PEAT WATER TREATMENT USING CHITOSAN-BENTONITE, SURFACTANT MODIFIED BENTONITE AND NATURAL ZEOLITE

by

SITI NOR FARHANA BT ZAKARIA

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OLAHAN AIR PAYA MENGGUNAKAN KITOSAN-BENTONIT, SURFACTANT TERUBAH SUAI BENTONIT DAN ZEOLITE ASLI

oleh

SITI NOR FARHANA BT ZAKARIA

Tesis yang diserahkan untuk

memenuhi keperluan bagi

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LIST OF ABBREVIATIONS

Ag_2SO_4	Silver Sulfate
BTC	Breakthrough curves
$CaCO_3$	Calcium Carbonate
CCD	Central Composite Design
COD	Chemical Oxygen Demand
DO	Dissolve Oxygen
FA	Fulvic Acid
Fe	Iron
GAC	Granular Activated Carbon
HA	Humic Acid
HCl	Hydrochloride Acid
HDTMA	Hexadecryltrimethylammonium Chloride
$HgSO_4$	Mercury (II) Sulfate
HMA	Hymatomelanic Acid
ICP	Inductively Coupled Plasma mass spectrometry
ICS	Ion Chromatography System
INWQS	Interim National Water Quality Standard
K_2CrO_7	Potassium Dichromate
NaOH	Sodium Hydroxide
NTU	Nephelometric Turbidity Units
OPC	Ordinary Portland Cement
PAC	Poly Aluminium Chloride
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy

SLR	Surface Loading Rate
SMB	Surfactant Modified Bentonite
TCU	True Colour Unit
UNDP	United Nations Development Programme
USEPA	United State Environmental Protection Agency
WWF	World Wild Fund Malaysia

LIST OF SYMBOLS

R^2	Coefficient of determination
K_L	Energy of adsorption in Langmuir Isotherm
K	Constant
q_m	Maximum capasity adsorbate adsorption in Langmuir isotherm
K_F	Capacity of adsorbate adsorption in Freundlich Isotherm
N	Level of adsorbent intensity to attract adsorbate in Freundlich Isotherm
p	Probability in ANOVA analysis

OLAHAN AIR PAYA MENGGUNAKAN KITOSAN-BENTONIT, SURFACTANT TERUBAH SUAI BENTONIT DAN ZEOLITE ASLI

ABSTRAK

Paya gambut merupakan salah satu kawasan lembap yang terbesar di Malaysia. Kebolehan paya untuk menyimpan air walaupun di dalam musim kemarau membuatkan paya gambut sangat berguna kepada flora dan fauna. Isu kekurangan air pada masa kini telah menjadikan air paya berpotensi untuk digunakan sebagai salah satu sumber bekalan air alternatif. Walaubagaimanapun, sifat air paya yang berasid, keperangan, mengandungi banyak unsur organik dan logam berat (besi) telah membuatkan air paya tidak sesuai disalurkan terus kepada pengguna. Oleh itu, kaedah untuk merawat air paya telah ditakrifkan di dalam kajian ini. Pemantauan kualiti air paya selama enam bulan di paya Beriah, Perak menunjukan air paya di sini mempunyai unsur besi, kekeruhan, keperangan dan asid yang tinggi. Di dalam kajian ini, terdapat dua kaedah telah digunakan iaitu kaedah balang dan kaedah penyulingan. Bahan yang digunakan di dalam kaedah balang adalah kitosan, bentonit semulajadi, bentonit diubah suai, gabungan bahan dan komposit. Sementara itu, dalam kaedah penyulingan, tambahan bahan penyerap seperti zeolite semulajadi dan karbon teraktif telah digunapakai untuk meningkatkan tahap pembersihan air paya. Eksperimen ini telah direka dan dianalisis menggunakan perisian Metodologi Tindakbalas Permukaan (RSM). RSM mampu menunjukan tindak balas yang berlaku diantara bahan dan juga sampel. Berdasarkan keupayaan untuk merawat air paya, gabungan kitosan-bentonit semulajadi menggunakan kaedah balang telah dipilih sebagai bahan terbaik diantara semua bahan. Gabungan ini telah menghilangkan 78% warna perang, 89% kekeruhan, 90% unsur besi dan 67% keperluan oksigen kimia (COD) di dalam air paya. Tindak balas itu berlaku pada pH air paya semulajadi iaitu 4.80.

Pembentukkan endapan zarah yang dilihat pada gambaran Imbasan Elektron Mikroskop (SEM) dan penambahan saiz yang direkod oleh mesin pengukur (Mastersizer) membuktikan gabungan ini benar-benar mempunyai kecenderungan untuk bertindak balas dengan unsur pencemar.

PEAT WATER TREATMENT USING CHITOSAN-BENTONITE, SURFACTANT MODIFIED BENTONITE AND NATURAL ZEOLITE

ABSTRACT

The peat swamp is one of the largest wet land coverage in Malaysia. Its ability to retain water even during drought makes the peat swamp a valuable resource to a variety of flora and fauna. In light of the recent water shortage issue, peat water was included in the list as one of the potential alternative water resources. However, due to its acidic nature, high organic matter and heavy metal (iron) contents, peat water is unsuitable to be supplied directly to consumers. Therefore, methods to remediate peat water from pollutant were defined in this study. After a six month monitoring at the Beriah swamp, Perak, it was found that peat water contains a high concentration of heavy metal iron, is turbid, brownish and acidic. In this study, two methods were used i.e. the jar test and the column study. The materials used in the jar test were chitosan, natural bentonite, modified bentonite, its combination and composite. In the column study, additional adsorbents such as natural zeolite and activated carbon were used to enhance the purification of the samples. The experiment was designed and analysed using Response Surface Methodology (RSM) in order to determine their interactions with the samples. Based on the efficiency in remediating peat water samples, the combination of chitosan-natural bentonite in the jar test was chosen as the best material. This combination had recorded removal 78% colour, 89% turbidity, 90% iron and 67% Chemical Oxygen Demand (COD) in natural peat water pH 4.80. The flocs formation which was observed in the Scanning Electron Microscopy (SEM) image and the size increment resulting from the Mastersizer analysis had proven that this combination had an affinity towards the pollutant elements.

CHAPTER 1

INTRODUCTION

1.0 Background of study

The earth is covered with almost 70 percent of water. Water presented in liquid form and become a main component in human life. By referring to hydrological cycle, there are six basic processes involved which are evaporation, transpiration, condensation, precipitation, runoff and infiltration. Water from the lake, river or ocean will evaporate to the atmosphere by depending on temperature. After it evaporates, the vapour or gases will condense. At this stage, the dark clouds are formed and give a sign that the day will be rain. A tiny drop of water falling down to the ground is called as precipitation process. At this stage, water particle can be drop in crystal ice form (snow or ice pellets) or liquid form (rain) depending on temperature at that area (Gilbert, 1990).

The process does not end with raining stage. It is continues by runoff and filtration process. Not all water will infiltrate into the ground because the soil itself has limited capability to filtrate water. Therefore, after the soil becomes saturated, water will flow according to the earth gravity on the ground as runoff. Finally, the lower place or wetland like reservoir, river, ocean and lake become a final destination for runoff before evaporation process repeated again (Gilbert, 1990).

The major water resource in this country is surface water. Abundant of surface water in Malaysia is coming from rainfall. The main surface water in this country is river. According to World Wild Fund for Nature Malaysia (WWF), there are 189 rivers in

Malaysia which came from highland. River have contributed almost 97% water supply for domestic, agriculture and industries uses. However, the increasing number of people, economies, development and water pollution make water demand increase in every year. Nowadays, current issue starts to mention about an alternative water resource since the water demand is increasing in every year as well as water pollution problem.

1.1 Wetland

One of the reservoir areas in Malaysia is wetland. Wetland is described as area which is covering mostly covered with water. Wetland itself has different characteristics depending on its soil, landscape, climate, water regime, and chemistry, vegetation and human disturbance. According to United State Environmental Protection Agency (USEPA) (2001), wetland also can be categorized into four general categories which are marshes, swamps, bogs and fens.

Marshes physically look like a pond surrounding by non-woody vegetation which adapted to wet soil conditions. Generally, these types of wet land general are periodically saturated, flooded and ponder with water. Basically marshes can be grouped into two groups which are tidal marsh and non-tidal marsh. Tidal Marsh occurs nearer the ocean (coastline) and surrounded by salt tolerant plants such as cordgrass and glasswort. The tidal marsh prevalent influence with tides and fresh water such river and rain (United State Environmental Protection Agency, 2001). Those source affecting the level of water and also water characteristic in tidal marsh pond. Non- tidal marsh is defined as forest of herbaceous plant and occurs in poorly

drained depression, floodplains and shallow water area such as at edges of lake and rivers (United State Environmental Protection Agency, 2001).

Subsequently, bogs had different physical and chemical properties from swamps and marsh. Bogs has characterized by its spongy soil, stagnant and acidic. Prevalently, bogs are located at higher area than its surrounding. The main source for bogs is precipitation and it is implies bogs as having lack of nutrient which is needed for plant to growth (United State Environmental Protection Agency, 2001). Stagnant physical in bogs make this wetland look like a pond without drainage and water is held by seepage. Different from bogs, swamp is major parts of wet land in this country and it is normally can be found at low land area. Malaysia has a lot of surface water (river) and this fresh water is the main water supply for swamp. Swamp is generally surrounded by woody vegetation such as mangrove and has ability to retain and provide water even in drought season because of its unique soil textile characteristic (Wetlands International, 2010).

Peat land in tropical area has a unique and difference characteristic compare to other places. Peat land is described as a wetland which is rich with organic matter and acidic. It is surrounded by large canopy tree and suitable as a habitat for numbers of fauna while Europe swamp is just cover with tall grasses. The plant in tropical swamp is also valuable and suitable for timbering (United Nations Development Programme Malaysia, 2006). Malaysia is located in South-East Asia and categorizes as tropical country which supports intact tropical peat land. In Malaysia, peat soils encompass 2,457,730 ha (7.45%) of total land area (32,975,800 ha). Sarawak having the largest area of peat soils in Malaysia (1,697,847 ha) followed by Peninsular Malaysia (642,918 ha) then Sabah (116,965 ha) (Wetlands International, 2010). Peat

land in Malaysia mostly is present in peat swamp forest. Peat swamp forests are waterlogged forests growing on a layer of dead leaves and plant material up to 20 meters thick (United Nations Development Programme Malaysia, 2006).

Peats in South-East Asia often contain more than 90% organic matter and they are acidic with pH level as low as 3.5 (Wetlands International, 2010). Swamp water is typically dark brown to black colour because of high humic substances (humus and humic acids) (United Nations Development Programme Malaysia, 2006). Humic substance was created during decomposition of organic matter and responsible for dark colour of water, capability of water to retain, friability and electrostatic conductivity. Because of the polar character of peat, the special adsorption potential for dissolved solids such as metals and polar organic molecules is quite high (Brown et al., 2000). Thus peat soil contains high metal composition. Composition of peat is complex and unique. The characteristic of peat is created based on its surrounding area such as feeding condition of peat land, geomorphologic position, geological settling of the region, environment condition and anthropogenic impact (Mall et al., 2011).

Peat land has an ability to store the water event in drought season. Advantageous by having very high porosity and water content make water retained in a one layer without seep into the ground. Moreover, the irreversible drying property also support water to retain and make peat swamp is suitable to become as an alternative of water resource. Disadvantageous of peat soil and its drainage are acidic, poor in nutrients and saturated with organic matter. Thus it is unsuitable to be used as water supplied without passing an extensive treatment (United Nations Development Programme Malaysia, 2006).

1.2 Problem Statement

Malaysia is a developed and modern country. Most households in this country are provided with basic facilities such as clean water, and electrical power supply. However, residents in many rural areas are facing difficulties in getting a continuous supply of clean water due technical and internal problems from the water suppliers. Therefore, an efficient alternative to the water supply especially to rural areas needs to be identified.

Malaysia is facing a major issue with water supply nowadays. According to Chan (2005), most Malaysians never expected that Malaysia will face water shortage problems until the water crises hit Melaka in 1991 and Selangor and Kuala Lumpur in 1998. Malaysia receives heavy rainfall every year and has more than 150 river systems which can supply more than 20, 000 m^3 of water per year. This fact keeps the Malaysian citizens secured but history had proven that Malaysia can also be struck with water crisis. Another major water problem cited by Chan (2005) was the high domestic water usage per-capita in Malaysia especially in urban areas. It is increasing every year due to development, industrial and agricultural growth. As a solution, an alternative water resource needs to be identified because water is essential to our lives and future generations.

Rural areas are surrounded by natural resources and one of the natural treasures found in the rural parts of Malaysia is the typical fresh peat swamp. The peat swamp has a unique water retention ability which makes it useful as water storage even in dry seasons. However, due to the high organic compound and iron contents and its acidity, peat water remains unutilized (Noraini et al., 2010). In order to make peat water one of our fresh water resources, pollutants inside the water need to be remove.

Several techniques are available to remediate peat water but most of them are costly. Thus, effective and economical techniques need to be determined (Kamari et al., 2011a). Low-cost materials such as chitosan, bentonite and limestone had proven their ability to remediate various types of waste water and samples in other research (Salam et al., 2011; Fu and Chung, 2011).

1.3 Objectives of Study

The aim of this study was to identify the potential of peat water as a water resource and determine the most suitable water treatment for treating peat water as drinking water.

The specific objectives of this study were:

1. To identify the optimum conditions of pH, reaction time and sorption dosage of chitosan, natural bentonite, surfactant modified bentonite (SMB), its combinations, composites, natural zeolite, limestone and activated carbon.
2. To assess the ability of chitosan, natural bentonite, modified bentonite, its combinations, composites, limestone, natural zeolite and activated carbon for treatment of peat water.

1.4 Scope of Study

The main purpose of this study is to identify new an alternative water resource and effective water treatment for treating peat water by using low cost adsorbents. Beriah swamp was chosen as location of sampling for this study. Water quality in the Beriah swamp was monitored and compared to the national standard for six months in terms of physical and chemical characteristics. In this study, ten types of low-cost coagulants and filtration media which were chitosan, natural bentonite, Surfactant

Modified Bentonite (SMB), combination chitosan-natural bentonite, combination chitosan-SMB, composite chitosan-natural bentonite, composite chitosan-SMB, natural zeolite, activated carbon and limestone were experimental to define their ability in remediate peat water. Optimum condition of each factorial such dosage, contact time and pH were studied for all coagulants involved as well as filtration media. Comparison between jar test and column filtration also made in order to determine the most suitable and relevant treatment can be applied on site.

1.5 Justification of the Research

The cardinal point of this study was to find the optimal condition of dosage, pH and contact time for those potential materials listed above in the remediation of peat water. Common coagulants and adsorbents such as chitosan, natural bentonite, lime stone, activated carbon and natural zeolite were chosen as the purifying media in this study based on their ability in removing unwanted substances as well as for economic and environmental reasons (Veli and Alyuz, 2007; Rizzo et al., 2008).

In recent years, the world is facing a lot of water-related problems; one of it is water scarcity. Even though Malaysia is located in the tropical region and enjoys high rainfall intensity, water demand still increases year by year. Development, industrial, manufacturing, agricultural and economic growth had contributed to increase water usage in this country. Indeed, an alternative water resource should be explored and studied in order to sustain lives. Malaysia possesses a large wet land area and those areas such as peat swamps have big potential to serve as water reservoirs owing to their ability to retain water. In short, peat swamps found mostly in rural areas are potentially valuable sources of water.

Chitosan is applied widely in cosmetics, pharmaceuticals, agriculture and biotechnology. This amino-biopolymer is also well known for its ability as a coagulant to remove organic matters and heavy metals. However, the application of chitosan was constrained in water treatment because of its high cost compared to other coagulants. In this study, an alternative by combining and composed natural material as a coagulant and filtration medium was tested in order to reduce the chitosan dosage yet providing clean water as the end product. The experiment was designed and analysed using response surface methodology (RSM). Modified bentonite with surfactant was also included in this study as an alternative to remediate peat water while limestone was used for increasing the pH of peat water.

In this study, two methods were applied in treating peat water which was the jar test and the column method. The jar test is a method of simulating the full scale of conventional water treatment in the field. Similar to the jar test, the column study also functions as method to remediate water samples from pollutant substances. The column study normally prefers aggregate minerals as their media because smaller sizes of media will cause clogging and reduce the effectiveness of the column. Finally, a comparison of both methods was done in order to find the best method that can be used to treat peat water.

1.6 Organization of the Dissertation

The thesis is divided into five chapters. Chapter 1 is a brief introduction and idea about this study including background study, problem statement, objective of research, justification as well as the organization of the thesis. Subsequently, Chapter 2 presents a literature review of previous researcher findings which is related to this

study. The literature review in this chapter is further divided into ten main topicswhich are peat swamp forest, characteristics of peat water, coagulant and coagulant aid properties, composite, adsorbent, batch study, column filtration process, response surface methodology, absorption isotherm model and summary of literature review.

Next, Chapter 3 explains the methodology of the research. In this chapter, the apparatus, materials, chemicals used, procedures of experiment, preservations and precautions taken, instruments involved and analysis of data are discussed in detailed. Additionally, a flow chart diagram is attached in this chapter in helping to explain the flow of this research clearly. The most complicated and interesting chapter is Chapter 4 which discusses the data obtained from the test and analysis finding. Finally, the summary and conclusion of the study are presented in Chapter 5. In this chapter, recommendations for further studies are also stated.

CHAPTER 2

LITERATURE REVIEW

2.0 General

Water is a basic necessity to living things. In Malaysia, surface water and rainfall become a main water resource for civilians and industries. Surface water was collected and undergoes to water treatment process before it can be supplied to consumer. The amount of water demand increase year by year especially in develops country and it has become a serious issue to be debated nowadays. An alternative water resource such as groundwater and swamp is seen to be a great potential for water supply.

Peat swamp is known as area which surrounding by surface water or rainfall and acidic. Peat swamps also one of the forest cover in Malaysia. Peat swamp has become a habitat for various types of flora and fauna. It has a unique ability to make our ecosystems place in good conditions such as preventing land from flooding, maintaining of based flow in river, toxicant removal and restoring water event in drought season. Advantageous in swamp itself make this wetland become a priority to be study as alternative water resource in this country.

2.1 Peat Swamp Forest

Generally, swamp is describing as wetlands which are covering with forest and usually located nearby the river or lake. There are more than 420 million hectare peat soil on earth (Wosten et al., 1997) especially in tropical region (72 million hectare)

(Ayob and Ahmad Khairi, 2003) and subtropical area. The distribution of peat swamp in South-East Asia and Malaysia is shown in Figure 2.1, Figure 2.2 and Figure 2.3. Based on Figure 2.1, Indonesia monopoly the area of peat swamp with 20 million hectare (Dwiyono and Rachman, 1996) followed by Malaysia 2.7 million hectare and remain belong to Brunei (Mutalib et al., 1992).

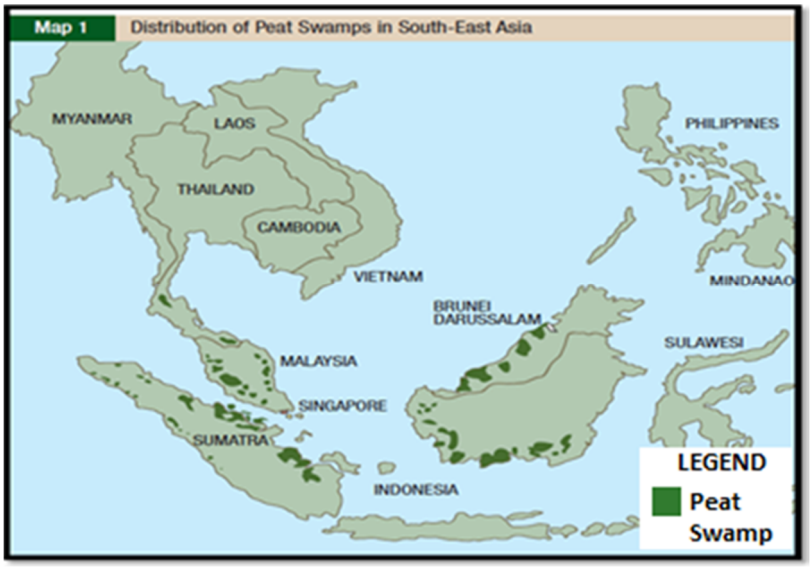


Figure 2.1.Distribution of peat swamps in South-East Asia
(United Nations Development Programme Malaysia, 2006)

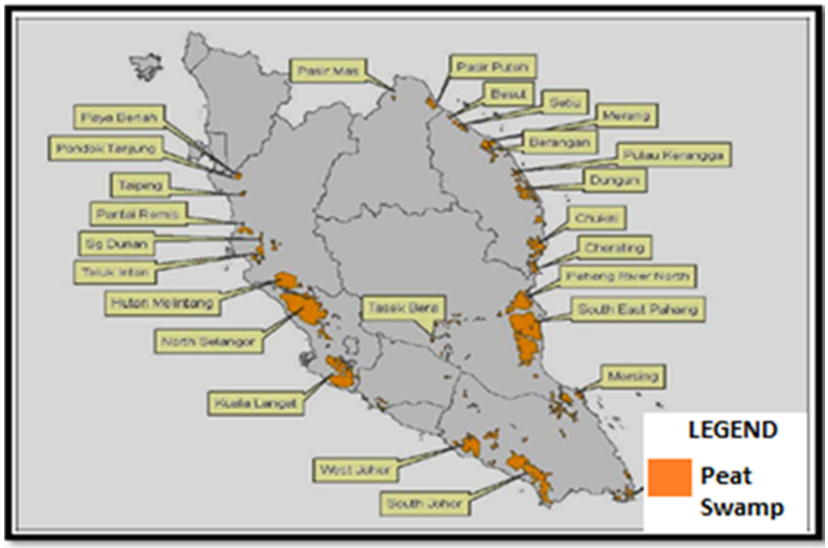


Figure 2.2.Distribution of peat swamps in Peninsular Malaysia
(Wetlands International, 2010)

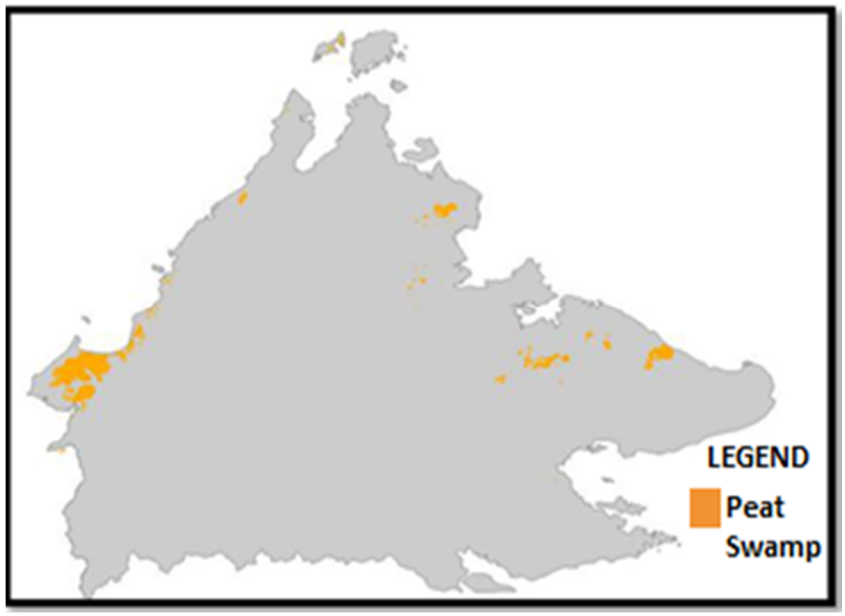


Figure 2.3.Distribution of peat swamps in Sabah (Wetlands International, 2010)

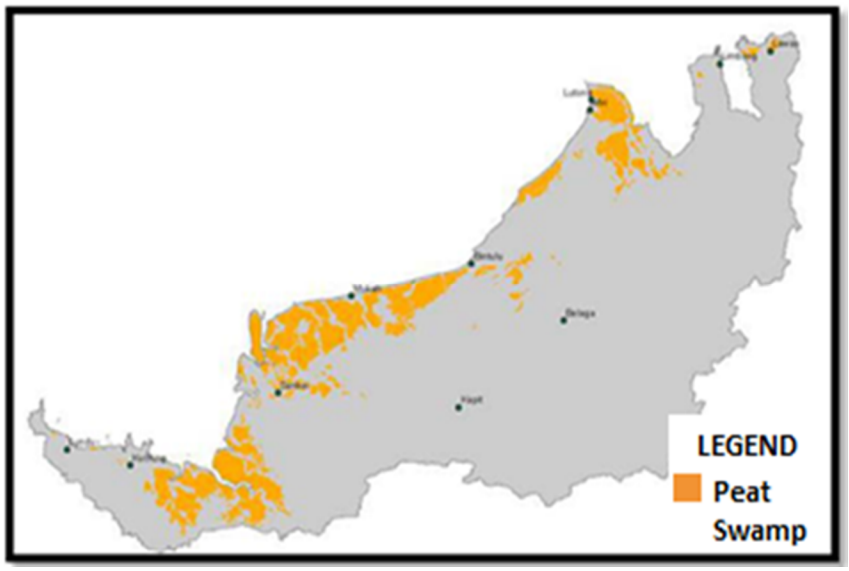


Figure 2.4.Distribution of peat swamps in Sarawak (Wetlands International, 2010)

Notably, seven percent from 22 million hectare of peat swamp in South East Asia are located in Malaysia as shown in Figure 2.1 (Mutalib et al., 1992) and based on United Nation Development Programme (2006), they estimate about 1.54 million hectare peat swamp covering Malaysia with large distribution in Sarawak 70 percent (Figure 2.4), follow by 20 percent at peninsular Malaysia (Figure 2.2) and remaining

is belong to Sabah (Figure 2.3). Those data clearly mention that Malaysia have an abundant of peat swamp as well as peat water.

Peat swamp globally representative a unique ecosystem and providing habitat for variety of flora and fauna. Each parts of this land including peat soil playing different roles in order to sustain our ecosystem and surrounding. Basically, formation of peat soil is form from decomposition of wood and dead vegetation around the swamp. The final product from this process is dark-brownish water which is rich with humic acid. Peat is an accumulation of decay vegetation or organic matter. It is non-decomposed and having high water content. The composition of peat is different in each region due to different types of vegetation occurs. The swamp characteristic also influence by temperature and climate zone (Mall et al., 2011).

Indeed, formation of peat produces unique ecosystem relation between hydrology, soil and vegetation. Decomposition of vegetation activities normally occur in high rainfall capacity and wet area such as tropical and subtropical region. Dead leaf will slowly decompose by bacteria until microbial degradation is retarded. In this condition, a dark brown non-soluble friction of peat with high molecular weight, capable to retain water, friability and electrostatic conductivity was formed (Mall et al., 2011). The formation phase of peat swamp is explained briefly in Figure 2.5.

Accumulation of organic material naturally build-up a layer of peat and become thicker by years. The different layers of peat with different characteristics make peat swamp have special ability to retain water and maintain the base flow of the river. There are three main layers in peat soil according to the degree of decomposition which are fibric, hemic and sapric. Fibric is the first decomposition of soil stage,

followed by hemic which is present in dark greyish brown to dark reddish brown and finally is sapric which occurs in very dark gray to dark colour (Hodgson and Palmer, 2012).

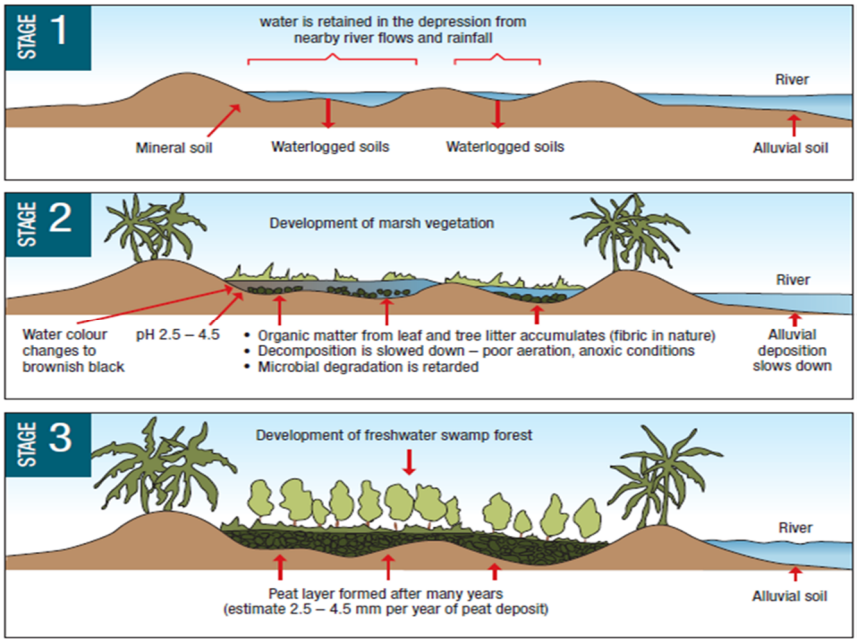


Figure 2.5 Stage of formatting peat swamp (United Nations Development Programme Malaysia, 2006)

Peat swamp served a lot of benefits to ecosystem and living things. Peat swamp starts to become favourable to human in agriculture sector for irrigation. Peat swamp is well known as having a great ability in restoring water even in drought season. The layer of peat soil is rich with organic matter which tends to be characterized as high porosity with lower bulk density and resulting high water retention in order to prevent water from seeping to the ground (Walazeck et al., 2002). Swamp can also acts as natural flood mitigation especially during raining season. The large area in swamp can cater flood water in certain time depending on its water holding capacity. The excessive water will be stored either in the surface area or underground and release it horizontally when the flooding is recovered. Other than that, it also

becomes a saver in maintaining base flow of the river. Peat soil behaves like a sponge which it can absorb and storage the water and releases when needed. Apart of critical role, tropical peat swamp being a house of variety species plant and advantageous gives an attraction to a lot of animal as their habitat (United Nations Development Programme Malaysia, 2006).

2.2 Peat water characteristic

Generally peat water is well known as dark-brownish colour and acidic. Decomposed of vegetation and accumulated organic material to form peat has directly donor, dark brownish colour, higher organic matter and acidic in peat water (Wosten et al., 2008). Even though peat water is labelled by contain higher concentration in certain element but peat water still have a great potential to become as one of water resource based on its capability in providing continuous water even in drought season.

2.2.1 Physical characteristics of peat water

Generally, physical characteristic is defined as characteristic which determined by sense of touch, sight, smell and taste. The example physical characteristic for water are temperature, colour, turbidity, suspended solid and odour.

2.2.1.1 Colour

Colour is one of the important parameters in water quality standard especially for drinking water. According to National Standard for Drinking Water discharge limit for colour is less than 15 TCU (true colour unit). Colour normally occurs because of other unwanted elements present inside the sample. For example, iron is tending to make water become red while manganese can give black-brownish colour into the

sample. Higher colour in water gives negative perspective from consumer toward water quality. Moreover, water supply with high TCU will lead a lot of problem especially in cloth washing, dyeing, paper industry, dairies and other food product (Malakootian and Fatehizadeh, 2010). Determination of colour can help in estimated costs which is relate to discolouration of the water.

Fundamentally in measurement, there are two types of colour which are true colour and apparent colour. True colour is describe as soluble chemical substances that cannot be separated by filtration while apparent colour is referring to suspended and colloid matters that can be isolated by filtration (Malakootian and Fatehizadeh, 2010). In short, true colour is a colour after the sample is filter while, the apparent colour is a raw colour of sample without filtration.

Water in peat swamp are typically dark brown to black colour because of incomplete decompose vegetation under lack of oxygen condition (Mall et al., 2011). The black colour appears when the water mixed with debris and little organic matter such as dead leave and wood in various and difference stages of decomposition (Noraini et al., 2010). The dark colour of peat water may also becaused by higher amount of certain mineral like iron and manganese. This fact matched well with data recorded in Beriah (Wan et al., 2005) and Sarawak swamp (Mall et al., 2011) which is having dark brownish colour.

2.2.1.2 Dissolved Oxygen

Every living thing needs oxygen to continue their life. Oxygen is a chemical element which can dissolve in water and known as dissolve oxygen (DO). Dissolve oxygen in water is important to aquatic life by providing oxygen for aquatic life to survive in

water. Solubility of oxygen in water is depending on temperature and pressure (Seneviratne, 2006). The concentration of DO also was effectuated by organism in aquatic itself like photosynthesis and respiration and oxidation by organism (Millero et al., 2002). Dissolve oxygen is extremely important parameter in water quality. By having data about DO, information about biological and biochemical reaction inside the water can also be defined. The major function of DO is used as indicator to measure BOD and COD value. The concentration of dissolved oxygen in natural water is used to measure the changes in chemical and biological processes like photosynthesis or respiration. The value of oxygen dissolved can also estimate the population of organisms as well as water quality of the sample. Normally, the concentration of oxygen will be increase due to photosynthesis by alga or aquatic plant and decrease because of respiration of bacteria (Millero et al., 2002).

Dissolve oxygen can be determined by using vary methods such as titration by Winkle method and an oxygen electrode using DO meter. Recently, a new study to improve measuring dissolve oxygen by using a reverse-flow injection analysis method was done. This method is developing based on classic method which is Winkle method and successfully deployed in tracking DO in either in laboratory or site (Muangkaew et al., 2002).

Peat water contains lower dissolve oxygen (DO). This characteristic can be seen directly in peat production process. Incomplete decomposition of vegetation is happening because of lack concentration of oxygen until anaerobic reaction occurs. Dissolve oxygen in peat water at Sarawak also present in low concentration as well as peat water in Beriah, Perak (Noraini et al., 2010; Wan et al., 2005).

2.2.1.3 Turbidity

Turbidity is referring to the level of water cloudiness which cause by suspended material inside the sample. Indeed, turbidity has provides the most direct measure of particular concentration by using scattering of a light beam. Measurement of turbidity however may affect by several factors such colour of sample, temperature, size and also type of mineral inside the sample.

Based on monitoring water quality at peat swamp in Sarawak, turbidity reading is still in the range of water quality standard and has been classified as in class I and II. The range of turbidity in that location is between range 0.3 to 9.8 NTU. This data implies that suspended solid in peat water is less and present in acceptable amount (Noraini et al., 2010).

2.2.2 Chemical Characteristics of peat water

The chemical characteristic of fresh water mostly reflection of the soils and rock which the water has contact with. In addition, microbial and chemical transformations also contributed to chemical characteristics of water.

2.2.2.1 Humic Substances

Humic substances are a part of high molecular weight compound called humus which functional to give the soil structure, porosity, cation and anion exchange as well as water holding capacity. Formation of humic substance is related with the breakdown of animals and vegetation matter normally in soil texture. Present of humic substance in high concentration will donate yellowish to brown colour in the sample. Theoretically, humic substance are form based on four theory which are

liginin modification, quinine-amino acid interaction, microbial synthesis of aromatics and lastly mallard reaction which is a sugar-amino acid reaction sequence. In each of theory, a variety of complex organic synthesis reactions occur and it shows that the availability in trace minerals is a requirement for the formation of humic substance.

Primarily, there are four types of humic substances that can be grouped based on their differences in solubility at different pH. First is humic acid (HA) which present in soluble water at higher pH value. Second is hymatomelanic acid (HMA) and it is soluble in etanol. Third is fulvic acid (FA) which flexible soluble in water under all pH condition and finally humin with hard characteristic not soluble into water in any pH condition. Besides, peat itself mostly contains HA, HMA and FA inside their composition and the concentration is rely on several factor such the depth of soil layer, age and type of peat soil (Mall et al., 2011).

Peats in South-East Asia often contain more than 90% organic matter and they are acidic with pH level as low as 3.5 (Wetlands International, 2010). Humic substance is one of element which describes the major processes and mechanism that occur in peat. Humic substance present in peat swamp as a part of decomposition product and the pH value in west Malaysia normally lies between 3.0 to 4.5 (Bujang et al., 2011). Other than that, natural factor such as absence of alkaline components from the organic parent material and the prevalence of precipitation over evaporation also responsible for acidic condition in peat water (Malawska et al., 2006). However, humic in peat have special gifted to absorb various biological molecule in water based on their chemical structure (Mall et al., 2011). Consequently, removal of humic acid in water and wastewater is very important. Currently, adsorption is

believed as a simple and effective technique to remediate humic and the success of the technique largely depends on efficient of adsorbent (Wang and Peng, 2010).

2.2.2.2 Chemical Oxygen Demand

Chemical oxygen demands (COD) also one of importance parameter in measuring water quality. The pollutant strength of sample can be defined using COD by reductive pollutant. COD is more preferable to be used as indicator for pollutant discharge because of its ability in measuring both organic and inorganic matter inside the sample. Chemical oxygen demand (COD) is referring to the amount of oxygen equivalent of organic matter inside the sample by oxidizing using strong chemical oxidant (Dan et al., 2000).

There are varying methods to determine chemical oxygen demand. The traditional test to estimates COD is by oxidative degradation of organic matter present in water and wastewater with strong oxidizing agents. Successfully determined, chemical oxygen demand at most of location peat swamp in Sarawak was recorded as in Class I based on Interim National Water Quality Standard (INWQS) and it is representing that peat water quality is in a good condition (0 – 17 mg/L) (Noraini et al., 2010).

2.2.2.3 Heavy metal

Heavy metal is one of unwanted elements inside the water. Most of heavy metal ions has been categorized as hazard to human health which contains high toxicity and difficult to degrade (Ning et al., 2011). Heavy metal such as Fe produce red discolouration and metallic taste which given a major problem in drinking water (Chaturvedi and Dave, 2012).

In aquatic environment, metals are present as dissolved ion and complexes, suspended and colloids ions. Those concentration metal ions are depending on biological process, redox potential, ionic strength and pH (Ozmen et al., 2004). The major of heavy metal inside the water is coming from domestic wastewater effluents, coal-burning power plants and power plants. Heavy metal also cause by industrial sector, geo-chemical structure and mining field.

Subsequently, because of the polar character of peat, the special adsorption potential for dissolved solids such as metals and polar organic molecules is quite high (Brown et al., 2000). Based on Supiandi (2010), colloidal organic in peat mostly is a negative charge and in theoretically it will tend to attract or catch positive element like iron (Fe^{3+}). Having iron in peat soil will increase the concentration of iron inside peat water as well. During heavy rain, precipitation will washout element (heavy metal) in unsaturated peat soil and increase the concentration inside the peat water (Klove, 2001).

2.3 Coagulant and Coagulant Aid

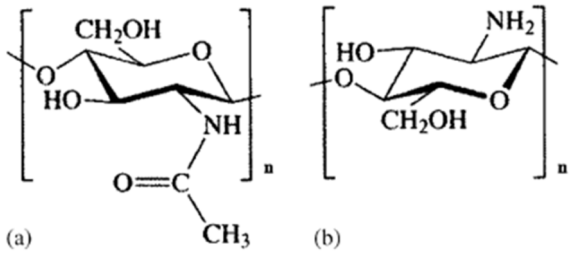
In order to make peat water as one of fresh water resources, unwanted elements such as suspended solid and heavy metal inside the water need to be remediated or removed. Conventional treatment using coagulation proses has been used widely now a day in order to treat water. Coagulant and coagulant aid are functional as purify agent in coagulation proses.

2.3.1 Chitosan

Several techniques are available to remediate water and soil contaminated by heavy metals, but many of them are inapplicable. Therefore, effective and suitable

techniques are needed to remediate metal contamination (Kamari et al., 2011a) especially in peat soil and water. Chitosan and treated chitosan were able to bind metal ions, even in the presence of K^+, Cl^- and NO_3^-, which are dominant ions in soil (Kamari et al., 2011b).

Chitosan which is known as a part of chitin family is produced from excessive deacetylation of chitin and present in a form of linear polysaccharide which mainly composed of two kinds linked structure, units *viz* . 2-amino-2-deoxy- d -glucose and *N* -acetyl-2-amino-2-deoxy- d –glucose (Pillai et al., 2009). Chitin (Figure 2.6a) is a structural biopolymer and it is second abundant material in the world. The main source of chitin is crustaceans which are a portion of fishing waste. Chitosan is regard as dissolved in dilute aqueous solution compared to chitin. Higher extended hydrogen bonded semi-crystalline structure of chitin make chitin disobey to be dissolve in solution (Pillai et al., 2009) and this characteristic become one of factor to differentiate both of material (Peniche et al., 2008). The chemical structure of chitin and chitosan can be seen in Figure 2.6.



(a) (b)

Figure 2.6 (a) Chemical structural of chitin (b) Chemical structural of chitosan in repeat unit (Marguerite, 2006)

Recently, chitosan has become a favourite material to be studied and applied in field due to its natural composition, harmless to humans, biodegradation, immunological and antibacterial (Miretzky and Cirelli, 2009). The pseudonatural cation polymer has

ability as a good coagulant in removing unwanted element and remediates polluted water (Marguerite, 2006). A unique structural of chitosan has excellent capability to bind metal in the sample effectively especially during coagulation and flocculation. The moderate to high molecular weight of chitosan help bridging mechanism in coagulation work effective (Roussy et al., 2005). The NH_2 groups on the chain (Figure 2.6b) are involved in specific interaction with metal such copper and iron (Marguerite, 2006).

Beside, chitosan also has a great potential to remediate fulvic acid (FA) from aqueous solution (Wang et al., 2008). This versatile biopolymer is not limited for used in water treatment industry only, but this material was widely used in biomedical, pharmacy, dentistry, cosmetics, agriculture and chemistry (Renault et al., 2009).

2.3.2 Natural Bentonite

Bentonite is the oldest mineral substance with strong affinity for absorbing water more than ten times of its capacity. Basically, bentonite is describing as a smectic soil composed of an expandable 2:1 of alumino silicate clay mineral. This rock is present in flat particle with characteristic size 102 to 192 mm with negative surface charge and sodium counter ions (Zhao, 2010).

Recently, bentonite has become one of low cost absorbent favourite to researcher because of its outstanding properties such as high swelling ability and cation exchange capacity. This mineral has been testing for its ability as alternative material in removing many cation elements such as dye, suspended solid and heavy metal (Mohammed, 2010). The optimum bentonite has been record can removed almost

100 percent of copper using combination of Na-bentonite and Ca-bentonite (Ding et al., 2009). Other than that, bentonite was also good to became as coagulant add (Susan and Donald, 1996).

2.3.3 Surfactant Modified Bentonite

Modification of adsorbent is referring to increase the ability of adsorbent to absorb the hydrophobic compound. Modification in ion exchange was done by using surfactant either cation or anionic surfactant. Modification bentonite using cation surfactant has been studied and it shows higher removal of organic matter (tannin) and also increase adsorption capacity of bentonite (Anirudhan and Ramachandran, 2007).

Fundamentally, natural bentonite have a lower capability to removed pollutant. In order to improve the capacity of adsorption in bentonite, surface charge of that clay need to be modified. The modification of cation surfactant to adsorbent involves replacement of inorganic exchange cation with quatenery amine cations $[(CH_3)2NHR]^+$ where R is a large alkyl hdrocaron chain, yield organoclays with organophilic clay surface. Theoretically, adsorption of hydrophilic long-chain quaternary ammonium cation into bentonite is happen based on the ion exchange mechanism (Anirudhan and Ramachandran, 2007). Figure 2.7 shows the chemical reaction during modification of organobentonite with hexadecyltrimethylammonium chloride (HDTMA).

Surfactant Modified Bentonite can be used as low-cost adsorbent for treatment of aqueous waste streams contaminated with humic substances. Humic acid adsorption was found to decrease with increase of ionic strength due to the formation of outer-

sphere surface complexes on surfactant modified bentonite (SMB) (Anirudhan and Ramachandran, 2007).

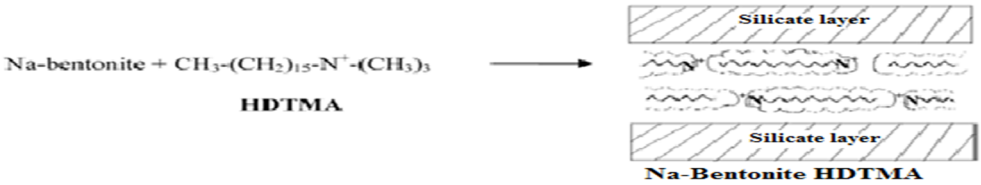


Figure 2.7 Preparation of organobentonite with HDTMA
(Anirudhan and Ramachandran, 2007)

Other than that, an excellent job in removing heavy metal (Shi et al., 2011) and toxic element like arsenic also has been studies (Su et al., 2011) and record a great removing using surfactant modified bentonite.

2.3.4 Limestone

Limestone is another abundant material widely available in Malaysia. Limestone contains high calcium carbonate ($CaCO_3$) and present in calcite mineral form (Aziz et al., 2001). Nowadays, limestone has become popular as alkaline media in neutralizing acidic aqueous because it is an inexpensive absorbent and easier to be found. Limestone able to increase pH and remove dissolve metal in acidic mine drain (Charles and Mary, 1999). The concentrations of dissolve metal like Mn, Cu, Co, Ni and Zn is decrease in effluent while pH is increase due to decreasing of $CaCo_3$. The following equation representing the chemical reaction that present during limestone function as neutralization media (Liu and Koenig, 2002).

$$CaCO_3(s) + H^+ = HCO^-_3 + Ca^{2+} \quad (2.1)$$

$$HCO^-_3 + H^+ = H_2CO_3 \quad (2.2)$$

$$H_2CO_3 = H_2O + CO_2 \quad (2.3)$$