POTENTIAL OF NATURAL CLAY DERIVED FUNCTIONALIZED ADSORBENTS FOR EFFECTIVE REMEDIATION OF SANITARY LANDFILL LEACHATE

by

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LIST OF ABBREVIATIONS

AOP	Advanced Oxidation Processes
API	Active Pharmaceutical Ingredients
DFT	Density Functional Theory
DOE	Department of Environment
EB	Electron Beam
EU	European Union
HRT	Hydraulic Retention Time
IUPAC	International Union of Pure and Applied Chemistry
LFG	Landfill Gasses
MOH	Ministry of Health
MHLG	Ministry of Housing and Local Government
MSW	Municipal Solid Waste
PBLS	Pulau Burung Landfill Site
PZC	Point of Zero Charge
SVI	Sludge Volume Index
UK	United Kingdom
UN	United Nations
USEPA	United States Environmental Protection Agency
VFA	Volatile fatty acids
VOC	Volatile Organic Compound

LIST OF SYMBOLS

q_e	Amount of adsorbate in the adsorbent at equilibrium (mg/g)
Q_o	Maximum monolayer capacity (mg/g)
b	Langmuir isotherm constant (dm^3/mg)
C_e	Equilibrium concentration (mg/L)
K_F	Freundlich isotherm constant (mg/g) $(dm^3/g)^n$ related to adsorbtion capacity
T	Temperature (K)
A_T	Tempkin isotherm equilibrium binding constant (L/g)
R	Universal gas constant 8.314 J/mol K
q_t	Amount of adsorbate in the adsorbent at time t, mg/g
k_1	Pseudo first order kinetic model rate constant, min^{-1}
k_2	Pseudo second order kinetic model rate constant, min^{-1}
ΔG_{ads}	Gibb`s free energy
ΔS_{ads}	Adsorption entropy
ΔH_{ads}	Adsorption enthalpy
q_{exp} (mg/g)	Equilibrium uptake experimentally
q_{cal}	Equilibrium uptake theoretically
$q_{m.exp}$	Average q_{exp} (mg/g)

POTENSI TANAH LIAT ASLI DIPEROLEHI MEMFUNGSIONALISASIKAN ADSORBEN UNTUK PEMULIHAN BERKESAN LARUT RESAP TAPAK PELUPUSAN SAMPAH SANITARI

ABSTRAK

Kajian ini dijalankan untuk mengkaji proses penyediaan adsorben semulajadi berasaskan tanah liat melalui pengubahsuaian asid untuk penjerapan permintaan kimia oksigen (COD) dan amonikal nitrogen dari tapak pelupusan sampah semi-aerobik. Kesan dos adsorben, masa sentuhan dan pH kepada proses penjerapan telah dinilai. Keputusan eksperimen menunjukkan penyingkiran serapan kepada COD dan amonikal nitrogen meningkat dengan bertambahnya dos adsorben dan masa sentuhan dengan penyingkiran serapan kepada COD dan amonikal nitrogen, masing-masing 71.93% dan 68.94%, pada dos adsorben 4.5 g/200 mL dan pH 7. Data eksperimen dianalisis dengan menggunakan dua model isoterma, iaitu model isoterma Langmuir dan Freundlich. Data keseimbangan penjerapan adalah bersesuaian dengan model isoterma Langmuir, dengan kapasiti penjerapan lapisan mono kepada COD dan amonikal nitrogen, masing-masing pada 89.17 mg/g dan 151.60 mg/g. Penjerapan kinetik teleh diuji dengan menggunakan model kinetik pseudo-tertib pertama dan pseudo-tertib kedua. Model kinetik pseudo-tertib kedua telah memberikan gambaran yang terbaik bagi penjerapan COD dan amonikal nitrogen terhadap asid-diaktifkan tanah liat semula jadi, dengan pekali kolerasi, R^2 bagi COD dan amonikal nitrogen, masing-masing pada 0.998 dan 0.997. Keputusan menunjukkan bahawa adsorben yang disediakan berasaskan tanah liat adalah sangat sesuai untuk pemulihan yang berkesan bagi larut resap tapak pelupusan sampah sanitari.

POTENTIAL OF NATURAL CLAY DERIVED FUNCTIONALIZED ADSORBENTS FOR EFFECTIVE REMEDIATION OF SANITARY LANDFILL LEACHATE

ABSTRACT

This study investigated the preparation of natural based adsorbent clay via acid modification for the adsorptive removal of chemical oxygen demand (COD) and ammonical nitrogen from the semi-aerobic sanitary landfill leachate. The effect of adsorbent dosage, contact time and pH on the adsorption process were evaluated. The experimental results manifested that the adsorptive removal of COD and ammonical nitrogen increased with increasing the adsorbent dosage and contact time, recorded the adsorptive removal of COD and ammonical nitrogen of 71.93% and 68.94%, respectively, at the adsorbent dosage of 4.5 g/200 mL and pH 7. The experimental data were modelled using two isotherm models, namely Langmuir and Freundlich isotherm models. The adsorption equilibrium data were favourably fitted to the Langmuir isotherm model, with a maximum monolayer adsorption capacity for COD and ammonical nitrogen of 89.17 mg/g and 151.60 mg/g, respectively. The adsorption kinetic was tested using pseudo-first-order and pseudo-second-order kinetic models. The pseudo-second-order kinetic model was best described the adsorption of COD and ammonical nitrogen onto the acid-activated natural clay, with the coefficients of correlation, R^2 for COD and ammonical nitrogen of 0.998 and 0.997, respectively. The result demonstrated that the prepared clay based adsorbent is highly feasible for the effective remediation of sanitary landfill leachate.

CHAPTER ONE

INTRODUCTION

1.1 The scenario of landfill leachate generation in Malaysia

Malaysia is a tropical country situated in the central part of Southeast Asia with a total landmass of 329,847 km^2. It lies between the longitudes 100^o and 120^o east and latitudes formed by the Equator and 7^o north. The country is separated into two regions – West Malaysia and East Malaysia – by the South China Sea. West Malaysia is the Peninsular, which comprises 11 states. East Malaysia comprises the two states of Sabah and Sarawak, which are situated on the Island of Borneo. Malaysia is well-endowed with natural resources in areas such as agriculture, forestry, and minerals. Its economy was once exclusively based on agricultural commodities, and now it is still one of the world's largest producers of rubber, tin, palm oil, timber, and pepper. However, the current government has aspired to shift the economy to manufacturing and service based industries (Latifah *et al.*, 2009).

Municipal Solid Waste (MSW) is generated by households, commercial activities and other sources whose activities are similar to those of households and commercial enterprises, for example, wastes from offices, hotels, supermarkets, shops, schools, institutions, and from municipal services such as street cleaning and maintenance of recreational areas (Ngoc and Schnitzer, 2009; Singh *et al.*, 2011). The MSW generation also increases, which makes MSW management crucial. In 2003, the average amount of MSW generated in Malaysia was 0.5–0.8 kg/person/day; it has increased to 1.7 kg/person/day in major cities (Kathirvale *et al.*, 2003). By 2020, the quantity of MSW generated was estimated at 31,000 tons. The composition of MSW in Malaysia differs from one place to another. The latest research data on composition of Malaysian MSW are given in Table 1.1. The main components of Malaysian MSW are food, paper and plastics, which make up approximately 80% of the waste by weight. Malaysian solid waste contains a very high concentration of organic waste and consequently has a high moisture content and a bulk density above 200 kg/m^3.

Table 1.1: The composition of Malaysian municipal solid waste in Malaysia (Sharifah *et al.*, 2008)

Composition	Percentage (%)
Organics	46.94
Plastics	20.28
Paper	17.89
Metals	4.31
Glass	2.60
Inorganics	0.17
Others	7.81

These composition characteristics reflect the nature and lifestyle of the Malaysian populations. Most studies on MSW generation used the load-account analysis, which is based on waste collected and disposed in the landfills. Among some of the factors that might influence the composition of MSW produced in a specific location are the extent of reduction, reuse and recycling (3R's) programs and also the duration of year. Changes in MSW generation rates are mostly caused by the demographic factors and facilities, which are provided by the respective departments

(Mohamed and Lee, 2006). A waste characterization study on the municipal solid waste is shown in Table 1.2.

Table 1.2: Various data on characteristics of Kuala Lumpur municipal solid waste (Khathirvale *et al.*, 2003)

Proximate analysis (wet)	**Weight (%)**
Moisture content	55.01
Volatile matter content	31.36
Fixed carbon content	4.37
Ash content	9.26
Elemental analysis (dry)	46.11
Carbon content	6.89
Hydrogen content	1.26
Oxygen content	28.12
Sulfur content	0.23
Heavy metals (dry)	ppm
Chlorine	8.840
Cadmium	0.99
Mercury	0.27
Lead	26.27
Chromium	14.41
Other parameter	
Bulk density (kg/m^3)	240
Net calorific value (kcal/kg)	2180

MSW has been and will continue to be a major issue worldwide. Over the past 20 years, Malaysia has achieved remarkable economic growth which has brought exponential population growth and high influx of foreign workers. This has resulted in an increase in the amount of MSW (Kadir *et al.*, 2013). Meanwhile, with limited resources, only basic technologies for treatment and disposal, and deficient enforcement of relevant regulations, serious problems remain for MSW. In Malaysia, solid wastes are generally categorized into three major categories, and each category is under the responsibility of the different government department, such as municipal solid waste is under Ministry of Housing and Local Government (MHLG), schedule/hazardous waste is under Department of Environment (DOE) and clinical waste is under Ministry of Health (MOH).

Essentially, MSW management in Malaysia is under the responsibility of the local authority, as stipulated in Section 72 of the Local Government Act 1976. Local authority is expected to provide, directly or through contract, public cleansing services of equitable and acceptable quality to all urban and semi-urban communities within its jurisdiction, and must dispose of all the waste collected in a sanitary manner. Therefore, the government has set up a new solid waste management structure. Under the Ministry of Housing and Local Government, Malaysia has set up the National Solid Waste Management Department as the regulatory body and the Solid Waste and Public Cleansing Management Corporation to conduct the operations Waste and Public Cleansing Management Corporation to conduct the operations.

According to the Municipal Waste Management Report: Status-quo and Issues in Southern and East Asians Countries 2010, defined municipal solid as any scrap materials or other unwanted surplus substances or rejected products arising from the application of any process; any substances required to be disposed of as being broken, worn out, contaminated, or otherwise spoiled, or any other material according to the Solid Waste and Public Cleansing Management Act (Act 672) or; other written law, is required by the authority to be disposed of such as public solid waste, imported solid waste, household solid waste, institutional solid waste, and special solid waste, for examples waste from commercial, construction, industrials and controlled activities.

At present, landfilling is the only method used for the disposal of MSW in Malaysia, and most of the landfill sites are open dumping areas, with serious environmental and social threats (Yunus and Kadir, 2003). Landfill is an area of land (normally derelict) where waste is deposited and concentrated for up to 20 years. The traditional method of MSW disposal in Malaysia is via land-filling practices. The evolution of landfill facilities has been traced. In 1988, there were only 49 landfills in operation. These increased to 155 in 2001, 161 in 2002 and 176 by 2007 (Sarkawi, 2011; Yahaya, 2007). Landfilling of MSW is a common waste management practice and one of the cheapest methods for organized waste management in many parts of the world (Jhamnani and Singh, 2009; Longe and Balogun, 2010).

Disposal of wastes through landfilling is becoming more difficult because existing landfill sites are filling up at a very fast rate. At the same time, constructing new landfill sites is becoming more difficult because of land scarcity and the increase of land prices and high demands, especially in urban areas due to the increase in population. In 2001, there were 155 disposal sites under the responsibility of local authorities in Malaysia (Wan and Kadir, 2001) ranging in size from 8 to 60 ha. Most of these sites are open dumpsites, and the capacity has been overloaded. Table 1.3 shows the distribution of the numbers operational and non-operational landfills in each state and the Federal Territories in Malaysia.

The landfills in Malaysia were initially under the Local Authorities (Section 72, Local Government Act 1976). They have since been placed under the Ministry of Housing and Local Government (MHLG). In Action Plan 1988, the government has tried stepwise increase in the efficiency of disposal sites by creating four targeted levels of improvement (Manaf *et al.*, 2009). These levels are, controlled dumping, sanitary landfill with daily cover, sanitary landfill with leachate circulation and sanitary landfill with leachate treatment. The non-sanitary nature of these facilities have led to serious environmental problems like fire outbreak, pollution of rivers and underground facilities by leachate, and other health-related problems.

The disposal of municipal solid waste in sanitary landfills is the most common and desirable integral indispensable solid waste management strategy, due to its simplicity of design, lower operating cost, and landscape-restoration of holes from mineral workings (Sandip *et al.*, 2012). However, the production of highly contaminated leachate is a major drawback of this method (Wiszniowski *et al.*, 2007; Kurniawan *et al.*, 2006). At present, there are over 230 landfills in Malaysia, mostly old dumpsites. The resulting leachate is discharged directly into water courses without any treatment, which can threaten the surrounding ecosystem, particularly in cases where landfills are located upstream of water intakes. If poorly managed, the landfill leachate could become a major source of hydro-geological pollution to groundwater table and the natural environment (Liu *et al.*, 2012).

Table 1.3: The operational and non-operational landfill distribution in Malaysia (National Solid Waste Management Department, Kuala Lumpur, Malaysia, 2010)

State	Landfills in operation	Landfills not in operation
Johor	13	21
Kedah	10	5
Kelantan	13	4
Melaka	2	5
Negeri Sembilan	8	10
Pahang	19	13
Perak	20	9
Perlis	1	1
Pulau Pinang	1	2
Sabah	21	1
Sarawak	51	12
Selangor	6	12
Terengganu	9	12
FT Kuala Lumpur	1	7
FT Labuan	1	0
FT Putrajaya	0	0
Total	178	114

The chemical and microbiological composition of landfill leachate is complex and variable, since apart from being dependent upon features of residual deposit, it is influenced by environmental conditions, the operational manner of the landfill and by the dynamics of the decomposition process that occurs inside the cells. Solid waste landfills may cause severe environmental impacts if leachate and gas emissions are not controlled. Leachate generated in municipal landfill contains large amounts of organic and inorganic contaminants (Raghab *et al.*, 2013). According to Bashir *et al.*, (2012) and Halim *et al.*, (2012) the most common and serious features of unprocessed stabilized leachate produced from Malaysian landfill sites are its high strength of recalcitrant compounds (as reflected by its COD value) and high level of ammoniacal nitrogen (NH3-N). The migration of leachate can pollute the surrounding soil and groundwater, thereby causing serious health problems to human beings. Due to the lack of emphasis on landfill management aspects, Malaysia is currently facing grave problems associated with landfill pollution and improper waste disposal practice; the latter is considered as one of the three main environmental problems faced by most municipalities, besides water and air pollution (Fauziah *et al.*, 2012).

According to World Bank's 2012 report, a decade ago, 2.9 billion residents used to generate about 0.64 kg of MSW per capita per day (0.68 billion tonnes per year), but now, 3 billion residents generate 1.2 kg per capita per day (1.3 billion tonnes per year). These adverse trends in waste generation demand consideration of various issues, most importantly, public health, impact on environment, and waste management (UN, 2010). All over the world landfills are still the most common practice of waste disposal, especially in developing countries owing to its economic advantages and also because of its decomposition capability under controlled conditions until its eventual transformation into relatively inert and stabilized material (George *et al.*, 1993; Christian *et al.*, 2000; Sponza and Agdag 2004; Chai *et al.*, 2007). Solid waste explicitly is linked to urbanization and economic development. Up to 95 % of total MSW collected worldwide is disposed off in the landfills (El-Fadel *et al.*, 1997). In 2009, nearly 54 % of the 243 million tons of MSW generated in the USA were discharged to landfills (USEPA 2010), while more than 90 % of the refuse in China was discarded in landfills (Chai *et al.*, 2007).

Figure 1.1 illustrates the importance of landfill over other disposal routes worldwide. Unlike in developed countries, there is a considerable dearth of scientifically engineered landfills in most under developed and developing countries; so, open dumping is frequently practiced (Singh *et al.*, 2014).

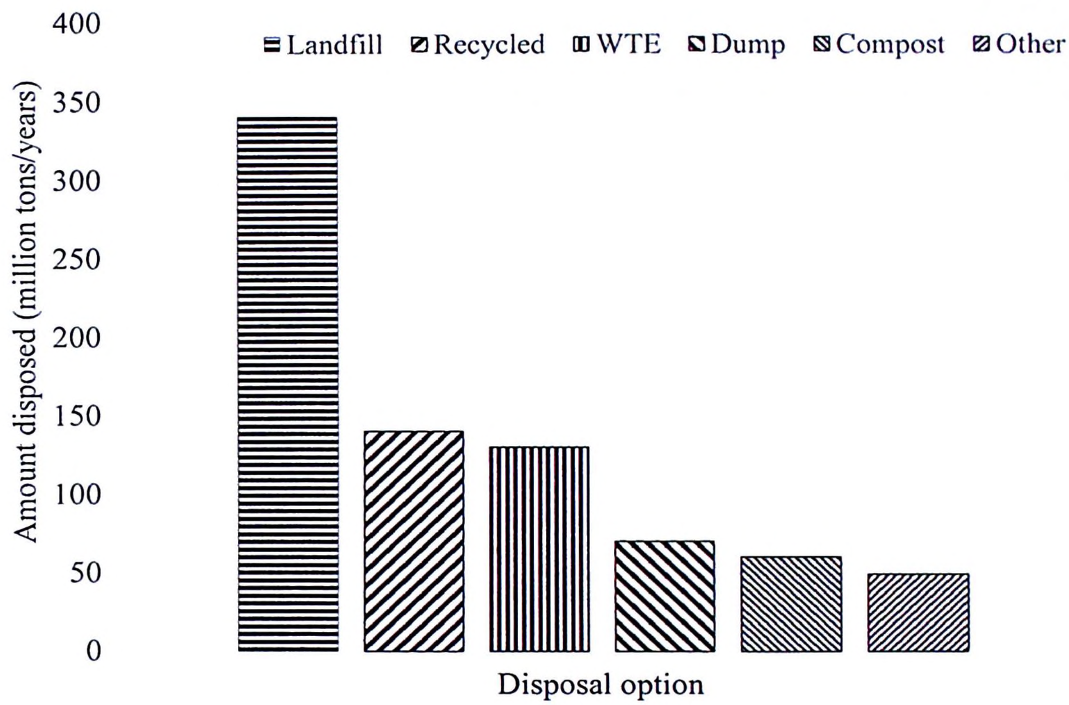

Figure 1.1: The global generation of MSW (World Bank Report 2012)

Open dumpsites provide a perfect breeding ground for disease vectors and their proliferation and cause odor problems. If landfilling is not properly managed, it may cause potential adverse effects to the environment, including groundwater and surface water pollution, release of landfill gasses (LFGs), and dust (Read *et al.*, 2001). In landfills, solid waste undergoes physicochemical and biological changes; as a consequence, decomposition of the organic fraction of MSW along with percolation of rainwater and moisture content of MSW leads to the production of highly contaminated liquid called "leachate" (Kurniawan *et al.*, 2006). Leachate may contain large amount of organic matter (biodegradable, but also refractory to be biodegraded), ammonia-nitrogen, heavy metals, and chlorinated organic compounds and inorganic salts. With the passage of time, leachate becomes mature and difficult to treat due to refractory organics.

The cases of water pollution due to landfill leachate are a global issue, particularly in European countries, China, and Australia (Ngo *et al.*, 2009). Emissions from landfill take a number of forms: gaseous emissions of volatile organic compounds (VOCs), airborne particulate matter and leachate. While landfilling provides a simple and economic means of waste disposal, if not suitably managed it can lead to serious contamination of the environment. Up to 95% of generated refuse is placed in landfill, both worldwide and in Australia. Past instances whereby inappropriate landfilling methods have caused serious environmental pollution.

The issue of greatest concern is the contamination of surrounding ground and surface waters by toxic materials (organic and inorganic) leached from the waste. Moreover, some of these impacts may last for centuries. That is why China has closed more than 1,000 landfill sites (Chai *et al.*, 2007), and the European Union (EU) had adopted landfill directive; according to which the quantity of biodegradable MSW disposed of to landfill must be reduced to: 75 % of 1995 baseline levels by 2006, 50 % by 2009 and 35 % by 2016 (Council of the EU, 1999). The risk of groundwater the pollution is probably the most severe environmental impact from landfills because historically most landfills were built without engineered liners and leachate collection systems.

Internationally, almost 70% of MSW is disposed of to landfill (Zacarias-Farah and Geyer-Allely, 2003). Household waste, any waste produced from a domestic source, represents over two-thirds of the municipal solid waste (MSW) stream (OECD, 2001). Figure 1.2. illustrates the total MSW generation by materials worldwide. MSW contains hazardous substances in the form of paints, vehicle maintenance products, mercury-containing waste, pharmaceuticals, batteries and many other diffuse products which are discussed in the review paper by Slack *et al.* (2004). Previous studies have found that, even without landfill co-disposal, leachates from MSW are very similar in composition to those from mixed or hazardous landfills (Schrab *et al.*, 1993; Kjeldsen *et al.*, 2002).

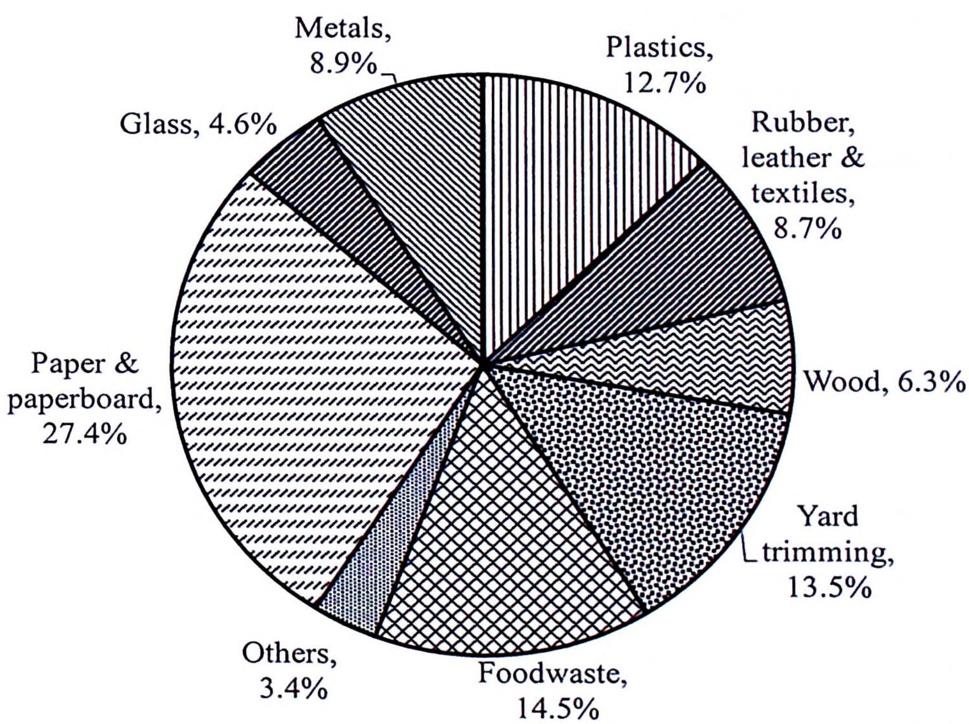

Figure 1.2: Total MSW generation in 2012, 251 million tonnes (before recycling) (USEPA, 2014)

More recently, regulations in many countries have required the installation of liners and leachate collection systems as well as a plan for leachate treatment. Christensen *et al.* (1994 and 2001) reviewed the characteristics of leachate plumes down gradient of landfills. Whilst leachate contamination of the groundwater environment is less likely from modern landfills as a consequence of engineered barriers and leachate collection, the risk still exists. Knowledge of leachate composition is necessary for the implementation of site remediation following barrier breakdown and for installation of practicable treatment processes. Although major components of landfill leachate, especially ammonical nitrogen, can be predicted with some certainty using models to predict the possible typical leachate resulting from the deposition of generic waste groups, the trace composition of leachate is inherently variable due to the heterogeneity of specific waste composition and other factors relating to the landfill (Slack *et al.*, 2005). Leachate composition is also an indication of the types of waste disposed and the processes occurring within the landfill.

1.2 The availability and cost effectiveness of clays

Clay minerals are members of the class of layered aluminosilicates and are ubiquitous at or near the surface of the Earth. Clay minerals exist in nature mostly as nano- to micro-sized particles with high capacity for adsorption, ion exchange capability, and acid sites. Advances in scientific knowledge and technology on clay minerals have made substantial contribution to human society through the many uses of clay-based products from traditional ceramics to modern functional nanocomposites. Knowledge of clay minerals is essential to effective management of the environment and is also proving to be a useful tool for interpreting paleoclimates on earth and possibly even the early state and evolution of extraterrestrial worlds (Pearson *et al.*, 2002). Naturally abundant clay minerals such as montmorillonite, kaolinite and illite are a class of layered alumosilicates (Yu *et al.*, 2013).

Recently, the attention of clay scientists has been focused particularly on the properties of clay minerals as natural nano-sized particles with uses in adsorption, catalysis and biology, in line with the rapid growth in nanotechnology research on synthetic materials. Generally, soils contain larger amount of clay fraction. Clay minerals are the essential component of a soil in controlling its engineering characteristics and are essential to support the plant growth on soils. Simultaneously, the use of clay minerals has been expanded. Soils are used for the manufacture of construction materials such as burnt clay bricks, which are consumed in bulk quantities. It is used in the form of stabilised soil for the manufacture of blocks and in-situ construction (Reddy and Latha, 2014).

Human society has been using clays and clay minerals since the Stone Age, due primarily to the fact that clay minerals are common at the Earth's surface and are widely utilized for agriculture (soils), ceramics, and building materials, with a very long history. Soil is formed due to natural weathering of rocks and it takes millions of years for soil formation. Clay is a mineral coming from the decomposition of rock. The mineral clay is formed specially from a mixing of hydrated phyllosilicate. It is combined with a different mineral like, carbonate, a ferriferous mineral oxide and hydroxide of aluminium (Mounir *et al.*, 2014).

Clay minerals are natural materials with a high capacity to adsorb organic compounds via different mechanisms of interaction. These minerals can be used, alone or mixed with soil, as barriers against organic pollutants. In soils, secondary clay-size minerals are the most reactive inorganic components. They occur commonly in association with the most reactive organic materials in soils. Clay minerals often associate with valuable minerals in a great range of ore bodies and have a substantial impact on the efficiency of many processes including grinding, pumping and dewatering, when valuable minerals are extracted (Zhao and Peng, 2012). In soils, clay dispersibility is influenced by various properties, such as clay content, composition and surface charge characteristics, electrolyte composition and concentration, Fe, Al and Si oxide contents and organic matter content (Mujinya *et al.*, 2013).

The natural clay minerals are good option as for natural adsorbents because of their abundance. Clays are finding growing application in wastewater treatment as adsorbents due to their wide availability, low-cost, and good intrinsic adsorption characteristics. Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. The clays invariably contain exchangeable ions on their surface and play important role in the environment by acting as a natural scavenger of pollutants by taking up cations and/or anions either through ion exchange or adsorption or both. The prominent ions found on clay surface are Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+, Na^+, and SO_4^{2-}, Cl^-, PO_4^{3-}, NO_3^-. These ions can be exchanged with other ions easily without affecting the structure of clay mineral (Bhattacharya and Guptta, 2008). Because of their low cost, abundance in most continents of the world, high sorption properties and potential for ion exchange, clay materials are strong adsorbents.

Vermiculite clay has the largest surface area and the highest cation exchange capacity. Its current market price about US$ 0.04–0.12/kg, is considered to be about 20 times cheaper than that of activated carbon (Babel and Kurniawan, 2003). In recent years, there has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite, diatomite and Fuller's earth for their capacity to adsorb not only inorganic ions but also organic molecules. Moreover, Fuller's earth is an interesting adsorbent since its average price is US$ 0.04/kg whereas commercial activated carbon costs US$ 20/kg. The use of natural siliceous adsorbents such as silica, glass fibers and perlite for waste water is increasing because of their high abundance, easy availability and low cost. Zeolites are highly porous aluminosilicates with different cavity structures. They consist of a three dimensional framework, having a negatively charged lattice. The electro neutrality is maintained by exchangeable counter ions.

Natural zeolites are an interesting option at between 100 and 200 times cheaper (Catalfamo *et al.*, 2006). High ion-exchange capacity and relatively high specific surface areas, and more importantly their relatively cheap prices, make zeolites more attractive adsorbents. Their price is about US$ 0.03–0.12/kg, depending on the quality of the mineral (Raffatullah *et al.*, 2010). Several alternative low cost adsorbents have been developed from minerals, agricultural and industrial waste materials amongst others. Clay minerals application in pollution control has received gross attention over the past decades. These adsorbents applicability for treatment of dye and heavy metals wastewaters, gas and pharmaceutical wastes pollution and oil spillage control have been investigated (Auta and Hameed, 2014). Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world.

In spite of its prolific use, activated carbon remains an expensive material since higher the quality of activated carbon, the greater its cost. Due to the problems mentioned previously, attention has been focused on the various adsorbents which have low cost and local availability. Similar to zeolites, clay minerals are also important inorganic components in soil. Their sorption capabilities come from their high surface area and exchange capacities. Clay is one of potential alternatives to activated carbon as well. The negative charge on the structure of clay minerals gives clay the capability to attract metal ions. Nowadays, researchers turn their interests on using adsorbents, which will be both effective and of low-cost, reducing drastically the synthesis cost. Raw and modified clays have been used extensively for adsorption purposes but the fact that new challenges of pollution problems keeps emanating, it calls for a continuous research towards finding a cheaper, effective and efficient solution to the problems (Auta and Hameed, 2013).

A sorbent must be eco-friendly, cost-effective, industrially viable and efficient for a wide range of concentration of different pollutant metals. In recent years, there has been growing interest in finding inexpensive and effective adsorbents such as tea waste, Fe_3O_4, wood, sawdust, kaolin, bentonite and peat (Hashemian and Salimi, 2012). Various treatments techniques have been developed for treating water and wastewaters. However, the sorption technique can be a preferred treatment technique, provided that the adsorption process is cost-effective (Foo and Hameed, 2011; Nasuha and Hameed, 2011; Albadrin *et al.*, 2011; Salman *et al.*, 2011). Adsorption can also remove soluble and insoluble organic pollutants. Adsorption is considered as the best wastewater treatment method due to its universal nature, inexpensiveness and ease of operation. The cost of water treatment using adsorption is 5.0-200 US$ per cubic meter of water (Ali *et al*., 2012).

Basically, adsorption is the accumulation of a substance at a surface or interface. In case of water treatment, the process occurs at an interface between solid adsorbent and contaminated water. The removal capacity by this method may be up to 99.9%. Due to these facts, adsorption has been used for the removal of a variety of organic pollutants from various contaminated water sources. Fuller's earth has long been used industrially for its decolourising properties all the world over and it is an inexpensive and readily available mineral. Due to their wide availability, low-cost, and good intrinsic adsorption characteristics, clays are finding growing application in wastewater treatment as adsorbents.

1.3 Problem Statement

During the past several decades, the exponential population and social civilization growth, changes in the productivity and consumption habits, increasingly affluent lifestyles and resources use, and continuing development of the industrial and technologies has been accompanied by the rapid generation of municipal and industrial solid wastes, which create the most intransigent paradox around the world (Renou *et al*., 2008). Rapid urbanization and industrialization changed the characteristics of solid waste generated. In 1994, the global municipal solid waste production rate was recorded at 1.3 billion tonnes per day, or equivalent to an average of two-thirds of a kilogram per capita per day, 10 times per capital body weight per year (Beede and

Bloom, 1995). In 2008, the figure has risen by 31.1%, designated a generation rate of 1.7 billion tonnes per day (Foo and Hameed, 2009).

The Malaysian population has been increasing at a rate of 2.4% per annum or about 600,000 per annum since 1994. The MSW generation also increases, which makes MSW management crucial (Latifah *et al.*, 2009). Of major interest, sanitary landfilling is recognized as the most common and desirable integral indispensable solid waste management strategy for sustainable disposal. Sanitary landfill is the most common MSW disposal method due to such advantages as simple disposal procedure, low cost, and landscape-restoring effect on holes from mineral workings (Bashir *et al.*, 2010). An important aspect related to the planning, operation and long-term management of municipal solid waste landfills is the generation of landfill leachate.

Landfill leachate is a complex mixture of soluble organic and mineral compound, formed by the interaction of waste layers with excess water percolating within the landfills. Here, it should be noted that the essence of leachate recirculation is to provide MSW with moisture. Besides, in order to save the valuable landfill air space, the landfilled MSW is usually compacted as much as possible. The compacted MSW will prevent biogas from diffusing, leading to biogas accumulation which may affect the interaction between waste and leachate. Lack of moisture in conventional landfills is generally responsible for the retarded stabilization of MSW, leading to a long-term environmental problem (Hao *et al.*, 2008). As science and technology developed, the management of an ever increasing volume of waste became a very organised, specialised and complex activity. The mass of waste produced in the world has been growing considerably for many decades especially in affluent countries.

In 2006, the 15 countries of the EU (Austria, Belgium, Denmark, Finland, France, Germany, Greece, Italy, Ireland, Luxembourg, Netherlands, Portugal, Spain, Sweden, United Kingdom) generated 219 million tonnes of MSW, or 560 kg/year/capita (Giusti, 2009). China produced 190 million metric tons of MSW in 2004 and became the world's largest MSW generator. A number of serious and highly publicised pollution incidents associated with incorrect waste management practices, led to public concern about lack of controls, inadequate legislation, environmental and human health impact. In Europe, landfilling is the main disposal method. Landfills have been the dominant disposal method for MSW management in China as they are cost-effective and can accept mixed waste without requirements for separation. In many developing countries, they are dumped in an uncontrolled manner without any precaution to deal with gas emissions and leachate generation, which pose a threat to the environment (Nagendran *et al.*, 2006).

A landfill is an extremely variable and heterogeneous environment, as evident from the diversity of refuse composition with respect to location and time. More than 90% of the MSW generated in India are directly disposed of in open areas in an unsatisfactory manner (Biswas *et al.*, 2010). The resulting leachate is discharged directly into water courses without any treatment, which can threaten the surrounding ecosystem, particularly in cases where landfills are located upstream of water intakes. In spite of various exploitations, emphasis and researches have been proliferated, such implementations are handicapped by the inherent drawbacks of the extensive emissions of highly variable quantity and quality of landfill leachates, which enriched in numerous organic, inorganic, ammonium and toxic constituents, resulting in the threatening of surrounding soil, groundwater, and surface water (Aktas and Cecen, 2001).

If not treated and safely disposed, landfill leachate could be a potential source of surface and ground water contamination, as it could seep into soils and sub-soils, causing severe pollution to receiving waters. Due to the pollution potential to the surrounding environment such as local surface water and groundwater, landfill leachate must be treated to meet the local standard for discharge into the receiving water (Kumar and Alappat, 2005). The major pollutants contained in leachate are biodegradable/non-biodegradable organic material, ammonia, and inorganic salts, with anthropogenic organic chemicals, such as phthalates and other endocrine disrupting compounds, becoming an increasing concern (Lu *et al.*, 2008; Zheng *et al.*, 2009). Therefore, landfill leachate is recognised as an important environmental problem. Landfilling as a waste management option has potential to pollute all the three main natural factors of the environment which are land/soils, air, and waters. In scientific terms these are lithosphere, atmosphere and hydrosphere respectively (Butt *et al.*, 2011).

Landfill leachate specifically can pollute all of the three a fore said principal factors. For instance, leachate vapours or fumes can find their way into the ambient atmosphere in sufficient amounts to present danger to human health and the environment, whereas these vapours or fumes can be containing chemical and/or biological hazards and volatile organics. In addition, leachate contaminants can pollute land/soils as it moves through the ground either mixed with water or on its own such as, through the unsaturated zone under a landfill. Therefore, in general, landfill leachate can be seen as a lot more hazardous product and presents a lot more substantial environmental threat. The main environmental problems at landfill sites are the infiltration of leachate and its subsequent contamination of the surrounding land and aquifers. Leachate from a biodegradable landfill will contain significant concentrations of substances such as ammoniacal-nitrogen, which is toxic to many organisms or run-off arising from a landfill containing only soil and rubble may contain suspended solids, be turbid, and threaten fish and other aquatic organisms.

An excess of 200 organic compounds have been identified in municipal landfill leachate, with more than 35 of them having the potential to cause harm to the environment and human health (Slack *et al.*, 2005). Many reviews suggested an association between proximity and exposure to landfill sites and ill health. For example, increased risk of birth defects and some cancers for the population living near landfill sites. Elliott *et al.* (2001) included about 80% of the UK population residing within 2 km of 9565 landfill sites (7803 non-special, 774 special, 988 unclassified) between 1983 and 1998. Given the influence of confounding factors and data artefacts, no clear cause could explain the slight excess risk of birth defects and low birth weights that was found. Human exposure to substances released at waste management facilities can be acute, in case of a serious accident causing short term exposure to high levels of potentially hazardous substances, ionising radiation, bioaerosols, dusts and; chronic, when it involves long-term exposure to low concentrations of these substances or radiation.

1.4 Objectives

a. To explore the potential of natural clays as renewable resources for preparation of functionalized adsorbents.
b. To optimize the best operating conditions for preparation of clay derived functionalized adsorbent.
c. To characterize the physical, chemical and physiochemical properties of the functionalized adsorbent.
d. To examine the novel application for the effective remediation of sanitary landfill leachate.
e. To evaluate the best treatment conditions for the remediation of sanitary landfill leachate.
f. To establish the adsorption isotherm of the treatment process.
g. To determine the adsorption kinetic of the treatment process.

1.5 Scope of study

The primary purposed of this study strategy is to address the health, environmental, aesthetic, land-use, resource, and economic concerns associated with the remediation of sanitary landfill leachate. The impact produced by municipal solid waste (MSW) landfills has received special social and environmental attention in recent decades. These issues are an ongoing concern for nations, municipalities, corporations, and individuals around the world. The degradation of the organic fraction of the wastes in combination with percolating rainwater leads to the generation of leachate. Landfill leachate is considered a high strength wastewater, which is characterized by extreme pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), inorganic salts and toxicity. Leachate needs to be pre-treated on site to meet the standards for its discharge into the sewer or its direct disposal into surface water.

Therefore, there is a need to develop reliable and sustainable options to manage leachate generation and treatment effectively. A natural clay will derived as functionalized adsorbent for the effective remediation of sanitary landfill leachate. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances. The development of low-cost adsorbents such as natural like clay materials, has received the greatest attention and recognition as a good adsorbent. The reason for study is to provide assurance that the treatment method does not cause harm to human health or the environment.

1.6 Organization of study

Chapter 1 contains a relatively short summary of the scenario of landfill leachate generation in Malaysia and the availability of cost effectiveness of clays as adsorbents in landfill leachate remediation. Problem statement, research objective and scope of the study also presented in this chapter.

A description of clay, natural clay derived functionalized adsorbents, sanitary landfill leachate, adsorption process, advance application of natural clay and its composite in adsorption process and the potential of clay for the treatment sanitary landfill leachate are given in Chapter 2. Meanwhile, description of landfill leachate treatment system and batch adsorption studies, physical and chemical characterization of prepared clay based adsorbent, and performance analysis are described in Chapter 3. The method used for the preparation clay based adsorbent is also outlined.

Chapter 4 presents the result of physical and chemical characterization of prepared clay based adsorbent, effect of adsorbent dosage, effect of contact time and effect of pH on the adsorptive uptake of COD and ammonical nitrogen, adsorption isotherm and adsorption kinetic.

In Chapter 5 conclusions and recommendations are made and suggested respectively.