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Stripping/flocculation/membrane bioreactor/reverse osmosis treatment of municipal landfill leachate

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ABSTRACT

This study presents a configuration for the complete treatment of landfill leachate with high organic and ammonium concentrations. Ammonia stripping is performed to overcome the ammonia toxicity to aerobic microorganisms. By coagulation–flocculation process, COD and suspended solids (SS) were removed 36 and 46%, respectively. After pretreatment, an aerobic/anoxic membrane bioreactor (Aer/An MBR) accomplished the COD and total inorganic nitrogen (total-N_i) removals above 90 and 92%, respectively, at SRT of 30 days. Concentrations of COD and total-N_i (not considering organic nitrogen) in the Aer/An MBR effluent decreased to 450 and 40 mg/l, respectively, by significant organic oxidation and nitrification/denitrification processes. As an advanced treatment for the leachate, the reverse osmosis (RO) was applied to the collected Aer/An MBR effluents. Reverse osmosis provided high quality effluent by reducing the effluent COD from MBR to less than 4.0 mg/l at SRT of 30 days.

1. Introduction

Leachate is a high-strength wastewater formed as a result of percolation of rain-water and moisture through waste in landfills. During the formation of leachate, organic and inorganic compounds are transferred from waste to the liquid medium and pose a hazard to the receiving water bodies. Production of landfill leachate begins with introducing moistured waste into disposal area and continues for several decades following the landfill closure. Leachate contains high organic matter and ammonium nitrogen and its composition depends upon the landfill age, the quality and quantity of waste, biological and chemical processes that took place during disposal, rainfall density, and water percolation rate through the waste in the landfill. Depending upon what was placed in the landfill, leachate may contain many types of contaminants, and if not removed by treatment, these contaminants may be toxic to life or simply alter the ecology of receiving streams. Leachate should be treated before reaching surface water or ground water bodies, because it can accelerate algae growth due to its high nutrient content, deplete dissolved oxygen in the streams, and cause toxic effects in the surrounding water life. Since the composition of a leachate consists of a wide range of contaminants, it cannot be easily treated by conventional methods. Therefore, a number of scientists around the world have intensively focused on the combination of biological and physico-chemical treatment systems for effective leachate treatment.

The physical and chemical treatment processes include chemical oxidation, coagulation–flocculation, chemical precipitation, activated carbon absorption, ozonation, and pressure-driven membrane processes. Ozonation and reverse osmosis could be considered following an effective biological treatment to reach a better effluent quality. In general, physico-chemical units are not enough to remove organics from leachate. The disadvantage of treating leachate with coagulation and precipitation process is that excess sludge is produced after the treatment application, which is difficult to manage. On the other hand, biological treatment alone does not achieve high removal efficiency due to inhibition effect of some contaminants such as ammonium and heavy metals. For example, as physico-chemical treatment ensures the removal of metals and partially ammonium, biological treatment is necessary for the stabilization and degradation of organic matter, and also for the nutrient removal.

Among advanced biological treatment processes, membrane bioreactor (MBR) is the most important process, which consists of a

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membrane module and a bioreactor containing generally activated sludge with high mixed liquor suspended solids (MLSS) of greater than 10,000 mg/l. The application of membrane bioreactor as a main treatment after physico-chemical application seems to be promising due to the expected high effluent quality. However, ozonation and reverse osmosis could be used as a post-treatment following biological treatment to remove the residual organic matters.

This study presents an effective treatment configuration for landfill leachate. The objectives of this study are to investigate: (1) the performance of coagulation as a pretreatment for leachate, (2) the potential of ammonium stripping for ammonium removal under different conditions, (3) the performance of membrane bioreactor placed after the coagulation and ammonium stripping, (4) the effect of solid retention time on the aerobic/anoxic MBR (Aer/An MBR) performance, (5) the relationship between viability and inert COD in Aer/An MBR, and (6) the final effluent quality if reverse osmosis is used as an optional post-treatment for the removal of residual organic matter after aerobic/anoxic MBR.

2. Mini review on treatment trials

Unfortunately, most of the landfills in the world do not have an appropriate leachate treatment system. Although some treatment options are available, treatment alternatives for leachate are very limited because they are not usually designed by considering the leachate characteristics [1–2]. Hence, it is necessary to develop leachate treatment systems with reduced footprint and effective efficiency. High ammonium and phosphorus deficiency in young leachate constrain the biological treatment applications such as nitrification–denitrification processes following phosphorus addition [3–6].

Some researchers received nitrification efficiency higher than 95% for leachates containing high ammonium by using some expensive biological methods [7–10]. It has been realized that biodegredation mechanism depends upon the age and origin of the landfill, and the type and operation of the treatment system [7,9,11–15]. In general, almost all treatment schemes used for landfill leachate consist of a combination of physico-chemical and biological treatment units [5]. In order to asses the performance of biological treatment; COD efficiencies have generally been evaluated according to the intensity of leachate, number of treatment steps, hydraulic retention time (HRT), and organic loading rate. Alvarez-Vazquez et al. [16] estimated that the percentages of treatment systems used for leachate treatment were 72% biological processes, 11% flocculation/coagulation, 5% filtration, 4% air stripping, 4% chemical oxidation, 2% activated carbon, and 2% ion exchange.

2.1. Biological treatment for landfill leachate

Biological processes are very effective when applied to young leachates, but their efficiency decreases with an increased leachate age [17–18]. In particular, conventional biological systems cannot significantly treat old leachates, which contain contaminants resistant to biodegradation. Furthermore, old leachates have inhibition effect on activated sludge due to their high ammonium concentrations [19]. However, the phosphorus deficiency hampers the production of microorganisms and consequently the treatment performance [20]. It is found that the most studied aerobic processes for leachate treatment are aerobic lagoons which account for 21% of biological treatment systems available around the world. Other biological systems are; 18% UASB, 17% activated sludge, and 8% MBR. Recently, many researchers have been intensively focusing on the treatment of leachate by using membrane bioreactor (MBR) due to the recent advances in membrane technology. MBR seems to be a good alternative for all wastewaters with high organic and nutrient loadings, as well as high suspended solid content. In addition, MBR has also a significant effect on nitrification because high SRT promotes the growth of nitrifying bacteria. Some researchers demonstrated that both nitrification and denitrification processes could occur in a single bioreactor when an intermittent aeration is adapted to the system [21–22]. A study by Visvanathan et al. [23] showed 60–80% COD removal, 97–99% BOD removal, and 60–80% ammonium removal in a thermophilic MBR.

2.2. Physico-chemical treatment for landfill leachate

Various methods of physico-chemical treatment are used to treat wastewaters containing toxic contaminants such as heavy metals, non-biodegradable organics and ammonium. These physico-chemical treatment methods are selected based on wastewater characterization, investment and operating cost, and some local regulations. Up to now, many researchers have used a number of physico-chemical methods to treat leachate. These processes include chemical oxidation [19,24–26], coagulation and precipitation [17,27–31], electro-coagulation [32–33], adsorption [34], photooxidation [35–38], ammonium stripping [39], ozonation [40–43], and membrane processes [44–45].

Nanofiltration (NF) and reverse osmosis (RO) are used alone to purify the water microfiltration (MF) and ultrafiltration (UF) and are generally coupled with a biological process. Bodzek et al. [46] applied RO unit directly to leachate treated in activated sludge system and faced the recovery reduction significantly due to the excess fouling of membranes. Chan et al. [47] used the vibrating share mechanism to reduce the fouling potential in the RO and consequently increased the running time of membrane. The system accomplished 97% removal of non-biodegradable matter and 99% removal of ammonium.

2.3. Combination of biological and physico-chemical processes for landfill leachate

Physico-chemical treatment units are placed either as pretreatment to reduce the loading rate for biological processes or as post-treatment to reach a high quality discharge standard. For example, Bae et al. [48] studied the COD and ammonia removal by using Fenton process following the conventional activated sludge system. Haapea et al. [49] applied the processes of ozonation and ozonation/hydrogen peroxide before the biological process for the treatment of landfill leachate. Activated carbon [50] and ammonia stripping/coagulation [51] have been commonly used as pretreatment of sequencing batch reactor (SBR). On the other hand, some researchers combined the aerobic and anaerobic processes [3,52–56]. Bohdziewicz and Kwarciak [57] showed an effective removal of leachate contaminants by using reverse osmosis following upflow anaerobic sludge blanket (UASB).

3. Materials and methods

3.1. Experimental plan

Experimental study was conducted at various steps (Fig. 1), including leachate characterization, pretreatment (coagulation and ammonia stripping), main treatment (aerobic/anoxic MBR), and post-treatment (reverse osmosis). Soil and sludge samples taken from a landfill area and a municipal activated sludge treatment plant were placed into a 5-l batch reactor and the reactor was operated by continuous feeding of diluted leachate at a SRT of 5 days for 45 days. Then, the Aer/An MBR was inoculated by activated sludge obtained from the batch reactor.

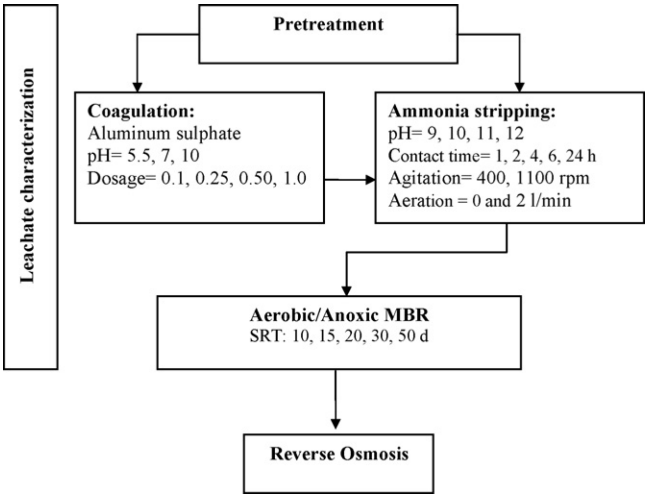


Fig. 1. Running plan of study.

3.2. *Leachate characterization*

The leachate used in this study was supplied from the landfill area in City of Diyarbakir, Turkey. The properties of leachate used in this study are given in Table 1. Inert COD indicated that the leachate used was very young because the ratio of inert COD to total COD varied over a range of 3–10%. The BOD/COD ratio also justified the idea that the leachate was very young. Ammonium concentration varied over a range of 1100–2150 mg/l. Nitrate in leachate could be considered as a partial nitrification resulted from leachate flow in non-covered disposal area.

3.3. *Ammonia stripping*

The ammonia stripping experiments were performed in four reactors with different pH values. In the beginning, pH values were adjusted to be 9.0, 10.0, 11.0, and 12.0, respectively, in reactors 1 through 4. First, the reactors were mixed with 400 rpm by using a magnetic stirrer. Secondly, they were either mixed with 400 rpm or aerated with an air flow rate of 2 l/min. Then, mixing rate was increased to 1100 rpm without aeration. Finally, aeration with an air flow rate of 2 l/min was carried out at a mixing rate of 1100 rpm. 0.1 ml of liquid was withdrawn from the reactors to measure ammonium concentrations at any time.

Table 1
Properties of leachate used in the study.

Parameter	Concentration, mg/l except for pH and ratios
pH	6.45–7.50
BOD_5	5700–10,800
COD	8500–19,200
BOD/COD	40–70%
NO_3^--N	5–47
NO_2^--N	0.16–3
NH_4^+-N	1100–2150
Total phosphorus	17–24
Ortho-phosphate	8–18
Inert COD/total COD	3–10%
Cu^{+2}	2–3.5
Mn^{+2}	35–42
Fe^{+2}	600–720
Cd^{+2}	ND
Co^{+2}	1–1.6
Cr^{+6}	ND
Zn^{+2}	10–12

ND = Not determined.

Table 2
Properties of membrane used in Aer/An MBR.

Property	Unit	Value
Company	–	Zena membranes
Material	–	Polypropylene
Type	–	Converted to hydrophilic
Pore size	mm	0.1
Effective fiber length	cm	10
Fiber outer diameter	mm	310
Total surface area	cm^2	390
Fiber number	–	400

3.4. *Coagulation/flocculation*

Coagulation experiments were performed at Al^{+3} dosages of 0.10, 0.25, 0.50, and 1.0 g/l at three pH values (5.5, 7.0, and 10.0). Optimal dosage and pH value were determined according to COD and SS removals. Experiments were carried out at a rapid mixing of 1000 rpm (30 s), at a slow mixing of 100 rpm (90 min), and at a gravity settling (30 min).

3.5. *Aerobic/anoxic membrane bioreactor (Aer/An MBR)*

The experimental set-up consisted of a membrane unit and a bioreactor. The bioreactor, Aer/An MBR, was either aerobic, provided with oxygen to allow aerobic nitrification and organic COD oxidation, or anoxic, in the absence of oxygen to allow denitrification. The membrane was immersed into a bioreactor having total volume of 2.0 l and effective volume of 1.5 l. The membrane manufactured from polypropylene material had an average pore size of 0.1 μm and total surface area of 390 cm^2. Hydrophobic membranes supplied from Zena Membranes Company (The Czech Republic) were converted to hydrophilic by using the method of alcohol/water in the laboratory. The properties of membrane used in the bioreactor are tabulated in Table 2. The influent of Aer/An MBR was driven by a peristaltic pump. The filtrate was suctioned by another peristaltic pump and collected in 5 l covered storage tank.

Leachate was pumped into Aer/An MBR following pretreatment (coagulation and ammonia stripping) for 150 days. The phosphorus deficiency was overcome by adding an external phosphorus source (H_2PO_4). The Aer/An MBR was operated at solid retention times (SRT) of 10, 15, 20, 30, and 50 days. The conditions in Aer/An MBR were presented in Table 3. Aeration was kept at 45 min on and 15 min off by means of a time role.

3.6. *Reverse osmosis*

Reverse osmosis study was carried out by using a pilot scale apparatus which is reported in detail by Ipek [58]. The filter used in the experimental work, manufactured by Osmonics, has extended blown microfiber technology to meet the requirements for a pure polypropylene deep filter with an exceptional dirt holding capability. This translates into a longer life on fewer changes than existing string-wound or resin-bonded filters. The Desal-11, a thin-film membrane, was used throughout the work. This membrane (AG4021FF) manufactured by Desal (Osmonics) is characterized by high flux and excellent sodium chloride rejection. The properties and operating parameters of the membrane are given in Table 4. Granular activated carbon (AquaSorb 1000) was manufactured by steam activation from selected grades of bituminous coal. The perfect balance between adsorption and transport pores provides optimal performance in a wide range of water treatment applications. The product is a high-density adsorbent and provides maximum volume activity. The total pore volume and apparent density of the adsorbent, whose surface area is 950 m^2/cm, are 0.88 cm^3/g and 500 kg/m^3, respectively. The bed height and inner

Table 3
Operating conditions in Aer/An MBR.

Stage	Operating time (d)	HRT (h)	SRT (d)	ΔP (atm)	DO (mg/l)		Phase time for aeration (min)	
					On	Off	On	Off
I	1–30	3.6–7.2	30	0.4–0.7	1.5–3.0	<0.3	45	15
II	31–62	5.1–6.9	20	0.6–0.65	1.5–3.0	<0.3	45	15
III	63–97	6.8–16.4	10	0.65–0.75	1.5–3.0	<0.3	45	15
IV	98–125	10.0–14.4	15	0.65	1.5–3.0	<0.3	45	15
V	126–150	12.9–15.0	50	0.65	1.5–3.0	<0.3	45	15

Table 4
Membrane properties and operating parameters in RO.

Model	AG4021FF
Cross reference	BW30-4021
GPD, m/d	1.050 (3.97)
NaCl rejection, % (avg/min)	99.4/99.0
Active area, m^2	3.72
Membrane	Thin-film (TFM)
Typical operating pressure, kPa	1.379
Maximum pressure, kPa	2.758
Maximum temperature, °C	50
Recommended pH:	
Optimum rejection	6.5–7.5
Operating range	4.0–11.0
Cleaning range	2.0–11.5

diameter of the pretreatment units are 50 and 6.5 cm, respectively. The bed dimensions of the membrane are 63.5 cm in height and 12.5 cm in outside diameter, and the general dimensions of the entire system are 45 cm × 45 cm × 80 cm.

Leachate treated in Aer/An MBR following pretreatment was stored for one month at 4 °C to provide sufficient amount of water to be used in RO system. The system was operated at a pressure of 1100 kPa.

3.7. Analytical methods

Aer/An MBR performance was monitored by analyzing influent and effluent samples. All samples were immediately filtered through a 0.2-μm membrane filter (Pall Corp., Ann Arbor, ML). The nitrogen species and COD were analyzed by Merck kit (Nova 60 Merck). Total inorganic nitrogen (total-N_i) was calculated as the sum of NO_3^--N, NO_2^--N and NH_4^+-N. Since all samples were filtered, the analytical results represent only soluble concentration such as soluble COD (sCOD). Non-biodegradable COD was analyzed according to the method reported by Eremektar et al. [59]. Heavy metals were determined by using Atomic Absorption Spectrophotometry (UNICAM 929 model). The mixed liquor suspended solid (MLSS) and mixed liquor volatile suspended solid (MLVSS) in the MBR were determined in accordance with Standard Methods for the Examination of Water and Wastewater [60]. Dissolved oxygen and pH were measured by a multi-meter (Hach HQ40D).

4. Results and discussion

4.1. Pretreatment of leachate

4.1.1. Coagulation and flocculation

Coagulation–flocculation is a relatively simple technique that may be employed for the treatment of older or stabilized landfill leachate. However, this method may result in only moderate removals of COD (or TOC). Coagulation–flocculation has thus been proposed mainly as a pretreatment method for fresh leachate, or as a post-treatment technique for partially stabilized leachate [28].

In this study, the leachate pH varied in the range of 6.45–7.50. During the coagulation experiments, COD and SS of leachate used were 11,400 and 5200 mg/l, respectively, while pH was 7.24. Experiments were conducted at three pH adjustments (5.5, 7 and 10) for different dosages of aluminum sulphate (0.1, 0.25, 0.5, and 1.0 g Al^{+3}/l). Although COD removal reached to 52% at pH of 10.0 and at 1.0 g Al^{+3}/l, optimum conditions for coagulation–flocculation process were satisfied at pH 7.0 and at 0.25 g Al^{+3}/l of alum dosage. Fig. 2 shows that COD and SS removals were 36 and 46%, respectively, thus reducing the COD removal from 11,000 to 7300 mg/l and SS from 5200 to 2800 mg/l. These removal rates were achieved at pH of 7.0 and Al^{+3} dosage of 0.25 g/l. Maranon et al. [31] reported that, while the high turbidity removal was obtained in coagulation and flocculation, no clear differences were observed in COD removal for different dosages, ranging between 11.5% for 0.3 g Al^{+3}/l and 20% for 0.5 g Al^{+3}/l at pH of 6.0.

4.1.2. Ammonia stripping

Ammonia stripping involves passage of large quantities of air over the exposed surface of leachate, thus causing the partial pressure of the ammonia gas within the water to drive the ammonia

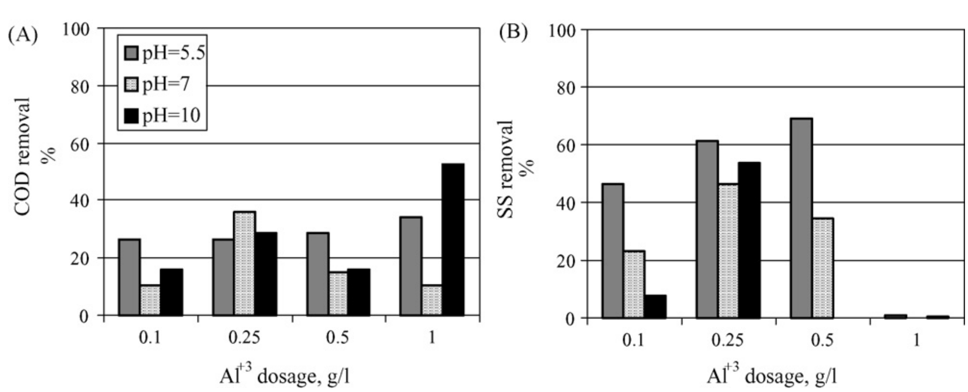


Fig. 2. Coagulation with Al^{+3} at different pH and dosages.

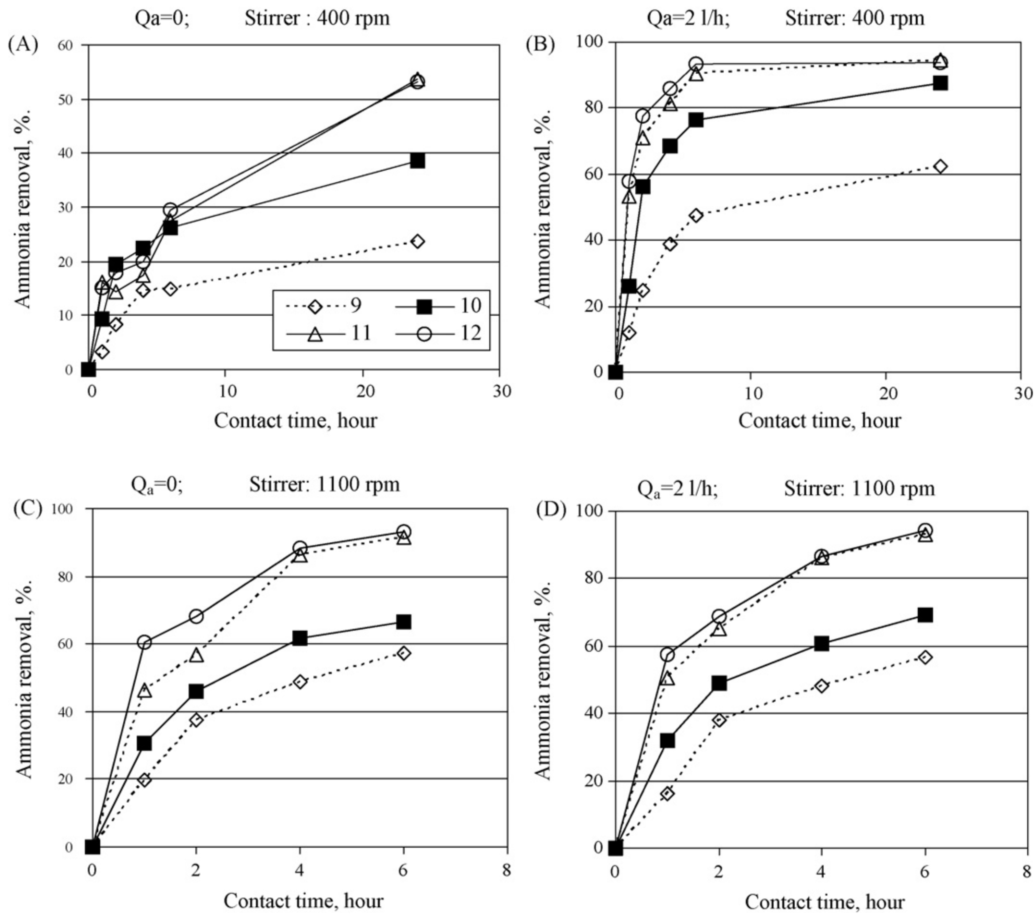


Fig. 3. Ammonia stripping results at different conditions.

from the liquid to the gas phase. The process is further subject to careful pH control and involves the mass transfer of volatile contaminants from water to air. Free ammonia begins to form when the pH is above 7. Over 85% of ammonia present may be liberated as gas through agitation in the presence of air at pH greater than 11 [61]. Ammonium hydroxide (NH_4OH) is formed as an intermediate product in the reaction at pH between 10 and 11. The bubbling of air through ammonium hydroxide solutions results in the freeing of ammonia gas. Solubility increases at low ambient temperatures since ammonia is highly soluble in water. Cheung et al. [39] investigated air flow rate and pH as critical parameters for the optimization of ammonia stripping in a stirred tank. After one day, they achieved a significant ammonia removal between 86 and 93% at air flow rate of 5 ml/min and pH greater than 11. In this study, the ammonia removal was 30% at contact times of 1–6 h, at agitation of 400 rpm and, in the absence of air flow. The removal efficiencies were very close to each other at pH 11 and 12 (Fig. 3A). Ammonia removal increased clearly and reached to 76.4% at pH 10, 90.6% at pH 11, and 93.2% at pH 12 when the air flow rate was kept at 2 l/min, agitation at 400 rpm and contact time at 6 h (Fig. 3B). Since NH_4OH formed at high pH values, it was converted to free ammonia by only giving air through the leachate, and the aeration affected significantly the performance of ammonia stripping. When the agitation rate was increased to 1100 rpm in the absence of air flow, ammonia removal reached to 66.4% at pH 10, 91.7% at pH 11, and 93.3% at pH 12 at contact time of 6 h (Fig. 3C). When the air flow rate was kept at 2 l/min at the same agitation rate, the ammonia removal increased slightly (Fig. 3D). Hence, pretreatment experiments of leachate were carried out in the absence of aeration, at pH 10 and agitation speed of 1100 rpm.

4.2. Biological treatment of leachate by aerobic/anoxic MBR

Visvanathan et al. [23] studied the treatment of landfill leachate at different BOD/COD ratios in a thermophilic MBR. They reported that the COD removal increased as the ammonia removal decreased with an increase in BOD/COD ratio. Moreover, they showed that the system was not in favor of wastewaters with high nitrogen content. Hence, in this study, the pretreatment units (coagulation and ammonia stripping) were applied to raw leachate before the membrane bioreactor. Leachate was fed into a membrane bioreactor after a pretreatment application described in Table 5.

4.2.1. Effect of SRT on performance in Aer/An MBR

Many researchers reported that the membrane bioreactors are effective treatment alternatives for the young leachates [62–64]. Leachate used during this study was young because it contained readily biodegradable organic matter. MBR was operated at five SRTs and fed with leachate pretreated by coagulation and ammonia stripping. Fig. 4 shows how the performance of MBR for COD removal is affected from different SRTs.

Table 5
Conditions in pretreatment for landfill leachate.

Coagulation		Ammonia stripping	
pH	6.45–7.50	pH	10
Rapid mixing	1000 rpm at 30 s	Contact time	6 h
Slow mixing	100 rpm at 90 min	Agitation rate	1100 rpm
Precipitation	30 min	Aeration	Off
Al^{+3} dosage	0.25 g/l	10N NaOH dosage	18 ml/l
		1N H_2SO_4 dosage	118 ml/l

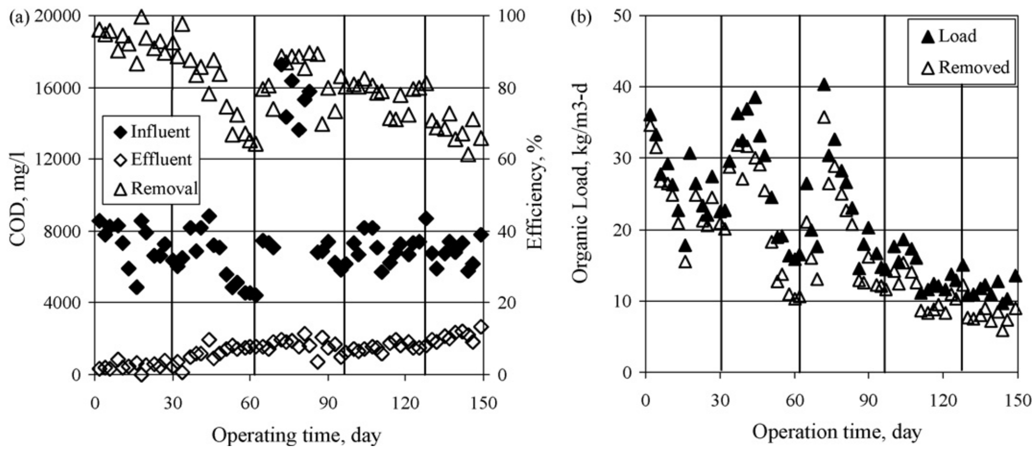


Fig. 4. Biological oxidation in Aer/An MBR along operating time; (A) changes in COD, (B) specific organic loading and removed organic load.

The MBR accomplished the organic oxidation above 90% when the SRT was kept at 30 days. The COD value in the effluent was 450 mg/l in the MBR, which was fed with influent COD of 7300 mg/l (Fig. 4A) and the organic loading rate was kept in the range of 20–35 kg/m^3 d (Fig. 4B). At SRT of 20 days, the COD of MBR effluent increased to 1230 mg/l as the COD of pretreated leachate was 6300 mg/l on average (the organic loading rate was kept in a wide range of 10–40 kg/m^3 d), and the removal efficiency decreased dramatically from 90 to 60%. At SRT of 10 days, the COD in the effluent increased to 1600 mg/l when the organic loading rate was kept in the range of 10–40 kg/m^3 d. When the SRT was increased to 15 days, the COD in the effluent decreased from 7100 to 1550 mg/l at the organic loading rate of 10–20 kg/m^3 d. At SRT of 50 days, the COD in the effluent increased to 2100 mg/l when the organic loading rate was kept in the range of 10–15 kg/m^3 d, which resulted in a removal efficiency of 68%. Results showed that the COD removal decreased at other SRTs except for 30 days, although the organic loading rate was decreased. It can be concluded that the MBR performed a significant COD removal at SRT of 30 days, when the results were compared in terms of organic oxidation.

Fig. 5 indicates the behavior of nitrogen species found in the leachate. Nitrite was determined to be less than 0.8 mg/l in the leachate and less than 0.2 mg/l in the Aer/An MBR effluent during the experiments. Nitrate in the leachate varied in the range of 5–47 mg/l, although the leachate contained nitrate in low concentrations. The landfill from which the leachate was supplied is not a municipal solid waste landfill and was not designed taking into account the engineered gauges. Leachate exists in the form of small puddles within the landfill area or flows through the landfill area open to the atmosphere. Hence, it is thought that nitrate in the leachate occurs from a partial nitrification because the leachate contacted with oxygen and nitrifying bacteria in the open landfill area. After applying the Aer/An MBR to pretreated leachate, nitrate in the effluent varied in the ranges of 0.5–8.0 mg/l at SRT of 30 days, 6.0–13.9 mg/l at SRT of 20 days, 11.5–23.0 mg/l at SRT of 10 days, 12.5–28.0 mg/l at SRT of 15 days, and 14.0–73.0 mg/l at SRT of 50 days. Ammonia in the leachate varied in the range of 200–600 mg/l and was reduced to less than 15.0 mg/l in the Aer/An MBR at SRT of 30 days, which translates into nitrification rate higher than 90%. At SRT of 20 days, specific nitrification rate increased due to high ammonium concentration although the nitrification capacity appeared to decrease as percentage. Ammonium decreased from 730 mg/l to about 85 mg/l in the MBR. At SRT of 10 days, ammonium in the effluent was determined to be 85 mg/l, similar to the previous stage, which had a nitrification capacity of 91%. Operating the Aer/An MBR at SRT of 15 days resulted in a nitrification capacity of 87%, and gave an effluent with 100 mg/l ammonium

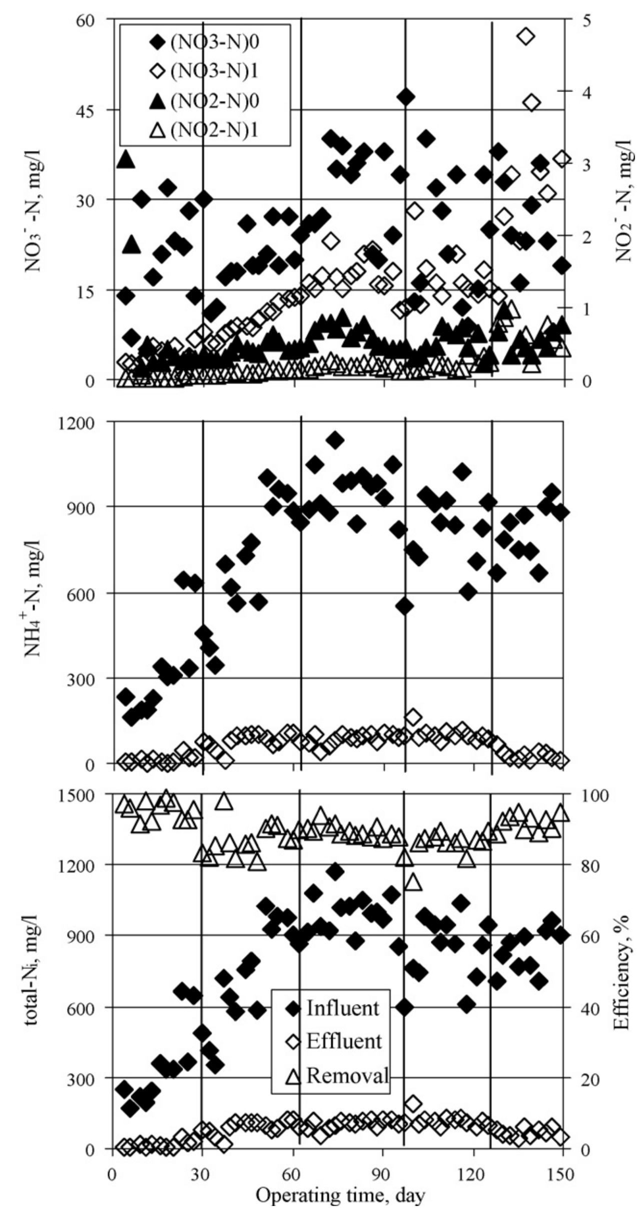


Fig. 5. Nitrogen species in Aer/An MBR; (A) changes in oxidized nitrogen species, (B) changes in ammonium nitrogen, (C) changes in total-N$_i$ (NO_3^- + NO_2^- + NH_4^+).

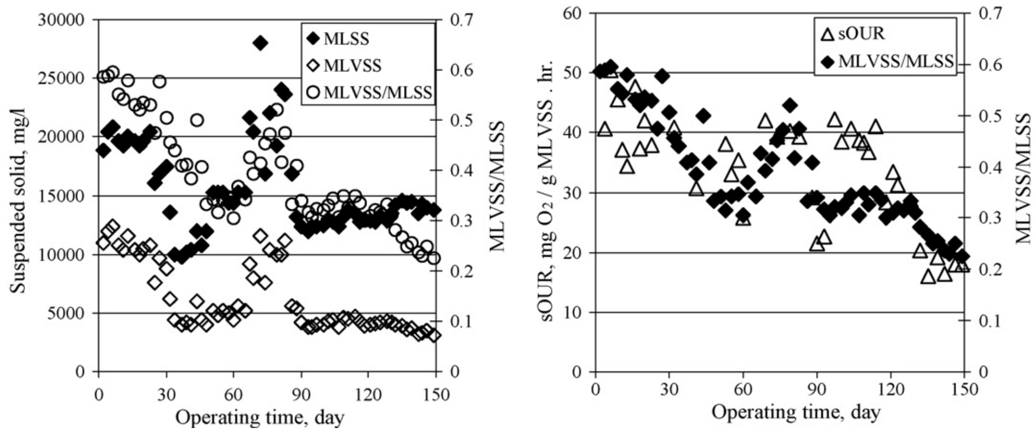


Fig. 6. Biomass behavior in Aer/An MBR; (A) changes in solid concentration, (B) changes in specific oxygen uptake rate.

concentration. On the other hand, significant nitrification (98%) was achieved at SRT of 50 days. In this stage, NH_4^+ was less than 30 mg/l while ammonium concentration of pretreated leachate was about 800 mg/l. Operation of the MBR at SRT of 50 days accomplished a significant nitrification but not noticeable COD removal. On the other hand, the nitrification rate was higher than 90% at SRT of 30 days and the COD removal was very satisfactory. It is not possible to assess nitrification and denitrification processes separately in the Aer/An MBR because both aerobic and anoxic conditions were provided in a single reactor by means of intermittent aeration. Hence, the total-N_i behavior in the system should be investigated to give more meaningful result. In this study, total nitrogen was considered to be sum of nitrate, nitrite and ammonium by neglecting the organic nitrogen. Mean total-N_i removals were 92% at SRT of 30 days, 85% at SRTs between 10 and 20 days, and 90% at SRT of 50 days. In the last stage (SRT = 50 days), total-N_i removal was lower than that at SRT of 30 days due to the insufficient denitrification in spite of a high nitrification capacity. All the results for nitrogen species demonstrated that the Aer/An MBR process is a good alternative for nitrogen removal from leachate.

4.2.2. Behavior of biomass concentration in Aer/An MBR

Fig. 6 indicates the biomass concentration and specific oxygen uptake rate in the Aer/An MBR. At the end of Stage I, MLSS concentration was sharply decreased from 18 to 10 g/l to investigate the effect of MLSS on the total membrane resistance. Young activated sludge acclimated to leachate was inoculated again into the bioreactor to increase the MLVSS concentration since the MLVSS/MLSS ratio decreased from 0.50 to 0.30 in Stage III, and MLSS increased to 22 g/l. MLVSS/MLSS ratio increased to 0.45 by this application. In Stages IV and V, no similar interpretation was made for the sludge. While the MLVSS/MLSS ratio was 0.33 in Stage IV with SRT of 15 days, it fell down rapidly to 0.20 in Stage V with SRT of 50 days. Not only was the effect of SRT on accumulation of inert matter determined, but also the increase of inert matter in the bioreactor was observed with an increase in the operation time. As known, MLVSS is a parameter used to express the microorganism concentration within a reactor and to model the biological processes. However, MLVSS does not give reliable results because it also contains dead microorganisms. In particular, it is not possible to assess the viable microorganism intensity due to high solid retention time and low bacteria yield in very complex treatment plants like membrane bioreactors. In this study, the oxygen uptake rate was also measured along with solid concentration to have an idea about microorganism viability, but the relationship between sOUR and MLVSS is not clear because anoxic microorganisms also exist in Aer/An MBR. The sOUR decreased about 50% in the last stage (SRT = 50 days) where MLVSS/MLSS ratio dropped down to 0.20. On the other hand, inert COD was the lowest in the MBR effluent with SRT of 30 days, which meant sOUR and MLVSS/MLSS were the highest. In this optimal stage, inert COD in the effluent was found to be 420 mg/l as sOUR and MLVSS/MLSS ratios were 40 mg O_2/mg VSS day and 0.60 mg O_2/mg VSS day, respectively. The inert/total COD ratio was determined to be 0.93 and the biodegradable COD was almost completely removed.

4.2.3. Flux and membrane resistance

The membrane fouling is a result of accumulation of rejected particles at the top of the membrane (external fouling), or deposition and adsorption of small particles or macromolecules at the pores or within the internal pore structure (internal fouling) of the membrane. Membrane fouling is an issue of concern in membrane

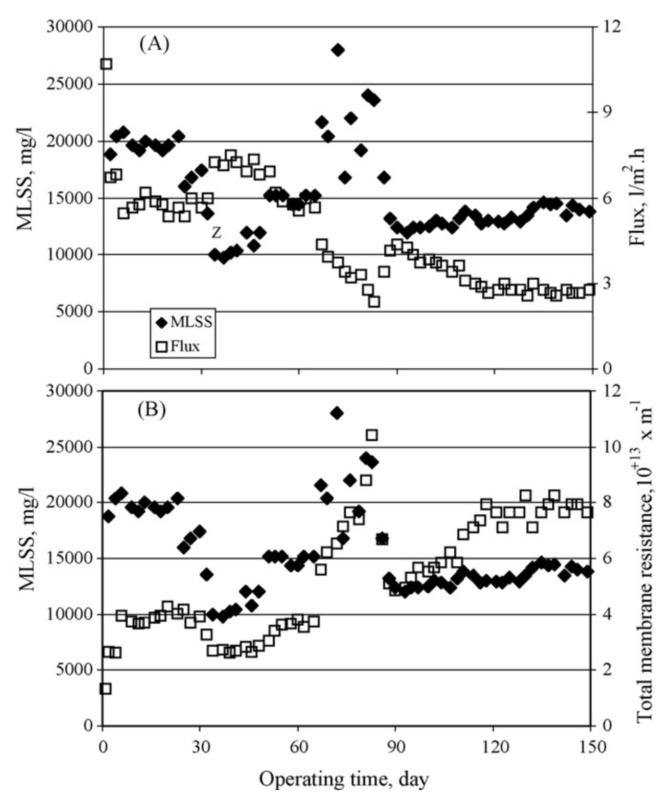
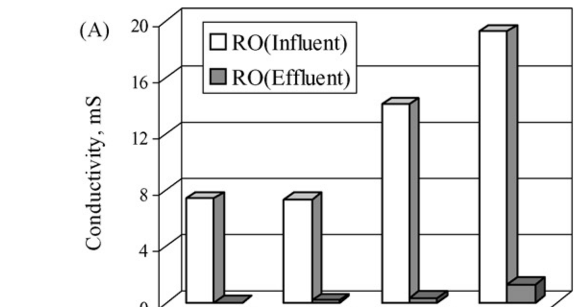
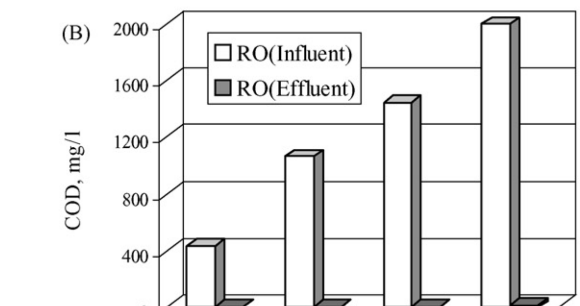


Fig. 7. Hydraulic properties of membrane in Aer/An MBR; (A) changes in the flux with MLSS concentration, (B) changes in total membrane resistance with MLSS concentration.



SRT, day	30	20	10	50
RO(Influent)	7.42	7.38	14.1	19.3
RO(Effluent)	0.02	0.18	0.37	1.34



SRT, day	30	20	10	50
RO(Influent)	438	1065	1450	2000
RO(Effluent)	3.4	9.6	7.6	13.6

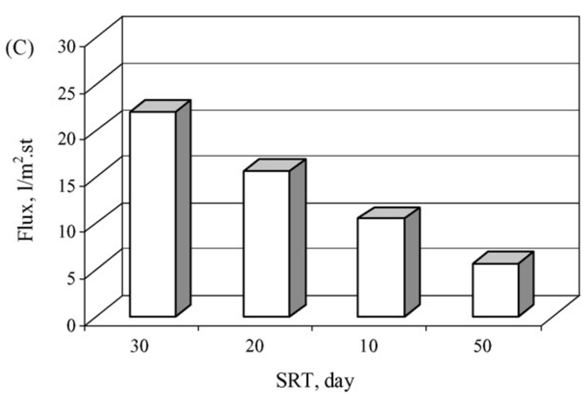


Fig. 8. Capacity of reverse osmosis as advanced treatment to the effluent of Aer/An MBR operated at differential conditions; (A) changes in conductivity, (B) changes in residual COD, (C) changes in the RO flux.

treatment as it causes considerable reduction in flux and shortens the membrane life, thus increasing the capital and operational cost for the MBR treatment. The membrane fouling is indicated by the sharp increase in the total membrane resistance. Flux decreased clearly with increasing of both operating time and solid concentration (Fig. 7A). While the membrane flux on the first day of operating time was 10.7 l/m^2 h, it decreased dramatically to 7.0 l/m^2 h on the second day, and then continued to decrease. Stable membrane flux was maintained at about 3.0 l/m^2 h between 125 and 150 days of operation time. While flux decreased sharply when the solid concentration in the bioreactor increased, it increased again when the solid concentration decreased. The results showed that the total membrane resistance increased significantly with the increase in both operating time and solid concentration in the bioreactor (Fig. 7B). Total membrane resistance decreased from 4×10^{13} to 2.5×10^{13} m^{-1} when the MLSS decreased from 16 to 10 g/l during Stage II. It increased dramatically to 1×10^{14} m^{-1} when MLSS increased during Stage III. MLSS concentration was reduced again in Stage IV, and the total membrane resistance decreased. In Stages IV and V, the resistance continued to increase and became stable at 8×10^{13} m^{-1} although the MLSS concentration remained constant.

4.3. Reverse osmosis as a tertiary treatment of leachate

Reverse osmosis seems to be one of the most promising and efficient methods among the new processes for landfill leachate treatment. In the past, several studies, performed at both lab and industrial scale, have already demonstrated RO performances on the separation of pollutants from landfill leachate [65–66]. Values of the rejection coefficient referred to COD parameter and heavy metal concentrations higher than 98 and 99%, respectively, were reported [44,47]. Chan et al. [47] applied the RO system directly to the stabilized leachate including high COD (8000 mg/l) and NH_3-N (2620 mg/l). They reported that RO membrane system accomplished the local effluent limits for COD of lower than 200 mg/l and for NH_3-N of less than 5 mg/l. This suggests that RO is technically applicable and appealing for the treatment of stabilized leachate. Ahn et al. [62] also reported that dissolved non-biodegradable organic matters are effectively removed by a subsequent reverse osmosis following a membrane bioreactor. In this present study, RO reduced conductivity of treated leachate from 7.40 to 0.02 mS, and residual COD from 440 to 3.5 mg/l at optimal conditions. It was established that MBR performance affected either water quality or hydraulic conditions for reverse osmosis (Fig. 8). In the case of applying the reverse osmosis to secondary effluent treated in MBR, the results in Stage I were very important because the flux was the highest (~22 l/m^2 h) due to the lowest loading rate although RO provided an excellent quality for the effluents obtained at all conditions of Aer/An MBR. In the case that effluent COD was 2000 mg/l, the RO flux decreased to 5.69 l/m^2 h (Fig. 8C).

5. Conclusions

The suggested treatment configuration in this study for complete treatment of the landfill leachate consisted of ammonia stripping, coagulation/flocculation, Aer/An MBR and reverse osmosis. By this configuration, leachate could be used even for all the reuse applications at the optimal conditions because the final COD value decreased to less than 4 mg/l. The flux reduction in reverse osmosis was acceptable for the effluent of Aer/An MBR operated at SRT 30 days, which is an optimal condition for the biological treatment.

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References

[1] D. Frascari, F. Bronzini, G. Giordano, G. Tedioli, M. Nocentini, Long-term characterization, lagoon treatment and migration potential of landfill leachate: a case study in an active Italian landfill, Chemosphere 54 (2004) 335–343.
[2] Z. Salem, K. Hamouri, R. Djemaa, K. Allia, Evaluation of landfill leachate pollution and treatment, Desalination 220 (2008) 108–114.
[3] J. Im, H. Woo, M. Choi, K. Han, C. Kim, Simultaneous organic and nitrogen removal from municipal landfill leachate using an anaerobic-aerobic system, Water Res. 35 (2001) 2403–2410.

[4] J. Jokela, R.H. Kettunen, K.M. Sormunen, J.A. Rintala, Biological nitrogen removal from municipal landfill leachate: low-cost nitrification in biofilters and laboratory scale in situ denitrification, Water Res. 36 (2002) 4079–4087.
[5] S. Renou, S. Poulain, J.G. Givaudan, P. Moulin, Treatment process adapted to stabilized leachates: lime precipitation-prefiltration-reverse osmosis, J. Membr. Sci. 313 (2008) 9–22.
[6] W. Xing, H.H. Ngo, S.H. Kim, W.S. Gou, P. Haqare, Physico-chemical processes for landfill leachate treatment: experiments and mathematical models, Sep. Sci. Technol. 43 (2008) 347–361.
[7] N.J. Horan, H. Gohar, B. Hill, Application of a granular activated carbon-biological fluidised bed fort he treatment of landfill leachates containing high concentrations of ammonia, Water Sci. Technol. 36 (1997) 369–375.
[8] U. Welander, T. Henrysson, T. Welander, Biological nitrogen removal from municipal landfill leachate in a pilot scale suspended carrier biofilm process, Water Res. 32 (1998) 1564–1570.
[9] E. Klimiuk, D. Kulikowska, Organics removal from landfill leachate and activated sludge production in SBR reactors, Waste Manage. 26 (2006) 1140–1147.
[10] R. He, D.S. Shen, Nitrogen removal in the bioreactor landfill system with intermittent aeration at the top of landfilled waste, J. Hazard. Mater. 136 (2006) 784–790.
[11] H. Garcia, J.L. Rico, P.A. Garcia, Comparison of anaerobic treatment of leachates from an urban-solid-waste landfill at ambient temperature and at 35 degrees C, Bioresour. Technol. 58 (1996) 273–277.
[12] H. Timur, I. Ozturk, M. Altinbas, O. Arikan, B.S. Tuyluoglu, Anaerobic treatability of leachate: a comparative evaluation for three different reactor systems, Water Sci. Technol. 42 (2000) 287–292.
[13] A.Z. Ding, Z.H. Zhang, J.M. Fu, Biological control of leachate from municipal landfills, Chemosphere 44 (2001) 1–8.
[14] J. Kang, J.L. Wang, Influence of chemical oxygen demand concentrations on anaerobic ammonium oxidation by granular sludge from EGSB reactor, Biomed. Environ. Sci. 19 (2006) 192–196.
[15] M.S. Bilgili, A. Demir, B. Ozkaya, Quality and quantity of leachate in aerobic pilot-scale landfills, Environ. Manage. 38 (2006) 189–196.
[16] H. Alvarez-Vazquez, B. Jefferson, S.J. Judd, Membrane bioreactors vs conventional biological treatment of landfill leachate: a brief review, J. Chem. Technol. Biotechnol. 79 (2004) 1043–1049.
[17] A. Amokrane, C. Comel, J. Veron, Landfill leachate pretreatment by coagulation–flocculation, Water Res. 31 (1997) 2775–2782.
[18] F. Kargi, M.Y. Pamukoğlu, Adsorbent supplemented biological treatment of pre-treated landfill leachate by fed-batch operation, Bioresour. Technol. 94 (2004) 285–291.
[19] X.Z. Li, Q.L. Zhao, X.D. Hao, Ammonium removal from landfill leachate by chemical precipitation, Waste Manage. 19 (1999) 409–415.
[20] R.J. Chaudhari, F. Basheer, I.H. Farooqi, Combined treatment of landfill leachate and domestic wastewater in Submerged Aerobic Fixed Film (SAFF) reactor, Asian J. Water Environ. Pollut. 5 (2008) 97–101.
[21] H. Hasar, C. Kınacı, A. Unlü, U. İpek, Role of intermittent aeration in domestic wastewater treatment by submerged membrane activated sludge system, Desalination 143 (2002) 287–293.
[22] H. Hasar, C. Kınacı, Comparison of a sMBR with a CASP system for wastewater reclamation and re-use, Filtr. Sep. 41 (2004) 35–39.
[23] C. Visvanathan, M.K. Choudhary, M.T. Montalbo, V. Jegatheesan, Landfill leachate treatment using thermophilic membrane bioreactor, Desalination 204 (2007) 8–16.
[24] D.J.L. Forgie, Selection of the most appropriate leachate treatment methods. Part I: a review of potential biological leachate treatment methods, Water Pollut. Res. J. Can. 23 (1988) 308–329.
[25] S.K. Marttinen, R.H. Kettunen, K.M. Sormunen, R.M. Soimasuo, J.A. Rintala, Screening of physical-chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachates, Chemosphere 46 (2002) 851–858.
[26] A. Gunay, D. Karadag, I. Tosun, M. Ozturk, Use of magnesit as a magnesium source for ammonium removal from leachate, J. Hazard Mater. 156 (2008) 619–623.
[27] M.I. Aguilar, J. Saez, M. Liorens, A. Soler, J.F. Ortuno, Nutrient removal and sludge production in the coagulation–flocculation process, Water Res. 36 (2002) 2910–2919.
[28] A.A. Tatsi, A.I. Zouboulis, K.A. Matis, P. Samaras, Coagulation–flocculation pre-treatment of sanitary landfill leachates, Chemosphere 53 (2003) 737–744.
[29] A.C. Silva, M. Dezotti, G.L. Sant'Anna, Treatment and detoxification of a sanitary landfill leachate, Chemosphere 55 (2004) 207–214.
[30] M.A. Zazouli, Z. Yousefi, Removal of heavy metals from solid wastes leachates coagulation–flocculation process, J. Appl. Sci. 8 (2008) 2142–2147.
[31] E. Maranon, L. Castrillon, Y. Fernandez-Nava, A. Fernández-Méndez, A. Fernández-Sánchez, Coagulation–flocculation as a pretreatment process at a landfill leachate nitrification–denitrification plant, J. Hazard. Mater. 156 (2008) 538–544.
[32] F. Ilhan, U. Kurt, O. Apaydin, M.T. Gonullu, Treatment of leachate by electrocoagulation using aluminum and iron electrodes, J. Hazard. Mater. 154 (2008) 381–389.
[33] S. Veli, T. Ozturk, A. Dimoglo, Treatment of municipal solid wastes leachate by means of chemical- and electro-coagulation, Sep. Purif. Technol. 61 (2008) 82–88.
[34] J. Rodriguez, L. Castrillon, E. Maranon, H. Sastre, E. Fernandez, Removal of non-biodegradable organic matter from landfill leachates by adsorption, Water Res. 38 (2004) 3297–3303.
[35] H. Yoo, S. Cho, S. Ko, Modification of coagulation and Fenton oxidation processes for cost-effective leachate treatment, J. Environ. Sci. Health A36 (2001) 39–48.
[36] S. Kim, S. Geissen, A. Vogelpohl, Landfill leachate treatment by a photoassisted Fenton reaction, Water Sci. Technol. 35 (1997) 239–248.
[37] A. Lopez, M. Pagano, A. Volpe, A.C. Di Pinto, Fenton's pre-treatment of mature landfill leachate, Chemosphere 54 (2004) 1005–1010.
[38] O. Primo, M.J. Rivero, I. Ortiz, Photo-Fenton process as an efficient alternative to the treatment of landfill leachates, J. Hazard. Mater. 153 (2008) 834–842.
[39] K.C. Cheung, L.M. Chu, M.H. Wong, Ammonia stripping as a pretreatment for landfill leachate, Water Air Soil Pollut. 94 (1997) 209–221.
[40] S.S. Huang, V. Diyamandoglu, J. Fillos, Ozonation of leachates from aged domestic landfills, Ozone Sci. Eng. 15 (1993) 433–444.
[41] J.J. Wu, C.C. Wu, H.W. Ma, C.C. Chang, Treatment of landfill leachate by ozone-based advanced oxidation processes, Chemosphere 54 (2004) 997–1003.
[42] C. Tizaoui, L. Bouselmi, L. Mansouri, A. Ghrabi, Landfill leachate treatment with ozone and ozone/hydrogen peroxide systems, J. Hazard. Mater. 140 (2007) 316–324.
[43] T. Poznyak, G.L. Bautista, I. Chairez, R.I. Cordova, L.E. Rios, Decomposition of toxic pollutants in landfill leachate by ozone after coagulation treatment, J. Hazard. Mater 152 (2008) 1108–1114.
[44] T.A. Peters, Purification of landfill leachate with reverse osmosis and nanofiltration, Desalination 119 (1998) 289–293.
[45] J. Bohdziewicz, M. Bodzek, J. Gorska, Application of pressure-driven membrane techniques to biological treatment of landfill leachate, Process Biochem. 36 (2001) 641–646.
[46] M. Bodzek, E. Lobos-Moysa, M. Zamorowska, Removal of organic compounds from municipal landfill leachate in a membrane bioreactor, Desalination 198 (2006) 16–23.
[47] G.Y.S. Chan, J. Chang, T.A. Kurniawan, C.X. Fu, H. Jiang, Y. Je, Removal of non-biodegradable compounds from stabilized leachate using VSEPRO membrane filtration, Desalination 202 (2007) 310–317.
[48] J. Bae, S. Kin, H. Chang, Treatment of landfill leachates: ammonia removal via nitrification and denitrification and further COD reduction via Fenton's treatment followed by activated sludge, Water Sci. Technol. 36 (1997) 341–348.
[49] P. Haapea, S. Korhonen, T. Tuhkanen, Treatment of industrial landfill leachates by chemical and biological methods: ozonation, ozonation + hydrogen peroxide, hydrogen peroxide and biological post-treatment for ozonated water, Ozone Sci. Eng. 24 (2002) 369–378.
[50] F. Kargi, M.Y. Pamukoğlu, Repeated fed-batch biological treatment of pre-treated landfill leachate by powdered activated carbon addition, Enzyme Microb. Technol. 34 (2004) 422–428.
[51] A. Uygur, F. Kargı, Biological nutrient removal from pre-treated landfill leachate in a sequencing batch reactor, J. Environ. Manage. 71 (2004) 9–14.
[52] C.Y. Lin, F.Y. Chang, C.H. Chang, Co-digestion of leachate with septage using a UASB reactor, Bioresour. Technol. 73 (2000) 175–178.
[53] T.H. Hoilijoki, R.H. Kettunen, J.A. Rintala, Nitrification of anaerobically pre-treated municipal landfill leachate at low temperature, Water Res. 34 (2000) 1435–1446.
[54] O.N. Ağdağ, D.T. Sponza, Anaerobic/aerobic treatment of municipal landfill leachate in sequential two-stage up-flow anaerobic sludge blanket reactor (UASB)/completely stirred tank reactor (CSTR) systems, Process Biochem. 40 (2005) 895–902.
[55] O.N. Ağdağ, D.T. Sponza, Sequential anaerobic, aerobic/anoxic treatment of simulated landfill leachate, Environ. Technol. 29 (2008) 183–197.
[56] J. Bohdziewicz, E. Neczaj, A. Kwarciak, Landfill leachate treatment by means of anaerobic membrane bioreactor, Desalination 221 (2008) 559–565.
[57] J. Bohdziewicz, A. Kwarciak, The application of hybrid system UASB reactor-RO in landfill leachate treatment, Desalination 222 (2008) 128–134.
[58] U. Ipek, Removal of Ni(II) and Zn(II) from an aqueous solution by reverse osmosis, Desalination 174 (2005) 161–169.
[59] G. Eremektar, F.G. Babuna, D. Orhon, Inert COD fractions in two-stage treatment of a pulp and paper mill effluent, J. Chem. Technol. Biotechnol. 72 (1998) 7–14.
[60] APHA, AWWA&WEF, (American Public Health Association, American Water Works Association and Water Environment Federation), Standard Methods for the Examination of Water and Wastewater, 18th ed., Washington, DC, USA, 1995.
[61] B. Wichitsathian, S. Sindhuja, C. Visvanathan, K.H. Ahn, Landfill leachate treatment by yeast and bacteria based membrane bioreactors, J. Environ. Sci Health. Part A, Toxic/Hazard. Substances Environ. Eng. 39 (2004) 2391–2404.
[62] W.Y. Ahn, M.S. Kang, S.K. Yim, K.H. Choi, Advanced landfill leachate treatment using an integrated membrane process, Desalination 149 (2002) 109–114.
[63] N. Laitinen, A. Luonsi, J. Vilen, Landfill leachate treatment with sequencing batch reactor and membrane bioreactor, Desalination 191 (2006) 86–91.
[64] H. Hasar, U. Ipek, C. Kinaci, Associated treatment of landfill leachate with municipal wastewater by submerged membrane bioreactor, in: IWA Regional Conference for Membrane Technologies in Water & Waste Water Treatment, 2–4 June 2008, Moscow, Russia, 2008.
[65] T. Bilstad, M.V. Madland, Leachate minimization by reverse osmosis, Water Sci. Technol. 25 (1992) 117–120.
[66] K. Linde, A.-S. Jonsson, R. Wimmerstedt, Treatment of three types of landfill leachate with reverse osmosis, Desalination 101 (1995) 21–30.