ADSORBENT SUPPLEMENTED TREATMENT OF LANDFILL LEACHATE IN SEQUENCING BATCH REACTOR

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SEQUENCING BATCH REACTOR

by

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ABBREVIATIONS

AN	Ammoniacal nitrogen
BET	Brunauer, Emmett and Teller
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EDX	Energy Dispersive X-ray
FAAS	Flame Atomic Absorption Spectrometer
FTIR	Fourier Transform Infrared Spectrophotometer
HRT	Hydraulic Retention Time
MLBSS	Mixed Liquor Biomass Suspended Solids
MLCSS	Mixed Liquor Carbon Suspended Solids
MLRSS	Mixed Liquor Modified Rice Husk Suspended Solids
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids
MRH	Ethylenediamine-Modified Rice Husk
$NO_2^- \text{-N}$	Nitrite nitrogen
$NO_3^- \text{-N}$	Nitrate nitrogen
$NO_x^- \text{-N}$	Oxidized nitrogen
PAC	Powdered Activated Carbon
PACT	Powdered Activated Carbon Treatment
PE	Polyethylene
PTFE	Polytetrafluoroethylene
RRH	Raw Rice Husk
SBR	Sequencing Batch Reactor

SEM	Scanning Electron Microscope
SND	Simultaneous Nitrification and Denitrification
SOUR	Specific Oxygen Utilization Rate
SRT	Sludge Retention Time
SS	Suspended Solids
SV_{30}	Settled Sludge Volume
SVI	Sludge Volume Index
TDS	Total Dissolved Solids

PENGOLAHAN AIR LARUT RESAP TAPAK PELUPUSAN SAMPAH DALAM REAKTOR KELOPOK BERTURUTAN DENGAN MENGGUNAKAN BAHAN PENJERAP

ABSTRAK

Tujuan penyelidikan ini adalah untuk mengkaji kesan penambahan bahan penjerap terhadap penyingkiran nitrogen ammoniakal (AN) dan tuntutan oksigen (COD) daripada air larut resap tapak pelupusan sampah di bawah operasi reaktor kelompok berturutan (SBR). Dua buah SBR "plexiglass" dioperasikan mengikut mod operasi PENGISIAN, TINDAK BALAS, PEMENDAPAN, PENGELUARAN dan REHAT dengan nisbah tempoh masa 2:12:2:1:7 dalam tempoh 24 jam/kitaran. Reaktor R-PAC menerima campuran air buangan sintetik bersama air larut resap yang kepekatannya meningkat (115-170 mg/L AN) serta dosej serbuk karbon teraktif (PAC) yang meningkat (0.5-1.5 g/kitaran). Reaktor R-MRH pula menerima campuran air buangan sintetik bersama air larut resap yang kepekatannya meningkat (115-215 mg/L AN) dan dosej serkam padi teraktif-etilenadiamina (MRH) yang meningkat (0.5-1.0 g/kitaran).

Keputusan menunjukkan bahawa selepas penambahan air larut resap, kecekapan penyingkiran COD menurun dari 90% untuk kedua-kedua reaktor kepada 72% untuk reaktor R-PAC and 79% untuk reaktor R-MRH. Pengolahan air larut resap pada kepekatan yang tinggi dapat dikekalkan jika PAC atau MRH ditambah. Kelebihan MRH yang diperhatikan ialah kebolehannya untuk mengekalkan penyingkiran COD dalam reaktor R-MRH pada 70% ke atas

dengan kepekatan air larut resap pada 215 mg/L AN bersama 0.5 g MRH/kitaran. Secara perbandingan, penyingkiran COD yang melebihi 70% dengan kepekatan air larut resap pada 170 mg/L AN hanya dapat dikekalkan jika dosej PAC ditambah pada 1.5 g/kitaran dalam reaktor R-PAC.

Kecekapan penyingkiran AN adalah hampir 100% untuk kedua-dua reaktor sebelum dan selepas penambahan air larut resap pada kepekatan 115 mg/L AN tetapi merosot apabila kepekatan air larut resap ditingkatkan. Pada kepekatan air larut resap 170 mg/L AN, kecekapan penyingkiran AN adalah hampir 100% dalam reaktor R-PAC dan dapat dikekalkan dengan penambahan 1.5 g PAC/kitaran. Kecekapan penyingkiran AN yang sama dicapai dalam reaktor R-MRH pada kepekatan air larut resap 215 mg/L AN dengan 0.5 g MRH/kitaran.

Keputusan kajian kinetik menunjukkan bahawa kadar penyingkiran COD dan AN semasa tempoh TINDAK BALAS dapat dihuraikan dengan kinetik tertib pertama. Penambahan air larut resap menyebabkan penukaran nitrogen nitrit (NO_2^- -N) ke nitrogen nitrat (NO_3^- -N) terbantut. Penambahan PAC dan MRH masing-masing mengekalkan kadar penyingkiran COD dan AN pada kepekatan air larut resap setinggi 170 dan 215 mg/L AN. Ini menunjukkan bahawa penambahan bahan penjerap telah meminimakan kesan toksik air larut resap dengan MRH menunjukkan kecekapan yang lebih tinggi daripada PAC.

ADSORBENT SUPPLEMENTED TREATMENT OF LANDFILL LEACHATE IN SEQUENCING BATCH REACTOR

ABSTRACT

The objective of this study is to evaluate the performance of the sequencing batch reactor (SBR) with and without the addition of adsorbent in the removal of oxygen demand (COD) and ammoniacal nitrogen (AN) from landfill leachate. Two identical plexiglass SBRs were operated with FILL, REACT, SETTLE, DRAW and IDLE periods in the ratio of 2:12:2:1:7 for a cycle time of 24 h. Reactor R-PAC was fed with a mixture of synthetic wastewater and increasing strength of leachate (115-170 mg/L AN) as well as increasing dosage of powdered activated carbon (PAC) (0.5-1.5 g/cycle). Whilst reactor R-MRH received a mixture of the same synthetic wastewater and increasing strength of leachate (115-215 mg/L AN) as well as increasing dosage of ethylenediamine-modified rice husk (MRH) (0.5-1.0 g/cycle).

The results showed that after the introduction of leachate, the COD removal efficiency was reduced from 90% for both reactors to 72% for reactor R-PAC and 79% for reactor R-MRH. Treatment of leachate at higher strength was sustainable only if PAC or MRH was added. The beneficial effect of MRH was seen in its ability to sustain the COD removal in R-MRH of above 70% at the leachate strength of 215 mg/L AN with the dosage of 0.5 g/cycle. In comparison, the COD removal in R-PAC above 70% at the leachate strength of 170 mg/L AN was sustainable if higher PAC dosage of 1.5 g/cycle was added.

The AN removal efficiency for both reactors was almost 100% before and after the introduction of leachate at the strength of 115 mg/L AN but deteriorated when the leachate strength was increased. At the leachate strength of 170 mg/L AN, the AN removal efficiency in reactor R-PAC was sustained at almost 100% with PAC addition of 1.5 g/cycle. The same AN removal efficiency was achieved in reactor R-MRH at a lower MRH dosage of 0.5 g/cycle for the leachate strength of 215 mg/L AN.

The results of kinetic study showed that the rates of COD and AN removal during the REACT period can be described by first-order kinetics. The addition of leachate resulted in the effective inhibition of the conversion of nitrite nitrogen (NO_2^- -N) to nitrate nitrogen (NO_3^- -N). The addition of PAC and MRH, respectively, helped to sustain the rates of COD and AN removal at higher leachate strength of up to 170 and 215 mg/L AN. This indicates that the addition of adsorbents had minimized the toxic effect of leachate with MRH showing more effectiveness than PAC.

CHAPTER 1
INTRODUCTION

Human population which has increased exponentially in recent decades produces huge amounts of solid wastes. The solid wastes generated have become a threat to human health and the environment. Therefore, proper waste management and disposal should be practiced to reduce the possibility of pollution. The major strategies of waste management include incineration and landfilling, but for the moment, landfilling remains the cheapest option. The purpose of landfill disposal is to stabilize the solid waste through proper storage of waste and use of natural metabolic function (The Role of Landfill Site, 2003).

1.1   Landfill Leachate

Landfill leachate is generated from the mixing of soluble materials in solid wastes disposed off and liquid mostly from rain water that percolates through the landfill cell. As the liquid moves through the landfill, many organic and inorganic compounds are transported in the leachate. A vast majority of the solids in the leachate is in the soluble form as most suspended solids are filtered out by the soil around the compacted refuse.

1.1.1   Characteristics of Landfill Leachate

There are a number of factors that affect the quality and quantity of leachate: seasonal weather variation, landfilling technique, compaction method, waste composition and age of the landfill (Ehrig, 1983; Baig *et al.*, 1999; Kang *et al.*, 2002). The flow rate and composition of leachate vary from site to site. Young leachate normally contains a large amount of volatile fatty acids which

are readily degradable and mostly account for the chemical oxygen demand (COD) concentration (Lema *et al.*, 1988). On the other hand, old leachate is rich in ammoniacal nitrogen (AN) due to hydrolysis and fermentation of the nitrogenous fraction of biodegradable wastes (Matthew, 2001) and the low BOD_5/COD ratio. Young landfill leachate are usually more easily treated compared to the old ones (Kargi & Pamukoglu, 2004a). Thus, the treatment strategy mainly depends on the characteristics of the leachate.

1.1.2 Environmental Pollution due to Leachate

Landfill leachate can cause environmental problems when it comes into contact with the surrounding soil, ground and surface water. The environmental impact of leachate is due to several factors, such as high load of organic matter, high content of ammonium ions, inorganic salts, heavy metals and mass flux of transported contaminants (Isidori *et al.*, 2003). Leachate is a high strength wastewater which may cause significant pollution such as dissolved oxygen depletion, increasing toxicity of water body, eutrophication and methemoglobinemia (Gerardi, 2002).

The high load of organic matter and ammonium ions may cause dissolved oxygen depletion in receiving waters. The depletion occurs when dissolved oxygen is consumed by microbial activities for the oxidation process. During oxidation, ammonium ions will be converted to nitrite ions and further to nitrate ions. Besides, the nitrogenous wastes also serve as nutrient for aquatic plants. When the plants die, oxygen is consumed to decompose the dead plants. Nitrogenous wastes as one of the main plant nutrients may also cause the

eutrophication phenomenon in the pond or lake. The excess nutrients discharged to water bodies may stimulate the bloom of aquatic plants. When the plants die, the freshwater will be filled with dead plants thus resulting in water pollution.

Some constituents in leachate like heavy metals, ammonium ions and other contaminants may be toxic to aquatic life in receiving waters. Ammonium ions may be oxidized to nitrite ions which are among the toxic nitrogenous species. Ammonium ions will be toxic to aquatic life when appearing as an ammonia species at high pH.

1.1.3 Landfill Leachate Management

In the past, it was acceptable to allow leachate to seep slowly and disperse through the ground. Old landfill sites had no leachate or gas management facilities, so the land was contaminated. Chemicals were leached into the groundwater and the air was polluted with gases generated from the fermentation of organic materials. New sanitary landfill sites are based on the idea of containment. Landfills are lined with clay and flexible synthetic membranes to prevent leachate contaminating the groundwater. Leachate is drained through the horizontal array of pipes and collected at the bottom of the landfill site. Methane gas is also collected at the top, and is either vented to the air or tapped off for industrial or heating use (Pollution from Landfill, 2005).

Traditional landfill practices the single pass leaching strategy whereby the leachate generated is collected and pre-treated before it is discharged for

further treatment involving physical, chemical and biological processes. Recirculation management collects the leachate at the base of the landfill and flushes it back through the landfill many times. Recirculation turns the landfill into an anaerobic bioreactor. This increases the rate of waste decomposition and reduces time required for landfill stabilization from several decades to 2-3 years (Matthew, 2001). Leachate recycling may reduce the volume of leachate but increases the toxicity of leachate by concentrating it. Recirculation of leachate will produce stabilized leachate containing low concentration of degradable carbon compounds but high concentration of ammonia (Knox, 1985).

1.1.4 Treatment of Landfill Leachate

Landfill leachate is a high strength wastewater with large variables of organic, inorganic and heavy metal contents (Lin & Chang, 2000). Thus, it is difficult to obtain a satisfactory treatment of leachate. The type of method utilized for the treatment of leachate depends upon the specific characteristics of a particular landfill site. Treatment processes for landfill leachate can be classified as physical, chemical or biological processes and the processes are usually used in combination for better treatment efficiency. Among the major physical processes for leachate treatment are sedimentation, air-stripping, adsorption, and membrane filtration (Morawe *et al.*, 1995; Amokrane *et al.*, 1997; Bohdziewicz *et al.*, 2001; Trebouet *et al.*, 2001). Major chemical processes for leachate treatment are coagulation-flocculation (Amokrane *et al.*, 1997; Ahn *et al.*, 2002), chemical precipitation and chemical-electrochemical oxidations (Steensen, 1997; Lin & Chang, 2000; Chiang *et al.*, 2001; Marttinen *et al.*, 2002). Biological processes used for the removal of biodegradable

compounds in leachate can be classified as aerobic, anaerobic or anoxic process (Kargi & Pamukoglu, 2004a).

1.1.4.1 Chemical Treatment

The treatment of landfill leachate by Fenton process was carried out in a batch reactor by Zhang *et al.* (2005). It was found that Fenton's reagent effectively degraded leachate organics in 30 min. The efficacy of Fenton process was improved by adding Fenton's reagent in multiple steps rather than in a single step. The disadvantage of this process is that ammoniacal nitrogen (AN) in the landfill leachate is not removed.

1.1.4.2 Biological Treatment

Biodegradation process could follow either an aerobic or anaerobic path. For instance, the processes in activated sludge systems, aerated lagoons, and rotating biological contactors follow an aerobic path whereas those in anaerobic lagoons, up-flow anaerobic sludge blanket units (UASB) and anaerobic fixed film reactors follow an anaerobic path. Aerobic biological process is recommended for low-strength (COD < 500 mg/L) leachate. For medium-strength (COD range 500-5000 mg/L) leachate, the choice could be either aerobic or anaerobic. Anaerobic treatment is suitable for high-strength (COD > 5000 mg/L) leachate, provided toxic metals are removed by chemical pre-treatment. The reason for choosing the anaerobic path for high-COD waste is that the higher the strength of leachate, the higher is the energy required (to run the aeration compressor) for the aerobic treatment whereas the anaerobic

system is a potential energy producer (by virtue of its ability to produce methane) (Martin, 1991).

Biological processes are quite effective when applied to young leachate, but less efficient for old leachate. The refractory organic contaminants in old leachate must be treated by a physico-chemical process (Forgie, 1988).

The most popular treatment of landfill leachate in the past was the anaerobic or aerobic activated sludge process (Lema *et al.*, 1988). Agdag & Sponza (2005) investigated the treatability of leachate from food solid waste in a two-stage sequential up-flow anaerobic sludge blanket reactor (UASB)/aerobic completely stirred tank reactor (CSTR). Experiments were performed in two UASB reactors and a CSTR reactor. As the organic loading rates increased from 4.3 to 16 kg/m^3 per day, the COD removal efficiency reached a maximum of 80% while the AN removal was 99.6% after the aerobic stage. AN was converted to nitrate in the aerobic system via nitrification, so further studies need to be conducted for the removal of nitrate nitrogen (NO_3^- -N) via denitrification.

Leachate from food solid waste might be treated with merely biological treatment but not for municipal landfill leachate. The anaerobic or aerobic process alone is inadequate to treat the municipal landfill leachate satisfactorily since leachate is a high strength wastewater with various constituents which may exert inhibitory effect on the treatment. Therefore, alternative leachate

treatment approaches involving a combination of biological, chemical and physical treatment processes are applied.

1.1.4.3 Physical-Chemical Treatment

An integrated technique consisting of ozonation and coagulation/flocculation processes was adopted by Ntampou *et al.* (2005) for the treatment of pre-treated leachate. The coagulation of leachate samples was achieved by the addition of ferric chloride or poly-aluminium chloride agents at various dosages. Pre-ozonation followed by coagulation/flocculation was not efficient in COD removal with the percentage of COD removal less than 82%, but coagulation/flocculation followed by ozonation proved to be an efficient process as the reduction of COD was found to be greater than 82%. However, high coagulant and/or ozone doses are required due to the presence of refractory organic compounds in the leachate sample thus indirectly increase the cost of treatment.

1.1.4.4 Physical-Biological Treatment

Aktas & Cecen (2001a) investigated the biological treatment of combined landfill leachate and domestic wastewater in an activated sludge system in the presence of powdered activated carbon (PAC). The removal of COD and AN decreased with increasing landfill leachate and domestic wastewater mixing ratio. But overall, the percentages of removal for COD and AN were greater than 90%. PAC was found to be beneficial for both COD removal and nitrification. However, high nitrite accumulation was observed in this study.

Kargi & Pamukoglu (2004a) treated the pre-treated leachate using an aeration tank operated in repeated fed-batch mode in the absence and presence of PAC as adsorbent. The PAC addition increased COD removal to 94% compared to 87% with PAC-free biological treatment. The removal of COD was also affected by the mode of the fed-batch operation. AN removal was not affected by the type of the fed-batch operation used. The removal of AN was only 30%.

Kargi & Pamukoglu (2004b) compared PAC and powdered zeolite (PZ) as adsorbents in the removal of COD and AN concentrations from pre-treated landfill leachate using fed-batch operation. Nearly 87 and 77% COD removal were achieved with PAC and PZ concentrations of 2 g/L, respectively. AN removal efficiencies were 30 and 40% with PAC and PZ concentrations of 5 g/L, respectively, at the end of 30 h fed-batch operation. Percent COD removal with PAC addition was significantly higher that of PZ. On the other hand, PZ performed better in the removal of AN. However, a mixture of PAC and PZ (1+1 g/L) did not prove to be as effective as PAC (2 g/L) for COD and AN removal.

1.1.4.5 Treatment with the Sequencing Batch Reactor (SBR)

The most cost-effective form of treatment for high levels of biochemical oxygen demand (BOD), COD and AN is intense biological oxidation in which the sequencing batch reactor (SBR) is the most commonly used system. The SBR employs activated sludge treatment. The fundamental difference between the process in a SBR and a traditional activated sludge/settlement process is that

biological degradation and solids settlement are carried out in the same tank for a SBR system.

Timur & Ozturk (1999) treated landfill leachate using lab-scale anaerobic sequencing batch reactors (ASBR). The results have shown that about 83% of COD removed during the treatment was converted to methane and biomass. The removal of AN which is very important in the landfill leachate treatment was not studied.

Treatment of old landfill leachate by combined chemical and biological processes was investigated by Lin & Chang (2000). The electro-Fenton method assisted by chemical coagulation was employed and found to be efficient in removing a large amount of refractory organic and inorganic compounds in the leachate. The SBR was capable of further elevating the quality of leachate effluent to the discharge standard. The only disadvantage of this treatment was that it had to go through a few steps for efficient treatment of landfill leachate.

Loukidou & Zouboulis (2001) used an attached-growth biomass system for the treatment of leachate in terms of nitrogen, organic matter (expressed as BOD_5 and COD), colour and turbidity removal. Free-floating polymeric (polyurethane) elements and granular activated carbon (GAC) as biofilm carriers in moving-bed biofilm SBR process were compared. In the GAC moving-bed biofilm SBR process, large amount of residual suspended solids were produced and had to be subsequently treated and separated. Thus, porous polyurethane showed an advantage for the process.

Uygur & Kargi (2004) utilized the SBR system in the removal of biological nutrients from pre-treated landfill leachate. Landfill leachate with high COD concentration was pre-treated by coagulation-flocculation with lime followed by air-stripping of ammonia at pH 12. Domestic wastewater and PAC were introduced to the pre-treated landfill leachate. Three different operations consisting of different numbers of anaerobic (An), anoxic (Ax) and oxic (Ox) steps were tested. These operations consisted of three-step (An/Ax/Ox), four-step (An/Ox/Ax/Ox) and five-step (An/Ax/Ox/Ax/Ox) operations with a total residence time of 7 h each. The results showed that the five-step operation gave the lowest effluent nutrients levels, with 75% COD, 44% AN and 44% orthophosphate-phosphorus (PO_4^{3-}-P) removal. However, the nutrients removal efficiency needs to be improved.

1.2 Sequencing Batch Reactor (SBR)

1.2.1 Activated Sludge Process

Activated sludge process is the most commonly used system for the treatment of industrial and domestic wastes around the world. It is a biological system that uses microorganisms to treat the waste. The process is very similar to the biological processes which take place in the upper layers of soil that contain vast quantities of microorganisms, except that the activated sludge process maintains the microorganisms in a controlled liquid environment (Junkins *et al.*, 1983). The original design of an activated sludge system was a single tank batch reactor where aeration and settlement took place in the same tank (Arden & Lockett, 1914; Allemen & Prakasam, 1983). This design was

developed into the conventional system used today in which aeration and settlement occur in separate tanks.

The aeration tank is a biological reactor where dissolved oxygen is provided for chemoheterotrophic bacteria to metabolize organic substrates. Dissolved oxygen is also needed for chemoautotrophic nitrifying bacteria for the oxidation of AN to oxidized nitrogen (NO_x^- -N) The degradation of the wastes by the bacteria results in growth of the bacteria population. Successful operation of the system depends on a complete separation of liquid phase from solid cell biomass in the clarifier, as the treatment effluent leaves the reactors (Seviour & Blackall, 1999).

1.2.2 Operation of SBR System

Renewed interest in batch operation has led to the introduction of the SBR system (Irvive & Ketchum, 1983). A SBR system is an activated sludge process which is operated as a batch process rather than a continuous one. It is run on the fill and draw principle in a single reactor. A single reactor permits better operation management of the mixed liquor with good control over oxygen and redox conditions. The sequence of operation used will depend on the type of treatment required. In this study, the sequence of operational phases comprising FILL, REACT, SETTLE, DRAW and IDLE was utilized with alternating aerobic-anoxic processes during the REACT period.

The SBR is used throughout the world for scientific studies, bench-scale testing, and full-scale applications for small and medium-sized wastewater

treatment plants (Gray, 2004). The use of SBR has been emphasized in this study due to some advantages including:

- High degree of process flexibility in terms of cycle time and sequence;

- Ability to incorporate aerobic and anoxic phases in a single reactor;

- Near ideal quiescent settling conditions;

- No separate clarifier required;

- Elimination of short circuiting.

The greater process flexibility of SBR is particularly important when considering the treatment of landfill leachate with its high degree of variability in quality and quantity (Kennedy & Lentz, 2000).

1.3 Nutrient Removal in Activated Sludge Process

1.3.1 Nitrogen Removal

1.3.1.1 Nitrification

Nitrification is a process in which reduced nitrogen compounds, generally ammonium ions, are microbiologically oxidized to nitrate ions via nitrite ions under aerobic conditions (Belser & Schmidt, 1980; Glover, 1985; Kuenen & Robertson, 1988; Powell & Prosser, 1991; Robertson & Kuenen, 1991; Randall, 1992; Fang *et al.*, 1993; Halling-Sorensen & Jorgensen, 1993; Laanbroek *et al.*, 1994). Nitrification is a two-stage oxidation process carried out by two groups of autotrophic bacteria, collectively called the nitrifying bacteria (Watson *et al.*, 1989; Bock & Koops, 1992; Randall, 1992; Bryan, 1993).

Nitrosomonas and *Nitrobacter* are the two main genera of autotrophic bacteria that mediate the nitrification process (Gerardi, 2002). The general reactions for which they are responsible are as follows:

$$2NH_4^+ + 3O_2 \longrightarrow 2NO_2^- + 2H_2O + 4H^+ + energy \qquad (1.1)$$

$$2NO_2^- + O_2 \longrightarrow 2NO_3^- + energy \qquad (1.2)$$
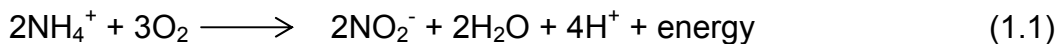
The overall nitrification reaction is

$$2NH_4^+ + 4O_2 \longrightarrow 2NO_3^- + 2H_2O + 4H^+ + energy \qquad (1.3)$$
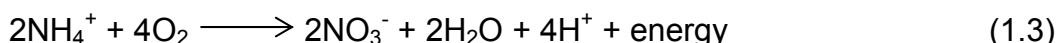
Nitrifying bacteria obtain their energy by oxidizing inorganic substrates. Not all the ammonium ions are used as an energy source. Some of the ammonium ions are used as a nutrient source of nitrogen for the growth of new cells in activated sludge. Carbon dioxide serves as the carbon source for synthesis of cellular material for nitrifying bacteria.

Nitrosomonas and *Nitrobacter* are Gram-negative bacteria and are strict aerobes that require dissolved oxygen in order to oxidize substrate. Oxygen is used to carry and removed electrons from the bacteria cell as they are released during the oxidation of ammonium ions and nitrite ions. In activated sludge, nitrifying bacteria are found adsorbed on the surface of the floc particles, suspended in the bulk solution, and on the biological growth on the sides of the aeration tank. Only nitrifying bacteria that are exposed to free molecular oxygen nitrify (Gerardi, 2002).

The nitrifying bacteria obtain a small amount of energy from the oxidation of ammonium ions and nitrite ions, so their growth rate is slow compared to the heterotrophs (Bock *et al.*, 1986, Bock *et al.*, 1988; Prosser, 1989; Fang *et al.*,

1993). The population size of nitrifying bacteria within the activated sludge is very small, typically 2-5% (Randall, 1992) in comparison to the population size of organotrophs. Organotrophs often are referred to as heterotrophs because they obtain the carbon needed for cellular growth from organic waste, not from carbon dioxide. Heterotrophs releases far more energy from the oxidation of organic compounds than the oxidation of nitrogenous compounds by the nitrifiers (Prosser, 1989; Randall, 1992). Heterotrophs play the role of removing the biodegradable carbonaceous compounds in activated sludge flocs (Painter, 1986; Randall, 1992; Andreadakis *et al.*, 1993). The presence of organic compounds may inhibit the activities of nitrifying bacteria (Gerardi, 2002).

The population size of *Nitrosomonas* is larger than *Nitrobacter*. *Nitrosomonas* obtain more energy from the oxidation of ammonium ions than what is obtained from the oxidation of nitrite by *Nitrobacter*. *Nitrosomonas* has a shorter generation time and is able to increase quickly in number as compared to *Nitrobacter*. The difference in generation time between *Nitrosomonas* and *Nitrobacter* is responsible for the buildup of nitrite ions during unfavorable operational conditions including cold temperature, hydraulic washout, low dissolved oxygen level, toxicity and so on.

The activated sludge process must be operated with a proper sludge age which has been suggested to be 0.5-5.0 d (Junkins *et al.*, 1983) to maintain a strong population of nitrifying bacteria in the sludge (Forster, 2003). By increasing the sludge age or sludge retention time (SRT), washout of nitrifying bacteria is often avoided and the nitrite/nitrate removal efficiencies increase

(Jones & Sabra, 1980; Arquiaga *et al.*, 1993). Other conditions which are required to achieve nitrogen removal include an adequate hydraulic retention time (HRT) (Halling-Sorensen & Jorgensen, 1993), suitable dissolved oxygen (DO) tension (Jones & Sabra, 1980; Painter, 1986), pH (Jones & Sabra, 1980; Painter, 1986), temperature (Painter, 1986) and the level of inhibitors (Jones & Sabra, 1980; Painter, 1986). The effect of DO on rates of nitrification differs considerably in the literature reports, which probably due to environmental variability. Toerien *et al.* (1990) suggested that the optimal DO for nitrification to be between 2-3 mg/L. Others have confirmed that rates are independent of the DO levels above 1.0 mg/L for *Nitrosomonas* and 2.0 mg/L for *Nitrobacter* (Randall, 1992). Younos (1987) reported that the optimum temperature condition for nitrification usually falls between 24-35 ºC. In general, the activity of nitrifying bacteria increases by a factor of 2 for every 10 ºC rise above optimum temperature conditions. Nitrification has an optimum pH of between 7.0 and 8.2 (Antoniou *et al.*, 1990) or between 7.5 and 8.5 (Painter & Loveless, 1983). Nitrification is inhibited at a pH below 6.5 and above 10.0 (Downing *et al.*, 1964; Painter & Loveless, 1983).

1.3.1.2 Denitrification

Denitrification is a process in which nitrate can be converted via nitrite to gaseous nitrogen under low DO conditions (Robertson & Kuenen, 1992). Denitrification process removes nitrogen from wastewater in the following sequence (Gray, 2004):

$$NO_3^- \xrightarrow{reductase} NO_2^- \xrightarrow{reductase} NO \xrightarrow{reductase} N_2O \xrightarrow{reductase} N_2$$

Nitrate serves as the terminal electron acceptor and is converted to insoluble gases which escape to the atmosphere.

Denitrification can only proceed under anoxic conditions with the DO concentration < 2% saturation (Kiff, 1972), and when a suitable carbon source is available to act as an electron donor. The process is carried out by a wide range of facultative anaerobes, the most common genera are *Pseudomonas*, *Alcaligenes*, *Denitrobacillus*, *Micrococcus*, *Xanthomonas*, *Achromobacterium* and *Spirillum* (Painter, 1970; Tiedje, 1988). Denitrifying bacteria degrade organic carbon using nitrite ions and nitrate ions in the absence of free molecular oxygen to obtain energy for cellular activity and carbon for cellular synthesis (Gerardi, 2002).

The rate of denitrification is affected by nitrate/nitrite and carbon source concentrations, temperature and pH. The optimum pH is 7.0 with both the pH and alkalinity increasing as denitrification proceeds. Thus, about half of the alkalinity consumed during nitrification is replaced by denitrification. The optimum temperature is 25-30 ºC (Gray, 2004).

1.4   Adsorption Study

An adsorption study was conducted using PAC as the adsorbent in the landfill leachate. The adsorption capacity of PAC obtained in the adsorption study may not necessarily be applicable for the SBR system. An adsorption in the reactor would be more complicated due to the presence of activated sludge which can act as an adsorbent as well. In the presence of activated sludge,

PAC can be bioregenerated provided the adsorbate is biodegradable (Lee & Lim, 2005). Activated sludge has different adsorption affinity and capacity from PAC. Thus, the adsorption study could only provide a rough description of adsorption by PAC in the reactor.

The commonly used equilibrium adsorption models are the Langmuir, Freundlich and Brunauer, Emmett and Teller models. Langmuir and Freundlich models were selected to fit the data obtained in the adsorption study of PAC in landfill leachate.

1.4.1 Langmuir Model

The Langmuir isotherm was developed by Irving Langmuir in 1916. The basic idea behind the Langmuir model is monolayer adsorption. It is assumed that all surface sites are equivalent and can accommodate, at most, one adsorbed molecule. The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites. Molecules already adsorbed have a probability of desorbing. At equilibrium, equal numbers of molecules adsorb and desorb at any time. The Langmuir model is applicable when there is a strong specific interaction between the surface and the adsorbate so that a single adsorbed layer and no multilayer adsorption occurs. The Langmuir model is expressed as:

$$\frac{m}{x} = \frac{1}{Q_o} + \left(\frac{1}{bQ_o}\right)\frac{1}{C_e} \tag{1.4}$$

where,

x　　=　amount of adsorbate (mg).

m　　=　amount of adsorbent (g).

C_e　　=　concentration of adsorbate in the solution at equilibrium (mg/L).

Q_o　　=　amount of adsorbent required to cover the entire adsorbing surface with monomolecular layer. It is also known as maximum adsorption capacity (mg/g).

b　　=　Langmuir constant for the adsorption affinity between adsorbent and adsorbate (L/mg).

1.4.2　Freundlich Model

The Freundlich model is basically an empirical model and is valid for heterogeneous surfaces. The Freundlich equation can be expressed as:

$$\frac{x}{m} = K_f C_e^{1/n} \qquad (1.5)$$

where,

$\dfrac{x}{m}$　　=　amount of adsorbate per gram of adsorbent (mg/g).

C_e　　=　concentration of adsorbate in the solution at equilibrium (mg/L).

K_f　　=　constant, a relative measurement of adsorbent adsorption capacity by adsorbate $(mg/g)(L/mg)^{1/n}$.

n　　=　constant, affinity of interaction between adsorbate and adsorbent.

When 1/n=1, the reaction is linear and called "partitioning"; When 1/n<1, the adsorption is said to be "favourable" as the incremental change in amount sorbed decreases with increasing concentrations; While 1/n>1, the adsorption is

"unfavorable" because the reverse is true. Most natural adsorbents exhibit either linear or favorable adsorption. The Langmuir and Freundlich models for $1/n<1$, are concave downwards, so both models can be fitted to similar data.

1.5 Simultaneous Biodegradation and Adsorption Processes for Wastewater Treatment

Landfill leachate is a high strength wastewater which may contain non-biodegradable substrates and inhibitory constituents. Thus, biological treatment alone may not be sufficient since non-biodegradable substrate cannot be removed (Cecen & Cakiroglu, 2001). Certain difficulties have been encountered in the biomass growth and inhibition of nitrification in landfill leachate treatment. It has been reported that the refractory organics and heavy metals can often be removed by adsorption (Aktas & Cecen, 2001a).

1.5.1 Powdered Activated Carbon (PAC) as Adsorbent

To enhance the performance of the SBR system in treating the leachate, adsorbents have been added. Introduction of PAC into the activated sludge system is known as Powdered Activated Carbon Treatment (PACT) and was patented by du Pont Company. The PACT process involves simultaneous biodegradation and adsorption processes. The benefits of the PACT process over conventional activated sludge are as follows:

- Improvement of the removal of COD and BOD;
- Improvement of the stability to shock loads and toxic upsets;
- Enhancement of the removal of toxic substances and priority pollutants;
- Effective colour removal;

- Improvement of sludge settling and dewatering;

- Suppression of stripping of volatile organics;

- Less tendency to foam in aerator.

In the PACT system, the PAC particles are predominantly associated physically with the floc. The inhibitory species are concentrated in the floc, while the concentration in the bulk solution is reduced. Thus, PAC can stimulate biological activity by preventing the inhibitory substrates from exerting their toxic effect (Sublette *et al.*, 1982).

On the other hand, the biomass is in intimate contact with the wastewater to be treated, thus optimizing the conditions for enhanced biodegradation of pollutants. As the adsorbed material is biodegraded, it releases active sites on the carbon surface which allow further adsorption of substrate (Iwami *et al.*, 1992). The renewal of adsorptive capacity of activated carbon through the action of microorganisms is defined as bioregeneration (Sublette *et al.*, 1982).

Lim & Er (2000) used the PACT process under SBR operation to treat wastewater containing Acid Blue 25 (AR) and Basic Yellow 2 dyes (BR). The average COD and AR removal efficiencies were 89 and 93%, respectively, with PAC addition compared to 76 and 7%, respectively, without PAC addition. In the case of BR, the average removal efficiencies of COD and dye increased from 52 and 9% to 90 and 93%, respectively, with PAC addition.

Lim *et al.* (2002) used the PACT process to treat the copper and cadmium-containing synthetic wastewater. In the presence of 10 mg/L Cu(II) and 30 mg/L Cd(II) respectively, the average COD removal efficiencies were above 85% with the PAC dosage of 143 mg/L compared to around 60% without PAC addition.

Lee & Lim (2005) studied the extent of bioregeneration of PAC loaded with phenol, p-methylphenol, p-ethylphenol and p-isopropylphenol, respectively, in the simultaneous adsorption and biodegradation processes using oxygen uptake as a measure of substrate consumption. For the treatment of phenol and p-methylphenol in the SBR reactors, the effluent quality of COD ≤ 100 mg/L was achieved when the applied PAC dosage was 0.115 and 0.143 g PAC per cycle, respectively. When no further PAC was added, the treatment performance deteriorated to the case without PAC addition after 68 and 48 cycles of SBR operation, respectively, for phenol and p-methylphenol. Bioregeneration for phenol-loaded PAC was found to be greater than p-methylphenol-loaded PAC.

1.5.2 Chemically-Modified Rice Husk as Adsorbent

Rice husk is the by-product of the rice milling industry and is produced in large quantities as an agricultural waste, creating an environmental problem. Rice husk mainly comprised hemicellulose, lignin, cellulose and silica (20 wt %) (Low & Lee, 1997). The high silica content of rice husk makes it unsuitable as a feed for livestock and bestows very low fuel value. On the other hand, the presence of silica in the rice husk provides sufficient structural strength without

cross linking. Thus it has a potential as an adsorbent (Suemitsu *et al.*, 1986; Marshall *et al.*, 1993).

In recent decade, activated rice husk has been utilized by a number of researchers as an alternative adsorbent to the conventional activated carbon. Different methods were employed to chemically modify the rice husk. Lim *et al.* (2000) had treated wastewater containing copper and phenol respectively with two types of activated rice husk. The first one was prepared by treatment with concentrated nitric acid for 15 h at 60-65 ºC, whereas the other one was pyrolysed at 600 ºC for 5 h in a nitrogen atmosphere. Performance between the 2 types of activated rice husk was compared. Lee & Lim (2003) investigated the performance of activated rice husk as an adsorbent to treat wastewater containing phenol, p-methylphenol, p-ethylphenol and p-isopropylphenol. The rice husk was pyrolysed as described in Lim *et al.* (2000).

Qi *et al.* (2004) carbonized and activated the rice husk using sodium hydroxide and potassium hydroxide. The activated rice husk had cage-like structures and the specific surface area exceeded 2500 $m^2 g^{-1}$. The product was used to adsorb the phenolic compounds from aqueous medium. Yalcin & Sevinc (2000) carbonized and activated the rice husk by $ZnCl_2$ /CO_2 and other salt solutions /CO_2. The product had the specific surface area of 480 $m^2 g^{-1}$.

Rahman *et al.* (2000) activated the rice husk using merely HNO_3. The product was used to adsorb Zn^{2+} ions which are commonly found in industrial waste. Mmari *et al.* (1998) compared the adsorptive activity of pyrolysed and

treated pyrolysed rice husk on the Cu^{2+} ions. The treated pyrolysed rice husk was prepared by treating the pyrolysed rice husk with a mixture of 20% H_2SO_4 and 20% HNO_3. Low & Lee (1997) quaternized the rice husk with NaOH followed by N-(3-chloro-2-hydroxy-propyl)-trimethylammonium chloride and finally washed to pH 2 with diluted HCl. The quaternized rice husk was used as a sorbent for reactive dyes. Munaf & Zein (1997) activated the rice husk with 1% HCl and used it to remove the toxic metal from wastewater.

Despite the reported success of chemically-modified rice husk as an adsorbent, very little has been reported on the application of the activated rice husk in the PACT process to treat landfill leachate. In this study, the rice husk was activated with ethylenediamine which involved amination process. The proposed reaction postulated to have taken place is shown as follows:

$$S_h\text{-COOH} + H_2NCH_2CH_2NH_2 \longrightarrow S_h\text{-COHNCH}_2CH_2NH_2 + H_2O \quad (1.6)$$
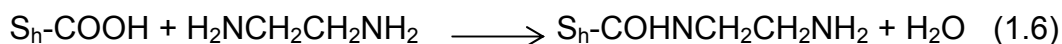
where S_h represents the surface of rice husk.

The activation process to produce ethylenediamine-modified rice husk (MRH) was believed to involve carboxyl groups on the rice husk. Upon reacting rice husk with ethylenediamine, the resultant husk contained primary amide and primary amines. The elemental analysis (CHN) showed that there was an increase in the nitrogen content of the sorbents thus confirming the introduction of nitrogen group to rice husk through amination process (Tang, 2001).

Ethylenediamine activation which is in the alkaline pH range was used instead of acid activation so that the nitrification and denitrification process in the SBR system would not be affected as nitrification is inhibited at pH below

6.5 (Section 1.3.1.1). In addition, ethylenediamine is a chelating agent with a bidentate ligand containing 2 amino groups. The bidentate ligand is crucial for chelation with metals and organic compounds (Tang, 2001). This will be useful for leachate treatment.

1.6   Bio-kinetic Models

Landfill leachate is a complex wastewater with various constituents, some of which may inhibit the removal of COD and nitrogen species. Thus preliminary evaluation of the kinetic data was conducted by employing the Halden and Edwards models using the *Matlab-Curve Fitting* program. However, the result from the evaluation showed relatively low correlation for both models. Therefore, the simpler first-order model was used.

1.6.1   Removal of COD

The rate of COD removal during the REACT period is assumed to follow the first-order kinetics as follows:

$$[COD]_t = [COD]_0 exp(-k_{COD}.t) \tag{1.7}$$

where,

$[COD]_t$ =   Concentration of COD at time t

$[COD]_0$ =   Initial concentration of COD during REACT period

k_{COD} =   Pseudo first-order rate constant for the removal of COD

t =   Time of reaction