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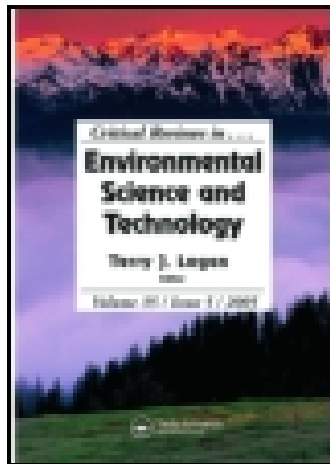
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Contemporary environmental issues of landfill leachate: assessment & remedies

Sumona Mukherjee¹, Soumyadeep Mukhopadhyay², Mohd Ali Hashim², Bhaskar Sen Gupta^{3*}

Abstract

Landfills are the primary option for waste disposal all over the world. Most of the landfill sites across the world are old and are not engineered to prevent contamination of the underlying soil and groundwater by the toxic leachate. The pollutants from landfill leachate have accumulative and detrimental effect on the ecology and food chains leading to carcinogenic effects, acute toxicity and genotoxicity among human beings. Management of this highly toxic leachate presents a challenging problem to the regulatory authorities who have set specific regulations regarding maximum limits of contaminants in treated leachate prior to disposal into the environment to ensure minimal environmental impact. There are different stages of leachate management such as monitoring of its formation and flow into the environment, identification of hazards associated with it and its treatment prior to disposal into the environment. This review focuses on: (i) leachate composition, (ii) Plume migration, (iii) Contaminant fate, (iv) Leachate plume monitoring techniques, (v) Risk assessment techniques, Hazard rating methods, mathematical modeling, and (vi) Recent innovations in leachate treatment technologies. However, due to seasonal fluctuations in leachate composition, flow rate and leachate volume, the management approaches cannot be stereotyped. Every scenario is unique and the strategy will vary accordingly. This paper lays out the choices for making an educated guess leading to the best management option.

Keywords: landfill leachate plume, pollution, hazard identification, treatment technologies

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1 Introduction

Landfill leachate is defined as any liquid effluent containing undesirable materials percolating through deposited waste and emitted within a landfill or dump site. Often, its route of exposure and toxicity remains unknown and a matter of prediction due to extremely complicated geochemical processes in the landfill and the underlying soil layers (Koshi et al., 2007; Taulis, 2005). The prevalence of landfill waste dumping with or without pre-treatment is on the rise around the globe due to increasing materialistic lifestyle and planned obsolescence of the products. According to Laner et al. (2012), in 2008 up to 54% of the 250×10^6 metric tons of municipal solid waste (MSW) in USA was disposed off in landfills. Also, 77% MSW in Greece, 55% MSW in the United Kingdom, and 51% MSW in Finland was landfilled in 2008 while about 70% of MSW in Australia has been directed to landfills without pre-treatment in 2002 (Laner et al., 2012). In Korea, Poland and Taiwan around 52%, 90% and 95% of MSW are dumped in landfill sites, respectively (Renou et al., 2008a). In India, the accumulated waste generation in four metropolitan cities of Mumbai, Delhi, Chennai and Kolkata is about 20,000 tons d^{-1} and most of it is disposed in landfills (Chattopadhyay et al., 2009). Most of the landfill sites across the world are old and are not engineered to prevent contamination of the underlying soil and groundwater by the toxic leachate.

Leachate presents high values of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), total suspended solid (TSS), total dissolved solid (TDS), recalcitrant organic pollutants, ammonium compounds, sulfur compounds and dissolved organic matter (DOM) bound heavy metals which eventually escape into the environment, mainly soil and groundwater, thereby posing serious environmental problems (Gajski et al., 2012; Lou et al.,

2009). Around two hundred hazardous compounds have already been identified in the heterogeneous landfill leachate, such as aromatic compounds, halogenated compounds, phenols, pesticides, heavy metals and ammonium (Jensen et al., 1999). All of these pollutants have accumulative, threatening and detrimental effect on the survival of aquatic life forms, ecology and food chains leading to enormous problems in public health including carcinogenic effects, acute toxicity and genotoxicity (Gajski et al., 2012; Moraes and Bertazzoli, 2005; Park and Batchelor, 2002). Broadly speaking, landfill leachate has deep impact on soil permeability, groundwater, surface water, and nitrogen attenuation all of which will be discussed in Section 4.1.

A leachate is characterized by two principle factors viz., its composition and the volume generated, both of which are influenced by a variety of parameters, such as type of waste, climatic conditions and mode of operation. The most important factor influencing landfill leachate composition is the age of the landfill (Kulikowska and Klimiuk, 2008; Nanny and Ratasuk, 2002). The regulatory bodies around the world have set specific maximum discharge limits of treated leachate that has to be maintained prior to the disposal of treated leachate into any surface water bodies, sewer channels, marine environment or on land to ensure minimal environmental impact. These are discussed in the Section 2. Monitoring of the contaminated leachate plume is an arduous but essential task necessary for measuring the extent of spread of pollution and taking management decisions regarding leachate treatment. A number of techniques have been followed for the past three decades for leachate plume migration monitoring, such as hydro-geological techniques for groundwater sampling for geo-chemical

analysis, use of stable isotopes, electromagnetic methods, electrical methods and bacteriological experiments, all of which will be discussed in details in Section 3.2.

Assessing the effect of leachate on the environment needs systematic study procedure. The task is extremely difficult and largely prediction based, due to unpredictability of the soil environment, groundwater flow and variation of soil permeability in different parts of the world. However, an educated guess can be taken on the pollution scenario and risk assessment can be done either by using relative hazard assessment systems or by using stochastic and deterministic models after gathering background physico-chemical data. Softwares are also used for this purpose. Section 4.2 describes the procedure of risk assessment of landfill leachate.

Once the landfill leachate plume is monitored and risk assessment has been performed, then the management decision regarding leachate treatment can be taken. Already some comprehensive reviews on various leachate treatment technologies have been published (Alvarez-Vazquez et al., 2004; Deng and Englehardt, 2006; Foo and Hameed, 2009; Kim and Owens, 2010; Kurniawan et al., 2006b; Laner et al., 2012; Renou et al., 2008a; Wiszniowski et al., 2006). So we have included a brief but detailed description of only the most recent developments in this field, mainly in tabular form in Section 5 (Tables 6-12).

This review elucidates the complete leachate management process, beginning with leachate composition, plume migration, fate of contaminant, plume monitoring techniques, risk assessment techniques, hazard assessment methods, mathematical modeling up to the recent innovations in leachate treatment technologies. This paper also steers clear from the topics in which good reviews are already available and only the most relevant information has been included.

2 Landfill leachate: Characteristics and regulatory limits

Landfill leachate can be categorized as a soluble organic and mineral compound generated when water infiltrates into the refuse layers, extracts a series of contaminants and triggers a complex interplay between the hydrological and biogeochemical reactions (Renou et al., 2008a). These interactions act as mass transfer mechanisms for producing moisture content sufficiently high to initiate a liquid flow (Aziz et al., 2004a), induced by gravitational force, precipitation, surface runoff, recirculation, liquid waste co-disposal, groundwater intrusion, refuse decomposition and initial moisture content present within the landfills (Achankeng, 2004; Foo and Hameed, 2009). The knowledge of leachate characteristics at a specific landfill site is the most essential requirement for designing management strategy. This knowledge is equally important for designing containment for new landfill where leachate will be extracted, as well as for managing the old landfill that lacks proper safeguards installed to contain leachate (Rafizul and Alamgir, 2012). Typical composition of a municipal landfill leachate is given in Table 1.

Two most important factors for characterizing leachate are volumetric flow rate and its composition. Leachate flow rate depends on rainfall, surface run-off, and intrusion of groundwater into the landfill (Renou et al., 2008a). According to a number of researchers (Baig et al., 1999; Christensen et al., 2001; El-Fadel et al., 2002; Harmsen, 1983; Nanny and Ratasuk, 2002; Rapti-Caputo and Vaccaro, 2006; Rodríguez et al., 2004; Stegman and Ehrig, 1989), leachate composition is influenced by a number of factors viz., (i) climatic and hydro-geological conditions (rainfall, groundwater intrusion, snowmelt); (ii) operational and management issues at the landfill (compaction, refuse pre-treatment, vegetation cover, re-circulation, liquid waste co-disposal, etc.); (iii) characteristics of waste dumped in the landfill (particle size, density,

chemical composition, biodegradability, initial moisture content); (iv) internal processes inside landfill (decomposition of organic materials, refuse settlement, gas and heat generation and their transport); (v) age of the landfill. The leachate quality varies, not only from landfill to landfill but also, between different sampling points at the same landfill site from time to time due to the variation in the above factors.

Among all the above factors, leachate characterization depending on age may be used for making initial management decisions since others are too complex to estimate instantly. Although leachate composition may vary widely within the successive aerobic, acetogenic, methanogenic, stabilization stages of the waste evolution, four types of leachates can be defined according to landfill age viz., young, intermediate, stabilized and old as shown in Table 2. However, detailed management decision may be taken only after considering all the above factors.

The characteristics of the landfill leachate can usually be represented by the basic parameters COD, BOD₅, BOD₅/COD ratio, pH, suspended solids (SS), ammonium nitrogen (NH₄-N), total Kjeldahl nitrogen (TKN) and heavy metals. The landfill age was found to have significant effect on organics and ammonia concentrations (Kulikowska and Klimiuk, 2008). The concentration and biodegradability of leachate usually decrease with its age. Young leachate fractions have low molecular weight organic compounds characterized by linear chains, which are substituted through oxygenated functional groups such as carboxyl and alcoholic groups. Old leachate have organic compounds with a wide range of molecular weight fractions having complex structures with N, S and O containing functional groups (Calace et al., 2001). Hence, the management decision can be generalized and the treatment approach can be chalked out depending on the age of the landfill.

Landfill leachates cause enormous harm when they get released into the environment without proper treatment, as will be discussed in section 4.1. In order to minimize their environmental impact, regulatory bodies around the world require that the leachate volume is controlled and its toxicity and contaminant level reduced by using proper treatment technologies (Robinson, 2005). The regulatory limits of various leachate components in different countries are discussed in Table 3. India, has specific regulations regarding construction, maintenance and operation of a landfill and the post closure steps required to be taken for pollution prevention under Schedule III of the Municipal Solid Wastes (Management and Handling) Rules, 2000. The recent stricter discharge limits for leachate demands the application of advanced treatment techniques such as electrochemical treatments, membrane filtrations, advanced oxidations and so on, all of which involve high installation and operational cost. According to a World Bank (1999) study, equipment donated by bilateral organizations remains idle due to lack of training or funds for operation. The regulatory authorities managing landfills inspect the incoming waste but are not very observant towards the environmental impacts of waste disposal, which results in poor enforcement of the discharge standards (The World Bank, 1999). The increased private sector participation in leachate management can lead to better enforcement of standards. Better incentives such as low taxes, institutional support etc., can draw private sector companies to the field of leachate management.

3 Leachate plume migration and methods of its monitoring

It is a well established fact that leachate plumes are formed from landfills with or without liners and these infiltrate into subsurface aquifers, subsequently forming an even larger plume (Baun et al., 2004; Bloor et al., 2005; Isidori et al., 2003; Kjeldsen et al., 2002; Slack et al., 2005). The processes associated with leachate plume formation has also been discussed by other researchers (Kjeldsen et al., 2002). Leaching tests designed to assess the release of toxic leachate from a solid waste into the surrounding environment has been earlier reviewed (Scott et al., 2005). A large number of research has already been done to study the migration of leachate plume through landfill liners (Baun et al., 2003; Chalermtanant et al., 2009; Edil, 2003; Haijian et al., 2009; Lu et al., 2011; Varank et al., 2011). Two distinctive routes of landfill leachate transport were identified by some researchers (Foose et al., 2002; Katsumi et al., 2001). The first route is the advective and dispersive transport of contaminants through defects in the geomembrane seams and through clay liner underlying the geomembrane. The second route is the diffusive transport of organic contaminants through the geomembrane and the clay liner. It was reported that every 10,000 m² of geomembrane liner contains 22.5 leaks on an average facilitating the leachate plume formation (Laine and Darilek, 1993). Chofqi et al. (2004) deduced that there were several factors that determine the evolution of groundwater contamination, such as (1) depth of the water table, (2) permeability of soil and unsaturated zone, (3) effective infiltration, (4) humidity and (5) absence of a system for leachate drainage. Leachate plumes often contain high concentrations of organic carbon such as volatile fatty acids, humic like compounds and fulvic acids (Christensen et al., 2001), ammonium (Christensen et al., 2000) and a variety of xenobiotic compounds (e.g. BTEX compounds, phenoxy acids, phenolic compounds, chlorinated aliphatic compounds and a

variety of pesticides) (Baun et al., 2004; Kjeldsen et al., 2002). Non-volatile dissolved organic carbon (DOC), ferrous iron, methane, ammonium, sulfate, chloride, and bicarbonate are also present in the leachate plume 10–500 times higher than natural aquifer conditions (Bjerg et al., 2003; Christensen et al., 2001).

3.1 Fate of contaminants in leachate plume

The generation of leachate plume depends upon the quantity and quality of leachate, which varies seasonally depending upon the composition and moisture content of the solid waste, hydro-geological conditions, climate, local population densities, annual precipitation, temperature and humidity. All these factors add to the complexity in landfill leachate characteristics and composition (Christensen et al., 2001; Miyajima et al., 1997). The contaminant migration greatly depends upon the composition of the leachate or contaminants entering the ground-water system. Similar contaminants may behave differently in the same environment due to the influence of other constituents in a complex leachate matrix (Abu-Rukah and Al-Kofahi, 2001). Redox environments were found to vary greatly inside contaminant plumes due to variation in contaminant load, groundwater chemistry, geochemistry and microbiology along the flow path (Christensen and Christensen, 2000; van Breukelen et al., 2003). Existence of redox gradients from highly reduced zones at the source to oxidized zones towards the front of the plumes was supported by detailed investigation of the terminal electron acceptor processes (Bekins et al., 2001; Ludvigsen et al., 1999). Some researchers also studied the steep vertical concentration gradients for contaminants and redox parameters in plume fringes, where contaminants mix with electron acceptors by dispersion and diffusion processes

(Lerner et al., 2000; Thornton et al., 2001; van Breukelen and Griffioen, 2004). The fates of nitrogenous, sulfurous, heavy metals and organic contaminants are discussed under different paragraphs.

3.1.1 Inorganic pollutants

3.1.1.1 Nitrogenous pollutants

The landfill leachate having NH_4 poses long-term threat of pollution once it escapes into ground or surface waters (Beaven and Knox, 2000; IoWM, 1999). In the UK, average concentrations of about $900 \text{ mg NH}_4(+\text{NH}_3)\text{-N L}^{-1}$ have been reported for landfill leachates (Burton and Watson-Craik, 1998) while legislation probably requires concentrations below $0.5 \text{ mg NH}_4\text{-N L}^{-1}$ for any discharge in the environment (EA, 2003). The laboratory experiments revealed that most biological nitrogen removal processes are carried out by the combination of aerobic nitrification, nitrate reduction, anoxic denitrification and anaerobic ammonium oxidation processes or (anammox) (Fux et al., 2002; Jokella et al., 2002; Pelkonen et al., 1999). The NH_4^+ in leachate can undergo sequential bacterial transformation to NO_3^- under oxidizing environment. Although NO_3^- is less toxic than NH_4^+ it still presents a pollution threat and bacterial denitrification to 'harmless' N_2 is required under anaerobic conditions, to eliminate it. When oxygen is depleted, nitrate can be converted to nitrite and finally to nitrogen gas by denitrification. Also, when nitrite is present under anaerobic conditions, ammonium can be oxidized with nitrite as an electron acceptor to dinitrogen gas (anammox) (Mora et al., 2004). The attenuation of N pollution resulting from disposal of organic wastes in landfill sites therefore requires fluctuating redox conditions favouring the transformations: $\text{NH}_4^+ \rightarrow \text{NO}_3^- \rightarrow \text{N}_2$. Anaerobic conditions prevent

the formation of NO_3^- , so N attenuation by denitrification in landfills is not regarded as a significant process (Burton and Watson-Craik, 1998). Heaton et al. (2005) acquired data for the isotope ratios ($^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$ and $^{34}\text{S}/^{32}\text{S}$) and dissolved gas (N_2 , Ar, O_2 and CH_4) composition of groundwater in and around a landfill site in Cambridgeshire, England. Decomposition of domestic waste, placed in unlined quarries produced NH_4^+ rich leachate dispersing as a plume into the surrounding middle chalk aquifer at approximately 20 m below ground level. Few boreholes around the edge of the landfill extending to the west and north in the direction of plume flow showed evidence of methanogenesis, SO_4^{2-} reduction, and denitrification. The first two processes are indicative of strongly reducing conditions, and are largely confined to the leachate in the landfill area. Denitrification does not require such strong reducing conditions and beyond those strong reducing zones, clear evidence of denitrification comes from data for elevated $\delta^{15}\text{N}$ values for NO_3^- ($>+10\text{‰}$) and the presence of non-atmospheric N_2 . This distribution of redox zones is therefore consistent with an environment in which conditions become progressively less reducing away from the landfill (Christensen et al., 2001; Heaton et al., 2005).

3.1.1.2 Reduction of sulfate pollutants

Sulfate reduction is a major process for degradation of organic matters and many anaerobic subsurface environments have been found to experience this process (Krumholz et al., 1997; Lovley, 1997; Ulrich et al., 1998). The sulfate reduction is controlled by factors such as availability of utilizable organic matter as electron donors (McMahon and Chapelle, 1991; Ulrich et al., 1998), water potential, sediment pore throat diameter, pH and availability of thermodynamically more favorable electron acceptors (Ludvigsen et al., 1998; Routh et al.,

2001). In anoxic aquifers, lithologic, climatic, hydrological, and biogeochemical processes controlling the sulfate supply may determine sulfate reduction (Martino et al., 1998; Ulrich et al., 1998). Ulrich et al. (2003) undertook field and laboratory techniques to identify the factors affecting sulfate reduction in a landfill leachate contaminated shallow, unconsolidated alluvial aquifer. Depth profiles of ^{35}S -sulfate reduction rates in aquifer sediments revealed a Michaelis–Menten-like relationship with an apparent K_m and V_{\max} of approximately 80 and $0.83 \mu\text{M SO}_4^{-2} \text{ day}^{-1}$, respectively. The rate of sulfate reduction was in direct correlation with the concentration of the sulfate. Near the confining bottom layer of the aquifer, sulfate was supplied by advection of groundwater beneath the landfill and the reduction rates were significantly higher than rates at intermediate depths (Ulrich et al., 2003).

3.1.1.3 Heavy Metals (HMs)

Although HMs tend to be leached out of fresh landfill, they later became largely associated with MSW-derived dissolved organic matter (DOM) which plays an important role in heavy metal speciation and migration (Baumann et al., 2006; Baun and Christensen, 2004; Li et al., 2009). Christensen et al. (1996) conducted experiments to determine the metal distribution between the aquifer material and the polluted groundwater samples (K_d) and the difference in distribution coefficients indicated that DOC from landfill leachate polluted groundwater can form complexes with Cd, Ni and Zn. DOM derived from MSW landfill leachate was observed to have a high affinity for metals such as Cu, Pb, Cd, Zn and Ni, enhancing their mobility in leachate-polluted waters (Christensen et al., 1999). However, Ward et al. (2005) deduced that the heavy metal binding capacities largely fluctuated among various leachates due to variable compositions. Earlier, it was demonstrated that HMs mobilization was enhanced by reduced pH of the leachate

with oxygen intrusion in landfill (Flyhammar and Ha°kansson, 1999; Ma°rtensson et al., 1999) and by the presence of large quantity of fatty acids generated at the initial phase of solid waste degradation (He et al., 2006). In some recent studies, it was revealed that less than 0.02% of HMs in landfills may leach out over 30 years of land filling (Kjeldsen et al., 2002; Øygard et al., 2007). Qu et al. (2008) monitored mobility of some heavy metals including Cd, Cr, Cu, Ni, Pb and Zn released from a full-scale tested bioreactor landfill (TBL) in the Tianziling MSW Landfill in Hangzhou City, China over the first 20 months of operation. The size of the TBL was approximately 16,000 m² with a combined GCL-HDPE bottom liner, and had four layers of 6–8 m thick MSW layers. At the initial landfill stage, the leachate exhibited high HMs release, high organic matter content (27,000–43,000 g l⁻¹ of TOC) and low pH (5–6). By the fifth month of land filling, the methanogenic stage was established, and HMs release was reduced below the Chinese National Standards. At a landfill age of 0.5 years, 15% of Cr, 25% of Cu, 14% of Ni, 30% of Pb and 36.6% of Zn in solids were associated with amorphous metal oxides and crystalline Fe oxides. At 1.5 years of filling age, these HMs were largely transformed into alumino-silicates forms or released with the landfill leachate. Computer modeling revealed that the humic acid (HA) and fulvic acid (FA) could strongly bind HMs (Qu et al., 2008). Chai et al. (2012) found strong interactions between HA and Hg. They proposed that the overall stability constant of Hg(II)–HA was determined by the abundant O-ligands in HA. Compared to HA, the FA having relatively high content of carboxylic groups had a much higher Hg(II)-complexing capacity. Thus FA played an important role in binding Hg(II) in early landfill stabilization process.

3.1.2 Organic contaminants

Organic contaminants in the form of hydrocarbons usually undergoes degradation by bacterial activity in the vadose zone producing carbonic and organic acids which enhance the mineral dissolution of the aquifer materials (McMahon et al., 1995). This leads to the production of a leachate plume with high total dissolved solids (TDS) resulting in the increased groundwater conductance observed in and around the zones of active biodegradation (Atekwana et al., 2000; Benson et al., 1997). The acidogenic phase in young landfills is associated with rapid anaerobic fermentation, leading to the release of free volatile fatty acids (VFA), whose concentration can be up to 95% of the TOC (Welander et al., 1997). Figure 1 illustrates an anaerobic degradation scheme for the organic material, measured by COD, inside a sanitary landfill. High moisture content enhances the acid fermentation in the solid waste (Wang et al., 2003). The methanogenic phase takes over with the maturity of the landfill. Methanogenic microorganisms converts VFA into biogas (CH_4 , CO_2) and in such old landfills, up to 32% of the DOC in leachate consists of high molecular weight recalcitrant compounds (Harmsen, 1983).

van Breukelen et al. (2003) delineated the leachate plume inside a landfill (Banisveld, The Netherlands) using geophysical tests by mapping the subsurface conductivity to identify the biogeochemical processes occurring. Methane was found to form inside the landfill and not in the plume. Precipitation of carbonate minerals was confirmed by simulation of $\delta^{13}\text{C}$ -DIC [dissolved inorganic carbon]. Ziyang et al. (2009) investigated the COD compositions in leachate based on the molecular weight distribution and hydrophobic/hydrophilic partition characteristics as shown in Figure 2. The COD composition varied over the age of the leachate and the ratio of TOC/TC decreased over time, indicating decrease in the percentage of organic matters in

leachate and increase in inorganic substances. Giannis et al. (2008) monitored long-term biodegradation of MSW in relation to operational characteristics such as air importation, temperature, and leachate recirculation in an aerobic landfill bioreactor over a period of 510 days of operation in a lab-scale setup. It was evident from the leachate analysis that above 90% of COD and 99% of BOD₅ was removed by the aerobic bioreactor. Tuxen et al. (2006) used microcosm experiments to illustrate the importance of fringe degradation processes of organic matters within contaminant plumes and identified increased degradation potential for phenoxy acid herbicide governed by the presence of oxygen and phenoxy acids existing at the narrow leachate plume fringe of a landfill. Anaerobic processes taking place in a leachate contaminated alluvial aquifer was studied near Norman Landfill, Oklahoma (USA), along the flow path of aquifer. The center of the leachate plume was characterized by high alkalinity and elevated concentrations of total dissolved organic carbon, reduced iron, methane, and negligible oxygen, nitrate, and sulfate concentrations. Occurrence of anaerobic methane oxidation inside the plume was suggested by values of methane concentrations and stable carbon isotope ($\delta^{13}\text{C}$). Methane $\delta^{13}\text{C}$ values increased from about -54‰ near the source to $>-10\text{‰}$ down gradient and at the plume margins. Oxidation rates ranged from 18 to 230 μM per year while first-order rate constants ranged from 0.06 to 0.23 per year. Hydro-chemical data suggested a sulfate reducer-methanogen consortium mediating this methane oxidation. So natural attenuation of organics through anaerobic methane oxidation was found to be an important process in the plume (Grossman et al., 2002)

3.1.3 Biological contaminants

Survival of micro-organisms in groundwater, septic tank and leachate plumes have been investigated by few researchers (Crane and Moore, 1984; Grisey et al., 2010; Sinton, 1982; Tuxen et al., 2006). Grisey et al. (2010) monitored total coliforms, *Escherichia coli*, *Enterococci*, *Pseudomonas aeruginosa*, *Salmonella* and *Staphylococcus aureus* for 15 months in groundwater and leachate beneath the Etueffont landfill (France). They coupled the microbiological tests to tracer tests to identify the source of contamination. Groundwater was found to have high levels of faecal bacteria (20,000 CFU 100 mL⁻¹ for total coliforms, 15,199 CFU 100 mL⁻¹ for *E. coli* and 3290 CFU 100 mL⁻¹ for *Enterococci*). Bacterial density was lower in leachates than in groundwater, except for *P. aeruginosa* which seemed to adapt favourably in leachate environment. Tracer tests indicated that bacteria originated from the septic tank of the transfer station and part of these bacteria transited through waste. Microcosm experiments were used to measure the fringe degradation of phenoxy acid herbicide across a landfill leachate plume by microbial activity in lab scale experiments. High spacial resolution sampling at 5 cm interval was found to be necessary for proper identification of narrow reaction zones at the plume fringes because samples from long screens or microcosm experiments under averaged redox conditions would yield erroneous results. The samples were collected by a hollow stem auger drilled down to the desired level of the cores. The collected cores were sealed with aluminium foil and plastic stoppers to maintain the redox conditions and stored at 10 °C to be used within 4 days. These were divided into smaller parts for the microcosm experiments, pore-water extraction, and sediment analyses, determination of MPN, solid organic matter (TOC), and grain size distribution. A multi-level sampler installed beside the cores measured the plume position and

oxygen concentration in the groundwater. Microcosm experiments were performed in 50 mL sterilized infusion glass bottles, each containing aquifer material from the sediment samples. In each microcosm, the oxygen concentration was individually controlled to mimic the conditions at their corresponding depths. The number of phenoxy acid degraders was enumerated by a most probable number (MPN) method. The results illustrated the importance of fringe degradation processes in contaminant plumes (Tuxen et al., 2006).

3.2 Monitoring of plume generation and migration: techniques & methodology

The leachate plume migration have been monitored by using a broad range of techniques and methods, such as, hydro-geological techniques, electromagnetic techniques, electrical resistivity and conductivity testing, ground penetrating radars, radioactive tracing systems and microcosm experiments. Historically, investigations by conventional sampling or electromagnetic methods were applied only at sites suspected of contamination. However, early detection and monitoring of leachate plume migration into subsurface is essential for preventing further contamination. Whatever be the technology, the monitoring wells and their placement is a matter of common interest, except for electromagnetic techniques. Usually, monitoring wells are constructed at different depths in and around the landfill site, mostly in the down-gradient of groundwater flow and the probes and sampling devices are lowered into these wells for measuring various parameters. This positioning of monitoring wells and a cross section of such a well is shown in Figure 3. USEPA (2004), in one of its reports, discussed several technologies for detecting the contaminant leaks in the vadose zone such as advanced tensiometers, cable network sensors,

capacitance sensors, diffusion hoses, electrochemical wire cables, electrode grids, intrinsic fibre optics sensors, lysimeters, neutron probes, portable electrical systems, time domain reflectometry detection cables and wire net designs (USEPA, 2004). Therefore, most of these technologies is not discussed in this review and the interested readers are advised to access the referred document. Table 3 gives an overview of the plume monitoring techniques discussed in this section.

3.2.1 Hydro-geological techniques for groundwater sampling for geo-chemical analysis

The hydro-geological sampling devices had been most frequently used for the past few decades to collect groundwater samples around leachate plumes to measure and map the plume migration (Cherry et al., 1983; Chofqi et al., 2004; Christensen et al., 1996; Kjeldsen, 1993; Nicholson et al., 1983). Cherry et al (1983) used six types of devices for groundwater monitoring to detect migration of the plume of contamination in the unconfined sandy aquifer at the Borden landfill. The monitoring devices included (i) standpipe piezometers, (ii) water-table standpipes, (iii) an auger-head sampler, (iv) suction-type multilevel point-samplers, (v) positive-displacement-type multilevel point-samplers, and (vi) bundle-piezometers. The last four devices can provide vertical sample profiles of groundwater from a single borehole. Standpipe piezometers, multilevel point-samplers and bundle-piezometers were also used by MacFarlane et al. (1983) for measuring the distribution of chloride, sulfate, electrical conductance, temperature, hydraulic conductivity, density and viscosity of the leachate & groundwater. The auger-head sampler yields samples from relatively undisturbed aquifer zones providing a rapid means of acquiring water-quality profiles for mapping the distribution of a contaminant plume. A suction-type multilevel sampler consists of twenty or more narrow polyethylene or polypropylene tubes

contained in a **polyvinyl chloride (PVC)** casing capped at the bottom. Each tube extends to a different depth and is attached to a small-screened sampling point that extends through the casing to draw water from the aquifer of depth of 8 or 9 m when suction is applied. A positive-displacement multilevel sampler can be used for deeper aquifers since each sampling point is connected to a positive-displacement pumping device. A bundle-piezometer consists of flexible polyethylene tubes, fastened as a bundle around a semi-rigid centre-piezometer. In shallow water-table areas water is withdrawn from each of the tubes and from the PVC piezometer by suction. In areas with a deep water table, samples are obtained by bailing with a narrow tube with a check valve on the bottom or by displacement using a double- or triple-tube gas-drive sampler. Coupling the positive-displacement multilevel sampler or the gas-drive samplers with the bundle-piezometers is an excellent option for collecting samples that can be filtered and have preservatives added without the water being exposed to oxygen. The multilevel samplers and bundle-piezometer can be installed to establish permanent networks for groundwater-quality monitoring by means of hollow-stem augers in which eight or more polyethylene tubes are included conveniently in each bundle-piezometer (Cherry et al., 1983).

3.2.2 Use of stable isotopes to monitor landfill leachate impact on surface waters

The uniqueness of isotopic characteristics of municipal landfill leachate and gases (carbon dioxide and methane) is utilized for monitoring leachate plume migration in groundwater. Few researchers (Hackley et al., 1996; North et al., 2006; Rank et al., 1995; Walsh et al., 1993) examined the application of stable isotopes $\delta^{13}\text{C}$ -DIC, δD - H_2O , and $\delta^{18}\text{O}$ - H_2O measurements of groundwater from landfill monitoring wells to detect leachate infiltration. The $\delta^{13}\text{C}$ of the CO_2 in landfills is up to +20 ‰ enriched in ^{13}C . The $\delta^{13}\text{C}$ and δD values of the methane fall within a

range of values representative of microbial methane produced primarily by the acetate-fermentation process. The δD of landfill leachate is strongly enriched in deuterium, by approximately 30 ‰ to 60 ‰ relative to local average precipitation values due to the extensive production of microbial methane within the limited reservoir of a landfill (Hackley et al., 1996). So monitoring of these isotopic characteristics of leachate provides some insight into its migration. The biologically mediated methanogenic processes associated with refuse decomposition resulted in isotopic enrichment of carbon ($\delta^{13}C$) in dissolved inorganic carbon (DIC) and of hydrogen (δD) and oxygen ($\delta^{18}O$) isotopes of water in landfill leachate (Grossman et al., 2002). $\delta^{13}C$ -DIC was also used to investigate the seepage of leachate-contaminated groundwater into stream water (Atekwana and Krishnamurthy, 2004). Carbon isotopes can also be used for monitoring biological activity in the aquifers (Grossman, 2002). North et al. (2006) measured δD -H₂O using a dual inlet VG SIRA12 mass spectrometer after reduction to H₂ with chromium. The $\delta^{13}C$ of DIC was measured on CO₂ liberated from the sample with 103% phosphoric acid using a Thermo Finnigan Gas Bench and Delta Plus Advantage mass spectrometer. The use of compound-specific isotope analysis may also help clarify sources of contaminants in surface waters, although applications of this technique to landfill leachate are still being developed (Mohammadzadeh et al., 2005). Vilomet et al. (2001) used strontium isotopic ratio to detect groundwater pollution by leachate. Natural groundwater and landfill leachate contamination are characterized by different strontium isotopic ratios ($^{87}Sr/^{86}Sr$) of 0.708175 and 0.708457 respectively. Piezometers were used for sampling of groundwater and The mixing ratios obtained with strontium in groundwater revealed a second source of groundwater contamination such as fertilizers having $^{87}Sr/^{86}Sr$ of 0.707859. Pb isotopic ratios

($^{206}\text{Pb}/^{207}\text{Pb}$) (Vilomet et al., 2003) and Tritium isotopes (Castañeda et al., 2012) were also used for the same purpose.

Heaton et al. (2005) determined the changes in N speciation and defined redox conditions in a leachate plume by using the data for isotope ratios ($^{15}\text{N}/^{14}\text{N}$, $^{13}\text{C}/^{12}\text{C}$ and $^{34}\text{S}/^{32}\text{S}$) and dissolved gas (N_2 , Ar, O_2 and CH_4) concentrations. Groundwater was sampled in and around a landfill site in Cambridgeshire, England. They analysed the dissolved gases for determining these isotopic ratios. The CO_2 gas was collected by using cryogenic trap cooled with dry ice and liquid N_2 and was analysed for $^{13}\text{C}/^{12}\text{C}$ ratios. The other gases such as N_2 , O_2 , Ar and CH_4 , were collected on activated charcoal cooled in liquid N_2 . Gas yield and their proportions were measured by capacitance manometer and mass spectrometry respectively. $^{15}\text{N}/^{14}\text{N}$, $^{13}\text{C}/^{12}\text{C}$ and $^{34}\text{S}/^{32}\text{S}$ ratios were determined in VG SIRA, VG Optima, and Finnigan Delta isotope ratio mass spectrometers. In addition to identifying zones of methanogenesis and SO_4^- reduction, the analysis of the data indicated processes of NH_4^+ transformation by either assimilation or oxidation, and losses by formation of N_2 i.e. nitrification & denitrification in a system where there are abrupt temporal and spatial changes in redox conditions (Heaton et al., 2005). Bacterially mediated methanogenesis in municipal solid waste landfills cause an enrichment of carbon stable isotope ratios of dissolved inorganic carbon and hydrogen stable isotope ratios of water in landfill leachate

3.2.3 Electromagnetic methods

Over the past couple of decades, electromagnetic methods including the resistivity cone penetration test (RCPT), geophysical exploration such as ground penetrating radar (GPR) and time domain reflectometry (TDR) have been proposed and developed as potential alternatives to conventional methods of on-site sampling and laboratory analysis (Atekwana et al., 2000; Börner et al., 1993; Campanella and Weemees, 1990; Francisca and Glatstein, 2010; Fukue et al., 2001; Lindsay et al., 2002; Oh et al., 2008; Pettersson and Nobes, 2003; Redman, 2009; Samouëlian et al., 2005). GPR is one of the most widely used techniques and will be discussed here in brief.

The antenna of GPR transmits and receives high-frequency electromagnetic energy and its reflections into the subsurface. The transmitted energy reflects at a boundary with sufficient contrast in dielectric permittivity and the amplitude of such reflection depends on the size of change in dielectric permittivity across the boundary and proximity of the boundary to the surface (Figure 4a). The resulting data are presented as a plot, or trace, of amplitude versus two-way travel-time (TWT), so that a reflection from a boundary is located on the trace at the time taken for the energy to travel to the boundary and back again (Figure 4b) (Redman, 2009).

Pettersson and Nobes (2003) used a Sensors and Software pulse EKKO™ 100 radar unit with 200-MHz antennas for the GPR surveying of contaminated ground at Antarctic research bases. Readings were taken at 20-cm intervals along straight lines with a time window of 300 ns, and traces were stacked 16 times to enhance the signal-to-noise ratio. Atekwana et al. (2000) conducted GPR surveys at the Crystal Refinery located in Carson City, MI constructed in the 1930s releasing hydrocarbons into the subsurface from tanks and pipeline leaks using

Geophysical Survey Systems, (GSSI) SIR-10A equipment with a 300 MHz bistatic antenna. A three-scan moving average filter was applied to the data resulting in slight horizontal smoothing. The GPR study identified three distinct layers; (i) regions of low apparent resistivity, coinciding with attenuated GPR reflections, (ii) a central region of high apparent resistivity/Low conductivities with bright GPR reflections below the water table and (iii) an upper GPR reflector subparallel to the water table, approximately a few meters above the current free product level and coincident with the top of an oil-stained, light-gray sand layer (Atekwana et al., 2000).

Splajt et al. (2003) investigated the utility of GPR and reflectance spectroscopy for monitoring landfill sites and found strong correlations between red edge inflection position, chlorophyll and heavy metal concentrations in grassland plant species affected by leachate contaminated soil. Reflectance spectroscopy by using spectroradiometer containing contiguous bands at sufficient spectral resolution over the critical wave range measuring chlorophyll absorption and the red edge (between 650 and 750 nm) was found to identify vegetation affected by leachate-contaminated soil. The GPR data identified points of leachate breakout. An integrated approach using these techniques, combined with field and borehole sampling and contaminant migration modeling may offer cost-effective monitoring of leachate plume migration. Hermozilha et al. (2010) combined 3D GPR and 2D resistivity over a heterogeneous media for obtaining information on landfill structure. They complemented 3D GPR profiling with a constant offset geometry with 2D resistivity imaging using GPS location techniques to overcome lateral resistivity variations arising from complexity and heterogeneity of landfill. The 3D GPR was performed by PulseEcho IV GPR system, using unshielded 100 MHz antennas in 1999 and then by a Ramac system with a 100 MHz shielded antenna in 2005. ReflexW software was used for

the GPR data treatment. Boudreault et al. (2010) obtained GPR profiles with a Ramac CU II system from Mala Geoscience (Mala, Sweden) using 100 MHz center frequency antenna having a vertical resolution of approximately 33 cm and an actual center frequency of 75 MHz. The transmitter and receiver antennae were spaced 1 m using a rigid frame in broadside common offset mode. Data were processed using the REFLEX software from Sandmeier Scientific Software (Karlsruhe, Germany). No gain was given to the signal in order to compare wave amplitude between the reflectivity profiles. The two-way travel time was converted to depth using an average wave velocity of 0.1 m ns^{-1} as determined from the wave diffraction patterns observed in the radar images.

3.2.4 Electrical methods

Geophysical investigation techniques involving electrical conductivity measurements are the most widely researched of all methods due to easy installation with relatively inexpensive electrical components. The landfill leachate plumes usually possess elevated ionic load and enhanced electrical conductivity. So, an aquifer system containing groundwater with a naturally low electrical conductivity, when contaminated with a leachate plume, will result in a bulk electrical conductivity anomaly that is readily detectable using both surface, borehole or cross-borehole electrical resistivity imaging methods (Acworth and Jorstad, 2006).

3.2.4.1 Electrical resistivity and very low frequency electromagnetic induction (VLF-EM)

Benson et al. (1997) conducted electrical resistivity and very low-frequency electromagnetic induction (VLF-EM) surveys at a site of shallow hydrocarbon contamination in Utah County, USA. Water chemistry was analyzed through previously installed monitoring wells to enhance

the interpretation of the geophysical data. The electrical resistivity and VLF data helped map the contaminant plume by generating the vertical cross-sections and contour maps as an area of high interpreted resistivity. Karlık and Kaya (2001) also integrated geophysical methods with soil chemical and hydro-geological methods for investigating groundwater contamination by leachate. They collected qualitative data from direct current (DC) resistivity geo-electrical sounding and fast and inexpensive data from VLF-EM survey. The results of VLF-EM method was expected to have good correlation with those of the DC-resistivity method in which the signature of a contaminant plume is a low resistivity zone, the depth of investigation being approximately the same for both methods. The near-surface bodies or discontinuous areas are more responsive towards galvanic VLF-EM method rather than inductive DC resistivity and thus simultaneous application of these two methods can very well monitor leachate plume migration. Al-Tarazi et al. (2008) conducted VLF-EM measurements in a landfill near Ruseifa city at Jordan with a Geonics EM 16 unit. The transmission from the Russian station (UMS) with a 17.1 kHz and 1 MW power, was used for reliable VLF measurements. They integrated data from previous DC resistivity study with this VLF-EM data for successfully locating shallow and deep leachate plume with resistivity less than 20 Ωm , and mapped anomalous bodies down to 40 m depth. He noticed sign of groundwater contamination resulting in high number of faecal coliform bacteria and the increase in inorganic parameters such as chloride.

3.2.4.2 Electrical resistivity, cross-borehole tomography and depth-discrete groundwater electrical conductivity

Acworth and Jorstad (2006) correlated surface resistivity data with cross-borehole tomography data and depth-discrete groundwater electrical conductivity (Fluid EC) data measured from

bundled piezometers, to create a continuous, high-resolution image of the distribution of the leachate plume. Electrical imaging was done using 2 multi-core cables connected to an ABEM LUND ES464 switching unit slaved to an ABEM SAS4000 Terameter, using the Wenner equispaced electrode configuration. Data were inverted to produce a distribution of true resistivity using the RES2DINV software. A bundled piezometer with sample tubes at vertical spacing varying from 0.5 to 1 m was installed to 15 m depth using hollow stem auger technique. Two 15 m strings of 15 gold-plated electrodes in each of them at 1 m intervals were installed one on either side of the bundled piezometer in a line approximately normal to the groundwater flow direction and 8 m apart. The strings were then addressed with a current source attached to the top electrode (1 m depth) in one bore and a current sink in the top electrode in the second bore. Potential measurements were made between corresponding electrodes at similar depth in the 2 boreholes. The current electrodes were then moved down one position and the process repeated until the base of the hole was reached. Finally, the results of the cross-borehole tomography survey demonstrated a strong correlation with the results of the surface resistivity transects and the groundwater chemistry profiles from the bundled piezometer (Acworth and Jorstad, 2006).

3.2.4.3 Electrode Grids

Applications of electrode grids method in landfill sites essentially rely upon the electrical conductivity of homogeneous mixtures of soil and landfill leachate, insulating properties of the geo-membrane liners and ionic concentration of the pore fluid (Frangos, 1997; White and Barker, 1997). Electrode grid systems cover the entire area beneath a containment unit and can be used to identify releases and track their migration in the subsurface (USEPA, 2004). The whole system structurally consists of grid-net electric circuit, electrical conductivity measuring

sensors adapting two-electrode measurement method, and measuring instruments including connection system, source meter, and data logger. The electric circuit consists of two arrays of parallel armored electric wires arranged orthogonally installed in a sub-layer beneath the landfill liner using simple and durable parts made of high-grade, stainless steel alloy or non-corrosive, liner compatible conductive HDPE, usually installed during the initial construction of the landfill facility. One array of electric wires is installed at a specific interval in parallel while the other array is arranged orthogonally with a same specific interval. Each electrode of two-electrode sensor is connected to each orthogonal wire at intersections of grid-net electric wires. Finally, one end of each electric wire forming the grid-net should be connected by branch wires that lead to a control box of measuring system. The first measurement of electrical conductivity should be performed to obtain the baseline conditions of the site. Then, electrical conductivity data are collected with specific time intervals during operation of containment facilities. The location of contaminant release could be found by searching for deviation points in the distribution of electrical conductivity (Oh et al., 2008).

3.2.4.4 **Electrical resistivity imaging (ERI)**

In this process, artificially generated electric currents are supplied to the soil and the resulting potential difference patterns provide information on the form of subsurface heterogeneities and their electrical properties as shown in Figure 5 (Kearey et al., 2002). The greater the electrical contrast between the soil matrix and heterogeneity, the easier is the detection (Samouëlian et al., 2005). Measurement of electrical resistivity usually requires four electrodes: two electrodes used to inject the current (current electrodes), and two other electrodes used to record the resulting potential difference (potential electrodes). Groundwater contamination can also be monitored,

identified and mapped using an electrical resistivity device (Guérin et al., 2002; Karlik and Kaya, 2001; Samouëlian et al., 2005). Boudreault et al. (2010) performed ERI with a Terrameter SAS 4000 and an ES10-64 switch box with two multiple electrode cables from ABEM (Sundbyberg, Sweden). Two north-south and four west-east ERI profiles were measured. The electrodes were pushed into the fill at a regular interval of 1 m to obtain a sufficiently high resolution and a depth of investigation of about 5 m. A dipole–dipole configuration was used to improve the horizontal sensitivity of the method since the typical urban fill composition has a large short-scale lateral variability. Robust inversion (with a convergence limit fixed at 1%) of the measured data was done using the RES2DINV software from Geotomo Software (Boudreault et al., 2010).

3.2.5 Monitoring the fate of dissolved organic matter (DOM) in landfill leachate

Persson et al. (2006) characterized DOM along a groundwater gradient to understand its interaction with pollutants, such as molecular weight distribution and aromaticity. Groundwater samples were collected downstream from an old municipal landfill in Vejen, Denmark through preinstalled Teflon tubes lowered into nitrogen purged iron pipes. The mass spectrometric analysis of the DOM was carried out on a Micromass Quattro II tandem mass spectrometer (Manchester, UK), with an electrospray interface, used in the negative ion mode. Estimations of molecular weight distributions were performed by electrospray ionisation mass spectrometry (ESI-MS) and size exclusion chromatography (SEC). SEC by Waters Ultrahydrogel 250 column, a Waters model 2690 LC-pump and a UV-detector at 254 nm was carried out to separate molecules according to their size rather than their molecular weight. Mass spectrometric results indicated that in the middle of the gradient, the molecular weight and aromaticity of DOM decreased to a minimum value while polydispersity increased. However, the aromaticity

increased to a higher value at the end of the gradient. The molecular weight distribution of DOM in the groundwater samples as measured with SEC resulted in the same pattern as the mass spectrometric analysis, showing decreasing molecular weight with increasing distance from the landfill which can be seen as a process where the DOM gradually becomes more similar to groundwater fulvic acids (Persson et al., 2006).

Humic substances containing ionizable functional groups such as carboxylic and phenolic groups exhibit strong affinities toward metal ions (Hernández et al., 2006; Terbouche et al., 2010).

Research on metal binding properties of DOM in the leachate from MSW landfill is lacking. Wu et al. (2011) utilized fluorescence excitation-emission matrix (EEM) spectroscopy to characterize the binding phenomenon of DOM with MSW leachate. EEM is a simple, sensitive, non-destructive technique providing insights into molecular structure of DOM. In combination with a quenching method, EEM spectroscopy can elucidate the binding properties of metal ions with DOM (Plaza et al., 2006a, b). However, due to various types of overlapping fluorophores, the EEM spectra of in situ DOM cannot be easily identified (Henderson et al., 2009). So, a multivariate chemometric method namely, parallel factor (PARAFAC) analysis, may be used for decomposing fluorescence EEMs into different independent groups of fluorescent components, which can then reduce the interference among fluorescent compounds allowing a more accurate quantification (Engelen et al., 2009). In a recent study, nine leachate samples from various stages in MSW management were collected and then titrated using four heavy metals (Cu, Pb, Zn and Cd) as fluorescent quenching agents. Four components with characteristic peaks at Ex/Em of (240, 330)/412, (250, 300, 360)/458, (230, 280)/340 and 220/432, were identified by the DOMFluor-PARAFAC model. The results suggested that all the fluorescence EEMs could be

successfully decomposed by PARAFAC analysis into a four-component model, despite the dissimilar fluorescence characteristics of the nine leachate samples and the different quenching effects of different metals at various concentrations. The combination of EEM quenching and PARAFAC was found to be a useful indicator to assess the potential ability of heavy metal binding and migration through landfill leachate (Wu et al., 2011).

4 Environmental impact of landfill leachate and its assessment

Leachate is the main toxic compound released from sanitary landfill into the environment, characterized by high concentrations of numerous toxic and carcinogenic chemicals including heavy metals and organic matter (Halim et al., 2005). In addition to these chemical mixtures, the leachates can be contaminated with bacteria, including aerobic, psychrophilic and mesophilic bacteria, faecal coliforms, and spore-forming-bacteria, including *Clostridium perfringens* (Matejczyk et al., 2011). It takes only a small amount of landfill leachate to contaminate large volume of groundwater, which in turn can contaminate and affect biodiversity and enter the food chains (Bakare et al., 2007; Garaj-Vrhovac et al., 2009). Multiple chemical exposures may also pose a higher risk than a single substance. The genotoxic potential of leachates have been confirmed by several researchers who reported a significant increase in frequencies of micronuclei, DNA disturbances, sister chromosomal aberrations, chromatid exchanges and also cut-downs of mitotic indexes in different cell types and model systems (Bakare et al., 2005; Gajski et al., 2011; Gajski et al., 2012). Different environmental impacts by leachate are being discussed in the following paragraphs.

4.1 Environmental impact

4.1.1 Effects on groundwater

Several researchers (Godson and Moore, 1995; Heron et al., 1998; Kerndorff et al., 1992; Lee and Jones-Lee, 1993; Massing, 1994; Mato, 1999; Mikac et al., 1998; Riediker et al., 2000) have repeatedly mentioned about the environmental impact of the landfill leachate, particularly on groundwater quality, regardless of an ideal site selection and a monitoring network design of the landfill. The danger of leachate infiltration in groundwater is great considering that even the best liner and leachate collection systems will ultimately fail due to natural deterioration (Needham et al., 2006; Ouhaldi et al., 2006a, b). In addition, the infiltration of leachate may cause the variation of groundwater pH and Eh (Rapti-Caputo and Vaccaro, 2006), inducing a metal dissolution from the subsoil matrix (Prechtai et al., 2008) into the groundwater, even when the leachate itself is not highly polluted (Kumar and Alappat, 2005; Vadillo et al., 2005). The presence of organic matter and the modification of pH and redox conditions of the aqueous phase of the soil may extract a wide number of metals, by the dissolution of several mineral species (Barona et al., 2001; Martinez, 2000; Peters, 1999; Voegelin et al., 2003; Xiaoli et al., 2007). Risk assessments and environmental regulations for polluted soils are therefore based on batch extractions of metals, assuming that the results are related to the risk of metal leaching into ground water or plant uptake (Voegelin et al., 2003). Groundwater quality monitoring systems being the main indicator to determine the likelihood, and severity of contamination problems, is of great importance in the overall design of a landfill.

Van Duijvenbooden and Kooper (1981) investigated the effects of a waste disposal site on the groundwater flow and groundwater quality in the Netherlands. Measurement of electrical resistivity and an electromagnetic investigation revealed intrusion of a very large vertical flow component of landfill plume in the fresh water - salt water boundary at about 40 m depth. However, local flow patterns indicated an all-sided migration of pollutants into the aquifer (Van Duijvenbooden and Kooper, 1981). The leachate from the Ano Liosia landfill in Greece was found to contain high levels of colour, conductivity, TS, COD, $\text{NH}_3\text{-N}$, PO_4^{3-} , SO_4^{2-} , Cl^- , K^+ , Fe and Pb. The low BOD/COD ratio (0.096–0.195), confirmed that the majority of this organic matter was not easily biodegradable. The sites nearest to the landfill were most polluted, indicating pollution transfer and the leachate movement through fractures or karstic cavities, geological and hydrological characteristics of the area under study (Fatta et al., 1999). Mor et al. (2006) measured concentration of various physico-chemical parameters including heavy metal and microbiological parameters in groundwater and leachate samples from Gazipur landfill site near Delhi. The groundwater was found to contain moderately high concentrations of Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Phenol, Fe, Zn and COD indicating leachate percolation. Interestingly the water contamination dropped fast with depth up to 30m and further percolation of viscous leachate became gentler probably due to the hindrance from the solid soil matter (Mor et al., 2006).

Rapti-Caputo and Vaccaro (2006) performed hydrogeological and geochemical monitoring of two principal aquifer systems, one unconfined, and another confined at 17m depth, below the landfill of Sant'Agostino in Italy. In the shallower unconfined aquifer, the existence of high concentration values of K, Na, Cl^- and SO_4^{2-} and heavy metals such as Cr, Ni, Co, Mo and Sr were found along the flow direction. pH values between 7.16 and 7.9 and redox potential

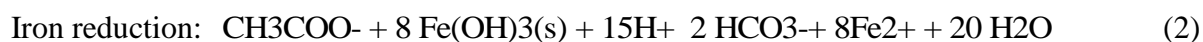
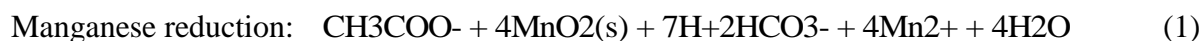
between -17 and -35 mV indicated the occurrence of basic water in a reducing environment favouring the adsorption of ionic substances in soil. The deeper confined aquifer had higher concentrations of NH_4^+ , Cl^- , Pb, Cu and Zn than that in the regional aquifer indicating local diffusion from leachate (Rapti-Caputo and Vaccaro, 2006).

4.1.2 Reduction of soil permeability and modification of soil

Field observations, such as the ponding of leachate at landfills (Nelson, 1995) suggest that some of the unlined landfills underwent significant reductions in hydraulic conductivity. Other laboratory and field observations also show that soils can undergo significant reduction in hydraulic conductivity during leachate permeation (Cartwright et al., 1977; Yanful et al., 1988), even leading to clogging of leachate collection systems (Brune et al., 1994; Rowe et al., 1997). Reductions in the soils' hydraulic conductivity have been linked to the formation of continuous biofilms (Rowe et al., 1997; Taylor and Jaffé, 1990) or presence of discontinuous microbial aggregates in soil pores (Vandevivere and Baveye, 1992), metal precipitation (Rowe et al., 1997), and gas production by denitrifiers and methanogens (deLozada et al., 1994; Islam and Singhal, 2004; Taylor and Jaffé, 1990). However, the relative significance of these mechanisms in controlling the extent of clogging and the dynamics of microbial-metal precipitation interactions is not yet properly researched.

Continuous flow experiments were conducted by Islam and Singhal (2004) using sand-packed columns for investigating the relative significance of bacterial growth, metal precipitation, and anaerobic gas formation on biologically induced clogging of soils. Natural leachate from a local municipal landfill was amended with acetic acid and then was fed to two sand-packed columns.

Based on observed transformations the following microbial reactions are assumed to occur in the columns in presence of acetic acid:



Changes in the observed concentrations of dissolved acetic acid, sulfate, Fe(II), and Mn(II) with time suggest that methanogenesis and the reduction of manganese, iron, and sulfate occur simultaneously. Several physical, geochemical, and biological interactions were observed during leachate transport in soils resulting in a reduction of its permeability. An increase in the substrate concentration resulted in rapidly increasing pH, inorganic carbon (total dissolved carbonate), and attached biomass at the column inlet, leading to enhanced precipitation of Fe^{2+} , Mn^{2+} , and Ca^{2+} at the column inlet thereby decreasing the hydraulic conductivity from an initial value of 8.8×10^{-3} to $3.6 \times 10^{-5} \text{ cm s}^{-1}$. However, mathematical modeling showed that bioaccumulation and gas formation played more significant role in reducing hydraulic conductivity, while metal precipitation had a negligible effect (Islam and Singhal, 2004). In another simulation work by the same researchers, it was deduced that higher substrate concentrations may increase the extent of the zone of reduced hydraulic conductivity, but may not lead to further decreasing the conductivity. Also, finer-grained soils are likely to experience higher conductivity reductions than larger-grained soils (Singhal and Islam, 2008).

The percolation of landfill leachate even in absence of a high concentration of a specific pollutant may induce a strong modification of soil chemical and physical characteristics due to the alteration of the natural equilibrium between the aqueous phase and the soil matrix. As a result, a huge amount of cations can be solubilised, thus inducing groundwater pollution. Di Palma and Mecozzi (2010) performed batch and column experiments for studying metal mobilization from a soil sampled down gradient of a municipal waste landfill in Northern Italy at different pH and Eh. At first, the column was washed with distilled water and then a groundwater, sampled down-gradient in the same site, was used for column leaching. The concentrations of Fe, Mn, and Ni were evaluated when the pH & Eh were altered. Results indicated a greater release when acidic conditions were achieved, a positive effect in this case of the addition of an oxidant and a great Mn mobilization when negative redox potentials were established. The effect of the addition of oxidant or reductant solutions on soil characteristics modification during a remediation treatment involving the percolation of an aqueous solution was investigated. In the case of a pH lowering, the addition of an oxidant such as H_2O_2 proved to be effective in decreasing metal dissolution, and could also have a positive effect on aerobic biological degradation reactions. Conversely, the addition of a reductant, such as dithionite, strongly enhanced Ni and, mainly, Mn mobilization, even under alkaline conditions (Di Palma and Mecozzi, 2010).

Chen and Chynoweth (1995) calculated hydraulic conductivities of dry municipal solid waste (MSW) samples by compacting them in plexiglas columns which were set-up as constant head permeameters to densities of 160, 320 and 480 kg m^{-3} . Water flowed continuously through the columns under hydraulic gradients of $2\text{--}4.0 \text{ m m}^{-1}$. Darcy's equation was used to calculate

hydraulic conductivity which was found to be time-dependent. The temporal variation was attributed to varying degrees of saturation due to gas formation and relative movement of fine particles in the columns. The average hydraulic conductivities at 160, 320 and 480 kg m⁻³ were found to be 9.6×10^{-2} , 7.3×10^{-4} and 4.7×10^{-5} cm s⁻¹, respectively. Francisca and Glatstein (2010) deduced that physicochemical interactions such as changes in the double-layer thickness and chemical precipitation of carbonates had negligible effect on the hydraulic conductivity of highly compacted silt–bentonite mixtures. However, bioclogging due to accumulated biomass from bacteria and yeast significantly reduced the hydraulic conductivity and blocked up the soil pores. The experimental data confirmed the biofilm formation .

Wu et al. (2012) measured water retention curves (WRC) of MSW using pressure plate method representing the shallow, middle, and deep layers of the landfill and the WRC was found to be well-reproduced by the van Genuchten–Mualem model, which was then used to predict the unsaturated hydraulic properties of MSW, such as water retention characteristics and unsaturated hydraulic conductivity. With the increase in the landfill depth and age, the overburden pressure, the highly decomposed organic matter and finer pore space increased, hence the capillary pressure increased causing increases in air-entry values, field capacity and residual water content. Steepness of WRC and saturated water content decreased. The unsaturated hydraulic properties of MSW showed more silt loam-like properties as the age and depth increased (Wu et al., 2012).

4.1.3 Effects on surface water

Yusof et al. (2009) studied the impact of landfill leachate from three different types of landfills, namely active uncontrolled, active controlled and closed controlled, were characterized, and their relationships on the river water chemistry. The organic contents in the closed or older landfills were found to be lower than in the active landfill. Moreover, the higher BOD/COD (0.67) in the active controlled landfill indicated it to be in the acetogenic phase. Conversely, the lower BOD/COD (0.16) shown by both the active uncontrolled and the closed controlled landfills is a typical characteristic of the methanogenic phase of an old landfill (Calli et al., 2005; Fan et al., 2006). The impact of leachate from an active uncontrolled landfill was the highest, as the organic content, $\text{NH}_4\text{-N}$, Cd and Mn levels appeared high in the river. At the same time, influences of leachate were also observed from both types of controlled landfills in the form of inorganic nitrogen ($\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$) and heavy metals (Fe, Cr, Ni and Mn). Improper treatment practice led to high levels of some contaminants in the stream near the closed controlled landfill. Meanwhile, the active controlled landfill, which was located near the coastline, was exposed to the risk of contamination resulting from the pyrite oxidation of the surrounding area (Yusof et al., 2009).

4.2 Hazard assessment of landfill leachate

Numerous models and approaches ranging from deterministic water balance analyses such as Hydrologic Evaluation of Landfill Performance (HELP) (Schroeder et al., 1994) and Flow Investigation of Landfill Leachate (FILL) (Khanbilvardi et al., 1995) and stochastic simulation models such as LandSim (GolderAssociates, 1996) and EPA's Composite Model for Leachate

Migration with Transformation Products (EPACMTP) (USEPA, 2003) to relative hazard assessment systems for evaluating landfill hazards have been developed. Each one of these models and approaches has some advantages and disadvantages. While deterministic and stochastic models need large amounts of data, involve complex analytical procedures and thus are time consuming, relative hazard assessment systems, often referred to as hazard rating/ranking systems, suffer from the subjectivity involved in their scoring methodologies. However, considering their simplicity, such relative hazard assessment systems are considered to be more suitable when only a comparative assessment as in the case of priority setting, is the objective.

4.2.1 Relative hazard assessment systems

In order to comply with the legislations regarding the management of municipal solid waste, it is necessary to undertake a diagnosis and characterisation of the landfill impacted areas in order to develop an adequate action plan. However, the remedial and preventive measures cannot be undertaken at all the existing closed and active landfill sites because of financial constraints. So, a gradual approach is needed based on a system of prioritization of actions to establish which landfills need immediate attention for the remediation works. In most cases, the diagnostic methods made it possible to compare landfills on an environmental basis, but not to take decisions about their control, closure, capping, or recovery. All of the assessments were related to the release point, without taking into account the characteristics of their environment (Calvo, 2003).

A number of relative hazard assessment systems for waste disposal sites have been developed over the past three decades and reported in literature (Singh et al., 2009). Usually, three hazard

modes are used to evaluate the waste sites: 1. migration of pollutants away from the site via groundwater, surface water, or air routes, or a combination thereof, 2. fire and explosion potential, and 3. direct contact with hazardous substances. In most of the systems, site ranking is based either on the combined score for various routes under migration mode or the score for the dominant route *i.e.* the route returning highest score. In course of calculating site hazard, more information is considered by a system, more accurate is the assessment and evaluation. However, more data signifies increased complexity, cost, time and chances of error. This reduces the acceptability of a system among users who always want maximum output with minimum inputs. Some parameters can be termed as simple parameters that can be determined without any complex analytical methods such as by site walkover, visual survey, local inhabitant survey, regional maps of groundwater, soil type, geology etc. The parameters which are difficult to collect e.g. by field drilling and sampling as well as laboratory testing are considered as complex parameters. More number of complex parameters in a system reduces its user friendliness. Table 4 lists the number of parameters considered by different hazard rating systems. In this subsection, we will discuss mainly four significant hazard rating systems.

4.2.1.1 Leachate Pollution Index (LPI) Method

Kumar and Alappat (2005) discussed about LPI, a quantitative tool having an increasing scale index based on Delphi technique (Dalkey, 1969), for calculating the leachate pollution data of landfill sites. In this method, 18 leachate pollutants (e.g. pH, TDS, BOD, COD, heavy metals, phenolic compounds, chlorides, total coliform) were selected for inclusion in the index and were awarded some significance and pollution weight, that added up to 1.00 for the 18 pollutants.

The LPI can be calculated using the equation:
$$LPI = \sum_{i=1}^n w_i p_i \quad (5)$$

Where, LPI = the weighted additive leachate pollution index, w_i = the weight for the i th pollutant variable, p_i = the sub index score of the i th leachate pollutant variable, n = number of leachate pollutant variables used in calculating LPI and $\sum_{i=1}^n w_i = 1$. However, when the data for all the leachate pollutant variables included in LPI are not available, the LPI can be calculated using the concentration of the available leachate pollutants. In that case, the LPI can be calculated by the equation:

$$LPI = \frac{\sum_{i=1}^m w_i p_i}{\sum_{i=1}^m w_i} \quad (6)$$

where m is the number of leachate pollutant parameters for which data is available.

The procedure for calculating LPI for a given landfill site at a given time involves the following three steps: Firstly, testing of the 18 leachate pollutants, secondly, calculating sub-index values (p) based on the concentration of the leachate pollutants obtained during the tests and lastly, aggregation of sub-index values obtained for all the parameters by multiplying it with the respective weights assigned to each parameter. For the last step, the above two equations are used depending upon the situation. High value of LPI indicates higher contamination potential (Kumar and Alappat, 2005).

4.2.1.2 Global Environment–Landfill Interaction Index or Impact Index (E–LI)

Calvo et al. (2005) studied a new methodology for environmental diagnosis of landfill sites. This methodology was based on the formulation of a general index called Global Environment–Landfill Interaction Index or Impact Index (E–LI). In order to calculate this index, some aspects in each landfill have to be analysed viz, environmental interaction between the release point and certain affected environmental parameters, environmental values of the surface water, groundwater, atmosphere, soil and health and operational conditions of the landfill from the point of view of environment. The rate expression is as follows:

$$E-LI = \sum E-LI_i = \sum (ERI_i \times EWC_i) = (ERI_{\text{groundwater}} \times EWC_{\text{groundwater}}) + (ERI_{\text{surfacewater}} \times EWC_{\text{surfacewater}}) + (ERI_{\text{atmosphere}} \times EWC_{\text{atmosphere}}) + (ERI_{\text{soil}} \times EWC_{\text{soil}}) + (ERI_{\text{health}} \times EWC_{\text{health}}) \quad (7)$$

where

E–LI = Global Environment–Landfill Interaction Index or Impact Index

E–LI_{*i*} = the Environmental–Landfill Interaction Index for parameter *i*

i = the parameters: groundwater, surface water, atmosphere, soil, and health

EWC_{*i*} = the Environmental Weighting Coefficient

ERI_{*i*} = the Environmental Risk Index for the Environmental Effect of parameter *i*

Ranges of scores are obtained for E–LI to classify the overall environmental impact of landfills as low (0-35), average (31-70) and high (71-105). The ERI aims to gauge the potential for environmental impact for each observed parameter, reflecting whether or not interaction exists between the processes in the release point and the characteristics of the environment.

The E-LI determines the state of potential landfill impact on the landfill's own environment. Focusing on the study of each landfill individually, the ERI enables us to determine which parameters are most affected by the landfill, making it easier to prioritize suitable control actions. Analysis of index results provides information about the suitability of the release-point locations on the basis of which, it would be possible to draw up action plans for the remediation or closure of the landfill site (Calvo et al., 2005).

4.2.1.3 Hazard rating system by Singh et al. (2009)

Singh et al. (2009) assessed existing site hazard rating systems and came up with a new groundwater contamination hazard rating system for landfills. The proposed system was based on source-pathway-receptor relationships and evaluated different sites relative to one another by the Delphi technique (Dalkey, 1969). The proposed system is more sensitive to the type of waste and exhibited greater sensitivity to varied site conditions. In this system, 15 parameters are studied as depicted in Figure 6. Each of them is assigned a best and worst value. The overall groundwater contamination hazard rating of a waste disposal site was obtained by the following relationship:

$$HR_{GW} = (H_S \times H_P \times H_R) / SF \times 1000 \quad (8)$$

where H_S , H_P and H_R were the source hazard rating, pathway hazard rating and receptor hazard rating, respectively; and SF is a scaling factor (equal to 1,000,000). The scaling factor is equal to the product of the source, pathway, and receptor hazard ratings of a waste disposal site having all its parameters at the worst values. The overall hazard score obtained from the Equation 8 is limited to a maximum of 1000 for MSW landfills, 5000 for HW landfills, and 200 for C&D

waste landfills. The application of different systems to six old municipal solid waste landfills showed that whereas the existing systems produced clustered scores, the proposed system produced significantly differing scores for all the six landfills improving decision making in site ranking (Singh et al., 2009).

4.2.1.4 Assessment of Toxicity Index

Baderna et al. (2011) also proposed an integrated strategy to evaluate the toxicity of the leachate using chemical analyses, risk assessment guidelines and *in vitro* assays using the hepatoma HepG2 cells as a model. Human risk assessment was done based on chronic daily intake (CDI (mg kg⁻¹ day)) for each compound, which was calculated using the formula:

$$CDI = [(C_{\text{water}} \times WI \times ED \times EF) / (BW \times AT)] \quad (9)$$

where C_{water} =pollutant's concentration in water; WI=water intake=2 L day⁻¹; ED=exposure duration=30 years; EF=exposure frequency=350 days year⁻¹; BW=body weight of the target=70 kg (adult); AT=exposure average time: 30 years for non-carcinogenic compounds, 70 years (lifetime) for carcinogenic compounds.

The hazard index (HI) was calculated for each compound in order to estimate possible toxic effects on humans due to the ingestion of leachate-contaminated water, using the formula:

$$HI = CDI/RfD \quad (10)$$

where HI is the hazard index, CDI the calculated chronic daily intake, RfD the reference dose for the selected compounds (mg kg⁻¹ day). The RfD is a numerical estimate of a daily oral exposure

to the human population, including sensitive subgroups such as children, that is not likely to cause harmful effects during a lifetime (USEPA, 2006).

The assessment of carcinogenic effects was calculated using the cancer risk equation:

$$CR = CDI \times SF \quad (11)$$

where CR is the cancer risk, SF the slope factors (kg day mg^{-1}): an upper-bound estimate of risk per increment of dose that can be used to estimate risk probabilities for different exposure levels (USEPA, 2005).

The ecological risk assessment was based on the dilution scenario used for human risk assessment. For risk analysis we used traditional risk procedures focused on the Hazard Quotient defined as follows:

$$HQ = PEC / PNEC \quad (12)$$

where PEC is the predicted environmental concentration (resulting from chemical analysis) and PNEC the predicted no-effect concentration. The evidences from *in vitro* studies on HepG2 suggested that leachate inhibited cell proliferation at low doses probably inducing a reversible cell-cycle arrest that becomes irreversible at high doses. This study confirmed the hypothesis that cells that survive the initial insult from leachate constituents maintains the potential to proliferate until the effects on cell metabolism lead to death (Baderna et al., 2011).

4.2.2 Deterministic and stochastic models for monitoring environmental impact of landfill leachate

Mathematical models are powerful predictive tools to address issues related to landfill leachate management. However, inadequate and wrong field data and insufficient understanding of the complex physico-chemical and biochemical reactions going on in the landfill limit the predictive capabilities of these mathematical models. So, these models are advised to use for an educated guesswork and to evaluate the relative importance of selected variables for management purpose. Numerous mathematical models have been developed since 1980s to simulate the generation and transport of leachate in landfills (El-Fadel et al., 1996, 1997; Suk et al., 2000). A detailed review on pre-1995 models was done by El-Fadel et al. (1997). However, these models have their own disadvantages as a whole (Scott et al., 2005).

4.2.2.1 Assessing the reduction in hydraulic conductivity

Islam and Singhal (2004) came up with a simple mathematical model to assess the total reduction in hydraulic conductivity in a landfill. It was expressed in terms of the fractional reduction due to biomass accumulation, metal precipitation, and gas formation, as follows:

$$\text{Total reduction} = 1 - k(t)/k_0 = 1 - (1 - (f(x) + g(m)))(1 - h(g)) \quad (13)$$

where, $f(x)$, $g(m)$, and $h(g)$ are functions for fractional reduction in hydraulic conductivity due to bioaccumulation, metal precipitation, and gas formation, respectively, k_0 is the initial soil permeability (L^2), and $k(t)$ is the soil permeability at time t . The term $(1-(f(x)+g(m)))$ represents

the fraction of the initial intrinsic permeability remaining, and $(1-h(g))$ acts similarly to the relative permeability function in representing the effect of gas flow on soil permeability.

The impact of biomass accumulation on the permeability was described using a simple permeability reduction model proposed by Clement et al. (1996), as follows

$$f(x) = 1 - (1 - n_s/n_0)^{19/6} \quad (14)$$

where $n_s (=X^s \rho_k / \rho_s)$ is the volume fraction of the soil-attached biomass (L^3 biomass L^{-3} total), n_0 is the initial soil porosity, X^s is the microbial mass per unit mass of aquifer solids ($M M^{-1}$), ρ_k is the bulk density of aquifer solids ($M L^{-3}$), and ρ_s is the biomass density ($M L^{-3}$). The biomass density was estimated as 70 mg-volatile solids cm^{-3} (Cooke et al., 1999). Assuming that approximately 50% of the cellular carbon is protein the biomass density is estimated as 35 mg-protein cm^{-3} . The study suggested that stimulation of anaerobic activity at the base of landfills might lead to creation of impermeable barriers and pore clogging of leachate collection systems (Islam and Singhal, 2004).

Yıldız et al. (2004) developed a mathematical model to simulate landfill leachate behavior and its distribution throughout the landfill, taking into consideration the hydraulic characteristics of waste and composition of leachate. The model incorporated governing equations describing processes taking place during the stabilization of wastes, including leachate flow, dissolution, acidogenesis and methanogenesis. To model the hydraulic property changes occurring during the development stage of the landfills, a conceptual modeling approach was proposed. This approach considered the landfill to consist of columns of cells having several layers. Each layer was

assumed to be a completely mixed reactor containing uniformly distributed solid waste, moisture, gases and micro-organisms.

4.2.2.2 Assessment of degradation products of landfill leachate components

Butt et al. (2008) reviewed the advantages and shortcomings of various risk assessment techniques related to landfill leachate contamination. Also, Butt and Oduyemi (2003) briefly outlined a holistic procedure for the concentration assessment of the contaminants and a computer model for the risk assessment of landfill leachate (Butt et al., 2008; Butt and Oduyemi, 2003). Reinhart et al. (1991) used a mathematical mass transport model, the Vadose Zone Interactive Processes model to describe the fate of organic compounds in sanitary landfills. The model was used to solve a convective-dispersive equation incorporating the transport and transformation processes of dispersion, advection, chemical and biological transformation, and sorption in unsaturated porous media. The model was optimized using input data from laboratory column operations and the physical/chemical phenomena from the field and it predicted low mobility of hydrophobic compounds and high mobility of more hydrophilic compounds in the landfill. Gau and Chow (1998) investigated the characteristics of landfills using different kinds of waste combinations. COD concentrations of leachate from semiaerobic and anaerobic landfills were processed by using a numerical method to get a simulation model for the estimation of variations in the organic pollutants in the leachate. The degradation of the leachate quality was approximately similar for both types of landfills .

4.2.2.3 Mathematical simulation and long-term monitoring of leachate components

Ozkaya et al. (2006) simulated the refuse age and leachate components spread out using a mathematical formula in cells with and without leachate recirculation (C1 & C2 respectively). The leachate from Odayeri Sanitary Landfill, Istanbul, Turkey was monitored for 920 days by for the sulfate (SO_4^{2-}), chloride (Cl^-), COD and BOD. The relationship between these parameters and refuse age was simulated by a non-linear exponential function:

$$y=a_0+a_1e^{-t}+a_2te^{-t} \quad (15)$$

where a_0 , a_1 and a_2 are unknown constants of the function, the a_0 constant is residual concentration and y is pollutant concentration at time t as g L^{-1} and t is refuse age as months. This model could predict reaching rate to the peak value of pollutant concentration to ensure optimization of leachate treatment. Constants in the non-linear equation were solved by the least squares method, minimizing the total square deviations from the model of the experimental data, using a MATLAB 7.0 computer program. A good fit was obtained between the measured data and model simulations. The results showed that there appeared to be little improvement in leachate quality by leachate recirculation in terms of COD and BOD values, however, it was determined that the pollution loads more rapidly reached minimum values within the C2 test cell (Ozkaya et al., 2006)

4.2.2.4 Reliability assessment of groundwater monitoring networks at landfill sites

Monitoring well networks at the landfill sites can be used for detecting leakage plumes. Yenigül et al. assessed the reliability of groundwater monitoring systems at landfill sites through a hypothetical problem where the detection probability of several monitoring systems was

compared by a simulation-based model. A Monte–Carlo approach was used to simulate a large number of contaminant plumes resulting from the failure of the landfill. A single Monte–Carlo realization consists of the following five steps, namely, (i) Generation of a realization of a random hydraulic conductivity field, (ii) Solution of the steady state groundwater flow model to determine the velocity field, (iii) Generation of a random leak location, (iv) Solution of the random walk transport model to determine the concentration field of the contaminant plume until it reaches the compliance boundary, (v) Check whether the concentration value at a given monitoring well location exceeds a given threshold concentration (detection limit), to determine whether a plume is detected or not detected by the monitoring system.

The movement of contaminants in the subsurface was represented by the advection–dispersion equation (Bear, 1972). The contaminant was assumed to be conservative and to have no interaction with the solid matrix. The two-dimensional advection–dispersion equation for this case can be written as:

$$\frac{\delta C}{\delta t} + v_x \frac{\delta C}{\delta x} + v_y \frac{\delta C}{\delta y} - \frac{\partial \left[D_{xx} \frac{\delta C}{\delta x} + D_{xy} \frac{\delta C}{\delta y} \right]}{\partial x} - \frac{\partial \left[D_{yx} \frac{\delta C}{\delta x} + D_{yy} \frac{\delta C}{\delta y} \right]}{\partial y} = 0 \quad (16)$$

where C is the concentration of the contaminant at time t at location (x,y) , v_x and v_y are average groundwater flow velocity components in the x and y -directions, respectively, and D_{xx} , D_{xy} , D_{yx} , D_{yy} are the components of the hydrodynamic dispersion tensor (Bear, 1972). The analysis revealed the lateral dispersivity of the medium as one of the most significant factor affecting the efficiency of the systems, since it is the primary parameter controlling the size of the plume. It was also concluded that the reliability of the common practice of three down-

gradient monitoring wells is inadequate for prevention of groundwater contamination due to landfills (Yenigül et al., 2005).

4.2.2.5 Computer aided modeling for risk assessment

Hazards can be quantified, simulated and accurate risk analysis can be undertaken by using computational methods and modelling precise systems, leading to a more effective risk management. Butt et al. (2008) discussed about some techniques used in landfill risk assessment. Some computer models and software programme have been described in the Table 5 and their shortcomings have been pointed out.

5 Recent technological developments for landfill leachate treatment and remediation

The knowledge of the impact of landfill leachate on the environment has forced authorities to apply more and more stringent standards for pollution control. In addition, the ever increasing toxic load in MSW has caused the leachate generated in landfills to become more varied and complex in composition and thus difficult to treat. For many years, simple biological and physico-chemical treatments such as aerated lagoons, simple aerobic and anaerobic digesters, advanced oxidation treatments using ozone or Fenton reagents, adsorption using GAC or PAC, chemical and electrical coagulation etc., were considered sufficient for treatment and management of highly concentrated effluents such as landfill leachates. However, it was found that the simple treatments were insufficient to meet the present stricter effluent disposal standards targeted towards complete reduction of the negative impact of landfill leachate on the environment. This implies that new treatment alternatives must be developed. Therefore, in the

last two decades, a host of new technologies based on membrane filtration, electrochemical oxidation and combination of different reagents or technologies have been developed as viable treatment alternative. It was found that integration of age old technologies with advanced treatment processes yielded excellent treatment efficiency in terms of COD, $\text{NH}_4\text{-N}$, heavy metals, TOC, DOM etc., removal (Kjeldsen et al., 2002).

Treatment techniques vary depending on the age of the leachate and on the leachate disposal standards set by the local authorities (Castrillón et al., 2010; Ozturk et al., 2003; Renou et al., 2008a). Reasonable treatment efficiency can be achieved by using biological treatments for the removal of COD, $\text{NH}_3\text{-N}$ and heavy metals in case of young leachates. However, for treating old stabilized leachate having low biodegradability, physico-chemical treatments have been found to be suitable as a refining step for biologically treated leachate. Integrated chemical–physical–biological processes, in any order, negates the drawbacks of individual processes contributing to a higher efficacy of the overall treatment (Bohdziewicz et al., 2001; Lin and Chang, 2000).

Due to the climatic conditions and a combination of various physical, chemical and biological processes occurring in the landfill, the leachate composition can fluctuate over both short and long periods of time. According to Scott et al. (2005) the variation is particularly pronounced in an active landfill. Therefore the leachate treatment system must be flexible enough to produce the same quality effluent despite all the variations (Kochany and Lipczynska-Kochany, 2009). In spite of different views on the leachate treatment, many experts agree that on-site treatment facilities are more suitable both in terms of cost and in terms of efficiency.

Many good reviews on leachate treatment technologies have been published over the years (Alvarez-Vazquez et al., 2004; Deng and Englehardt, 2006; Foo and Hameed, 2009; Kim and

Owens, 2010; Kurniawan et al., 2006b; Laner et al., 2012; Renou et al., 2008a; Wiszniowski et al., 2006). So, this section concentrates only on the recent developments in this area post 2005.

Different leachate treatment techniques have been classified as illustrated in Figure 7.

5.1 Application of natural attenuation for leachate remediation

According to USEPA (1999), the amalgamation of different physical, chemical and biological processes occurring in nature, which can efficiently reduce concentration, toxicity, and/or mobility of contaminants can be defined as natural attenuation. The application of constructed wetlands (CW) for natural treatment of leachate has been practised for many years in different countries with varying degrees of success (Pendleton et al., 2005; Vrhovšek et al., 2000). CWs are mainly of two types, free surface water system and subsurface flow system depending on the nature of wastewater flow. The treatment of wastewater in CWs involves a combination of biological and biochemical processes (Yalcuk and Ugurlu, 2009). The wetlands provide suitable milieu for rapid natural attenuation of organic contaminants due to the presence of large variety of microorganisms, nutrients in the discharging groundwater and a wide range of redox conditions in the surrounding groundwater or surface water interfaces (Lorah et al., 2009; Tobias et al., 2001). Microbial communities present in CWs can break down the complex organic compounds in wastewaters and with age as the microbial population increases in a CW the rate of organic removal increases (Calli et al., 2006). Fluorescence results reveal the predominance of bacteria in CWs, including heterotrophic and autotrophic, which are responsible for BOD₅ removal (Sawattayothin and Polprasert, 2007). However, different treatment plants support

different bacterial populations and even within a given treatment plant significant variations in community profile has been observed.

Phytoremediation is an attractive technology for landfill remediation and according to Kim and Owens (2010), it can stabilize soil while simultaneously remediating landfill leachate. Figure 8 illustrates the interaction between the soil and plant systems for leachate remediation in a CW. Plants influence the redox potential in planted CWs by supplying oxygen to the soil in the root rhizospheric zone. Enhanced nitrification by nitrifying bacteria takes place in this zone, thereby reducing the $\text{NH}_4\text{-N}$ concentration in the landfill leachate (Białowiec et al., 2012b). The amount of oxygen in the rhizosphere shows diurnal and seasonal fluctuations depending upon various factors like photosynthesis, light intensity, stomatal aperture, and temperature (Białowiec et al., 2012a). The plants that are commonly used in CWs are cattail (*Typha latifolia* L.), willow-coppice (*Salix* sp.), poplars, reed (*Phragmites australis* Trin ex Steudel), rush (*Juncus effusus* L.), yellow flag (*Iris pseudacorus* L.), and mannagrass (*Glyceria maxima*) (Białowiec et al., 2007; Duggan, 2005; Rosenqvist and Ness, 2004; Wojciechowska et al., 2009; Wojciechowska and Obarska-Pempkowiak, 2008; Yalcuk and Ugurlu, 2009; Zalesny et al., 2008).

The HM content in leachates from old landfill sites are usually low and do not represent much difficulty in purification procedures (Christensen et al., 2001; Kjeldsen et al., 2002; Long et al., 2009). Different biotic and abiotic processes such as complexation, precipitation, flocculation, adsorption, cation and anion exchange, oxidation and reduction, adsorption, microbial activity and plant uptake are responsible for heavy metal removal in a CW (Kosopolov et al., 2004; Sinan Bilgili et al., 2007; Ujang et al., 2005). The mobility and eco-toxicity of HMs depends on the metal speciation and the fraction of DOM to which it is bound.

CWs show high BOD₅, TN and fecal coliforms (FC) removal efficiency of 91%, 96% and more than 99%, respectively (Bulc, 2006; Mehmood et al., 2009; Sawaitayothin and Polprasert, 2007; Yalcuk and Ugurlu, 2009). Examples of leachate treatment in CWs and the achieved efficiency is tabulated in Table 6. According to Picard et al. (2005) about 98–99% of nitrogen and phosphorus removal may be achieved in a constructed wetland. Irrespective of the microorganism density and the type of plants used, the prevailing weather conditions have significant influence on the treatment capacity of a CW (Akratos and Tsihrintzis, 2007). There are certain drawbacks associated with the land application of leachate as a phytoirrigant, the most important being high nitrogen and salinity loadings. Salinity loading due to leachate irrigation can be managed, by judiciously controlling the leachate application rate and by providing intermittent fresh water irrigation. According to Smesrud et al. (2011) fresh water irrigation can be 30% of the total irrigation water supplied.

5.2 Application of biological and biochemical techniques in reactors

Traditionally, landfill leachates have been treated along with sewage in sewage treatment plants. According to Robinson and Barr (1999), combinations of different biological and physico-chemical treatment methods for landfill leachate treatment, is more efficient than using any single treatment system such as Sequential Batch Reactors (SBR), Upflow Anaerobic Sludge Blanket Reactor (UASB), Anaerobic Digesters, and others. Leachate contains high COD and NH₄-N content and some other noxious substances such as heavy metals which are difficult to be remediated by biological treatments alone (Uygur and Kargi, 2004; Xu et al., 2008).

In the SBR systems, reaction and sludge settling are completed in the same reactor, sequentially (Aziz et al., 2011b). The time dependent character of the process facilitates the alteration of SBR operation cycles in response to variation in waste, which occurs frequently in case of landfill leachate (Laitinen et al., 2006; Trois et al., 2010). According to Klimiuk and Kulikowska (2006), the treatment strategy in SBRs maybe designed as follows: dump filling of wastewater into the SBR over a relatively short period of time, elimination or reduction of aeration and mixing during filling stage and increasing the volumetric exchange ratio. A long sludge age allows the growth of slow growing microorganisms in mixed culture of the activated sludge, which eventually participate in the removal of slow biodegradable substrates. However, for SBRs operated under aerobic conditions short hydraulic retention time is more favourable as long hydraulic retention time can cause reduction in biomass concentration due to cell decay (Klimiuk and Kulikowska, 2006). Many researchers found that the addition of activated carbons like PAC, GAC and biometric fat cells increased the efficiency of SBRs by effectively removing stable hydrophobic organic chemical species from biologically treated landfill leachate (Aziz et al., 2011c; Kargi and Pamukoglu, 2004; Liyan et al., 2009). Neczaj et al. (2007) found that a pretreatment of landfill leachate by sonication increased COD and nitrogen removal efficiency in a SBR.

Di Iaconi et al. (2006) proposed an aerobic Sequencing Batch Biofilter Granular Reactor having high organic removal efficiency of about 80% in terms of COD. Systems with granular biomass are known to have up to 15g L^{-1} biomass concentrations and conversion capacities of 6-7 kg of COD m^{-3} and relatively low sludge production rates (Di Iaconi et al., 2005). This treatment technique was further modified by addition of a pre-treatment step for nitrogen removal by

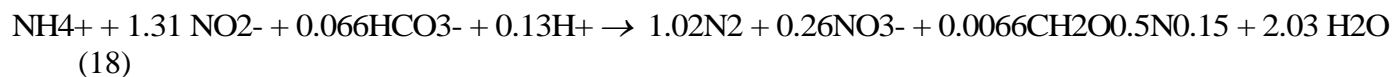
struvite precipitation, and subsequent biological degradation by ozone which increased nitrogen removal efficiency (Di Iaconi et al., 2011). Gálvez et al. (2012) and Gálvez et al. (2006) used submerged biofilter under aerobic and anaerobic conditions for leachate treatment.

Anaerobic digestion is a simple and effective biotechnological process that has been used extensively to treat organic wastes. Anaerobic processes involve the sequential breakdown of complex organic compounds by several effectively interacting metabolic groups of microorganisms (Huang et al., 2003). According to Erses et al. (2008) and Mertoglu et al. (2006), better organics, nitrogen, phosphorous and alkali metal removal is achieved under aerobic condition as compared to anaerobic conditions. Co-digestion of sewage and leachate is an effective leachate treatment option if the leachate is young and the sewage treatment facility is located near the landfill site (Garg and Mishra, 2010). Mixing of leachate and sewage increases the total organic carbon and causes the biogas yield to increase. The biogas yield from the co-fermentation of sewage sludge and intermediate leachate mixture at the ratio of 20:1 is 13% higher than the biogas yield using sludge alone (Montusiewicz and Lebiocka, 2011).

Single-stage mesophilic mixed anaerobic digestion reactor is extensively used for reduction of organic sludge volume from wastewater treatment processes (Song et al., 2004). Kheradmand et al. (2010) combined anaerobic digester under mesophilic condition with an activated sludge unit and achieved 94% and 93% COD reduction at a loading rate of 2.25 g COD L⁻¹d⁻¹ and 3.37 g COD L⁻¹d⁻¹ respectively. The system also achieved heavy metal removal, however ammonia was not removed by the combined system. A schematic diagram of the laboratory scale combined anaerobic and aerobic leachate treatment system is shown in Figure 9.

The Upflow Anaerobic Sludge Blanket (UASB) reactor has been combined with many physical and chemical treatment techniques for obtaining higher removal efficiencies (Bohdziewicz and Kwarciak, 2008; Marañón et al., 2006). Bohdziewicz and Kwarciak (2008) combined UASB with RO while Marañón et al. (2006) effectively combined nitrification–denitrification treatment with UASB reactors to obtain the desired removal standards. The moving-bed biofilm reactor (MBBR) is an effective biological treatment process, which was developed by combining conventional activated sludge process and fluidized-bed reactor (Chen et al., 2008; Loukidou and Zouboulis, 2001). Chen et al. (2008) was able to achieve 92-95% COD removal due to methanogenesis along with 97% NH₄-N removal in an anaerobic MBBR.

Lab-scale anoxic rotating biological contactor is highly effective for the removal of nitrate from a mature landfill leachate and is an example of biological attached growth filter technology (Teixeira and Oliveira, 2000; Wiszniowski et al., 2006). Cortez et al. (2011) was able to achieve almost 100% nitrate nitrogen removal efficiencies without nitrite or nitrous oxide accumulation, however the reactor could not achieve the desired carbon removal standards. In this reactor ammonium is partly converted to nitrite by ammonium oxidizing bacteria and subsequently the heterotrophic denitrifying bacteria uses nitrite as the final electron acceptor and nitrogen gas is released as shown in Equation 17 (Hellinga et al., 1999). In some instances Anammox bacteria converts ammonium and nitrite directly to nitrogen gas as given in Equation 18 (Strous et al., 1998; van Dongen et al., 2001).



Kim et al. (2006) noted that nitrification treatment in a leachate treatment plant was severely affected due to high free ammonia content of leachate. At high pH the free ammonia concentration increases which inhibited nitrite oxidizing and ammonia oxidizing bacteria especially under high $\text{NH}_4\text{-N}$ condition.

The coupling of partial nitrification process with Anammox is a very economical process, however Anammox is not suitable for wastewater with COD and $\text{NH}_4\text{-N}$ ratio greater than one (van Dongen et al., 2001; Xu et al., 2010). Berge et al. (2006) experimented with a completely aerobic nitrification–denitrification bioreactor for $\text{NH}_4\text{-N}$ removal from landfill leachate and found that nitrification–denitrification could occur simultaneously in an aerobic landfill cell, without having two separate anoxic and aerobic cells.

Liang and Liu (2008) combined a partial nitrification reactor, Anammox reactor and two underground soil infiltration systems. The combined system was effective for leachate treatment and worked stably over a long period of time under the experimental conditions. The underground soil infiltration system has low construction and operation expenditure. Due to complex interplay between hydraulic flow and purification processes of filtration, sorption, chemical reactions, biotransformation, predation and plant uptake, significantly higher purification can be attained by the underground soil infiltration systems (Van Cuyk et al., 2001). Underground soil infiltration system is a promising option for advanced treatment of landfill leachate.

Puig et al. (2011) used microbial fuel cells to treat landfill leachate containing 6033 mg L^{-1} of nitrogen and a conductivity of $73,588 \text{ }\mu\text{S cm}^{-1}$, for production of electricity. The microbial fuel cell had an air-cathode and was run over a period of 155 days. The system was able to remove up

to $8.5 \text{ kg m}^{-3} \text{ d}^{-1}$ of biodegradable organic matter and generated 344 mW m^{-3} of electrical energy.

MSW degradation inside a landfill can be enhanced by leachate recirculation as observed by a number of researchers who used recirculation bioreactors for the purpose of leachate treatment (Iglesias et al., 2000; Jiang et al., 2007; Jun et al., 2007; Li et al., 2010a). Jiang et al (2007) made recirculation reactors by packing landfill waste in anaerobic columns, the schematic diagram of which is as shown in Figure 10. In another experiment Li et al., (2010) used eight years old aged refuse excavated from Shanghai Refuse Landfill for leachate treatment. In both the cases excellent organic removal was observed as discussed in Table 7. Han et al. (2011) modified the aged refuse biofilter by making it semi-aerobic. This new semi-aerobic aged refuse biofilter reactor showed superior efficacy for nitrogen removal as compared to other aged refuse biofilter systems. Sometimes the landfills are engineered to act as bioreactor landfills so as to provide a more controlled means of reduction in greenhouse gases and methane migration (Warith, 2002). In bioreactor landfills the stabilization and settlement process of MSW is accelerated by optimizing the conditions for microbial degradation of MSW, this also allows for additional MSW disposal or faster land reuse (Kelly, 2002). In both aerobic and anaerobic bioreactors, leachate recirculation increases the moisture content, distributes nutrients and enzymes between bacteria and the waste, causes pH buffering, dilutes inhibitory compounds, and distributes methanogens (Bilgili et al., 2007; Sponza and Agdag, 2004). However, there are certain disadvantages associated with leachate recirculation such as, too much leachate recirculation can cause ponding, saturation, accumulation of ammonia nitrogen, development of acidic conditions and/or the inhibition of methanogenesis due to the accumulation of volatile

fatty acids (Ledakowicz and Kaczarek, 2002; Reinhart and Al-Yousfi, 1996; San and Onay, 2001; Sponza and Agdag, 2004). Hence, internal leachate characteristic in the solid waste landfill site during recirculation needs to be done by the introduction of monitoring wells (Sormunen et al., 2008). In bioreactor landfills clog formation during leachate recirculation can be effectively controlled by methanogenesis of leachate prior to recirculation (Lozecznik et al., 2010). Khire and Mukherjee (2007) identified the key design variables for leachate recirculation system in a landfill consisting of vertical wells using the finite-element model HYDRUS-2D numerical model.

5.3 Application of physical and chemical processes for leachate treatment

5.3.1 Advance Oxidation Treatments

Advanced oxidation processes (AOPs) is used to enhance the bio-treatability of recalcitrant and/or non-biodegradable organic substances, through the generation of highly reactive chemical species, such as hydroxyl radicals ($\cdot\text{OH}$) (de Morais and Zamora, 2005; Deng and Englehardt, 2008; Doocey and Sharratt, 2004; Kurniawan and Lo, 2009; Parsons and M. Williams, 2004; Wang et al., 2006; Wiszniowski et al., 2004; Yu et al., 1998). The $\cdot\text{OH}$ breaks the organic molecules by abstracting a hydrogen atom or by introducing double bonds in the molecule (Sarria et al., 2002). The $\cdot\text{OH}$ decompose even the most recalcitrant molecules into biodegradable compounds such as, CO_2 , H_2O and inorganic ions (Bauer et al., 1999; Gogate and Pandit, 2004a, b). There are different ways of producing hydroxyl radicals, which enhances the versatility of AOPs. Some of the methods by which hydroxyl radicals can be generated are: TiO_2/UV , $\text{H}_2\text{O}_2/\text{UV}$, Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), photo-Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$), electro-Fenton, electro-photo-

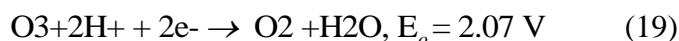
Fenton and ozone (O_3 , O_3/UV , and O_3/H_2O_2) (Altin, 2008; Atmaca, 2009; Cho et al., 2002; Frontistis et al., 2008; Hermosilla et al., 2009; Jia et al., 2011; Kurniawan et al., 2006c; Poznyak et al., 2008; Tizaoui et al., 2007). A disadvantage of some of the AOPs is the high demand for electric power, which increases the operational cost of the process (Lopez et al., 2004). However, the introduction of renewable solar energy as the UV photon source has lowered the demand of electric power (Rocha et al., 2011). This technique is also known as solar photocatalysis. A combination of AOP and other treatment process, has been found to be an economical as well as efficient (Kurniawan et al., 2006c).

Meeroff et al. (2012) experimented with a new technique, photochemical iron mediated aeration (PIMA) process and compared its efficiency with TiO_2 photocatalysis for both real and simulated leachate. Table 8 illustrates the efficiency of the technique for real landfill leachate. In another novel approach, Galeano et al. (2011) experimented the applicability of catalytic wet peroxide oxidation (CWPO) for leachate treatment. It was found that CWPO treatment in the presence of Al/Fe-pillared clay catalyst was able to remove 50% COD and simultaneously enhance the biodegradability of the leachate from 0.135 to 0.321 in 4 h of reaction at 18 °C and 72 kPa.

Among the individual AOPs discussed herein, ozonation and/or Fenton oxidation are the most commonly applied techniques for leachate treatment. Selection of suitable AOP depends on the leachate characteristics, technical applicability and other parameters such as, effluent discharge standards, cost-efficiency, regulatory requirements and long-term environmental impacts.

5.3.1.1 Ozonation

Ozone is known to degrade organic compounds and is effective for the removal of nitrogen, color and odour (Haapea et al., 2002; Poznyak et al., 2008; Wang et al., 2002). Ozone has a high oxidation potential (E_0) of 2.07V as shown in Equation 19, and can be used for the treatment of contaminated wastewater of high strength (Al-Kdasi et al., 2004; Camel and Bermond, 1998):



However, ozonation alone can remove only 35% COD and 50% $\text{NH}_4\text{-N}$ from leachate (Kurniawan et al., 2006a). So, it is applied in conjunction with other treatment techniques for better efficiency (Kerc et al., 2003). Application of GAC to ozone treatment improved the process efficiency by accelerating the kinetic rate of the ozone decomposition through the formation of nascent $\cdot\text{OH}$ radicals which have higher oxidation potential of 2.80V as seen in Equation 20. It can easily oxidize the organic matter present in leachate (Wang et al., 2004).



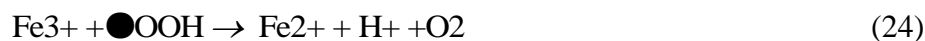
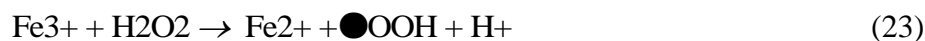
Ozone is incapable of degrading humic substances (Wang et al., 2004). However, it is highly suited for ammonia removal as shown in Equation 21 (Kurniawan et al., 2006a):



Ntampou et al. (2006) found that ozonation followed by coagulation-flocculation was less efficient in COD removal as compared to coagulation-flocculation followed by ozonation, which could reduce COD from an initial value of 1010 mg L^{-1} to less than 180 mg L^{-1} .

5.3.1.2 Fenton Oxidation

Treatment of landfill leachate using Fenton process has been widely reported in recent years (de Morais and Zamora, 2005; Deng and Englehardt, 2006; Gotvajn et al., 2009; Kang and Hwang, 2000; Kim et al., 2001; Pala and Erden, 2004; Stuber et al., 2005; Sun et al., 2009; Zhang et al., 2005). The mechanism of free radical generation in a Fenton oxidation reaction involves the following key steps as illustrated in Equations 22 through 27:

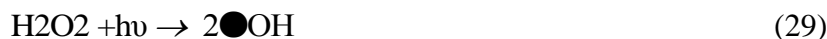


The $\bullet\text{OH}$ radical can attack and initiate a series of oxidation reactions leading to the degradation of the organic pollutant as seen in Equation 28:



The primary processes involved for leachate treatment by Fenton Reagent are pH adjustment, oxidation, neutralization, coagulation and precipitation (Kang and Hwang, 2000). According to Wu et al. (2010) Fenton treatment is highly effective in removal of about 95.8% HS in 24h period. The photo-Fenton process is much more efficient than heterogeneous TiO_2 , $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$ or homogeneous $\text{H}_2\text{O}_2/\text{UV}$ photocatalysis. The initial reaction rate of photo

Fenton is 20 times higher and leads to almost complete mineralization of the wastewater (Moraes and Bertazzoli, 2005; Vilar et al., 2011). The H₂O₂ molecule is cleaved with a quantum yield of two •OH radicals per quanta of absorbed radiation, as shown in Equation 29 (Esplugas et al., 2002):



The •OH radicals significantly improve the biodegradability. The BOD₅/COD ratio improves from 0.13 to 0.37 or 0.42, which is seen to result in an almost total COD and color removal (de Morais and Zamora, 2005; Malato Rodríguez et al., 2004).

5.3.2 Adsorption

Adsorption is recognized as one of the most efficient and extensively used fundamental approach in wastewater treatment processes (Daifullah et al., 2004; Kurniawan et al., 2006b). Traditionally activated carbon has been used for leachate treatment due to its large porous surface area, controllable pore structure, thermal stability and low acid/base reactivity (Li et al., 2008; Méndez-Díaz et al., 2012). Activated carbon has a superior ability to remove a wide variety of organic and inorganic pollutants dissolved in aqueous and gaseous environments (Chingombe et al., 2005; Singh et al., 2012).

Activated carbon adsorption was effective for ammonium nitrogen removal from landfill leachate samples (Foo and Hameed, 2009). The addition of powdered activated carbon (PAC) improved the performance of biological treatment of leachate (Kargi and Pamukoglu, 2003a, b).

Lim et al. (2010) used EDTA modified rice husk in a SBR and achieved better COD and nitrogen removal efficiency as compared to commercially available PAC.

Activated carbons can be prepared from a large variety of carbon-containing materials through pyrolysis. Large number of agricultural by-products such as sugarcane bagasse, rice straw, soybean hulls, rice hulls, peat moss, nutshells and other lignocellulosic wastes has been used to prepare inexpensive and renewable additional source of activated carbons (Ahmedna et al., 2000; Kadirvelu et al., 2003; Sahu et al., 2010). Activated carbon made from tamarind wood and chemically activated by zinc chloride was used for the removal of lead and chromium from wastewater with significant success (Dwivedi et al., 2008; Sahu et al., 2009a; Singh et al., 2008). Other low cost adsorbents that has been successfully used for heavy metal removal are peat and rubber wood ash (Hasan et al., 2000; Sen Gupta et al., 2009). These adsorbent may also be used for the treatment of leachate. A basic two stage process consisting of carbonization followed by activation is followed for the production of activated carbons. In the first step the carbon content is enriched for the creation of an initial porosity and second activation stage helps in enhancing the pore structure (Acharya et al., 2009a; Acharya et al., 2009b). Some reviews have been published on the preparation of activated carbon, which can be subsequently utilized for leachate treatment (Demirbas, 2009; Dias et al., 2007).

In addition to activated carbon other materials like clinoptilolite, Zeolite (CV-Z) synthesized from coal fly ash , limestone, peat, blast furnace slag and pine bark have been utilized for leachate treatment with good results (Aziz et al., 2004b; Heavey, 2003; Karadag et al., 2008; Luna et al., 2007; Nehrenheim et al., 2008; Orescanin et al., 2011; Söukand et al., 2010).

Clinoptilolite has a high $\text{NH}_4\text{-N}$ removal efficiency (Hankins et al., 2005). Li et al. (2011b) used

coal flyash, treated with initiator C for landfill leachate treatment. The efficiency of the above mentioned adsorbents is discussed in Table 9. Oti et al. (2011) used an iron oxide based adsorbent Kemiron for the removal of As(V) and As(III) from leachate. Fuller earth beads and cylinders containing chitosan and sodium silicate as binders was used successfully by Hasan et al. (2007) for the removal of cesium from wastewater. This can also be replicated for leachate treatment.

Composite adsorbent media made by combining different materials like zeolite and activated carbon, carbon and low-cost materials such as limestone or rice husk, carbon waste with Portland cement as a binder and so on (Azhar et al., 2006; Gao et al., 2005). The combinations of hydrophilic and hydrophobic groups in the adsorbents make an excellent adsorption system which can remove both metallic ions and organic substances (Okolo et al., 2000). Studies show that ammoniacal nitrogen was better adsorbed by composite adsorbents towards than zeolite and activated carbon (Halim et al., 2010a). Halim et al. (2010b) studied the performance of such composite adsorbent media via a lab-scale column study which is shown schematically in Figure 11.

Studies have shown that the combination of activated carbon and ozone is a suitable and feasible option for the treatment of landfill leachate (Fettig et al., 1996; Rivas et al., 2003). Addition of PAC to activated sludge reactors has shown to enhance the biological treatability of leachate (Aktaş and Çeçen, 2001). Sahu et al. (2009b) used activated rice husk in a three phase modified multi-stage bubble column reactor and achieved 77.15% and 19.05% lead and BOD₅ reduction respectively, under optimum conditions. This technique can also be used for leachate treatment, specifically for the removal of HMs. Li et al. (2010b) applied coagulation flocculation followed

by adsorption using PAC and obtained 86%, 97.6%, 99.7% and 78%, removal of COD, Pb, Fe and toxicity respectively under optimum operating conditions.

5.3.3 Coagulation-flocculation

Coagulation and flocculation have been used successfully in treating stabilized and old landfill leachates and is most effective for colour removal (Kang and Hwang, 2000; Manu and Chaudhari, 2002; Monje-Ramirez and Velásquez, 2004; Silva et al., 2004). The different types of coagulation processes include classical chemical coagulation using salts of iron and aluminium, electrocoagulation and biocoagulation. Four major types of chemical coagulants are aluminium (III) sulfate (alum), ferric (III) chloride, ferrous (II) sulfate and ferric (III) sulfate. Studies have shown that ferric (III) sulfate has the highest coagulation efficiency followed by aluminium (III) sulfate and ferric (III) chloride (Comstock et al., 2010). Tatsi et al. (2003) worked with three conventional coagulants viz., ferric chloride, aluminium sulfate and lime and four commercial polyelectrolytes among whom one was anionic, two cationic and another was non-ionic polymer. He found that although ferric chloride removed 80% COD from partially stabilized leachate, the removal decreased below 35% when coagulants were added to raw leachate.

Zouboulis et al. (2004) experimented with bioflocculants produced by the bacterium *Rhizomonas* sp. The application of bioflocculant was efficient for the removal of humic acids from synthetic solutions and reducing COD content from real landfill leachates. More than 85% humic acid removal was observed at 20 mg L⁻¹ bioflocculant dose and at pH 7-7.5.

Electrocoagulation is a simple and efficient electrochemical method used for the purification of many types of water and wastewaters and is able to remove large variety of pollutants (Adhoum and Monser, 2004; Alinsafi et al., 2005; Bayramoglu et al., 2006; Can et al., 2006; Daneshvar et al., 2006; Ilhan et al., 2008; Kobya et al., 2006; Li et al., 2011a). In electrocoagulation, electric current destabilizes the suspended, emulsified, or dissolved contaminants in the wastewater (Emamjomeh and Sivakumar, 2009). Mariam and Nghiem (2010) achieved about 67% TOC and 80% turbidity removals by the electrocoagulation while the removal percent by chemical coagulation was only 10% TOC and 65% turbidity. The treatment of leachate is easier due to their high conductivity and chloride content (Labanowski et al., 2010). Several materials have been used as anode such as Pt, TiO₂, SnO₂, Al and Fe. Among them, Al and Fe are most frequently used (Top et al., 2011). The COD removal for Fe and Al electrodes were 35% and 56% respectively, in 30 min contact time as discussed in Table 11. Fe electrodes transfer higher numbers of Fe ions into solution leading to higher rate of electrode dissolution, formation of more sludge with less COD removal. Since, the costs of both Al and Fe electrodes are comparable, Al electrodes will be a better choice due to its higher efficiency (Ilhan et al., 2008). However, Bouhezila et al. (2011) estimated a higher operational cost for Al electrode, thus preferring Fe electrode material.

Coagulation is also used as a pre and post treatment technique for membrane filtration to achieve higher removal efficiency (Mariam and Nghiem, 2010; Theepharaksapan et al., 2011; Top et al., 2011). Vedrenne et al. (2012) used chemical coagulation-flocculation with ferric (III) chloride in conjunction with photo Fenton oxidation and was successful in removing about 56% of COD, 95% TC, 64% NH₄ -N, 46% As, 9% Hg and 85% Pb from an aged leachate sample.

Dissolved air flotation (DAF) technique is used in conjunction with various coagulation-flocculation techniques to separate the flocculated particles from the wastewater, by bringing the particles to the surface of the liquid. DAF is also helpful in reduction of BOD₅, COD and turbidity (Al-Shamrani et al., 2002a, b; Palaniandy et al., 2010). Studies show that separation by flotation presents some advantages compared to separation by settling (Pouet and Grasmick, 1995). Adlan et al. (2011) combined chemical coagulation by ferric (III) chloride and DAF for the treatment of semi-aerobic leachate.

5.3.4 Electrochemical treatment

Stabilized or methanogenic leachates are alkaline and have less than 1% of biodegradable organic matter as evident by BOD/COD value of 0.004, making electrochemical treatment techniques more feasible (Tauchert et al., 2006). According to a number of researchers, electrochemical oxidation of leachate is superior to light-enhanced oxidation, Fenton treatment, combined UV and O₃/H₂O₂, ultrasound and other physico-chemical processes since it can efficiently reduce concentrations of organic contaminants, ammonia, and color in leachate (Gonze et al., 2003; Ince, 1998). Pretreatment techniques, anode materials, pH, current density, chloride concentration, and additional electrolytes significantly influence the performance of electrochemical oxidation. During electro-oxidation treatment of leachate, COD reduction can range from 70% up to >90% and the achieved NH₃-N removal efficiency is almost 100%, under optimum conditions (Chiang et al., 2001; Ihara et al., 2004).

According to Feng et al. (2003) direct oxidation of organic matter at the anode surface is also possible. Several anode materials have been used for electrocoagulation, such as boron-doped diamond binary Ru-Ti oxide-coated titanium anode also called the Dimensional Stable Anode

(DSA), Ti/SnO₂ and Ti/PbO₂, Ti/Pt, graphite and PbO₂ and Sn–Pd–Ru oxide coated titanium (SPR), graphite and DSA (Anglada et al., 2011; Cabeza et al., 2007b; Chiang et al., 1995; Cossu et al., 1998; Feki et al., 2009; Feng et al., 2003; Moraes and Bertazzoli, 2005; Pérez et al., 2010; Tauchert et al., 2006).

During the electrolysis, the pollutants are degraded either by direct or indirect oxidation processes as shown in Figure 12 (Chen, 2004; Deng and Englehardt, 2007; Szpyrkowicz et al., 2001). Deng and Englehardt (2007) found that NH₄-N removal is higher than COD removal, indicating the dominance of indirect oxidation during electrolysis reaction. The hypochlorite ion or hypochlorous acid generated during electrochemical oxidation is the main oxidizing agents:



The chlorine and hypochlorite oxidize NH₄⁺ and are reduced to chloride ions in the process as given in Equation 33 (Cabeza et al., 2007a; Chen, 2004)



Schoeman et al. (2005) experimented with electrodialysis to desalinate/concentrate the leachate to effectively reduce the volume pollution control. However, there are two basic drawbacks of electro-oxidation viz., high energy consumption and possible formation of chlorinated organics (Deng and Englehardt, 2007). For treating old stabilized landfill leachate, Orescanin et al. (2012) pre-treated extremely low biodegradable leachate with ozone, followed by simultaneous

ozonation and electro-oxidation and it was finally subjected to microwave treatment. The removal percentages obtained were 98.43% colour, 99.48% turbidity, 98.96% suspended solids, 98.80% ammonia, 94.17% COD and 98.56% iron. However, this process uses complex treatment schedule, high energy and much resource.

5.3.5 Filtration and membrane bioreactors

In recent years advance treatment techniques like, membrane filtrations which were originally used for of drinking water purification are being applied for leachate treatment. Nanofiltration, ultrafiltration and reverse osmosis are the major membrane filtration techniques that applied for leachate treatment. Among them, reverse osmosis is considered to be the most promising treatment technique available in recent years due to its high removal pollutant efficiency (Chan et al., 2007; Jenkins et al., 2003; Renou et al., 2008a; Renou et al., 2008b; Ushikoshi et al., 2002). However, leachate treatment by involves high pre and post treatment cost and frequent membrane fouling also affects its performance (Trebouet et al., 2001). It was found that membrane fouling is increased if the humic acid concentration in the leachate increases (Šír et al., 2012). Frequent membrane fouling in reverse osmosis can be overcome by the application of vibratory shear-enhanced processing reverse osmosis (VSEPRO) system for treating stabilized leachate. Leachate containing recalcitrant organics can be effectively treated in a VSEPRO system due to the shearing force (Chan et al., 2007).

Nanofiltration exhibits treatment characteristics between reverse osmosis and ultrafiltration (Zouboulis and Petala, 2008). Studies have shown that nanofiltration is highly efficient in removal of metals like K^+ and Na^+ and boron from landfill leachate (Dydo et al., 2005; Ortega et al., 2007). Zouboulis and Petala (2008), found that the application of vibratory shear enhanced

unit (VSEP) on nanofiltration membranes enhanced the treatment efficiency of raw stabilized leachate. The humic acid removal efficiency was about 97%. The VSEP unit also prevented membrane fouling by creating shear waves (Zouboulis and Petala, 2008). Xu et al. (2006) found that Humic substances (HS) in mature leachate from inorganic components could be effectively removed by ultrafiltration.

The addition of successive membrane operations to biological treatments offered new advantage in the field of landfill leachate treatment (Bodzek et al., 2006) and the combination is called Membrane Bioreactors (MBR) (Tarnacki et al., 2005). A MBR thus combines the goodness of a biological reactor and membrane filtration system. The presence of the membrane allows for long sludge retention time with high organic loading rate and low hydraulic retention time. According to Robinson (2007) landfill leachate treatment can be highly challenging for MBRs as high chloride content of the leachate may corrode the membrane system. However Ahmed and Lan (2012) reported that excellent organics (BOD) and ammonia removal capacity up to 90% or more can be achieved by MBRs even when dealing with mature or stabilized landfill leachate. In recent years much attention has been given to MBRs for landfill leachate treatments owing to their efficiency and small foot-print (Ahn et al., 2002; Alvarez-Vazquez et al., 2004; Chaturapruek et al., 2005; Melin et al., 2006; Robinson, 2005; Setiadi and Fairus, 2003; Vasel et al., 2004). Various authors have worked with MBRs obtaining high removal efficiency as cited in Table 12.

6 Summary and Discussion

Landfill leachate is extremely toxic due to high concentration of recalcitrant organics and ammonia nitrogen along with variable quantities of other phosphorus, chlorides, calcium, magnesium, sulfate, dissolved solids, heavy metals, BTEX and other xenobiotic compounds. In view of the grave impact of landfill leachate on environment, the regulatory authorities have been forced to fix increasingly stringent discharge water standards. In developed countries, directives regarding prevention of leachate seepage into groundwater and soil, collection, treatment and its disposal exist to some extent. A discussion is provided in Table 3 regarding the maximum limit of contaminants in treated leachate prior to its disposal into the surrounding environment. However, due to extreme variation of leachate composition and operating conditions in different landfills, no guideline or standard operating procedures for leachate treatment and disposal can be effectively chalked out. While most of the old landfills do not contain adequate pollution containment mechanisms, these safety considerations are being integrated into the new landfills during the design phase. So management of old and new landfills and their troubleshooting should follow different approaches which have been shown in the Figure 9.

1. Leachate plumes have a widely varying characteristic and composition. Both vertical and horizontal gradient in redox potential and contaminant concentration dictates the transformation of nitrogenous, sulfurous, carbonaceous and heavy metal species along the leachate plume. While ammonium compounds undergo aerobic nitrification, nitrate reduction, anoxic denitrification and anaerobic ammonium oxidation processes to form harmless nitrogen gas under fluctuating redox conditions, the sulfate reduction depends on available organic electron

donors and sulfate electron acceptors. Carbonaceous compounds or organics in the leachate plume is reflected by the COD which keeps on decreasing over age of the landfill due to natural anaerobic methane oxidation and natural attenuation. The HMs are found to undergo very less mobilization as they became stabilized by complexing with DOM, HA and FA.

2. The leachate plume migration can be monitored by using a large number of techniques and methods. The monitoring techniques are site specific and each landfill site should be carefully studied before the application of any specific monitoring technique. Construction of monitoring wells or insertion of hollow stem augers are very common and essential for sampling purposes and for inserting various probes and electrodes for geo-chemical and electrical monitoring techniques. Hydro-geological equipment such as piezometers and various samplers are historically the most used instruments. Isotope mapping and electrical monitoring such as tomography, ERI, VLF-EM, electrode grid, etc are comparatively new, but very convenient field techniques. The electromagnetic methods such as GPR, RCPT and TDR can be performed without monitoring wells and permanent facilities. Sometimes, two or more of these techniques can be used to complement each other and obtain a clearer picture regarding leachate plume migration. Bacteriological monitoring can also point out the fringe of the leachate plume by distinct degradation potentials inside and outside of leachate plume. The suitability of these different monitoring methods will vary from site to site depending upon groundwater flow, soil porosity, pore water content, electrical conductivity of soil matrix, soil texture, and logistic issues.

3. Landfill leachates pose significant risk towards the soil and groundwater environment. It is well established fact that small amount of leachate can pollute a large volume of groundwater

once it infiltrates an aquifer by changing its pH and Eh and introducing toxic chemicals. Soil texture, porosity, permeability and HRT changes mostly due to bioclogging from biomass and biofilm produced by microbes, gas pocket formation and metal precipitation. Additionally, water bodies present near landfills may experience higher organic load, inorganic nitrogen content, and heavy metal concentration.

4. In order to assess the extent of impact of landfill leachate on environment, both qualitative and quantitative methods are available. However, none of them guarantees an exact assessment of the actual scenario due to extreme complexity of the leachate plume and soil environment. Relative hazard assessment systems rank a number of landfills by a comparative rating system to prioritize the treatment efforts. Around 22 hazard-rating systems have been cited in section 4.2 and four systems have been discussed in details, viz. LPI, E-LI, hazard rating by Singh et al. (2009) and a toxicity index. All of them stress upon different factors. While some concentrates on the environment as a whole, some other specializes on the toxic effect of leachate on human beings. Necessity would decide which hazard rating system is to be used. However, the subjectivity associated with the scoring system of these hazard rating systems is their main drawback. In most of the systems, site ranking is based either on the combined score for various routes under migration mode or the score for the dominant route *i.e.* the route returning highest score.

5. Numerous mathematical models that have been developed for different issues related to risk assessment of landfill leachate are completely dependent on the data input. The results can be misleading if any input is wrong and the complex chemical and biochemical processes undergoing in the landfill is predicted wrongly. In this paper, we have reviewed few

mathematical models for assessing permittivity reduction of soil, degradation of leachate pollutants, long term fate of leachate components, reliability of groundwater monitoring systems and also softwares used for modeling purpose. The use of softwares is supposed to be a very good option. However, in spite of presence of a number of softwares in the market, none is exactly suitable for leachate plume modeling and a lots of adjustment is required to work with these generic softwares. These stochastic models should be used for guesswork in case the leachate composition and biogeochemical and bacteriological processes are fully understood. Otherwise, the management decisions taken based on the wrong predictions may cost dear.

6. Leachate control systems may include installation of geo-synthetic or other liners at the bottom of the landfill and leachate collection systems. Treatment of leachate prior to discharge to surface water is also an integral part of that system (Damgaard et al., 2011). According to the Department of Environment Food and Rural Affairs (UK) landfills both hazardous and non-hazardous should have a bottom liner in addition to the geological barrier (DEFRA, 2009). The danger of leachate infiltration in groundwater is great considering that even the best liner and leachate collection systems will ultimately fail due to natural deterioration. Nooten et al. (2008) proposed a semi-passive treatment of leachate during post closure remediation of old landfills, thereby replacing conventional energy consuming wastewater treatment systems. The system can also be installed along the gradient of leaking landfills for mitigation of contaminated groundwater plumes. In another novel approach Ziyang et al. (2011) proposed the introduction of functional layers embedded in landfill so that leachate strength may be reduced source, thereby reducing the cost of leachate treatment. Leachate treatment techniques differ depending on the nature and age of leachate. Biological treatments are most suitable for treatment of young

leachate while physico chemical treatments like membrane filtration, electrochemical and advanced oxidation treatments are suitable for stabilized acidogenic leachate. Membrane filtration in combination with biological treatment was found to be extremely effective. However, installation of membrane treatment facilities is much expensive than other treatment techniques. The treatment costs of landfill leachate will vary depending on its capacity and the composition of waste it has to deal with. Other factors that will contribute towards determining the treatment cost include the technology employed, the local condition of the site, and the disposal standards it has to comply with. The total treatment cost will take into account the construction as well as operational and maintenance costs. While the construction cost usually depends on the capacity of the landfill and target quality of the effluent, the operation and maintenance cost will cover manpower, energy, chemicals and maintenance over its lifetime and even after its closure.

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Table 1: Typical range of leachate composition in municipal waste (Excludes volatile and semi-volatile organic compounds) (Canter et al., 1988; Lee and Jones-Lee, 1993; Lee and Jones, 1991)

Parameter	Typical Range (milligrams per liter, unless otherwise noted)	Upper Limit (milligrams per liter, unless otherwise noted)
Total Alkalinity (as CaCO ₃)	730–15,050	20,850
Calcium	240–2,330	4,080
Chloride	47–2,400	11,375
Magnesium	4–780	1,400
Sodium	85–3,800	7,700
Sulfate	20–730	1,826
Specific Conductance	2,000–8,000 $\mu\text{mhos cm}^{-1}$	9,000 $\mu\text{mhos cm}^{-1}$
TDS	1,000–20,000	55,000
COD	100–51,000	99,000
BOD	1,000–30,300	195,000
Iron	0.1–1,700	5,500
Total Nitrogen	2.6–945	1,416
Potassium	28–1,700	3,770
Chromium	0.5–1.0	5.6
Manganese	Below detection level – 400	1,400
Copper	0.1–9.0	9.9
Lead	Below detection level – 1.0	14.2
Nickel	0.1–1.0	7.5

Table 2: Physicochemical parameters of leachate of different age

Parameters	Landfill age (years)				Reference
	Young (0-5)	Intermediate (5-10)	Stabilized (10-20)	Old (>20)	
pH	<6.5	6.5–7.5	>7.5	-	(Foo and Hameed, 2009)
	3-6	6-7	7-7.5	7.5	(El-Fadel et al., 1997; Scott et al., 2005)
TDS (mg L ⁻¹)	10,000-25,000	5000-10,000	2000-5000	<1000	(El-Fadel et al., 1997; Scott et al., 2005)
BOD ₅ (mg L ⁻¹)	10,000-25,000	1000-4000	50-1000	<50	(El-Fadel et al., 1997; Scott et al., 2005)
COD (mg L ⁻¹)	>10,000	4,000–10,000	<4000	-	(Foo and Hameed, 2009)
	15,000-40,000	10,000-20,000	1000-5000	<1000	(El-Fadel et al., 1997; Scott et al., 2005)
BOD ₅ /COD	0.5–1.0	0.1–0.5	<0.1	-	(Foo and Hameed, 2009)
	0.66-0.625	0.1-0.2	0.05-0.2	<0.05	(El-Fadel et al., 1997; Scott et al., 2005)
Organic compounds	80% volatile fatty acids (VFA)	5–30% VFA+ humic and fulvic acids	Humic and fulvic acids	-	(Foo and Hameed, 2009)
Ammonia nitrogen (mg L ⁻¹)	<400	N.A	>400	-	(Foo and Hameed, 2009)
	500-1500	300-500	50-200	<30	(El-Fadel et al., 1997; Scott et al., 2005)
TOC/COD	<0.3	0.3–0.5	>0.5	-	(Foo and Hameed, 2009)
Kjeldahl nitrogen (mg L ⁻¹)	100-200	N.A	N.A	-	(Foo and Hameed, 2009)
	1000-3000	400-600	75-300	<50	(El-Fadel et al., 1997; Scott et al., 2005)
Heavy metals (mg L ⁻¹)	Low to medium	Low	Low	-	(Foo and Hameed, 2009)
Ca (mg L ⁻¹)	2000-4000	500-2000	300-500	<300	(El-Fadel et al., 1997; Scott et al., 2005)
Na, K (mg L ⁻¹)	2000-4000	500-1500	100-500	<100	
Mg, Fe (mg L ⁻¹)	500-1500	500-1000	100-500	<100	
Zn, Al (mg L ⁻¹)	100-200	50-100	10-50	<10	
Cl ⁻ (mg L ⁻¹)	1000-3000	500-2000	100-500	<100	
Sulfate (mg L ⁻¹)	500-2000	200-1000	50-200	<50	
P (mg L ⁻¹)	100-300	10-100	-	<10	

Table 3: Regulatory limits of leachate contaminants

Parameter → Country ↓	C O D (m g L ⁻¹)	BO D ₅ (m g L ⁻¹)	T O C (m g L ⁻¹)	N H ₄ -N (m g L ⁻¹)	P O ₄ -P (m g L ⁻¹)	Disso lved Solids (m g L ⁻¹)	S S (m g L ⁻¹)	Total nitrog en (m g L ⁻¹)	Phenoli c Compo unds (m g L ⁻¹)	Hg (m g L ⁻¹)	A s (m g L ⁻¹)	Pb (m g L ⁻¹)	Refere nces
UK	-	60	-	-	-		-	-					(Ngo et al., 2008)
Hong Kong	20 0	800	-	5	25		-	100					
Vietnam	10 0	50	-	-	6		-	60					
France	12 0	30	-	5	25		-	30					
South Korea	50		-	50	-		-	150					
Taiwan	20 0		-	-	-		50	-					
Poland	12 5	30	-	10	-		-	-					
Australia		10	15	0.5	0.1		20	5	0.05	0.0001	0.005	0.005	
Germany	20 0	20	-	-	3	-	-	70	-	0.05	-	0.5	(Steg mann et al., 2005)
Turkey	10 0	50	-	-	1.0 (T P)		10 0	-					(Oztur k et al., 2003)
South Korea	40 0	-	-	50	-	-	-	150 (inorg anic N)	-	-	-	-	(Ahn et al., 2002)
Malaysia	10 0	50	-	-	-	-	10 0	-	-	-	-	-	(Aziz et al., 2007)
China	10 0	-	-	15	0.5 (T P)	-		-	-	-	-	-	(Yido ng et al., 2012)

Bangladesh		200	50	-	50	-	2100	150	-	-	-	-	-	(Mahmud et al.)
India	Inland surface water	250	30	-	50	-	2100	100	100	1.0	0.01	0.2	0.1	(MoEF, 2000)
	Public sewers	-	350	-	50	-	2100	600	-	5.0	0.01	0.2	1	
	Land disposal	-	100	-	-	-	2100	200	-	-	-	0.2	-	

Table 4 : Monitoring of plume formation & migration: techniques & methodology

Techniques	Devices or analytical process used	Purpose	References
Hydro-geological techniques for monitoring and sampling of water for geo-chemical analysis	Standpipe piezometers	To monitor piezometric water levels	(Cherry et al., 1983;
	Water-table standpipes	To measure water level in aquifer.	MacFarlane et al., 1983)
	Auger-head sampler	Provides samples from relatively undisturbed aquifer zones.	
	Suction-type multilevel point-samplers	Collects groundwater samples from different depth of the aquifer up to 8 or 9 m when suction is applied.	
	Positive-displacement-type multilevel point-samplers	Collects groundwater samples from different aquifer depth more than 9 m.	
	Bundle-piezometers	Collects groundwater samples from different depth of the aquifer through a bunch of dedicated piezometer tubes up to 8 or 9 m when suction is applied.	
Isotopic techniques	Measurements of $\delta^{13}\text{C}$ -DIC, δD - H_2O , and $\delta^{18}\text{O}$ - H_2O from leachate	All these isotopes have elevated levels in leachate plume. Monitoring of these isotopes gives some indication of its migration	(Atekwana and Krishnamurthy, 2004; North et al., 2006)
	Measurement of isotopic ratios of $^{15}\text{N}/^{14}\text{N}$, $^{13}\text{C}/^{12}\text{C}$ and $^{34}\text{S}/^{32}\text{S}$ and dissolved gas (N_2 , Ar, O_2 and CH_4) concentrations in leachate plume	To identify the zones of methanogenesis, nitrification-denitrification and $\text{SO}_4^{=}$ reduction.	(Heaton et al., 2005)
Electromagnetic methods	Direct current (DC) resistivity geo-electrical sounding survey	To identify a low resistivity zone signifying the presence of leachate plume	(Atekwana et al., 2000; Hermozilha et al., 2010; Karlık and Kaya, 2001; Petterson and Nobes, 2003; Redman, 2009)
	Ground Penetrating Radar (GPR)	To identify the change in dielectric permittivity across the soil profile to indicate the boundary of leachate plume	
Electrical Methods	Very-low-frequency electromagnetic (VLF-EM) survey	Near-surface bodies of leachate plume responds galvanically	(Al-Tarazi et al., 2008; Benson et al., 1997; Karlık and Kaya, 2001)

	Cross-borehole tomography and depth-discrete groundwater electrical conductivity	To create a continuous, high-resolution image of the distribution of the leachate plume	(Acworth and Jorstad, 2006)
	Electrode Grids	To detect the location of contaminant release or leakage from the landfill containment system	(Frangos, 1997; Oh et al., 2008; White and Barker, 1997)
Bacteriological Experiments	High resolution microcosm experiments Pore water extraction Sediment analyses Determination of MPN Solid organic matter (TOC) Grain size distribution	It can measure the variation in phenoxy acid herbicide degradation across a landfill leachate plume fringe, indicating spread of plume.	(Tuxen et al., 2006)
Characterization of DOM	Molecular weight distribution by electrospray ionization mass spectrometry and size exclusion chromatography Aromaticity measured with UV-vis spectrophotometer at 280 nm and 254 nm wavelength Fluorescence excitation-emission matrix (EEM) quenching combined with parallel factor (PARAFAC) analysis	At the middle of the leachate plume, molecular weight of DOM decreases, polydispersity increases. Aromaticity increases at the fringes of leachate plume. Molecular structure and binding property of DOM with MSW. PARAFAC analysis was used for decomposing fluorescence EEMs into different independent groups for reducing interference for more accurate quantification.	(Persson et al., 2006) (Wu et al., 2011)

Table 5: Summary of various existing hazard-rating systems adopted from Singh et al. (2009)

Hazard Rating System	Hazard migration routes	Evaluation of	Parameters to be measured			Algorithm used	Reference
			Simpl e	Comple x	Tota l		
LeGrand Method	G	site hazard for groundwater route alone	2	3	5	Ad	(LeGrand, 1964)
Soil-waste Interaction Matrix	G		7	9	16	Ad-M	(Phillips and Nathwani, 1977)
DRASTIC	G		5	3	8	Ad	(Canter, 1996)
HRS: Hazard Ranking System 1982	G, SW, A, F, D	multiple hazard migration routes, each one separately producing separate scores for all the routes	11	3	14	Ad-M	(Wu and Hilger, 1984)
HRS: Hazard Ranking System 1990 (USEPA)	G, SW, A, S		13	5	18	Ad-M	(USEPA, 1990)
DPM: Defense Priority Model	G, SW, A/S		11	2	13	Ad-M	(National Research Council, 1994)
WARM: Washington Ranking Method	G, SW, A, MS		13	3	16	Ad-M	(Science Applications International Corporation, 1990)
NCAPS: National Corrective Action Prioritization System	G, SW, A		10	2	12	Ad-M	(DOE, 1996)
ISM: Indiana Scoring Model	G, SW, A, F, D		11	3	14	Ad-M	(Solid Waste Management Board, 2001)

ERPHRS: Environmental RepA Program Hazard Ranking System	G, SW, A, F, D		14	4	18	Ad-M	(Wisconsin Department of Natural Resources, 2001)
RSS: Risk Screening System	G, SW, D		6	2	8	M	(Ministry for the Environment, 2004)
RASCL: Risk Assessment for Small & Closed Landfills	G, SW, A, D		11	1	12	M	(Golder Associates (NZ) Ltd, 2002)
Toxicity Index	H, E		Concentration of 24 toxic chemicals were measured			M	(Baderna et al., 2011)
HR-FCP: Hazard Ranking using Fuzzy Composite Programming	G, SW, A	various routes concurrently and produce a composite score for all the routes	13	4	17	FL	(Hagemeyer et al., 1996)
SRAP: Standardized Risk Assessment Protocol	G, SW, A, S		11	4	15	B	(Marsh and Day, 1991)
NCS: National Classification System	G, SW, D		12	2	14	Ad	(Canadian Council of Ministers for the Environment, 1992)
NPC: National Productivity Council	G, SW, A		12	2	14	Ad	(National Productivity Council, 2003)
JENV system	G, SW, A		11	3	14	Ad	(Joseph et al., 2005)
LPI: Leachate Pollution Index	L, S, G		0	18	18	Ad	(Kumar and Alappat, 2005)

E-LI: Global Environment–Landfill Interaction Index	L, G, SW, A, S, H	61 variables under 5 parameters are assigned different grades depending on their numerical values	Ad-M	(Calvo et al., 2005)
Hazard rating system by Singh et al. (2009)	Source-pathway-receptor	15	Ad-M	(Singh et al., 2009)

G - Groundwater; S - soil; SW - surface water; L - leachate ; A - air/atmosphere; E - Environment; H - health; F - fire and explosion; D - direct contact; MS - marine sediment; V - volatiles; Ad - additive model; Ad-M - additive-multiplicative model; M - multiplicative model; B - binary approach; FL - fuzzy logic

Table 6: Softwares for landfill risk assessment

Softwares	Description	Shortcomings	References
LandSim	Used for landfill risk assessment allowing for temporal and spatial variations. It estimates the probable boundary of migration of leachate plume & it's concentrations a given point in the ground (e.g., groundwater abstraction point) in a certain time, in terms of years. Biodegradation and longitudinal dispersion can be modeled in all pathways, retardation in both the unsaturated zone and the aquifer, and attenuation in the mineral component of liners taking account of loss of membrane liner and cap degradation and of active operational/institutional control.	Exposure analysis is not quantified, e.g. the amount of exposure for people (or livestock) if they consume the contaminated groundwater. It mainly focuses on groundwater as a receptor and not particularly other environmental receptors such as human population, livestock, and crops. No allowance for the categorization of hazards into toxic, non-toxic, carcinogenic, and non-carcinogenic groups. LandSim is a part of the total risk assessment not the total system itself.	(Environment Agency, 1996, 2001, 2003c; Slack et al., 2007)
Hydro-geological Evaluation of Landfill Performance (HELP)	It's a quasi-two-dimensional hydrologic model that can calculate water balance of landfills and other solid waste containment facilities using soil, weather and design data. It can also estimate effects of snowmelt, surface runoff, evapotranspiration, infiltration, vegetative growth, soil moisture storage, leachate recirculation, lateral subsurface drainage, unsaturated vertical drainage, and leakage through geo-membrane, soil or composite liners.	It does not address many risk assessment modules and sub-modules such as toxicity, chemical reactions, soil features, etc.	(Schroeder et al., 1994; Scientific Software Group, 1998)
GasSim	GasSim is principally designed for assessing landfill gas and deals with some risk assessment modules relevant to landfill gas generation, migration, impact and	Not suitable for leachate risk assessment Not a complete risk assessment models in a categorical and	(Attenborough et al., 2002; Golder Associates, 2003)

	exposure.	algorithmic manner	
GasSimLite	Similar to GasSim and developed for calculating landfill gas emissions.	-do-	(Environment Agency, 2002)
Repository Integration Programme (RIP)	It is an integrated probabilistic simulator for environmental systems having any potential pollutant source in the ground. RIP has to be adapted accordingly in landfill scenario by risk assessors.	Not specifically developed for landfill risk assessment. So adaptation is time consuming and difficult task. RIP may be applied to landfills for contaminant release and transport, but it does not readily provide a straightforward total risk assessment procedure for landfill leachate in a sequential and systematic way.	(Environment Agency, 2002; Landcare Research, 2003)
GoldSim	It is a general-purpose simulation software to support environmental systems modeling, business and economic modeling, and engineered system modeling	Not specifically developed for landfill risk assessment. So adaptation is time consuming and difficult task.	(Golder Associates, 2003)
ConSim	It is a tool for risk assessment associated with groundwater pollution originating from contaminated land	This was not been specifically designed for use with landfills having a leachate head and/or liners as in the modern engineered landfills.	(Environment Agency, 2003a; Whittaker et al., 2001)
Contaminated Land Exposure Assessment (CLEA)	It considers only human health hazards from landfills. Other environmental receptors such as plants, animals, buildings and controlled waters are not taken into account.	Designed for use with contaminated land and not specifically for landfills. Pathways are considered only from the perspective of soil as an exposure medium and not leachate.	(Environment Agency, 2003b; Environment Agency et al., 2002)
Multimedia, Multipathway, and Multireceptor Risk Assessment (3MRA), EPA	It evaluates five waste management unit types, viz waste pile, landfill, aerated tank, surface impoundment and land application unit. The model is generalized towards considering all of these types of units.	The model does not include a complete set of exposure routes e.g., some human exposure pathways such as dermal exposure are not included. Simultaneous exposures	(Bardos et al., 2003; Environment Protection Agency (EPA), 2004; Leavesley and

		towards multiple contaminants are not considered. Living receptors are taken into account but does not include non-living items as standalone receptors.	Nicholson, 2005; Weinberg et al., 2003)
Hazardous Waste Identification Rule (HWIR) modeling technology	It represents the methodology followed in United States national-scale assessment to determine human and ecological risks. It is appropriate for establishing contaminant-specific exemption levels from different industrial waste streams. The HIWR modeling technology has been developed to automate the risk assessment methodology and to avoid the possible over regulation.	Living receptors are taken into account but does not include non-living items as standalone receptors. It focuses on the wastes rather than a given landfill scenario.	(Construction Industry Research and Information Association (CIRIA), 2001; Environment Agency, 2003c; Environment Agency et al., 2002; Environmental Protection Agency (EPA), 1992)
Spatial Analysis and Decision Assistance (SADA)	It is a free software incorporating tools from environmental assessment fields such as integrated modules for visualization, geospatial analysis, statistical analysis, human health risk assessment, ecological risk assessment, cost/benefit analysis, sampling design, and decision analysis to form an integrated environment. The integration of the human health risk capabilities of SADA with modules for ecological risk assessment can help accomplish various Govt agencies' guidelines.	SADA is one of the softwares addressing different scenarios and right combinations of these different software programmes have to be selected each time while carrying out a landfill risk analysis The focus of the SADA appears to be more spatial than temporal in approach.	(The Institute of Environmental Modelling (TIEM), 2012)
Adaptable risk assessment modeling system	It is a modeling and database driven analysis system developed for the US Army for estimating the human and ecological health	It is a difficult task to adapt ARAMS into a landfill leachate scenario. ARAMS appears to	(Engineer Research and Development Center

(ARAMS)	impacts and risk associated with military relevant compounds (MRCs) and other constituents. Users can select particular model and/or existing database for calculating exposure, intake/update, and effects (health impacts) and incorporate them into conceptual site-models.	concentrate mostly on the exposure assessment facet of a risk analysis, but does not include a baseline study section comprising, for instance, geology, hydrology, hydrogeology, topography, etc. that are necessarily required in a landfill risk analysis.	(ERDC), 2012)
Multimedia Environmental Pollutant Assessment System (MEPAS)	It is a suite of environmental models developed to assess environmental problems by integrating transport and exposure pathways for chemical and radioactive releases to determine their potential impact on the surrounding environment, individuals, and populations. MEPAS modules have been integrated in the FRAMES software platform to allow MEPAS models to be used with other environmental models to accomplish the desired analysis.	In the context of landfills, it does not present an overall risk assessment methodology of landfill leachate.	(Pacific Northwest National Laboratory (PNNL), 2012b)
Framework for Risk Analysis Multimedia Environmental Systems (FRAMES)	It is a software platform for selecting as well as implementing environmental risk assessment software models by assisting users in developing environmental scenarios and by providing options for selecting the most appropriate computer codes for conducting human and environmental risk management analyses. It incorporates models that integrate across scientific disciplines, allowing for tailored solutions to specific activities.	FRAMES is a generic programme. It does not contain software especially for landfill leachate, which could guide a landfill assessor to perform a landfill risk analysis.	(Evangelidis, 2003; Pacific Northwest National Laboratory (PNNL), 2012a)
RESRAD	RESRAD is an acronym for Residual Radiation environmental analysis. It is a family of computer codes to provide useful tools for	None of the RESRAD family softwares is specifically for landfill leachate. These members in combination are not	(Decision Mapping System (DMS), 2006; Environmental

	<p>evaluating human health risk from residual contamination. The family consists of the following:</p> <p>RESRAD for soil contaminated with radio-nuclides;</p> <p>RESRADBUILD for buildings contaminated with radio-nuclides;</p> <p>RESRAD-CHEM for soil contaminated with hazardous chemicals;</p> <p>RESRADBASLINE for risk assessments against measured (baseline) concentrations of both radio-nuclides and chemicals in environmental media;</p> <p>RESRAD-ECORISK for ecological risk assessments;</p> <p>RESRAD-RECYCLE for recycle and reuse of radio-logically contaminated metals and equipment; and</p> <p>RESRAD-OFFSITE for off-site receptor dose/risk assessment.</p>	<p>able to address all factors and aspects of risk analysis of landfill leachate and to combine these would be a cumbersome task to execute each time a landfill risk assessment is performed for different landfill scenarios.</p>	<p>Assessment Division (EAD), 2012)</p>
RISC-HUMAN 3.1, RUM, Vlier-Humaan	<p>These software packages deal with risk analysis with a main emphasis on exposure assessment</p>	<p>These are designed for use with contaminated land and not specifically for landfills</p>	<p>(Scott and Stone, 2004)</p>

Table 7: Overview of leachate treatment techniques involving Natural processes

Technology	Mechanism & Process	Scope	Efficiency	Country	Advantage	Disadvantage	Selected References
Constructed Wetlands	Phytoremediation by cattail and insitu microorganisms	BOD ₅ TN FC Total P Cd	91% 96% >99% 98-99% 99.7%	Thailand	Low operation and maintenance cost	Buildup of excessive salts in soil due to poor understanding of soil plant system and improper management	(Sawattayothin and Polprasert, 2007)
	Phytoremediation by reeds and cattail	BOD ₅ COD NH ₃ -N Total P Fe Chloride	50% 59% 51% 53% 84% 35%	Slovenia	Low operation and maintenance cost	Slow operation in the initial phase	(Bulc, 2006)
	Phytoremediation by cattail (<i>Typhalatifolia</i>)	COD NH ₄ -N PO ₄ -P Fe (III)	27.3% 62.3% 52.6% 21%	Turkey	Low operation and maintenance cost	Low removal in the initial phase Long stabilization period	(Yalcuk and Ugurlu, 2009)
	Phytoremediation by <i>Phragmitesaustra lis</i> and <i>Salix purpurea</i>	SS BOD ₅ NH ₄ -N Total P Phenols	83.7% 65.5% 41.9% 38.4% 61.7%	Slovenia	Leachate reuse as fertilizer for the growth of energy crops	Large amount of elements percolate back into the waste layers after irrigation	(Justin and Zupancic, 2009)

Aerated Lagoons	Microbial oxidation, plant uptake	COD TN	75% 80%	United Kingdom	Low operation and maintenance cost. Suitable for the removal of N	Long Hydraulic Retention Time	(Mehmood et al., 2009)
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Table 8: Application of biological processes in reactors for leachate treatment

Technology	Mechanism & Process	Scope	Efficiency	Country	Advantage	Disadvantage	Selected References
Recirculation Bioreactor	Anaerobic digestion	COD	96.9%	China	Increased methane production Increased landfill capacity due to increased air space Acceleration of refuse decomposition	Full scale landfill operation may cause ponding, flooding or clogging especially in areas with increased precipitation	(Jiang et al., 2007)
	Anaerobic digestion with intermittent aeration for phase separation	COD BOD ₅ NH ₄ -N Total N	80% 81% 75% 74%	China	Accelerated conversion and stabilization of solid-waste by promoting rapid development of desired microbial population of denitrifiers, nitrifiers and methanogens	-	(Jun et al., 2007)
Two stage bioreactor with aged refuse (AR)	Anaerobic degradation	COD NH ₄ -N BOD ₅ Total N	93% 96.9- 99.8% 95.8- 99.8%	China	The landfilling after excavation may be	Blockage of the AR biofilter	(Li et al., 2010a)

biofilter media			49-63%		used for re-landfilling, leading to longer service life of landfills		
Combined Sequencing Batch Biofilter Granular Reactor (SBBGR)	Aerobic decomposition by submerged biofilter with aerobic granular biomass	COD	80%	Italy	High conversion capacity Low sludge production High compactness	Low ammonia removal due to high salinity and presence of inhibitory compounds	(Di Iaconi et al., 2006)
Sequential Batch Bioreactors		COD	97.5%	Poland	Time oriented nature of operation in SBR facilitates the alteration of operating cycle depending on the variation in leachate	--	(Klimiuk and Kulikowska, 2006)
Anaerobic–anoxic–aerobic (A2/O) bioreactor	Anaerobic fermentation	NH ₄ –N COD Total N	96.5 81.7% 61%	China	Suitable for N removal	Only diluted leachate is treated	(Yu et al., 2010)
Simultaneous aerobic and anaerobic (SAA) bio-	Combined aerobic and anaerobic digestion	COD NH ₄ –N	94% 95%	China	The system of SAA bioreactor is very simple Requires few	Long stabilization period	(Yang and Zhou, 2008)

reactor					specialized skills for operation Low energy consumption Chemicals rarely applied		
Aerobic bioreactor	Aerobic degradation	COD BOD ₅	90% 99.6%	Greece	Aerobic bioreactor enhance removal process Achievement of optimum waste stabilization Reduce methane production	-	(Giannis et al., 2008)
Simultaneous Leachate and Sludge Digester	Co-fermentation of leachate and sludge	Biogas generation	1.30 m ³ kg ⁻¹ of removable volatile solids (sludge: leachate ratio of 20:1)	Poland	Enhanced biogas and methane generation	Small quantity of leachate being treated	(Montusiewicz and Lebiocka, 2011)
Combined anaerobic digester and activated sludge system	Anaerobic digestion	COD Ammonia Alkalinity Zinc Fe, Cu, Mn, Ni Methane	94% 48.6-64.7% 49-60% 50% 88.8-99.9% 0.02-0.04L g ⁻¹	Iran	Reduced sludge production Effective HM removal	Excessive inorganic scale deposition in the interior of the reactor leading to operational problems	(Kheradmand et al., 2010)

		producti on rate	¹ COD _{rem}				
Swim-bed bio fringe reactor	Combined aerobic and anaerobic treatment	COD BOD Total N NH ₄ -N Nitrite Nitrate Phospha te Colour SS	82.6% 90.7% 21.8% 53.2% 36.4% 52.4% 86.3% 63.2% 3.5%	Malay sia	Swim-bed BF achieved higher performanc e for nitrite, nitrate and phosphorus removal due to its aerobic and anaerobic phase structure The technique is less sensitive to adverse environme ntal conditions Less sludge production	Humic acids were not treated adequately as a result colour removal was very low	(Aziz et al., 2011a)
Fixed bed biofilm reactor (micro- organisms developed on GAC bed)	Aerobic degradatio n (controlled aeration)	Dissolv ed Organic Carbon NH ₄ -N	95% 90%	Tested on artifici al leachat e	Denitrificat ion occurred even in the absence of external carbon supply due to partial bio-mass decay No excess sludge formation Can be operated as	Tested only on artificial leachate	(Ismail and Toshihiko, 2012)

an
automated
system for
leachate
treatment
Cost
effective

Table 9: Application of advanced oxidation processes for leachate treatment

Technology	Scope	Efficiency	Country	Advantage	Disadvantage	Selected References
Ozonation	Organics (Simple acids, Fulvic acids, humic acids)	-	Mexico	Complete removal of colour Significant removal of organics	Pretreatment with coagulation required	(Poznyak et al., 2008)
Photo-Fenton Oxidation	Improvement of biodegradability	64%	Brazil	Suitable for treatment of stabilized leachate.	Other subsequent treatment techniques required for effective removal of organics	(de Morais and Zamora, 2005)
Fenton Oxidation	HS COD TOC	95.8% 65% 55%	China	Effective removal of humic substances	Large reaction tanks required due to foaming during mixing and oxidation	(Wu et al., 2010)
Oxone/Co ²⁺ Oxidation	COD SS Colour	57.5% 53.3% 83.3%	China	More suitable for large scale application than Fenton treatment	Longer reaction time for higher degradation More number of stepwise addition of reagent as compared to Fenton treatment	(Sun et al., 2009)
PIMA	COD BOD ₅ Pb Ammonia	<50% <50% >90%		Effective for removal of certain metal	Presence of colour and turbidity	(Meeroff et al., 2012)

	Colour	21% >90%	USA	oxyanions (arsenite, arsenate, vanadate and chromate) and HMs	lowers the photocatalytic degradation	
UV/TiO ₂	COD Ammonia Colour	86% (BOD/COD ratio increase from 0.09 to 0.14) 71% 90%		Effective for colour removal The photocatalytic particles may be used more than 4 times with no loss in removal efficiency	-	
UV/TiO ₂ and Fe(III) as catalyst	TOC	95%	Spain	Effective degradation of HA Utilization of the waste TiO ₂	Treatment tested only for diluted leachate	(Poblete et al., 2011)
Thin gap annular UV/H ₂ O ₂ photo reactor	Colour COD	91% 87%	Taiwan	Good removal of colour and COD	Effective removal exhibited only under diluted conditions	(Shu et al., 2006)
FeGAC/H ₂ O ₂ system	HA FA	83% 86%	Taiwan	Efficient for treating stabilized landfill leachate	Not suitable for treatment of raw landfill leachate Pre-treatment of leachate with other techniques required	(Fan et al., 2007)

Table 10: Application adsorbents for leachate treatment

Adsorbents	Scope	Efficiency	Country	Advantage	Disadvantage	Selected References
Zeolotised coal fly ash	COD NH ₄ -N SS	43% 53% 82%	Spain	Utilization of fly ash in leachate treatment	For effective waste removal process needs to be combined with other treatment techniques	(Luna et al., 2007)
Pine Bark Blast Furance Slag	Metal removal	-	Sweden	Pine very effective in metal retention	No colour removal	(Nehrenheim et al., 2008)
Composite Zeolite-Carbon	NH ₃ -N COD	90% 93.7%	Malaysia	Combined adsorption properties of zeolite and carbon Low cost adsorbents	-	(Halim et al., 2010b)
Clinoptilolite	NH ₄ -N	-	Turkey	Regeneration of adsorbent after exhaustion lead to higher removal efficiency, so the same column can be used repeatedly	Competitive ions decrease efficiency	(Karadag et al., 2008)
Ozone modified GAC	COD NH ₃ -N	86% 92%	China	System robust enough to handle large variations in	The process needs to be combined with other treatment	(Kurniawan et al., 2006a)

			leachate composition and strength	techniques to achieve desired effluent standards
Anion Exchange Resins	Colour COD SS Turbidity	91.5% 70.3% 93.1% 92.4%	Malaysia Good removal efficiency Ease in operation Low running cost Low energy consumption	Overall treatment cost needed to cover the total resins required, Inability of anionic resin to exchange the positive ion substances such as $\text{NH}_3\text{-N}$ due to its mobile ion charge Not suitable for young leachate treatment since biological treatment could be effectively used prior to an ion exchange. The process needs to be combined with other treatment techniques to achieve desired effluent standards

(Bashir et al., 2010)

Sequential application of anion and cation exchange resin	Colour COD NH ₃ -N	96.8% 87.9% 93%	Malaysia	Good removal efficiency Low energy consumption	Not suitable for young leachate treatment since biological treatment could be effectively used prior to an ion exchange.	(Bashir et al., 2011)
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Table 11: Application of Chemical and Electrical coagulation techniques for leachate treatments

Technology	Materials Used	Scope	Efficiency	Country	Advantage	Disadvantage	Selected References
Chemical Coagulation	Ferric chloride (FeCl ₃)	Colour Turbidity SS COD	92% 95% 94% 51%	Malaysia	Effective colour removal	Excessive chemical coagulant addition for treatment will result in adverse effect on the receiving environment	(Aziz et al., 2007)
	Ferric chloride (FeCl ₃)	Di-(2-ethylhexyl) phthalate (DEHP) Di-butyl phthalate (DBP) Bisphenol A	100% 99.6% 98%	Thailand	The treatment helped to reduce bio-toxicity of leachate to non-mortality Degree of DNA damage was similar to non-exposure level	The chemical coagulation had to be followed by sand filtration and Reverse Osmosis to achieve the standards	(Theepharaksapan et al., 2011)
Electrocoagulation	Al Electrode	Sulfate COD	67% 56% (after 30min treatment)	Turkey	Effective sulfate removal is accomplished	High operational cost due to electrical current requireme	(Ilhan et al., 2008)
	Fe	Sulfate	65%				

Electrode	COD	35% (after 30min treatment)				nt.
Al Electrode	COD	45% (after 30min treatment)	Turkey	Effective for treatment of nanofiltration concentrate	High operational cost due to current requirement.	(Top et al., 2011)
	Colour	91.8 % (after 30min treatment)				
	Phosphorous	60% (after 30min treatment)				
Al Electrode	COD	70%	Algeria	-	Higher operating cost	(Bouhezila et al., 2011)
	TN	24%				
	Colour	56%				
	Turbidity	60%				
Fe Electrode	COD	68%		Energetically more efficient	-	
	TN	15%				
	Colour	28%				
	Turbidity	16%				

Table 12: Application of Electrochemical techniques for leachate treatment

Materials Used	Scope	Efficiency	Country	Advantage	Disadvantage	Selected References
Dimensional Stable Anode (DSA)	Colour COD	90% 60%	Brazil	The overall process is effective for treatment of recalcitrant leachates	High operational cost Photo-electrochemical process can be improved by previous clarification process to reduce colour since, dark colour of leachate has negative impact on photochemical reaction	(Tauchert et al., 2006)
Oxide-coated Titanium anode	COD TOC Colour NH ₄ ⁻ N BOD	73% 57% 86% 49% 71%	Brazil	Effective for treatment of low biodegradability leachates	High operational costs	(Moraes and Bertazzoli, 2005)
Ti/IrO ₂ -RuO ₂	COD TC	90% 65%	Stabilized leachate obtained from lab scale bioreactor landfill used	Effective for treatment of stabilized leachate	High electricity consumption for 90% COD removal, removal decreases to 75% even after the addition of NaCl for the decrease of resistance	(Turro et al., 2012)

Table 13: Leachate treatment by membrane filtration

Technology	Scope	Efficiency	Country	Advantage	Disadvantage	Selected References
Nanofiltration	Al ³⁺ Ca ²⁺ Mg ²⁺ Mn ²⁺	84-100%	Canada	Nanofiltration can be run at lower pressure as compared to reverse osmosis Has lower operating cost	High capital cost and frequent membrane fouling	(Ortega et al., 2007)
Nanofiltration with vibration shear enhanced filtration	COD Humic Acid	60% 97%	Greece	System was able to handle large fluctuations in leachate composition	The desired effluent standards were achieved only when applied in combination with microfiltration or ultrafiltration	(Zouboulis and Petala, 2008)
Reverse Osmosis with vibration shear enhanced filtration	COD NH ₃ -N	96% 98%	Hong Kong	The vibratory shear enhanced reverse osmosis could handle large variation in leachate composition Limited membrane fouling	High capital and maintenance cost	(Chan et al., 2007)
Combined UASB reactor	COD (UASB reactor)	76%	Poland	Suitable for concentrated leachate	The startup of UASB reactor is difficult due	(Bohdziewicz and Kwarciak,

and RO treatment	COD BOD Chloride NH ₄ -N	95.4% 90.2% 85.4% 88.7%		Production of biogas Low sludge production Low operating cost	to low biodegradability of leachate and presence of toxic compound	(2008)
Aerobic thermophilic membrane bioreactor	COD BOD NH ₃ -N	79% 97-99% 60%	Thailand	Thermophilic system is highly suitable for COD and BOD removal especially at elevated organic loading	The system is unable to treat high nitrogen content wastewater High operation and capital cost	(Visvanathan et al., 2007)
Membrane sequencing batch reactor	COD TN Phosphate	<60% 88% 35-45%	Greece	A high nitrification and denitrification was achieved resulting in negligible ammonia nitrogen concentration and low nitrate nitrogen concentration	High capital and operating cost determined by the cost of the membrane Very low COD removal due to high solids retention time (SRT) Frequent membrane fouling	(Tsilogeorgis et al., 2008)
Composite PNR and Anammox reactor	NH ₄ -N TN COD	97% 87% 89%	China	Compared to the conventional biological treatment technologies, the composite PNR and Anammox	-	(Liang and Liu, 2008) (Liang and Liu, 2008)

reactor
promising
technical and
economic
advantages
as it involves
less oxygen
consumption
,
no organic
source
addition and
low sludge
production

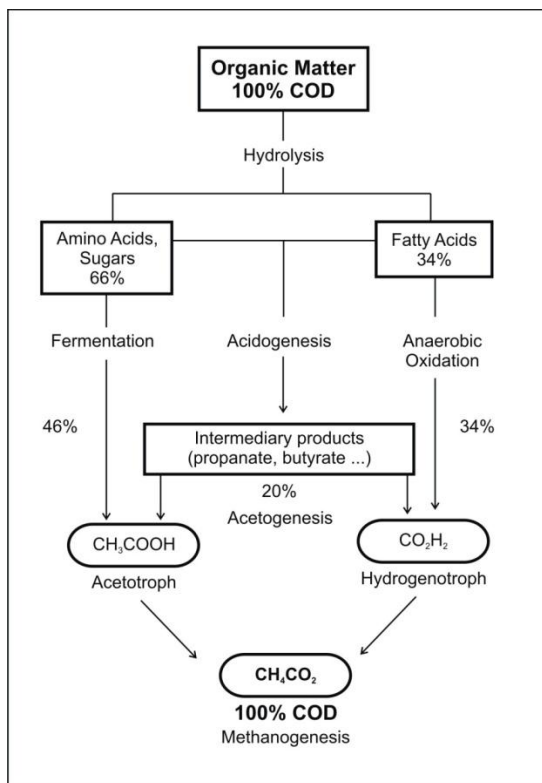


Figure 1: COD balance of the organic fraction in a sanitary landfill (Lema et al., 1988)

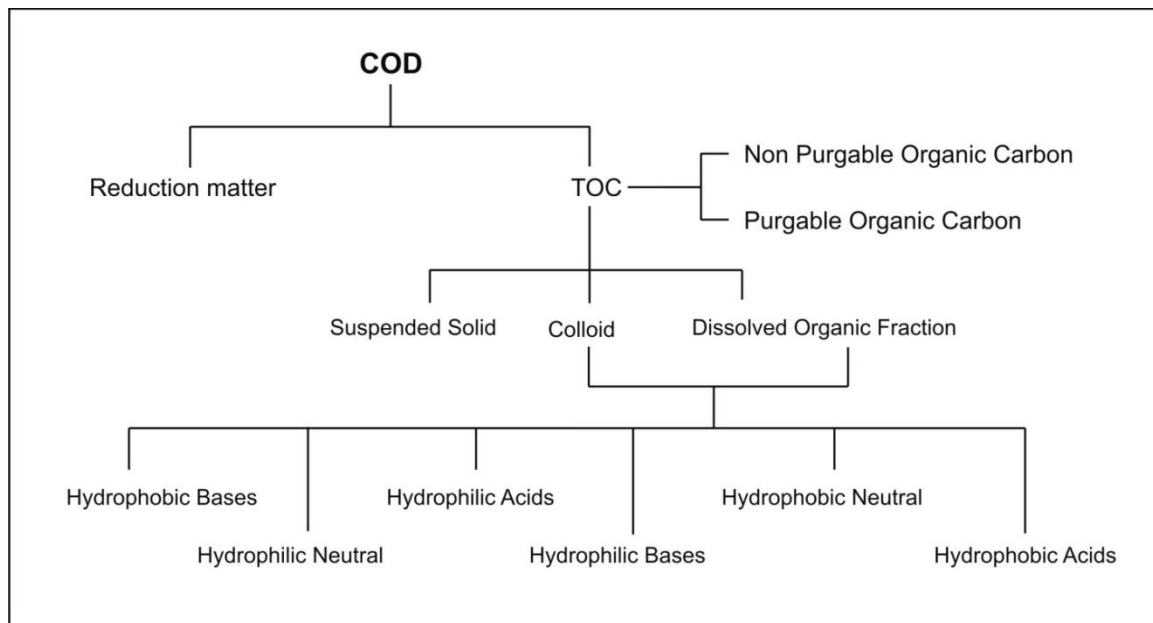


Figure 2: Fractions of COD in leachate during the stabilization phase of landfill (Ziyang et al., 2009)

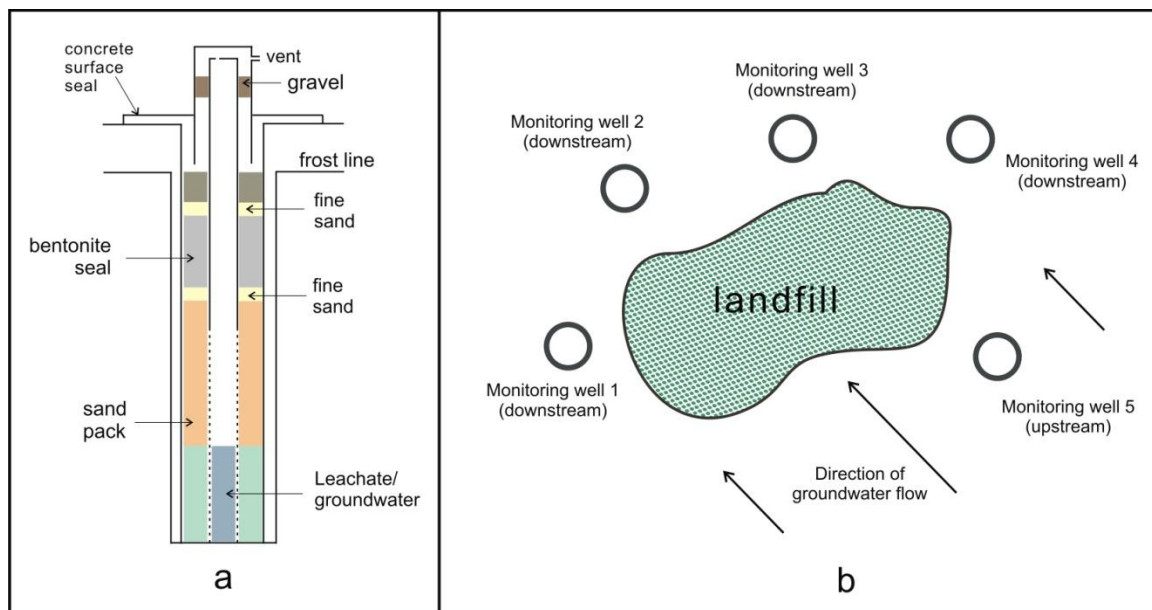


Figure 3: a. Cross section of a monitoring well; b. positioning of monitoring wells around a landfill.

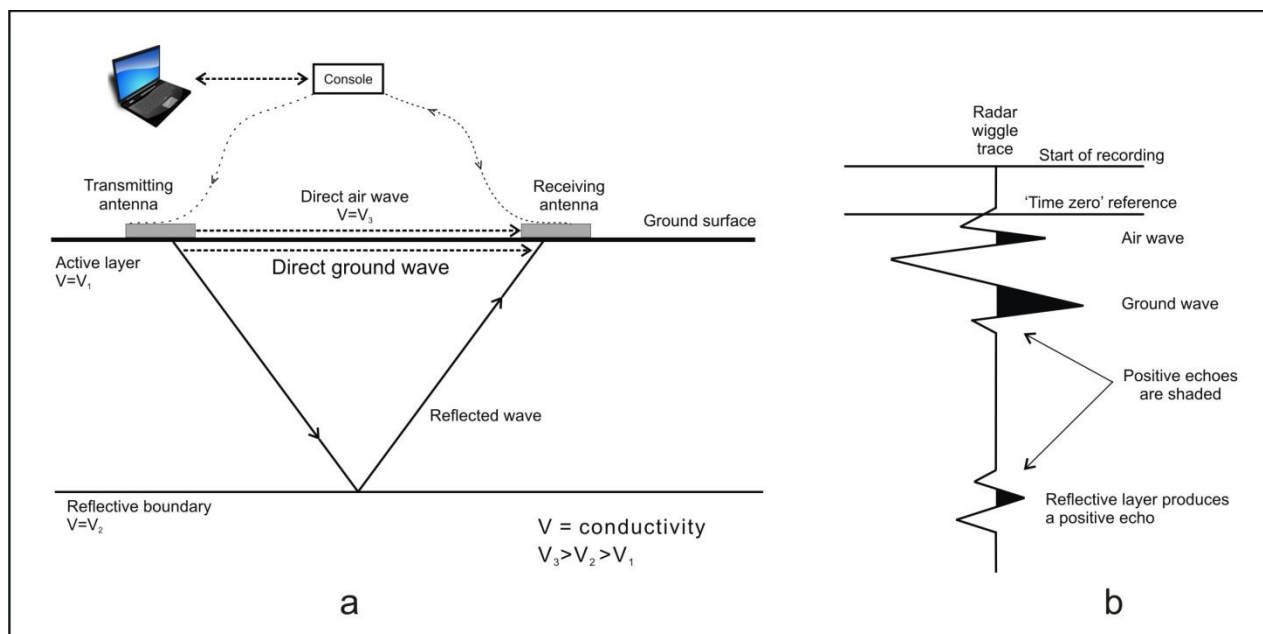


Figure 4: (a, b) Basic principles of GPR, adapted from Redman (2009)

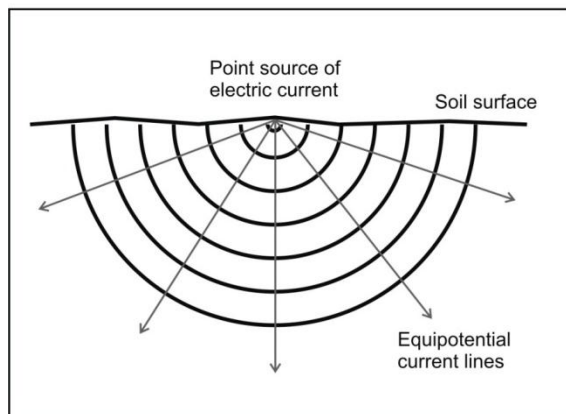


Figure 5: Distribution of the current flow in a homogeneous soil (Kearey et al., 2002)

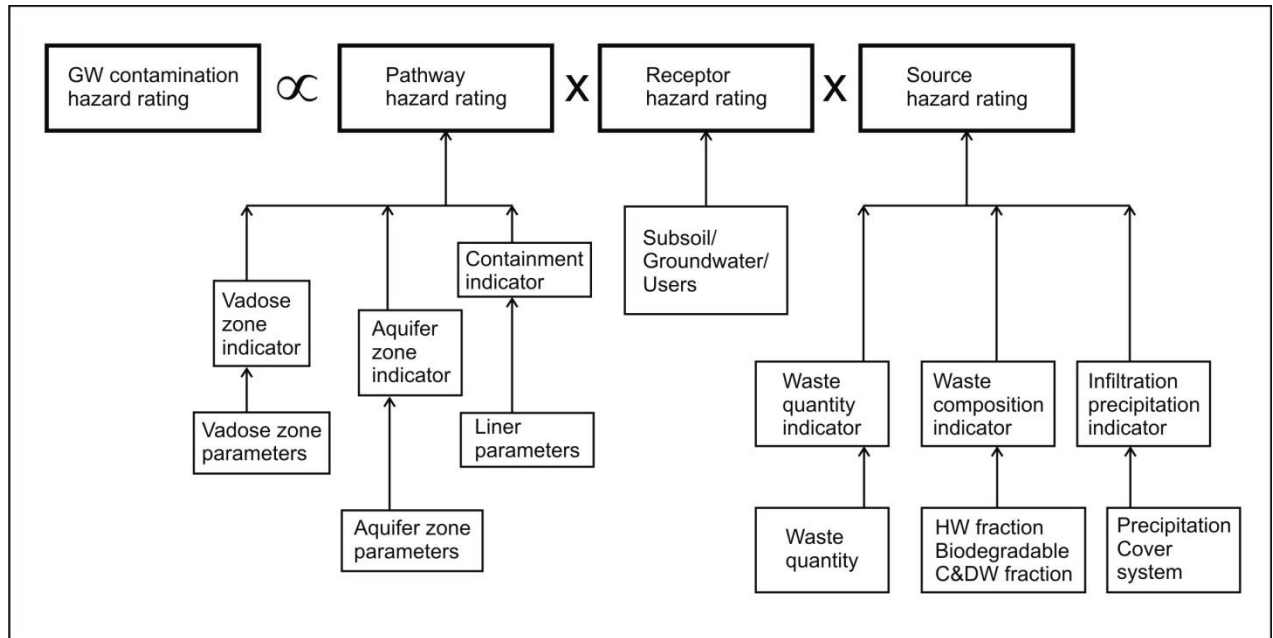


Figure 6: A conceptual diagram of the framework of the proposed system (Singh et al., 2009)

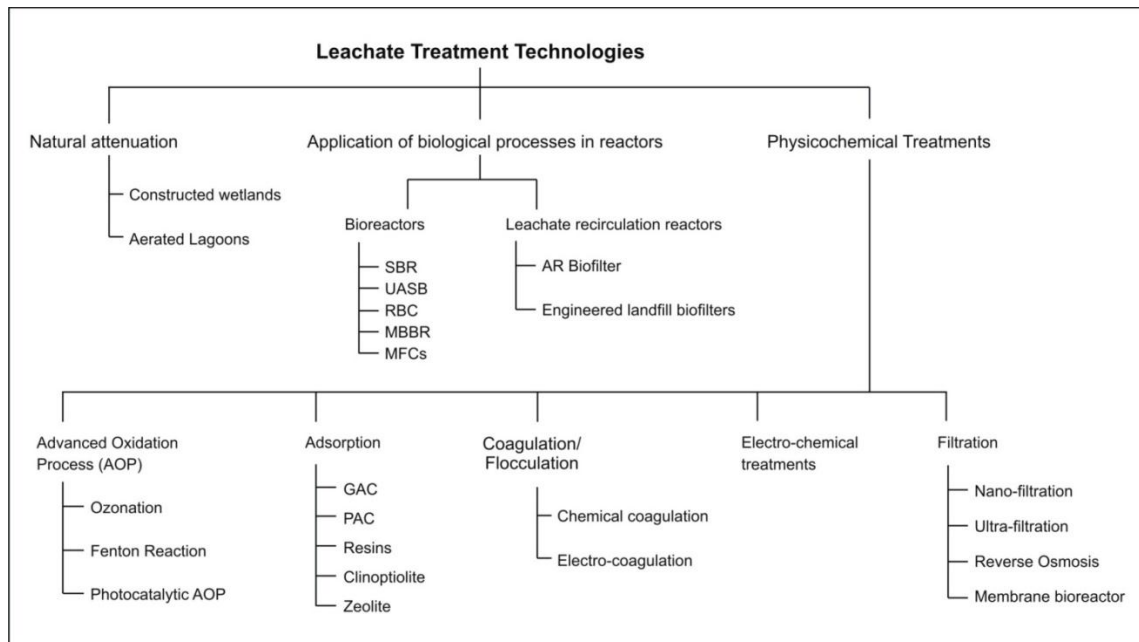


Figure 7: Classification of leachate treatment technologies

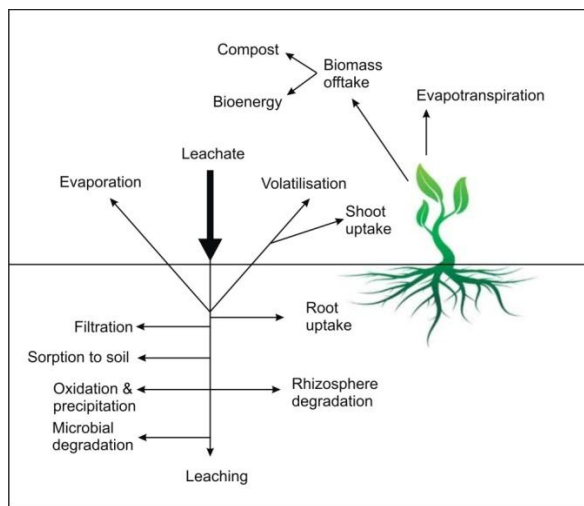


Figure 8: Representation of soil plant system in a CW adapted from Jones et al. (2006)

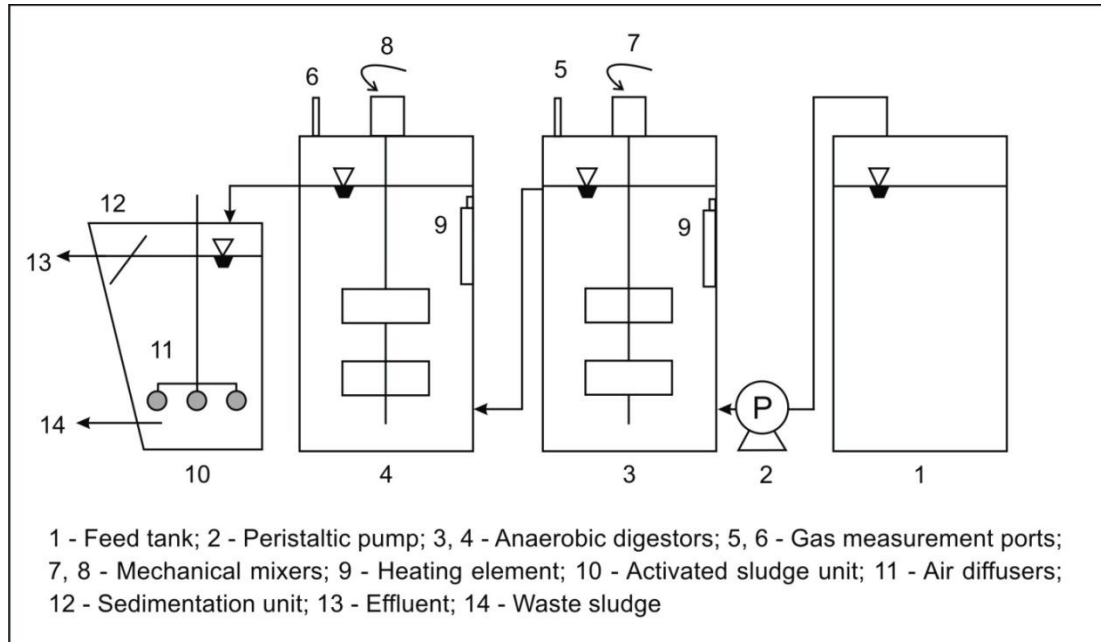


Figure 9: Laboratory scale combined Anaerobic- aerobic leachate treatment system adapted from Kheradmand et al. (2010)

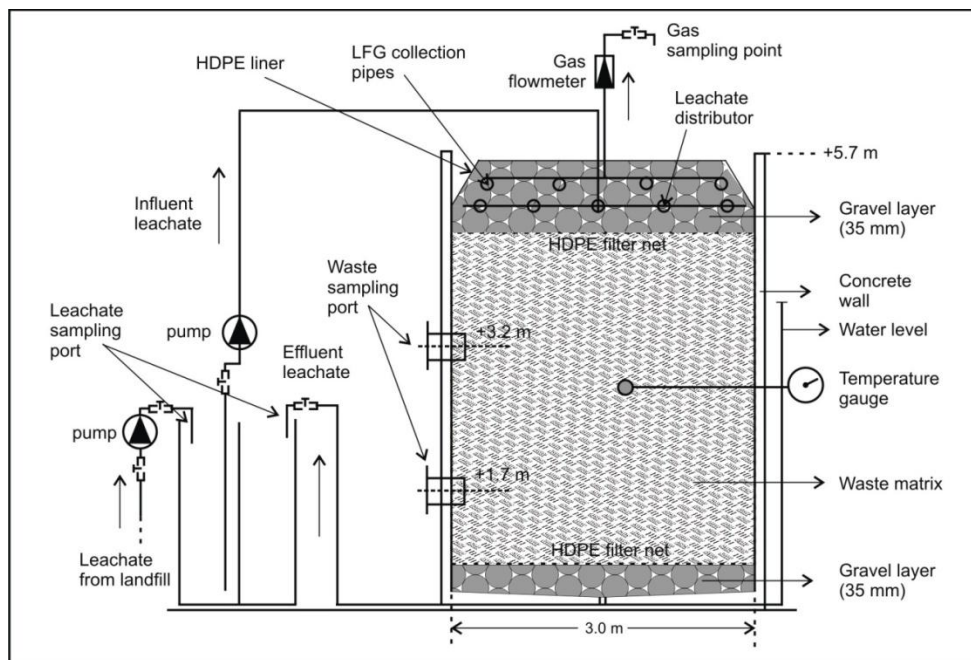


Figure 10: Pilot Scale recirculation bioreactor system adapted from Jiang et al (2007)

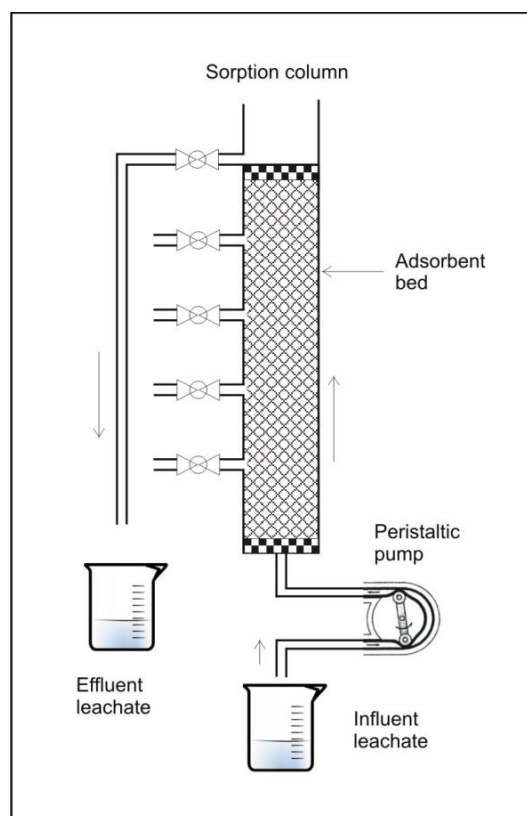


Figure 11: Schematic diagram of lab-scale column study adapted from Halim et al (2010b)

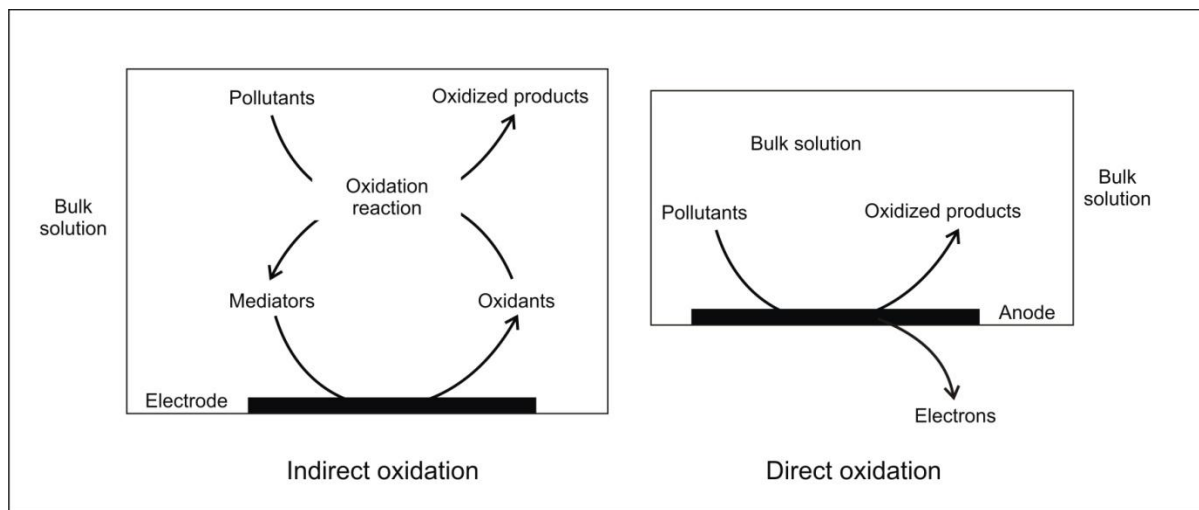


Figure 12: Pollutant removal pathways in electrochemical oxidation adapted from Deng and Englehardt (2007)

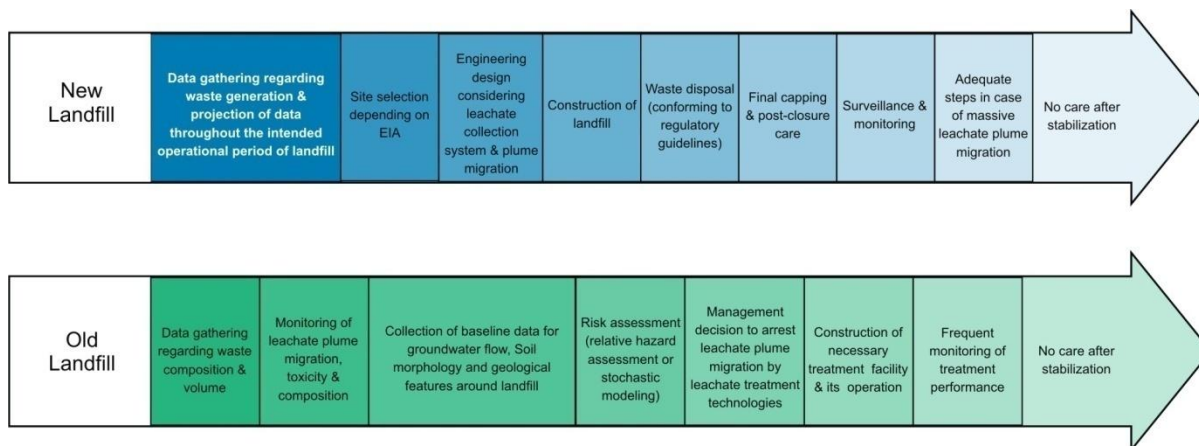


Figure 13: Management approaches towards old and new landfills