

Qualitative Study of Landfill Leachate from Different Ages of Landfill Sites of Various Countries Including Nepal

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Abstract: The present paper describes the qualitative analysis of landfill leachate at different ages of landfill sites (LFS) around the world and it has been prepared on the basis of extensive survey of literatures. The main objective of this study was to explore the knowledge on qualitative analysis of municipal solid waste landfill leachate. This paper provides a reliable and robust database for the prediction of leachate quality when new landfills are to be developed in Nepal and other parts of the world.

Large amount of biodegradable organic matter is indicated though high ratio of BOD/COD. This in turn leads to relative high concentration of Fe, Mn, Ni and Zn. The lower concentration of VFAs and high pH represents "old" leachate from the late methanogenic phase. The humic substances give a dark color to stabilized leachate. Due to the decreasing solubility of many metal ions with increasing pH, the concentration of metal ions is low in general. The strength of the leachate decreases with time with precipitation of soluble elements such as heavy metals as the organic compounds break down biologically. This is the reason why leachate management is problematic due to complexity in its design, operation, and composition, age of landfill, specific climate conditions and moisture routing through the landfill. In order to avoid pollution and toxicity level in the water bodies, it is legal necessity to treat landfill leachate before discharging it.

Key Words: Acetogenesis, Landfill Leachate, Methanogenic, Leachate, Bio-degradable

I. Introduction

Solid waste is the unwanted or useless solid materials produced in a given area. Human settlements, industrial, institutional and commercial areas as well as agriculture activities are the major sources of the solid waste. The quantity and the frequency of the waste generation goes with the rise in the population of any area. The refuse produced by the urban dwellers is comprehensibly heterogeneous. The city communities produce both organic and inorganic waste. However, the garbage resulting from agriculture and industrial activities are more homogeneous in nature. Issue of waste comes up with health and environmental concerns [1]. The ill-managed or unmanaged solid waste threatens human health and environment. The indiscriminate littering and improper waste handling causes variety of complications that results in impurity of water, festering of pests and rodents, which carries various diseases. Lack of proper solid waste management pollutes surrounding environment, threatens human health and status of aquatic creatures [2].

Despite the possible safety hazards from fire or explosion due to the gas formed in the landfill site or waste dump, the lack of proper waste management also increases greenhouse gas (GHG) emissions thereby contributing to climate change. The proper disposal of the collected waste in landfill is the only solution of above mentioned problems [3]. Landfilling is likely to be the most appropriate and cost-effective final disposal option for solid waste in developing countries. Facing the accelerated generation of solid waste caused by an ever-increasing population, migration from country side, urbanization, and industrialization, the problem has become one of the primary environmental issues in low and middle income Asian countries [1].

Nepal is situated in the Himalayan belt has a geometric growing population with high urbanisation rate. Factors like lack of proper solid waste management practices, leakage of hazardous substances to soil and surrounding aquatic systems, and health problems are causing problems connected to municipal solid waste (MSW). There are differences in waste generation and composition within and between urban areas and semi rural areas of Nepal. The household survey conducted by the solid waste management and technical support center, Nepal in support of Asian Development Bank (ADB) in 2011 [4] generated that an average per capita household waste generation rate of 0.17 kg/capita/day. The same study also uncovered that the household waste generation rates vary with the economic status and climatic conditions in Nepal. Households in Terai municipalities generate nearly 80% more waste than those in mountain region municipalities. Based on the analysis and findings, it is estimated that waste from households in general contributes about 50%–75% of the total MSW generated in Nepal. The analysis of household waste composition indicated that the highest waste category was organic waste with 66%, followed by plastics with 12%, and paper and paper products with 9%. The average MSW generation was found to be 0.317 kg/capita/day. MSW generation in municipalities of

Nepal was estimated at about 1,435 tons/day and 524,000 tons/year [4]. This indicates great potential for producing leachate in landfill sites of Nepal as landfill leachate depends upon the waste composition [5]. At present in Nepal out of 191 municipalities only 6 municipalities have landfill sites. At these landfill sites there are provision of leachate collection and leachate treatment plants but are not functioning at all. These cause the serious health and environmental problems in nearby areas, streams and rivers. A little study has been conducted in Nepal in order to gain the knowledge in field of the leachate composition. A study conducted by first author of this review paper initially found that the leachate water analyses showed high levels of BOD, COD, ammonia, iron, manganese, chromium and lead. In order to retrieve a broad picture of the current waste management situation, landfill and leachate problems serious investigation is needed at present. In Nepal it can be concluded that the urban areas of Nepal are very much in need of a more structured waste management system.

II. Landfill Processes

In this section, different dimensions of landfill process are discussed. Touching upon the physical and chemical process of the land filling briefly, the main focus in this paper will be the biological process of proper waste dumping. Nevertheless, biological process is greatly influenced by physical and chemical process [6]. The concluding part of this section will have the consequences resulting from these three types of process.

2.1 Physical

Broadly, there are 3 aspects of physical process of landfill. Compaction, dissolution and absorption are the steps involved in physical process of the fill. The process of settlement and compression goes together. Similarly, dissolution and transport are closely associated phenomena, although not to the same degree as compression and settlement. All components of the buried fills are subjected to these three processes. Compaction is the process that starts with the compression and size reduction of the particles by compacting mechanism and it goes on after the waste is in place [7]. The continuing compression is due to the weight of the wastes and that of the soil cover (burden). Sifting of soil and other fines are responsible for some consolidation. Settling of the completed fill is an end result of compression. This settling is in addition to the settlement brought about by other reactions (e.g., loss of mass due to chemical and biological decomposition).

The amount of water that enters a landfill has important bearing on physical reactions. Water acts as a medium for the dissolution of soluble substances and for the transport of untreated materials [8]. The untreated materials consist of animate and inanimate particulates. Particle sizes range from colloidal to several millimeters in cross-section [9]. In a typical landfill, the broad variety of components and particle sizes of the wastes provides conditions that lead to an extensive amount of adsorption, which is the adhesion of molecules to a surface. Of the physical phenomena, adsorption is one of the more important processes because it brings about the immobilization of living and non-living substances that could pose a problem if allowed to reach the external environment. It could play an important part in the containment of viruses and pathogens and of some chemical compounds [10].

Absorption does have its limits, one of which is its questionable permanency. One or several factors can alter permanency. For example, it can be altered by the effect of biological and chemical decomposition on adsorption sites. Absorption is another of the physical phenomena that takes place in a fill [11]. It is significant in large part because it immobilizes dissolved pollutants by immobilizing the water that could transport them and suspended pollutant particulates out of the confines of the landfill. Absorption is the process whereby substances are taken in by capillarity. Municipal waste is attributable to its cellulosic content. However, it should be recognized that, accepting fills located in arid regions, eventually all absorbent material in a fill becomes saturated. Consequently, absorption may be regarded as being only a delaying action as far as pollutant release is concerned.

2.2 Chemical

Oxidation is one of the two major forms of chemical reaction in a landfill. Obviously, the extent of the oxidation reactions is rather limited, in as much as the reactions depend upon the presence of oxygen trapped in the landfill when the landfill is made. Ferrous metals are the components likely to be affected [12].

The second major form of chemical reaction includes the reactions that are due to the presence of organic acids and carbon dioxide (CO_2) synthesized in the biological processes and dissolved in water (H_2O). Reactions involving organic acids and dissolved CO_2 are typical acid-metal reactions [13]. Products of these reactions are largely the metallic ions and salts in the liquid contents of the fill. The acids lead to the solubilization and, hence, mobilisation of materials that otherwise would not be sources of pollution [14]. The dissolution of CO_2 in water deteriorates the quality of the water, especially in the presence of calcium and magnesium [13].

2.3 Biological

The importance of biological reactions in a landfill is due to the following two results of the reactions:

- i. The organic fraction is rendered biologically stable and, as such, no longer constitutes a potential source of nuisances.
- ii. The conversion of a sizeable portion of the carbonaceous and proteinaceous materials into gas substantially reduces the mass and volume of the organic fraction.

At this point, it should be remembered that a fraction of the nutrient elements in the waste is transformed into microbial protoplasm. Eventually, this protoplasm will be subject to decomposition and, hence, it makes up a reservoir for breakdown in the future [15]. The wide varieties of landfill components that can be broken down biologically constitute the biodegradable organic fraction of MSW. This fraction includes the garbage fraction, paper and paper products, and "natural fibres" (fibrous material of plant or animal origin). Biological decomposition may take place either aerobically or anaerobically [7]. Both modes come into play sequentially in a typical fill, in that the aerobic mode precedes the anaerobic mode. Although both modes are important, anaerobic decomposition exerts the greater and longer lasting influence in terms of associated landfill characteristics [9].

2.3.1 Aerobic decomposition

The greater part of decomposition that occurs directly after the wastes are buried is aerobic. It continues to be aerobic until all of the oxygen (O_2) in the interstitial air has been removed. The duration of the aerobic phase is quite brief and depends upon the degree of compaction of the wastes, as well as the moisture content since the moisture displaces air from the interstices [16]. Microbes active during this phase include obligate as well as some facultative aerobes. Because the ultimate end products of biological aerobic decomposition are "ash", CO_2 and H_2O , adverse environmental impact during the aerobic phase is minimal. Although intermediate breakdown products may be released, their amounts and contribution to pollution usually are small [16].

2.3.2 Anaerobic decomposition

When the oxygen supply in a landfill soon is depleted, most of the biodegradable organic matter eventually is subjected to anaerobic breakdown. This anaerobic decomposition is biologically much the same as that in the anaerobic digestion of sewage sludge [17]. Microbial organisms responsible for anaerobic decomposition include both facultative and obligate anaerobes. Unfortunately, the breakdown products of anaerobic decomposition can exert a highly unfavorable impact on the environment unless they are carefully managed. The products can be classified into two main groups: volatile organic acids and gases [16]. Most of the acids are malodorous and of the short-chain fatty-acid type. In addition to chemical reactions with other components, the acids serve as substrates for methane-producing microbes. The two principal gases formed are methane (CH_4) and CO_2 [16]. Gases in trace amounts are hydrogen sulphide (H_2S), hydrogen (H_2) and nitrogen (N_2).

The nature, rate, and extent of biological decomposition in a fill are greatly influenced by the environmental factors that affect all biological activities. The nature of biological decomposition determines the nature of the decomposition products. The principal factors that influence biological decomposition in a conventional fill are moisture, temperature, and the microbial nutrient content and degree of resistance of the waste to microbial attack [1]. Moisture is a limiting factor in a fill at moisture content levels of 55% to 60% or lower, because microbial activity is increasingly inhibited as the moisture drops below the 55% level. The activity of most microbes increase with rise in temperature until a level of about $40^\circ C$ is reached. For some types of microbes, the upper temperature is on the order of 55° to $65^\circ C$. Because temperatures in tropical regions are more favorable, decomposition can be expected to proceed more rapidly and to a greater extent. With respect to nutrients, wastes characterized by a high percentage of putrescible matter approach the ideal in terms of decomposition [18].

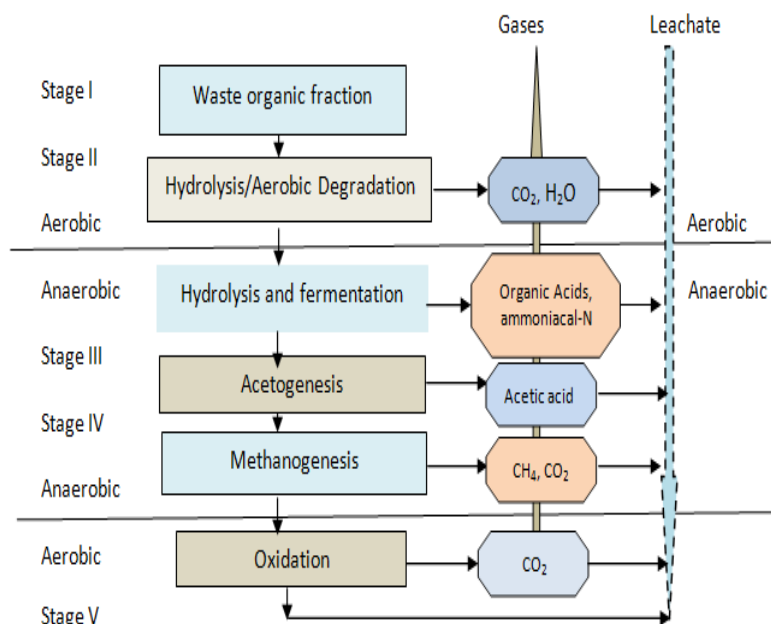


Figure 1: Biological Decomposition Process in a Landfill [19]

III. Water Balance And Leachate In Landfills

Leachate is the liquid that extracts solutes, suspended solids or any other component of the wastes as it passes through different layers of landfill. Leachate differs in composition according to the age of landfill and the type of the waste that it contains [5]. The rate of the production of the leachate can be found out by performing the value of a water balance. The water balance includes all the sources of water entering and leaving the landfill site, water used for the biochemical reaction and the water lost in the form of vapour from the landfill site [18]. The primary of sources of water are water entering the fill through the cover (precipitation), moisture in the cover material, groundwater inflow and inherent moisture in the solid waste. And also the water formed as a by-product of decomposition of the wastes. Water leaves the landfill in the form of saturated vapour in the landfill gas, and through transpiration. The remainder of the water is either stored by the wastes or becomes leachate. The various components of a water balance for a landfill are presented in the figure 2. The vegetation on the cover utilizes water to build plant tissue and results in water loss by transpiration. The total amount of moisture that can be stored in a unit volume of soil is a function of two variables the field capacity (FC) and the wilting point (WP) of the soil. The FC of a soil is defined as the quantity of liquid that remains in the pore space following a prolonged period of gravitational drainage [18]. The WP of a soil is defined as the quantity of water that remains in a soil after plants are no longer capable of extracting any more water. The difference between the field capacity and the wilting point is equivalent to the quantity of moisture that can be stored in a particular type of soil [3]. Since a potential major contributor to the formation of leachate is precipitation, an estimation of its infiltration into the cover is an important aspect of establishing the water balance on the landfill system as shown in figure below.

The components of the water balance for a landfill can be expressed by the following equation if groundwater infiltration is insignificant [18]:

$$MC = W_{sw} + W_c + W_p - W_{RO} - W_{lfg} - W_v - W_{evap} + W_{leach}$$

Where,

MC = change in the quantity of moisture stored in the landfill (kg/m³);

W_{sw} = quantity of water in the incoming solid waste (the moisture content of solid waste ranges from 30% to 60% in developing countries, depending on the location) (kg/m³)

W_c = quantity of water in the cover material (kg/m³)

W_p = quantity of water from precipitation and other outside sources (kg/m³)

W_{RO} = quantity of water from precipitation diverted as runoff (kg/m³)

W_{lfg} = quantity of water utilised in formation of landfill gas (on order of 0.2 kg/m³ of gas)

W_v = quantity of water lost as saturated vapour with the landfill gas (on the order of 0.04 kg/m³ of gas)

W_{evap} = quantity of water lost due to evapotranspiration (kg/m³)

W_{leach} = quantity of water leaving the (control volume) landfill as leachate (kg/m³).

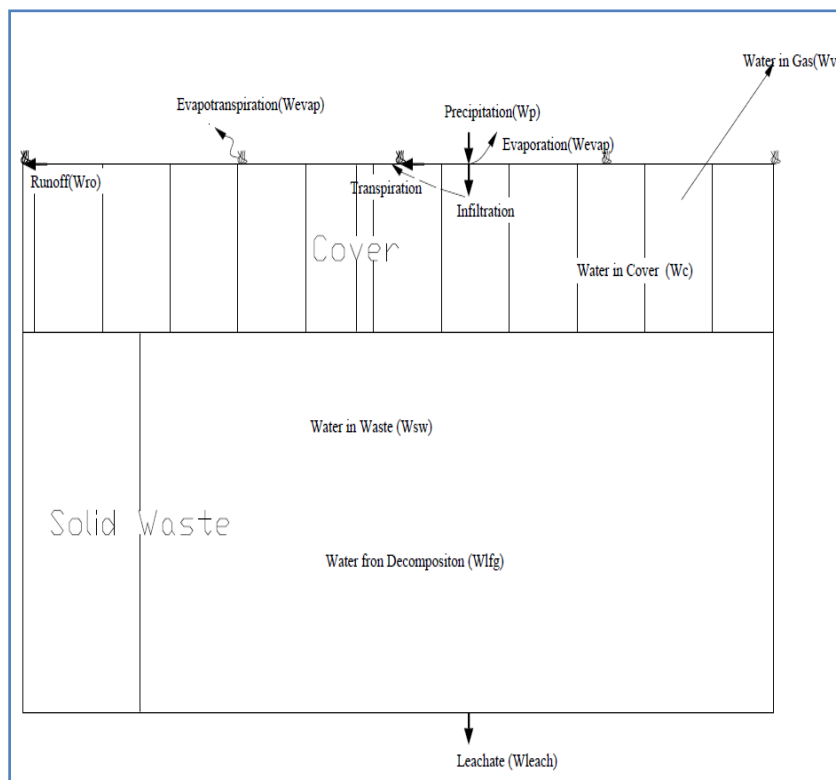


Figure 2: Water balance for a landfill sites [19]

Landfill leachates are one of the most pollution problems caused by Municipal Solid Waste landfill. The characteristics of Leachate can be explained in terms of many chemicals like Organic matters, inorganic matters and xenobiotic organic compounds. Inside landfill many complex events occur which can be classified as physical, chemical and biological process [16]. As outcome of these processes, waste is disintegrated or transformed and when the water flows through the transformed waste, it contains leached with the water which include inorganic soluble matters, soluble biodegraded matters of complex organic processes, soluble matters from chemical reactions and inorganic fine suspended and colloidal solid. Leachate generated in this way are affected by many factors like quality of solid waste, degree of compaction in landfill, age of waste, climatic condition and hydrogeological condition of landfill site, pH, chemical and biological process occurs during degradation [1].

After the closing of landfill site also, the harmful and contaminated leachate production continues for 30 – 50 years. The main component of leachate is organic matters though it also contains ammonia-nitrogen, heavy metals, inorganic salts and chlorinated organic pigments [16, 17]. And these are the major threat to the surrounding pollution mainly soil and water pollution. These pollutants can be categorized into organic matters, such as COD (chemical oxygen demand), BOD (biological oxygen demand) and TOC (total organic carbon); specific organic compounds, inorganic compounds and heavy metals. The stabilization of the waste occurs in acetogenic, early methanogenic, late methanogenic and stabilization successive and distinctive phases [1, 18]. Landfill contains areas of refuse of varying ages and states of decomposition. Thus, where leachate from older methanogenic refuse is mixed with leachate from fresher refuse in the acid phase, it is not possible to relate leachate composition to processes within the waste layers. Furthermore, where leachate from refuse in the acid phase percolates through well-decomposed refuse, the leachate can be expected to reflect the composition of methanogenic leachate [19]. This is because the high COD of the acid phase leachate will be consumed as the leachate passes through the well decomposed, and thus, there is carbon limited refuse. In cases where leachate is released to groundwater, such as in the case of older landfills that are not lined, the spatial distribution of the leachate quality is especially important to evaluate the leaching to the underlying strata. This requires a large number of sampling points [19].

IV. Leachate Sample Collection Technique

Since there is variation in the composition of leachate due to the factors like waste composition, waste age, landfilling technology, leachate sample collection techniques may also influence the measured leachate quality [5]. For example, colloids have a high affinity for heavy metals thus the concentration of heavy metals measured in a leachate sample may depend strongly on the amount of colloidal matter present in the sample and

the handling of the sample. No standard protocols for sampling, filtration, and storage of leachate samples exist. The content of colloidal matter in a sample depends to a large extent on the sampling technique used [20] where samples are obtained from groundwater monitoring wells. A high pumping rate will increase the colloid content of the sample significantly [17], and the heavy metal concentration may also be increased. Thus leachate samples should be filtered in the field before analysis of heavy metals, especially when the sampling is done quickly. Alternatively, samples could be withdrawn under very low pumping rates and after sufficient removal of the well. Leachate samples should be maintained under anaerobic condition until they are preserved because metal solubility varies according with their oxidation stage.

V. Characteristics Of Landfill Leachate

Generally saying, leachate from acid phase young landfill comprise of huge quantity of biodegradable organic matter [19]. Volatile fatty acid is found more than 95% in dissolved organic carbon (DOC) with little amount of high molecule weight compounds. Likewise, leachate from methanogenic phase mature landfill is highly dominated by refractory compounds and the DOC content consists of high molecular weight compounds [17]. Tables 3 and 4 summarize the ranges of leachate composition in detail. Values of COD vary from 70,900 mgL⁻¹ with leachate sample obtained from the Thessaloniki Greater Area (Greece) to 100 mg L⁻¹ with sample from more than 10-years old landfill near Marseille (France). With few exceptions, the pH of leachates lies in the range 5.8–8.5 as a result of the biological activity that takes inside the tip. It also shows the majority of TKN is ammonia, which can range from 0.2 to 13,000 mg L⁻¹ of N. But the ratio of BOD/COD is from 0.70 to 0.04 which is in decreasing pattern in relation to the age of landfill site due to the release of the large recalcitrant organic molecules from the solid wastes. The old landfill sites produce leachate with low ratio of BOD/COD and fairly high NH₃-N. Thus, the age of land fill sites is the determining factor for the production of leachate composed of diverse elements including stabilization stages of the waste evolution [19].

Table- 1: Characteristics of leachate at different ages of landfill sites

Parameters	Young	Intermediate	Mature
Age	<5	5-10	>10
pH	6.5	6.5-7.5	>7.5
COD mg/l	>10,000	4,000-10,000	<4,000
BOD mg/l	>2,000	150-2,000	<150
BOD/COD	>0.3	0.1-0.3	<0.1
Organic compound	80% VFA	5-30% VFA+humic & fomic	Humic & fomic
Heavy Metals	Medium	low	low
Biodegradability	Imp	Medium	Low

Source: [16]

Table- 2: Typical concentrations in landfill leachate comparing with sewage and groundwater

Parameters	Young leachate	Old leachate	Typical sewage	Typical ground water
COD (mg/l)	20,000-40,000	500-3,000	350	20
BOD (mg/l)	10,000-20,000	50-100	250	0
TOC (mg/l)	9,000-25,000	100-1,000	100	5
Volatile fatty acids (mg/l)	9,000-25,000	50-100	50	0

Source: [21]

Table- 3: Heavy Metals Composition in Landfill Leachate

Y-Young, MA- Medium age, O- Old; (all values except pH and BOD/COD are in mg/l)

Age	LFS	Fe	Mn	Ba	Cu	Al	Si	Ref.
Y	Italy	2.7	0.04	–	–	–	–	[72]
MA	Canada	1.28-4.90	0.028-1.541	0.006-0.164	–	<0.02–0.92	3.72-10.48	[63]
MA	Hong Kong	3.811	0.182	–	0.12	–	–	[73]

MA	South Korea	76	16.4	–	0.78	–	–	[62]
MA	Spain	7.45	0.17	–	0.26	–	–	[74]
O	Brazil	5.5	0.2	–	0.08	<1	–	[32]
O	France	26	0.13	0.15	0.005–0.04	2	<5	[69]
O	Malaysia	4.1–19.5	15.5	–	–	–	–	[42]
O	South Korea	–	0.298	–	0.031	–	–	[74]

Table- 4: Leachate composition (COD, BOD, BOD/COD, pH, SS, TKN, NH3-N)

Age	LFS	COD	BOD	BOD:COD	pH	SS	TKN	NH3-N	Ref.
Y	Canada	1870-13800	90-9660	0.05-0.7	5.8-6.58	–	75-212	10.0-40	[60]
Y	China, Hong Kong	13000-50,000	4200-22000	0.27-0.44	6.8–9.1	2000-5000	3200-13000	2260-13000	[61]
Y	China, Mainland	1900–3180	3700–8890	0.36–0.51	7.4–8.5	–	–	630–1800	[17]
Y	Greece	70,900	26,800	0.38	6.2	950	3,400	3,100	[18]
Y	Italy	10540-19900	4000-4000	0.2-0.22	8-8.2	1666	–	3917-5210	[16]
Y	South Korea	24,400	10,800	0.44	7.3	2400	1,766	1,682	[62]
Y	Turkey	10,750–50000	6380–25000	0.5–0.67	5:6–8.2	2630–3930	2,370	1,946–2,002	[40]
MA	Canada	3210–9190	–	–	6.9–9.0	–	–	–	[63]
MA	Nepal	2500-4000	325-1500		6.4-7.8	-	-	-	[5]
MA	China, Hong Kong	7439	1436	0.19	8.22	784	–	–	[64]
MA	Germany	3180-4000	800-1060	0.20.33	–	–	1,135	800-884	[65]
MA	Greece	5350	1050	0.2	7.9		1,100	940	[18]
MA	Italy	3840-5050	1200-1270	0.25-0.31	7.9-8.38	480	1100-1670	940-1330	[66]
MA	Poland	1180	331	0.28	8	–	–	743	[67]
MA	Taiwan	6500	500	0.08	8.1	–	–	5,500	[24]
MA	Turkey	9500	–	–	8.15	–	1,450	1,270	[32]
O	Brazil	3460	150	0.04	8.2	–	–	800	[68]
O	Estonia	2170	800	0.37	11.5	–	–	–	[16]
O	Finland	340–920	62-84	0.09–0.25	7.1–7.6	–	192	159–560	[69]
O	France	100-1930	3-7.1	0.01-0.03	7-7.7	13–1480	5–960	0.2-430	[70]
O	Malaysia	1533–2580	48–105	0.03–0.04	7.5–9.4	159–233	–	–	[42]
O	South Korea	1409	62	0.04	8.57	404	141	1,522	[71]
O	Nepal	100-320	80-350		7.9-8.8	-	-	-	[5]
O	Turkey	10,000	–	–	8.6	1600	1,680	1,590	[53]

5.1 QUALITATIVE PARAMETERS FOR THE LANDFILL LEACHATE

5.1.1 Color and Odor

The leachate samples are of color orange brown or dark brown or black. Leachates produces malodorous smell, mainly due to the presence of organic acid, which arises because of the high concentration of organic matter when decomposed. The presence of high organic substances is responsible for the high concentration of color in landfill [21]. Generally, leachate produced by an old landfill with low biodegradability is classified as stabilized leachate. Such leachate contains high levels of organic substances such as humic and fluvic compounds, which can be indicated by leachate color [22]. The humic substances are natural organic matter and are made up of complex structures of polymerized organic acids, carboxylic acids and carbohydrates [1].

5.1.2 pH

The pH in a landfill varies according to the age of landfills. Generally stabilized leachate has higher pH than of young leachate [1]. Leachate generally is found to have pH between 4.5 and 9. The pH of young leachate is less than 6.5 while old landfill leachate has pH higher than 7.5 [22]. Little variation is seen in stabilized leachates which have fairly constant pH ranging 7.5 to 9 [18]. In acid formation phase, pH levels are expected to be lower due to the production of volatile organic acids (VOAs). While in the methanogenic phase, as the intermediate acids are consumed by methanogenic bacteria the pH values increase. Some other researchers [23] reported that the pH of leachate increases with the decrease of the partially ionized free volatile fatty acids [24]. Increase in the pH suggest that a steady state has been reached between acid producing processes (e.g., cellulose and lignin degradation) and acid consuming processes (e.g., methane formation) at the landfill [25]. Leachates exposure to the atmosphere could cause some removal of carbon dioxide from the leachate which tends to raise the pH [26]. Some studies even suggest that the higher pH levels of leachate in the leachate collection pond may be the result of carbon dioxide being utilized by algae.

5.1.3 Dissolved Organic Matter

It is quantified as Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC), volatile fatty acids (that accumulate during the acid phase of the waste stabilization [27], and more refractory compounds such as fulvic-like and humic-like compounds. From the leachate many researchers tested Fe (II), Mn (II), and sulfide contributed up to one-third of the COD. Poor sampling methods that expose anaerobic leachate to oxygen may cause Fe (II) to oxidize to Fe (III) and precipitate out of the leachate. COD decreases relative where Fe (II) gets oxidized as part of the COD analysis [6]. This could be observed when the sample was maintained under anaerobic conditions until after filtration, at which point it could be acidified to reduce iron oxidation. Dissolved organic matter in leachate includes a bulk parameter covering a variety of organic degradation products ranging from small volatile acids to refractory fulvic and humic-like compounds [26]. The complex properties of the high-molecular-weight component of the dissolved organic matter are the constituents through which dissolved organic matter can affect leachate composition. At the most general level, a low BOD/COD ratio suggests a leachate with low concentrations of volatile fatty acids and relatively higher amounts of humic and fulvic-like compounds [1]. In the acid-phase leachate, more than 95% of the DOC content of 20,000 mg/l consisted of volatile fatty acids and only 1.3% of the DOC consists of high molecular-weight (MW) compounds (MW > 1000). No volatile acids, amines, or alcohols are detected, and 32% of the DOC (2100 mg/l) consisted of higher-molecular-weight compounds (MW > 1000) in the methanogenic-phase leachate. According to [6] methanogenic-phase leachate, described more than 60% of the DOC content as humic-like material. Whereas 11. While some other researches [28] found that only 6 to 30% of the DOC could be described as fulvic acids in leachate.

5.1.4 BOD, COD and BOD/COD ratio

The amount of oxygen required or consumed for the microbiological decomposition (oxidation) of organic material in water or wastewater is measured through BOD. Unit of Measurement: mg/l of oxygen consumed in 5 days at a constant temperature of 20°C in the dark. BOD measures the biodegradable organic mass of leachate and that indicates the maturity of the landfill which typically decreases with time [29]. Due to the degradation of BOD in the leachate the waste constituents percolate down along with rainwater thus polluting groundwater nearby to MSW landfill site. The value of BOD varies according to the age of landfills. The value of BOD values for new landfills were 2000-30000 mg/l; while for mature landfills, BOD value varies from 100-200 mg/l [30]. The concentration of BOD and COD appears to remain low (less than 1500 mg/l) throughout the life of the landfill, most likely due to dilution and stimulation of methanogenesis. The elevated pH in the acidogenic phase is indicated by the stimulation of methanogenesis [6]. COD represents the amount of oxygen needed to oxidize the organic waste components chemically to inorganic end products. The dilution and stimulation of methanogenesis makes the BOD and COD concentration to appear low as the life of landfill sites increases. The pH in the acidogenic phase supports the stimulation of methanogenesis [18]. Leachate from the shredded waste fill has significantly higher concentration of organic pollutants than that of un-shredded waste landfills as evidenced in the high COD and BOD levels from the South Dade Shredded Landfill [1]. In other words, leachate from shredded waste fills has significantly higher concentrations of organic pollutants than leachate from un-shredded landfills.

COD Versus Age of Landfill:

The highest concentration in leachate contains organic compounds which are volatile fatty acids (e.g. acetic, propionic, and butyric) produced during the decomposition of lipids, proteins, and carbohydrates. Similarly, in the lower concentrations Aromatic hydrocarbons, including benzene, various xylenes, and toluene, are also found frequently [27]. These compounds were considered to be components of gasoline and fuel oils. In other study researchers [27] reported that the presence of the more soluble, less volatile aromatic components of

gasoline meant that the more volatile components were being stripped by the gas from the landfill. Even nicotine, caffeine, and phthalate plasticizers are found in small fraction in several leachates [19]. In a similar other study, researchers reported [30] through their observation identified the total of 150 different organic compounds in several studies but only 29 were identified in more than one. With this observation they concluded that leachate composition was quite site specific. The ongoing microbial and physical / chemical process within the landfill is the reason why the dominant organic class in leachate shift as the age of the landfill increases. An investigation of leachates obtained from landfills operated from one to twenty years found that the relative abundance of high molecular weight humic-like substances decreases with age, while intermediate sized fulvic materials (e.g. high density carboxyl and aromatic hydroxyl groups) showed significantly smaller decreases [31]. The relative abundance of organic compounds present in leachate was observed to decrease with time in the following order: free volatile fatty acids, low molecular weight aldehydes and amino acids, carbohydrates, peptides, humic acids, phenolic compounds, and fulvic acids [30].

BOD/COD Ratio:

Different level of biodegradability characterizes the organics in leachate. Generally, the age of landfill is known through the BOD/COD ratio, which is the degree of its biodegradation. Lower range of BOD/COD ratio indicated higher concentration of non- Biodegradable organic materials which with difficulty degrades biologically [27]. In a landfill through BOD/COD ratio degradation of organic materials can be known. This instead can be used as an indicator to differentiate the acetogenic phase from methanogenic phase in this landfill. To differentiate acetogenic phase from methanogenic phase, the indicator for degradation of organic matter in this landfill. The quality of leachate affects by microbial activity which determines the duration of waste placement in landfill [27]. As BOD is predominantly a biochemical parameter, it generally reflects biodegradability of organic matter in leachate thus making BOD/COD ratio the good indicator of the proportion of biochemically degradable organic matter to total organic matter [32]. It is summarized that BOD/COD ratio is a best indicator for degrees of both biological and chemical decompositions that are taken place in the landfill and can also be taken as an indicator of degradation of organic matter in landfill. It will be good information source for designing and managing of leachate of landfill that will be made realistic prediction for future trends. An eventual decline in BOD and COD concentrations is often observed as organic matter is being removed via washout and degradation [5].

5.1.5 Ammonia

A study was conducted for ammonia concentration [33] and it was concluded that ammonia concentrations between 50 and 200 mg/L have been shown to be beneficial to anaerobic processes. Ammonia concentrations between 200 and 1000 mg/L have been shown to have no adverse effects on anaerobic processes while concentrations ranging from 1500 to 3000 mg/L have been shown to have inhibitory effects at higher pH levels. Concentrations above 3000 mg/L were toxic to microorganisms. Ammonia and organic nitrogen produced by decomposition of organics are stable in an anaerobic environment, and therefore represent a high percentage of the soluble nitrogen compounds in leachate [22]. Leachates of older landfills generally have lower concentrations and percentages of these constituents [6]. In leachate the ammonia generally produced from organic matter. So that, it is expected that the BOD, COD, and ammonia concentrations would be lower in the leachate from ash fills due to the lack of organic matter in MSW incinerator ash. Many investigations report shows that of ammonia-nitrogen in the range of 500 to 2000 mg/l, and no decreasing trend in concentration with time. Ammonia came from the waste by decomposition of proteins. The only mechanism by which the ammonia concentration can decrease during refuse decomposition is leaching because there is no mechanism for its degradation under methanogenic conditions [34]. While in other study scientist [35] reports that there is no significant change in ammonia concentrations from the acidic to methanogenic phase, and that the average value is 740 mg-N/l. Ammonia concentrations will remain high even in leachate from older landfills that is otherwise low in organic content.

5.1.6 Inorganic Macro-components

The major inorganic macro components detected in landfill leachate are Calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), ammonium (NH_4^+), iron (Fe^{2+}), manganese (Mn^{2+}), chloride (Cl^-), sulfate (SO_4^{2-}) and hydrogen carbonate (HCO_3^-). Borate, sulfide, arsenate, selenate, barium, lithium, mercury, and cobalt are also found in very low concentrations and are only of secondary importance [10]. The concentrations of some inorganic macro-components in leachate depend on the stabilization of the landfill. The cations calcium, magnesium, iron, and manganese are lower in methanogenic phase leachate due to a higher pH (enhancing sorption and precipitation) and lower dissolved organic matter content, which may form complexes with the cations. Sulfate concentrations are also lower in the methanogenic phase due to microbial reduction of sulfate to sulfide. The effects of sorption, complexation and precipitation are minor for macro-components like

chloride, sodium, and potassium [33]. Concentration of these pollutants may decrease with time due to leaching, but did not observe any decrease in concentration for these parameters after up to 20 years of leaching.

5.1.7 Inorganic Compounds

Major heavy metals found in leachate are Cadmium (Cd^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), lead (Pb^{2+}), nickel (Ni^{2+}) and zinc (Zn^{2+}). The variations in heavy metals among landfills are wide and varied. There are some heavy metals are sometimes found in landfill leachates including zinc, copper, cadmium, lead, nickel, chromium, and mercury [36]. Heavy metal concentrations in leachate do not appear to follow patterns of organic indicators such as COD or BOD, nutrients, or major ions [36]. Heavy metal release is a function of characteristics of the leachate such as pH, flow rate, and the concentration of complexing agents. With increasing pH Metal solubility's generally decrease. In addition, the hydrogen ion concentration will indirectly influence metal solubility by its impact on such processes as the dissociation of an acid to yield a precipitant anion and reduction-oxidation reactions [37].

With time, moderate to high molecular weight humic-like substances are formed from waste organic matter in a process similar to soil humification. These substances tend to form strong complexes with heavy metals. The formation of complexes between heavy metals and ligands tends to increase metal solubility although there are conditions under which the opposite may be expected [38]. Sulfide, however, effectively competes with most complexing agents, and consequently many heavy metals will precipitate as sulfides rather than remain in solution as complexes [36]. In a study researcher also reported [26] that the formation of metal sulfides under anaerobic conditions effectively eliminated the majority of heavy metals in leachate. In some instances, a remobilization of metals occurs once the organic content has been stabilized and oxic conditions begin to be reestablished [39]. Adsorption is another important mechanism controlling the heavy metal concentration. Under oxidizing conditions, adsorption can regulate the concentration of metals well below the level controlled by precipitation effects [36].

Electrochemical processes can influence metal speciation and behavior both directly by modifying the nature of the metal itself and indirectly through conversion by other species in the landfill environment. For example, the toxic non-metal, selenium, can be removed from landfills by reduction to the neutral element or conversion to the selenide ion which will be readily precipitated by ferrous ions [40]. Specific conductance is a gross indicator of the total concentration of dissolved inorganic matter or ions present in leachate. The primary metal species contributing to specific conductance are calcium, magnesium, sodium, and potassium [41].

Heavy Metal Attenuation and Mobilization in Landfills:

Only 0.02% of heavy metal leaches out from the total heavy metals deposited at landfill at the period of 30 years, so low concentrations of heavy metals is seen in methanogenic leachate [42]. Waste contains soils and organic matter, which, especially at the neutral to high pH values prevailing in methanogenic leachate, has a significant sorptive capacity [42]. In addition, the solubilities of many metals with both sulfides and carbonates is low, and these anions are typical in landfills. Sulfide is formed from sulfate reduction during waste decomposition in landfills, and sulfide precipitation is often cited as an explanation for low concentrations of heavy metals [43, 44].

Sulfides and carbonates are capable of forming precipitates with Cd, Ni, Zn, Cu, and Pb. While carbonates are abundant in landfill leachate, the solubilities of metal carbonates are generally higher than that of metal sulfides [5]. In general, sulfide precipitation is expected to dominate heavy metal attenuation compared with complexation agents [45]. Cr is an exception to this because it does not form an insoluble sulfide precipitate [43]. However, Cr tends to form insoluble precipitates with hydroxide [44, 46]. Investigations of the sulfur content of landfilled waste have shown that the waste does not contain sufficient sulfur to bind all the heavy metals present in the waste. The landfill sampled by [47] contained only enough sulfur to bind 5% of metals present. Occasionally, phosphates and hydroxides will also precipitate metals [45]. Hydroxide precipitates form at pHs at or above neutral, which is typically the case in methanogenic leachates [45]. There are many processes including complication to inorganic and organic ligands, and sorption to colloids are capable of mobilizing heavy metals by increasing the concentration in the mobile aqueous phase. A highly varying fraction of the heavy metals was incorporated with colloidal fractions. Researcher also reported [48] that in an American landfill a significant fraction of the Zn, Pb, and Cr were in colloidal fractions. Further, in the same study at a German landfill that the main fraction of the heavy metals was associated with the colloidal matter, primarily the 0.001 to 0.01 μm fraction, which is dominated by humic material. In all these investigations, comparison of the distribution of organic matter and heavy metals between the size fractions indicated that the heavy metals in the colloidal fractions were not only related to organic matter, even though the colloidal humic substances are suspected to play a major role with respect to the speciation of the heavy metals. Free divalent Cd^{2+} only made up a few percent of the total cadmium content. Most of the complexed fraction was characterized as labile complexes that easily could be redistributed to other dissolved species [6]. However, a

small fraction (5 to 15%) was characterized as stable soluble complexes, defined as lack of ability to exchange with a cation exchange resin [37].

The stable complexes were considered to be organic. In leachate from three landfills containing industrial waste [49] found by use of dialysis, ion exchange, and thermodynamic calculations, large variation with respect to the speciation of Cd. In two of the investigated leachates about 20% of the total Cd content was determined to be Cd²⁺, while most of the Cd was identified as chloride complexes. The third leachate had a high dissolved organic carbon content (3200 mg C/I), and most of the Cd in this leachate was complexed with the organic matter. In a study it was found that both low-molecular-weight compounds (<500) comparable to simple carboxylic acids and high-molecular-weight compounds (>10000) contributed significantly to cadmium complexation [50]. A study was performed [41] with some speciation calculations on four leachates. Their calculations showed that 38% of Cd was present in complexes with organic ligands and 32% with inorganic ligands, while Zn and Ni were present in complexes (36% and 68%, respectively) exclusively with organic ligands. Suspended and colloidal solids presence and their types largely determine the electrical conductivity. In closed LFS many of the solids are already settled and concentration of those solid decreases with time. Intermediate age of landfill sites have greater Electric conductivity than the closed landfill sites [37].

5.1.8 Microbiology

MSW is a shelter for microbes and therefore solid waste may be heavily contaminated with pathogenic microorganisms [45]. MSW landfills contain human excreta, animal excreta, dead bodies of animal, sanitary pads and baby diapers, wastes from hospital, and sometimes sewages, all of which are potentially health hazardous [36].

5.1.9 Bacteria

Several studies have shown that there can be a significant bacterial population associated with municipal landfill leachates. The actual bacterial content of leachate, particularly the numbers of total coliforms, fecal coliforms, fecal streptococci, and total plate counts, varies dramatically with the age, and thus, chemical properties of the leachate [47]. A limited number of bacterial pathogens have been found in leachates from commercial and experimental landfills, and environmental lysimeters [51]. A comprehensive review of studies on the survival of bacteria in leachates was conducted by [46] who found increases in bacterial mortality with time of leaching or refuse age due to the bactericidal effects of the leachate and landfill. Relatively high temperatures achieved in the aerobic stage of refuse biodegradation can reduce bacterial growth and survival [36]. Also, bacterial inactivation is more rapid at lower pH [36]. Together, temperature and pH act to accelerate bacterial inactivation [52].

5.1.10 Viruses

As Solid Waste is collected from various sources so, it is possible that it contains pathogen as virus. However, the chances of occurrences of lethal virus are less [37]. In a study researcher detected no viruses in leachates produced by a large [53], field-scale MSW lysimeter that had been experimentally contaminated with poliovirus type 1 during the filling operation. Municipal leachate and landfills apparently pose a harsh environment for the survival of viruses, though the mechanisms of viral destruction are unknown [36]. The activation of virus is inversely related to temperature in leachate and inactivation augments at higher temperatures (20 to 22oC). Thus, high landfill temperature helps in the inactivation of viruses [36].

5.1.11 Nutrients

Xenobiotic Organic Compounds (XOCs) in landfill leachate:

Xenobiotic organic compounds are produced from household or industrial chemicals and are present in relatively low amount (usually less than 1 mg/l of individual compounds). Aromatic hydrocarbons, phenols, chlorinated aliphatic, pesticides, and plastizers are commonly present in XOCs compounds [40]. Varieties of XOCs are observed dependent in waste composition, landfill technologies, and waste age. The most abundant found XOCs are the monoaromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) and halogenated hydrocarbons such as tetrachloroethylene and trichloroethylene and their concentration is high in solid waste [33]. The reason for comprehensive investigations focusing on these two groups of pollutants is their well-documented negative effects in the aquatic environment. In addition, these organic compounds are quite easy to analyze despite the complicated matrix of leachates from landfills. The observed quantities of these phenols are generally in the tg/l level. MTBE (methyl-tert-butyl-ether), which is used as gasoline additives, has been found in concentrations up to 35 mg/l in the leachate test from eight Swedish landfills [54].

In a research more than 200 individual compounds or classes of compounds in a screening for XOCs in three Swedish landfills [55]. Compounds identified were dioxanes and dioxolans, which were not reported previously in landfill leachates. These are synthetic cyclic ethers showing very low odor threshold and high odor

intensity. Disposal from alkyd resin production and from disposed products from painting and coating give rise dioxanes and dioxolans [56]. The cumulative range given by [57] was 30 to 27,000 µg/l, but in many cases Absorbable Organically Bound Halogens (AOX) results were in the range of 200 to 5000 ug/l. The virtue of AOX mapping is challenged by the lack of information on identities and concentrations on individual compounds, often with quite dissimilar health effects, and also by poor correlation between the measured AOX in the leachate, and the concentrations of identified, halogenated pollutants [58]. In a study researcher saw similar issue employing the related parameter TOX (Total Organic Halogens) in leachate from two Danish landfills. Using screening procedures for organic pollutants, the individual halogenated compounds behind the TOX could not be found [59]. In this study researcher also argued the frequent presence of halogenated hydrocarbons at relatively high concentrations, reflecting the co-disposal of hazardous waste at some of the sites.

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