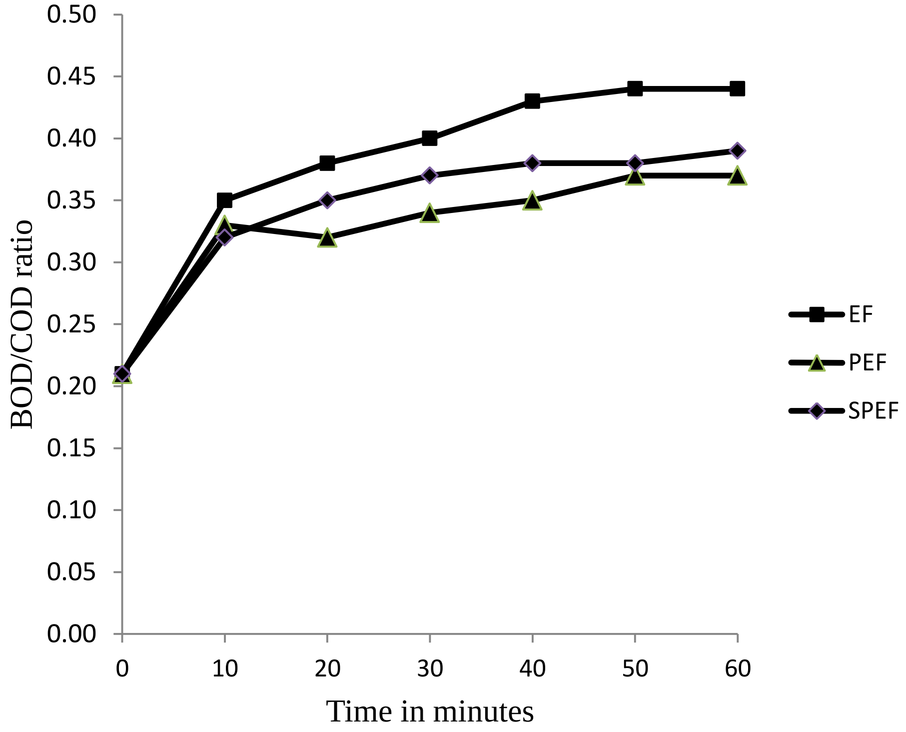

Fig. 4.9 Variation in biodegradability index with time for EF, PEF and SPEF processes

4.5 Effect of operating variables on the performance of Electro Fenton process and optimizing the operating variables using Response surface methodology

The experiment design, optimization, and the contour plots were accomplished using the MINITAB 17 software. Box Benhken Design was adopted for the experiment design in order to find the relation between response functions and the input variables.

Table 4.4Design of experiment and response for Electro Fenton treatment

SL. No:	**pH**	**CD (A/m^2)**	**Dosage (%)**	**Time (min)**	**COD (%)**	**NH_{3-} N(%)**	**Cl^- (%)**	**SO_4^- (%)**	**S^- (%)**	**PO_4^- (%)**	**BI**
1	2	15.0	50.0	37.5	74.2	39.1	59.0	56.1	52.0	59.1	0.364
2	4	15.0	50.0	37.5	72.0	37.3	57.2	52.9	50.0	57.4	0.323
3	2	150.0	50.0	37.5	78.2	41.8	63.1	58.8	56.0	62.4	0.431
4	4	150.0	50.0	37.5	77.9	42.0	60.5	59.0	55.0	62.1	0.419
5	3	82.5	20.0	15.0	74.2	37.2	59.7	57.6	52.5	57.1	0.252
6	3	82.5	80.0	15.0	78.1	39.3	62.9	57.2	54.6	59.3	0.330
7	3	82.5	20.0	60.0	78.0	39.0	60.9	56.3	54.0	59.4	0.298
8	3	82.5	80.0	60.0	76.3	40.9	61.0	58.1	54.0	61.2	0.361
9	2	82.5	50.0	15.0	76.4	40.0	60.7	56.9	53.0	60.1	0.359
10	4	82.5	50.0	15.0	73.9	38.3	59.2	57.2	52.0	58.3	0.341
11	2	82.5	50.0	60.0	74.8	41.7	60.0	57.3	53.0	62.3	0.402
12	4	82.5	50.0	60.0	78.0	40.1	60.2	56.8	54.0	60.0	0.373
13	3	15.0	20.0	37.5	73.1	37.2	58.3	52.0	51.0	57.4	0.246
14	3	150.0	20.0	37.5	76.5	40.8	61.0	58.8	56.4	61.2	0.338
15	3	15.0	80.0	37.5	75.0	38.2	60.0	57.0	52.9	58.1	0.312
16	3	150.0	80.0	37.5	77.9	41.0	63.8	59.9	56.1	60.0	0.392
17	2	82.5	20.0	37.5	76.0	40.0	60.0	56.9	53.2	59.8	0.309
18	4	82.5	20.0	37.5	74.2	37.1	59.4	55.4	51.9	57.4	0.281
19	2	82.5	80.0	37.5	76.0	40.0	61.1	59.2	54.0	60.2	0.368
20	4	82.5	80.0	37.5	76.2	40.2	59.4	57.1	53.2	60.1	0.350
21	3	15.0	50.0	15.0	73.0	37.2	58.2	53.6	51.3	57.3	0.298
22	3	150.0	50.0	15.0	78.4	39.9	62.1	59.2	54.0	60.0	0.405
23	3	15.0	50.0	60.0	74.0	40.1	59.0	54.0	52.0	60.4	0.358
24	3	150.0	50.0	60.0	77.9	42.0	62.5	58.9	57.3	62.3	0.412
25	3	82.5	50.0	37.5	77.8	40.9	62.9	60.0	55.9	61.6	0.439
26	3	82.5	50.0	37.5	78.0	41.0	62.8	60.0	56.2	61.7	0.435
27	3	82.5	50.0	37.5	78.0	41.1	63.0	59.6	56.1	61.8	0.435

Table 4.4 indicates the design of experiments based on Box Behnken design and responses COD, ammonia nitrogen, chloride, sulfate, sulfide, phosphate reduction and biodegradability index (BI). The independent variables affecting the Electro Fenton process were pH, H_2O_2 dosage, current density (CD) and reaction time. A second order polynomial model was fitted to the experimental data for Biodegradability index as given underneath (Eq 4.1).

$$Y = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 \qquad \text{- Eq (4.1)}$$

Where Y is the predicted response, X_1, X_2, X_3, X_4 are the input variables, b_o is a constant, b_1, b_2, b_3, $b_4$are regression coefficients for linear effects. b_{11}, b_{22}, b_{33}, b_{44} are second order coefficients and b_{12}, b_{13}, b_{14}, b_{23}, b_{24}, b_{34} are the coefficients of interaction.

Table 4.5 shows the range of the independent variables were decided based on the preliminary runs and literature review

Table 4.5 Range of variables used for Electro Fenton treatment

Independent variable	**Unit**	**Notation**	**Range of value**
pH	-	X_1	2- 4
Current density (CD)	(A/m^2)	X_2	15-150
H_2O_2 dosage	% of theoretical value	X_3	20- 80
Reaction time	minutes	X_4	15- 60

The optimum value of every variable and the impact of their associations on the BI were analyzed by plotting two-dimensional contour lines (Fig 4.10-4.15).

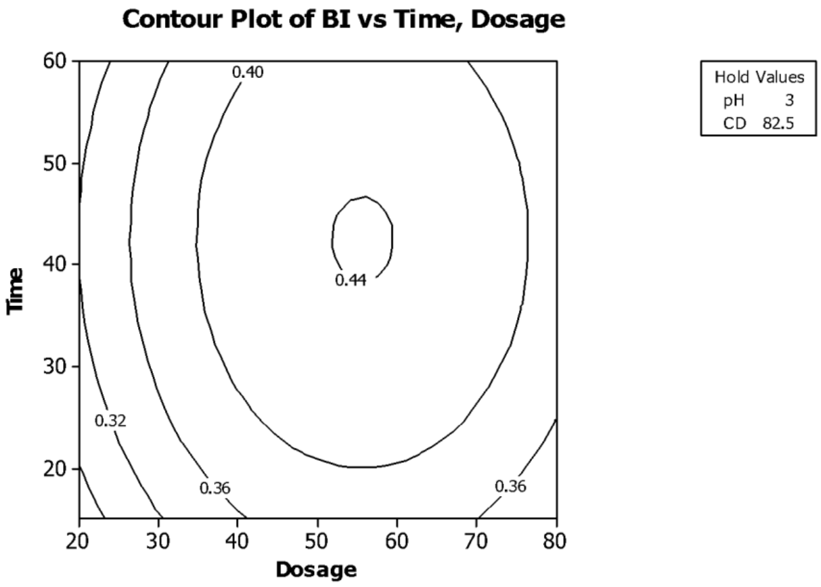

Fig. 4.10 Effect of time and H_2O_2 dosage on BI at pH-3 and CD-82.5A/m^2

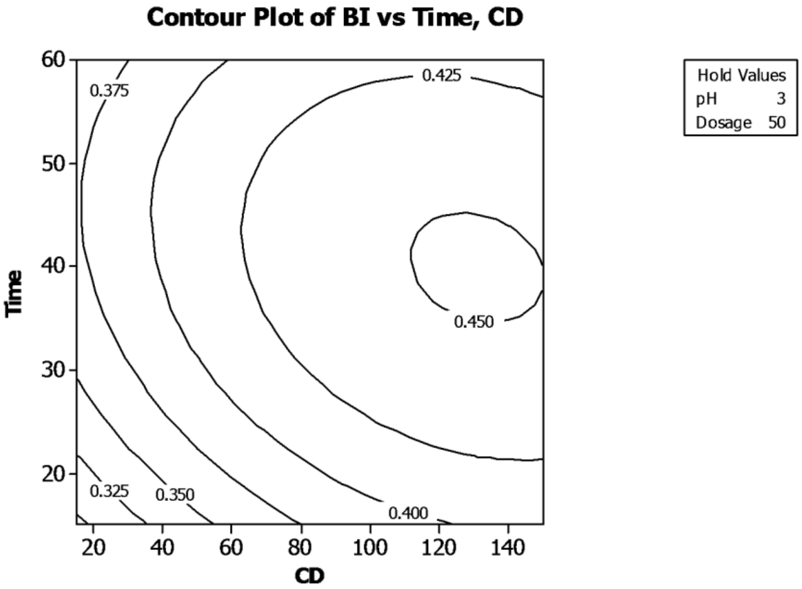

Fig. 4.11 Effect of time and CD on BI at H_2O_2 dosage-50% and pH- 3

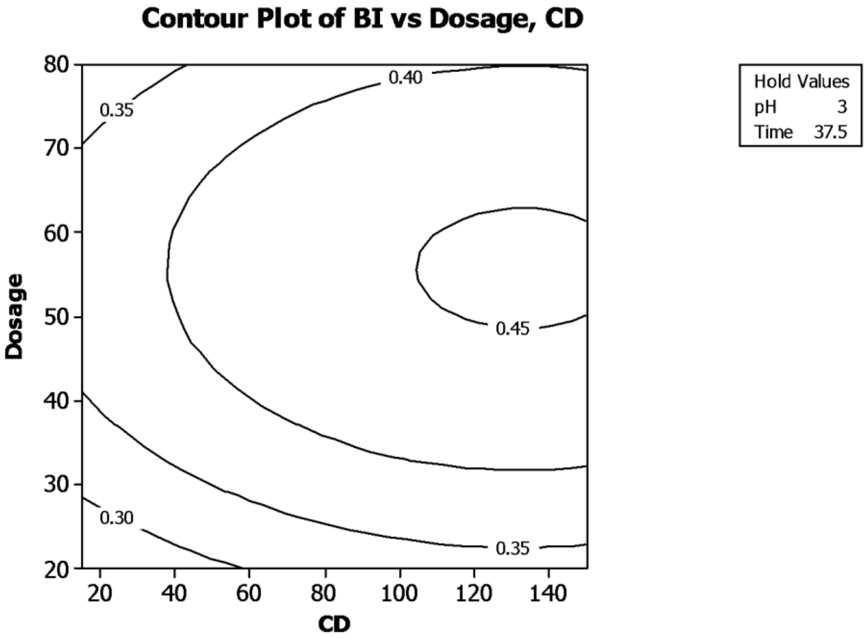

Fig. 4.12 Effect of H_2O_2 dosage and CD on BI at pH-3 and time-37.5minutes

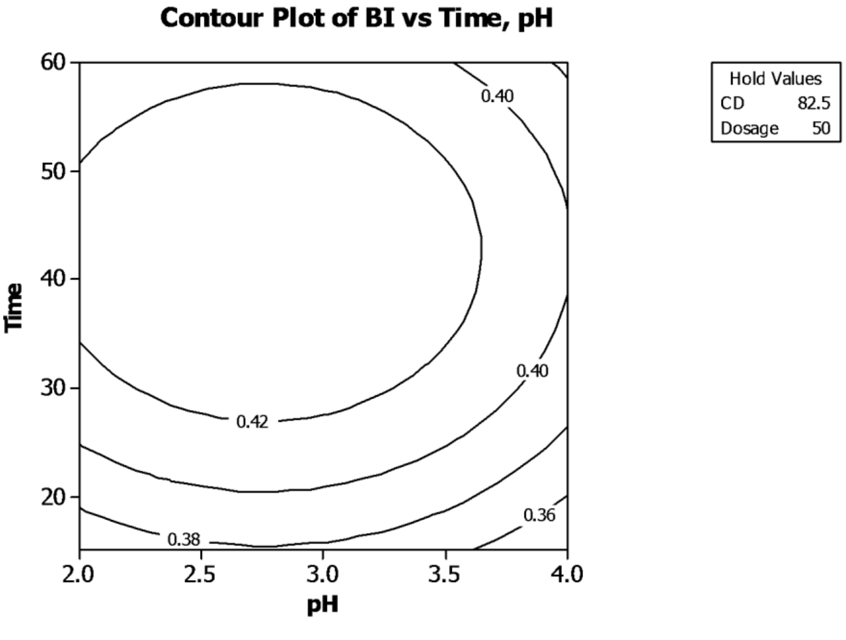

Fig. 4.13 Effect of time and pH on BI at H_2O_2 dosage-50% and CD-82.5A/m^2

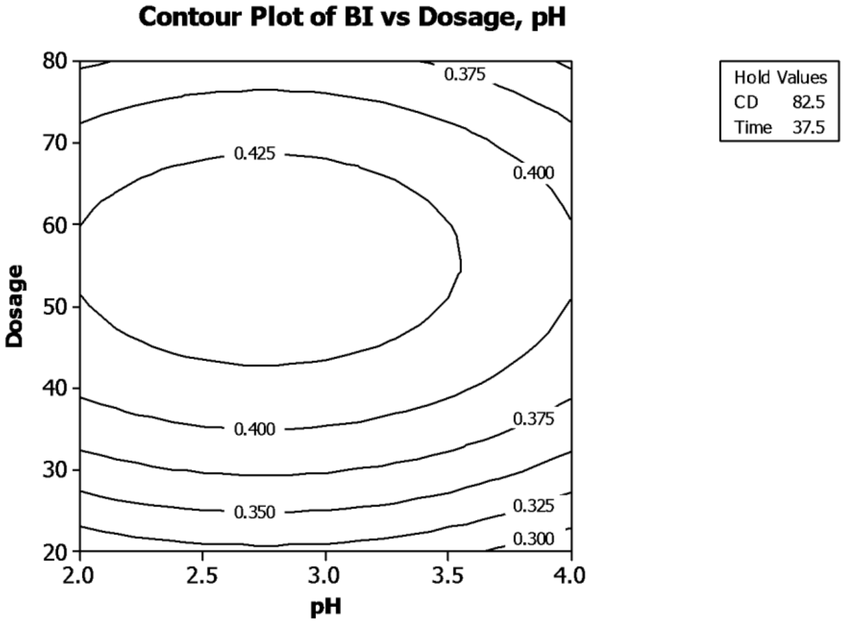

Fig 4.14 Effect of H_2O_2 dosage and pH on BI at CD-82.5A/m^2 and Time-37.5minutes

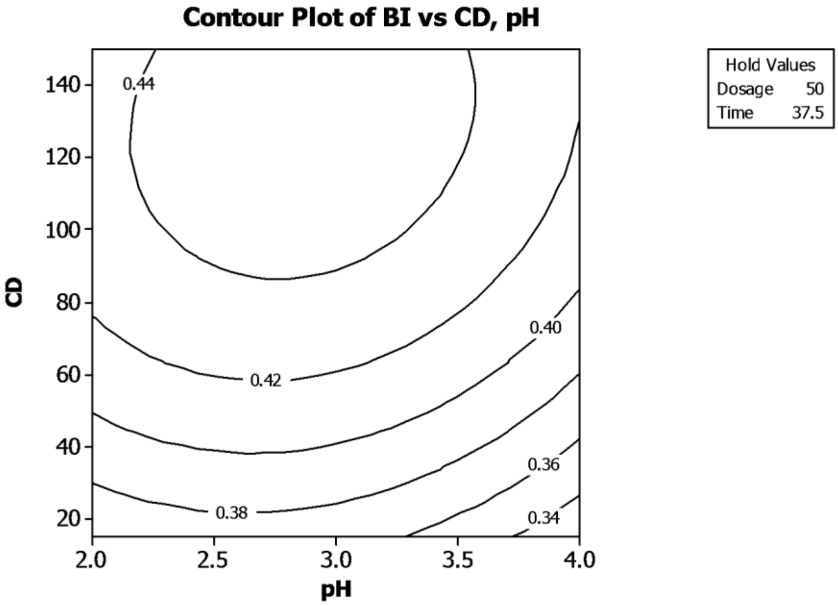

Fig. 4.15 Effect of CD and pH on BI at H_2O_2 dosage-50% and Time-37.5minutes

The figures depend on equation (4.1) with two variables kept steady at its centre point and changing the other factors within the experimental range.The trend of variation of BI with respect to the parameters in consideration is similar as seen in Fig.4.10 – 4.15. As the parameter value increased, BI value increased to an extent and then decreased.

As read from figure 4.10 BI is directly in relation with both the parameters H_2O_2 dosage and reaction time at the initial stage of the treatment. BI decreases after a treatment duration of 40 minutes and an H_2O_2 dosage of 55.76%. This can be explained due to the formation of a strong oxidizing agent hydroxyl radical in the process. The organic matter having long chain structure gets transferred to lower molecular weight compounds by the action of hydroxyl radicals. This will not significantly reduce the COD of the solution but will improve the BOD which results in higher BI.

After a definite period of reaction time, the ratio of readily degradable component to gradually degradable components changes which result in the lowering of BI. Also, the reaction amongst H_2O_2 and Fe^{2+} was finished inside this time interim.

The effect of current density can be interpreted by the oxidation mechanism of a strong oxidizing agent. After the optimum value of current density- 129.5A/m^2, the oxidizing agent started attracting easily degradable organic components thus lowering the BI.

The trend of the relation between BI and pH was also similar as seen in Fig. 4.13. Maximum BI was obtained at pH 2.85. The formation of hydroxyl radicals was high in the acid range. At low pH, H_2O_2 would stay stable because of the generation of oxonium ion (H_3O^{2+}) which resulted in lower BI (Nidheesh and Gandhimathi, 2012). As pH increased above optimum value, there was a reduction in the formation of hydroxyl radical thus lowering the BI. As the concentration of H_2O_2 builds the hydroxyl radical concentration likewise increases. In any case, when the dosage of H_2O_2 was increased further, COD removal diminishes because of the hydroxyl radical scavenging effect of H_2O_2.

Table 4.6 Regression coefficients for biodegradability index with P and T values

Term	Coefficient	SE Coefficient	T	P
Constant	-0.29751	0.021851	-13.616	0.000
pH	0.128889	0.009591	13.439	0.000
CD	0.001693	0.000107	15.877	0.000
Dosage	0.010638	0.000255	41.657	0.000
Time	0.008293	0.00034	24.355	0.000
pH*pH	-0.02492	0.001417	-17.59	0.000
CD*CD	-6E-06	0.00000	-19.532	0.000
Dosage*Dosage	-9.5E-05	0.000002	-60.212	0.000
Time*Time	-8.2E-05	0.000003	-29.15	0.000
pH*CD	0.000107	0.000024	4.432	0.001
pH*Dosage	0.000083	0.000055	1.528	0.152
pH*Time	-0.00012	0.000073	-1.681	0.119
CD*Dosage	-0.000001	0.000001	-1.834	0.092
CD*Time	-0.000009	0.000001	-8.101	0.000
Dosage*Time	-0.000006	0.000002	-2.293	0.041

Increasing the H_2O_2 dosage caused hydroxyl ion to react with H_2O_2 forming hydroperoxyl radical which has lesser oxidizing capacity than hydroxyl radicals. These radicals attacked more on the easily degradable organic matter which resulted in lower BI.

For BI, the acquired coefficient of determination (R^2) is 0.9966. This infers 99.66% of the variations in BI are clarified by the independent variables.

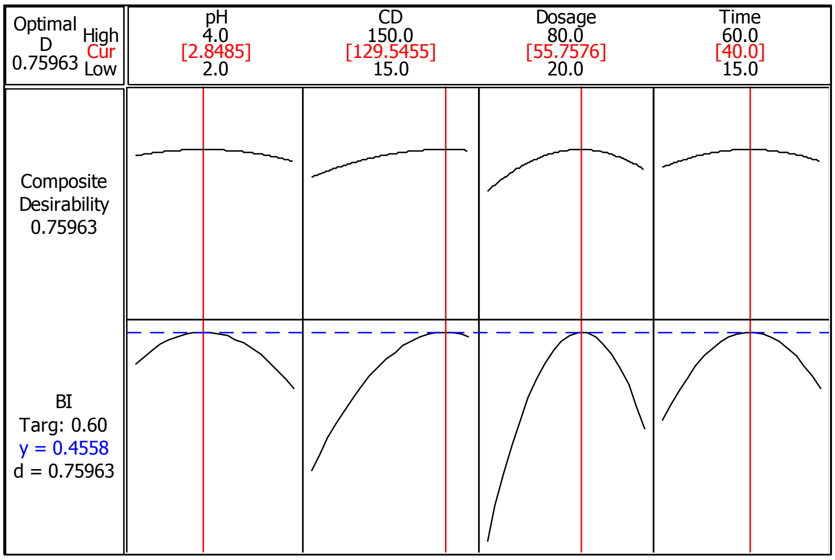

Fig. 4.16: Graph indicating Optimum values of the independent variables for maximum BI

Table 4.6 demonstrates the regression coefficients and a p-value of various independent variables for BI. The low p-value shows that the corresponding coefficient value is more significant. For this situation, the linear effect and quadratic effect of the factors were huge. The higher p-value for interaction coefficients demonstrates their lesser influence. pH- current density and current density - reaction time were related and had a huge interactive impact. Regression coefficients of other responses are shown in Table 4.7.

Fig.4.16 demonstrates the optimum estimations of every parameter for maximum BI. The optimum conditions obtained for maximum BI are pH = 2.85, current density = 129.5 A/m^2, H_2O_2 dosage = 55.76% and reaction time = 40 min with maximum predicted BI being 0.456.

The procedure was approved by running the experiment at ideal working conditions. The average COD removal after EF treatment was 78.2% i.e., the COD value was diminished to 5058mg/l and BOD to 2275mg/l (Table 4.8). The test estimation of BI practically agrees with the anticipated BI.

Table 4.7 Regression coefficients of other responses

Term	**COD**	**NH_3-N**	**Chloride**	**Sulphate**	**Sulphide**	**Phosphate**
b_0	62.6564	33.5074	35.6568	34.8576	31.1687	46.9973
b_1	3.927780	-0.177780	10.477800	7.427780	9.302780	2.030560
b_2	0.069433	0.029380	0.075981	0.092812	0.054540	0.054184
b_3	0.150463	0.093980	0.183611	0.186204	0.170000	0.169537
b_4	0.053827	0.149753	0.162222	0.212222	0.154444	0.209630
b_{12}	-1.333300	-0.400000	-1.858330	1.408330	-1.845830	-0.654167
b_{22}	0.000284	-0.000115	-0.000273	-0.000402	-0.000221	-0.000185
b_{32}	-0.000968	-0.001375	-0.000995	-0.001301	-0.001148	-0.001838
b_{42}	-0.001349	-0.001260	-0.002041	-0.002905	-0.002559	-0.001663
b_1b_2	0.007037	0.007407	-0.002963	0.012593	-0.003704	0.005185
b_1b_3	0.016666	0.025833	-0.009167	-0.005000	0.041167	0.019167
b_1b_4	0.063333	0.001111	0.018889	-0.008889	0.022222	-0.005555
b_2b_3	-0.000062	-0.000099	0.000136	-0.000481	-0.000272	-0.000235
b_2b_4	-0.000247	-0.000132	-0.000066	-0.000115	0.000428	-0.000132
b_3b_4	-0.020741	-0.000074	-0.001148	0.000814	-0.000778	-0.000148
R^2	0.9506	0.9563	0.9521	0.9582	0.9700	0.9308

Table 4.8 Average result of experimental runs at optimal conditions

Parameter	**COD**	**BOD**	**NH_3-N**	**Cl^-**	**SO_4^-**	**PO_4^-**	**S^-**
Value mg/l	5058	2275	1295.6	1009.3	240.7	72.3	8.9
Average % removal	78.2	53.3	41.0	62.2	59.0	60.9	55.8

Table 4.9Performance of EF process based on the relevant Indian Standards

Parameter	**Before Treatment**	**After EF Treatment**	**General standards for discharge of environmental pollutants as per The Environment (Protection)**	
			Inland surface	**Land for irrigation**
TSS(mg/l)	498	102	<100	<200
COD (mg/l)	23200	5058	<250	----
BOD(mg/l)	4872	2275	<30	<100
Ammonia Nitrogen (mg/l)	2196	1295.6	<50	----
Chloride (mg/l)	2670	1009.3	<1000	<600
Sulphate (mg/l)	587	240.7	<1000	<1000
Phosphate (mg/l)	185	72.3	<5	----
Sulphide (mg/l)	20.1	8.9	<2	----

BOD/COD ratio of the landfill leachate after Electro Fenton treatment increased from 0.21 to 0.45 which indicates that the biodegradability of the wastewater has enhanced. Nitrate content increased to 4.9 mg/l due to the oxidation of NH_3-N. The concentration of nitrate was below the discharge limits indicating the conversion of nitrate to nitrogen. The volume of sludge formed was 147ml/ l of leachate treated. The sludge volume index of the sludge was 83 mL/g (Eq.3.2). According to Metcalf and Eddy, 2013, SVI value below 100 is desirable. Hence the settling characteristic of the sludge was good. EF process oxidizes the refractory organic or inorganic compounds of the landfill leachate in a more efficient manner.

As indicated by the general standards for release of environmental pollutants as irrigation water Part-A: Effluents [Schedule VI] according to

The Environment (Protection) Rules, 1986, Govt. of India, the BOD ought to be under 100 mg/l (Table 4.9). Also the chloride content was above 600mg/l. However, after EF treatment the effluent concentrations of TSS, COD, BOD, NH_3-N, phosphate, sulphate, sulphide and chloride were 102, 5058, 2275, 1295.6, 72.3, 240.7, 8.9 and 1009.3 mg/l respectively, all of them over the permissible limit for inland surface water discharge standards in India except sulphate. Also, the leachate effluent after EF treatment can't be securely released as irrigation water to land and hence require additional post- treatment.

For complete biodegradation, the effluent must have a BOD to COD ratio (biodegradability index) of no less than 0.4 (Soloman et al 2007). This demonstrates the EF process oxidizes the refractory natural or inorganic compounds of the landfill leachate in a more proficient way. Matured landfill leachate after EF treatment can be subjected to subsequent biological treatment for further degradation.

The weight of anode dissolved for EF pretreatment was 1.125 kg/m^3. Hence the Specific anode consumption for removing 1 kilogram of COD from matured landfill leachate was 0.062 kg/kg of COD removed.

Energy consumed for EF pretreatment was obtained as 1.79 kWh /m^3 using the Eq. 3.3. Specific energy consumption for the degradation of 1kg COD was obtained as 0.0987 kWh.

4.6 Estimating the biological treatability of the treated matured landfill leachate by determining the kinetic coefficients k and Ks of untreated and treated landfill leachate

Biological treatability of untreated and EF treated matured landfill leachate were estimated. Kinetic coefficients were determined using the formula derived from Monod’s Eq. 3.4. The acclimatized inoculum was added to the matured leachate and EF treated landfill leachate under aerobic condition.

COD reduction and MLSS were measured each day. A graph was plotted with 1/S on x-axis and $X\Theta/S_0$-S on y-axis. The slope of the linear graph indicates Ks /k value and 1/k value is indicated by the y-intercept (Fig.4.2 & 4.17). Table 4.10 shows the k and Ks values of raw matured leachate and EF treated landfill leachate.

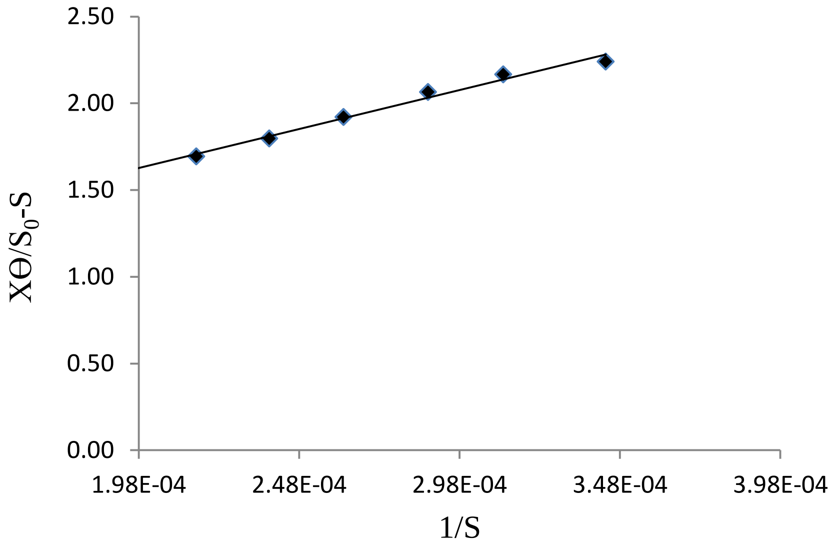

Fig.4.17 Graph for determining kinetic coefficients k and Ks for EF treated matured leachate

Table 4.10 Kinetic coefficients of untreated and EF treated matured leachate

Kinetic coefficient	**Untreated landfill**	**EF treated landfill**
k (day^{-1})	1.146	1.357
Ks (g/l)	6.366	6.096

The maximum substrate utilization rate constant (k) was higher for EF treated leachate indicating faster degradation. Hence a considerable reduction in reactor volume can be achieved. Half velocity constant (Ks) which represents the substrate concentration at one half the maximum specific biomass growth rate was lower for EF treated matured landfill leachate when compared to untreated landfill leachate. Lower Ks value indicates faster microbial growth in EF treated matured landfill leachate.

4.7 Evaluation of the bio compatibility (toxicity) of the raw landfill leachate and Electro Fenton treated landfill leachate using Poecillia Reticulata fish Bioassay

Static test was conducted to determine the medium lethal concentration (LC50) at 24 hr and 96 hr according to IS 6582-1971. LC 50 is the leachateconcentration at which the mortality of the test organism reaches 50%. Based on the preliminary bioassay test range of leachate concentration selected was 10-100%. A group of 10 fish (Poeicilia Reticulata) of similar size were exposed to different leachate concentrations (10-100%) at pH 7. Fish mortality was measured after 24hr and 96 hr and plotted against leachate concentration (Fig.4.18 &Fig.4.19). From the graph, leachate concentration at which 50% mortality of test species occurs is the lethal medium concentration. LC 50 after 24hr for untreated landfill leachate was estimated as 61.1% and LC 50 after 96hr was 42.6%. 50% fish mortality after 96hrs was observed in lower leachate concentration than the concentration obtained after 24hrs. Test species could not survive in the leachate sample for a longer time and hence 50% mortality occurred at lower leachate concentration. For EF pretreated landfill leachate mortality of test organism after 96 hr was 0%. All test organisms survived in EF pretreated landfill leachate after 96hrs of observation.

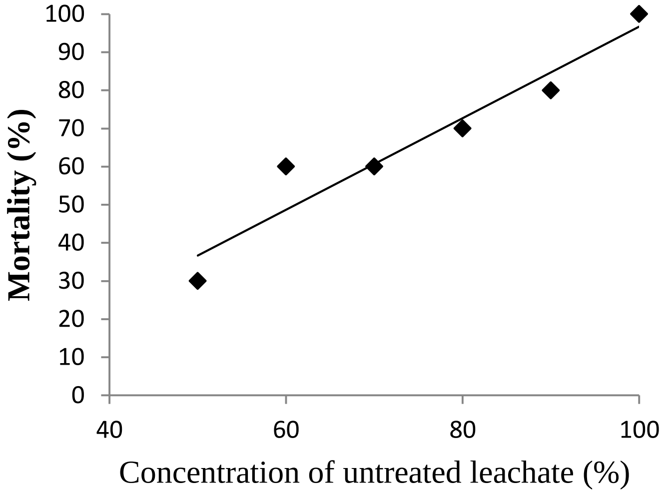

Fig. 4.18 Fish mortality Vs concentration of untreated landfill leachate (After 24hr)

Fish are influenced by toxic substances mainly in two ways 1) Epithilia-Absorb toxic materials, getting impaired in the process, for example, gills stick together to get congested with mucus and gets ruined 2) harmful materials are adsorbed by way of gills, skin or intestine, thereby damaging physiological functions. These impacts may ultimately lead to the fish death (Kulshreshtha et al. 2019).

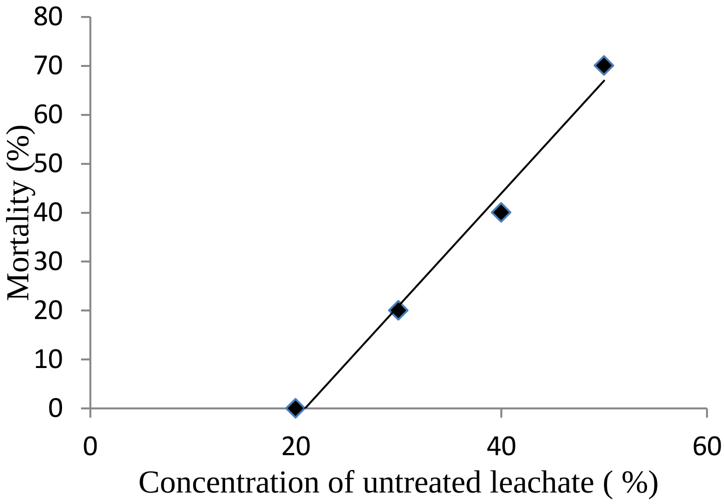

Fig. 4.19 Fish mortality Vs concentration of untreated landfill leachate (After 96hr)

4.8 Treatment of Electro Fenton pretreated matured landfill leachate by Membrane bioreactor

4.8.1 Membrane bioreactor treatment for Electro Fenton pretreated landfill leachate

The matured landfill leachate sample was subjected to EF process at optimum conditions (pH =2.85, H_2O_2 dosage = 55.76%, current density = 129.5 A/m^2 and time = 40 minute). EF treated leachate was further treated by the MBR process to degrade the biologically active organic matter. Fig.4.20 shows the COD at different Hydraulic retention times. At optimum HRT of 4 days, percentage removal of other parameters was found which is shown in Table 4.8.

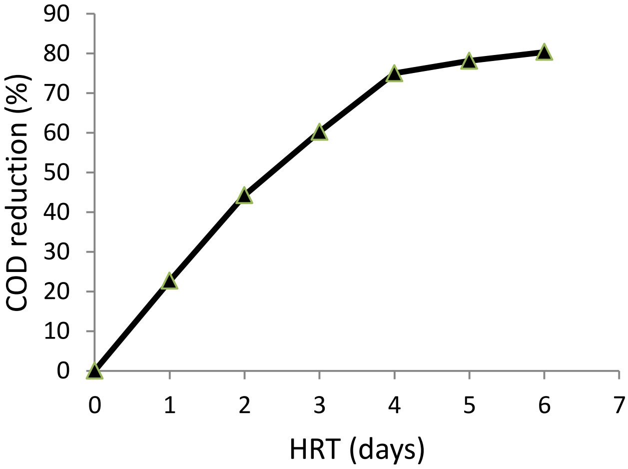

Fig. 4.20 COD reduction at different HRTs in membrane bio reactor

Flocs in a bioreactor were found to be smaller in size which can explain improved mass transfer for both oxygen and carbon. It also explains the higher removal rate and more adaptability to changes in the influent quality and quantity. Magnified biodegradation efficiency is due to high biomass concentration which increases their bio-availability and the real concentration of the substrates in the bioreactor. (Ahmed and Lan, 2012). The performance of MBR can also be explained by the existence of dispersed bacteria that are beneficial when Food to microorganism ratio is low and sludge age is high.

Microbial analysis of the membrane bioreactor sludge was done at the Department of Microbiology, Kerala Agriculture University, Vellanikkara. The identification of the microorganism was done by 16 Svedberg unit Ribosomal RNA (16SrRNA) method. The presence of heterogeneous bacteria (pseudomonas aeruginosa) in the MBR sludge was seen in the microbial analysis. The heterogeneous bacteria are responsible for the consumption of the COD and denitrification in the reactor (Galleguillos Torres, 2011). Low nitrate content in the effluent (2.6mg/l) confirmed denitrifying process in the reactor. Fig. 4.21 shows the picture of pseudomonas bacteria.

Fig. 4.21 Bacteria of the genus pseudomonas

The COD concentration measured at biomass concentrations 10, 15 and 20 g/l was in the range 1238-1264 mg/l and Ammonia nitrogen concentration was in the range of 330- 337 mg/l. COD and Ammonia nitrogen removal were found lesser at lower biomass concentration of 5g/l (Fig.4.22). This indicated that increasing biomass concentration beyond 10g/l did not show an increase in pollutant removal. This may be due to insufficient food for the excess microorganisms present in the reactor and low oxygen transfer efficiency (Germain et al., 2007; Radejnovic et al., 2007). Also the volumetric permeate flux reduced from 17.5x10^{-6} m^3/m^2/sec to 11.5 x $10^{-6}$$m^3/m^2$/sec as biomass concentration increased from 5g/l to 20g/l (Fig. 4.23). This indicated faster fouling with increased biomass. Hence an optimum biomass concentration of 10g/l was selected for maximum removal efficiency and reduced membrane fouling.

The table 4.11 summarizes the result of integrated treatment applied to landfill leachate. The EF pretreatment reduced the loading on the subsequent MBR treatment and substantially improved the water quality. The average influent COD of the leachate 23200 mg/l was treated to a level of 5058 mg/l by EF treatment and 1264.5 mg/l after MBR respectively with the final removal rate of 94.55%. The average influent Ammonia nitrogen of the leachate 2196 mg/l was treated to a level of 1295.6 mg/l by EF treatment and 336.8mg/l after MBR respectively with the final removal rate of about 84.66%.

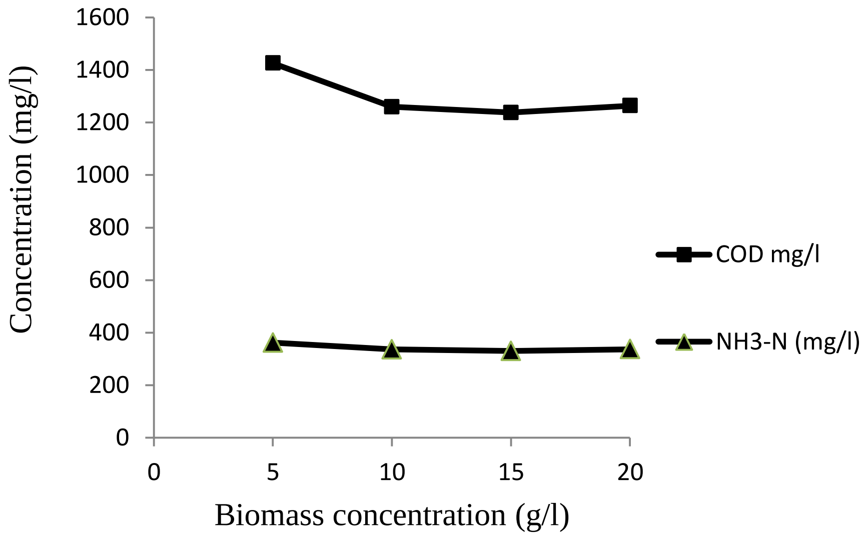

Fig.4.22 Variation of COD and NH_4-N concentration with biomass

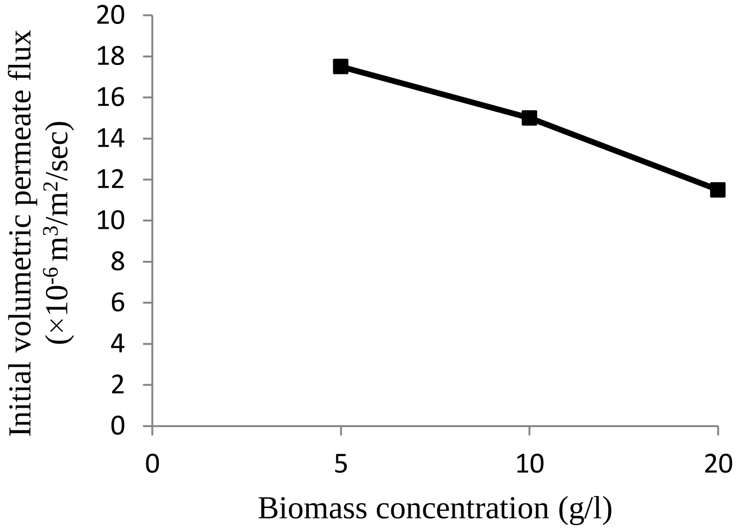

Fig.4.23 Variation of initial volumetric flux with biomass concentration

Table 4.11 Percentage reduction of pollutant after EF + MBR treatment

Parameter	**Initial characteristics**	**Characteristics after EF process**	**Pollutant removal (%)**	**Characteristics after EF + MBR**	**Total removal (%)**
TSS(mg/l)	498	273	45.2	29	94.2
BOD(mg/l)	4872	2175	55.4	456.8	90.62
COD(mg/l)	23200	5058	78.2	1264.5	94.55
NH_3-N(mg/l)	2196	1295.6	41.0	336.8	84.66
Phosphate (mg/l)	185	72.3	60.9	BDL	100
Sulphate (mg/l)	587	240.7	59.0	98.7	83.19
Sulphide(mg/l)	20.1	8.9	55.8	3	85.07
Chloride(mg/l)	2670	1009.3	62.2	444.1	83.37
BOD/COD	0.21	0.45		0.36	

BDL= Below detectable level

Nitrification in the bioreactor is an oxic process of transformation of ammonia nitrogen to nitrite and then eventually to nitrate. The process includes two steps involving two different categories of bacteria, the ammonia-oxidizing bacteria that oxidize ammonia to nitrite and the nitrite-oxidizing bacteria that oxidizes nitrite to nitrate (Galleguillos Torres, 2011). The basic requirement of nitrification to occur is that the withdrawal rate of biomass is lesser than the rate of growth of nitrifying bacteria. Regarding nitrification, MBR is really a feasible treatment technology. Around 74 % of Ammonia nitrogen reduction is attained in the membrane bioreactor. The low Nitrate content of 2.6mg/l in the MBR effluent indicated no accumulation of nitrate/ nitrite nitrogen in the reactor which is due to the de-nitrification process in the reactor. Heterotrophic bacteria are the most common denitrifying organisms. The presence of pseudomonas aeruginosa species in the membrane bioreactor sludge indicated the presence of heterotrophic bacteria (Rajta et al. 2020). The total suspended solids, phosphate, sulphate, sulphide and chloride contents in the effluent after EF-MBR treatment met the irrigation discharge standards but BOD content exceeded the discharge limits of 100mg/l. The implementation of membrane bioreactor post Electro Fenton treatment enhanced the quality of effluent. The BOD/ COD ratio reduced from 0.45 to 0.36 which indicated degradation of the easily biodegradable portion from the EF treated landfill leachate.

4.8.2 Membrane fouling

Fouling occurs as an aftereffect of interactions between the mixed liquorand themembrane, and is one of the main limitations of the MBR process. The main causes of membrane fouling are:

1. Adsorption of colloidal and macromolecular matter
2. Biofilm growth on the membrane surface

3. Precipitation of inorganic compounds
4. Ageing of the membrane

Membrane fouling is classified into reversible and irreversible fouling.

a) Reversible fouling: If the cake layer formed over the membrane surface is easily removable by simple physical washing then it is called reversible fouling (Chang et al., 2002).

b) Irreversible fouling: Internal fouling due to the adsorption of dissolved matter onthe membrane pores and pore blocking is considered as irreversible. This type of fouling is generally cleared by chemical cleaning. Sometimes a gel layer is formed over the membrane resulting in irreversible fouling (Radjenovic et al., 2007). Feed wastewater pre-treatment through screening is necessary for Hollow Fibre (HF) and Flat sheet (FS) membrane modules.

It was observed that membrane flow rate decreased with time indicating fouling of membrane. Membrane flow rate decreased from 3cm^3/s to 0.4cm^3/s after 150 min of filtration. This may be attributed towards membrane clogging. The membrane was backwashed and the flow rate was found after 2 minutes of backwash. From figure 4.24 it was seen that around initial dischargewasrecovered by back washing indicating that reversible fouling had taken place. Reversible fouling was formed on the membrane, which suggests that there is no need for frequent chemical cleaning. Intermittent physical backwashing enhanced the membrane flow rate in the overall process. Fig. 4.25 shows the degree and nature of fouling of the membrane after EF- MBR treatment of matured leachate.

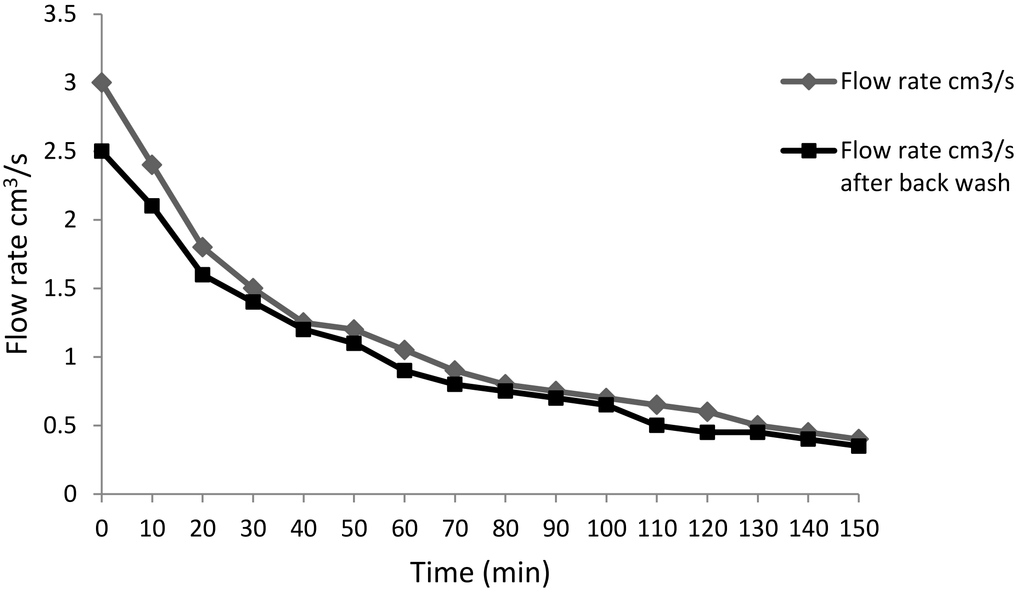

Fig. 4.24 Variation in membrane flow rate with time before and after backwash

The degree of fouling and nature of fouling of membrane was found as per Eq.3.4 - Eq.3. 11 (Swierczynska Anna et al., 2016).

Volumetric flux of the waste water $J_w = V_w/S*t = 15 * 10^{-6}$ m^3/m^2/sec

Volumetric flux of the deionized water prior to waste water filtration

$J_{dp} = V_{dp}/S*t = 50*10^{-6}$ m^3/m^2/sec

Volumetric flux of the deionized water after wastewater filtration

$J_{da} = V_{da}/S*t = 45*10^{-6}$ m^3/m^2/sec

Where, V_w = volume of waste water filtered through membrane in m^3

V_{dp}= volume of deionized water prior to waste water filtration in m^3

V_{da}= volume of deionized water after waste water filtration in m^3

t = time of filtration in seconds S = membrane surface area in m^2

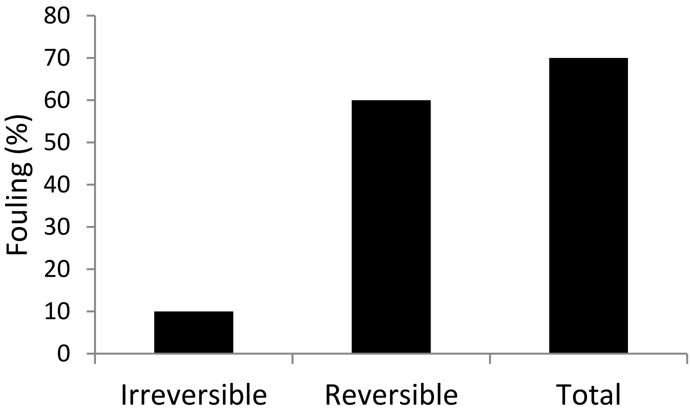

Fig. 4.25 Degree and nature of membrane fouling after MBR process

Relative permeability of the membrane for wastewater flux

$$J_w*100/J_{dp} = 30\ \%$$

Relative permeability of the membrane for deionized water flux

$$J_{da}*100/J_{dp} = 90\ \%$$

Reversible fouling $R_{rf} = (J_{da}-J_w)*100/J_{dp} = 60\ \%$

Irreversible fouling $R_{if} = (J_{dp}-J_{da})*100/J_{dp} = 10\ \%$

Total fouling $R_f = (1-J_w/J_{dp})*100 = 70\%$

4.9 Post treatment of the effluent from Membrane Bioreactor by Electro Fenton process

Effluent from MBR process was subjected to EF process to meet the land disposal standards. Optimum conditions were found by varying each parameter and measuring COD reduction. pH was fixed at 2.85. Reaction time, H_2O_2 dosage and current density were varied one at a time to find the optimum conditions. Other parameters were analyzed at the optimum conditions (Fig.4.26-4.28).

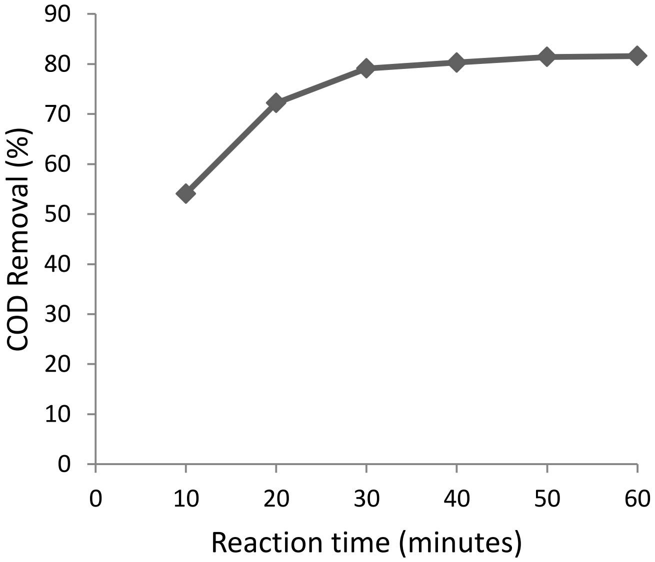

Fig.4.26 Variation in COD reduction with reaction time

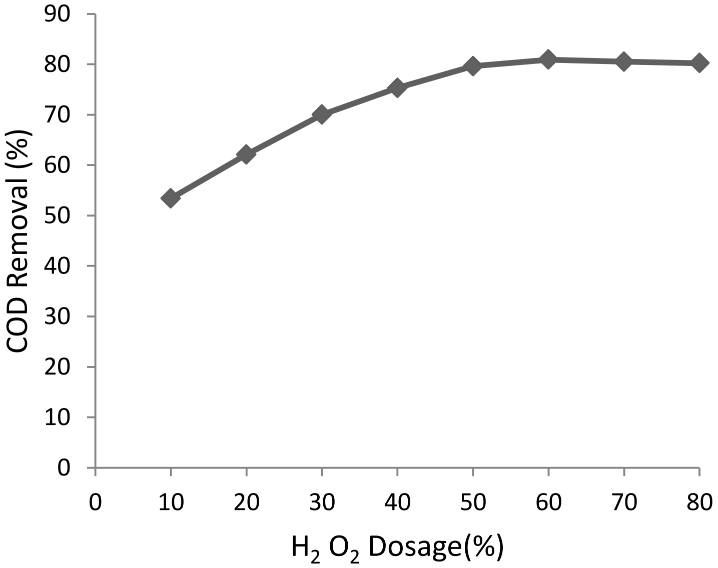

Fig.4.27 Variation in COD reduction with H_2 O_2 Dosage (%)

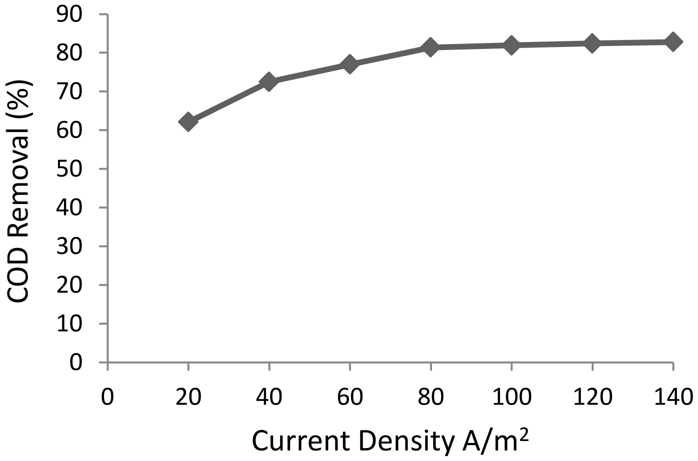

Fig.4.28 Variation in COD reduction with current density

COD removal was higher at a higher current density (Fig.4.28) which might be because of the higher hydroxyl radical concentration. As the concentration of H_2O_2 builds the hydroxyl radical concentration likewise increases. In any case, when the dosage of H_2O_2 was increased further, COD removal diminishes because of the hydroxyl radical scavenging effect of H_2O_2 and development of hydroperoxyl radical ($HO_2^{\bullet}$) which has lesser oxidation capacity than that of hydroxyl radical. Maximum COD removal is acquired after 30minutes of reaction time. The reaction amongst H_2O_2 and Fe^{2+} was finished inside this time interim. Optimum COD removal was obtained at H_2O_2 dosage of 60% and a current density of 80 A/m^2.

Table 4.12 Concentration of parameters after EF-MBR integrated treatment of matured landfill leachate

Parameter	**Initial concentration (mg/l)**	**After EF treatment (mg/l)**	**% Removal**	**After EF +MBR (mg/l)**	**% Removal**	**After EF +MBR+EF (mg/l)**	**% Removal**	**Total % Removal**
TSS	498	102	79.5	29	94.2	10	65.5	98.0
BOD	4872	2175	55.4	456.8	90.62	97.7	78.6	97.9
COD	23200	5058	78.2	1264.5	94.55	234.6	81.4	98.9
Ammonia Nitrogen	2196	1295.6	41.0	336.8	84.66	40.4	88	98.1
Phosphate	185	72.3	60.9	BDL	100	-	-	100
Sulphate	587	240.7	59.0	98.7	83.19	34.5	65	94.1
Sulphide	20.1	8.9	55.8	3	85.07	0.93	69	95.8
Chloride	2670	1009.3	62.2	444.1	83.37	75.5	83	97.2

Table 4.13Performance of EF, EF and MBR integrated processes based on the relevant Indian Standards

Parameter	Before Treatment	After Treatment			General standards for discharge of environmental pollutants [Schedule VI] , The Environment (Protection) Rules, 1986, Govt. of	
		EF	EF+MBR	EF+MBR+EF	Into surface water	Land for irrigation
TSS (mg/l)	498	102	29	10	<100	<200
BOD (mg/l)	4872	2175	456.8	97.7	<30	<100
COD (mg/l)	23200	5058	1264.5	234.6	<250	----
NH_3 N (mg/l)	2196	1295.6	336.8	40.4	<50	----
Phosphate (mg/l)	185	72.3	BDL	BDL	<5	----
Sulphate (mg/l)	587	240.7	98.7	34.5	<1000	<1000
Sulphide (mg/l)	20.1	8.9	3	0.93	<2	----
Chloride (mg/l)	2670	1009.3	444.1	75.5	<1000	<600

Table 4.12 shows the concentration of parameters after EF-MBR integrated treatment at optimum conditions. All parameters met the land disposal standards after post EF treatment but could not meet surface water disposal standards because BOD concentration was higher than that specified limit 30mg/l (Table.4.13). After post-EF treatment total reduction in TSS, COD,

BOD, NH_3-N, phosphate, sulphate, sulphide and chloride were 98, 98.9, 97.9, 98.1, 100, 94.1, 98.5 and 97.2 percent. pH has to be increased to 5.5 before land disposal. BOD/ COD ratio enhanced from 0.36 to 0.41 after post treating with EF process which indicated the mineralization or oxidation of non degraded pollutants in the EF reactor.

4.10 Treatment of young landfill leachate by Membrane bioreactor integrated with Electro Fenton process

4.10.1 Membrane bioreactor treatment for young landfill leachate

Young landfill leachate was filled in the membrane bioreactor. The reactor was provided with oxygen at the rate of 5litre/min using an aerator. This acclimatized sludge was used as inoculum for the bioreactor system. The reactor was operated in batch mode with Mixed Liquor Suspended Solid (MLSS) concentration maintained at 10 g/l. The supernatant from the bioreactor was transferred through the hollow fiber membrane module of pore size 0.1 micrometer and the treated effluent was analyzed. The process was repeated with different hydraulic retention times at neutral pH. The COD of the effluent at different HRTs were analyzed (Fig.4.29). Optimum HRT was obtained as 6 days. Table 4.14 shows other parameters at optimum HRT. The biodegradability index reduced from 0.49 to 0.24 after the MBR process which indicated the removal of the biodegradable part from the wastewater. The reduction of NH_3-N was as good as COD reduction. NH_3-N removal efficiency was 86% while the effluent NH_3-N concentration was 21.4mg/l. However typical surface water discharge standard for phosphate in India is 5mg/l. Phosphate concentration in the effluent from MBR was below a detectable level indicating 100% removal efficiency.

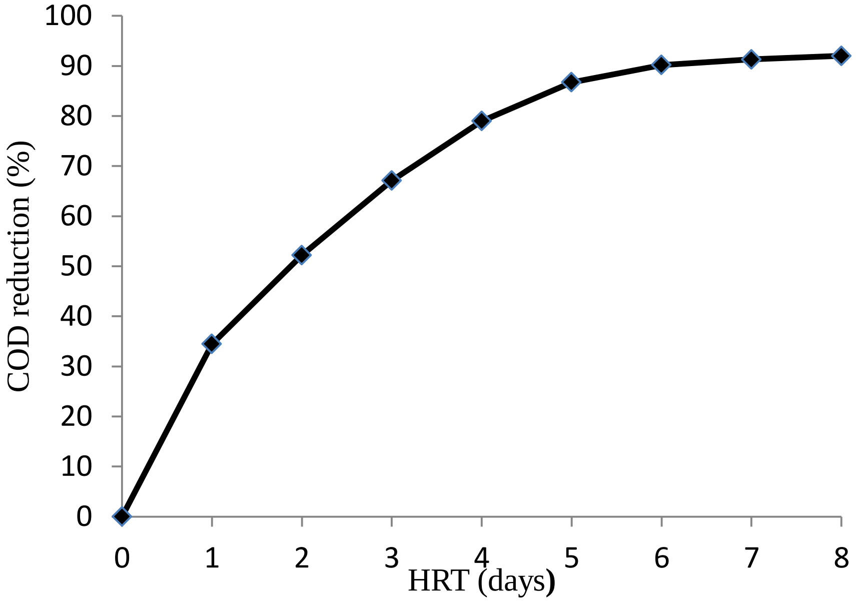

Fig. 4.29 Percentage COD reduction with hydraulic retention time

Table 4.14 Effluent parameters after MBR treatment of young leachate at optimum HRT

Parameter	**Before MBR treatment mg/l**	**After MBR treatment mg/l**	**% Removal**
TSS	568	79.0	86.1
COD	20180	1977.6	90.2
BOD	9850	482.6	95.1
Ammonia nitrogen	153	21.4	86.0
Sulphate	392	101.9	74.0
Phosphate	98	BDL	100
Sulphide	122	17.3	85.8
Chloride	2640	821	68.9
BOD/COD	0.49	0.24	

High biomass concentration in bioreactor increases biodegradation efficiency. The existence of dispersed bacteria that are beneficial when Food to microorganism ratio is low enhances the performance of MBR.

Membrane bioreactor consists of ultra-filtration membrane (UF). UF is a pressure-driven method by which particulate, colloids and high molecular mass soluble species are retained by size exclusion, andalso provides a means for concentrating, separating or filtering suspended or dissolved species. UF permits most ionic inorganic species to pass by the membrane and retains particulate matter and ionic and nonionic organic species. UF is a unique process that removes many water-soluble organic materials and microbiological contaminants.

4.10.2 Membrane fouling

Membrane flow rate variation with time is shown in Fig.4.30. The degree of fouling and its nature was measured by passing deionized water through the membrane after the waste water filtration. Relative permeability of the membrane and percentage fouling were calculated as per Eq (3.4)-Eq (3.11).

Volumetric flux of waste water $J_w=V_w/S*t =13.5x\ 10^{-6}\ m^3/m^2/sec$

Volumetric flux of the deionized water prior to waste water filtration

$$J_{dp}=V_{dp}/S*t = 50*10^{-6}\ m^3/m^2/sec$$

Volumetric flux of the deionized water after wastewater filtration

$$J_{da}=V_{da}/S*t = 45*10^{-6}\ m^3/m^2/sec$$

Relative permeability of the membrane for wastewater flux

$$J_w*100/J_{dp} = 27\ \%$$

Percentage fouling $R_f = R_{rf} + R_{if}$

Reversible fouling $R_{rf} = (J_{da}-J_w)*100/J_{dp} =63\%$

Irreversible fouling $R_{if} = (J_{dp}-J_{da})*100/J_{dp} =10\%$,

Total fouling $R_f= (1-J_w/J_{dp})*100 = 73\%$

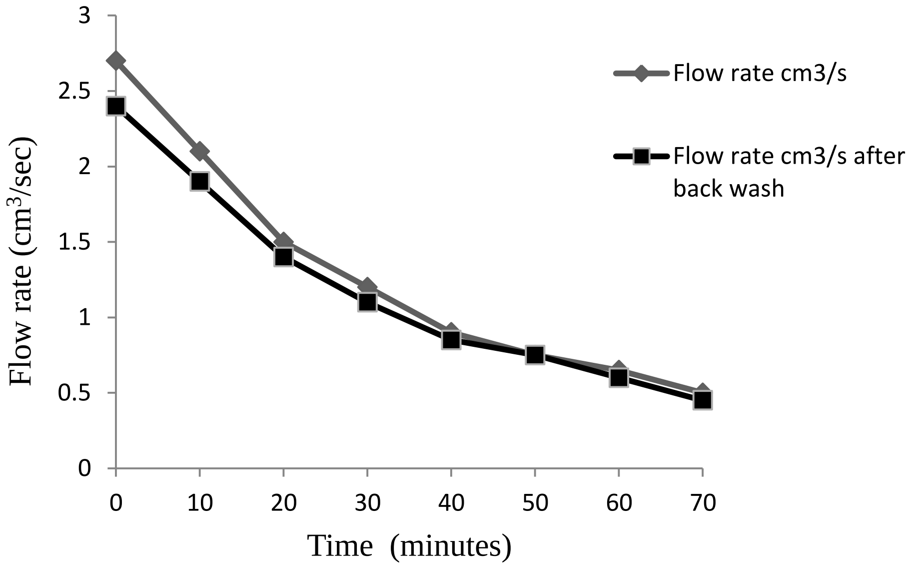

Fig.4.30 Variation of membrane flow rate with time

Reversible fouling of 63% indicated that chemical cleaning is not required frequently. After 70 minutes of wastewater flow the flow rate reduced to 0.4cm^3/sec. By physical backwashing almost initial flow rate was achieved.

4.10.3 Integrating MBR with EF process to meet discharge standards

Landfill leachate is an intricate liquid that contains extreme amount of non-biodegradable and biodegradable products which cannot be easily separated by biological process alone. The biodegradability index of young leachate was 0.49. However, after treatment in the MBR the effluent characteristics of TSS, COD, BOD, Ammonia nitrogen, phosphate, sulfate, sulfide and chloride were 79, 1977.6, 481.6, 21.4, below detectable level (BDL), 101.9, 17.3 and 821 mg/l respectively (Table 4.15). All parameters except TSS, ammonia nitrogen, phosphate and sulfate were above discharge standards (Table. 4.16).

Table 4.15 Effluent parameters after MBR- EF integrated treatment of young landfill leachate

Parameter	**Influent characteristics (mg/l)**	**Concentration of Parameter after MBR process(mg/l)**	**Concentration of Parameter after MBR+ EF process(mg/l)**	**Total removal (%)**
TSS	568	79.0	22	96.1
COD	20180	1977.6	246.2	98.8
BOD	9850	482.6	98.5	99.0
NH_3-N	153	21.4	5.0	96.7
Phosphate	98	BDL	-	100
Sulphate	392	101.9	34.2	91.2
Sulphide	122	17.3	2.7	97.7
Chloride	2640	821	129.5	95.1
BI	0.49	0.24	0.4	

BDL – below detectable level

Quality of the effluent from MBR system was not appropriate for discharging into receiving waters or for irrigation purpose requiring additional post treatment. Hence, after MBR primary treatment and EF treatment was used as post treatment for separating the non-degraded pollutants to meet the irrigation disposal standards. The factors affecting the treatment were varied one at a time and optimum conditions were determined by measuring COD reduction. The efficiency of the AOP was studied by analyzing all other parameters at optimum conditions and compared with the discharge standards. Optimum conditions were found by varying each parameter and measuring COD reduction. pH was fixed as 2.85.

Table 4.16 Evaluation of the performance of EF-MBR integrated process for the treatment of young leachate based on the relevant Indian Standards

Parameter	**Before Treatment**	**After Treatment**		**General standards for discharge of environmental pollutants [Schedule VI]. The Environment (Protection) Rules, 1986, Govt. of India.**	
		MBR	**MBR+EF**	**Inland surface water**	**Land for irrigation**
TSS (mg/l)	568	79.0	22	<100	<200
BOD (mg/l)	9850	482.6	98.5	<30	<100
COD (mg/l)	20180	1977.6	246.2	<250	----
NH_3 -N (mg/l)	153	21.4	5.0	<50	----
Phosphate (mg/l)	98	BDL	-	<5	----
Sulphate (mg/l)	392	101.9	34.2	<1000	<1000
Sulphide (mg/l)	122	17.3	2.7	<2	----
Chloride (mg/l)	2640	821	129.5	<1000	<600

Parameters varied were reaction time, H_2O_2 dosage and current density. Optimum conditions were reaction time -30 minutes, H_2O_2 dosage - 50% of theoretical value and current density- 80A/m^2. At optimum condition other parameters were analyzed which is shown in table 4.12. pH was adjusted to the range 5.5 - 9 before discharge. All parameters met the Indian land disposal standards (Table 4.16) and biodegradability index enhanced from 0.24 to 0.4 after EF treatment. Except BOD all other parameters were within the discharge limits of inland surface water.

4.11 General strategy for the treatment of landfill leachate

As mentioned earlier, EF process has been used to improve the biodegradability of matured landfill leachate constituting various organic compounds that are toxic to microorganisms or recalcitrant. This process is expensive and a favorable alternative to oxidize completely bio recalcitrant compounds to more readily biodegradable intermediates which permits subsequent biological treatment to be attained in short period and meet the disposal standards.

Advanced biological process like MBR oxidizes these readily biodegradable intermediates to biomass, CO_2 and water. As a first step of the EF-MBR integrated treatment, it must be confirmed that the landfill leachate is non-biodegradable by analyzing the BI, since biological treatments are the most economical and environmentally compatible, for biodegradable leachate.

In case of treating young leachate, EF process is applied as a polishing step to remove the non-biodegradable fraction after MBR process. A general strategy was developed that can be used to integrate EF process and MBR process for both matured and young landfill leachate (Fig. 4.31). This general method has to be adapted in order to fulfill the discharge standards at low financial cost. Fig. 4.32 shows the scheme for treating landfill leachate at Brahmapuram MSW disposal site, Kochi, Kerala and table 4.14 shows the values of parameters at different stages of the EF- MBR integrated treatment system.

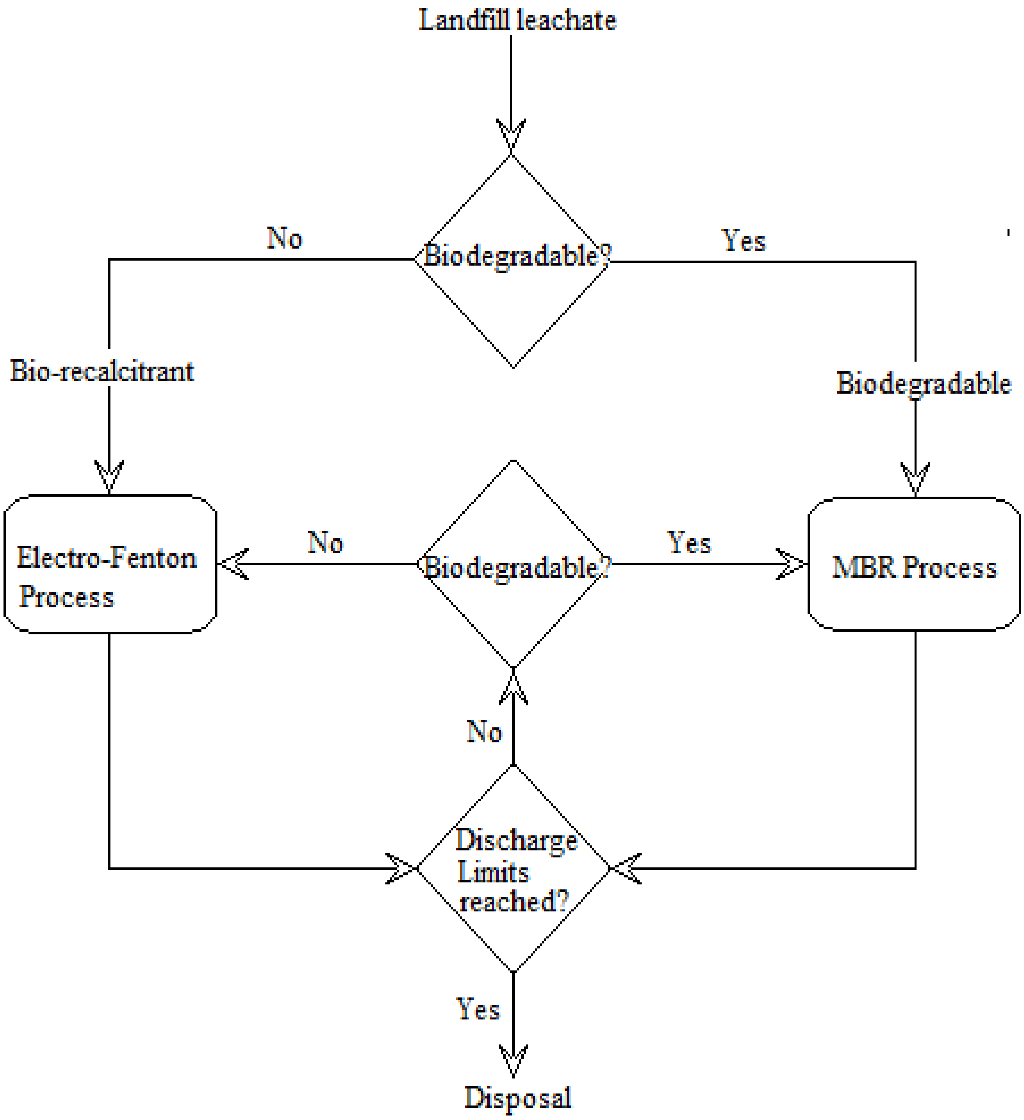

Fig. 4.31 General strategy for the treatment of landfill leachate

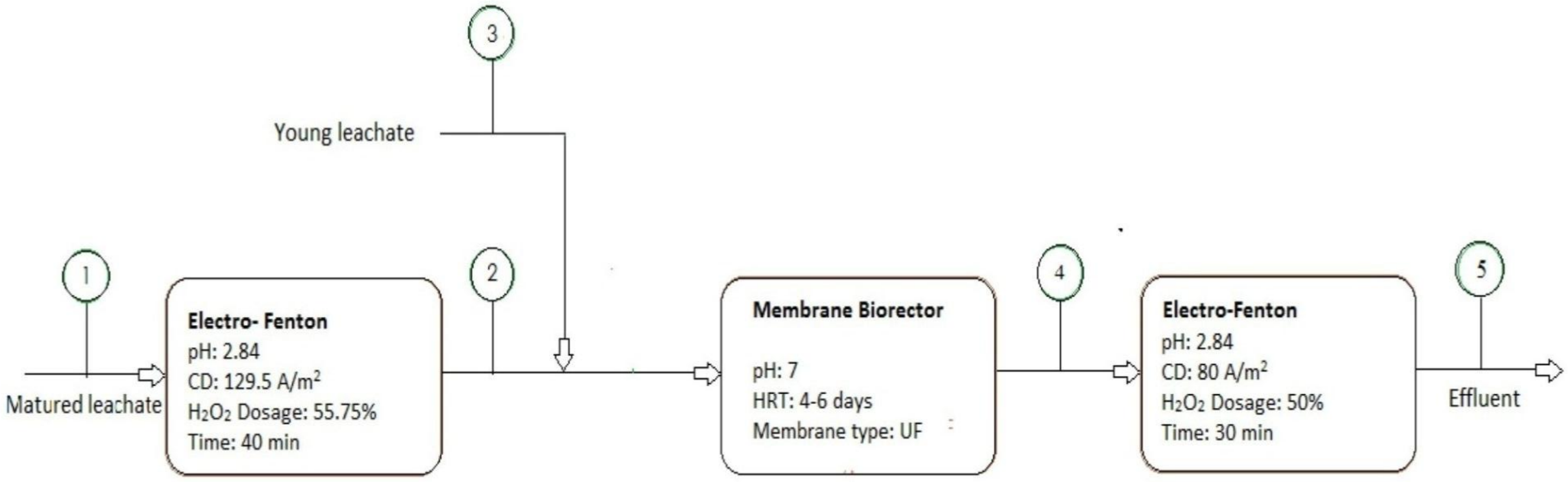

Fig. 4.32 Scheme for the treatment of matured and young leachate generated at Brahmapuram MSW disposal site, Kochi

Table 4.17 Values of the parameters at different stages of integrated EF – MBR treatment system

	Matured landfill leachate				Young landfill leachate		
Parameters	1	2	4	5	3	4	5
TSS (mg/l)	498	102	29	10	568	79.0	22
BOD (mg/l)	4872	2175	456.8	97.7	9850	482.6	98.5
COD (mg/l)	23200	5058	1264.5	234.6	20180	1977.6	246.2
NH_3 N (mg/l)	2196	1295.6	336.8	40.4	153	21.4	5.0
Phosphate (mg/l)	185	72.3	BDL	BDL	98	BDL	-
Sulphate (mg/l)	587	240.7	98.7	34.5	392	101.9	34.2
Sulphide (mg/l)	20.1	8.9	3	0.93	122	17.3	2.7
Chloride (mg/l)	2670	1009.3	444.1	75.5	2640	821	129.5
BOD/COD	0.21	0.45	0.36	0.41	0.49	0.24	0.41

4.12 Cost comparison of the Electro Fenton-Membrane Bioreactor integrated system for the treatment of matured and young landfill leachate

An economic comparison of the treatment of matured and young landfill leachate was performed. The comparison is based on the annualized capital cost and operational cost. Operational cost included energy cost, chemical cost, electrode cost and sludge management cost. Labour cost has not been considered. Specific energy consumption and specific anode consumption for EF pretreatment was found according to Eq 3.13 and Eq 3.14 (Table 4.18).

According to Robinson A.H. (2005) specific energy consumption for treating landfill leachate using MBR process is 3 kWh/m^3. Assuming 100m^3 of landfill leachate quantity per day, annualized operating cost and capital cost were determined. Annualized capital cost of each unit was determined by multiplying annualisation factor (Eq 3.12) and the amount of each unit. 10 percent interest rate was assumed for the design period.

Table 4.18 Specific energy and anode consumption for EF treatment of matured and young landfill leachate

	Pre-treatment of matured landfill leachate	**Post-treatment of MBR treated young landfill leachate**
Specific energy consumption kWh/ m^3	1.8	0.83
Specific anode consumption kg/m^3	1.125	0.92

Table 4.19 and table 4.20 show the details of annualized capital cost and operating cost calculation of matured landfill leachate respectively. Appendix-III shows the design of the bioreactors for treating landfill leachate for MBR process.

Table 4.19 Annualized capital cost for treating 100m^3 of matured landfill leachate by EF+MBR

Units	**Amount (Rs)**	**Design life (yrs)**	**Annualized capital cost (Rs./year)**
EF treatment Unit (12.5m^3)	125,000	15	16,434
Pumps (3HP-2 no.s)	50,000	15	6,574
Power supply unit	375,000	15	49,303
MBR- aeration tank (400m^3)	720,000	50	72619
MBR- Membrane (100m^2 UF hollow fibre membrane)	150,000	5	39,570
Pumps (feed-3HP, backwash-5HP)	200,000	15	26,295
Backwash water tank	20,000	15	2,629
Total cost			Rs.213,424

Table 4.20 Operating cost for treating matured landfill leachate by EF+MBR

Items	**Rate**	**Unit**	**Operating cost Rs / yr**
Chemical cost	669	Rs/m^3	24,418,500
Electrode cost	90	Rs/m^3	3,285,000
Electricity cost (EF)	9.9	Rs /m^3	361,350
Electricity cost (MBR)	16.5	Rs /m^3	602,250
Sludge management cost	15	Rs /m^3	547,500
Total operating cost			29,214,600

In the EF pretreatment process, chemical cost contributed more towards operating cost. Operating cost of matured landfill leachate treatment by EF-MBR integrated system was found Rs. 800.4 per m^3 and annualized capital cost as Rs. 5.8 per m^3. The total cost for treating $1m^3$ of matured landfill leachate was around Rs 806.2 (10.68$/$m^3$). The total expense for digesting 1 kg of COD from matured landfill leachate using the EF-MBR system was Rs 36.8 (0.48$/kg of COD).

The annualized capital cost for young landfill leachate was found to be Rs 6.5 per m^3 (Table 4.21). Operating cost for treating young landfill leachate by MBR – EF integrated system was calculated to be Rs. 151.1 per m^3 (Table 4.22). The total cost for treating $1m^3$ of young landfill leachate was around Rs 157.6 per m^3 (2.09$/$m^3$). Figure 4.33 shows the total cost of digesting 1 kg of COD from young leachate by MBR-EF integrated treatment system which is Rs 7.9 (0.105$/kg of COD).

Table 4.21 Annualized capital cost for treating $100m^3$ of young landfill leachate by MBR+ EF processes

Units	**Amount (Rs)**	**Design life (yrs)**	**Annualized capital cost (Rs./year)**
EF treatment Unit	125,000	15	16,434
Pumps (3HP-2 no.s)	50,000	15	6,574
Power supply unit	375,000	15	49,303
MBR- aeration tank	888,000	50	89,563
MBR- Membrane ($100m^2$ UF hollow fibre	150,000	4	47,321
Pumps (feed, backwash)	200,000	15	26,295
Backwash water tank	20,000	15	2,629
Total			238,119

Table 4.22 Operating cost for treating young landfill leachate by MBR+EF processes

Items	**Rate**	**unit**	**Operating cost Rs/yr**
Chemical cost	52	Rs/m^3	18,98,000
Electrode cost	68	Rs/m^3	24,82,000
Electricity cost (EF)	4.56	Rs /m^3	1,66,623
Electricity cost (MBR)	16.5	Rs /m^3	6,02,250
Sludge management	10	Rs /m^3	3,65,000
Total			55,13,873

Treating matured leachate was found to be 5 times costlier than the young leachate. Based on the economic analysis it was found that treating the leachate initially with biological methods will reduce the cost of treatment. Since the mature leachate is high ammonia containing waste water (NH_3-N often above 1100mg/l) and high concentration of ammonia is toxic to microorganisms, biological treatment methods cannot be adopted as primary treatment for matured leachate.

Reducing the formation of leachate is the best method of precaution that can be adopted. Formation of leachate can be prevented by providing proper temporary caps and final covers for landfills as per the Municipal Solid Wastes Management & Handling Rules, (2000).

EF process being a primary treatment for matured landfill leachate, showed higher treatment cost as the chemical and electrode consumption and energy use were higher. The energy cost for EF treatment of matured and young leachate was Rs. 9.9 per m^3 and Rs. 4.56 per m^3 respectively. The energy cost for the MBR process was the same (Rs16.5 per m^3) for both matured and young leachate.

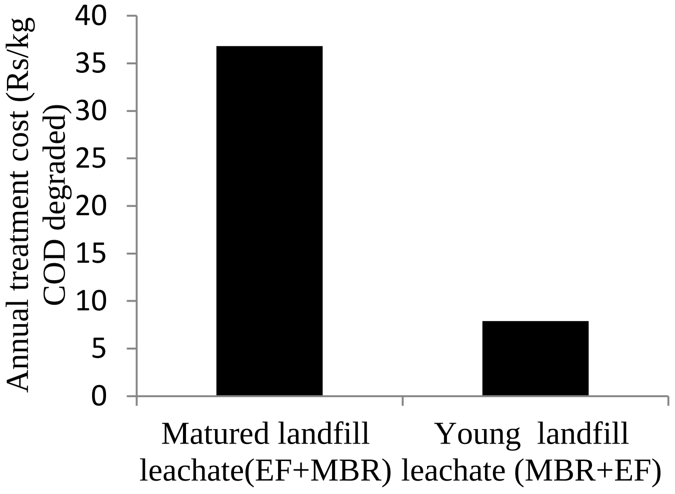

Fig.4.33 Annualized treatment cost for degrading 1kg of COD using EF-MBR integrated system

Also in post EF process sludge production was less. While treating young leachate, EF was used as a secondary treatment after the MBR process. Since the sludge production, chemical and energy consumptions were less for post EF treatment, the operating cost of young leachate was lesser compared to matured leachate.

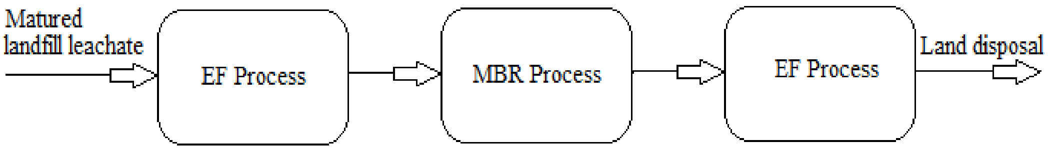

Fig.4.34 Block diagram of EF – MBR integrated treatment system for matured landfill leachate

Table 4.22 shows the annual cost of the EF-MBR integrated treatment system for treating $1m^3$ of matured and young landfill leachate. Block diagram for the EF-MBR integrated treatment system for matured and young landfill leachate are shown in Fig. 4.34 and fig. 4.35 respectively. Table 4.23 shows the annual treatmentcost of matured and young landfill leachate by EF- MBR integrated system.

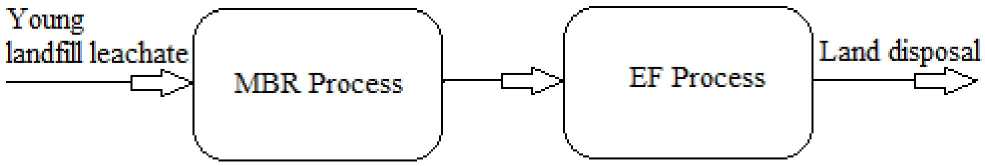

Fig.4.35 Block diagram of MBR - EF integrated treatment system for young landfill leachate

Table 4.23 Annual treatment cost of matured and young landfill leachate by EF- MBR integrated system

	Matured leachate (EF +MBR)	**Young leachate (MBR +EF)**
Annual capital cost (Rs/m^3)	5.8	6.5
Annual operating cost (Rs/m^3)	800.4	151.1
Total annual cost (Rs/m^3)	806.2	157.6

CHAPTER - 5

CONCLUSIONS

5.1 Summary and conclusions

Landfill leachate, if not properly collected and treated, will cause significant contamination of surface water and groundwater. Analysis of the characteristics of leachate samples showed that the biodegradability index of the landfill leachate (matured) was less than 0.3. Ammonia nitrogen content in matured leachate was high. Hence the biological treatment is not feasible for matured leachate. EF process was compared with PEF and SPEF processes, both PEF and SPEF showed higher degradation of organic matter than EF process but the Biodegradability Index (BOD to COD ratio) was less than 0.4.

RSM was used to statistically design the experiments of EF process to investigate the influence of operating parameters viz. pH, current density, H_2O_2 dosage and reaction time on BI and to optimize the parameters for maximum BI. BOD to COD ratio of the matured leachate enhanced to 0.45 from 0.21 by 40 min of EF treatment at optimum operating condition (pH-2.85, H_2O_2 dosage -55.76%, current density -129.5A/m^2). An empirical model was developed for the response BI with a coefficient of determination (R^2) value 0.9966. The pollutant removal (COD -78.2%, BOD -53.3%, NH_3-N -41%, PO_4^--60.9%, SO_4^--59%, Cl^--62.2%, S^--55.8%), specific energy consumption (0.0987 kWh/kg COD removed) and specific anode consumption (0.062 kg/kg of COD removed) at optimum operating condition are promising. EF was found to be more appropriate for pretreatment of matured leachate before biological systems (Biodegradability Index >0.4). Electro Fenton process can be used as a pretreatment method to improve the biological treatability of wastewater, thus favoring their processing by means of common microorganisms.

Toxicity of the matured landfill leachate was noticed to be reduced after EF treatment. Mortality of Poecillia Reticulata fish species reduced from 100% in raw leachate to 0% in EF treated leachate, after 96hr exposure. The biological treatability was found to be improved after treating with EF process (k =1.357day^{-1}, Ks =6.096 g/l) compared to raw leachate (k =1.146day^{-1}, Ks =6.366 g/l).

High biomass concentration combined with the membrane filtration increases the concentration of the substrates in the MBR. Bioavailability of substrates in the bioreactor lead to enhanced biodegradation efficiencies of EF treated matured leachate (COD -94.2%, BOD -90.62%, NH_3-N -84.66%, PO_4^--100%, SO_4^- -83.19%, S^--85.07%, Cl^--83.37%) at optimum operating conditions (HRT- 4days and biomass concentration- 10g/l). Presence of heterogeneous bacteria, pseudomonas aeruginosa in the MBR sludge indicated the occurrence of the denitrifying process in the bioreactor. Post EF treatment is directed towards the removal of those contaminants which are not completely degraded during the biological treatment. Thus for treating matured landfill leachate, integrating EF and MBR processes enhanced treatment efficiency (COD -98.9%, BOD -97.9%, NH_3-N -98.1%, PO_4^--100%, SO_4^--94.1%, S^--95.8%, Cl^--97.2%) and land disposal standards were attained.

MBR process degraded major part of the biodegradable compounds in young leachate (COD -90.2%, BOD -95.1%, NH_3-N -86%, PO_4^--100%, SO_4^- -74%, S^--85.8%, Cl^--68.9%) at optimum HRT of 6 days. Since MBR treatment alone could not achieve the land disposal standards, post EF treatment was applied. It was found to improve the treatment efficiency of young leachate (COD -98.8%, BOD -99%, NH_3-N -96.7%, PO_4^--100%, SO_4^- -91.2%, S^--97.7%, Cl^-- 95.1%) and meet the land disposal standards.

Fouling of the membrane was faster for young leachate when compared to that of EF treated matured landfill leachte effluent. Intermittent physical backwashing improved the life of the membrane. Around 85% of the total fouling was reversible.

Total expense for degrading 1 kg of COD from matured landfill leachate by the EF-MBR integrated system was found to be Rs 36.8 (0.48 $/kg of COD removed) and that for young landfill leachate by the MBR - EF treatment system was Rs 7.9 (0.105 $/kg of COD removed). Treating matured landfill leachate is 5 times costlier than treating young leachate (Matured leachate - Rs 806.2 per m^3, Young leachate - Rs 157.6 per m^3).

Integrating the Electro Fenton process withthe membrane bioreactor process effectively controls the landfill leachate contamination of groundwater and surface water. The research not only establishes the technical feasibility of integrated Electro Fenton process and Membrane bioreactor in the reduction of organic load and other pollutants from high strength landfill leachate but also shows that the method is more attractive in comparison with the existing practice of physicochemical processes or biological processes or their combinations in protecting our environment by meeting the discharge standards.

5.2 Scope for future studies

1. A proper collection system for the landfill leachate generated at the MSW disposal site can be designed.

2. Impact assessment of the landfill leachate on the surrounding environment and people can be investigated.

3. Experiments may be conducted by mixing landfill leachate with highly biodegradable wastewater like Municipal sewage, Dairy wastewater etc. and treatment efficiency and cost estimation can be studied.

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APPENDIX -I

Characteristics of matured lechate samples collected from November 2015 to May 2016

Parameters	Nov-2015 1st week	Nov-2015 2nd week	Nov-2015 3rd week	Nov-2015 4th week	Dec-2015 1st week	Dec-2015 2nd week	Dec-2015 3rd week	Dec-2015 4th week	Jan-2016 1st week	Jan-2016 2nd week	Jan-2016 3rd week	Jan-2016 4th week	Feb-2016 1st week	Feb-2016 2nd week
pH	8	8.6	8.7	8.4	8.6	8.5	8.5	8.6	7.5	7.6	7.5	7.6	8	8.6
TSS(mg/l)	435	542	545	451	552	457	495	458	498	560	540	563	435	542
COD(mg/l)	19960	24100	22950	19040	25720	22200	25890	21950	22490	23810	24550	22820	19960	24100
BOD(mg/l)	3962	5320	5472	3496	5700	3170	5674	4710	4570	5150	4930	4870	3962	5320
Sulphate(mg/l)	485	666	580	585	584	494	587	485	578	680	648	582	485	666
Phosphatemg/l	155	187	215	160	188	146	188	182	171	162	192	165	155	187
Sulphide(mg/l)	20	20	30	17	21	16	21	15	19	20	21	20	20	20
Chloride(mg/l)	2680	2765	2641	2658	2620	2710	2910	2648	2652	2399	2630	2655	2680	2765
NH_3-N (mg/l)	2152	2210	2185	2150	2155	2408	2150	2314	1940	2205	2190	2310	2152	2210
Nitrate(mg/l)	1.1	1	1.7	1.3	1.7	1.2	1.8	0.9	1.2	1.7	1.8	1.5	1.1	1
BOD/COD	0.2	0.22	0.24	0.18	0.22	0.14	0.22	0.21	0.2	0.22	0.2	0.21	0.2	0.22

APPENDIX –I (continued)

Parameters	Feb-2016 3rd week	Feb-2016 4th week	Mar-2016 1st week	Mar-2016 2nd week	Mar-2016 3rd week	Mar-2016 4th week	Apr-2016 1st week	Apr-2016 2nd week	Apr-2016 3rd week	Apr-2016 4th week	May-2016 1st week	May-2016 2nd week	May-2016 3rd week	May-2016 4th week
pH	8.7	8.4	8.6	8.5	8.5	8.6	7.5	7.6	7.5	7.6	8.6	8	8.4	8.5
TSS(mg/l)	545	451	552	457	495	458	498	560	540	563	552	435	451	495
COD(mg/l)	22950	19040	25720	22200	25890	21950	22490	23810	24550	22820	25720	19960	19040	25890
BOD(mg/l)	5472	3496	5700	3170	5674	4710	4570	5150	4930	4870	5700	3962	3496	5674
Sulphate(mg/l)	580	585	584	494	587	485	578	680	648	582	584	485	585	587
Phosphatemg/l	215	160	188	146	188	182	171	162	192	165	188	155	160	188
Sulphide(mg/l)	30	17	21	16	21	15	19	20	21	20	21	20	17	21
Chloride(mg/l)	2641	2658	2620	2710	2910	2648	2652	2399	2630	2655	2620	2680	2658	2910
NH_3-N (mg/l)	2185	2150	2155	2408	2150	2314	1940	2205	2190	2310	2155	2152	2150	2150
Nitrate(mg/l)	1.7	1.3	1.7	1.2	1.8	0.9	1.2	1.7	1.8	1.5	1.7	1.1	1.3	1.8
BOD/COD	0.24	0.18	0.22	0.14	0.22	0.21	0.2	0.22	0.2	0.21	0.22	0.2	0.18	0.22

APPENDIX -II

Characteristics of young lechate samples collected from November 2015 to May 2016

Parameters	Nov-2015 1st week	Nov-2015 2nd week	Nov-2015 3rd week	Nov-2015 4th week	Dec-2015 1st week	Dec-2015 2nd week	Dec-2015 3rd week	Dec-2015 4th week	Jan-2016 1st week	Jan-2016 2nd week	Jan-2016 3rd week	Jan-2016 4th week	Feb-2016 1st week	Feb-2016 2nd week
pH	7.1	7.7	7.8	7.5	7.7	7.6	7.6	7.7	6.6	6.7	6.6	6.7	6.7	6.9
TSS (mg/l)	425	342	415	361	322	427	665	428	468	510	410	533	472	548
COD (mg/l)	18620	20900	19750	19040	22520	19000	22690	18750	19290	20610	21350	19620	20250	22670
BOD (mg/l)	3962	5320	5472	3496	5700	3170	5674	4710	4570	5150	4930	4870	5582	5603
Sulphate (mg/l)	485	451	385	380	359	299	322	290	383	290	453	387	493	383
Phosphate mg/l	67	99	97	88	86	90	92	94	89	84	94	87	96	115
Sulphide (mg/l)	20	120	125	117	121	116	125	115	124	118	119	120	122	120
Chloride (mg/l)	2680	2565	2441	2488	2620	2710	2910	2648	2652	2369	2600	2625	2800	2612
NH_3-N (mg/l)	92	85	88	93	88	91	103	117	77	118	123	133	133	143
Nitrate (mg/l)	1.4	1.3	1.4	1.6	1.4	1.5	1.1	1.2	1.5	2	2.1	1.8	1.9	1.6
BOD/COD	0.52	0.54	0.52	0.46	0.48	0.42	0.5	0.49	0.48	0.5	0.45	0.47	0.52	0.48

APPENDIX –II (continued)

Parameters	Feb-2016 3rd week	Feb-2016 4th week	Mar-2016 1st week	Mar-2016 2nd week	Mar-2016 3rd week	Mar-2016 4th week	Apr-2016 1st week	Apr-2016 2nd week	Apr-2016 3rd week	Apr-2016 4th week	May-2016 1st week	May-2016 2nd week	May-2016 3rd week	May-2016 4th week
pH	6.6	6.6	7.7	7.6	7.7	7.8	6.7	6.7	6.7	6.9	7.7	7.1	7.5	7.6
TSS (mg/l)	568	610	612	527	748	615	772	760	743	648	782	645	781	775
COD (mg/l)	19290	21350	20900	19000	18750	19750	20250	20610	19620	22670	22520	16760	15840	22690
BOD (mg/l)	4570	4930	5320	7790	9710	10472	10582	10150	9870	10603	10700	8962	8496	10674
Sulphate(mg/l)	383	453	471	295	290	385	489	485	387	393	389	310	430	448
Phosphate mg/l	93	104	99	98	94	117	118	99	97	112	98	107	104	114
Sulphide (mg/l)	118	119	120	126	125	130	134	132	135	132	141	132	137	141
Chloride(mg/l)	2652	2630	2765	2710	2648	2641	2770	2369	2625	2582	2620	2650	2668	2880
NH_3-N (mg/l)	167	148	173	161	167	158	193	210	233	243	238	236	245	217
Nitrate (mg/l)	1.5	2.1	1.7	1.5	1.2	2.2	1.9	2	1.8	2.5	2.1	1.5	2	2.2
BOD/COD	0.45	0.48	0.5	0.41	0.45	0.52	0.55	0.51	0.49	0.54	0.52	0.48	0.46	0.55

APPENDIX-III

Design of bioreactors for MBR process

	Matured landfill leachate	Young landfill leachate
Detention period(days)	4	6
Quantity of leachate produced (m^3/day)	100	100
Volume of the reactor(m^3) = detention period(days) × quantity of leachateformed /day	400	600

LIST OF PUBLICATIONS

Journal Articles

1. Minimol Pieus T., Soloman P.A., (2020), “Integrated electro fenton and membrane bioreactor system for matured landfill leachate treatment”, *Journal of hazardous, toxic and radioactive waste management*, American Society for Civil Engineers, 25(1), p.04020004.

2. Minimol Pieus T., Soloman P.A., (2018), “Degradation of matured landfill leachate by Electro fenton treatment and optimization by response surface methodology”, *International Journal of Engineering and Technology,* 7(3.8), pp. 101-105.

3. Minimol Pieus T., Soloman P.A., (2018), “Matured landfill leachate treatment by electro fenton and photo electro fenton process”, *International Journal of Management, Engineering and Technology*, 8(X), pp. 1231-1240.