AMMONIACAL NITROGEN REMOVAL FROM LANDFILL LEACHATE BY HEAT ACTIVATED ZEOLITE

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SCHOOL OF CIVIL ENGINEERING
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By

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I hereby declare that all corrections and comments made by the supervisor(s) and examiner have been taken into consideration and rectified accordingly.

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ABSTRAK

Kajian ini dilakukan untuk menilai prestasi zeolit semulajadi dan zeolit pengaktifan haba dalam merawat air larut lesapan dari tapak pelupusan Alor Pongsu, sebagai tapak kajian kes. Pengambilan sampel air larut lesapan dilakukan sebanyak tiga kali dari 19^{th} Februari hingga 25^{th} Mac 2019 dikuti pencirian parameter utama larut lesapan. Manakala, media zeolit semulajadi dan zeolit pengaktifan haba dicirikan menggunakan X-Ray Diffraction (XRD), X-Ray Fluorescene (XRF), Scanning Electron Microscopy (SEM) dan Brunauer-Emmelt-Teller (BET). Kemudian, zeolit disediakan dalam saiz 2-4mm dan digunakan sebagai media penjerap. Kesan dos penjerap dan pH terhadap rawatan telah dikaji. Kajian penjerapan zeolit semulajadi dan pengaktifan haba telah dijalankan dengan menggunakan model isoterma Langmuir dan Freundlich. Perbandingan prestasi rawatan dilakukan antara zeolit semulajadi dan zeolit yang diaktifkan pada suhu 150°C, 200°C serta 250°C. Keputusan menunjukkan bahawa air larut lesapan mempunyai nilai pH 8.09, suhu 25.5°C, nitrogen ammonia 1080mg/L, oksigen terlarut 1.0mg/L, Permintaan Oksigen Kimia 3743mg/L, warna jelas 16250PtCo, warna sebenar 13077PtCo, zeta potensial -21.0mV dan jumlah pepejal terampai 388mg/L. Berdasarkan analisis XRD dan XRF, zeolit telah dikenalpasti sebagai kuartza. Hasil kajian menunjukkan bahawa penggunaan zeolit yang diaktifkan pada suhu 150°C adalah optimum untuk rawatan. Menggunakan zeolit semulajadi pada dos 10g, penyingkiran nitrogen ammonia pada pH optimum 7 adalah 55.8%. Walau bagaimanapun, pada pH optimum 4, penyingkiran COD dan warna sebenar adalah masing-masing 24.3% dan 73.8%, pada dos yang sama (10 g). Untuk zeolit yang diaktifkan pada suhu 150°C, pada dos optimum 10 g, penyingkiran nitrogen ammonia adalah 67.0 % pada pH optimum 8. Namun begitu, pada pH optimum 4, penyingkiran

COD adalah 46.3%, dan pengurangan warna sebenar adalah 91.4% pada pH optimum pH 5; kedua-duanya pada dos yang sama (10g). Peningkatan penyingkiran selepas pengaktifan haba adalah sebanyak masing-masing 11.2%, 22%, dan 17.5%, untuk nitrogen ammonia, COD, dan warna sebenar. Kapasiti penukaran ion oleh zeolit juga dijangka menyumbang terhadap penyingkiran bahan pencemar. Analisis penjerapan isotherma menunjukkan bahawa kedua-dua isotherma Langmuir dan Freundlich berpadanan dengan data eksperimen. Secara umumnya, model Freundlich dapat menggambarkan data keseimbangan yang lebih baik berbanding dengan model Langmuir berdasarkan nilai-nilai R^2 yang tinggi bagi parameter COD, NH_3-N dan warna sebenar.

ABSTRACT

This study was undertaken to determine the performance of raw zeolite and heat activated zeolite to treat the landfill leachate from Alor Pongsu landfill, as a case study site. The landfill leachate was collected for three times between 19th February and 25th March 2019 and then was characterized for the main leachate parameters. The raw zeolite was characterized by the X-ray diffraction, X-ray fluorescence, Scanning electron microscopy and Brunauer-Emmett-Teller instrument, later sieved to size 2-4mm and was used as the adsorbent. Batch studies were undertaken at different adsorbent dosages and pH values. The Langmuir and Freundlich isotherm parameters were also determined. The performance of raw zeolite was compared with the activated zeolite, heated at 150°C, 200°C and 250°C. Results indicated that the average leachate parameters monitored were pH 8.09, temperature 25.5°C, ammoniacal nitrogen 1080mg/L, dissolved oxygen 1.0mg/L, chemical oxygen demand 3743mg/L, apparent colour 16250PtCo, true colour 13077PtCo, zeta potential -21.0mV and total suspended solid 388mg/L. Based on the X-ray diffraction and X-ray fluorescence analysis, the zeolite was identified as quartz. Based on the batch results, the activated zeolite heated at 150°C showed better performance. Using raw zeolite, at an optimum dosage of 10 g, the ammoniacal nitrogen removal was 55.8% at an optimum pH 7. However, at an optimum pH 4, the removal for COD and the true color was 24.3% and 73.8%, respectively, at the same dosage (10 g). For activated zeolite heated at 150°C, at optimum dosage of 10 g, the ammoniacal nitrogen removal was 67.0 % at an optimum pH 8. However, at an optimum pH 4, the removal for COD was 46.3%, and the reduction of true color was 91.4% at an optimum pH 5; both at the same dosage (10 g). The improvements in the removal performance after heat treatment were 11.2%, 22%,

and 17.5%, respectively, for ammoniacal nitrogen, COD and true colour. The cation exchange capacity of the zeolite is also expected to contribute to the removal of the pollutants. The adsorption isotherm analysis revealed that both Langmuir and Freundlich isotherms fitted well with the experimental data. However, the Freundlich isotherm model is more suitable than Langmuir isotherm for evaluating the adsorption equilibrium required for COD, NH_3-N and true colour as verified by the high R^2 values.

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CHAPTER 1

INTRODUCTION

1.1 Background

Landfilling is an engineered disposal method to minimize potential environmental impacts. It is normally practiced in developing countries. Wastes cause two main types of pollutions which consist of water pollution and air pollution. Water pollution is caused by the leachate which is the liquid that leaches or drains from a landfill. Leachate from municipal solid waste (MSW) landfills normally exceeds the standard discharge limit of effluents. It contains chemicals which are harmful to the environment. The characteristics of leachate are determined by the siting, design and the mode of operation of the landfill, and also depend on the age of the landfill.

The total number of landfill site in Malaysia in 2015 is 296 including 165 operating landfill site and 131 of closed landfill site (JPSPN, 2015). The leachate produced from these landfill needs to be controlled and treated, even after the landfill/dumpsites have been closed. Leachate is still being produced even after 20 years of the closure of landfill (Kjeldsen et al., 2002).

1.2 Problem Statement

Leachates are normally treated using physical/chemical, biological and combined processes. Advanced oxidation technology, air stripping methods, adsorption methods, membrane treatment methods have also been applied. Due to the operating costs and secondary pollution, the physical and chemical treatment method is normally used as a pre-treatment and a post-treatment method in the leachate treatment process.

Various media had been used to treat leachate in previous studies such as activated carbon, chitosan, zeolite, clay and others (Mojiri et al., 2015); (Rashid, 2009); (Kasmuri et al., 2018); (Chaari et al., 2011). Zeolites are crystalline hydrated aluminosilicates with a framework structure containing pores occupied by water, alkali and alkaline earth cations which are one of the low cost adsorbents. Due to their high cation-exchange ability and molecular sieve properties, zeolites have been widely used as adsorbents in water and wastewater treatment in the past decades.

Alor Pongsu Landfill site (APLS) in Kerian Perak is one of the typical landfills in Malaysia which has a collection pond of leachate. The main purpose of the pond is just for leachate collection which will reduce the volume via evaporation. There is no associated treatment process incorporated with this ponding system. The landfill leachate in APLS is categorized as stabilized landfill leachate as the $BOD_5/COD<0.1$ which is hard to be treated biologically (Zakaria and Aziz, 2018). Hence, the research was conducted to investigate the potential use of zeolite as an adsorbent in treating the NH_3-N, COD and true colour from this leachate. Previous studies have reported that the levels were 1241mg/L, 3852mg/L and 14984PtCo respectively, (Zakaria and Aziz, 2018), far beyond the acceptable discharge limit of effluent under the Laws of Malaysia Environmental Quality Act (MEQA) 1974 (MDC, 1997).

The performance of raw and activated zeolite heated at different temperatures will be investigated, both act as an adsorbent. This is due to the fact that the raw zeolite may contain impurities, hence, heat activation is expected to improve its adsorption ability. Previous studies have shown the improvement in the performance of zeolite as adsorbent after heat activation (Kurniasari et al., 2011); (Merissa et al., 2013); (Wibowo et al., 2017). Adsorbents have a very high surface area that allows the adsorbate to be adsorbed.

1.3 Objectives

The research aimed to evaluate the performance of raw and heat activated zeolite in removing COD, ammoniacal nitrogen, colour and suspended solids from the leachate. The specific objectives are:

i. To characterize the raw zeolite and the leachate from Alor Pongsu landfill.

ii. To activate the zeolite using heat activation method and then to characterize the material.

iii. To evaluate the removal performance and to determine the adsorption isotherms.

1.4 Scopes of Work

The leachate sample was taken three times from Alor Pongsu landfill site. They were then characterized. The raw and activated zeolite were prepared in the laboratory with the particle size of 2-4mm. Physical activation was done at temperatures of 150°C, 200°C and 250°C. The performance and the adsorption isotherm (Langmuir and Freundlich) was determined in a batch study. The leachate parameters tested were COD, ammoniacal nitrogen, colour and suspended solids. The investigation only involves the zeolite as adsorbent and not as ion-exchanger.

1.5 Expected Outcomes

The addition of zeolite as an adsorbent is expected to work well in removing the unwanted pollutants such as COD, ammoniacal nitrogen, colour and suspended in the leachate. The physical activation by heat treatment is expected to improve the performance.

1.6 Dissertation Outline

The thesis is categorized into five chapters, namely introduction, literature review, methodology, results and discussion and conclusion and recommendations.

Chapter 1: Introduction- this chapter introduces and provides an overview of the research that is to be undertaken. It includes the background of leachate treatment, the problem statement of this study, objectives and the expected outcome.

Chapter 2: Literature Review- this chapter gives a detailed explanation to the technical terms, findings, topics and results related to the research with reference to the research papers published earlier. It gives some ideas and guidelines to the researcher for them to have a better understanding of the topic and proceed with their respective research.

Chapter 3: Methodology- this chapter describes the methodology to obtain the expected outcomes and ways to achieve the project objectives in detailed. The particular equipment, processes, or materials used in this research are clearly stated.

Chapter 4: Results and Discussions- this chapter records all the findings and results obtained after the research. The data analysis, either quantitative or qualitative, is intended to abridge a mass of information to answer the research questions, test the theory, examine the encountered issues and explore the conjectures. The results will be analysed and discussed in this chapter to answer the research objectives. The results are expected to be consistent with the previous research conducted in a similar context.

Chapter 5: Conclusion and Recommendations- this chapter summarises all the results and findings of the research. The research question will be answered and all objectives and expected outcomes are addressed. Recommendations are suggested for action that is based upon the results and the applicable literature, with consideration for the limitations of both.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Leachate

Leachate is the fluid that penetrates through the solid waste and is produced from liquids present within the waste and outside water that has entered the landfill from external sources such as rainfall, surface drainage and others (Jayawardhana et al., 2016). It is normally identified as a turbid dark brown colour. At the point when water percolates through solid waste, the effluent is drained with both natural and chemical substance materials. Water pollution occurs when the leachate carries the contaminants flows into the natural environment. The leachate generated may vary with the composition and depth of waste, availability of moisture and oxygen, landfill design, operation and age (Reinhart and Grosh, 1998). Malaysia is one of the developing countries that practices landfilling to dispose of the waste materials and the total number of landfill site in Malaysia in 2015 is shown in Table 2.1.

Table 2.1 Total Number of Landfill Site in Malaysia

State	No of Operating Landfill Site	No of Closed Landfill Site	Total
Johor	14	23	37
Kedah	8	7	15
Kelantan	13	6	19
Melaka	2	5	7
Negeri Sembilan	7	11	18
Pahang	16	16	32
Perak	17	12	29
Perlis	1	1	2
Pulau Pinang	2	1	3
Sabah	19	2	21
Sarawak	49	14	63
Selangor	8	14	22
Terengganu	8	12	20
WP Kuala Lumpur	0	7	7
WP Labuan	1	0	1
Total	165	131	296

2.1.1 Characteristic of Leachate

Landfill leachate may be described as a water-based solution that comprises of trace metals, major elements, organic compounds and microbiological components carrying both dissolved and suspended materials. The pollutants make it hard to be dealt with. The pollutants in the urban landfill leachates may be divided into four fundamental groups: dissolved organic matters; inorganic compounds such as calcium, potassium, sodium, ammonium, magnesium, sulphates and chlorides; heavy metals such as lead, nickel, copper, cadmium, chromium and zinc; xenobiotic organic materials (Aziz et al., 2010). Along these lines, the leachate should not be discharged directly into the water stream as they cause negative impacts to the amphibian biological community, subsequently threatening the wellbeing of the living things.

2.1.2 Leachate Treatment

There are numerous leachate treatment methods such as physical/chemical, biological and combined processes. The physical and chemical treatment method are normally used as a pre-treatment and a post-treatment method in the leachate treatment process due to the operating costs and secondary pollution (Kurniawan et al., 2006). The biological treatment method decomposes organic and nitrogenous matter from young leachates with the use of microorganisms (Madu, 2008). However, leachate is normally hard to be treated completely by only one single method as the characteristics of the leachate is differ. A combined process is usually used. A few treatment methods have been applied to landfill leachate, such as advanced oxidation technology, air stripping methods, adsorption methods, membrane treatment methods, etc (Kalcikova et al., 2015). Biological treatment methods, such as the anaerobic techniques are normally done for energy recovery (Kheradmand et al., 2010).

Other biological treatment methods include aerated lagoons, activated sludge and sequence batch reactors (SBR) (Gao et al., 2015). Aerated lagoons, known as stabilization ponds are the most popular wastewater treatment methods due to their low operation and low maintenance costs (Renou et al., 2008). The reduced compounds from the lower anaerobic part are oxidized in the upper part of a lagoon which is aerobic. Activated sludge systems comprise of a completely mixed aeration reactor where biodegradation takes place and clarifies where sludge is settled. Some portion of the sludge is recycled whereas excess sludge together with clarified water is discharged appropriately. These systems offer more intensive treatment than aerated lagoons because they operate with intensive aeration and large populations of acclimatized microbes (Rooksby, 2007). Sequencing batch reactors (SBR) are systems which allow aerobic biological treatment, equalization, sludge settling and clarification to take place in the same tank over a period succession. This sort of operation makes a treatment process which is robust and less affected by the regular variation of organic load or ammonium nitrogen (Laitinen et al., 2006).

The adsorption process has become more important in water and wastewater treatment over the last few decades. Adsorption processes are a good alternative method for water purification because of the high reliability, energy efficiency, design flexibility, technological maturity and the ability to be regenerated. A large specific surface area of adsorbent pores provides a large adsorption capacity. The presence of the large numbers of small sized pores between adsorption surfaces due to the large internal surface area in a limited volume. Adsorbents such as activated carbon and zeolite can be specifically engineered with precise pore size distributions and thus utilised in wastewater treatment (Slejko and Frank, 1985).

2.2 Introduction to Zeolites

Zeolites are microporous crystalline solids with well-defined structures that are made up of a three dimensional network of SiO_4 and AlO_4 tetrahedra sharing all the corners with each other (Lassinantti, 2001). The word zeolite originates from a Greek term meaning "boiling stone". This terminology entails the property of this material to swell and to lose water when heated. Zeolite has an open structure with pores and voids where the movement of ions and molecules is permitted. At least 60 species of natural zeolites are known to exist, normally occurring in soils, sediments, and rocks. The most common natural zeolites that have been identified are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite and phillipsite during the past 2 centuries (U.S., 2015). Some of the types of synthetic zeolites are A, beta, Y, ZSM-5 and others. Natural zeolites are mined around the worlds but synthetic zeolites are used more frequent in the commercial. The physical properties of the crystal and chemical composition define for the main contrast. Besides, zeolite varies relying upon the genesis and purity, the following characteristics: void volume, degree of hydration, cation exchange properties, ability to absorb and adsorb and molecular sieve properties (Hogg, 2003).

2.2.1 Formation of Zeolite

Most natural zeolites are formed because of volcanic action. When the eruption occurs, magma gets through the earth’s crust and flows out in the form of lava accompanied by gases and residue. In situations where such locations are on an island or close to a sea, the lava and ash frequently flow into the sea. After achieving the sea, the hot lava, water and the salt from the sea undergo reactions which, through the span of thousands of years, have prompt the generation of crystalline solids known as zeolites (de' Gennaro et al., 2000). Figure 2.1 shows the formation of natural zeolite.

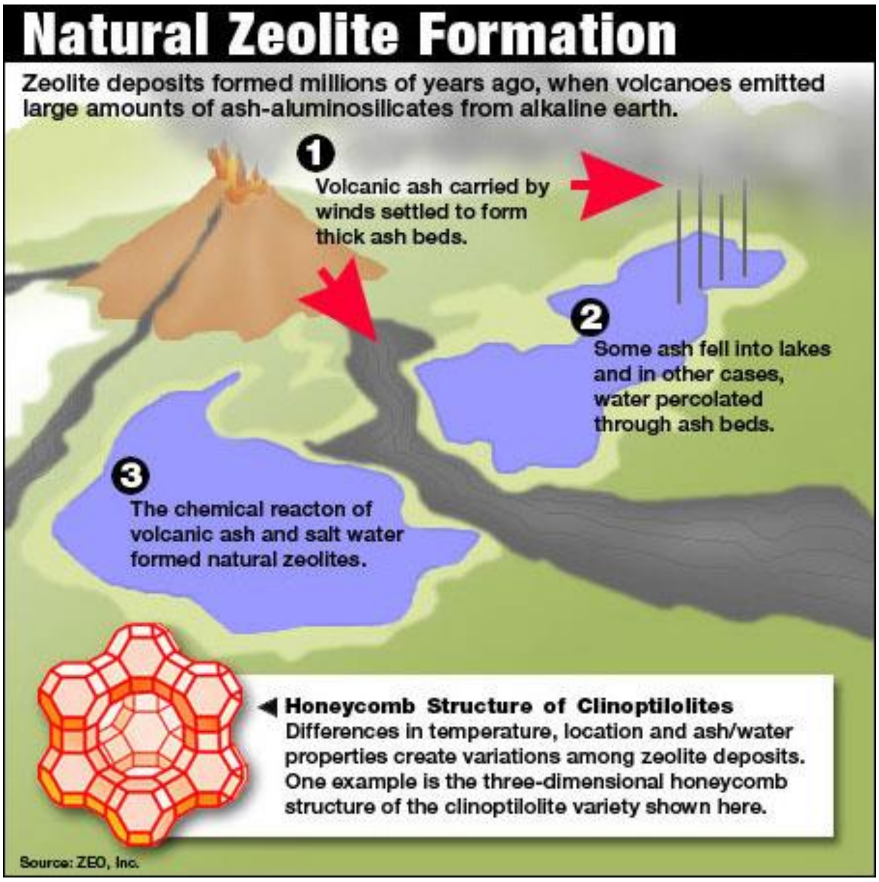

Figure 2.1 Formation of Zeolite (ZEO, 2013)

Zeolite synthesis normally involves the hydrothermal crystallization of alumina silicate gels (formed upon mixing an aluminate and silica solution in the presence of alkali hydroxides and/or organic bases) or solutions in a basic environment. The crystallization is in a closed hydrothermal system at increasing temperature, autogenous pressure and varying time (a couple of hours to a few days) (Markovska, 2009).

2.2.2 Structural and Properties of Zeolite

The structural formula of zeolite is based on the crystallographic unit cell: $M_{x/n}$ $[(AlO_2)_x(SiO_2)_y]$ wH_2O, where M is a soluble base or alkaline earth cation, n is the valence of the cation, w is the amount of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell, and the proportion y/x most has values of 1 to 5, however for the silica zeolite, y/x raged from 10 to 100 (Jacobs et al., 2001).

Zeolite promotes ion exchange processes. Since silicon ion typically exists in a +4 oxidation state while the aluminium exists in the +3 oxidation state, therefore there is an overall negative charge on the alumina silicate framework. The cations, for example, metal or hydrogen ion that are highly mobile balance the net negative charge on the alumina silicate framework. The isomorphous positioning of aluminium in tetrahedral coordination within their Si/Al frameworks prompt the cation exchange properties (Cejka, 2005).

Zeolite has a large surface area with significant porosity which makes it a good adsorbent. The surface area of zeolites is in the range of 600-800 m^2/g. Due to the high surface area, zeolites can adsorb large quantities of adsorbate relying upon adsorbate size, opening size, temperature and surface acidity of zeolites.

Zeolite has high thermal stability that most of them can withstand up to 400^{o}C. Its stability increased with the increasing silica content. Thermal stability of zeolites can be quantified by the Stability Index which based on the zeolite breakdown temperatures from X-ray diffraction studies. From the results, it was shown that zeolites with Si/Al$\geqslant$3.80 are very stable; zeolites with Si/Al$\leqslant$1.28 are quite unstable; and zeolite stability in the intermediate Si/Al range cannot directly be predicted from the Si/Al ratio (Cruciani, 2006).

2.2.3 Zeolite Applications

A significant amount of zeolites occur naturally as minerals while the others are synthetic, and are made commercially for explicit uses, or produced by scientists for research purposes. By the mid-1930s, there is literature described the ion exchange, adsorption, molecular properties of zeolite minerals (Jacobs et al., 2001). Due to their unique porous, open structure and negatively charged, zeolites are utilized in an assortment of uses with a worldwide market of several million tonnes per annum. In the western world, significant utilizations are in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction (Wong, 2009). The adsorption ability of zeolite is affected by the exchangeable cation, Si/Al ratio, surface area and the size of zeolite pore (Suyato et al., 2017).

Zeolite had been used in a few studies to treat the landfill leachate. A zeolite-feldspar mineral composite adsorbent had been used to identify their optimum ratio in the ammoniacal nitrogen and COD removal. A composite had been created utilizing feldspar and zeolite with feldspar as the alternative adsorbent media to replace a portion of zeolite in decreasing the treatment cost (Ibrahim et al., 2016). Besides that, there was additionally study in regards to zeolite and activated carbon combined with biological treatment for metals removal from mixtures of landfill leachate and household wastewater (Mojiri et al., 2015).

2.3 Activation Method

Activation of zeolite aims to improve the function of zeolite as an adsorbent. There are two types of activation methods, physical activation method by heat and chemical activation method by dissolving into acid or base solution. The adsorption ability of zeolite is influenced by the exchangeable cation, Si/Al ratio, surface area and the size of zeolite pore. Natural zeolite contains organic and inorganic impurities, consequently caused the pore to be clogged and active sites of the zeolite surface to be covered. Therefore, zeolite is usually activated before applied in wastewater treatment (Athanasiadis and Helmreich, 2005).

Zeolite heating process or calcination is carried out at a constant temperature and duration with hot air or a vacuum system to release water molecules. The temperature and heating duration should be controlled to avoid damage to the zeolite structure due to excessive warming. Zeolite heating process will reduce the water content of natural zeolite and the loss of this water molecule will increase the number of empty pores of the natural zeolite for the adsorption process. Chemical activation is carried by using chemicals, either acid or base. The acid or base aims to wash the pores on the zeolite surface. The impurities are dissolved so to form zeolite-H^+ or zeolite-Na^+. Acidic solutions (H_2SO_4, HCl, HNO_3) and basic solutions (NaOH, KOH) can be used for chemical activation of zeolite (Wiyantoko and Rahmah, 2017).

2.4 Adsorption

The technological, environmental and biological usage of adsorption have been a worry since the earlier century. Adsorption was known amid pioneering experimental age in which the first quantitative observations were carried out by Scheele in 1773 and Fontana in 1777 who turned out with the experiments of the uptake of gases by charcoal and clay (Dąbrowski, 2001). Adsorption can be described as an attachment of chemical molecular species on the surface of a liquid or solid (Worch, 2012). Adsorption occurred due to the interaction between the molecules in which the molecules that accumulate on the surface is termed adsorbate while the material that provides the surface for the adsorption to occur is termed adsorbent.

Adsorption techniques for wastewater treatment have turned out to be increasingly prevalent in recent years due to their efficiency and cost saving. Activated carbon has undoubtedly been the most well known and widely used adsorbent in wastewater treatment due to its highly porous with a large surface area (Babel and Kurniawan, 2003). However, activated carbon is an expensive material and non-economical to recover (Gupta and Suhas, 2009).

Efforts had been done by scientist to find a good alternative for activated carbon to substitute its usage in recent years. Research and investigation had been done on the capability of various adsorbents to remove pollutants from wastewater at low cost. Natural materials such as chitosan, zeolites, clay and other materials are produced at low costs (Babel and Kurniawan, 2003).

Chitosan is a type of fibre produced from chitin. It is present in the exoskeleton of shellfish and crustaceans. Low cost chitosan can be produced from the fishery wastes such as shrimp, lobster, and crab shells since the sources are abundantly available (Rorrer et al., 1993). Research on ammonium concentration removal had been done by using Chitosan-coated meso-microporous zeolite CS/MCM-41-A (Guo et al., 2015).

Zeolite had been used in a few studies to treat the wastewater. Natural zeolites also gained significant interest among scientist, mainly due to their valuable properties such as ion exchange capability. Zeolite had been used to treat the leachate in a batch reactor. This result is consistent with other research that zeolite can be a good substitution to the advanced wastewater chemical treatment system. This is because of its porous structure, which in this case offers an excellent ability to adsorb ammoniacal nitrogen and heavy metals (Kasmuri et al., 2018).

Clay is also one of the possibilities to replace the activated carbon in wastewater treatment. Similar to zeolite, clay has its adsorption capability due to high surface area and negatively charge on its structure. Montmorillonite with the highest exchange capacity among the clay species is 20 times cheaper than activated carbon (U.S., 2015).

Adsorption had been proved to have the capability to remove organic substances either in drinking water or wastewater treatment. There are other adsorbents applied in water purification. However, the application is limited to the type of adsorbates or types of water. The focus has been directed to compare the removal capability of the adsorbates on the pollutants and their overall cost for future aspect.

2.4.1 Types of Adsorption

Adsorption can be classified into two types, physical adsorption and chemical adsorption relying upon the type of interactions between adsorbate and adsorbent, the forces of attraction exist between adsorbate and adsorbent. These forces of attraction can be divided into van der Waals forces of attraction which are weak forces or due to chemical bond which are strong forces of attraction.

Physical adsorption happens with the development of multilayer of adsorbate on the adsorbent. It is an exothermic process which has a low enthalpy of adsorption (20-40kJ/mol) and takes place at low temperature below the boiling point of the adsorbate. The physical adsorption decreases as the temperature increase since it occurs more readily at lower temperature based on (Le-Chatelier's Principle). This type of adsorption is reversible due to weak attraction forces and low activation energy, therefore it can be reversed by heating or by decreasing the pressure.

Chemical adsorption happens with the development of unilayer of adsorbate on the adsorbent. It is also an exothermic process which has a high enthalpy of adsorption (80-240kJ/mol). It can take place at all temperature. Chemical adsorption increases with the increases in temperature until a certain limit and then decreases. It is also known as Langmuir adsorption. Since the chemical adsorption has a higher force of attractions and activation energy, therefore adsorption is practically irreversible (Atkins and de Paula, 2010).

2.5 Adsorption Isotherms

Adsorption equilibrium is built up when the concentration of adsorbate in the bulk solution is in dynamic balance with that of the interface. The equilibrium can be described as the state of the adsorption system at which there is no net adsorption takes place between adsorption and desorption process (Vadivelan and Kumar, 2005).

Adsorption isotherm models are used to describe the adsorption equilibrium. An adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent, q_e, to the concentration of the solute in the liquid, C_e, with which it is in contact. This equilibrium is also described by expressing the amount of solute absorbed per unit weight of adsorbent q_e, as a function of C_e, the concentration of solute remaining in solution. The Langmuir and Freundlich isotherms are commonly used isotherms for the application of media in water and wastewater treatment.

The amount of adsorption at equilibrium state, q_e (mg/L) can be calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M}$$

where C_0 and C_e represent the initial and equilibrium of the liquid-phase concentration (mg /L); V is the volume (mL) of the sample solution and M is the weight of the adsorbent (mg).

2.5.1 Langmuir Isotherm

In 1916, Irving Langmuir published a new model isotherm for gases adsorbed to solids, which held his name. It was first theoretically analyzed in the adsorption of gases on solid surfaces (Langmuir, 1918).

Assumptions of the Langmuir model are:

a) All adsorption occurs through the same mechanism.
b) Homogeneous surface (all adsorption sites are uniform)
c) No interaction between adsorbed molecules (Each active site can only react with only one adsorbate)

The Langmuir isotherm assumes that the adsorption takes place at specific homogeneous sites on the surface of the adsorbent and form a monomolecular adsorbed layer. Based on the assumptions, Langmuir can be expressed by the equation:

$$q = \frac{q_{max} b C_t}{1 + b C_t}$$

Langmuir adsorption parameters are determined by transforming the Langmuir equation into linear form (Huang et al., 2019).

$$\frac{C_t}{q} = \frac{C_t}{q_{max}} + \frac{1}{b q_{max}}$$

Where:

C_t = the equilibrium concentration of adsorbate (mg/L^{-1})

q_{max} = the amount of anion adsorbed per gram of the adsorbent at equilibrium (mg/g).

b = constant related to the affinity of binding sites

2.5.2 Freundlich Isotherm

In 1909, Freundlich expressed an empirical equation for representing the isothermal variation of adsorption of a quantity of gas adsorbed by a unit mass of solid adsorbent with pressure. The Freundlich isotherm is used to define the adsorption characteristics for the heterogeneous surface (Freundlich, 1906).

Freundlich adsorption isotherm is given by the equation:

$$Q_e = K_f C_e^{\frac{1}{n}}$$

Where K_f = Freundlich isotherm constant (mg/g)

n = adsorption intensity

C_e = the equilibrium concentration of adsorbate (mg/L)

Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)

Freundlich adsorption parameters are determined by transforming the Freundlich equation into a linear form.

$\log Q_e = \log K_f + (l/n) \log C_e$

Where, $Q_e = (x/m)$, is the amount of material adsorbed (mg g^{-1}) per unit mass of the adsorbent at equilibrium; m is mass of the adsorbent (g L^{-1}), K_f and 1/n are the Freundlich constants, which indicates adsorption capacity (mg g^{-1}) and strength of adsorption respectively. The value of 1/n $[0 < (1 / n) < 1]$ is a fraction, so that, the value of n is a whole number (n > I), which is the order of adsorption. A plot of Q_e vs C_e is an exponential plot. On the other hand, straight line plots are obtained when the values of log Q_e are plotted against log C_e values, with log K_f, values as the intercept and (1/n) value as the slope (A.O et al., 2012).

2.6 Summary of Literature Review

Landfill leachate is produced at the point when the water passes through the solid waste. It is normally identified as a turbid dark brown colour with high pollutants concentrations. The leachate generated from the landfill should be handled and treated properly before discharged into the water bodies. There are numerous leachate treatment methods such as physical/chemical, biological and combined processes in the current practices. Previous studies have been reported the coagulation processes using tin (IV) chloride, dimocarpus longan seeds, polyaluminium chloride, tobacco leaf and others as the coagulants in the leachate treatment from Alor Pongsu landfill. The practices of adsorption processes in the leachate treatment from Alor Pongsu landfill are quite minor. Adsorption is then practiced using the zeolite in this study. Due to its open structure and molecular sieve properties, the zeolite act as a good adsorbent in wastewater treatment. However, the raw zeolite has limited adsorption capacity. In recent years, the preparation of surface modified zeolite using various methods to improve the potential of zeolite for pollutants has been an important field of research. Physical activation, one of the activation methods in which the zeolite heating process or calcination is carried out at a constant temperature and duration to improve the function of the zeolite as adsorbent. In this study, the performance and limitations of using physical activation of zeolite by the heating process at 150°C, 200°C and 250°C with 3 hours duration are evaluated. Adsorption isotherm models are used to describe the adsorption equilibrium. Langmuir and Freundlich isotherms are applied to analyse the equilibrium data. Thus, the use of the zeolite and activation method will contribute to the understanding of the early stages of the process, limitations and future research.

CHAPTER 3

METHODOLOGY

3.1 Overview

This chapter describes the methodology and testing used in the research. Figure 3.1 shows the flow chart of the methodology of this research. The methodology can be divided into 4 sections: characterization of landfill leachate; characterization of raw zeolite and heat activated zeolite; batch studies (effect of dosage and pH) on adsorption processes using raw zeolite and heat activated zeolite; modelling and interpretation of adsorption isotherms.

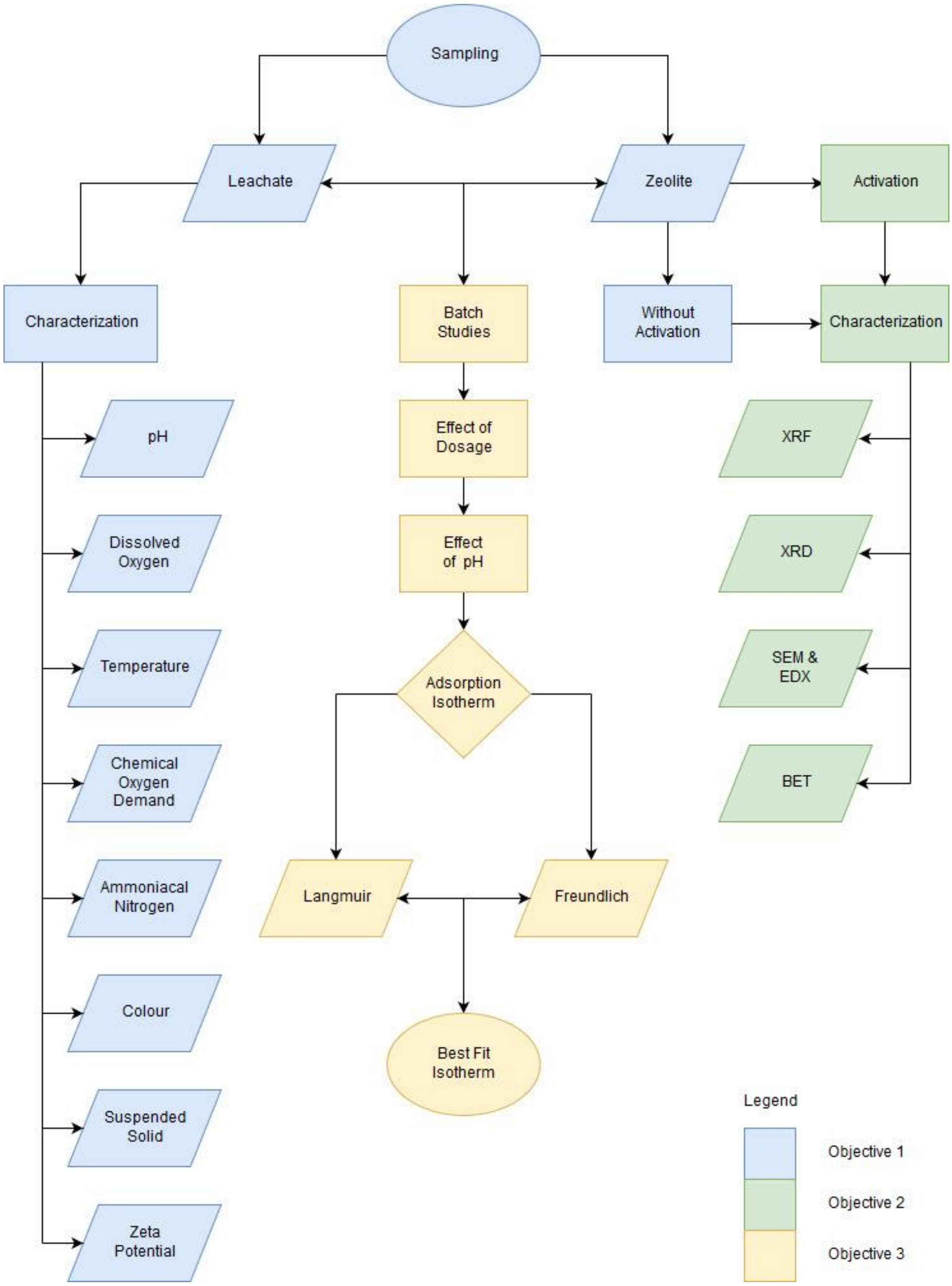

Figure 3.1 Flow Chart (Methodology)

3.2 Leachate Sampling

Raw leachate samples were collected from Alor Pongsu Landfill Site (APLS). It is located in Alor Pongsu, Perak, Malaysia, at coordinates of 5°04' N, 100°35' E. The leachate samples were taken directly from the pond using the bucket. The samples were filled into HDPE plastic bottles, transported to the laboratory and stored at 4°C to minimize the biological and chemical reactions. The leachate was collected for three times throughout the project period on 19th February, 4th March and 25th March 2019 respectively. Figure 3.2 shows the leachate sampling pond (last pond) at Alor Pongsu landfill site. Figure 3.3 shows the Alor Pongsu site condition and Figure 3.4 shows the second pond on site.

Figure 3.2 Leachate Sampling Pond (Last Pond) at Alor Pongsu Landfill Site

Figure 3.3 Alor Pongsu Landfill Site Condition

Figure 3.4 Second Pond in Alor Pongsu Landfill Site

3.3 Leachate Characterization

The samples were analysed for pH, temperature, dissolved oxygen (DO), zeta potential, ammoniacal nitrogen (NH_3-N), chemical oxygen demand (COD), colour and total suspended solids (TSS) in accordance to the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WEF, 1992). Table 3.1 shows the list of parameters and method references used in this study.

Table 3.1 List of Parameters and Method References

No	Parameter	Method Number	Equipment
1	pH	-	YSI Pro Plus Multi-Parameter Water Quality Meter
2	Temperature	-	YSI Pro Plus Multi-Parameter Water Quality Meter
3	Dissolved Oxygen	-	YSI Pro Plus Multi-Parameter Water Quality Meter
4	Zeta Potential	NCL method PCC-2 (Jeffrey D, 2009)	Malvern Zetasizer Nano ZS
5	Ammoniacal Nitrogen	Method 8038 (APHA, 2012d)	HACH DR2800 spectrometer
6	Chemical Oxygen Demand	Method 8000 (APHA, 2012a)	HACH DR2800 spectrometer
7	Colour	Method 8025 (APHA, 2012c)	HACH DR2800 spectrometer
8	Suspended Solids	Method 8006 (APHA, 2012b)	HACH DR2800 spectrometer

3.4 Adsorbent

Figure 3.5 shows the zeolite granules used in this project. The zeolite was packed and distributed by YM Multi Trading. It had the pH value in the range of 6.5-7.5. Figure 3.6 shows the processes of sieving and crushing of the zeolite. Since the