HIBISCUS ROSA-SINENSIS LEAF AS COAGULANT IN WASTEWATER AND LEACHATE TREATMENTS

By

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LIST OF ABBREVIATIONS

Alum	Aluminium sulphate
BF	Breakage Factor
BOD	Biochemical Oxygen Demand
CA	Coagulation Activity
COD	Chemical Oxygen Demand
FAU	Formazin Attenuation Unit
FTIR	Fourier Transform Infrared
FTU	Formazin Turbidity Unit
HBaqs	Extract of *Hibiscus rosa-sinensis* leaves with water
HBpowd	Extract of *Hibiscus rosa-sinensis* leaves in powder formed with acid treated
IEP	Isoelectric Point
NH_3-N	Ammonia Nitrogen
PBLS	Pulau Burung Landfill Site
PZC	Point of Zero Charge
RE	Removal Percentage
RF	Recovery Factor
SF	Strength Factor
SP	Sediment Percentage
SS	Suspended Solid

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DAUN BUNGA RAYA SEBAGAI BAHAN PENGGUMPAL DALAM OLAHAN AIR SISA DAN LARUT LESAPAN

ABSTRAK

Penggunaan bahan penggumpal makromolekul semulajadi mempunyai masa depan yang cerah memandangkan sumbernya yang mudah diperolehi, murah, fungsi yang pelbagai dan kebolehrosotannya berbanding bahan penggumpal berasaskan kimia. Penggunaan daun *Bunga Raya* sebagai bahan pengumpal masih belum dibincangkan dalam literatur. Kajian ini mengkaji ekstrak bahan penggumpal karbohidrat menggunakan air (HBaqs) dan rawatan asid 'thioglycollic' (HBpowd) dari daun bunga raya, dan juga menguji sifat-sifat kimia ekstraknya (contoh, titik isoelektrik, berat molekul dan spektra dari Fourier Transform Infrared). Dikenali sebagai polimer yang bermolekul tinggi, HBaqs (183 kDa) and HBpowd (108 kDa) bertindak sebagai bahan penggumpal anion untuk mewujudkan mekanisme jambatan melalui kumpulan berfungsi yang utama, karboksil (C=O) dan hidroksil (OH). Kebolehan ekstrak daun bunga raya untuk berfungsi sebagai bahan penggumpal dan bahan pembantu penggumpal kepada alum, dinilai menggunakan larut lesapan dari Tapak Pelupusan Pulau Burung (TPPB) dan juga air sisa domestik dari kolam pengoksidaan Kampus Kejuruteraan, Universiti Sains Malaysia. Larut lesapan dari TPPB boleh dikategorikan sebagai larut lesapan yang stabil kerana mempunyai kepekatan nitrogen ammonia (NH_3-N) (2124 mg/L) dan keperluan oksigen kimia (COD) (2736 mg/L) yang tinggi. Sementara itu, boleh dikatakan, semua parameter yang diuji dalam air sisa domestik berada dibawah limit Piawaian B, Akta Kualiti Alam Sekitar, 1974, Peraturan 2009, Malaysia. Analisis Ujian Balang menjurus kepada aktiviti penggumpalan dan peratus penyingkiran, pepejal terampai (SS), kekeruhan, ferum, (Fe^{3+}), NH_3-N, COD dan warna. Selain itu, keadaan operasi semasa proses penggumpalan, kekuatan flok dan peratus enapcemar turut dikaji. Keputusan menunjukkan, 20 mg/L HBaqs pada pH 12 mencapai peratus penyingkiran paling tinggi untuk semua parameter dalam air sisa domestik, dan mampu menandingi alum dengan penyingkiran masing-masing, 74%, 98%, 35%, 59%, 87% dan 92% untuk SS, Fe^{3+}, NH_3-N, COD, kekeruhan dan warna pada nilai awal 38 mg/L, 1.68 mg/L, 8.75 mg/L, 203 mg/L, 63 FAU dan 182 PtCo. Sebagai perbandingan, 20 mg/L alum pada pH 6 hanya mampu menyingkirkan masing-masing 50%, 86%, 12%, 48%, 81% dan 40% untuk SS, Fe^{3+}, NH_3-N, COD, kekeruhan dan warna. Secara keseluruhannya, HBaqs dan HBpowd menunjukkan kadar penyingkiran yang rendah dalam sampel larut lesapan berbanding penggunaan 7000 mg/L alum pada pH 6. Walau bagaimanapun, pada kepekatan 2000 mg/L dan pH 10, HBaqs menghasilkan penyingkiran yang paling tinggi untuk NH_3-N dan kekeruhan (masing-masing, 54% dan 76%) berbanding alum (masing-masing, 25% dan 50% dengan nilai awal 2188 mg/L dan 303 FAU). Sebanyak 43% isipadu alum dapat dikurangkan dari dos optimum asal alum apabila, kombinasi dos HBaqs dan HBpowd yang digunakan adalah kurang dari 1000 mg/L, dimana kesan yang paling ketara terhadap penyingkiran Fe^{3+} dan faktor penyembuhan (RF) diperolehi. Purata penyingkiran Fe^{3+} (nilai awal, 2.69 mg/L) oleh alum sahaja pada dos 7000 mg/L dan 4000 mg/L adalah sekitar 65%, meningkat hampir 100% apabila kombinasi 1000 mg/L polimer dicampur dengan 7000 mg/L alum dan 500 mg/L polimer dicampur dengan 4000 mg/L alum digunakan. Selain itu, flok yang terbentuk hasil dari kombinasi 4000 mg/L alum dan 500 mg/L HBaqs menunjukkan kebolehan melawan 'shear' dengan mempunyai nilai faktor kekuatan (SF) yang tinggi, 114 berbanding alum sahaja, 87.

HIBISCUS ROSA-SINENSIS LEAF AS COAGULANT IN WASTEWATER AND LEACHATE TREATMENTS

ABSTRACT

Applications of natural macromolecular coagulants are having a bright future because of their abundant source, low price, multifunction and its biodegradibility as compared to conventional chemical-based coagulants. The use of extracts from *Hibiscus rosa-sinensis* leaves as coagulant has not been discussed in literature. This research determines water (HBaqs) and thioglycollic acid treated (HBpowd) extraction of carbohydrate coagulants from the leaves of *Hibiscus rosa-sinensis*, and examines its chemical characteristics (i.e. isoelectric point (IEP), molecular weight and Fourier Transform Infrared). Identified as polymers with high molecular weight, HBaqs (183 kDa) and HBpowd (108 kDa) act as anionic coagulants to promote bridging mechanism via main functional groups, carboxyl (C=O) and hydroxyl (OH). The ability of *Hibiscus rosa-sinensis* leaves extract to act as primary coagulant and coagulants aid in conjunction with alum was evaluated using the leachate collected from Pulau Burung Landfill Site (PBLS) as well as the domestic wastewater collected from oxidation pond of treatment plant in the Engineering Campus of Universiti Sains Malaysia. Leachate from PBLS could be classified as stabilized leachate by having a high concentraction of ammonia nitrogen (NH_3-N) (2124 mg/L) and chemical oxygen demand (COD) (2736 mg/L). Whilst, parameters tested in domestic wastewater was generally under the limits set in Standard B, Environmental Quality Act 1974, Regulation 2009, Malaysia. Jar test results were analyzed based on the coagulation activity and the removal percentage of suspended solids (SS), turbidity, iron (Fe^{3+}), NH_3-N, COD and colour. In addition, operating conditions during coagulation, floc strength and sediment percentage properties were also studied. Results revealed that 20 mg/L HBaqs at pH 12 achieved the highest removal of all parameters in the domestic wastewater and managed to suppress alum with 74%, 98%, 35%, 59%, 87% and 92% of SS, Fe^{3+}, NH_3-N, COD, turbidity and colour removal from its initial values of 38 mg/L, 1.68 mg/L, 8.75 mg/L, 203 mg/L, 63 FAU and 182 PtCo, respectively. In comparison, 20 mg/L alum at pH 6 had removed only 50%, 86%, 12%, 48%, 81% and 40% of SS, Fe^{3+}, NH_3-N, COD, turbidity and colour, respectively. Generally, HBaqs and HBpowd showed low removal rates for all parameter tested in leachate as compared to 7000 mg/L alum at pH 6. However, at 2000 mg/L and pH 10, HBaqs gave highest removal for NH_3-N and turbidity (54% and 76% with initial values of 2188 mg/L and 303 FAU, respectively) as compared to alum (25% and 50% reductions, respectively). A 43% reduction in the concentration of alum from its optimal dosage with doses of HBaqs and HBpowd below 1000 mg/L exhibited a synergic effect on Fe^{3+} (initial value, 2.69 mg/L) removal and recovery factors (RF). The average removal of Fe^{3+} using 7000 and 4000 mg/L alum as sole coagulant was around 65% and increased to nearly 100% when 1000 mg/L polymer was mixed with 7000 mg/L alum and 500 mg/L polymer was mixed with 4000 mg/L alum. Besides, flocs formed by 4000 mg/L alum mixed with 500 mg/L HBaqs also showed better ability to resist shear with the higher strength factor (SF) of 114 which was much higher than 87 for alum alone.

CHAPTER 1

INTRODUCTION

1.0 BACKGROUND OF THE STUDY

During the past several decades, the exponential population and social civilization growth, increasingly affluent lifestyle, continuing development of the industrial and technological sector has been accompanied by the rapid generation of municipal solid waste (MSW). Hence, it has created the most intransigent paradox around the world (Renou *et al.*, 2008; Foo and Hameed, 2009). Solid wastes that cannot otherwise be processed, and residues and other materials that are discarded after processing, are ultimately disposed via sanitary landfilling (Shekdar, 2009).

Compounds present in effluent and leachate could constitute a potential risk to the quality of receiving water bodies if it is not well treated prior to its discharge to the environment. Typically, high-strength wastewaters are characterized by the extreme values of pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), inorganic salts and toxicity (Oman and Hynning, 1993). In view of the above matter, a wide range of new tertiary treatment process has been abounded. Extensive work has focused on the enhanced coagulation-flocculation, clarification and biological processes (aerated lagoons, activated sludge, anaerobic filters, stabilization ponds etc.) for wastewater treatment (Foo and Hameed, 2009).

Highly polluted waters are both difficult and costly to treat. Although some communities in Malaysia are able to locate groundwater supplies or alternate less polluted surface sources within feasible pumping distance, the majority of nation's population draws water from nearby surface supplies. The challenge in waterworks operation is to process these waters into a safe and potable product acceptable for domestic use.

Aluminum salts are the most common synthetic coagulants used in water and wastewater treatment all over the world. However, recent studies have raised doubts on the advisability of introducing aluminum into the environment. Natural coagulants of vegetable and mineral origin were in use in water and wastewater treatment before the advent of synthetic chemicals like aluminum and ferric salts. Previous studies however, have not determined whether such natural coagulants are economically and environmentally more acceptable than chemical coagulants.

Since recently, there has been more interest in the subject of natural coagulants, especially to alleviate the problems of water and waste water treatment in developing countries. Natural macromolecular coagulants now, show bright future and are concerned by many researchers because of their abundant source, low price, multifunction and biodegradation (Zhang *et al.*, 2006). Encouraged by these facts, the author choose to test *Hibiscuc rosa-sinensis* leaves as natural coagulant in treating domestic wastewater and leachate via coagulation-flocculation process.

1.1 PROBLEM STATEMENT

Chemically enhanced wastewater treatment attracts substantial interest, especially for wastewater that is not amenable to treatment by conventional biological treatment strategies (Semerjian and Ayoub, 2003). Coagulation-flocculation is one of the employed chemical treatment options used for municipal wastewater and landfill leachate treatment. It helps to improve the quality of the treated effluent from treatment plant and also reduces the size, complexity and cost of secondary treatment in order to conform to environmental regulations and guidelines. In addition, coagulation-flocculation may be used successfully in treating stabilized and old landfill leachate. It has been employed as pre-treatment prior to biological or reverse osmosis step or as a final polishing treatment step in order to remove non-biodegradable organic compounds and heavy metals from landfill leachate (Renou *et al.*, 2008; Foo and Hameed, 2009).

Quite a number of researchers such as Aziz *et al.* (2007), Cheng (2002), Cheng *et al.* (2004), Duan and Gregory (2003) and Zouboulis *et al.* (2004) focused on coagulation-flocculation process using chemical based coagulants like alum and ferric salts. Reported studies mainly focused on the application of alum or ferric salts to treat leachate and synthetic wastewater consisting of humic acid, kaolin, dyes, phosphate and magnesium in combination or alone contributing to BOD_5, COD, colour, turbidity and SS.

However, there is not a great deal of published information on the application of natural coagulants for wastewater purification. The existing literature (Okuda *et al.*, 2001a and 2001b; Šćiban *et al.*, 2009; Anastasakis *et al.*, 2009, Beltrán-Heredia and Sánchez-Martín, 2009b) mostly tends to study the removals of SS and turbidity in synthetic water (as elucidated above), streams or river water sources, municipal effluent and dyes wastewater, but, no study has been carried out for the treatment of landfill leachate.

Several studies used synthetic polyelectrolytes as coagulant aid (Kam and Gregory, 2001; Zouboulis *et al.* 2004; Aguilar *et al.* 2005; Lee and Westerhoff, 2006). Unfortunately, not many studies using natural coagulant as coagulants aids has been documented. Hence, it is not easy to compare the efficiency of *Hibiscus rosa-sinensis* as a coagulant and to compare directly the results gained from other published works.

Natural coagulants of vegetable and mineral origin were used in water and wastewater treatment before the advent of inorganic coagulants. Unfortunately, existing studies do not give comprehensives facts whether such natural coagulants are economically and environmentally more acceptable than inorganic coagulants. Nowadays, natural coagulants are becoming a central focus of many researchers because of their abundant source, low price, multiple function, biodegradable qualities (Zhang *et al.* 2006) and wider effective dosage range for flocculation of various colloidal suspensions (Sanghi *et al.*, 2006). Natural coagulants also fit well in the previous definition of sustainability and accuracy for developing countries (Beltrán-Heredia *et al.*, 2009).

The importance of this study lies in ascertaining efficiency of a new natural coagulant in the treatment of wastewater with the hope that by using locally available material, the treatment cost could be reduced. Many developing countries could hardly afford the high cost of imported chemicals due to low availability of chemical coagulants. Apart from that, recent studies have also pointed out several serious drawback of using chemical coagulants.

For example, alum may cause Alzheimer's disease which is progressive brain disorder that gradually destroys a person's memory and ability to learn, respond, make judgments, communicate and carry out daily activities. Besides that, alum also affects the actual alkalinity present in the water leading to a reduction of pH. Thus, extra processes need to be done in order to fix the problem. Therefore, exploring an alternative natural coagulant will help in developing an economical, environmental friendly and safer method in water treatment.

The present study concentrates on leachate produced from a semi-aerobic Pulau Burung Landfill Site (PBLS) located in Seberang Perai, Penang and domestic wastewater collected from the oxidation pond in the Engineering Campus of Universiti Sains Malaysia. The study also focuses on the use of natural polymer extracts from *Hibiscus rosa-sinensis* leaves as primary coagulant and coagulant aid with alum as primary coagulant.

1.2 RESEARCH OBJECTIVES

The main objectives of this research could be summarized as below:

i. To characterize natural coagulant (HBaqs) and modified natural coagulant (HBpowd) based on isoelectric point (IEP), molecular weight and functional groups properties.

ii. To determine the optimum operating conditions based on rapid mixing time (T_R) and intensity (ω_R), slow mixing time (T_S) and intensity (ω_S) and settling time (T_{SET}) of HBaqs and HBpowd as sole coagulant to remove SS, Fe^{3+}, NH_3-N, COD, turbidity and colour from leachate and domestic wastewater samples.

iii. To determine the optimum pH and dosage of HBaqs and HBpowd as sole coagulant and coagulant aid in the presence of alum to remove SS, Fe^{3+}, NH_3-N, COD, turbidity and colour from leachate and domestic wastewater samples.

iv. To investigate the effects of HBaqs on floc strength and sediment percentage (SP) when used as coagulant aid.

1.3 SCOPE OF RESEARCH

This study mainly focuses on laboratory work as indicated below:

a) The performance of *Hibiscus rosa-sinensis* as coagulant and coagulant aid was determined by means of standard jar test in laboratory.

b) Only two types of wastewater sample were used which were leachate of PBLS and domestic wastewater of oxidation pond

c) Only Hibiscus leaves from Malvacea family namely *Hibiscus rosa-sinensis* were tested for coagulation efficiency.

d) Only SS, Fe^{3+}, NH_3-N, COD, turbidity and colour removal by alum, HBaqs and HBpowd were used as working parameters.

CHAPTER 2

WASTEWATER

2.0 INTRODUCTION

Generally, domestic or sanitary wastewater refers to liquid discharge from residences, business buildings and institutions. Whilst, industrial wastewater refers to discharge from manufacturing plants such as sanitary landfill leachate, metal finishing, automotive, steel industries, paint manufacturing and electronic industries. The term of municipal wastewater is applied to the industrial wastewater within municipal limits collected in domestic sewer in a municipal plant after pre-treatment. On the other hand, leachate refers to any contaminated liquid effluent percolating through deposited waste and emitted within a landfill or dump site through external source (Foo and Hameed, 2009).

In this chapter, only the general basic knowledge of processes that take place in a typical wastewater treatment plant and sanitary landfill leachate will be elucidated and summarized. The complete processes are far more complicated and require further study. Hence, these will not be discussed here since the main concern of this study is basically on coagulation and flocculation which is only a part of the whole processes.

2.1 SANITARY LANDFILL LEACHATE

2.1.1 Landfills

Sanitary landfills are recognized as the most common and desirable integral indispensable solid waste management strategy for sustainable disposal and elimination of residue wastes from separation, recycling and incineration, both in fully industrialized and developing countries in terms of its simplicity as well as the low exploitation and capital costs (Foo and Hameed, 2009). Besides its economic advantages, landfilling minimizes environmental issues and other inconveniences (Renou *et al.*, 2008) and it also allows most solid wastes to be decomposed under controlled conditions until their eventual transformation into relatively inert, stabilized materials (Tatsi and Zouboulis, 2002).

Landfill sites are classified into 5 types; anaerobic landfill, anaerobic sanitary landfill, improved anaerobic sanitary landfill, semi-aerobic landfill and aerobic landfill. In Malaysia, various components of solid waste management services have been privatized (Shekdar, 2009) in order to impose the possibility of upgrading landfill level.

2.1.2 Leachate

Leachate can be defined as any contaminated aqueous effluent generated as a consequence of rainwater percolation through deposited waste, biochemical processes in waste's cells and the inherent water content of waste themselves (Renou *et al.*, 2008). More precisely, it constitutes of soluble organic and mineral compounds formed when water infiltrates (*I*) into the refuse layers (Figure 2.1). The infiltrating water extracts a series of contaminants and instigates a complex interplay between the hydrological and biogeochemical reactions that act as a mass transfer mechanisms for producing moisture content sufficiently high to initiate the liquid flow (Aziz *et al.*, 2004; Foo and Hameed, 2009).

Production of leachate is induced by the gravity force, precipitation (*P*), irrigation, surface runoff (R_{int}, R_{ext}), rainfall, snowmelt, recirculation, liquid waste co-disposal, refuse decomposition, groundwater intrusion and initial moisture content present within the landfills (Renou *et al.*, 2008; Foo and Hameed, 2009). Landfilling technique (waterproof covers, liner requirements such as clay, geotextiles and/or plastics) remains primordial to control the quantity of water entering the tip and so, to reduce the threat of pollution. The climate has also a great influence on leachate production because it affects the input of precipitation (*P*) and losses through evaporation (EV) (Renou *et al.*, 2008).

Depending upon the nature of the waste (water content) and its degree of compaction into the tip, the production of leachate is generally greater whenever the waste is less compacted since compaction reduces the filtration rate (Lema *et al.*, 1988; Renou *et al.*, 2008). Usually, leachate is produced mainly due to the infiltration of rainwater through the refuse tips (Tatsi and Zouboulis, 2002).

The two factors characterizing leachate are the volumetric flow rate and the chemical composition (Tatsi and Zouboulis, 2002; Renou *et al.*, 2008) as showed in Figure 2.1. The variation of leachate characteristics were attributed to a number of factors such as, precipitation, waste type and composition (depending on the standard of living of the surrounding population, structure of the tip), hydrogeology of landfill site, the quality of refuse, specific climate conditions, moisture routing through the landfill and in particular, the age of the landfill (Trebouet *et al.*, 2001; Tatsi *et al.*, 2003; Renou *et al.*, 2008).

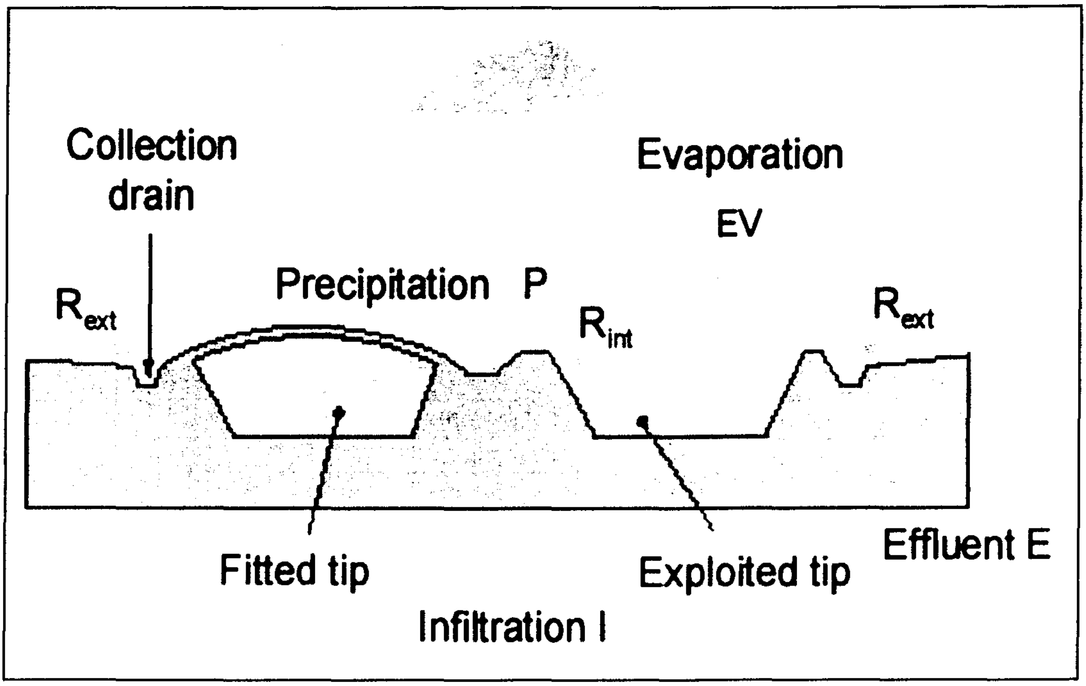

Figure 2.1: Water cycle in a sanitary landfill (Renou *et al.*, 2008).

As a landfill becomes older, there is a shift from a relatively shorter initial aerobic period to a longer anaerobic decomposition period, which has two distinct sub-phases i.e. an acidic phase followed by a methanogenic phase (Tatsi *et al.*, 2003). Basically, the characteristics of the landfill leachate can be best represented by COD, BOD_5, total organic carbon (TOC), BOD_5/COD ratio, pH, SS, NH_3-N, total Kjeldahl nitrogen (TKN), bacterial count, turbidity or heavy metals content which are critical to predict future trends of leachate quality and the design and operation of leachate management facilities (Foo and Hameed, 2009).

Table 2.1: Classification of landfill leachate according to the composition changes (Chian and DeWalle, 1976; Foo and Hameed, 2009).

Parameters	Type of Leachate		
	Young	Intermediate	Stabilized
Age (years)	<5	5 - 10	>10
pH	6.5	6.5-7.5	>7.5
COD (mg/L)	>10 000	4000-10 000	<4000
BOD_5/COD	>0.3	0.1-0.3	<0.1
Organic compounds	80% volatile fat acids (VFA)	5-30% VFA + humic and fulvic acids	Humic and fulvic acids
Ammonia nitrogen (mg/L)	<400	NA	>400
TOC/COD	<0.3	0.3-0.5	>0.5
Kjeldahl nitrogen (g/L)	0.1-0.2	N.A	N.A
Heavy metals (mg/L)	Low to medium	Low	Low
Biodegradability	Important	Medium	Low

Although leachate composition may vary widely within the successive aerobic, acetogenic, methanogenic, stabilization stages of the waste evolution, three types of leachates have been defined according to the age of a landfill which are young, intermediate and stabilized (Table 2.1). The leachate obtained from Pulau Burung Landfill Site (PBLS) was termed as stabilized leachate. The existing relation between the age of a landfill and the organic matter composition may provide useful criteria to choose a suitable treatment process.

2.1.3 Landfill leachate treatment technology

Leachate production and management is now recognized as one of the greatest problems associated with environmentally sound operation of a sanitary landfill (Tatsi and Zouboulis, 2002). The discharge of landfill leachate can lead to serious environmental problems as it may percolate through soils and sub soils causing extensive pollution of ground and surface waters if not properly treated and safely disposed. Hence, it should be adequately treated prior to its discharge to surface waters (Amuda, 2006).

The conventional treatments of leachate include leachate transfer (combined treatment with domestic sewage and recycling), physical/chemical process and biological treatment. Combined treatment of leachate with domestic sewage has been increasingly questioned due to the presence of organic inhibitory compounds with low biodegradability and heavy metals that may reduce treatment efficiency and increase the effluent concentration. Although positive effects have been reported from recycling leachate back through the tips, this approach also had some negatives effects such as high concentration of organic acids.

Hence, to overcome this problem, physical/chemical and biological treatment processes may be the best options in spite of their relatively higher operational costs as compared to other techniques such as leachate transfer. Biological processes are considerably effective for younger leachates (containing mainly volatile fatty acids), but less efficient for the treatment of stabilized leachates (Amokrane *et al.*, 1997). Reliability, simplicity and high cost-effectiveness of biological treatment (suspended/attached growth) causes it to be commonly used for the removal of the bulk of leachate containing high concentrations of BOD_5. Biodegradation is carried out by microorganism under aerobic or anaerobic conditions.

When treating young (biodegradable) leachate, biological techniques can yield a reasonable treatment performance with respect to COD and NH_3-N. Whilst, when treating stabilized (less biodegradable) leachate, biological treatment may not be able to achieve the permitted maximum COD levels for direct or indirect discharges due to recalcitrant characteristics of organic carbon in leachate (Kurniawan *et al.*, 2006a; Renou *et al.*, 2008; Foo and Hameed, 2009). Thus, some pre-treatment studies have been carried out by various researchers to improve the effectiveness of leachate treatment.

Physical/chemical treatment has been found to be suitable not only for the removal of refractory substances from stabilized leachate, but also as a refining step for biologically treated leachate. Numerous research studies on the treatment of stabilized leachate using different types of physical/chemical treatments likes flotation, coagulation-flocculation, chemical precipitation, adsorption, chemical oxidation and air stripping (Kurniawan *et al.*, 2006a; Renou *et al.*, 2008; Foo and Hameed, 2009) have been found in literature. Coagulation and flocculation are widely used in water and wastewater treatment due to their capability of removing high concentration organic pollutants (Wang *et al.*, 2002), heavy metals and some anions.

Tatsi *et al.* (2003) had emphasized coagulation-flocculation as a pre-treatment method for fresh leachate or as a post-treatment technique for partially stabilized leachate. To reduce the high fouling power of landfill leachate, Amokrane *et al.* (1997) studied coagulation–flocculation as a pre-treatment prior to biological or reverse osmosis, or as a final polishing treatment step in order to remove non-biodegradable organic compounds and heavy metals from landfill leachate. This technique facilitated the removal of colloidal particles from a solution by means of pH adjustment, mixing intensity and time, and addition of coagulants.

The application of coagulation to stabilized leachates (pH: 8.3, Turbidity: 432 NTU, Colour: 5537 PtCo units, COD: 4814 mg/L, BOD_5: 670) generated at the central landfill of Asturias was investigated by Castrillón *et al.* (2010). The optimum working pH was around 5.2 for ferric chloride and approximately 6.0 for aluminium sulphate without initial pH adjustment in the later case. The optimum dosages were 1700 mg/L ferric chloride and 3200 mg/L aluminium sulphate. In this case, the best results were obtained using ferric chloride, where 73%, 97.6% and 100% removals of COD, colour and turbidity were achieved, respectively. The respective removals of COD, colour and turbidity were 59.9%, 95.4% and 91.6% when aluminum was used as coagulant.

In addition, Palaniandy *et al.* (2010) claimed that the application of dissolved air flotation (DAF) in stabilized landfill leachate treatment showed a very distinctive result with and without alum coagulation. In the case of DAF without coagulation, only 36%, 33%, and 32% of colour, COD, and turbidity were removed, respectively. However, by applying coagulation followed by DAF, maximum removals of colour, COD, and turbidity were 70%, 79% and 42%, respectively. These results were obtained using 2.3 g/L alum, a pressure of 400 kPa, a flow rate of 6 L/min, an injection time of 4 min, and a retention time of 20 min.

The application of combined filtration and coagulation for stabilized leachate was investigated by Daud *et al.* (2009). Coagulation of semi-aerobic leachate from PBLS by adding 2000 mg/L PAC or 9000 mg/L aluminum sulphate led to maximum removal of colour (93% and 92%) and COD (56% and 46%). Results also demonstrated that filtration by a mixture of limestone–zeolite (15 : 25 ratio by volume) and limestone–GAC (15 : 25 ratio by volume) followed by coagulation at an optimum dosage of 800 mg/L PAC was efficient to reduce colour (98% and 99%) and COD (70% and 86%), respectively.

The integrated chemical-physical-biological processes (whatever the order used) ameliorates the drawbacks of the individual process, contributing to a higher efficacy of the overall treatment. With increasingly stringent discharge standards and the ageing of landfill sites (more stabilized leachate produced), a wide range of new tertiary treatment processes namely membrane technology, microfiltration, ultrafiltration, membrane bioreactors, nanofiltration and reverse osmosis has been introduced for the treatment of landfill leachate (Kurniawan *et al.*, 2006a; Renou *et al.*, 2008; Foo and Hameed, 2009).

Discharge of leachate from a landfill shall meet the standard requirements of the Environmental Quality Act 1974 and the limits set by the Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009, as presented in Table 2.2 (only parameters tested in this study are listed).

Table 2.2: Acceptable conditions for discharge of leachate as set by the Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009, under the Environment Quality Act, 1974.

Parameter	Unit	Standard
Temperature	°C	40
pH	-	6-9
COD	mg/L	400
SS	mg/L	50
NH_3-N	mg/L	5
Iron	mg/L	5
Colour	*ADMI	100

* ADMI: American Dye Manufactured Institute

2.2 DOMESTIC WASTEWATER EFFLUENT

2.2.1 Domestic wastewater collection system

The volume of wastewater generated by a community varies from 50 to 250 gal per capita per day (gpcd) depending on sewer uses (Hammer and Mark, 2004; WEF, 2008). In Malaysia, value for domestic wastewater flow was 225 gpcd. Where, the organic matter contributed per person per day in wastewater was approximately 68 g of SS and 55 g of BOD_5 (Aziz, 1999)

Domestic wastewater is collected in underground pipes which are called 'sewers'. The sewer or collection system is a network of pipes, conduits, tunnels, equipment and appurtenances used to collect, transport and pump wastewater. The wastewater flows through a network via conventional gravity sewers, which are designed in such a way that each pipe's size and slope will maintain flow towards the discharge point without a pump. Lift stations are used to move wastewater from lower to higher elevations (WEF, 2008).

There are three principal types of municipal sewers; sanitary sewers, storm sewers and combined sewers. Storm sewers convey stormwater runoff and other drainage. Today, municipalities rarely construct combined sewers and most have made efforts to separate stormwater from sanitary wastewater. Stormwater was conveyed to the nearest watercourse for discharge without treatment (Hammer and mark, 2004; WEF, 2008). In cities where the existing drainage systems cannot be easily upgraded, combined sewer overflow (CSO) can be controlled by storing the excess flows in retention basins for later redistribution to the combined sewer and to the wastewater treatment plant (Samrani *et al.*, 2008).

2.2.2 Wastewater treatment plant process

Conventional wastewater treatment is a combination of physical and biological processes designed to remove organic matter from solution (Hammer and Mark, 2004). Upon reaching the plant, wastewater first encounters preliminary treatment to remove the majority of SS, followed by secondary treatment to degrade the biodegradable dissolved organics and nitrogen, and perhaps advanced or tertiary treatment to remove most of the remaining organic and inorganic solids and pathogenic microorganisms (Shon *et al*, 2005) as showed in Figure 2.2.

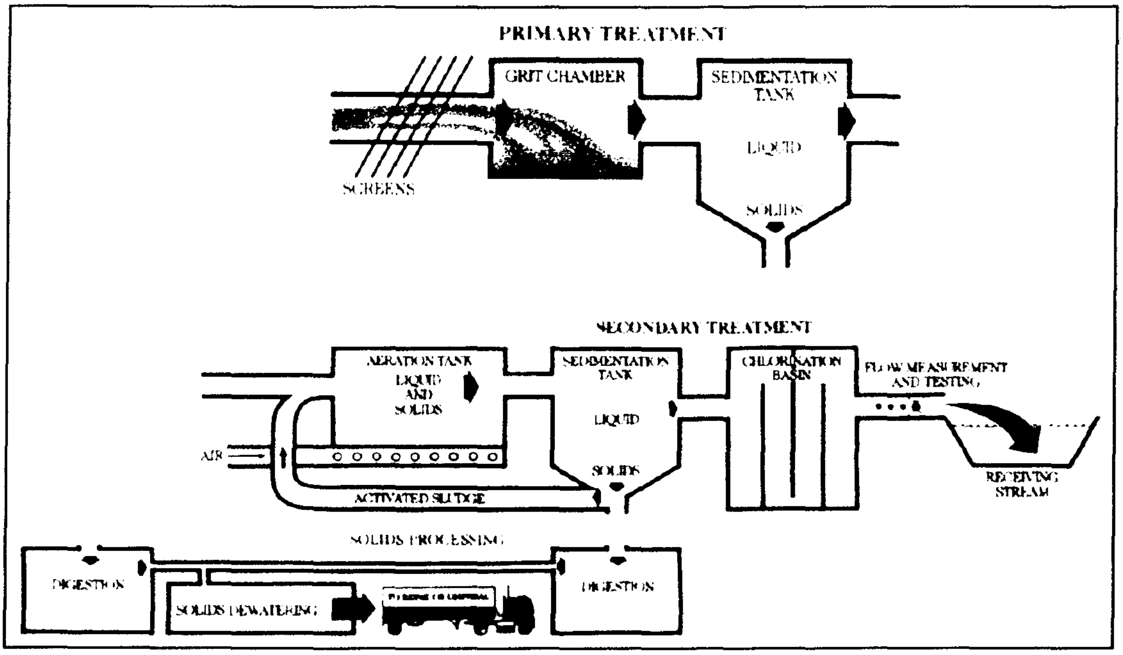

Figure 2.2: Typical schematic of a conventional municipal wastewater treatment plant (New York State Department of Environmental Conservation (NYSDEC) *et al.*, 2007).

Preliminary treatment basically begins with removing materials such as wood, cardboard, rags, plastic, grit, grease and scum. The purpose of this phase is to reduce the treatment load on the main plant as much as possible and to reduce wear and tear that might damage the plant headwork or impair downstream operations. These materials may be removed via chemical addition, pre-aeration, bar racks, screens, shredding devices or grit chambers.

Secondary treatment is a biological treatment process used to stabilize the dissolved solids. Microorganisms (e.g., bacteria) feed on the organic solids (food) in the wastewater and convert the organics into a cellular or biological mass that can later be removed. These biological processes are aerobic processes. Oxygen must be provided for these aerobic organisms to work properly and efficiently. An integral part of secondary treatment processes is another set of settling tanks or clarifiers. These secondary clarifiers (final clarifiers) remove the biological mass that has grown during biological treatment (NSYDEC *et al.*, 2007).

There are many different types of secondary processes that can be employed in secondary treatment such as conventional activated sludge and sequential batch reactor (SBR). SBR is different from conventional activated sludge system since it uses the aeration tank as a settling tank. In activated sludge treatment, the wastewater is mixed with organisms that are returned from the secondary clarifiers. In the aeration tank, oxygen is provided either by blowers and diffusers or by a mechanical mixing process. Lagoon systems and fixed film processes are also a form of biological or secondary treatment.

The treated wastewater is referred to as effluent. The effluent is discharged to a water body such as lake, river, stream, or groundwater (NSYDEC *et al.*, 2007). The effluents obtained are generally of good quality and can be used for irrigation of some crops (Goren *et al.*, 2008). An uncontrolled release of unproperly treated wastewater would degrade the water, land and air, which is where life are dependent upon (NSYDEC *et al.*, 2007).

Optional tertiary treatment upgrades the quality of secondary effluents to the unrestricted irrigation level, which is often performed by a sequence of coagulation-flocculation, filtration, membrane separation (microfiltration and ultrafiltration) and disinfection (Shon *et al.*, 2005; Fuchs *et al.*, 2006; Goren *et al.*, 2008). Shon *et al.* (2005) observed that pre-treatment by flocculation (with optimum $FeCl_3$ dose of 68 mg/L) has removed 75% of DOC, which led to only 9.6% additional DOC removal by ultrafiltration (UF) as post treatment. On the other hand, a partial $FeCl_3$ dose of 20mg/L removed only 34% DOC while the UF removed another 48%.

Fuchs *et al.* (2006) tried to compare the fouling behaviour during dead end membrane filtration of raw and flocculated wastewaters, and claimed that the effect of pre-flocculation was two-fold. Firstly, it decreased the resistance of the filter cake and secondly the filter cake was more easily removed during backflush which reduced the accumulation of particles on the membrane surface. However, it was demonstrated that no optimal concentration of the flocculent existed and the reduction of the fouling index occurred with higher flocculent additions.

Optimization of alum coagulation-flocculation for COD and TSS removal from wastewater collected from 4 wastewater treatment plants and a pilot plant was investigated at the University laboratory (Naples, Italy) to meet the Italian water quality discharge limits (Guida *et al.*, 2007). The jar test experiments provided evidence that the coagulation process could not provide sufficient COD removal efficiency in the

Cuma and the laboratory wastewater pilot plant even at an alum dosage of 450 mg/L. Wastewater treatment by coagulation using 150 mg/L alum at Nola and S. Giovanni plants was sufficient to meet COD (<160 mg/L) and TSS (80 mg/L) limits. The highest COD removal (80%) was obtained at pH 6.0–8.0 at the Nola plant. However, COD removal was lower in the Marcianese plant wastewater although its initial COD value was the same as the Nola plant wastewater. Nevertheless, COD removal of the University plant improved from 55 to 75–85% in parallel to TSS removals with the increasing pH (up to 8.0).

Solids that settle out in the primary and secondary clarifiers are referred as sludge. Sludge from biological treatment processes (e.g., activated sludge) is referred as biosolids. Proper handling of solids is of paramount importance to avoid health effects, odour problems and (NSYDEC *et al.*, 2007) the appearance of filamentous bulking due to poor activated sludge separation. The term bulking is defined as the phenomenon in which the activated sludge tends to be bulky, e.g. its density decreases as a consequence of the overa bundance of filamentous bacteria. The result is a higher risk of a loss of solids with the final effluent due to deterioration in both settling velocity and compaction of the activated sludge (Alsina *et al.*, 2009).

The government has developed a comprehensive set of laws and regulations for treating and disposing of wastewater and sludge. In Malaysia, the effluent quality of any discharge from a sewage treatment process to inland waters (other than those having an ocean outlet) shall meet the minimum requirements of the Environmental Quality Act 1974 and the limits set by the Environmental Quality (Sewage) Regulations 2009 as presented in Table 2.3 (only parameters tested in this study are listed).

Table 2.3: Acceptable conditions of sewage discharge of Standard A and B of Environmental Quality (Sewage) Regulations 2009, under the Environmental Quality Act 1974.

Parameter	Unit	Standard	
		A	B
Temperature	°C	40	40
pH	-	6.0 -9.0	5.5 - 9.0
COD	mg/L	120	200
SS	mg/L	50	100
NH_3-N (enclosed water body)	mg/L	5	5
NH_3-N (river)		10	20

2.3 CHARACTERISTICS OF WASTEWATER

One of the challenges in wastewater treatment is the continuous change in the volume and the physical, chemical and biological characteristics of wastewater. Some changes are temporary as a result of seasonal, monthly, weekly or daily fluctuations in the wastewater volume and composition. Other changes are long-term due to alterations in local populations, social characteristics, economies and industrial production or technology (WEF, 2008). Hence, for the design of efficient system, it is necessary to determine characteristics of the wastewater to be processed.

2.3.1 Turbidity

Turbidity is an optical property of water that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. It is caused by the molecules of water itself, dissolved substances, and organic and inorganic suspended matter (Thackston and Palermo, 2000). Turbidity particles can be waterborne pathogens or particles harboring them. The lower the turbidity, the less is the amount of the particulate matter (Sarai, 2006). The ability of a particle to scatter light depends on the size, shape, and relative refractive index of the particle and on the wavelength of the light (Barnes *et al.*, 1986).

Therefore, two samples with equal SS concentrations but different size distributions of particles will produce very different turbidity readings on the same nephelometer (Thackston and Palermo 2000). Hence, there is not a universal relationship between measured turbidity and the amount of material suspended in the water, although for specific samples there may be proportionality between turbidity and SS concentration (Barnes *et al.*, 1986).

2.3.2 Colour

Colour in water means that the water will absorb light energy in the visual spectral range, i.e. from 400 to700 nm (Tebbutt, 1983). Particles in suspension confuse the determination of colour because light is absorbed and scattered by the particles. True colour is determined on samples which have low turbidity or have been filtered (apparent colour can be removed by filtration) (Barnes *et al.*, 1986). True colour of water is considered to be only that attributable to substances in solution after removal of suspended material by centrifuging or filtration (Hammer and Mark, 2004).

It is well accepted that the colouring of wastewater is mainly caused by humic acid (Section 3.2.1.1). Humic acid is a natural organic matter resulting from the weathering and/or biodegradation of dead plants and animals (Cheng and Chi, 2002). According to Aziz *et al.* (2007), colour in landfill leachate was mainly contributed by organic matter with some insoluble forms that exhibited turbidity and SS readings. The decomposition of organic matter like humic acid causes the water to be yellow, brown or black

(Zouboulis *et al.*, 2004). Whereas, Méndez-Novelo *et al.* (2005) claimed that colouring of landfill leachate was mainly caused by colloidal particles of small diameter (<10 μm) while particles with larger diameter, colloidal or not, are responsible for turbidity.

Study by Sanghi et al. (2006) claimed that decolorization of dye solutions by coagulation method depended on the type of dye, pH and coagulant dosage. Color removal in the alkaline pH (9 to 9.5) by Poly-aluminum chloride (PAC) is presumably due to adsorption onto hydroxide flocs. In combination with a very low dose of (PAC), guar gum (GG) effectively decolorized 87% of Acid Sandolan Red (ASR).

2.3.3 Ammonium nitrogen, NH_3-N

Nitrogen exists in the form of organic nitrogen (nitrogen in the form of proteins, amino acids and urea), ammonia nitrogen (nitrogen as ammonium salts e.g. $(NH_4)_2CO_3$ or as free ammonia), in the oxidized form, nitrate (NO_3^-) and to lesser extent, nitrite (NO_2^-) (Barnes *et al.*, 1986) which can end up in lakes, rivers and drinking water reservoirs with effluent discharges. Ammonium is predominant at any pH less than 7. Unionized or free ammonia in concentrations above 0.2 mg/L has been shown to be fatal to several species of fish. Ammonia toxicity should not be a problem in receiving waters with pH below 8 and ammonia nitrogen concentrations less than about 1 mg/L^3 (Cheremisinoff, 1996).

Generally, ammonia nitrogen can be removed or decomposed by several methods such as air-stripping, biological denitrification, breakpoint chlorination, chemical precipitation with magnesium ammonium phosphate (Struvite,$MgNH_4PO_4 \cdot 6H_2O$), electrochemical conversion and microwave radiation (Renaou *et al.*, 2008). The ammonia stripping reaction is showed in Equation 2.1 (Davis and Cornwell, 2008).

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O \qquad \text{(Equation 2.1)}$$

Each method had their owned advantages and disadvantages. For example, even though air-stripping was the most common method for eliminating high concentration of ammonia nitrogen, apart from that, contaminated gas phase, NH_3 was also produced. The gas needs to be treated/adsorbed with either H_2SO_4 or HCl properly, and hence it will be costly (Renaou *et al.*, 2008). Whilst, biological denitrification method only suitable for removal of ammonia at relatively low concentraction (Carrera *et al.*, 2003).

It had been found that higher pH, 11 were favorable for the removal/volatilization of 98% ammonia (NH_3) by microwave (MV) radiation (Lin *et al.*, 2009). Removal of NH_3 rapidly increased as the solution pH (11 to 13) was further increased. This was in conjuction with result obtained by Kim *et al.* (2006) on electrochemical conversion characteristic of ammonia to nitrogen at the IrO_2 anodes of a divided cell without a membrane. Via this method, water discharge producing OH radicals (Comninellis, 1994) generated at the electrode surface under the oxygen evolution, help to decomposed nitrogen via oxidation process (Kim *et al.*, 2006).

2.3.4 Oxygen demand

Organic compounds are generally unstable and may oxidize biologically or chemically to stable, relatively inert form with the end product such as CO_2, NO_3, H_2O. An indication of the organic content of a waste can be obtained by measuring the