LANDFILL LEACHATE TREATMENT USING NANO COMPOSITE ADSORBENT

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ABSTRAK

Penjerapan melalui karbon yang diaktifkan adalah merupakan salah satu cara yang terbaik untuk merawat bahan larut lesapan di tapak pelupusan yang telah stabil. Walau bagaimanapun, teknik memerlukan kos yang tinggi diperlukan dan sumber karbon yang diaktifkan yang terhad. Oleh yang demikian, tujuan kajian ini djalankan adalah untuk menghasilkan media komposit bagi rawatan bahan larut resap yang dapat mengurangkan kos sekaligus efektif dalam menghakis bahan cemar di dalam bahan larut lesapan di tapak pelupusan. Kajian ini menggunakan hampas tebu sebagai karbon yang diaktifkan kerana kos yang rendah dan sumber biomass yang senang diperolehi dan banyak. Karbon yang diaktifkan dari hampas tebu telah digunakan untuk rawatan bahan larut resapan dari tapak pelupusan sampah anaerobik bagi penyingkiran permintaan oksigen kimia, warna dan ammonia. Karbon yang diaktifkan dari hampas tebu dikategorikan sebagai jenis kawasan permukaan, morfologi permukaan dan kelompok berfungsi. Penilaian prestasi agen penjerap dianalisa melalui proses kelompok dengan mengubah had kelajuan penggoncang, masa sentuhan. Dos agen penjerap dan pH agen penjerap. Hasil dari keputusan eksperimen yang dijalankan membuktikan bahawa prestasi agen penjerap mampu jerap dan membuang bahan cemar dari bahan larut resapan tapak pelupusan sampah. Penyingkiran permintaan oksigen kimia, warna dan ammonia kebiasaan diterangkan melalui isoterma Freundlich. Keputusan juga telah menunjukkan keadaan optimum eksperimen (200 rpm had laju gegaran, 60 min masa sentuhan, 2g dos karbon yang diaktifkan dan pH skala 4) membolehkan 96.36%,72.23% dan 92.36% penyingkiran warna, COD dan NH_3-N. Ia telah menunjukkan bahawa hampas tebu yang diaktifkan karbon dapat bertindak sebagai media dalam rawatan tapak pelupusan larut lesapan.

ABSTRACT

Adsorption via activated carbon (AC) is one of the best methods to treat stabilized landfill leachate. However, this technique required high cost and limited resource of AC precursor. Thus, aim of this research is to develop new composite media which could reduce the cost yet effectively remove the contaminants of landfill leachate. In this study, sugarcane bagasse, a cheap and abundant biomass from agricultural waste was used as activated carbon media. The prepared sugarcane bagasse activated carbon (SBAC) was tested for color, chemical oxygen demand (COD), and ammoniacal nitrogen (NH_3-N) removals from anaerobic stabilized landfill leachate. Sugarcane bagasse activated carbon (SBAC) was prepared using chemical activation and characterized for its surface area, surface morphology, and functional groups. The performance of the adsorbent was examined in a batch mode study by varying the shaking speed, contact time, adsorbent dosage, and pH. The experimental results indicated that SBAC could adsorb and remove the pollutants from anaerobic municipal stabilized landfill. Removal of color, COD, and NH_3-N were favorably described by Freundlich isotherm. The experimental results revealed that the optimum experimental conditions (e.g. 200 rpm shaking speed, 60 min contact time, 2 g AC dosage, and pH 4) resulted in 96.36%, 72.56%, and 92.36% removal of color, COD, and NH_3-N, respectively. It was indicated that the sugarcane bagasse activated carbon able to act as media in landfill leachate treatment.

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LIST OF ABBREVIATIONS

AC	**A**ctivated **C**arbon
APLS	**A**lor **P**ongsu **L**andfill **S**ite
BOD	**B**iological **O**xygen **D**emand
COD	**C**hemical **O**xygen **D**emand
JPSPN	**J**abatan **P**engurusan **S**isa **P**epejal **N**egara
MSW	**M**unicipa**l** **S**olid **W**aste
NZVI	**N**ano **Z**ero **V**alent **I**ron

NOMENCLATURES

C_o	Initial concentration
C_e	Final concentration
x	Mass of adsorbate
m	Mass of adsorbent
Q	Constant
b	Constant
q_e	Equilibrium uptake capacity
K_f	Adsorption capacity
n	Slope
W	Weighte
$ZnCl_2$	Zinc Chloride

CHAPTER 1

INTRODUCTION

1.1 Background

As the population of an area growths, the amount of wastes generated is greatly increased. Vast product innovation and as the power of buying and spending gains popularity among humans, wastes are uncontrollably produced day by day. Municipal solid waste has become the fastest-growing waste stream and its proper collection, recycling and final disposal is one of the most challenging and problematic tasks throughout the world (Bueno et al. 2015). Therefore, good management of solid waste is required to provide us with a comfortable environment for living. Solid wastes are mostly generated by the residential, municipal, commercial, industrial and others. The municipal solid waste separation can be done at source, residential, commercial and industrial facilities. By the time, the government has given more emphasized on recycling campaign. Some of the separated waste components are effectively reused and recovered. Thus, the amount of waste generated can be reduced. Even though, lots of effort has be done on waste reduction, recycling and transformation of technologies, disposal of residual solid waste in landfills still remains an important component in integrated solid waste management strategy.

Sanitary landfill method is widely accepted as the ultimate approach to dispose of solid waste material due to its economic advantage. Thus, sanitary landfills are important means of disposing municipal solid waste in developing countries. However, these landfills are associated with the generation of leachate, which if untreated may pose severe public health risk and may damage the ecosystem in the long term. Landfill leachate is a complex wastewater produced as a result of interaction of waste with water percolating through the body of a landfill (Abu Foul et al. 2009). Rainfall percolating through these open dumping sites triggers biological processes, chemical reactions and physical changes as the MSW degrades, generating a highly contaminated liquid known as leachate. Leachate is the wastewater generated from the biochemical reaction that occurs inside a waste deposit in a sanitary landfill. Leachate usually contains dissolved contaminants, volatile organic acids, toxic heavy elements, and high concentrations of organic matter, chemical oxygen demand (COD), ammonia nitrogen, and biochemical oxygen demand (BOD_5). Leachate which is generated from the matured sanitary landfill generally contains a combination of high strength of non-biodegradable organic pollutants (Mohajeri et al. 2010). When leachate containing high levels of dissolved contaminants is directly discharged into the environment, it may contaminate soil and water bodies, seriously threatening the environment and public health. Variation in leachate composition and in quantity of pollutants removed from waste are often attributed to the volume of water which infiltrates into the landfill and directly related to the natural processes occurring inside the landfill. Under favourable conditions, generally dictated by the presence of sufficient moisture to support microbial activity, landfills behave like large-scale anaerobic reactors. Simultaneously, in accordance with biochemical changes, physicochemical processes, including dissolution, precipitation, adsorption, dilution, volatization and others affect the leachate quality. Moreover, characterization of leachate is complicated by the fact that its composition may vary as a function of landfill age (Kulikowska and Klimiuk, 2008).

Leachate can be treated in various ways and the most efficient way is by integrating the treatment system. The major fraction of old or biologically treated leachate was large recalcitrant organic molecules that are not easy removed during biological treatment. So that, in order to meet strict quality standards for direct discharge of leachate into the surface water, a development of integrated methods of treatment, by a combination of biological, chemical, physical and membrane process steps, were required (Abbas et al. 2009).

1.2 Problem Statement

As the population increase, it was resulted in generation of large municipal and industrial waste (Ainee Zainol et al. 2012). These issue are leading to high generation of leachate from landfill activities, the possible of hazardous pollutants flow into the surface water is high, and become one of the greatest problems to human being , aquatic life and surrounding (Kamaruddin, 2011). The landfill operators are facing difficult problems in finding the suitable treatment method to overcome this problem

Generally, landfill leachate consist of relatively high COD as well as ammonia nitrogen concentration (Lim et al. 2010). Combinations of organic and inorganic pollutants being in landfill leachate need adsorbents that have the ability to remove various pollutants, including organic and inorganic species. It is well known that activated carbons are the most effective adsorbents for the removal of organic pollutants from the aqueous or the gaseous phase. Therefore, this type of adsorbent finds wide application as a commercial adsorbent in the wastewater treatment (Halim et al. 2010). Because of the weaknesses of AC when it comes to adsorbing polar or inorganic pollutant (Halim et al. 2011), much research has focused on modifying the AC surfaces, or on producing composite adsorbents that have the ability to interact with both organic and inorganic adsorbates.

Besides, due to high costs and specialized management requirement, the alternative method has to be taken. The aim of this study is to characterize a new composite adsorbent fabricated from chemically modified sugarcane bagasse for ammonia, colour and COD removal from stabilize landfill leachate.

1.3 Objectives

The objectives of this study are:

i. To develop new composite media to remove the contaminants of landfill leachate.
ii. To determine the capability of new composite media to remove the contaminants of landfill leachate.
iii. To establish the optimum condition using nano-composite for landfill leachate treatment.

1.4 Dissertation Outline

In chapter 1, there was an overview on the solid waste generation in Malaysia. The solid waste composition that related to the solid waste generation and also affect the quantity and quality of leachate. Problem statements, research objectives, and the dissertation outlines of this report. Next, chapter 2 was literature review covered the waste disposal by landfill and their impacts to environmental. Overview on leachate composition, factor affecting leachate quantity and quality, and the technologies of leachate treatment. In addition, some of information of activated carbon, their performance in treatment of leachate and also adsorption. Chapter 3, present the methodology of the experiment, list of materials and chemical reagents used in research work. The experimental procedure consist of preparation of precursor, activated carbon and batch studies analysis. It is followed with schematics flow diagram that showing overall activities in this research while for the chapter 4, it showed the results from experimental design used in preparing activated carbon, characterization and adsorption of activated carbon. It presents the optimization results based on the percentage of removal for COD, colour and ammoniacal nitrogen as well as the activated carbon yield for each activated carbon prepared. Next, discussed on the characterization of activated carbon that have been prepared. Lastly, more to adsorption study of activated carbon prepared. Last but not least, in chapter 5, conclusion that reflect to all objectives were obtain throughout the study as well as the recommendations for future research.

1.5 Scope of study

The samples were collected from the active detention pond with the leachate age of more than 5 years, and immediately transported to the laboratory, and stored in darkness at 4 °C prior to use to minimize the chemical and biological changes. The leachate was characterized according to Standard Method of Water and Wastewater (APHA, 2005).

Preparation of precursor by using sugarcane bagasse. Next, preparation of activated carbon by chemical activation process using zinc chloride. The activated carbon was then embedded by nano particle of ferric sulfate. Then the surface morphology of the activated carbon was scanned by SEM (Scanning Electron Microscope). Study the removal efficiencies of adsorbent based on COD, ammonia and colour of the leachate sample. The optimum condition was decided. The result of removal efficiency of sugarcane bagasse was supported graphically using Freundlich isotherm.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This chapter will briefly discuss the background information regarding waste disposal landfill, characteristic of leachate, leachate treatment by using batch adsorption study and activated carbon preparation.

2.2 Solid waste generation

Rapid economic development and population growth, inadequate infrastructure and expertise, and land scarcity make the management of municipal solid waste become one of Malaysia's most critical environmental issues. The increasing in population, the rapid economic growth and the rised in community living standards accelerate municipal solid waste (MSW) generation in developing cities. According to Manaf et al. (2009), the Malaysian population has been increasing at a rate of 2.4% per annum or about 600,000 per annum. With this population growth, the municipal solid waste (MSW) generation also increases, which makes MSW management crucial. The average amount of MSW waste generation in Malaysia is 1.17 kg/capita/day while for the whole of Malaysia is approximately 33,000 metric tonnes per day, with per capita waste generation ranging from 1 to 1.33 kg per person per day across the strata and housing type (K. Bandar, 2014).

2.3 Landfill facilities

According to Jabatan Pengurusan Sisa Pepejal Negara (JPSPN) record updated till 2015, there are 296 landfills in Malaysia and mostly it was old dumpsites. Aziz et al.

(2010) stated that most of landfill were simply dumping grounds without any environmental protection. Sanitary landfill is a treatment process in the solid waste management system. It can be defined as ‘‘a method of disposing of refuse on land without creating nuisances or hazards to public health or safety, by utilizing the principles of engineering to confine the refuse to the smallest practical area, to reduce it to the smallest practical volume, and to cover it with a layer of earth at the conclusion of each day’s operation or at such more frequent intervals as may be necessary” (Raghab et al. 2013).

To manage the solid waste in an efficient manner, four functional element interrelationships should be practiced well before the final disposal decision. The first function element is the material generated at the source. Materials that are no longer considered as having value are discarded as waste, and the quantity and the characteristic of that waste depends on the source. The second function element is waste handling, separation and storage at site. Wastes are separation before placing into the store containers. Paper, plastic, cardboard, ferrous metals, aluminum cans are some of these components. This action is very important before moving to the next point (collection). In collection, solid waste is picked up and placed into empty containers with separate parts for recyclable materials. Then, the collection vehicles collect the waste around the disposal centres manually before disposing into the disposal sites (Tarmudi et al. 2009).

In Malysia, solid waste is managed by the Ministry of Housing and Local Government, with the participation of the private sector. A new institutional and legislation framework which is The Solid Waste Management and Public Cleansing Corporation (SWCorp Malaysia) has been structured with the objectives to establish a holistic, integrated, and cost-effective solid waste management system, with an emphasis on National Solid Waste Management Department as the regulatory body and the Solid

Waste and Public Cleansing Management Corporation environmental protection and public health (Manaf et al. 2009).

However, there are lots of problem with landfills since most of them are simply dumping ground without any environmental protections. As a result, leachate is discharge directly into water courses without any treatment, which can threaten the surrounding ecosystem, particularly in cases where landfills are located upstream of water intakes (Aziz et al., 2010).

2.4 Leachate.

In general, Shim et al. (2012) stated that the landfill leachate is produced when rainwater infiltrates into the landfill and permeates through the decomposing waste within the landfill leaching out with it contaminants and pollutants. Untreated leachates can permeate ground water or mix with surface waters and contribute to the pollution of soil, ground water and surface water. Rain water percolating through a landfill leaches with it the decomposing organic matter, inorganic ions and heavy metals. This contaminant-laden concentrated effluent from the landfill is called landfill leachate. Landfill leachate can be regarded as a high strength wastewater with acute and chronic toxicity. Organic matter (biodegradable and refractory organics), ammonia and heavy metals are the three principal contaminants of the leachate. Depending upon the ratio of biodegradable and refractory organic compounds, the landfills can be classified as young, mature and old which is with stabilized leachate landfills as it can be seen from the Table 2.1 below. Generally, the risks of the leachate on the natural environment are determined by comparing leachate quality with Malaysia standards that has been published which is Environmental Quality (Control of Pollution From Solid Waste Transfer Station and Landfill) Regulations 2009.

Table 2.1 Landfill leachate classification vs. age (Abbas et al. 2009).

	Young	Medium	Old
Age (year)	< 1	1 - 5	> 5.0
pH	< 6.5	6.5 - 7.5	> 7.5
COD (g L^{-1})	> 15	3.0 - 15	< 3.0
BOD_5/COD	0.5 - 1	0.1 - 0.5	< 0.1
NH_3-N	< 400	400	> 400
Heavy metals	> 2.0	< 2.0	< 2.0

2.4.1 Characteristic and composition of leachate.

Generally, leachate is characterized by high values of COD (>400 mg/L), pH (>9.0), ammonia nitrogen (>5 mg/L) and heavy metals such like manganese (>0.20 mg/L) and zinc (2.0 mg/L), as well as strong colour and bad odour. The characteristics of the leachate vary with regard to its composition and volume, and biodegradable matter present in the leachate against time. All these factors make leachate treatment difficult and complicated. The previous study had indicated the concentration of COD, BOD and NH_3-N are very high in raw leachate, variable with seasons, climate, operational modes used, and location of the landfill (Raghab et al. 2013).

Landfill leachate characteristics varies and greatly depending on landfill age, rainfall, type of waste, site hydrology, landfill type and landfill operation (Kamaruddin et al. 2011) and (Tsarpali et al. 2012). In previous studies, the landfill leachate can be categorized into four major groups of pollutants. They are organic compounds (COD, BOD_5), nutrients (nitrogen, phosphorus), mineral compounds and heavy metals. It was shown that the principal pollutants in leachate were organics and ammonia. As the landfill age increased, organics concentration (COD) in leachate decreased and increase of ammonia nitrogen concentration. Fluctuation of other indexes (phosphorus, chlorides, calcium, magnesium, sulfate, dissolved solids, heavy metals, BTEX) depended rather on season of the year (seasonal variations) than landfill age (Kulikowska and Klimiuk, 2008).

2.4.2 Factor affecting leachate quality

Time is one of the factor that will affect the quality of the leachate. It was found that the ratio of TOC/TC in leachate decreased over time, indicating that the percentage of organic matters in leachate decreased while that of inorganic substances increased as the disposal time extended (Ziyang et al. 2009). Typically, the concentration of leachate parameters changes with the age of the leachate. The phases of leachate are transition (0–5 years), acid-formation (5–10 years), methane fermentation (15–20 years), and final maturation (greater than 20 years). The concentration of leachate contaminants at the anaerobic Kulim landfill is greater than that at the semi-aerobic PBLS which may due to the landfill's age (Aziz et al. 2010).

In general, Adhikari et al. (2014) stated there is a variation in composition and characteristics in the municipal wastes. The extent of biological activity was determined from the composition of the waste within the landfill sites. The greater concentrations of constituents are found in leachate from deeper landfill sites. But deeper landfills require more water to reach saturation. Similarly, it requires a longer time for decomposition, and distribution. Water entering the fill will travel down through the waste collected in the landfills. Generally when the water percolates through the landfill, it contacts the refuse and leaches chemicals from the wastes. Landfills of greater depth offer greater contact times between the liquid and solid phases which increase leachate strength.

The type of landfill will influenced the availability of free oxygen in a landfill. At the initial stage, aerobic decomposition occurs and the degradation may continue to occur at, and just below, the surface of the fill where oxygen is available. As a result, the chemicals released differ greatly from those produced during anaerobic degradation of the wastes in landfills compared to aerobic stage. During the process of aerobic decomposition, microorganisms degrade organic matter to CO_2, H_2O, and produce considerable amount of heat. Generally, high concentrations of organic acids, ammonia, hydrogen, carbon dioxide, methane, and water are produced during anaerobic degradation. Besides, temperature may affects bacterial growth and chemical reactions within the landfill. Temperature in the landfill sites is a largely uncontrollable factor influencing leachate quality. Decrease in optimum temperature, will decrease growth due to enzyme deactivation and cell wall rupture.

2.4.3 Factor affect the leachate quantity

According to the studies that have done, the infiltration to the landfill was estimated to be 50% of the daily rainfall. The leachate generated after a long-lacking period of rainfall had higher concentrations of pollutants. Variations of rainfall amount highly influenced the leachate characteristics that corresponded to the results obtained from the previous researches (Karnchanawong et al. 2009).

Besides, if the waste release pore water when squeezed, it will increase the quantity of leachate. Unsaturated waste will continues to absorb water until it reaches field capacity. High moisture sludge will increase the quantity of liquid retained by landfill and result higher volume of leachate may produce and it was lead to higher activity of biodegradation process and resulted in a higher concentration of pollutant in the leachate. The location of landfill sites plays an important role in leachate quantity. The landfill base sometimes constructed under the groundwater tables. When this happened, it will cause the increased of groundwater intrusion then increased the leachate quantity (Kamaruddin, 2011).

Besides, the composition of landfill leachate mainly depend upon weather condition. In January, compounds within body of the landfill probably do not undergo different degradation pathways, because of low temperatures and low amount of the rainfall. Due to the snow cover at the landfill, the lack of moisture could also reduce decomposition rates. On the other hand, increasing temperature and rainfalls probably lead to intensive degradation as well as increasing of pollution in March. During the months with high amount of rainfall which are May and November, the landfill leachate is diluted and because of it seems to be less polluted (Kalčíková et al. 2011).

2.5 Leachate treatment

Leachate treatment becomes a major concern in wastewater treatment with various approaches present such as physical, chemical and biological treatment. Sanitary landfill leachate, a highly polluted industrial wastewater, has been a cause for significant concern with landfilling being the most common technique in solid waste disposal (Wang et al. 2009). The application of the most suitable technique for the treatment of leachate is directly influenced by the characteristics of the leachate. Biological treatment processes are effective for young or freshly produced leachate, but are ineffective for leachate from older landfills (>10 years old). In contrast, physical–chemical methods which are not favored for young leachate treatment, are advised for older leachate (Ghafari et al. 2009).

2.5.1 Biological treatment

Aerobic treatment process applied the principle which used dissolved oxygen by microorganisms in the degradation process of organic wastes. Since oxygen is available to working aerobes as an electron acceptor, the biodegradation process can be significantly accelerated. The aerobic treatment system has many advantages including minimum odor when properly loaded and maintained, large biochemical oxygen demand (BOD) removals providing a good quality effluent and high rate treatment allowing smaller scale systems (Halim et al. 2012). the final discharge may contain dissolved oxygen which reduces the immediate oxygen demand on a receiving water, and the aerobic environment eliminates many pathogens present in agricultural wastes. Aerobic digestion of waste is the natural biological degradation and purification process in which bacteria that thrive in oxygen rich environments break down and digest the waste. During oxidation process, pollutants are broken down into carbon dioxide (CO_2), water (H_2O), nitrates, sulphates and biomass (microorganisms). By operating the oxygen supply with aerators, the process can be significantly accelerated (Bakar *et al.* 2010).

According to Li et al. (2011), anaerobic digestion (AD) is a method engineered to decompose organic matter by a variety of anaerobic microorganisms under oxygen-free conditions. The end product of AD includes biogas and an organic residue rich in nitrogen An anaerobic digestion for leachate treatment suitable dealing with high strength of organic effluent such as leachate streams from young tips. anaerobic digestion conserves energy and produces very few solids, but suffers from low reaction rates. Anaerobic bacteria transform the organic matter in waste water into biogas that contains large amounts of methane gas and carbon dioxide.

2.5.1 Chemicals and physical methods

Coagulation–flocculation is a relatively simple physical–chemical technique in treatment of old and stabilized leachate which has been practiced using a variety of conventional coagulants. Polymeric forms of metal coagulants which are increasingly applied in water treatment are not well documented in leachate treatment. This physical–

chemical methods are advised for old and stabilized leachate treatment; among which coagulation–flocculation is one of the simple and common methods. Although, there are many types of coagulants available to treat water and wastewater, opting the most effective coagulant for a particular wastewater still largely depends on the outcome of laboratory jar testing. PAC, a known coagulant for water treatment, but uncommon in leachate treatment, was investigated for leachate treatment in the present study (Ghafari et al. 2009).

Chemical oxidation processes are potential treatment options for the removal of specific organic and inorganic pollutants from landfill leachates, but are unlikely to provide full treatment of the wide range of contaminants present in typical samples. Oxidation involves the loss of one or more electrons from the element being oxidised the electron acceptor being another element, including an oxygen molecule, or a chemical species containing oxygen, such as hydrogen peroxide, ozone, or some other electron acceptor. Chemical oxidation has been widely studied method for the treatment of the effluent containing refractory compounds such as landfill leachate. Among the various types of physical-chemical treatments, advanced oxidation processes (AOPs) has been stated as one of the most effective method to degrade a variety of refractory compounds. This can be attributed to the role of a highly reactive radical intermediate such as hydroxyl radical (OH) as an oxidant. The radicals can be produced in ozone oxidation, Fenton oxidation, and electrochemical oxidation systems. The potential of oxidation , the OH radical rapidly degraded recalcitrant organics (Raghab et al. 2013a).

The adsorption process is used as a stage of integrated chemical-physical-biological process for landfill leachate treatment, or simultaneously with a biological process. The most frequently used adsorbent is granular or powdered activated carbon (PAC). Carbon adsorption permits 50-70% removal of both COD and ammonia nitrogen

(Demiral et al. 2008). Consequently, activated carbon adsorption aim is to ensure final polishing level by removing toxic heavy metals or organics. Other materials, tested as adsorbents, have given treatment performances close to those obtained with activated carbon. These are zeolite, vermiculite, illite, keolinite, activated alumina and municipal waste incinerator bottom ash (Abbas et al. 2009).

2.6 Leachate treatment via activated carbon adsorption process

AC adsorption is a physico-chemical process that has been reported as an effective method for removing high molecular weight refractory organic matter from landfill leachate. A number of unique characteristics such as high adsorption capacity, microporous structure, extended surface area, high degree of surface reactivity, thermo-stability, low acid/base reactivity and ability for broad range pollutants removal makes AC as one of the best filtration media in the world (Azmi et al. 2014). However, the major limitations of AC utilization in leachate treatment process are owing to the high production cost and expensive carbonaceous material. Thus, the use of non-conventional material such as agriculture waste and industrial by-product that are locally available like corncob, rattan sawdust and oil palm fiber can overcome this problem. These materials can be chemically modified and used as a low cost carbon adsorbent for landfill leachate treatment (Azmi et al. 2015).

2.7 Precursors for preparation of activated carbon from sugarcane bagasse.

There are a quite large number of studies regarding the preparation of activated carbons from agricultural wastes such as rambutan peels (Njoku et al. 2014), bagasse (Demiral et al. 2008), oil palm waste (Hameed et al. 2008), agricultural residues from sugarcane (Azmi et al. 2014), bamboo (Liu et al. 2010) and cotton stalk (Deng et al. 2010).

The large areas in Northern region of Malaysia are dedicated to sugarcane plantation to supply the required sugar. Sugar cane bagasse is the waste material produced by sugar factories after sugar juice extraction. The production of sugar cane can be anticipated to increase significantly in the future. The observations above show that sugar manufacturing processes produce a large amount of sugar cane bagasse wastes each year. Malaysia had produced 700,000 ton of sugarcane in 2009 (Shafie et al. 2012). These wastes are usually burnt in the open or left in the field, and only a small portion is used as paper pulp. This creates disposal and pollution problems. The activated carbon obtained from the agricultural wastes can provide useful, value-added products in the sugar factories and related industries. Activated carbon for commercial utilization can be obtained by thermal treatment of low-cost and low ash content materials. Sugar cane bagasse just conforms to the rule for it is a low ash content and availability (Liou, 2010). Sugar industries generate large amounts of pollution load particularly in terms of suspended solids, organic matter, press mud, bagasse pith and bagasse fly ash. These wastes especially bagasse fly ash does not find any use as such and causes a disposal problem. Currently, this is being used as filler in building materials. However, bagasse fly ash and otherwaste products have been used as adsorbent for the removal of various pollutants from the water (Ali et al. 2012).

2.8 Preparation of activated carbon.

Basically, there are two different processes for the preparation of activated carbon: physical activation and chemical activation. In comparison with physical activation, there are two important advantages of chemical activation. One is the lower temperature in which the process is accomplished. The other is that the global yield of the chemical activation tends to be greater since burn-off char is not required. Among the numerous dehydrating agents, zinc chloride in particular is the widely used chemical agent in the preparation of activated carbon. Knowledge of different variables during the activation process is very important in developing porosity of carbon which is sought for a given applications. For example, chemical activation done by $ZnCl_2$, H_3PO_4, H_2O_2, etc., can improve the pore distribution and increase the surface area of adsorbents in the structure because of using different chemicals. Besides, carbon content in precursor was increased due to pyrolytic effect at high temperature. Similar observations are reported on AC from bamboo waste, tamarind wood and coconut shell (Kamaruddin et al. 2011).

2.8.1 Physical activation

The physical activation requires high temperature and longer activation time as compared to chemical activation. However, in chemical activation, the activated carbon need a through washing due to chemical agent. In physical activation is a two steps process. It involves carbonization of a carbonaceous material followed by the activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures (Kamaruddin, 2010).

The carbonization temperature range normally between 400 to 850˚C and the activation temperature range between 600 to 900˚C (Guo et al. 2009). All carbonization temperatures were investigated both micropore and macropore volumes that showed maximum values at intermediate carbon burn-off whereas small amount of mesopore was developed. From that, as the level of burn-off increased, a rapid development in mesopore occurred.

2.8.2 Chemical activation with conventional heating

During the chemical activation, the precursor is impregnated with an activating agent such as $ZnCl_2$, H_3PO_4, KOH, H_2SO_4 or NaOH. Then, carbonized following conventional heating via an electrical furnace in an inert atmosphere at temperatures ranging from 400 to 800˚ C or alternatively carbonized with microwave heating (Demiral and Gunduzoglu, 2010). The impregnation ratio, activation temperature and activation time period were observed to be the vital factors in preparing AC from conventional heating. The impregnation ratio (defined as the ratio of the weights of chemical agent to precursor) is a variable that highly affects not only the pore size distribution of the resulting AC, but also the total surface area (Fierro et al. 2007).

2.9 Activated carbon characterization

2.9.1 Physical properties

The activated carbon was characterized physically (density, porosity, structure and surface morphology). The microscopic structure of activated carbon can be clearly seen from the SEM photograph (Foo et al. 2013b).

2.9.2 Chemical properties

The functional groups and chemical composition play important roles in the adsorption mechanism and capacity. Therefore, proximate and elemental analyses as well as surface chemistry are some of the important chemical properties of activated carbon to be studied.

2.9.3 Surface morphology and porosity of activated carbon

The surface morphological and pore structure of activated carbon can be seen by using a Scanning Electron Microscope (SEM). A scanning electron microscope (SEM) scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition. Based on previous studies (Azmi et al. 2014), during pyrolysis process non-carbon elements such as hydrogen, oxygen, and nitrogen released in the form of tars and gases leaving a rigid carbon skeleton with a rudimentary pore structure formed from the aromatic compounds. Consequently, activation by physico-chemical process enhanced the pore structure of sugarcane-derived AC. Pretreatment of the char with dehydrating agent ($ZnCl_2$) inhibits formation of tar and other undesired products, and at the same time generates porosity by carbon oxidation and hydroxide reduction. Consequently, CO_2 creates AC with larger micropore volume and narrower micropore size distribution leading to higher adsorption capacity (Azmi et al. 2015).

2.10 Adsorption performance

Adsorption process, a surface phenomenon by which a multi-components fluid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and form attachments via physical or chemical bonds, is recognized as the most efficient and promising fundamental approach in the wastewater treatment processes (Foo and Hameed, 2009). The adsorption of onto activated carbon can be attributed to the pore-filling effect (micropores and some narrow mesopores) and strong adsorptive interactions with the graphene surface or oxygenated groups. Regarding the surface area-normalized adsorption of TMP, porous activated carbon exhibited 50–500 times lower adsorption than nonporous carbon adsorbent due to the size-exclusion effect, especially when oxygen complexes presented on the edges of the pores of the activated carbon. From a system design point of view, a fast adsorption rate and high adsorption capacity are normally required, and these findings imply that activated carbon with high microporosity, a certain mesoporosity and approachable surface groups can have great application potential for TMP removal.

By knowing the adsorbate concentration at initial concentrations and equilibrium concentrations, the efficiency of adsorption by activated carbon can be calculated by using the following equation for efficiency of adsorption chromium (Cronje et al. 2011):

$$Adsorption\ (\%) = \frac{Co - Ce}{Co} \times 100 \qquad (2.1)$$

2.10.1 Effect of initial pH

Previous studies showed the removal of colour, iron and COD in the absence of media was slightly higher at a very acidic condition. This is due to the positive charge dominates the surface of the adsorbent, which slightly increases the electrostatic attraction existing between the negatively charged dye species and the positively charged surface of the adsorbent. Greater removal of COD at lower pH values because the precipitation of solids, corresponding to humic acids, will increase, which improves the removal efficiency of COD (Abu Foul et al. 2009).

Adsorption of lead and zinc was studied under similar condition at different pH. There is practically no removal at pH lower than 3 may be due to high H^+ ion concentration, which reverses the process of adsorption. There is a gradual increase in adsorption with increase in pH from 3 to 6 and the maximum adsorption is at pH 6. Again the percentage of adsorption increases gradually with increase in pH from 6 to 10 may be due to the formation of the precipitate of $Pb(OH)_2$ and $Zn(OH)_2$. So pH 6 was considered as optimum condition and was used for further study for both single and binary systems (Mishra and Patel, 2009).

2.10.2 Effect of contact time

In the early stage, there are larger surface sites that lead to higher adsorption capacity at a short period of time. However, as the contact time prolonged and approached to equilibrium, the availability of sorption sites decrease and becomes difficult to occupy due to repulsive forces between the solute molecules on the solid and bulk phases. As a consequence, the removal rates slow down due to the competition for the adsorption sites (Azmi et al. 2014).

2.10.3 Effect of adsorbent dosage

The adsorbent dosage conducted will affected both the rate of adsorption and the extent to which adsorption occurs. In general, the adsorption increase with the increases in adsorbent dosage. The increase in adsorption of certain parameters in adsorbate with adsorbate dosage can attributed to the increases of surface area adsorption sites (Kamaruddin, 2011).

Some of studied found that the adsorbent dosage influences the removal of pollutants in waste water. For example, from the research of Lin and Yang (2002) which the removal of pollutants from waste water by coal stated that the removal of COD and copper increase due to increase dosage of coal. This can explained that the amount of adsorbent influences the adsorption capacity.

2.11 Adsorption isotherm

Adsorption isotherm is helpful in describing the interaction of adsorbates with adsorbents, and the equilibrium distribution of adsorbate molecules between the liquid and solid phases (Njoku et al. 2014). The adsorption characteristics in this study were analyzed using the Langmuir and Freundlich isotherm models which are the most common models for describing the adsorption properties of adsorbents used in water and wastewater treatment (Azmi et al. 2014).

2.11.1 Langmuir isotherm.

The Langmuir theory was described the monolayer coverage of adsorbate over homogeneous adsorbent surface (Foo and Hameed, 2010). Basically, once the adsorbate is attached on the site, no further adsorption can take place at that site, that will concluded as adsorption process is monolayer in nature (Mohd Din et al. 2009). Langmuir equation is expressed by the following equation:

$$\frac{x}{m} = \frac{QbC}{1+bC} \qquad (2.2)$$

The linear form of Langmuir isotherm equation is given by equation 2:

$$\frac{1}{(\frac{1}{m})} = \frac{1}{\mathrm{QbC}} + \frac{1}{\mathrm{Q}} \qquad (2.3)$$

Where is the amount of material adsorbed (mg), is the weight of adsorbent (g); C is the equilibrium concentration of adsorbate in solution after adsorption is complete (mg/l); Q (mg/g) and are the Langmuir constant related to the maximum adsorption capacity and the energy adsorption.

2.11.2 Freundlich isotherm.

Freundlich isotherm was developed by Freundlich (1906) known that the relationship describing the nonideal and reversible adsorption, not restricted to the formation of monolayer (Foo and Hameed, 2010). The Freundlich isotherm also assumes that adsorption occurs on a heterogenous surface through a multilayer adsorption mechanism and that the adsorbed amount increases with the concentration according to the following equation:

$$q_e = K_F C_e^{1/n} \quad (2.4)$$

where qe is the amount of adsorbate adsorbed at equilibrium, (mg/g), Ce is the equilibrium concentration of adsorbate, (mg/l), KF is the Freundlich constant, (mg/g)(L/mg)1/n and n is the Freundlich heterogeneity factor.

The equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2.5)$$

A plot of (log q_e) against (log C_e) yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constant can be obtained from the slope and intercept of the linear plot of experimental data. The value of n indicates favourable adsorption when $1 < n < 10$.

CHAPTER 3

METHODOLOGY

3.1 Overview

This chapter will present the materials and method used in research. It was consist of general materials and equipment that been used. Followed by the design of experimental which are preparation and characterization of activated carbon. Next, the adsorptive uptake efficiencies of colour, COD, and heavy metals were investigated by testing the influence of operational variables including shaking speed, contact time, AC dosage, and pH. After each run, the media were filtered and the filtrates were kept for analysis of pollutants removal.

3.2 Flow schematic diagram

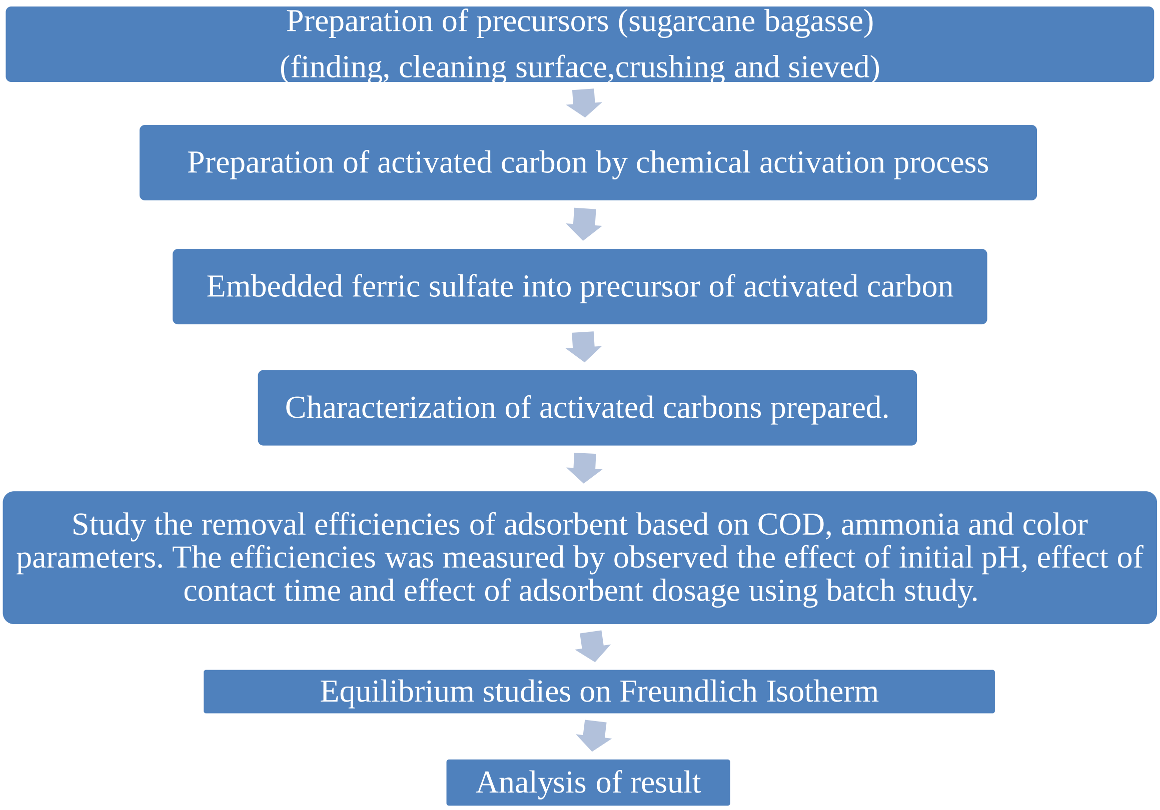

Figure 3.1: Flow chart of research study.