ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PARTICLE SIZE DISTRIBUTION BASED COD FRACTIONATION AND TREATABILITY OF ORGANIC WASTE LEACHATE

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ORGANİK ATIK SIZINTI SULARININ PARÇACIK BOYUT DAĞILIMI ESASLI KOİ FRAKSİYONLARININ BELİRLENMESİ VE ARITILABİLİRLİĞİ

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FOREWORD

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ABBREVIATIONS

ASM	: Activated sludge model
BOD	: Biochemical oxygen demand
COD	: Chemical oxygen demand
GAC	: Granular activated carbon
LLTP	: Landfill leachate treatment plant
LP	: Lime precipitation
MAP	: Magnesium ammonium phosphate
MBR	: Membrane bioreactor
MBBR	: Moving bed biofilm reactor
MF	: Microfiltration
NF	: Nanofiltration
MSW	: Municipal solid waste
OUR	: Oxygen uptake rate
OP	: Orthophosphate
PAC	: Powdered activated carbon
PE	: Polyelectrolyte
PHA	: Polyhydroxyalkanoate
PSD	: Particle size distribution
RBC	: Rotating biological contactor
RO	: Reverse osmosis
SBR	: Sequencing batch reactor
SS	: Suspended solids
TKN	: Total kjeldahl nitrogen
TOC	: Total organic carbon
TP	: Total phosphorus
TSS	: Total suspended solids
UASB	: Upflow anaerobic sludge blanket
UF	: Ultrafiltration
UV	: Ultraviolet
VSS	: Volatile suspended solids

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LIST OF SYMBOLS

b_H : Endogenous decay coefficient
C_I : Total Inert COD Concentration
C_S : Total Biodegradable COD Concentration
C_T : Total COD Concentration
f_{ES} : Fraction of soluble inert product
f_{EX} : Fraction of inert particulate metabolic product
k_h : Maximum spesific hydrolysis rate for S_H
k_{hx} : Maximum spesific hydrolysis rate for X_S
K_X : Half saturation coefficient for S_H
K_{XX} : Half saturation coefficient for X_S
S_H : Rapidly hydrolysable COD
S_I : Soluble inert COD
S_O : Dissolved oxygen concentration
S_S : Soluble readily biodegradable COD
X_A : Autotrophic biomass
X_H : Heterotrophic biomass
X_I : Particulate inert COD
X_P : Inert particulate product
X_S : Slowly hydrolysable COD
Y_H : Heterotrophic yield

PARTICLE SIZE DISTRIBUTION BASED COD FRACTIONATION AND TREATABILITY OF ORGANIC WASTE LEACHTE

SUMMARY

Various treatment methods are employed in treatment of leachtes, however determining the most appropriate treatment technology carries a great importance in for the environmental and economical issues. There is a need for the designation of the proper treatment alternative which requires a detailed wastewater characterization and treatability study.

Physico – chemical and biological methods are commonly utilized in leachate treatment, but also extensive investigation have been carrying out about the employment of membrane (ultrafiltration, nanofiltration, reverse osmosis) techniques in the treatment of leachate.

Considering the high pollution load of leachates, implemented treatment methods and obtained treatment efficiencies; the individual application of a treatment process does not provides the desired removal efficiencies. Therefore, the necessity ofintegration of various treatment processes is necessitated, so they can be implemented as adequate combined treatment processes.

The most important factor in in determining the appropriate treatment technology is the displayment of leachate characteristics. For that reason, after completion of detailed characterization studies physico – chemical and biological treatment methods were applied in this study and the observed efficiencies by these processes are reported. Along with these treatability studies sequential filtration/ultrafiltration was realized for the determination of organic matter fractions contained in leachate in terms their particle sizes. Finally, repirmetric tests were performed for the determination of biodegradability characterics of the organic matter involved in the leachate.

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ÖZET

Günümüzde çöp sızıntı sularının arıtılmasında çeşitli yöntemler kullanılmaktadır, ancak uygulanmakta olan bu farklı teknikler arasında en uygun arıtma teknolojisinin belirlenmesi çevresel ve ekonomik açıdan büyük önem taşımaktadır. En uygun arıtma teknolojisinin belirlenebilmesi doğrultusunda detaylı bir atıksu karakterizasyonu ve arıtılabilirlik çalışması yürütülmesi gerekliliği doğmuştur.

Çöp sızıntı sularının arıtımında fiziko-kimyasal ve biyolojik yöntemler yaygın olarak uygulanmaktadır, ancak fiziko-kimyasal ve biyolojik yöntemlerin yansıra membran sistemlerin (ultrafiltrasyon, nanofiltrasyon, ters osomos) çöp sızıntı suyu arıtımında kullanımı da yaygın olarak araştırılmaktadır.

Çöp sızıntı sularının yüksek kirlilik yükü, uygulanan arıtma yöntemleri, elde edilen arıtma verimleri ve atıksu deşarj standartları gözönünde bulundurulduğunda fiziko – kimyasal, biyolojik ve membran yöntemlerin tek başına uygulanması sonucunda istenen standartların sağlanmasının mümkün olmadığı görülmektedir. Bu bağlamda çöp sızıntı sularının arıtılması için farklı arıtma yöntemlerinin birbirleri ile entegre edilerek uygun kombinasyonlar halinde uygulanması gerekliliği doğmaktadır.

Uygun arıtma yönteminin belirlenmesinde en önemli faktör çöp sızıntı suyunun kompozisyonun ve karakteristik özelliklerinin belirlenmesidir. Bu bağlamda, bu çalışma kapsamında çöp sızıntı suyu için detaylı bir karakterizasyon çalışması yürütülmesinin ardından, fiziko-kimyasal ve biyolojik arıtma yöntemlerinin uygulanması ile elde edilen verimler ortaya konmuştur. Bu çalışmaların yanısıra sıra çöp sızıntı suyu içeriğindeki organic madde fraksiyonasyonunun parçacık boyut dağılımı bazında ortaya konmasına yönelik olarak ardışık filtrasyon/ultrafiltrasyon yöntemi uygulanmıştır. Çalışma sırasında yürütülen respirometrik testler yardımıyla da çöp sızıntı suyu içeriğindeki organik maddelerin biyolojik ayrışabilirk özellikleri ortaya konmuştur

1. INTRODUCTION

1.1 Significance of the Study

Adequate treatment of leachate carries a great importance, since the discharge of improperly treated leachate can cause severe environmental dangers due to its high pollution load and hazardous constituents. In addition to environmental dangers, it can lead to groundwater and surface water pollution which can constitute an important threat for human health. Therefore, leachates have to be treated to the desired level. Furthermore, strict discharge standards are set for leachates by governments all over the world. As a result of this situation, the necessity for the conduction of research studies on treatability of leachtes has risen.

1.2 Aim and Scope of the Study

The present study aims to investigate wastewater and treatability characteristics of leachate generated in the waste sorting and composting plant operated by South Antalya Association of Tourism Development and Infrastructure Operation (Güney Antalya Turizmi Geliştirme ve Altyapı İşletme Birliği, GATAB) in order to be able to betray appropriate treatment alternatives and to evaluate the applicability of implemented treatment processes.

GATAB is responsible for the activities of planning and operation of the infrastructure system in Kemer, Çamyuva, Tekirova and Kızıltepe (Göynük) regions. In the scope of these activities, the domestic wastewater treatment plants and the waste sorting and composting plant are operated by GATAB.

Organic waste is collected seperately by the hotels in the responsibility area of these four municipalities and GATAB compiles this organic waste from hotels. After the collection step the organic waste is transferred to the waste sorting and composting plant of GATAB. Organic waste is collected daily and it is subjected to the composting process demonstrated in Figure 1.1 during the same day. In case of malfunctions organic waste in stored only one day before it goes through the composting process.

After the arrival of the organic waste at the composting plant, the waste is weighted for the designation of its amount. In the next step the organic waste enters the composting unit, which consists of many stages such as pre – storage, sorting, grinding, drum screening, pressing, composting, final grinding, final screening. After the completion of these steps the composted waste is stored before sale. The flow chart of the process realized in the composting plant can been seen in Figure 1.1.

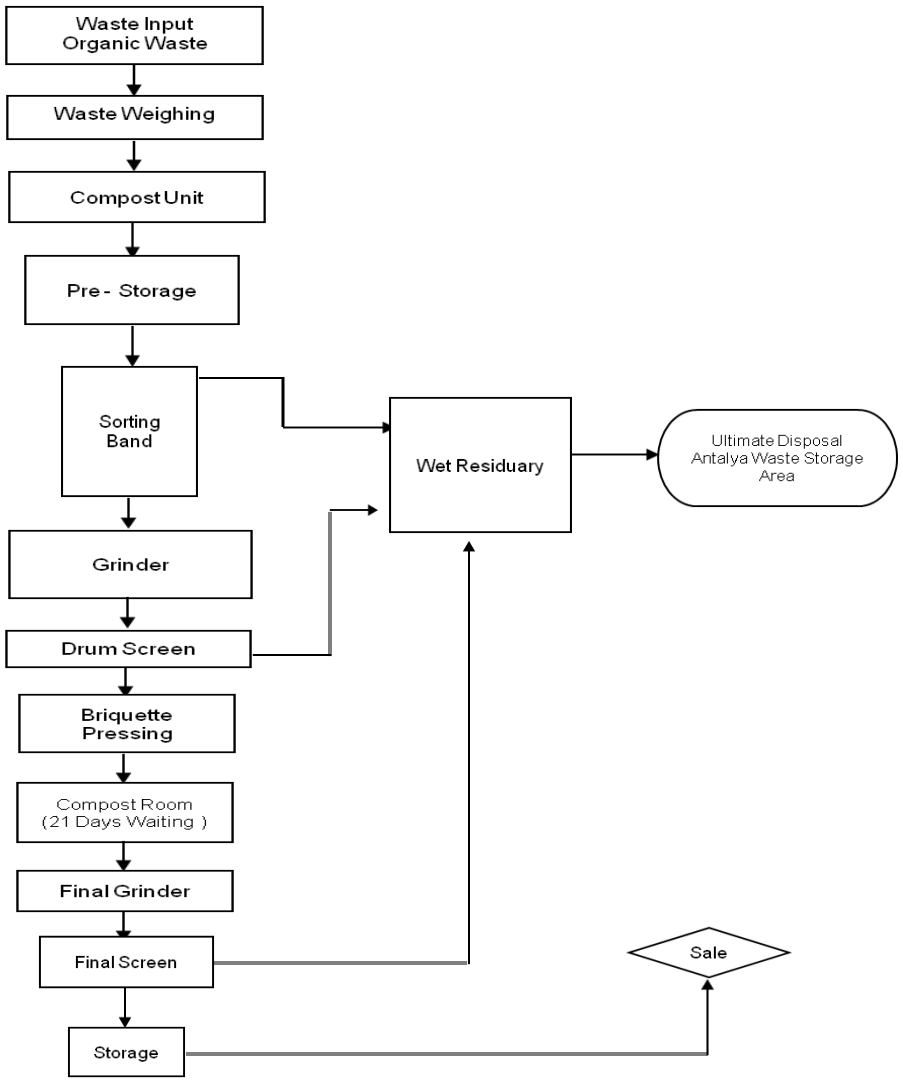

Figure 1.1: Flow chart of the compost plant

Following the pre – storage step organic waste is mixed with grinded plant waste and the prepared waste mixture is carried over the sorting band with the help of a loader. Glass and metal are sorted on the band. After the completion of the sorting step the waste mixture goes through the grinder and the drum screen, respectively. Inorganic waste such as trash bags and plastics are sorted with the help of the drum screen and the residual (organic) waste mixture is transferred to the briquette press machine. Organic waste is pressed as 85 cm x 85cm x 20 cm waste bales with help

of the briquette press machine. Generation of any kind of leachate does not occur during the briquetting step. Four or five bales are stowed on a pallet and they left to aerobic digestion as cubes with a height of 85 – 100 cm (a^3=0.85 – 1m^3) in composting rooms. After the composted waste leaves the composting rooms, it is subjected to final grinding and final screening. The purpose of both of these activities is to provide a high degree of sieving. The coarse material, which can not be sorted from the compost through the steps realized prior to briquette pressing, is removed with the help of these final stages.

In the compost plant, leachate is generated during the pre – storage process on the pre – storage area of the compost unit and during the whole composting process and that is why the pH value of the leachate generated on the compost plant is different compared to the pH value of the leachate generated in a solid waste landfill.

During the pre – storage period about 60 % of the water / moisture content of the organic waste is drained to leachate storage tanks in form of leachate. The remaining moisture content of the organic waste (approximately 40 %) is removed by the composting process (in composting room) either by evaporation or by leaching. The leachate generated in composting rooms is also drained to another leachate storage tank.

For the explanation of the amount of leachate generated in the pre – storage area and in the composting process following simplification can be made: The capacitiy of the composting plant is 150 t organic waste per day and the moisture content of 150 t of organic waste is approximately 100 t. If the moisture content of the organic waste thought to be 10 units, 6 units of this content is removed from the waste at the pre – storage area in form of leachate and the remaining 4 units is preserved in the waste, but during the composting process (in composting rooms) 3 units of the remaining moisture content is also removed during aerobic digestion in form of leachate, which means that the generated compost preserves 1 unit of the moisture content and the moisture content of the organic waste can not be removed totally by the application of the composting process. The generated compost has a mositure content of approximately 20 – 25 %. The leachates generated through the pre – stroge step and the composting process are drained to different leachate storage tanks. The leachate generated in the pre – storage area is stored in two tanks with total volume of 105 m^3 (20 m^3 + 85 m^3) and the leachate generated during the composting process is stored in a different tank with a volume of 50 m^3.

Leachates and wastewater generated during vehicle washing are stored in two tanks having a total volume of 105 m^3. The content of these tanks carries a lower pollution load compared to raw leachate, since the wastewater stored in these tanks is a mixture of raw leachate and wastewater generated during vehicle washing. The leachate generated in composting rooms are stored in a different tank with a volume of 50 m^3 as raw leachate. Every day the content of these three tanks is sucked into sewage trucks and tranferred to Tekirova and Kemer Treatment Plants. Leachates are stored in these tanks with a preiod of maximum one day.

In the winter period the amount of leachate and vehicle washing water mixture sent to the treatment plants of GATAB is 30 m^3, whereas the amount of raw leachate is 15 m^3. On the other hand, in summer period the amount of leachate and vehivle washing water mixture sent to the treatment plants of GATAB is 80 m^3, whereas the amount of raw leachate is 30 m^3. For the prevention of the possible negative influence of leachate and vehicle washing water mixture on the process of the treatment plants, the whole content of the storage tanks is not loaded out within a day.

The feeding of the leachate to these wastewater treatment plants designed for the treatment of domestic wastewater causes severe problems of capacity and odour, since the leachate carries a very high pollution load (50000 – 80000 mg COD/l) compared to domestic wastewater's pollution load (650 – 850 mg COD/l). Especially, in the summer period the pollution load is increased, so that the domestic wastewater treatment plants are only able to receive and treat a portion of the leachate generated in the waste handling and storage site.

The amount of leachate generated at the waste sorting and compost plant operated by GATAB is demonstrated in Table 1.1.

Table 1.1: Flow rate of generated leachate

Month	Average Daily Flow (m^3/day)	Average Monthly Flow (m^3/month)
January	50	1250
February	40	1000
March	50	1250
April	70	1750
May	100	3000
June	120	3600
July	150	4500
August	150	4500
September	150	4500
October	100	3000
November	60	1500
December	50	1250
Total	1090	31100

Considering the above mentioned problems, establishment of a leachate pre – treatment plant seemed to be proper to be able to decrease the pollution load to lower levels (20000 – 30000 mg COD/l), so that the leachate can be treated in the domestic wastewater treatment plants without any problems in the scope of their current capacities.

For the achievement of these specified targets, wastewater characterization studies were carried out for leachate in the first stage of the study. Following the completion of characterization studies, particle size distribution analyses were performed along with physico – chemical and biological treatability studies. For the determination of particle size distribution, sequential filtration/ultrafiltration method was employed. Lime precipitation and coagulation – flocculation with alum were the applied physico – chemical treatment methods. Activated sludge was utilized in the examination of biological treatment process. Respirometric tests were conducted and their results were utilized in modeling studies. For understanding of the

examined leachate’s biodegradability characteristics, the soluble inert fraction of organic matter contained in the leachate is figured out.

2. CONCEPTUAL APPROACH

2.1 Leachate Characteristics

Generation of leachate, an aqueous effluent, occurs as a result of rainwater percolation through wastes and biochemical processes in waste's cells and the inherent water content of wastes themselves (Wiszniowski et al, 2006).

Leachates generally contain large amounts of organic matter. The organic matter involved in leachate consists of a biodegradable and a non-biodegradable (refractory) portion. Humic-type constituents of leachate present an important group, as well as ammonia-nitrogen, heavy metals, chlorinated organic and inorganic salts. Considering the high pollution load and the hazardous components of leachates, chemical oxygen demand (COD), biological oxygen demand (BOD) and ammonium have to be removed from leachate before the discharge into receiving water bodies (Wiszniowski et al, 2006).

Toxicity analysis conducted by the use of various test organisms (Vibrio fisheri, Daphnia similes, Artemia salina, Brachydanio rerio) have confirmed the potential dangers of landfill leachates and the need for extensive treatment, so that the environmental hazards are eliminated and the discharge standards are met. Considering this fact, governments implement enhanced regulation for non-biodegradable organic matter and for nitrogenous compounds. In 1997, French authorities have set more stringent requirements concerning discharge into surface waters (Wiszniowski et al, 2006).

Determination of leachate characteristics carries a great importance, since the designation of the adequate treatment technology is based on specific characteristics of leachates. Only after completion of an extensive examination of wastewater characteristics, appropriate treatment alternatives can be proposed.

As the characteristics of waste dumped to each landfill differ, the features of generated leachates also differs, which means that comprehensive wastewater characterization and treatability studies have to be carried out in each case to be able to suggest proper treatment strategies, since the wastewater characteristics are case specific.

2.2 Leachate Treatment Methodologies

In the past decade, the municipal and industrial solid waste production has shown a rapid increase as a result of affluent lifestyles and continuing industrial and commercial growth in many countries around the world. The amount of municipal solid waste (MSW) generated grows both in per capita and overall terms day by day. For instance, waste production in Rio de Janeiro, Brazil, was 8042 t/day in 1997, whereas it was 6200 t/day in 1994, however the population growth during that period was practically zero. Furthermore waste production increased by 3% and 4.5% per year between 1992 and 1996, respectively, in Norway and in the USA (Warah, 2001).

The most widely accepted and applied method for the ultimate disposal of solid waste material is sanitary landfill method because of its economic advantages. According to the results obtained through comparative studies conducted on the investigation of the most advantageous ultimate disposal method for solid waste material, the cheapest method in terms of exploitation and capital costs is landfilling (Renou et al., 2008). Other than the economic advantages, lanfilling minimizes environmental threats and other indelicacies by allowing waste to decompose under controlled conditions until its eventual transformation into relatively inert, stabilized material. As a result of this situation the worldwide trend for the ultimate disposal of solid urban refuse and solid industrial waste has become controlled sanitary landfilling. In contrast to many advantages of sanitary landfill method there is an important drawback of this method, which has become the subject of recent interest: Release of leachate from landfills. Landfill leachate needs appropriate collection, storage and treatment, since it constitutes a threat for surface and ground waters because of its high pollution load (Di Palma et al., 2002). High concentration of organic and inorganic contaminants including humic acids, ammonia nitrogen, heavy metals, xenobiotics and inorganic salts are contained in leachates, therefore appropriate treatment techniques need to be implemented for the elimination of the adverse impacts of leachates on the environment. Comprehensive investigations have been conducted and been continuing for the determination of applicable treatment technologies for landfill leachate. Various treatment methodologies are applied in the scope of these research studies (Wiszniowski et al., 2006). For the classification of these different treatment methods three main groups of treatment technologies can be defined which are the conventional methods, the innovative treatment technologies and the hybrid process applications.

2.2.1 Conventional methods

2.2.1.1 Physico – chemical treatment

Physico - chemical treatment processes are applied for the reduction of suspended solids, colloidal particles, floating material, color, and toxic compounds and these treatment methods are commonly implemented by the treatment of landfill leachate as a pre-treatment step or as a polishing step in combination with other treatment techniques (Renou et al., 2008).

The need for the application of physico - chemical treatment processes as a pre-treatment step arises mostly in case of the treatment of old leachates (stabilized) because of the biorefractory contaminants, as these compounds are not amenable to conventional biological processes (Amokrane et al., 1997). Furthermore, the high ammonia content might also be inhibitory to activated sludge microorganisms (Li et al., 1999) and the deficiency of phosphorus generally encountered in case of old leachates can constitute another problematic issue by the individual employment of biological treatment methods. Therefore, a combination of physico – chemical and biological methods is often required for the efficient treatment of these heavily polluted wastewaters (Rautenbach and Mellis, 1994).

Physico – chemical processes commonly implemented by the treatment leachtes can be classified as following:

Coagulation/flocculation: Coagulation/flocculation is essential process in water and in industrial wastewater treatment. Many investigations have been carried out on the examination of coagulation–flocculation for the treatment of landfill leachates. These studies targeted optimization of process performance in terms of selection of the most appropriate coagulant, determination of experimental conditions, assessment of pH effect and investigation of flocculant addition (Sletten et al., 1995). Commonly used coagulants were aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate (Ehrig, 1984; Amokrane et al., 1997). Lime was also employed in combination with alum as a coagulant in the coagulation – flocculation process (Loizidou et al., 1992). Furthermore, some synthetic organic substances such as polyelectrolytes (cationic, anionic and neutral types) were utilized for the enhancement of the process efficiency. The research studies about coagulation – flocculation process mainly conducted on old landfill leachates, therefore information on the efficiency of this physico-chemical process still lacks in case of its application to young leachates. The coagulation – flocculation technique can provide

enhancement of subsequent leachate biodegradability, when applied prior to biological treatment (Tatsi et al., 2003).

The first step of coagulation – flocculation process is coagulation. At this step colloidal particles are destabilized by the addition of a coagulant. In the next step (flocculation), as a result of particle size increase unstable particles turn into bulky floccules and they settle. pH adjustment also plays an important role in this process. By the implementation of this method suspended solids and colloid particles can be removed.

Chemical precipitation: Chemical precipitation is a widely used pre-treatment step in case of leachate treatment, since through the employment of chemical precipitation prior to biological treatment high strength of ammonium nitrogen (NH_4 – N) can be removed, so that the negative impacts of ammonium nitrogen on the biological process efficiency can be eliminated. According to the results obtained through the research study conducted by Li et al. the COD removal efficiency declined from 95 to 79%, when the NH_4 – N concentration in wastewater increased from 50 to 800 mg/l (Li et al., 2002).

Chemical precipitation is based on the conversion of dissolved ions contained in the leachate into the insoluble solid form via chemical reactions. Typically, the metal precipitate from the leachate is in the form of hydroxide. Struvite (magnesium ammonium phosphate (MAP)) or lime is usually employed as the precipitant, depending on the target of the removal (either NH_4 – N or heavy metal) (Li et al., 2002; Yangın et al. 2002; Altınbaş et al. 2002).

The common implementation of chemical precipitation by leachate treatment does not only rely on the enhancement of subsequent biological treatment efficiency, but also the simplicity of the process and employment of cheap equipment by the process has made chemical precipitation one of the most applied methods among other treatment techniques. Through the implementation of chemical precipitation non-biodegradable organic compounds and heavy metals can also be removed from leachate as well as ammonium nitrogen (Kurniawan et al., 2005).

Adsorption: Adsorption is the most widely applied method for the removal of refractory organic compounds from landfill leachate. Adsorption can be defined as a mass transfer process during which a substance in liquid form is transferred onto the surface of a solid substance, and bounds on that surface area by physical and/or chemical interactions. Employment of granular activated carbon (GAC) or powder activated carbon (PAC) aided adsorption for the removal of organic and inorganic

pollutants from leachate has gained importance due to inherent physical properties, large surface area, microporous structure, high adsorption capacity and surface reactivity of these substances (Kurniawan et al., 2005).

The COD reduction levels obtained by adsorption (activated carbon columns, powdered activated carbon) are higher compared to the removal efficiencies observed through other chemical treatment methods. On the other hand, by the implementation of this method there is a need for frequent regeneration of columns or an equivalently high consumption of powdered activated carbon, which constitutes an important disadvantage due to high costs and for that reason the implementation of adsorption method for the treatment of leachate can be limited in developing countries. For the effective treatment of landfill leachate adsorption by activated carbon has been applied along with biological treatment (Ceçen and Aktaş, 2001; Ceçen et al., 2003). Through the employment of adsorption along with biological treatment non - biodegradable organics, inert COD and the color may be reduced to acceptable levels for biologically treated landfill leachate.

In the study of Rodriguez et al. (2004) PAC and different resins are examined for the observation of the efficiency in the reduction of non - biodegradable organic matter from landfill leachate. Among all resins activated carbon demonstrated the highest adsorption capacity with 85% COD removal. Furthermore, simultaneous adsorption and biological treatment has been tested in the study of Kargı and Pamukoğlu (2004). Pre-treated leachate (coagulation–flocculation and air stripping of ammonia) was subjected to biological treatment in an aeration tank operated in repeated fed-batch mode in the presence of adsorbent (PAC and powdered zeolite). Nearly 87% and 77% COD removals were achieved with PAC and zeolite concentrations of 2 g/l, respectively. Other adsorbent media such as peat and limestone have been investigated (Heavey, 2003; McLellan and Rock, 1988) and metal removal has been achieved by the use of these adsorbent media.

In addition to GAC or PAC, non-conventional materials that are locally available in large quantities, such as agricultural waste or industrial by – products, can be chemically modified and utilized as low-cost adsorbents. The use of waste and industrial by – products as adsorbent material in the adsorption process would add considerable economic value, in which the cost of waste disposal would be reduced and an inexpensive alternative to commercial activated carbon would be generated (Renou et al., 2008).

Chemical oxidation: Chemical oxidation is a commonly studied technique for the treatment of effluents involving recalcitrant compounds such as landfill leachates. Many investigations have been carried out advanced oxidation (AOP) processes. Most of them, except simple ozonation (O_3), use a combination of strong oxidants, e.g. O_3 and H_2O_2, irradiation, e.g. ultraviolet (UV), ultrasound (US) or electron beam (EB), and catalysts, e.g. transition metal ions or photocatalyst. Wang et al. (2003) confirmed that complete mineralization can be achieved by the application of AOP to leachte. Furthermore, they stated that the biodegradability of refractory organic pollutants can be improved to a level coherent with subsequent biological treatment.

In most of the research studies ozonation was employed as a tertiary treatment before discharge to the environment. Some studies investigated the combination of two oxidants (O_3 and H_2O_2) and addition of an irridation sytem (H_2O_2 /UV). Organic matter removal efficiency was reported as high as 90% in the studies of Wable et al. (1993), Bigot et al. (1994) and Schulte et al. (1995)for the O_3/H_2O_2 process. Through the implementation of H_2O_2/UV process, the BOD_5/COD ratio has been increased significantly from 0.1 to 0.45 by Qureshi et al. (2002). Moreover, Steensen (1997) reported 85–90% of COD reduction with a biologically pre-treated leachate by the employment of H_2O_2/UV process. Fenton and photo-Fenton processes resulted COD removal efficiency of, respectively, 45–75% and 70–78%. Recent works using Fenton process reported that BOD/COD ratios close to 0.5 have been achieved after oxidation, which means that the improvement of biodegradability was realized (Lopez et al., 2004; Kim et al., 2001). Photocatalytic treatment (Bekbölet et al., 1996; Wiszniowski et al., 2004) or electronbeam radiation treatment (Bae et al., 1999) of organic components from landfill leachates were also investigated at laboratory-scale. The purpose for the application of these technologies was treatment or degradation of principally humic substances.

Although satisfying removal efficiencies was observed in terms of COD, there are some disadvantages of AOP. High electrical energy demand induced by devices such as ozonizers, UV lamps and ultrasounds result in high treatment costs (Lopez et al., 2004). Furthermore, high oxidant doses are required for complete degradation of pollutants leading to high treatment costs. Beyond the high costs high doses of oxidants can lead to formation of some intermediate oxidation products resulting in increase of the toxicity of leachates (Silva et al., 2004).

According to Lopez et al. (2004) Fenton's process seems to be the best compromise among all AOP processes, since the application of the process is simple, there is no mass transfer limitation (homogeneous nature) and both of the chemicals iron and

hydrogen peroxide utilized in the process are cheap and non-toxic substances. On the other hand Fenton's process requires low pH, which means that this parameter needs to be adjusted.

Air stripping: Among various wastewater treatment technologies, air stripping has become the most commonly applied method for the removal of NH_4 – N. Generally, NH_4 – N, a toxic substance, is found in landfill leachates in high concentrations, but NH_4 – N can be eliminated from leachate through the employment of air stripping technique (Marttinen et al., 2002). The air stripping method should be applied at high pH values so the the desired efficiency can be reached and the contaminated gas phase must be treated with either sulfuric acid (H_2SO_4) or hydrochloric acid (HCl). Marttinen et al. (2002) reported a 89% ammonia reduction at pH = 11 and 20°C within 24 h retention time. Cheung et al. (1997) achieved high rates of ammonia removal in spite of high initial ammonia concentration (0.5 – 0.7 g N/l). According to the results obtained by their study 93% of 309–368 mg/l NH_4 – N was removed in free stripping tanks with 1 day retention time. Öztürk et al. (2003) and Silva et al. (2004) obtained 85 and 99.5% NH_4 – N removal, respectively. Air stripping seemed to be an efficient process for the removal of NH_4 – N, but the release of ammonia into the atmosphere constitutes a major concern, since it can cause severe air pollution if ammonia cannot be properly absorbed with either H_2SO_4 or HCl.

2.2.1.2 Biological treatment

Biological treatment is widely employed for the removal of the bulk of leachate containing high concentrations of biodegradable organic matter due to its reliability, simplicity and high cost-effectiveness. Biodegradation is performed by microorganisms, which can degrade organic matter to carbon dioxide, water and biomass under aerobic conditions and to biogas (a mixture composed of mainly CO_2 and CH_4) under anaerobic conditions (Lema et al., 1988). Biological processes seemed to be very efficient for the removal of organic and nitrogenous compunds from young (recently produced) leachates having a high value (>0.5) of BOD/COD ratio, whereas biological processes have only limited efficiency on the removal of refractory compounds (mainly humic and fulvic acids) contained in old (stabilized) leachates.

Aerobic biological treatment should result in a partial reduction of biodegradable organic pollutants and it should provide nitrification of the ammonium nitrogen as well. Aerobic biological processes can be classified as suspended-growth biomass

and attached-growth biomass systems. Aerated lagoons, conventional activated sludge process and sequencing batch reactors (SBR) have been widely studied methodologies among suspended-growth biomass systems (Li et al., 2001; Bae et al., 1999; Hosomi et al., 1989; Knox, 1985; Lin and Chang, 2000). On the other hand, moving-bed biofilm reactors (MBBR) and biofilters are interest attracting systems among attached-growth biomass systems. Membrane bioreactors, the combination of membrane separation technology and aerobic bioreactors, has become a novel focal point on leachate treatment.

Aerobic suspended-growth biomass systems and attached-growth biomass systems utilized for the treatment of leachates can be classified as following:

Aerated lagoons: Employment of aerated lagoons for wastewater treatment has been seen as an efficient method, since through the implementation of this low-cost method removal of pathogens, organic and inorganic materials can be realized. The low operation and maintenance costs have made aerated lagoons a popular choice among other wastewater treatment techniques (Robinson et al., 1988). Nevertheless, considering the strict standards determined by regulations aerated lagoons may not provide the desired treatment efficiency and therefore, they may not be the appropriate treatment alternative (Zaloum and Abbott, 1997). Furthermore, temperature dependence of lagooning constitutes an important limitation, since it influences microbial activity.

Activated sludge systems: Activated sludge processes are extensively implemented for the treatment of domestic wastewater or for the co-treatment of leachate and sewage, nevertheless in the more recent decades these processes have been seemed to be inappropriate for leachate treatment (Lin et al., 2000). Although activated sludge processes seemed to be effective for leachate treatment in terms of organic carbon, nutrient and ammonia removal, activated sludge processes are inconvenient for leachate treatment because of inadequate sludge settleability and the need for longer aeration times (Loukidou and Zouboulis, 2001) high energy demand and excess sludge production (Hoilijoki et al., 2000), microbial inhibition due to high ammonium-nitrogen strength (Lema et al., 1988).

Sequencing batch reactor: Sequencing batch reactor (SBR) systems are generally accommodated to nitrification–denitrification processes since they provide an operation regime compatible with simultaneous organic carbon oxidation and nitrification Diamadopoulos et al., 1997). Considering the variable characteristics of

leachates in quality and quantity, the process flexibility of SBR carries a significant importance (Kennedy and Lentz, 2000).

Trickling filter: Trickling filters have been investigated for the biological nitrogen removal from municipal solid waste landfill leachate. Due to their low-cost filter media biofilters remain an interesting and attractive option for nitrogen removal (Jokela et al., 2002).

Moving-bed biofilm reactor (MBBR): MBBR consists of suspended porous polymeric carriers, which are kept in continuous movement in the aeration tank, while active biomass is growing on the surface of these polymeric carriers as a biofilm. This process seemed to be very advantages compared to the conventional suspended-growth processes, since it can be operated at higher biomass concentrations, does not require long sludge-settling periods, has lower sensitivity to toxic compounds (Loukido et al, 2001) and provides high removal rates of organic matter and ammonia in a single process (Horan et al, 1997).

Anaerobic treatment process implementations for the treatment of landfill leachate seemed to be adequate because of the high organic matter removal capacity of anaerobic processes. Especially in case of treatment of young landfill leachate, application of anaerobic treatment processes is suitable due to the high concentration of organic substances contained in leachate (Pokhrel and Viraraghavan, 2004). Contrary to aerobic processes, anaerobic digestion conserves energy and produces very few solids, but reaction rates are very low by anaerobic processes (Berrueta and Castrillon, 1992). Furthermore, the methane gas produced by anaerobic reactions can be used for warming the anaerobic reactors, which usually work at 35°C and, under favourable conditions, for external purposes.

Anaerobic suspended-growth biomass systems and attached-growth biomass systems utilized for the treatment of leachates can be classified as following:

Digester: Typical values of achieved performances for COD reduction reached in conventional anaerobic suspended growth digesters are 80–90% in anaerobic lab-scale tank at 35°C and nearly 55% at ambient temperature (Bull et al., 1983; Lin, 1991; Sung Sung and Lee, 1997).

Sequencing batch reactor (SBR): Good performances of anaerobic sequencing batch reactors were achieved by some research studies. The SBR systems are able to provide solid capture and organic matter removal in a single reactor, so that the need for a clarifier is eliminated. Recently, nutrient reduction was investigated on pre-treated leachate by the use of a lab-scale SBR by Uygur and Kargı (Uygur and

Kargı, 2004). Sequential anaerobic–aerobic operation of the SBR resulted in COD, NH_4 - N and PO_4-P removal of 62%, 31% and 19%, respectively, at the end of cycle time (21 h). Moreover, in the initial period of the landfill, satisfactory organic matter reduction in the anaerobic reactor through methanogenesis and denitrification, can improve the nitrification process in the subsequent aerobic reactor. For that reason anaerobic–aerobic system is recommended for the removal of nitrogen and organic matter (Martienssen and Schops, 1997; Shiskoswski and Mavinic, 1998; Welander et al., 1998). For example, Kettunen and Rintala (1995) demonstrated that COD removal was 35% in the anaerobic stage, whereas the COD and BOD_7 removals were up to 75% and 99% by the combined process.

Up-flow anaerobic sludge blanket (UASB) reactor: UASB process can be described as a modern anaerobic treatment process which can render high treatment efficiency and a short hydraulic retention time (Lin et al., 2000). UASB reactors, subjected to high volumetric organic loading rate values (Garcia et al., 1996), have shown higher performances compared to other types of anaerobic reactors. The process temperatures reported for anaerobic treatment with UASB reactors have generally been 20–35°C. The average performance of COD removal efficiency under these conditions was always higher than 70% at ambient temperature (20–23°C) and 80% at 35°C. Kennedy and Lentz (Kennedy and Lentz, 2000) attained COD removal rates up to 92% at low and intermediate organic loading rates (between 6 and 19.7 g COD/l day^{-1}). Kettunen and Rintala (1998) demonstrated that leachate can be treated by the employment of an on-site UASB reactor at low temperature. Garcia et al. (1996) showed that COD reduction efficiency was not influenced by temperature between 15 and 35°C. These promising results demonstrated that high-rate treatment at low temperature may minimize the need for heating the leachate prior to treatment, which may thus provide an interesting cost-effective option (Kettunen et al., 1996). On the other hand, the main disadvantage of that type of a treatment remains as the sensitivity to toxic substances (Sung Sung and Lee, 1997).

Anaerobic filter: The anaerobic filter is a high rate system which is pulling the advantages of other anaerobic systems together and minimizing the disadvantages. In an up-flow anaerobic filter the biomass is sustained on support material such as plastic rings in form of biofilms (Nedwell and Reynolds, 1996). According to the results obtained by the research study of Henry et al. (1987) for different ages of a landfill, COD can be reduced by 90% in an anaerobic filter operated at loading rates varying from 1.26 to 1.45 kg $CODm^{-3}day^{-1}$. Total biogas production observed to be

between 400 and 500 l gas per 1 kg of removed COD and methane content of the gas varied between 75 and 85%.

Hybrid bed filter: Hybrid bed filter is made up of on an up-flow sludge blanket at the bottom and an anaerobic filter on top. This type of filter works as a gas–solid separator and develops the retention of solids without inducing channelling or short-circuiting (Timur and Öztürk, 1997). Improved performance of such a process is obtained through the maximization of the biomass concentration in the reactor. Nedwell and Reynolds (1996) reported steady-state COD reduction efficiencies of 81–97% by methanogenic digestion, depending on organic loading rate. Likewise by the employment of the anaerobic filter, the cost for the support media contained in the reactor constitutes a disadvantage by the use of hybrid bed filter.

Fluidized bed reactor: Suidan et al. (1993) and Imai et al. (1993, 1995, 1998) carried out studies on carbon-assisted fluidized beds. As a result of the combined biodegradation and adsorption processes examined in the scope of this study, removal of various organic compounds was achieved (Suidan et al., 1993). According to the observations attained throughout the study of Imai et al. (1993) the biological activated carbon fluidized bed process was much more effective for treating old landfill leachate than the conventional processes such as activated sludge and fixed film processes.

2.2.2 Innovative treatment technologies

Innovative treatment technologies utilized in leachate treatment can be classified as following:

Microfiltration (MF): In case of a need for the removal of colloids and suspended matter, for example as a pre-treatment step by the application of another membrane process (ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO)) or in partnership with chemical treatments, MF remains as an effective method, although is not appropriate to use MF alone. Piatkiewicz et al. (2001) examined the use of MF as a pre-filtration stage and reported that the achieved COD removal efficiency was between 25 and 35%.

Ultrafiltration (UF): UF is an effective method for the elimination of macromolecules and particles, whereas it is strongly dependant on the type of material, from which the membrane is made of. Beyond the use of UF as a separation method, it can also be employed as a useful tool for the determination of the fractionation of organic pollutants as it allows revealing of the predominant molecular mass of organic

pollutants in a given leachate. Furthermore, tests conducted on membrane permeates may give information about recalcitrance and toxicity of the permeated fractions (Renou et al., 2008).

Except Tabet et al. (2002), UF has seemed not to be appropriate to applied alone in leachate treatment due to strict discharge standards and high organic load of leachate. The study of Tabet et al. was an exception, in which membranes close to nanofiltration were used, the leachate had low organic matter content and local discharge standards were not so strict. Syzdek and Ahlert (1984) proposed the use of UF as a pre-treatment step for subsequent reverse osmosis (RO) process, since UF can be utilized to reduce the larger molecular weight components of leachate that tend to foul reverse osmosis membranes. The COD removal efficiency achieved by the application of UF varies between 10 and 75%. In a recent study UF has been employed in as a post-treatment treatment step after biological treatment (activated sludge) of landfill leachate (Bohdziewicz et al., 2001). Several hybrid processes such as activated sludge–ultrafiltration–chemical oxidation and activated sludge–ultrafiltration–reverse osmosis have been tested. Same authors showed that 50% of the organic matter content of the leachate could be separated alone by the UF stage. Moreover, by the employment of UF membranes in full scale membrane bioreactor plants (Van Dijk and Roncken, 1997) satisfactory results were obtained in terms of treatment efficiency of landfill leachate.

Membrane bioreactors: Membrane bioreactors have been a novel arising focal point in wastewater treatment, which constitute the combination of membrane separation technology and bioreactors. Membrane bioreactors are working at high biomass concentrations and they produce very low amounts of sludge by rendering an excellent effluent quality. The employment of membrane bioreactors at full scale on industrial wastewater treatment plants has become very common and some plants have been accommodated to leachate treatment (Van Dijk and Roncken, 1997). On the other hand, there are very few research studies related to landfill leachate treatment by the use of membrane bioreactors. Pirbazari et al. (1996) examined a hybrid technology known as the ultrafiltration-biologically active carbon (UF-BAC) process that unifies adsorption, biodegradation and membrane filtration. Observed removal efficiency of this process was between 95–98% in terms of TOC and it exceeded 97% for specific organic pollutants. Nitrifiers or organisms able to degrade slowly biodegradable substances were not washed out of this system contrary to conventional systems, so process activity was not decreased.

Nanofiltration (NF): Nanofiltration technology renders a versatile understanding in meeting multiple water quality objectives such as control of organic, inorganic and microbial contaminants. NF membranes are generally made of polymeric films with a molecular cut-off between 200 and 2000 Da. The rejection rate is high for sulfate ions and dissolved organic matter, whereas it is very low ate for chloride and sodium ions so that the volume of concentrate is reduced (Peters, 1998). Few studies investigated the employment of NF in leachate treatment (Marttinen et al., 2002; Trebouet et al., 1999; Rautenbach and Mellis, 1994; Trebouet et al., 2001; Linde et al., 1995; Trebouet et al., 1998). The observed removal efficiencies for COD and ammonia were nearly 60–70% and 50%, respectively in case of a transmembrane pressure between 6 and 30 bar and an average velocity of 3 m/s, whatever membrane material and geometry (flat, tubular, or spiral wounded) was. By the use of NF in combination with physical methods significant removal efficiencies were achieved in terms of recalcitrant COD (70–80%) (Trebouet et al., 2001). Nevertheless, prosperous implementation of membrane technology necessitates efficient control of membrane fouling.

A wide spectrum of constituents, which are dissolved organic and inorganic substances, colloidal and suspended particles, may lead to membrane fouling by nanofiltration of leachates (Trebouet et al., 2001). Furthermore, fouling caused by natural organic matter has recently acquired interest in particular (Braghetta et al., 1998; Hong, and Elimelech, 1997).

Reverse osmosis (RO): Among the novel technologies utilized for the treatment of leachate RO seems to be one of the most promising methods. Several studies carried out in the past demonstrated performances achieved by the application of RO technology for the separation of pollutants from landfill leachate (Linde et al., 1995; Bilstad and Madland, 1992). According to the reported values of the rejection coefficient referred to COD parameter and heavy metal concentrations were higher than 98 and 99%, respectively. The early RO systems utilized tubular and spiral wounded module. In 1988 an innovative technology, the disc-tube-module (DT-module), was introduced to the market of RO modules. The open channel module allowed systems be cleaned with high efficiency with regard to scaling, fouling and especially biofouling (Peters, 1996). However, the employment of pressure-driven membrane processes, and particularly RO, in landfill leachate treatment remained questionable until today because of two major disadvantages. The first one is membrane fouling which requires extensive pretreatment or chemical cleaning of the membranes, results in a short lifetime of the membranes and decreases process

productivity. The second disadvantage is the generation of large volume of concentrate which is unusable and has to be discharged or further treated.

2.2.3 Hybrid processes

The necessity for integration of different treatment methods for the efficient treatment of leachates has risen because of the variant nature and composition of leachate depending on landfill age, season, climatic conditions and strict discharge standards for leachate discharge (Wiszniowski et al., 2006). As a result of this situation, definition of a treatment strategy for landfill leachate is not easy. Furthermore, treatment of leachate is more difficult compared to domestic wastewater because of its high pollution load caused by recalcitrant compounds, organic and inorganic materials. Therefore, the implementation of hybrid processes is advantageous and necessary since, they enable the treatment of all types of contaminants present in the leachate (Bohdziewicz et al., 2001). Steensen (1997) denoted the experiences of 100 pilot treatment plants in Germany for the treatment of leachate operating and demonstrated that all were using a combination of several individual processes. The biological treatment step, constituting the first stage of the treatment, has been employed in more than 60% of the plants. The chemical oxidation process was implemented for further purification in 15 plants.

Integration of different treatment technologies were investigated by many research studies. Examined combinations of various treatment methods are summarized as following:

Nitrification/denitrification-O_3/UV-post-biological oxidation: Treatment Plant in Singhöfen (Germany) has been operated since 1994 and it is treating 107.4 m^3/d of landfill leachate. The system employed at this plan is an example of combined biological and chemical process. In the first step of treatment there are pre-denitrification and nitrification reactors with sedimentation tank and sand filter. The next stage is consists of ozonation-UV unit with sand filter followed by aerated packed bed as a post-biological stage. During the first operating period, it was observed that treatment with ozone without assistance of UV was effective enough to fulfill required standards. Furthermore, ozone treatment provided considerable increase of BOD fraction in leachate and this fraction was successfully removed in the subsequent biological treatment step. As a result of the post-biological stage overall treatment cost was reduced due to the reduction of ozone consumption and the required discharge standard was also reached (Wiszniowski et al., 2006).

Nitrification/denitrification–precipitation–ozonation: The landfill leachate treatment plants (LLTPs) in Bord-Matin landfill, near Saint-Etienne France) is treating the stabilized leachate generated in the landfill and it has been operated since 1972 (Poitel et al., 1999). The amount of leachate produced in the landfill was 12.5 m^3/d, contained 1750 mg/l and 850 mg/l of COD and ammonia, respectively. The system applied in the treatment plant consists of a biological stage involving nitrification and post-denitrification process followed by chemical precipitation with lime in a lamellar settling tank. In the final step of the treatment process ozonation is implemented in order to be able to achieve the required discharge standard by the removal of recalcitrant COD. Through the employment of this combined treatment process it was ensured that the effluent COD, ammonia and nitrate concentrations do not exceed 130 mg/l, 2 mg/l and 10 mg/l respectively, so that the national authority standards could be met (Wiszniowski et al., 2006).

Chemical precipitation-membrane bioreactor (MBR)—Reverse osmosis (RO): Ahn et al. (2002) reported observations attained from the landfill leachate treatment plant (LLTP) located at Chung-Nam Province in Korea that was retrofitted on April 2000. The LLTPs was treating 50 m^3 of leachate per day and the treatment process was consisted of contact aeration, rotating biological contactor (RBC) and granulated activated carbon (GAC) adsorption process. The leachate contained high concentrations of ammonia (200–1400 mg/l), nitrate (28–251 mg/l), COD (400–1500 mg/l) and BOD_5 (100–500 mg/l). However, removal of COD and total nitrogen (TN) was not stable and sufficient enough to achieve the regulatory national standards for discharge. Biomass was washed out of the system and there was a need for frequent activated carbon replacement.

The treatment process implemented in the LLTP has been modified by employment of membrane bioreactor and reverse osmosis (RO) stages instead of contact aeration reactor, RBC and GAC. Organic matter removal was developed with the help of a submerged membrane reactor. At the same time nitrification rate was increased and retention of biomass in the biological reactor was ensured. A spiral wound membrane module was utilized by RO process, which was installed for the enhancement of removal of non-biodegradable compounds and inorganic nitrogenous ions. The efficiency obtained by the application of MBR/RO process was more than 97% for COD and BOD_5 parameters, which corresponded to effluent concentrations of 6–72 mg/l and 1–7 mg/l for COD and BOD_5, respectively. Concentrations of ammonia and nitrate in the effluent ranged between of 10–47 mg/l

and 7–23 mg/l, respectively. The desired process efficiency in terms of meeting discharge limits was achieved.

Similar performance of treatment in the MBR/RO system was attained in LLTPs of Hersin-Coupigny landfill located in northen France. The plant has been operating since 1994 with maximal flow of treated leachate adding up to 40 m^3/d (Poitel et al., 1999).

Coagulation-2 stages of reverse osmosis (RO)—neutralization/sterilization: The dumped wastes to landfill located in Yachiyo Town (Japan) “Clean Park KINU” mainly consist of incinerated residue and incombustibles i.e. inert, non-biodegradable material. The capacity of the LLTP is 70 m^3/d, and it has been operating since April 1999. In the first step landfill leachate is collected in an equalization tank and then transferred to the settling settling tank. The settling tank is followed by sand filters, micron filters and 1st stage DT-Module units. For polishing purposes permeate from the 1st stage units is fed to the 2nd stage DT-Module units and neutralization – sterilization operations are applied to the permeate from the 2nd stage before disposal in the KINU River. Furthermore, retentat from the 1st stage DT-Module units is subsequently treated by nanofiltration (NF) unit, highpressure DT-Module units and finally dried to salts that are packed in a flexible container. Ushikoshi et al. (2002) reported that the operation (lasting 2.5 years) of the DT-Module RO system for leachate with high salinity and very high scaling ions (such as $CaCO_3$, $CaSO_4$, $SrSO_4$, $BaSO_4$ and SiO_2), was successful. The performance of the process was satisfactory providing a salt rejection rate higher than 99% and producing a potable level treated water.

2.3 Biodegradation of Organic Matter in Wastewater and COD Fractionation

The need for a clear description of organic matter involved in wastewaters has risen at the beginning of 1980’s for a better understanding of biodegradation process of organic material and a better estimation of kinetic constants utilized by these processes (Dold et al., 1980; Ekama et al.,1986).

For the definition of the organic pollution load of wastewaters commonly utilized parameters are BOD5, COD and TOC which are not able to give enough information about the characteristics of organic materials and the compounds utilizable by microorganisms involved in activated sludge systems. In order to be able to make a classification of biodegradable organic matter contained in wastewaters, it is divided into two categories which are defined as easily biodegradable and slowly

biodegradable (S_S and X_S) organic matter. Moreover, non-biodegradable (inert) organic matter is defined as dissolved and particulate fractions (X_I and S_I).

Task group (IAWQ) generated a new mathematical approach for the biological process of activated sludge. Activated Sludge Model No: 1 was developed by this group for the definition of the biological processes in wastewater treatment systems (Henze et al., 1987). The model matrix involves stoichiometric and kinetic coefficients utilized in the biological degradation process. Accurate determination of stoichiometric and kinetic coefficients carries a great importance for the specification of biological process rate and efficiency. In the scope of ASM1, organic matter fractions (in terms of COD) are also defined as model components, so accurate experimental determination of the organic fractions plays an important role in the designation of stoichiometric and kinetic coefficients, which can be useful tools for biological process identification (Henze et al., 1987; Ekama et al., 1986).

Organic matter fractions involved in wastewater are given detailed in Figure 2.1.

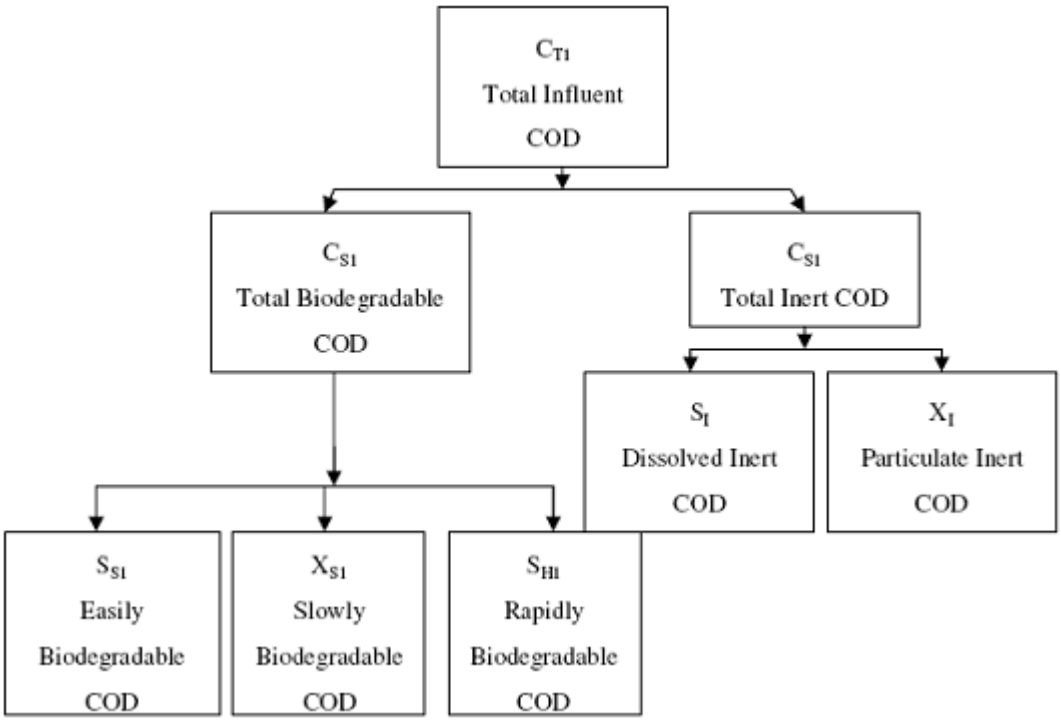

Figure 2.1: Organic matter components in wastewaters

For the exact determination of organic matter contained in wastewaters a lot of experimental techniques were investigated. For the designation of organic matter batch tests were conducted by performing Oxygen Uptake Rate (OUR) measurements and/or Nitrate Uptake Rate (NUR) measurements (Kriestensen et

al., 1982). OUR and NUR experiments are effective methods in rapid determination of organic matter.

Classification of organic matter on the basis of biodegradability may have a correlation with particle size and physical state in solution, showing that the biokinetic responses of activated sludge microorganisms to soluble and particulate organic matter differ. This difference may be induced by the contrast in the particle sizes of these soluble and particulate fractions (Wentzel et al., 1999;,Dulekgurgen et al., 2005).

2.4 Determination of Soluble Inert COD Fraction

The importance of soluble inert COD fraction (S_I) contained in wastewater has been expressed by many researchers. As this fraction does not undergo any biochemical reactions, the concentration of S_I in the effluent of the treatment system is the same as in the influent, which is an important factor in reaching the desired treatment efficiency and achieving the discharge limits. There are several methods available for the determination of this component (Ekama et al., 1986; Henze at al., 1987), but as a major disadvantage these methods are not able to differentiate the soluble inert organic substances from the soluble inert microbial end products, whereas other procedures based only on the measurement of COD allowed the direct experimental determination of soluble inert organic substances (Kappeler and Gujer, 1992; Orhon et al., 1994).

According to the method suggested by Germirli et al. (1991), involves the monitoring of COD in the soluble wastewater reactor and the glucose reactor of equivalent soluble COD content both seeded with minimal biomass (10 – 50 mg VSS/l) previously acclimated to the wastewater and the glucose substrate. The amount of biomass in both of the reactors is kept at minimum level for the prevention of possible interferences induced by soluble inert microbial products. These reactors eventually reach a stable threshold COD value obtained by COD monitoring after consumption of the total biodegradable substrate and ultimate mineralization of the biomass. The inert COD profiles to be attained by this method are presented in Figure 2.2 and Figure 2.3.

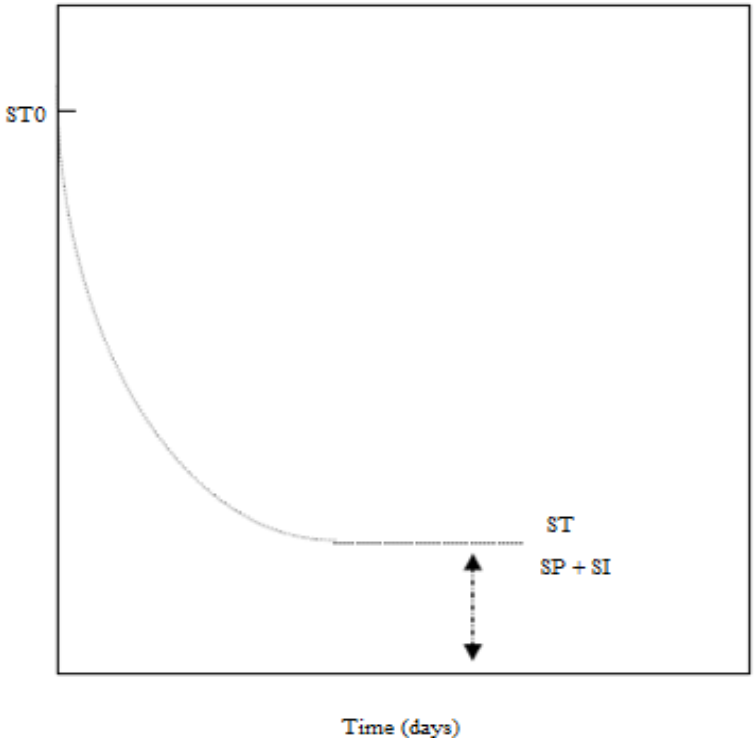

Figure 2.2: Raw wastewater reactor

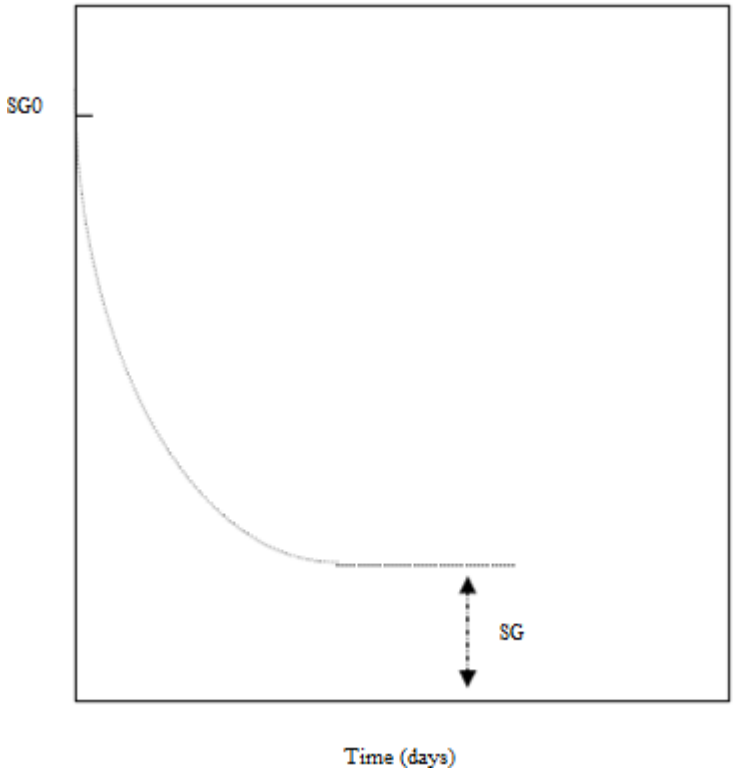

Figure 2.3: Glucose reactor

According to the assumption made by the application of this method, the residual soluble COD in the wastewater reactor is equal to the sum of soluble COD (S_I) and residual soluble microbial end products (S_P) generated in the reactor.

$$S_T = S_I + S_P \quad \textbf{(2.1)}$$

The generation of soluble microbial end products is defined as the conversion of the degradable COD content of the initial COD (S_{S0}) to soluble microbial end products with a certain yield (Y_{SP}). This yield can be calculated with the help of the initial and final COD concentrations measured in the glucose reactor. In order to be able to figure out the soluble inert COD fraction is assumed that $Y_{SP(wastewater)}$ $Y_{SP(glucose)}$ have approximately equal values.

$$Y_{SP} = S_{PG} / S_{G0} \quad \textbf{(2.2)}$$

This allows the calculation of SI from the following two equations with two unknowns (S_{T0} stands for initial soluble COD in wastewater reactor, S_T stands for final soluble COD in wastewater reactor):

$$S_{G0} + S_I = S_{T0} \quad \textbf{(2.3)}$$

$$Y_{SP}S_{S0} + S_I = S_T \quad \textbf{(2.4)}$$

2.5 Activated Sludge Modeling

Operational conditions and design of treatment plants play a significant role in developing the effluent quality. Therefore, the need for dynamic models has gained importance. Activated sludge modeling can be utilized as a useful tool for wastewater treatment plant design, control, organization and optimization of operational conditions. The structure of a model differs according to its intended use as design and control. Although models are described as useful tools simplifying complicated processes, they can only build simulations of real cases, since they are based on assumptions, depend on wastewater characteristics and the lack of knowledge in microbiology of treatment plants is anotherfactor affecting the reliability of model results negatively (Jördening and Winter, 2005).

For wastewater treatment plant design purposes generally deterministic models are used, whereas black-box type models that are also utilized for controlling purposes (Jördening and Winter, 2005). According to the common opinion design and operation of treatment plants are based on reliable experimental data, mechanistic description of kinetic processes and material balances. Multi-component modeling of activated sludge, assessed by means of multiple parameters, is a widely accepted

approach (Henze et al., 1997; Orhon and Artan, 1994). Determination of COD fractions is useful by the implementation of this approach for understanding particulate and soluble matter fractions, kinetic and stoichiometric coefficients which are affecting the biodegradation process in order to able to comprehend the concept of biological treatment (Henze et al., 1987; Orhon and Artan, 1994).

Most of the models are based on the IAWQ Activated Sludge Model No. 1, which is called ASM1 (Henze et al., 1987). Kinetic and stoichiometric parameters involved in basic processes are included in this model as model components. Through the development of ASM1 by the addition of new processes and components based on the complexity of design new models are introduced. ASM2 (Activated Sludge Model No. 2), ASM3 (Activated Sludge Model No. 3) are examples of activated sludge models (Jördening and Winter, 2005).

2.5.1 Activated sludge model 1

Processes, which enable calculation of oxygen consumption, ammonia, and nitrate in individual units of treatment plants and in effluents, are involved in ASM1. Beyond these parameters, mixed liquor suspended solids, solids retention time and sludge production can also be evaluated by the use of this type of models (Jördening and Winter, 2005).

In the multi component model, COD is determined as the most suitable parameter for the description of the carbon sources as it renders a linkage among electron equivalents in the organic substrate, biomass, and oxygen utilized. Organic carbon removal can be modeled by the use of ASM1 and ASM3, which include different processes.

Based on its solubility, biodegradability, biodegradation rate, and viability for biomass COD is branched into fractions in ASM1. The main COD fractions are described as soluble (S), and particulate (X) COD. These fractions are further divided into non-biodegradable fraction and biodegradable fraction. The non-biodegradable fraction is biologically inert, so it remains unchanged in an activated sludge system and leaves the system in an unchanged form. The inert soluble organic matter (S_I) leaves the system with the same concentration as it enters the system, whereas inert particulate organic fraction (X_I) in the influent is removed together with particulate organic matter produced via decay processes by sludge wastage (Orhon and Artan, 1994).

Basic processes included in ASM1 can be defined as growth, decay, and hydrolysis. According to the model, carbon removal is slightly coupled with nitrification. Heteretrophic bacteria use organic matter directly and/or after hydrolysis process, whereas autotrophic bacteria use ammonia for their growth.

The biodegradable matter consists of two major fractions which are defined as soluble readily biodegradable (S_S) fraction and slowly biodegradable fraction (X_S). A fraction of X_S is assumed to be soluble (S_H), so the fraction S_H can be defined as rapidly hyrolyzable fractions, whereas X_S can be described as slowly hyrolyzable fraction. S_S is assumed to be simple organic matter which can be directly used by heterotrophic organisms in the growth process. On the other hand, regeneration of slowly biodegradable particulate matter on nonviable biomass is observed in death-regeneration model while the rest of it is converted to inert particulate microbial products (X_P). Contrary to S_S, X_S consists of relatively complex molecules that require enzymatic breakdown as hydrolysis prior to utilization in the growth process. Heterotrophic biomass X_H and autotrophic biomass X_A are generated by growth on SS or by growth on ammonia nitrogen S_{NH}. The biomass is lost via the decay process and converted to some other particulate components (Orhon and Artan, 994).

In endogenous decay model, S_S is utilized in only growth process. Moreover, generation of inert particulate microbial products is linked to the active biomass decay, in which a fraction of biomass (f_{EX}) is converted into inert particulate microbial products, X_P. These products do not undergo any further reaction and accumulate in the system until they are removed by sludge wastage. On the other hand, soluble inert microbial product formation is assumed to be generated through the decay process, in which a fraction of biomass is converted to (f_{ES}) soluble inert microbial products. (Orhon and Artan, 1994).

The change of biomass concentration can be expressed as (McKinney, 1962):

$$\frac{dX}{dt} = \frac{dX_H}{dt} + \frac{dX_P}{dt} \qquad \textbf{(2.5)}$$

b_H is defined as the endogenous decay coefficient. The change in active biomass is demonstrated as:

$$\frac{dX_H}{dt} = -b_H X_H \qquad \textbf{(2.6)}$$

Generation rate of particulate inert products is given as following:

$$\frac{dX_P}{dt} = f_{EX}\frac{dX_H}{dt} \quad \textbf{(2.7)}$$

The maximum growth rate of heteretrophic bacteria and half saturation constant of substarte are defined as $\hat{\mu}_H$ and K_S respectively, so the biodegradation rate of S_S which is directly utilized in the growth process is demonstrated as following:

$$\frac{dS_S}{dt} = \frac{\hat{\mu}_H}{Y_H}\frac{S_S}{K_S + S_S}X_H \quad \textbf{(2.8)}$$

The rate of soluble inert microbial product formation associated by the decay process can be given as following:

$$\frac{dS_P}{dt} = f_{ES} b_H X_H \quad \textbf{(2.9)}$$

Where K_X and k_h are maximum spesific hydrolysis rate and half saturation coefficient for hydrolysis of slowly biodegradable substrate, hydrolysis of the slowly biodegradable substrate X_S to S_S is given as:

$$\frac{dX_S}{dt} = k_h \frac{X_S/X_H}{(K_X + X_S/X_H)}X_H \quad \textbf{(2.10)}$$

Matrix representation of basic relationships between process components of endogenous decay model is given in Table 2.1. The soluble and particulate inert components S_I and X_I are not included in the matrix because they do not take part in biochemical processes.

Table 2.1: Simplified matrix representation of ASM1 involving endogenous decay

Component → / Process ↓	1 S_S	2 X_S	3 X_H	4 X_P	5 S_P	6 S_O	Process Rate $ML^{-3}L^{-1}$
Growth	$-\frac{1}{Y_H}$	1				$-\frac{1-Y_H}{Y_H}$	$\frac{\hat{\mu}_H}{Y_H}\frac{S_S}{K_S+S_S}X_H$
Hydrolysis	1	-1					$k_h\frac{X_S/X_H}{(K_X+X_S/X_H)}X_H$
Decay			-1	f_{EX}	f_{ES}	$-(1-f_{EX}-f_{ES})$	$b_H X_H$
Parameter, ML^{-3}	COD	COD	Cell COD	COD	COD	O_2	

3. MATERIALS AND METHODS

3.1 Materials

In the present study, landfill leachate samples were taken from the landfill being operated by South Antalya Association of Tourism Development and Infrastructure Operation (Güney Antalya Turizmi Geliştirme ve Altyapı İşletme Birliği, GATAB). Different types of waste are collected and transferred to the waste storage and handling site under responsibility of GATAB. The site involves organic waste handling / composting plant and storage area for recyclable waste. After the waste collection step, waste sorting is realized in order to be able to separate organic waste and recyclable waste. Following the completion of waste sorting organic waste is handled and stored. The waste acceptance capacity of the plant is 120 tons per day.

Experimental studies were conducted on two leachate samples taken at different dates from the waste storage and handling site operated by GATAB. Sample numbers and sampling dates are as following:

Sample 1 – 4 October 2009

Sample 2 – 5 December 2009

Wastewater and treatability characteristics of leachate are investigated in the scope of the research work for the observation of treatment efficiency.

3.2 Methods

3.2.1 Experimental Approach

The steps followed by the experimental studies are demonstrated by enumeration to summarize the concept of the investigation and to introduce the experimental approach.

1. Conventional Wastewater Characterization
2. Physico – Chemical Treatment
3. Biological Treatment

4. Sequential Filtration – Ultrafiltration
5. Respirometry
6. Determination of Soluble Inert COD Fraction

3.2.1.1 Conventional wastewater characterization

Conventional wastewater characterization analyses were performed as described in the Standard Methods (APHA *et al.*, 1998), except for COD measurements, which were performed in accordance with the International Standard ISO 6060 (International Organization for Standardization, 1986). For the measurement of suspended solids (SS) and volatile suspended solids (VSS) Millipore AP40 glass fiber filters with an effective pore size of 1600 nm were used. SS and VSS analyses were performed by using the procedure defined in Standard Methods (1995).

3.2.1.2 Physico – chemical treatment

For the treatability studies conducted in the scope of physico – chemical treatment two different methods were applied. The first method was treatment with lime precipitation and the second method was coagulation – flocculation with alum. Physico – chemical treatment was performed by execution of jar test experiments. Hydrated lime, alum and anionic polyelectrolyte solutions are prepared to be used in jar test experiments. For the preparation of hydrated lime solution 50 g $Ca(OH)_2$ is solved in 1 l distilled water, whereas for the preperation of alum solution 20 g $Al_2(SO_4)_3.18H_2O$ is solved in 1 l distilled water. Anionic polyelectrolyte solution was prepared by solving 0.25 g of polyelectrolyte in 250 ml distilled water. A lab scale jar test apparatus is utilized for the jar test experiments.

The treatment with lime precipitation is carried for three different cases at three different pH values (pH 7, pH 9, pH 11). The jar test experiment procedure applied in all cases was 5 minutes of flash mixing at 100 rpm (after pH adjustment with hydrated lime solution) followed by 30 minutes of flocculation at 30 rpm (after addition of the anionic polyelectrolyte). After the completion of jar tests the treated samples settled for 30 minutes and COD analyses were performed on the supernatant decanted after precipitation for the observation of COD removal efficiency.

In the first case, the pH is adjusted to 7, 9 and 11 by the addition of hydrated lime solution and the jar test experiments were performed. In the second case, anionic polyelectrolyte with a dosage of 100 mg/l is added after the pH adjustment (pH 7, pH

9, pH 11) through the addition of hydrated lime solution and the flash mixing step for the examination of the effect of polyelectrolyte addition on COD removal efficiency. In the third case, 3 hours of aeration was realized prior to the pH adjustment step and after the aeration step the same procedure was applied as in the second case.

The treatment with alum coagulation – flocculation is conducted for five different alum dosages. Alum solution was added to samples so that the alum dosage for the samples were 250 mg/l, 500 mg/l, 1000 mg/l, 1500 mg/l, 2000 mg/l respectively. After the addition of alum solution the jar test experiments were realized. The jar test experiment procedure for alum coagulation – flocculation was 5 minutes of flash mixing at 100 rpm followed by 30 minutes of flocculation at 30 rpm. After the completion of jar tests the treated samples settled for 30 minutes and COD analyses were performed on the supernatant decanted after precipitation for the observation of COD removal efficiency. The same experimental procedure was realized for an aerated sample (3 hours) with an alum dosage of 2000 mg/l to examine the effect of aeration on COD removal efficiency.

3.2.1.3 Biological treatment

Biological treatability of raw (Sample 2 – 5 December 2009) and physico – chemically treated landfill leachate samples were investigated by operating two fill and draw reactors. Activated sludge contained in the first reactor was acclimated with raw landfill leachate sample and it had a working volume of 3 l, whereas the activated sludge in the second reactor was acclimated with physico – chemically treated landfill leachate sample and it had a working volume of 1.5 l. The physico – chemical treatment method to be applied prior to feeding was selected as aeration followed by lime precipitation at pH 11, since it was the most efficient treatment alternative in terms of COD removal according to the results obtained through physico – chemical treatability experiments. Beyond acclimation of the biomass with landfill leachate samples, all other macro and micronutrients necessary for biological growth were added into the reactors as Solution A and Solution B formulations in sufficient quantities (10 ml Solution A and Solution B for 1000 mg COD/l). Solution A and Solution B formulations served as an eliminator of the effects of nutrient limitation and they provided buffering of pH in reactors against possible variations. The components of Solution A and Solution B are given in Table 3.1. The reactors were operated at a sludge age of 10 days and a hydraulic retention time of 1 day. The system was operated under laboratory conditions until steady state was reached.

The performance of the first reactor fed with raw leachate sample was monitored in terms of COD removal. Acclimated biomass contained in both of the reactors was subjected to respirometric tests.

Table 3.1: Composition of solution A and solution B

Solution B		Solution A	
$MnSO_4.3H_2O$	0.5 g/l	K_2HPO_4	320 g/l
$ZnSO_4.7H_2O$	0.5 g/l	KH_2PO_4	160 g/l
$FeSO_4.7H_2O$	0.5 g/l	NH_4Cl	120 g/l
$MgSO_4.7H_2O$	15 g/l		
$CaCl_2$	2 g/l		

3.2.1.4 Sequential filtration – ultrafiltration

A continuously-stirred cell (Amicon, Model 8, 400; volume of 400 mL) was used for the filtration / ultrafiltration experiments, carried out under positive pressure (0.6–1.2 atm; N_2 as the inert gas). No quiescent-settling was applied and each sample was first filtered through AP40 glass-fibre filter (Millipore AP40; pore sizes of 1, 200-1,600 nm). Then, each filtrate were subsequently passed through conventional filters with a pore size of 450 nm (Durapore HV, polyvinylidene fluoride [PVDF]), and 220 nm (Durapore GV, PVDF) (Millipore Corp., Bedford, MA 01730). The permeates collected after filtering through 220 nm were then subjected to ultrafiltration experiments, during which a series of membrane discs with nominal molecular weight cut-off (MWCO) values of 100, 30, 10, 3, and 1 kDa (PL series, Millipore, MA), was used. All recommendations by the manufacturers, in terms of working and preservation conditions (pressure, temperature, washing, rinsing, preserving, regenerating, etc.) for the membranes were fulfilled.

Schematic presentation of the sequential filtration/ultrafiltration procedure is demonstrated in Figure 3.1.

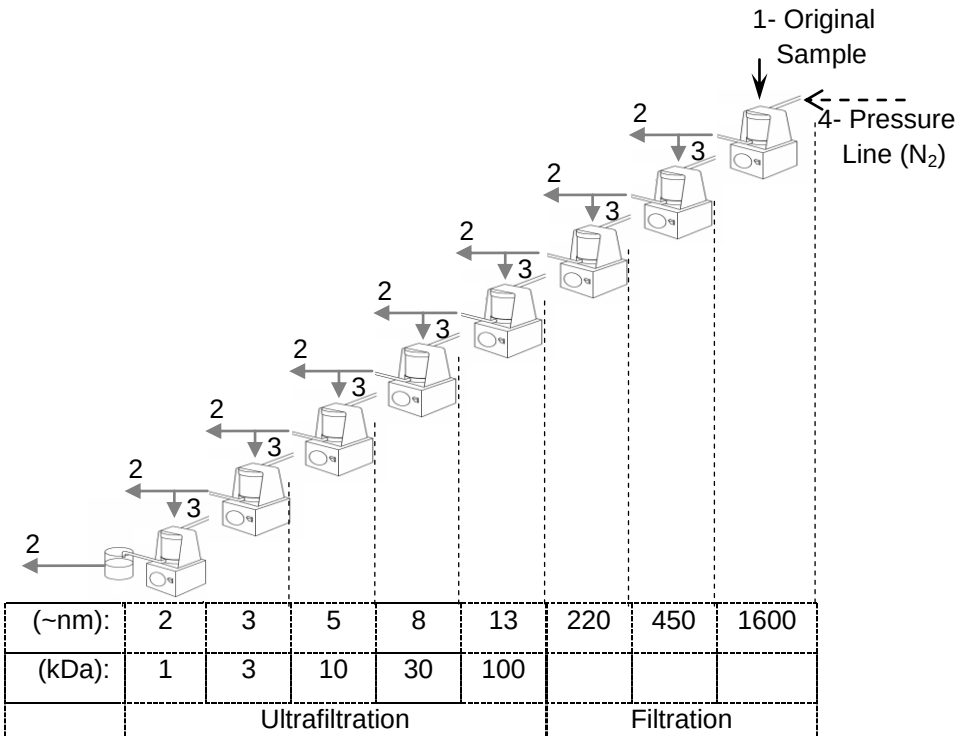

Figure 3.1: Schematic presentation of the sequential filtration/ultrafiltration

The explanations for the numbers in Figure 3.1 are summarized below.

1. Non-settled, non-filtered, but mixed original sample
2. Aliquot of filtrate from the previous step, subjected to COD measurements
3. Aliquot of filtrate from the previous step, subjected to subsequent filtration/ultrafiltration procedure
4. Gas line providing positive pressure

3.2.1.5 Respirometry

Respirometric analyses were performed on raw and physico – chemically treated landfill leachate samples (Sample 2 – 5 December 2009) with relevant acclimated biomass mentioned in 3.2.1.3 Biological Treatment. According to the results obtained through physico – chemical treatability experiments, the treatment method performing the highest COD removal efficiency was lime precipitation of aerated samples at pH 11. Therefore, the treatment method to be applied prior to the respirometric tests was selected as aeration followed by lime precipitation at pH 11.

Oxygen uptake rate (OUR) measurements were performed with a Ra-Combo (Applitek Co., Nazareth, Belgium) continuous respirometer. A nitrification inhibitor

(Formula 2533TM, Hach Company) was used to prevent any possible interference induced by nitrification. The concentration of the biomass in the reactor was adjusted to 1000 mg VSS/l and the reactor volume was 2 l. The tests were started with the biomass seeding alone to obtain the initial endogenous OUR level. After the observation of the initial endogenous OUR level, the sample was added into the reactor as substrate so that the initial total COD concentration of the substrate in the reactor was 100 mg/l. In order to be able to prevent the absence of nitrogen and phosphorus during the test, 1 ml of COD/l Solution A and Solution B were added for 100 mg/l COD by providing the suggested ratio 10 ml / 100 mg COD/l (O'Connor, J.T., 1972). While the OUR data was monitoring, samples were taken from the reactor in various time intervals in order to be able to observe the reactor performance in terms of COD removal and to generate useful data to be used in modeling studies. COD measurements were conducted on the filtered samples (0,45 µm Millipore membrane syringe filters) taken from the reactor.

For both of the samples (raw wastewater sample, physico – chemically treated wastewater sample) a reactor representing the same conditions as the respirometric tests (1000 mg VSS/l, 100 mg COD/l) were set up to conduct PHA and COD measurements on samples taken from these reactors. PHA and COD samples were taken in various time intervals. COD measurements were carried out on filtered samples (0,45 µm Millipore membrane syringe filters). Formaldehyde was added to PHA samples in order to prevent biological activity. Sampled biomass was washed with K–P buffer solution and freeze-dried. Extraction, hydrolysation, and esterification processe were performed at 100 °C in a mixture of hydrochloric acid, 1-propanol, and dichloroethane, as described by Beun et al. (2000). Then, free acids were removed through extraction with water. After the completion of the extraction step, organic phase was analyzed by gas chromatograph (Agilent 6890 N). Benzoic acid was used as the internal standard in the analysis.

3.2.1.6 Determination of soluble inert COD fraction

The soluble inert COD fraction of raw landfill leachate sample (Sample 2 – 5 December 2009) was determined according to the procedure described by Orhon et al. (1999). For the determination of the soluble inert COD, reactors with a volume of 3 l were set up for glucose and filtered wastewater. Appropriate amounts of glucose solution and filtered wastewater were added into the reactors, so that the initial COD concentration in the reactors was the same. The reactors were seeded with 50 mg VSS/l of acclimated biomass. For the acclimation purposes the biomass was fed

with a composition of 50 % leachate sample and 50 % glucose solution having equivalent COD values. The amount of the seed was intentionally kept minimal in order to prevent possible interferences induced by endogenous microbial products. Appropriate amounts of Solution A and Solution B (10 ml Solution A and Solution B for 1000 mg COD/l) were added to the reactor to eliminate the impacts of nutrient limitation. The reactors were constantly aerated and the filtered COD concentration in the reactors was monitored. The experiment was continued until all biological activity was completed and no appreciable COD change was detected. COD measurements were executed on the filtered samples (0,45 µm Millipore membrane syringe filters) taken from the reactors.

4. RESULTS

4.1 Characterization of Raw Leachate

4.1.1 Conventional wastewater characterization

The results of the conventional characterization for the first landfill leachate sample (Sample 1- 4 October 2009) are summarized in Table 4.1.

Table 4.1: Characterization of raw leachate (Sample 1)

PARAMETER	VALUE
Total COD (mg L^{-1})	74525
Settled COD (mg L^{-1})	67845
Filtered (1600 nm) COD (mg L^{-1})	57275
Filtered (450 nm) COD (mg L^{-1})	56330
Particulate COD (mg L^{-1})	18195
TSS (mg L^{-1})	9020
VSS (mg L^{-1})	7140
TKN (mg L^{-1})	2675
NH_3-N (mg L^{-1})	2335
TP (mg L^{-1})	38
OP (mg L^{-1})	20
pH	5.69
Cl^- (mg L^{-1})	2600

The results of the conventional wastewater characterization for the second landfill leachate sample (05.12.1009) are summarized in Table 4.2.

Table 4.2: Characterization of raw leachate (Sample 2)

PARAMETER	VALUE
Total COD (mg L^{-1})	47105
Settled COD (mg L^{-1})	41780
Filtered (1600 nm) COD (mg L^{-1})	35740
Filtered (450 nm) COD (mg L^{-1})	35240
Particulate COD (mg L^{-1})	11865
TSS (mg L^{-1})	5605
VSS (mg L^{-1})	4315
TKN (mg L^{-1})	1805
NH_3-N (mg L^{-1})	1645
TP (mg L^{-1})	25
OP (mg L^{-1})	12
pH	5.71
Cl^- (mg L^{-1})	1670

According to the results obtained by wastewater characterization (Table 4.1 and Table 4.2) it is obvious that the organic matter concentration is very high in both of the samples, but the pollution load of Sample 1 is higher compared to the pollution load of Sample 2, which may be induced due to seasonal variation of the composition of the organic waste handled.

It was observed that the wastewater characteristics of the examined leachate showed coherency with the default values found in literature for young landfill (recently produced) leachates. Young landfill leachates have a higher organic matter content compared to old landfill (stabilized) leachates, which demonstrates that the biodegradation reactions are almost completed in old landfills, whereas the biodegradation process continues in young landfills.

4.1.2 PSD based COD fractionation of raw leachate

The Particle Size Distribution based COD fractionation of raw leachate for both of the samples (Sample 1 and Sample 2) is given in Table 4.3 and Table 4.4.

Table 4.3: PSD-based COD fractionation of raw leachate (Sample 1)

Separation Technique	Particle size (nm)	Cumulative COD (mg L^{-1})	Size Category (nm)	Differential COD (mg L^{-1})
Total		74525		
Filtration				
AP40 filter	1600	57275	>1600	17250
HV filter	450	56330	450-1600	945
GV filter	220	55305	220-450	1025
Ultrafiltration				
100 kDa	13	54290	13-220	1015
30 kDa	8	53190	8-13	1100
10 kDa	5	52180	5-8	1010
3 kDa	3	50440	3-5	1740
1 kDa	2	46365	2-3	4075
			<2	46365

Table 4.4: PSD-based COD fractionation of raw leachate (Sample 2)

Separation Technique	Particle size (nm)	Cumulative COD (mg L^{-1})	Size Category (nm)	Differential COD (mg L^{-1})
Total		47105		
Filtration				
AP40 filter	1600	35740	>1600	11365
HV filter	450	35240	450-1600	500
GV filter	220	34690	220-450	550
Ultrafiltration				
100 kDa	13	34160	13-220	530
30 kDa	8	33600	8-13	560
10 kDa	5	33150	5-8	450
3 kDa	3	32305	3-5	845
1 kDa	2	30085	2-3	2220
			<2	30085

Through the observation of differential COD values obtained by the application of sequential filtration/ultrafiltration process, it can be seen that the particle size of a significant fraction of organic matter contained in both of the samples (Sample 1 and Sample 2) is below the particle size of 2 nm, which means most of the organic matter contained in the leachate samples is in soluble form. If the distribution of organic matter is analyzed by the consideration of particle size, it can be observed that the organic matter content of both of the samples consists of two major fractions. The first major fraction is composed of particles greater than 1600 nm and the second major fraction involves particles below the size of 2 nm.

Although the total organic matter concentrations of these two samples differ, the particle size distribution of Sample 1 and Sample 2 are nearly the same, which means that the seasonal variation of the organic pollution load leads to increased

concentrations of pollutants, but is does not impact the particle size distribution of the pollutant material, since almost the same particle size distribution profile is obtained for both of the samples.

The particle size distribution profiles for Sample 1 and Sample 2 are visualized in Figure 4.1 and Figure 4.2. As mentioned, the organic matter fractionation of these samples is very similar and compatible with each other.

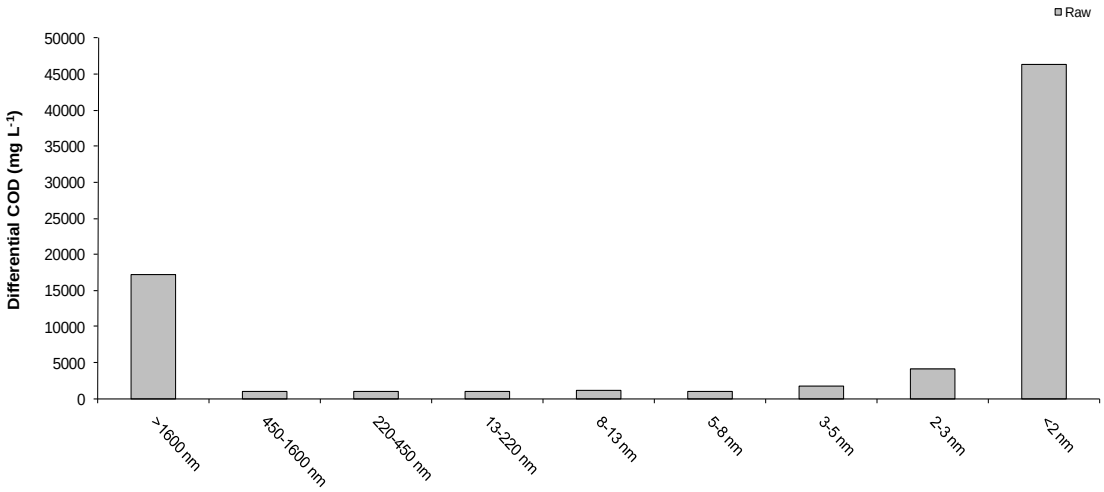

Figure 4.1: PSD-based COD fractionation of raw leachate (Sample 1)

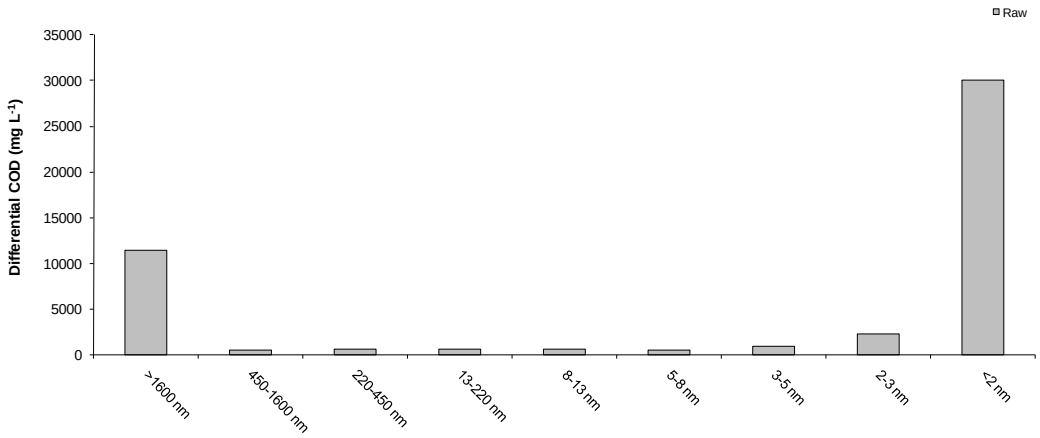

Figure 4.2: PSD-based COD fractionation of raw leachate (Sample 2)

In order to be able to compare the obtained particle size distributions of these two raw leachate samples, the distribution of variying particle sizes is demonstrated in Figure 4.3 as percentage. Figure 4.3 shows that the particle size distribution of Sample 1 and Sample 2 are very similar. It is also obvious in Figure 4.3 that the raw leachate samples have two major fractions such as the particles with a particle size greater than 1600 nm and the particles with a particle size lower than 2 nm as mentioned before.

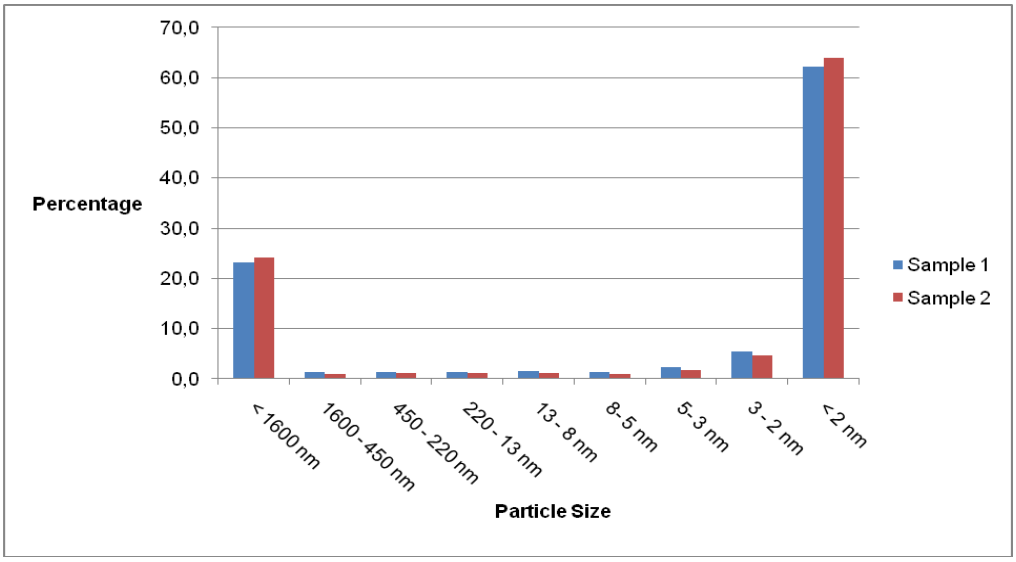

Figure 4.3: Comparison of the particle size distribution for raw leachate samples

4.2 Physico – Chemical Treatability

4.2.1 Lime precipitation

Table 4.5: Treatment with lime precipitation (Sample 1)

pH	Lime Dosage (mg L^{-1})	Total COD (mg L^{-1})	
		LP	LP + 100PE
7	2240	53395	49660
9	4270	49150	47540
11	7270	48840	46350

The results attained through the application of lime precipitation (LP) and lime precipitation with 100 mg/l polyelectrolyte addition for Sample 1 are summarized in Table 4.5. Treatment with lime is applied at three different pH values. The calculated pH values are also shown in Table 4.5. The total COD value of the raw sample was (Sample 1) approximately 75000 mg/l. COD measurements were performed after treatment with lime in order to be able to figure out the removal efficiencies by the applied treatment methods. According to the obtained results the removal efficiencies of total COD for lime precipitation was varied between 28-34%, whereas the removal efficiencies were between 33-38% by the addition of polyelectrolyte after treatment with lime. As it is obvious, polyelectrolyte assisted lime precipitation showed higher removal efficiencies. The effect of varying pH values on treatment efficiency can also be observed. The maximum efficiency was obtained by the highest pH value (pH 11).

Furthermore, the effect of aeration on the removal efficiency was also investigated. Total COD measurements were performed for the determination of the impact of 3 hour aeration period on the COD removal efficiency. The experiments are repeated for the same experimental conditions (pH 7, pH 9, pH 11 LP and LP+100PE). The results of these experiments are demonstrated in Table 4.6. The total COD removal efficiency at pH 7 was increased from 33% to 39%, at pH 9 from 36% to 40% and at pH 11 from 38% to 43%. According to the results, aeration is useful for the enhancement the COD removal efficiency.

Table 4.6: Aeration and treatment with lime precipitation (Sample 1)

Ph	Lime Dosage (mg L^{-1})	Wastewater	Total COD (mg L^{-1}) LP + 100PE
5.69	---	Non-aerated	74525
7	2240		49660
5.95	---	Aerated (3 h)	64830
7	1990		45775
5.69	---	Non-aerated	74525
9	4270		47540
5.95	---	Aerated (3 h)	64830
9	3800		44635
5.69	---	Non-aerated	74525
11	7270		46350
5.95	---	Aerated (3 h)	64830
11	6470		42730

Same experimental procedure was carried out on the Sample 2 and similar results were obtained. The results for Sample 2 are summarized in Table 4.7 and Table 4.8. According to the obtained results the removal efficiencies of total COD for lime precipitation was varied between 27-33%, whereas the removal efficiencies were between 32-36% by the addition of polyelectrolyte after treatment with lime.

Table 4.7: Treatment with lime precipitation (Sample 2)

pH	Lime Dosage (mg L^{-1})	Total COD (mg L^{-1})	
		LP	LP + 100PE
7	2140	34575	32265
9	4090	31890	30950
11	6960	31700	30195

Table 4.8: Aeration and treatment with lime precipitation (Sample 2)

pH	Lime Dosage (mg L^{-1})	Wastewater	Total COD (mg L^{-1}) LP + 100PE
5.71	---	Non-aerated	47105
7	2140		32265
5.96	---	Aerated (3 h)	42065
7	1900		30540
5.71	---	Non-aerated	47105
9	4090		30950
5.96	---	Aerated (3 h)	42065
9	3640		29780
5.71	---	Non-aerated	47105
11	6960		30195
5.96	---	Aerated (3 h)	42065
11	6190		28560

The effect of aeration on the removal efficiency was investigated also for the sample 2. The same experimental procedure was applied to the Sample 2 as the Sample 1. The experiments are repeated for the same experimental conditions (pH 7, pH 9, pH 11 LP and LP+100PE). The results of these experiments are demonstrated in Table 4.8. The total COD removal efficiency at pH 7 was increased from 32% to 35%, at pH 9 from 34% to 37% and at pH 11 from 36% to 39%. According to the results, aeration is useful for the enhancement the COD removal efficiency.

4.2.2 Coagulation – flocculation with alum

Physico – chemical treatability studies are carried out on both of the examined leachate samples (Sample 1 and Sample 2) by the application of coagulation – flocculation process with alum, as well as lime treatment. Coagulation – flocculation process is applied by various alum doses as described in 3.2.1.2 Physico – Chemical Treatment. Total COD measurements were performed for the determination of organic matter removal efficiency. The results obtained for Sample 1 can be summarized as following:

Highest removal efficiencies observed by the implementation of coagulation – flocculation process with alum were obtained with the greatest alum dose, which is 2000 mg/l. Total COD removal efficiencies varied between 29-35% (without

aeration), whereas the total COD removal efficiency of 40% was achieved by the employment of aeration process prior to coagulation – flocculation step.

The results obtained for Sample 2 can be summarized as following:

Highest removal efficiencies observed by the implementation of coagulation–flocculation process with alum were obtained with the greatest alum dose, which is 2000 mg/l. Total COD removal efficiencies varied between 27-33% (without aeration), whereas the total COD removal efficiency of 37% was achieved by the employment of aeration process prior to coagulation – flocculation step.

Considering the attained removal efficiencies, similar results came out for both of the samples (Sample 1 and Sample 2). An enhancement of removal efficiency was reached with the application of aeration before the coagulation – flocculation step. When lime treatment and coagulation – flocculation with alum are compared in terms of treatment efficiency, lime treatment showed higher removal efficiencies. Detailed information about the results can be found in Appendix A.1.

4.2.3 PSD based COD fractionation of physico - chemically treated leachate

PSD based COD fractionation was carried out on both of the samples (Sample 1 and Sample 2) after the physico – chemical treatment step. The applied physico – chemical treatment methods were aeration – lime precipitation and aeration – cogulation – flocculation. The results obtained by aeration – lime precipitation for Sample 1 are given in Table 4.9 and Figure 4.3. Other results obtained by aeration – lime precipitation for Sample 2 (Appendix A.2), aeration – coagulation – flocculation for Sample 1 and Sample 2 (Appendix A.3) can be found in appendices.

When the profiles of particle size distribution obtained for Sample 1 and Sample 2 (Figure 4.3 and Appendix A.2) after the application of aeration – lime precipitation is compared, it can be seen that very similar results were obtained in terms of COD removal for the particles in the same size interval. In order to be able to compare the particle size distribution after the implementation of aeration – lime precipitation the particle size distribution of Sample 1 and Sample 2 is visualized in Figure 4.4 as percentage. As it is obvious from Figure 4.4 the distribution of particles is nearly the same for both of the samples.

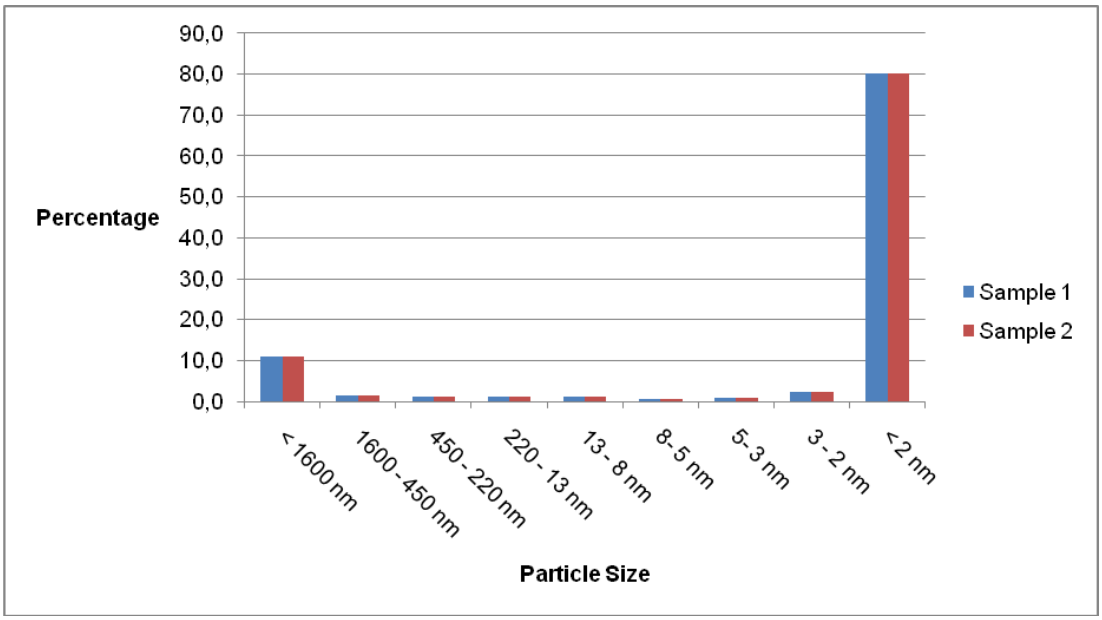

Figure 4.4: Particle size distribution after application of aeration – lime precipitation

The physico – chemical treatment process expected to remove the particles with higher molecular weights, but as it can clearly be seen on Figure 4.3, not only particles having a particle size greater than 1600 nm are removed, but also low molecular weight particles having a particle size below 2 nm are removed. The removal of low molecular weight particles may be enabled by the adsorption process.

4.2.3.1 Lime precipitation

The results for particle size distribution and COD removal (Sample 1) are demonstrated in Table 4.9 and Figure 4.5.

Table 4.9: Particle size distribution of COD after treatment by means of aeration and lime precipitation (Sample 1)

Separation Technique	Particle size in nm	Cumulative COD (mg L^{-1})				Size Category (nm)	Differential COD (mg L^{-1})			
		Aeration	Lime Precipitation				Aeration	Lime Precipitation		
			pH 7	pH 9	pH 11			pH 7	pH 9	pH 11
Total		64830	45775	44635	42730					
Filtration										
AP40 filter	1600	47590	40735	39720	38025	>1600	17240	5040	4915	4705
HV filter	450	46660	40095	39095	37425	450-1600	930	640	625	600
GV filter	220	45675	39545	38560	36910	220-450	985	550	535	515
Ultrafiltration										
100 kDa	13	44745	39025	38055	36425	13-220	930	520	505	485
30 kDa	8	43845	38475	37515	35915	8-13	900	550	540	510
10 kDa	5	43295	38200	37245	35660	5-8	550	275	270	255
3 kDa	3	42600	37835	36890	35320	3-5	695	365	355	340
1 kDa	2	40915	36705	35790	34265	2-3	1685	1130	1100	1055
						<2	40915	36705	35790	34265

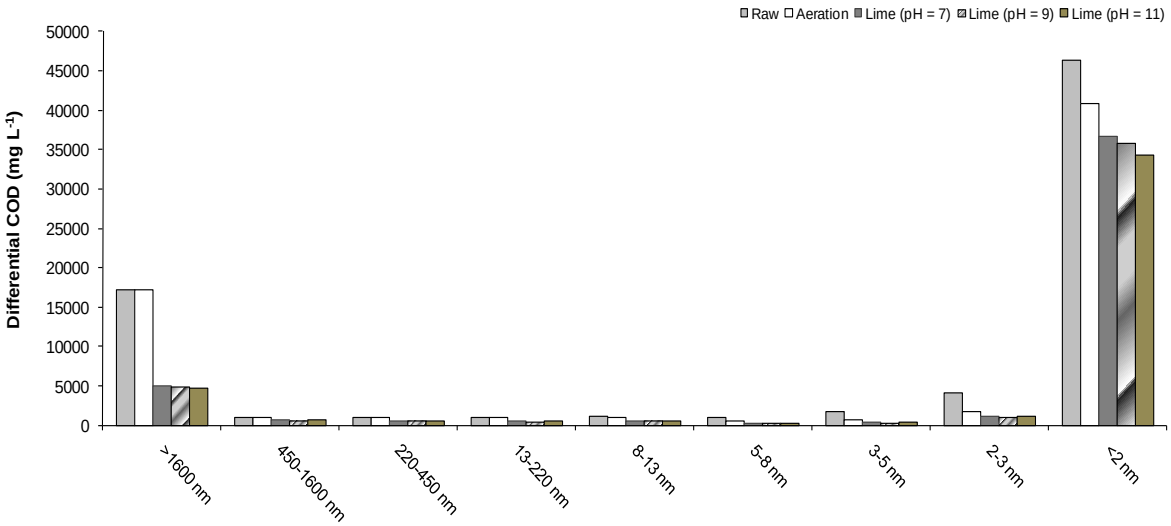

Figure 4.5: PSD of COD after treatment by means of aeration - lime precipitation

Table 4.10 and Table 4.11 summarize the observed COD removal efficiencies by the application of aeration – lime precipitation. Table 4.10 demonstrates the COD removal efficiencies obtained in each size interval and Table 4.11 demonstrates the individual removal efficiencies obtained for each size interval. The results showed that the aeration – lime precipitation is not only effective for the reduction of high molecular weight particles, but also it can remove some part of the low molecular weight particles. The enhancement of removal efficiency through aeration can also be recognized and the impact of pH on the process efficiency is displayed. The highest removal efficiency was achieved at pH 11. Although some part of the low molecular weight particles are removed by the employment of aeration and lime precipitation, the removal efficiency of high molecular weight particles (approximately 70%) are higher than that of the low molecular particles (approximately 20%) as expected.

Table 4.10: Fractions of the total removals observed in each size interval with aeration and lime precipitation (Sample 1)

Process	Removal efficiencies (%)									Total (%)
	>1600	450-1600	220-450	13-220	8-13	5-8	3-5	2-3	<2	
Aeration (t = 3 h)	0	0	0.1	0.1	0.3	0.6	1.4	3.2	7.3	13.0
Lime Precipitation (pH = 7)	16.4	0.4	0.6	0.7	0.7	1.0	1.8	4.0	13.0	38.6
Lime Precipitation (pH = 9)	16.6	0.4	0.7	0.7	0.8	1.0	1.9	4.0	14.2	40.1
Lime Precipitation (pH = 11)	16.8	0.5	0.7	0.7	0.8	1.0	1.9	4.1	16.2	42.7

Table 4.11: Individual removal efficiencies observed in each size interval with aeration and lime precipitation (Sample 1)

Process	Removal efficiencies (%)									Total (%)
	>1600	450-1600	220-450	13-220	8-13	5-8	3-5	2-3	<2	
Aeration (t = 3 h)	0.1	1.6	3.9	8.4	18.2	45.5	60.1	58.7	11.8	13.0
Lime Precipitation (pH = 7)	70.8	32.3	46.3	48.8	50.0	72.8	79.0	72.3	20.8	38.6
Lime Precipitation (pH = 9)	71.5	33.9	47.8	50.2	50.9	73.3	79.6	73.0	22.8	40.1
Lime Precipitation (pH = 11)	72.7	36.5	49.8	52.2	53.6	74.8	80.5	74.1	26.1	42.7

The particle size distribution profiles and observed COD removal efficiencies (total COD removal efficiencies and individual COD removal efficiencies for each particle size interval) of Sample 1 and Sample 2 after the application of aeration – lime precipitation can be compared through Figure 4.6 and Figure 4.7. Aeration – lime precipitation at pH 11 was the most successful application in terms of COD removal, so the results obtained by this implementation are visualized with the help of the data gained from Table 4.10 and Table 4.11. The fractions of the total removals observed in each size interval with aeration and lime precipitation and the individual removal efficiencies observed in each size interval with aeration and lime precipitation for both of the samples can be compared with the help of Figure 4.6 and Figure 4.7.

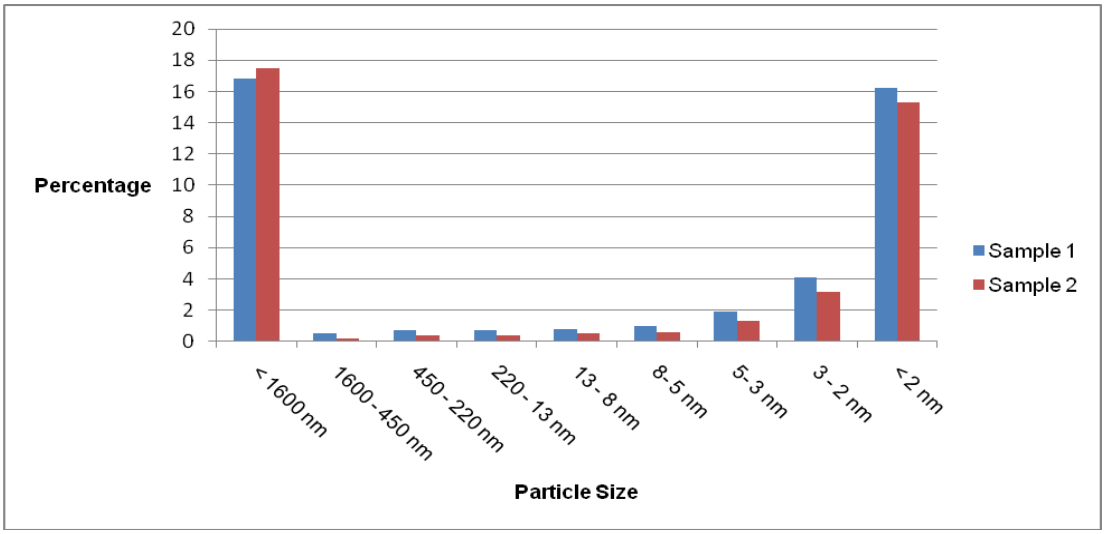

Figure 4.6: Fractions of the total removals observed in each size interval with aeration and lime precipitation

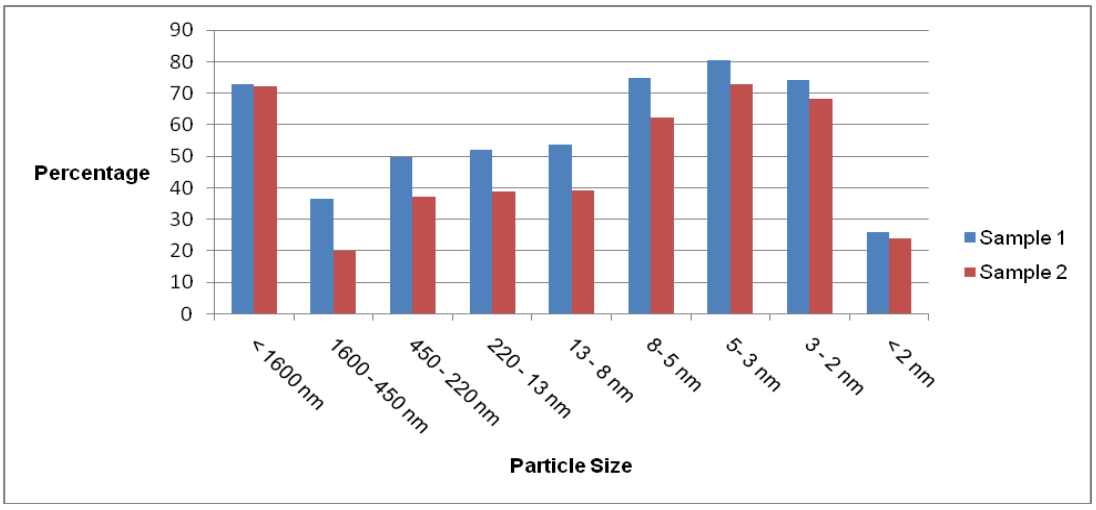

Figure 4.7: Individual removal efficiencies observed in each size interval with aeration and lime precipitation

4.2.3.2 Coagulation – flocculation with alum

The results of the experiments carried out on Sample 1 and Sample 2 by the implementation of aeration-coagulation-flocculation are given in Appendix A.3.

4.3 Biological Treatability

4.3.1 COD removal efficiency

The COD removal efficiency in the main biological reactor mentioned in 3.2.1.3 Biological Treatment was monitored. For that purpose samples were taken from the reactor following the feeding of the reactor with examined the leachate (Sample 2). Filtered COD (0.45 μm) measurements were performed and the change of the filtered COD concentration in the reactor over time was calculated. The change of filtered COD concentration in the reactor over time is demonstrated on Figure 4.8.

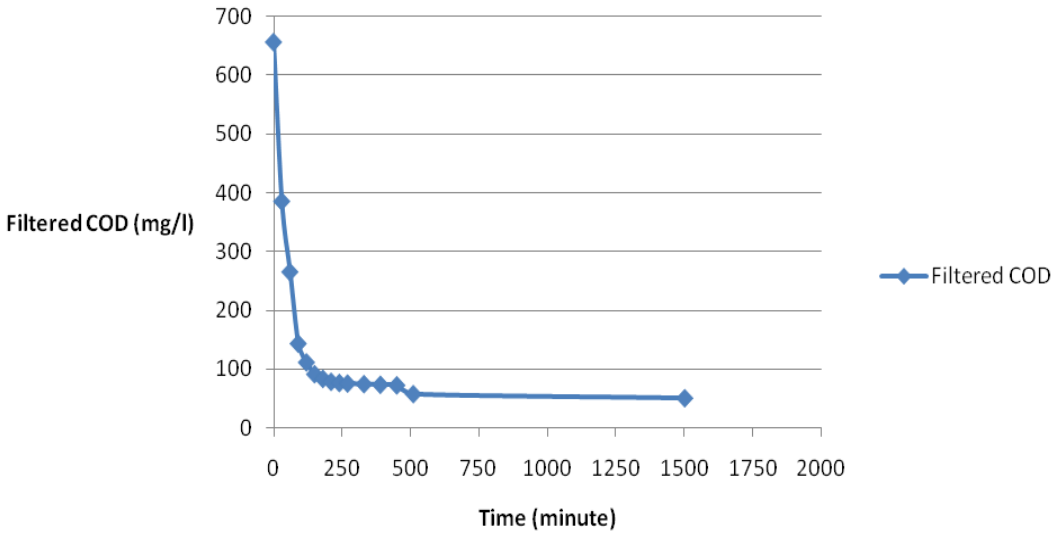

Figure 4.8: Monitoring of COD removal in the biological reactor

The COD removal efficiency in the reactor was satisfactory. The filtered COD concentration was decreased from 656 mg/l to 50 mg/l, so the removal efficiency was 92%. The observed removal efficiency indicates that the sample feed to the reactor has a high degree of biodegradability, so biological treatment can be an appropriate alternative for the organic matter removal.

4.3.2 Respirometric Analyses

4.3.2.1 Respirometric Analyses on Raw Leachate

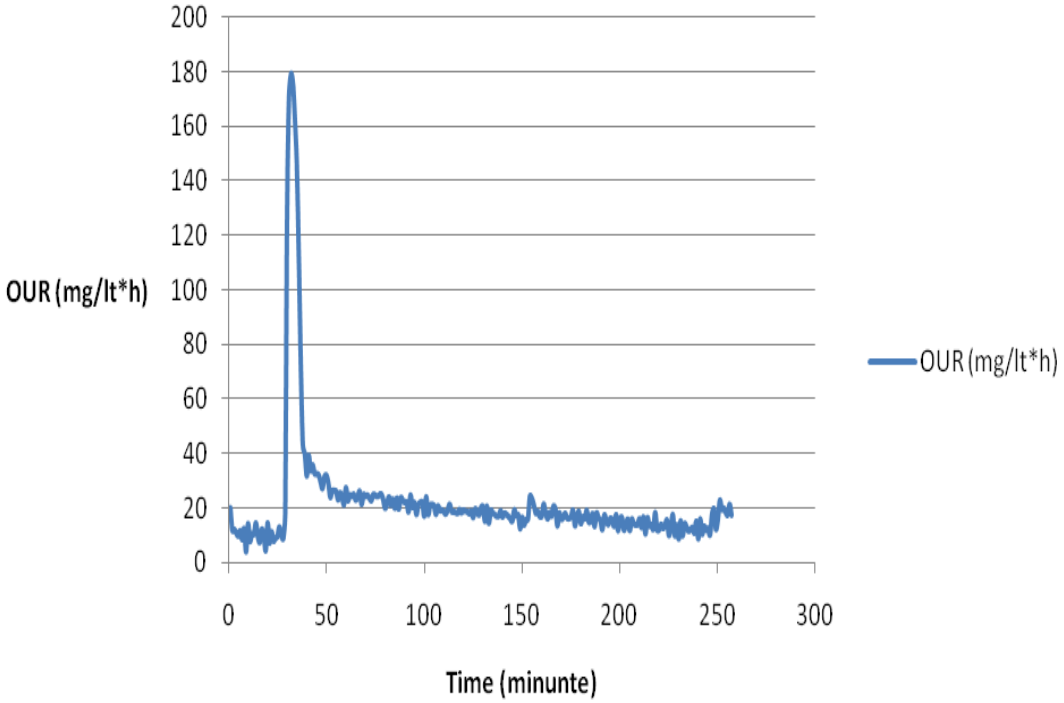

Figure 4.9: OUR profile observed with raw leachate

The obtained OUR profile in Figure 4.9 demonstrates that, easily biodegradable COD fraction (S_S) of the examined leachate (Sample 2) is very high, so that the oxygen uptake rate increases in a short period of time to the level of 180 mg/l*h, since the readily biodegradable substrate is consumed by biomass directly in the growth process.

During the OUR measurement COD samples were taken from simultaneously the reactor for the monitoring COD removal efficiency. The first COD sample was taken before feeding the reactor. The change of filtered COD concentration in the reactor over time is shown in Figure 4.10. The filtered COD concentration in the reactor showed a sudden decrease in a short period of time as expected in coherency with the results obtained through respirometric tests. This sudden increase may probably be due the rapid consumption of readily biodegradable organic matter by the reactor biomass.

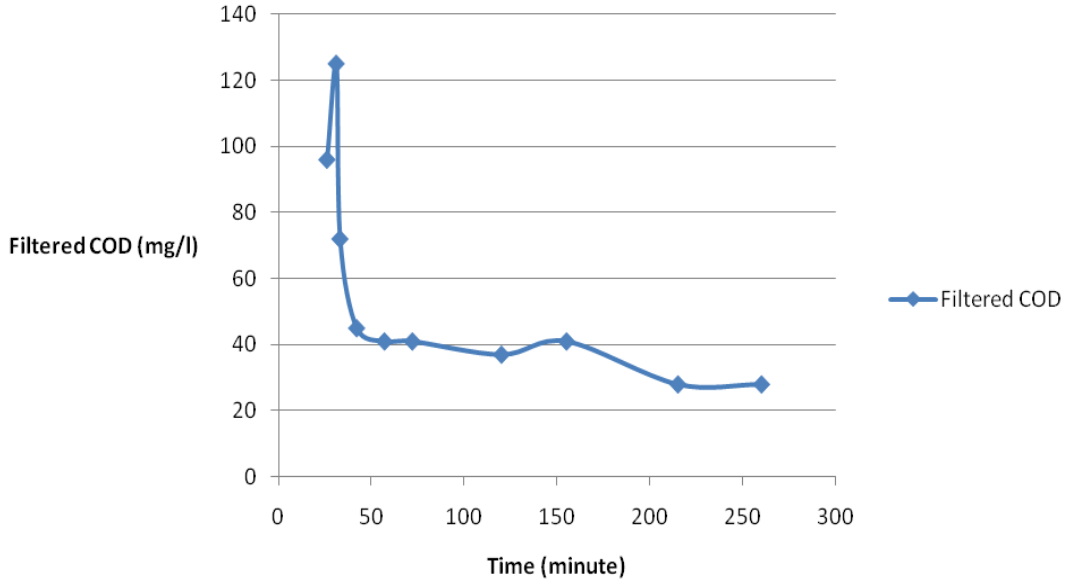

Figure 4.10: Monitoring of COD removal during OUR measurements

4.3.2.2 Respirometric analyses on physico - chemically treated leachate

Respirometric measurements and COD monitoring were performed also for the physico - chemically treated (aeration-lime precipitation at pH 11) leachate (Sample 2) in the same way as the raw leachate. Similar results are obtained for the physico - chemically treated leachate. The OUR profile and the change of filtered COD concentration in the reactor over time are demonstrated in Figure 4.11 and Figure 4.12.

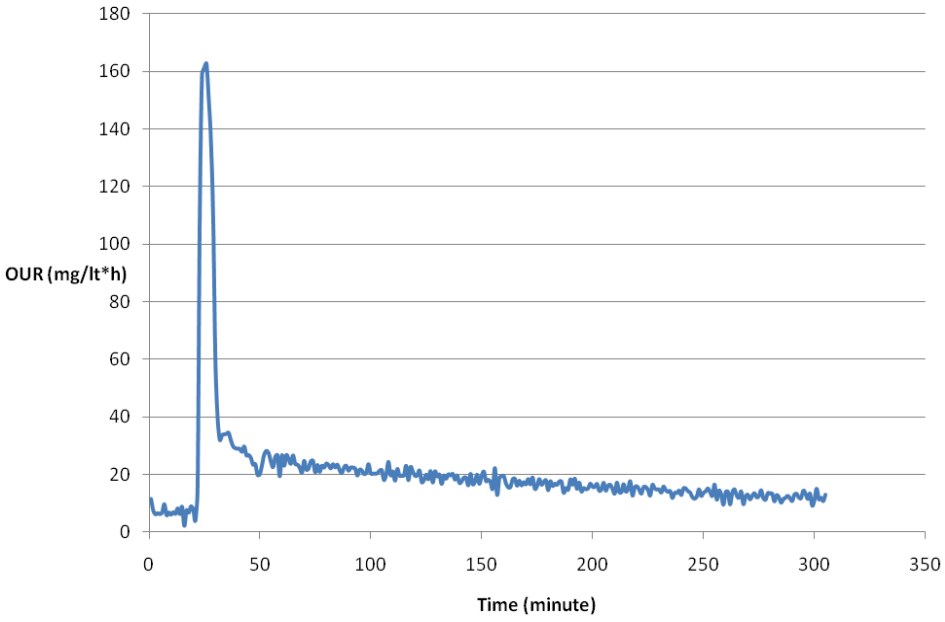

Figure 4.11: OUR profile observed with raw leachate

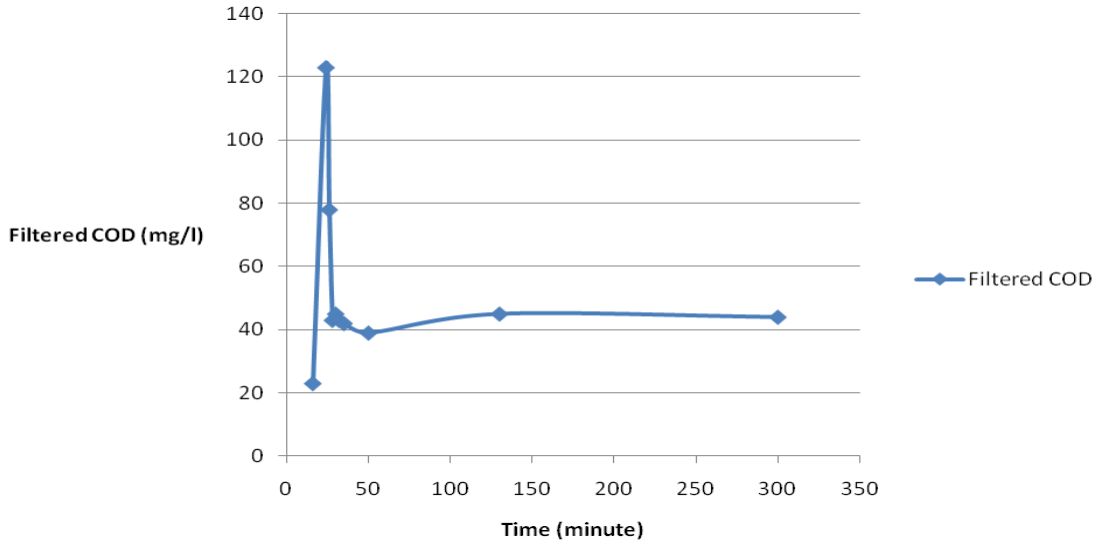

Figure 4.12: Monitoring of COD removal during OUR measurements

4.3.3 PSD Based COD Fractionation of Biologically Treated Leachate

The PSD based COD fractionation of biologically treated leachate is shown in Table 4.12 and Figure 4.13. According to the results obtained biological treatment provides an effective removal for the low molecular weight compounds with particle size below 2 nm. The removal efficiency observed with biological treatment is higher than that of attained by physico – chemical treatment for this type of pollutants (particle size below 2 nm).

Table 4.12: Particle size distribution of COD after biological treatment (Sample 1)

Separation Technique	Particle size in nm	Cumulative COD (mg L^{-1})		Size Category (nm)	Differential COD (mg L^{-1})	
		Influent	Effluent		Influent	Effluent
Total		1250				
Filtration						
AP40 filter	1600	961		>1600	289	
HV filter	450	945	396	450-1600	16	
GV filter	220	928	394	220-450	17	2
Ultrafiltration						
100 kDa	13	911	393	13-220	17	1
30 kDa	8	892	386	8-13	19	7
10 kDa	5	875	379	5-8	17	7
3 kDa	3	846	372	3-5	29	7
1 kDa	2	778	323	2-3	68	49
				<2	778	323

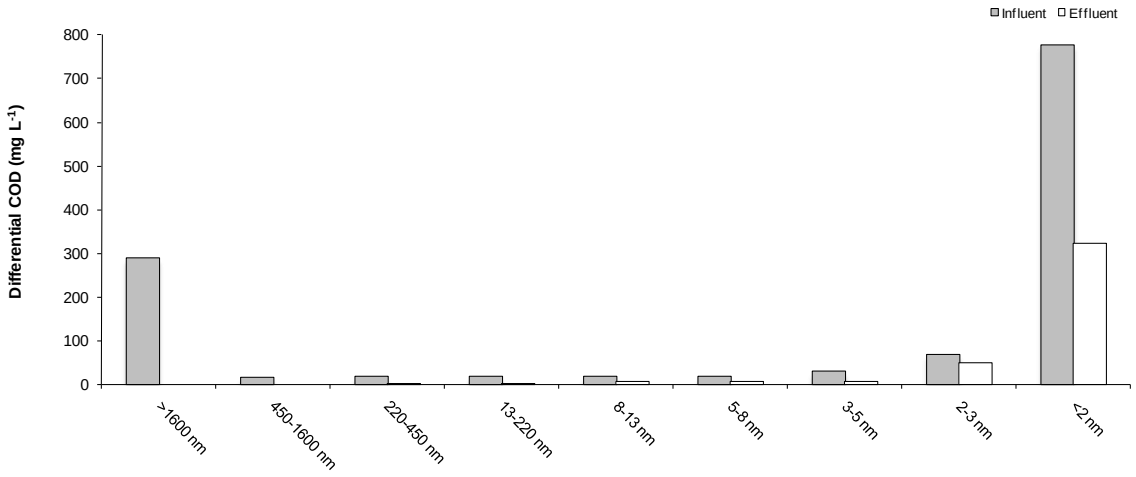

Figure 4.13: Particle size distribution of COD after biological treatment (Sample 1)

4.4 Model Application and Results

Resluts obtained through application of ASM1 is given in Table 4.13 and Table 4.14.

Table 4.13: ASM 1 model results

Model Parameter & State	Wastewater Type		
	Unit	Raw	Chemically Treated
Maximum Growth Rate, μ_{Hmax}	day^{-1}	9.0	9.0
Half Saturation Coefficient, K_S	mgL^{-1}	3	3
Hyrdolysis Rate for S_{H1}, k_{hs}	day^{-1}	8	8
Half Saturation Coefficient for S_{H1}, K_{XS}	mg COD/mg COD	0.02	0.02
Hyrdolysis Rate for X_{S1} , k_{hx}	day^{-1}	2.3	2.3
Half Saturation Coefficient for X_{S1}, K_{XX}	mg COD/mg COD	0.05	0.05
Endogeneous Decay Rate , b_H	day^{-1}	0.24	0.24
Heterotrophic Yield Coefficient , Y_H	mg COD/mg COD	0.65	0.65
Initial Inert COD	mg/L	2	3
Initial Biodegradable COD	mg/L	98	97
Initial Easily Biodegradable COD, S_S	mg/L	20(%20)	18(%18)
Initial Hydrolyzable COD, S_{H1}	mg/L	27(%27)	27(%27)
Initial Hydrolyzable COD, X_{S1}	mg/L	51(%51)	52(%52)
Initial Active Biomass Concentration	mg COD/L	1350	1245
Volatile Suspended Solids	mg VSS/L	1000	1000

Table 4.14: Experimental assessment of different COD fractions (mg/l)

Wastewater	C_{T1}	S_{T1}	X_{T1}	S_{S1}	S_{H1}	X_{S1}	C_{I1}
Raw	47000	35240	11760	9400	12690	23970	940
Chemically Treated	28560	25015	3545	5140	7710	14770	940

4.5 Determination of Soluble Inert COD Fraction

The soluble inert COD fraction is determined according to Orhon et al. (1994) and it was figured out as nearly zero, which means that the examined leachate sample is highly biodegradable and does not contain soluble inert organic matter.

5. CONCLUSIONS

Determination of wastewater characteristics for any kind of wastewater including leachates carries a great importance, since the degree of wastewater treatability and appropriate treatment alternatives to be applied can only be displayed in case of conduction of a detailed investigation of wastewater characteristics.

In the present study, the characteristics of organic waste leachate derived from the waste sorting and composting plant operated by GATAB was examined, in which raw, physico – chemically and biologically treated leachate samples were subjected to PSD based COD fractionation in order to be able to determine the wastewater characteristics of the leachate and to suggest appropriate treatment alternatives.

Conventional wastewater characterization studies were carried out on raw leachate samples and the organic pollution load (in terms of COD) of these samples was found to be very high. The organic pollutant concentration in the leachate samples was expected to be high due to the high organic matter content of the waste handled.

PSD based COD fractionation experiments conducted on raw leachate samples taken at different dates from the waste sorting and composting plant showed that the particle size distribution characteristics of these different samples were very similar. Likewise the raw leachate samples, physico – chemically treated leachate samples (Sample 1 and Sample 2) have also demonstrated similar particle size distribution characteristics. There were two major fractions involved in these samples. These two major fractions can be defined as the particles which have a particle size greater than 1600 nm and the particles which have a particle size lower than 2 nm.

Coagulation – flocculation with alum and lime precipitation were the implemented physico – chemical treatment methods in the scope of this study. The highest COD removal efficiencies were obtained through the application of lime precipitation at pH 11. The effect of anionic polyelectrolyte addition was also investigated and it found to be an enhancing factor in COD removal process. The removal efficiencies observed with lime precipitation at pH 11 with the employment of anionic polyelectrolyte was 43 % and 39 %, respectively for Sample 1 and Sample 2.

The PSD based COD fractionation experiments conducted on both of the samples demonstrated that, not only the particles having a particle size greater than 1600 nm can be removed through the employment of physico – chemical treatment, but also particles having a particle size lower than 2 nm can be removed. Through the application of physico – chemical treatment approximately 20 – 25 % of the particles with a particle size lower than 2 nm have been removed. The achievement of this removal rate for this sort of particles was not expected by the implementation of physico – chemical treatment. This situation may appear due to the adsorption process.

Activated sludge was employed as biological treatment and respirometric tests were conducted on acclimated biomass for the determination of biodegradability characteristics. According to the obtained COD removal efficiencies and respirometric test results the leachate samples had a high degree of biodegradability. Experiments were also conducted for the determination of soluble inert COD fraction in parallel and their results demonstrated that the soluble inert COD fraction of the leachate samples are very low, which means that the results obtained through these experiments are consistent with the results gained through respirometric tests.

In conclusion, physico – chemical treatment can be an appropriate treatment alternative for the pre – treatment of the leachate generated in the organic waste sorting and composting plant of GATAB, since the physico – chemical treatment can supply the desired level of COD removal before feeding of the leachate to the domestic wastewater treatment plants and it can serve as a supporting factor for the prevention of the possible negative effects on the process efficiency of these domestic wastewater treatment plants. On the other hand, biological treatment can also be employed in treatment of this type of leachate because the leachate has a high degree of biodegradability, but the high organic pollution load of the leachate constitutes a disadvantage in case of direct feeding of the leachate to a biological system such as aerobic activated sludge. Therefore, the application of activated sludge system would only be meaningful after appropriate pre – treatment of leachate, which can lower the organic pollution load to the suitable level for the activated sludge system or anaerobic treatment system can be implemented as a biological treatment method.

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APPENDICES

APPENDIX A.1: Experimental Results Obtained by Coagulation – Flocculation with Alum (Sample 1 and Sample 2)

APPENDIX A.2: Experimental Results Obtained by PSD after application of aeration and lime treatment (Sample 2)

APPENDIX A.3: Experimental Results Obtained by PSD after coagulation flocculation with alum (Sample 1 and Sample 2)

APPENDIX A.1:

Table A1.1: Coagulation-flocculation with alum (Sample 1)

Alum Dosage (mg L^{-1})	pH	Total COD (mg L^{-1})
250	5.66	53285
500	5.64	51430
1000	5.60	50320
1500	5.57	49945
2000	5.53	48285

Table A1.2: Aeration and coagulation-flocculation with alum (Sample 1)

Aeration Time (h)	pH	Wastewater	Total COD (mg L^{-1})
0	5.69	Raw	74525
3	5.95		64830
0	5.53	Alum – 2000 (mg L^{-1})	48285
3	5.69		44775

Table A1.3: Coagulation-flocculation with alum (Sample 2)

Alum Dosage (mg L^{-1})	pH	Total COD (mg L^{-1})
250	5.67	34575
500	5.65	33395
1000	5.61	32690
1500	5.58	32455
2000	5.54	31420

Table A.1.4: Aeration coagulation-flocculation with alum (Sample 2)

Aeration Time (h)	Ph	Wastewater	Total COD (mg L^{-1})
0	5.71	Raw	47105
3	5.96		42065
0	5.54	Alum – 2000 (mg L^{-1})	31420
3	5.69		29850

APPENDIX A.2

Table A.2.1: Particle size distribution of COD after treatment by means of aeration and lime precipitation (Sample 2)

Separation Technique	Particle size in nm	Cumulative COD (mg L^{-1})				Size Category (nm)	Differential COD (mg L^{-1})			
		Aeration	Lime Precipitation				Aeration	Lime Precipitation		
			pH = 7	pH = 9	pH = 11			pH = 7	pH = 9	pH = 11
Total		42065	30540	29780	28560					
Filtration										
AP40 filter	1600	30705	27180	26500	25415	>1600	11360	3360	3280	3145
HV filter	450	30210	26750	26085	25015	450-1600	495	430	415	400
GV filter	220	29675	26385	25730	24670	220-450	535	365	355	345
Ultrafiltration										
100 kDa	13	29180	26040	25390	24345	13-220	495	345	340	325
30 kDa	8	28705	25675	25035	24005	8-13	475	365	355	340
10 kDa	5	28465	25490	24855	23835	5-8	240	185	180	170
3 kDa	3	28125	25245	24615	23605	3-5	340	245	240	230
1 kDa	2	27125	24490	23880	22900	2-3	1000	755	735	705
						<2	27125	24490	23880	22900

Table A.2.2: Fractions of the total removals observed in each size interval with aeration and lime precipitation (Sample 2)

Process	Removal efficiencies (%)									Total (%)
	>1600	450-1600	220-450	13-220	8-13	5-8	3-5	2-3	<2	
Aeration (t = 3 h)	0	0	0	0.1	0.2	0.4	1.1	2.6	6.3	10.7
Lime Precipitation (pH = 7)	17.0	0.1	0.4	0.4	0.4	0.6	1.3	3.1	11.9	35.2
Lime Precipitation (pH = 9)	17.2	0.2	0.4	0.4	0.4	0.6	1.3	3.2	13.2	36.8
Lime Precipitation (pH = 11)	17.5	0.2	0.4	0.4	0.5	0.6	1.3	3.2	15.3	39.4

Table A. 2.3: Individual removal efficiencies observed in each size interval with aeration and lime precipitation (Sample 2)

Process	Removal efficiencies (%)									Total (%)
	>1600	450-1600	220-450	13-220	8-13	5-8	3-5	2-3	<2	
Aeration (t = 3 h)	0	1.0	2.7	6.6	15.2	46.7	59.8	55.0	9.8	10.7
Lime Precipitation (pH = 7)	70.4	14.0	33.6	34.9	34.8	58.9	71.0	66.0	18.6	35.2
Lime Precipitation (pH = 9)	71.1	17.0	35.5	35.8	36.6	60.0	71.6	66.9	20.6	36.8
Lime Precipitation (pH = 11)	72.3	20.0	37.3	38.7	39.3	62.2	72.8	68.2	23.9	39.4

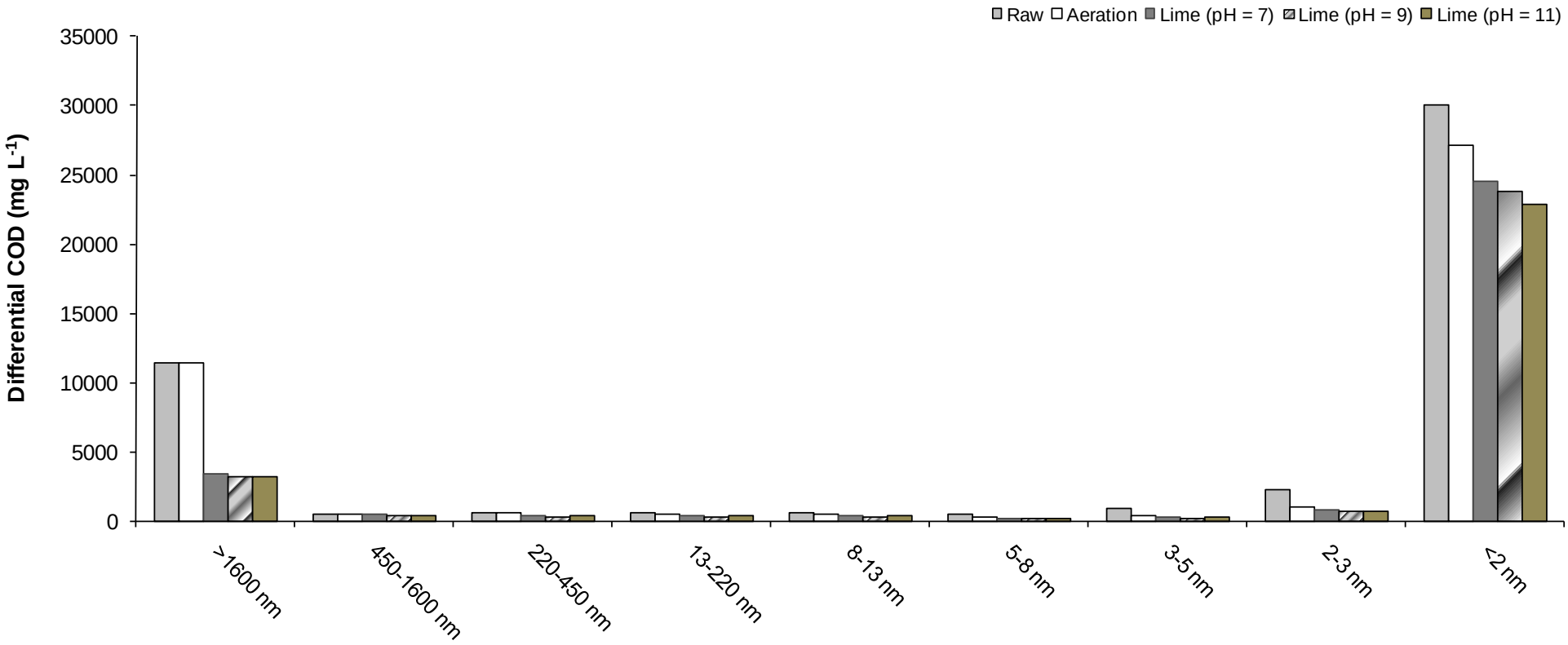

Figure A.2.1: Particle size distribution of COD after treatment by means of aeration and lime precipitation (Sample 2)

APPENDIX A.3

Table A.3.1: Particle size distribution of COD after treatment by means of aeration and alum coagulation (Sample 1)

Separation Technique	Particle size in nm	Cumulative COD (mg L^{-1})		Size Category (nm)	Differential COD (mg L^{-1})	
		Alum Coagulation (2000 mg L^{-1})	Aeration		Alum Coagulation (2000 mg L^{-1})	Aeration
Total		48285	44775			
Filtration						
AP40 filter	1600	42970	39465	>1600	5315	5310
HV filter	450	42295	38800	450-1600	675	665
GV filter	220	41715	38240	220-450	580	560
Ultrafiltration						
100 kDa	13	41165	37735	13-220	550	505
30 kDa	8	40580	37250	8-13	585	485
10 kDa	5	40290	37055	5-8	290	195
3 kDa	3	39905	36770	3-5	385	285
1 kDa	2	38715	35815	2-3	1190	955
				<2	38715	35815

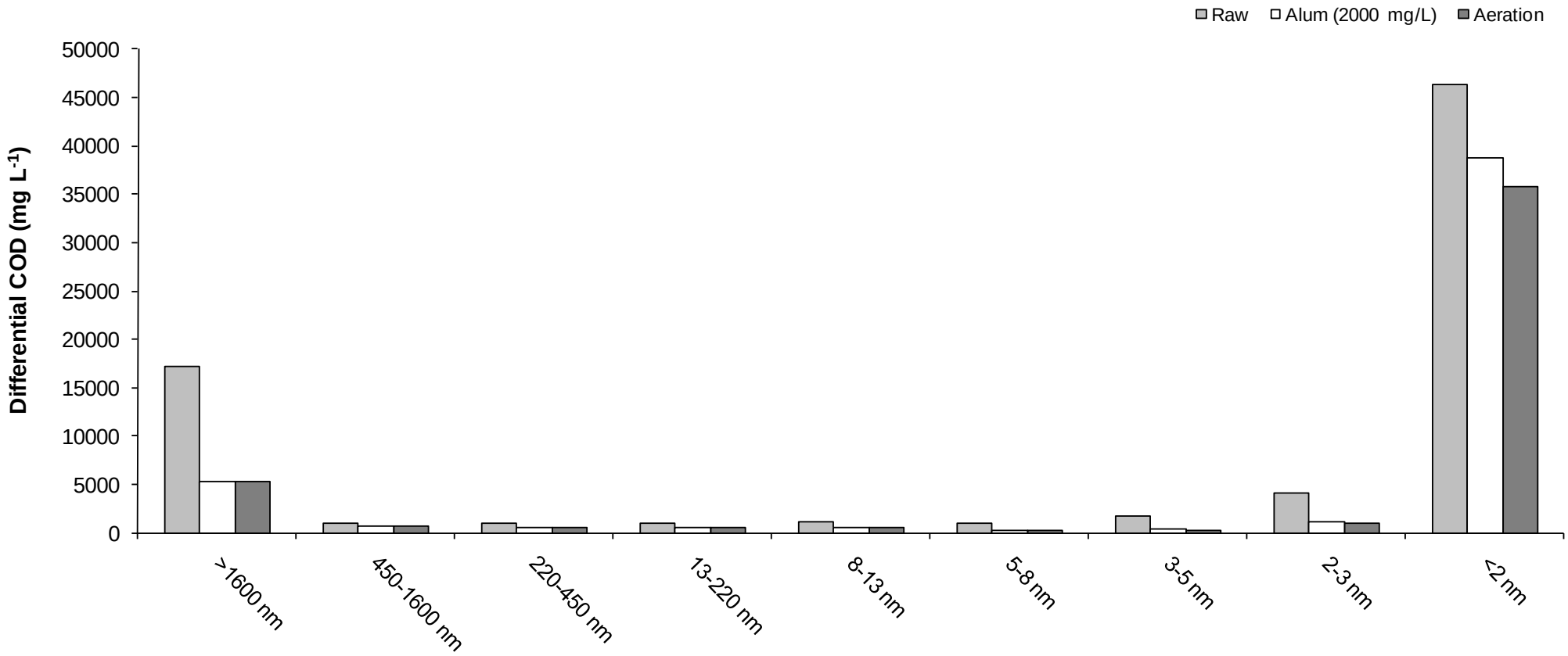

Figure A.3.1: Particle size distribution of COD after treatment by means of alum coagulation and aeration (Sample 1)

Table A.3.2: Fractions of the total removals observed in each size interval with alum coagulation and aeration (Sample 1)

Process	Removal efficiencies (%)									Total (%)
	>1600	450-1600	220-450	13-220	8-13	5-8	3-5	2-3	<2	
Alum Coagulation (2000 mg L^{-1})	16.0	0.4	0.6	0.6	0.7	1.0	1.8	3.9	10.3	35.2
Aeration (t = 3 h)	16.0	0.4	0.6	0.7	0.8	1.1	2.0	4.2	14.2	39.9

Table A.3.3: Individual removal efficiencies observed in each size interval with alum coagulation and aeration (Sample 1)

Process	Removal efficiencies (%)									Total (%)
	>1600	450-1600	220-450	13-220	8-13	5-8	3-5	2-3	<2	
Alum Coagulation (2000 mg L^{-1})	69.2	28.6	43.4	45.8	46.8	71.3	77.9	70.8	16.5	35.2
Aeration (t = 3 h)	69.2	29.6	45.4	50.2	55.9	80.7	83.6	76.6	22.8	39.9

Table A.3.4: Particle size distribution of COD after treatment by means of alum coagulation and aeration (Sample 2)

Separation Technique	Particle size in nm	Cumulative COD (mg L^{-1})		Size Category (nm)	Differential COD (mg L^{-1})	
		Alum Coagulation (2000 mg L^{-1})	Aeration		Alum Coagulation (2000 mg L^{-1})	Aeration
Total		31420	29850			
Filtration						
AP40 filter	1600	27960	26390	>1600	3460	3460
HV filter	450	27520	25955	450-1600	440	435
GV filter	220	27145	25590	220-450	375	365
Ultrafiltration						
100 kDa	13	26790	25255	13-220	355	335
30 kDa	8	26415	24925	8-13	375	330
10 kDa	5	26225	24795	5-8	190	130
3 kDa	3	25970	24595	3-5	255	200
1 kDa	2	25195	23900	2-3	775	695
				<2	25195	23900

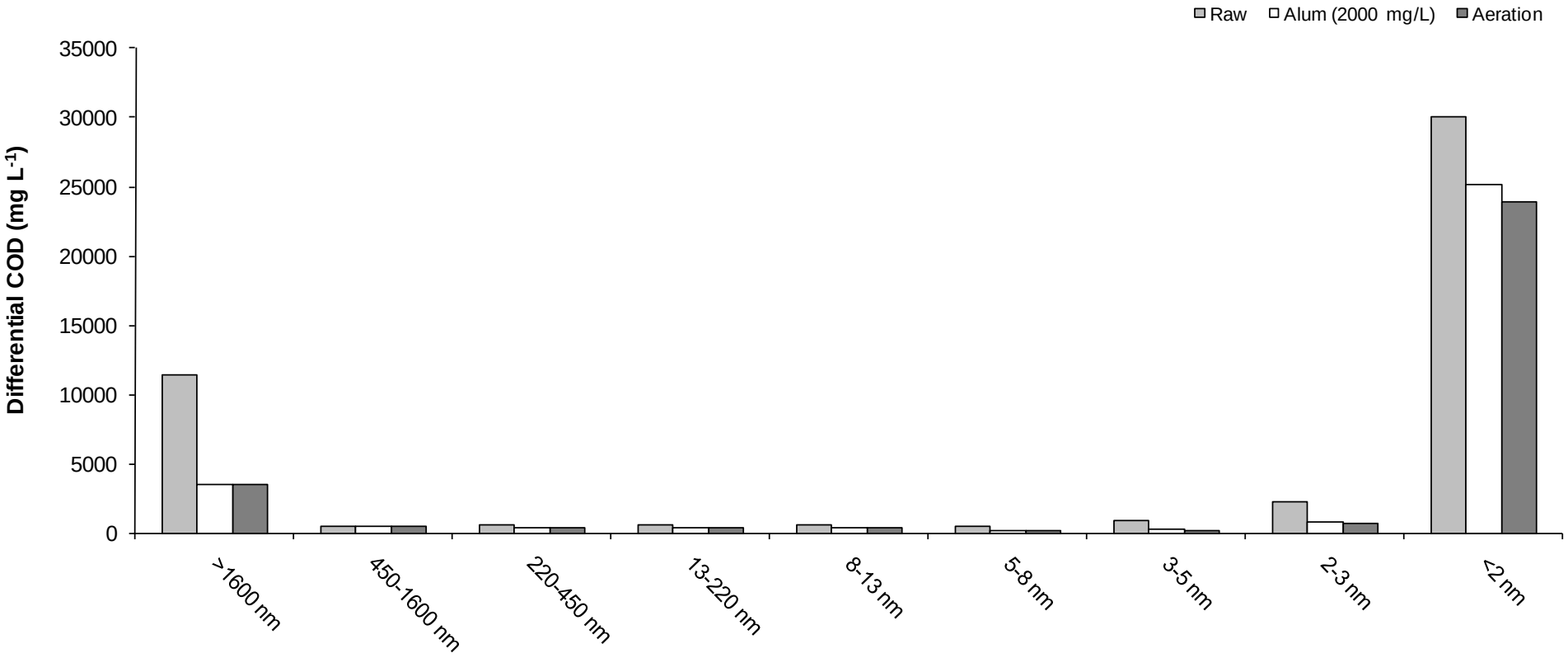

Figure A.3.2: Particle size distribution of COD after treatment by means of aeration and alum coagulation (Sample 2)

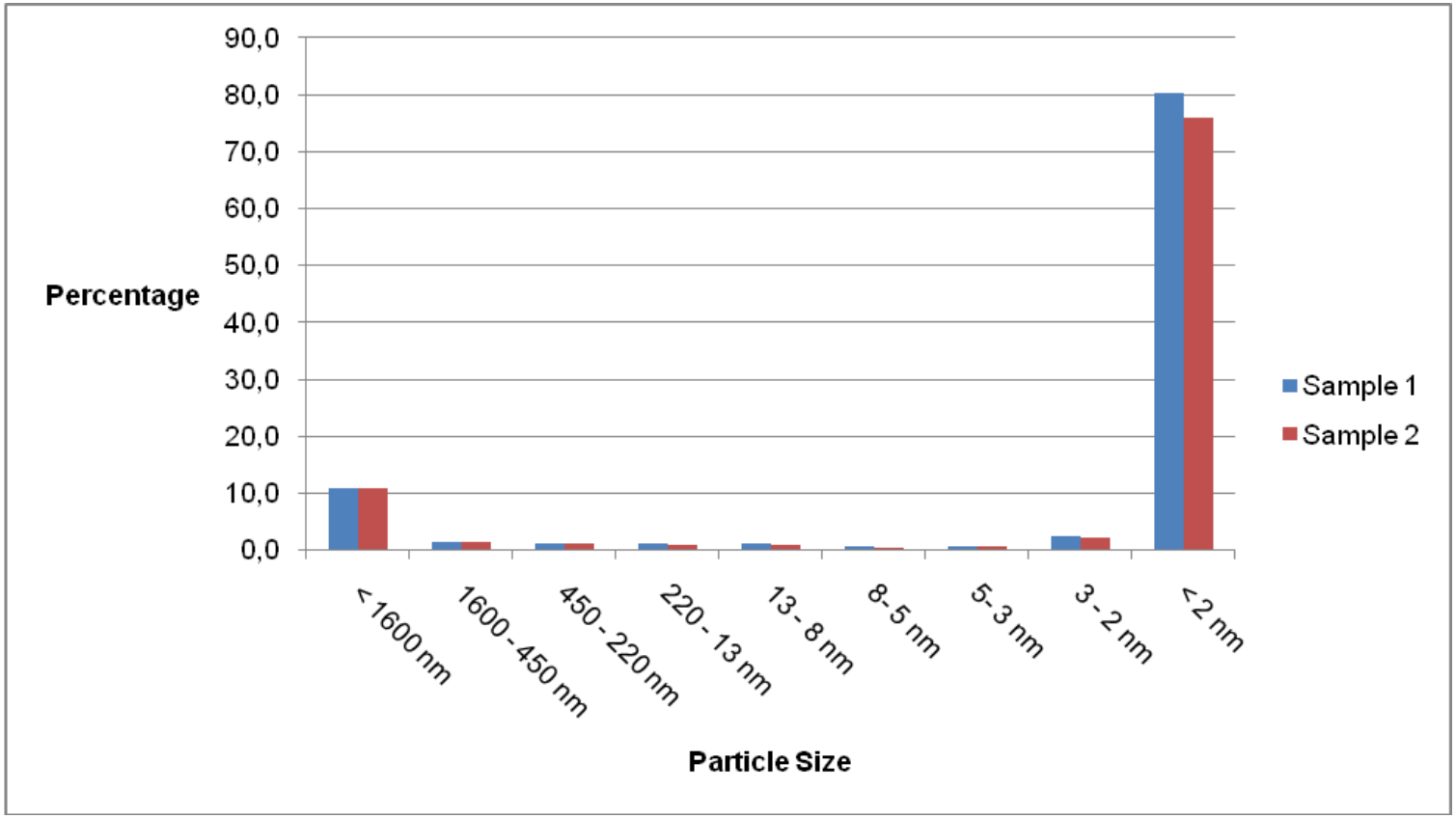

Figure A.3.3: Comparison of the particle size distribution after coagulation flocculation with alum

Table A.3.5: Fractions of the total removals observed in each size interval with aeration and alum coagulation (Sample 2)

Process	Removal efficiencies (%)									Total (%)
	>1600	450-1600	220-450	13-220	8-13	5-8	3-5	2-3	<2	
Alum Coagulation (2000 mg L^{-1})	16.8	0.1	0.4	0.4	0.4	0.6	1.3	3.1	10.4	33.3
Aeration (t = 3 h)	16.8	0.1	0.4	0.4	0.5	0.7	1.4	3.2	13.1	36.6

Table A.3.6: Individual removal efficiencies observed in each size interval with aeration and alum coagulation (Sample 2)

Process	Removal efficiencies (%)									Total (%)
	>1600	450-1600	220-450	13-220	8-13	5-8	3-5	2-3	<2	
Alum Coagulation (2000 mg L^{-1})	69.6	12.0	31.8	33.0	33.0	57.8	69.8	65.1	16.3	33.3
Aeration (t = 3 h)	69.6	13.0	33.6	36.8	41.1	71.1	76.3	68.7	20.6	36.6

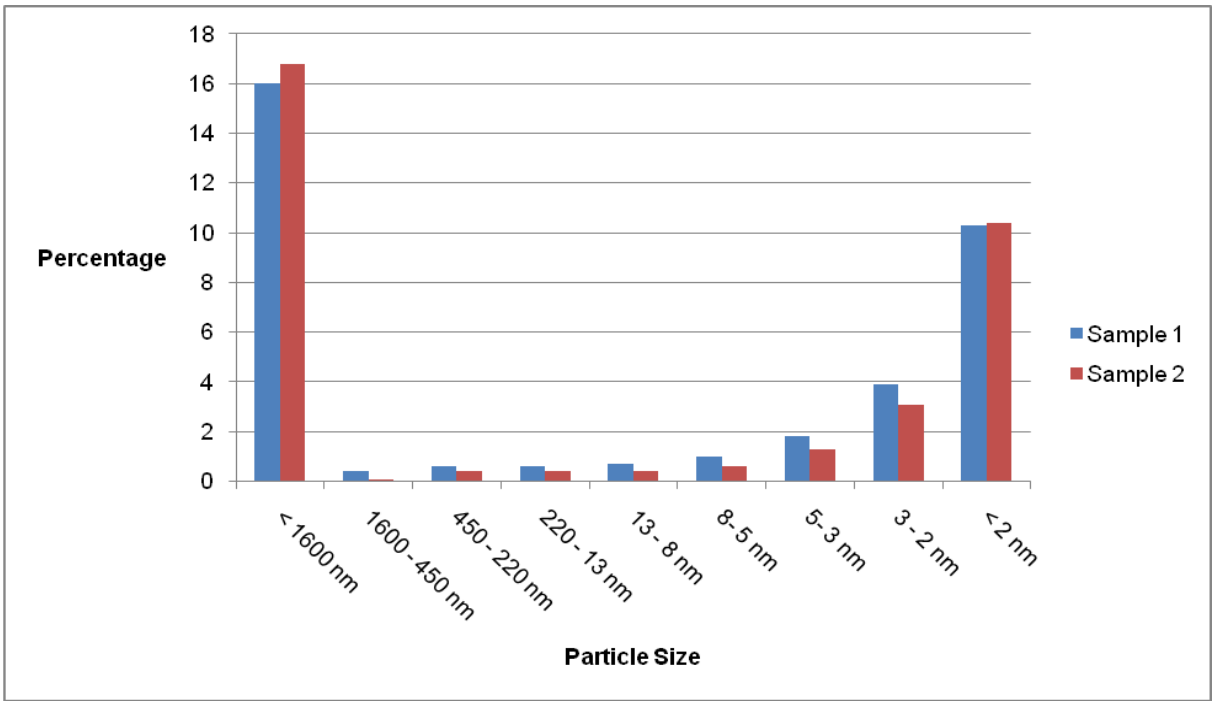

Figure A.3.4: Fractions of the total removals observed in each size interval with aeration and alum coagulation

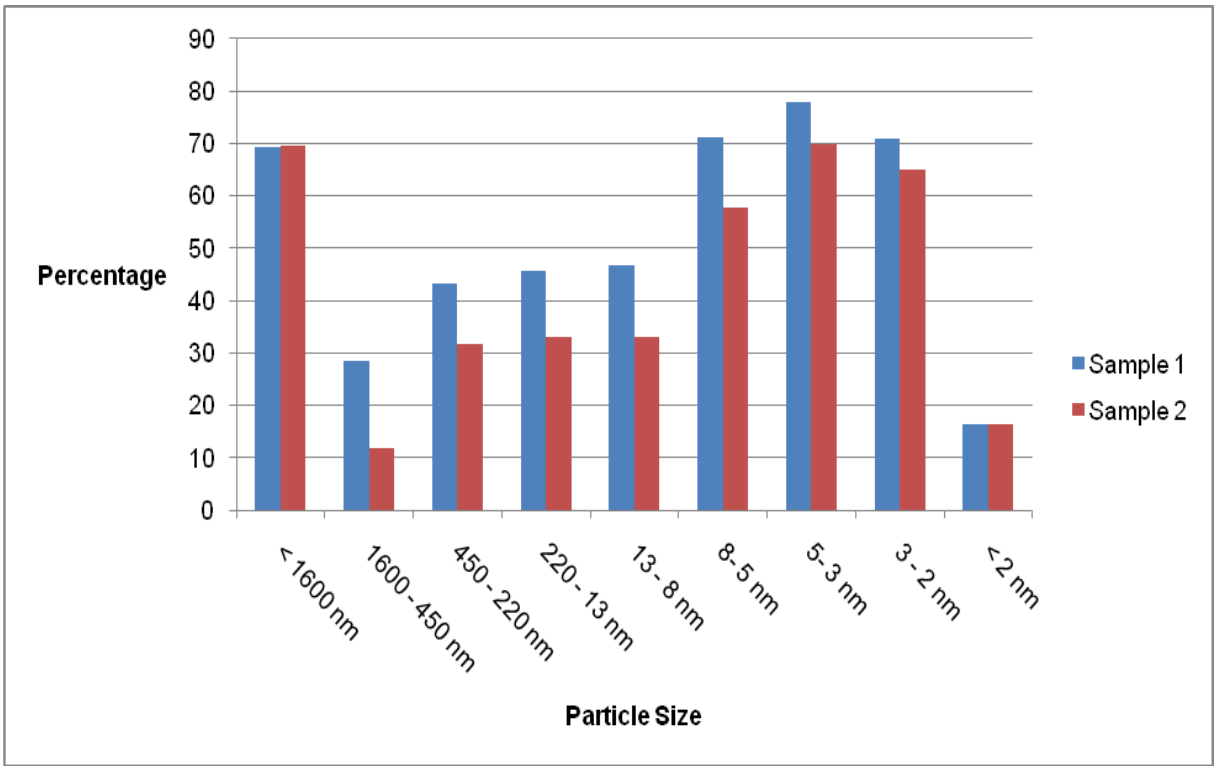

Figure A.3.5: Individual removal efficiencies observed in each size interval with aeration and alum coagulation

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