STUDY ON FOULING INDEX OF HUMIC ACID REMOVAL BY POLYETHERSULFONE ULTRAFILTRATION MEMBRANE

SAW WEN QI

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UNIVERSITI MALAYSIA PAHANG

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ABSTRACT

Over the past few decades, membrane processes has received overwhelming attention worldwide in drinkable water production offering advantages such as compact module, lower energy consumption, environmental friendliness and high quality of water product which is independently on the fluctuations in feed quality. Among those methods, ultrafiltration membrane process has receives the most attention publicly. Ultrafiltration (UF) membrane technology is a low pressure driven membrane separation process aimed to recover water from a saline solution pressurized to a point greater than the osmotic pressure of the solution. In essence, this membrane can filters viruses and microorganisms under low applied pressure and create high permeate flux. These will save a lot of cost as the process only consume little energy. However, for this successful application, the major critical issue is fouling. The major foulants come from the natural organic matters (NOM) where it is mainly in the river water. This NOM consists of humic acid where it is the main fouling factor to the UF membrane. Humic acid will cause pore blockage or cake formation on the membrane that will further decrease the permeate flux of the filtered water. In spite of that, there are also many fouling factor that increase the fouling index of humic acid on UF membrane such as trans-membrane pressure and pH of the feed solution which represent the feed characteristic and the operation parameter that will probably contribute to the fouling index of the membrane. Therefore, a study will be done on parameters, pH of the feed solution and addition of calcium ion in order to investigate the fouling index of humic acid on membrane. The experiments start with the pure water permeability test with different pressure. Then, the fouling experiments wil start with filtration of humic acid solution with different pH, 3, 6 and 9. The fouling index, flux and solute rejection has been studied. The result obtained showed that permeate flux was lower whenever the pH of humic acid solution was lowered due to fouling in contraty the flux was higher when the pH is high. This phenomenon showed that membrane is easier to foul when the pH is low. Besides that, since the flux was decrease, which means the membrane was fouled. Hence, the fouling index of the membrane was increased when pH was low while decreased when the pH was high. Lastly, the solute rejection is related with the fouling of the membrane. When the membrane was fouled under low pH, the rejection of the membrane was increased because the membrane pore was partially block. Adversely, the rejection of the membrane is lower under high pH as the membrane was less fouled. To achieve the desired volume, longer filtration time was taken.

ABSTRAK

Pada era globalisasi ini, proses membrana telah mendapat perhatian yang amat menggalakkan daripada pengaji-pengaji dalam industri air di seluruh dunia disebabkan proses ini dapat menawarkan pelbagai kelebihan seperti modul padat, penggunaan tenaga yang rendah, keramahan alam sekitar dan kualiti air yang dijamin. Antara kaedah-kaedah, proses membrana ultrafiltrasi telah menerima perhatian yang amat tinggi. Teknologi Ultrafiltrasi (UF) menggunakan tekanan yang lebih besar daripadatekanan osmotic untuk menjalani proses penapisan air yang bertujuan untuk mendapatkan air yang berkualiti. Hal ini demikian kerana membrana berkebolehan untuk manapis virus dan mikroorganisma selain daripada dalam keadaan tekanan rendah, mahupun juga boleh dapat fluks yang tinggi. Oleh itu, aplikasi ini dapat menjimatkan kos kerana hanya sedikit tekanan yang digunakan sahaja. Tetapi, bagi applikasi yang berjaya ini, isu kritikal yang utama bagi membrana adalah fouling manakala foulants utamanya ialah organic semula jadi (NOM) yang terdapat dalam air terutamanya air sungai. NOM ini mengandungi asid humik yang biasanya menjadi faktor utama fouling kepada membrane UF. Hal ini disebabkan asid humik akan menyebabkan penyumbatan laing membrana dan pembentukan kek yang secara tidak langsung akan menyebabkan fluks menurun. Selain itu, terdapatnya faktor-faktor lain yang menyumbang kepada membrana fouling seperti tekanan transmembrane dan pH sebagaimana factor tersebut akan menyebabkan fouling keadaan membrane menjadi lebih teruk. Dengan itu, satu kajian akan dijalankan dengan pH dan kewujudan kalsium ion dalam larutan asid humik sebagai parameter untuk mengkaji indeks fouling untuk UF membrana. Eksperimen itu akan bermula dengan penelapan air dalam tekanan yang berbeza. Selepas itu, kajian bagi penapisan larutan asid humik dengan pH berbeza, 3, 6, dan 9 akan dijalankan. Bagi kajian ini, indeks fouling, fluks dan penolakan bahan larut telah diselidik. Keputusan yang diperolehi telah menunjukkan fluks lebih rendah dalam keadaan pH rendah manakala fluks meningkat dalam keadaan pH tinggi. Hal ini disebabkan membrana senang terdedah kepada fouling apabila pH larutan asid humik rendah yang seterusnya menjejaskan fluks. Selain itu, indeks fouling mempunyai kaitan yang rapat dengan fluks kerana semasa fluks rendah maka maknnya indeks fouling membrana tersebut adalah tinggi. Akhir sekali, penolakan adalah berkaitan dengan indeks fouling membrana. Hal ini demikian kerana sebagaimana indeks fouling meningkat, penolakan bahan larutan dari membrana itu juga akan meningkat kerana sebahagian liang membrana telah blok. Maka, untuk mendapatkan jumlah air yang ditapis, masa yang diperolehi juga akan dipanjangkan.

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J	Water flux ($m^3/m^2.s$)
V	Volume of water (m^3)
A	Effective membrane area (m^2)
t	time (s)
P_m	Water permeability ($m^3/m^2.s.bar$)
ΔP	Pressure difference (bar)
FI	Fouling index of humic acid
F_o	Final fouling of humic acid
F_f	Initial fouling of humic acid

LIST OF ABBREVIATIONS

HAs	Humic acidsAdvanced oxidation processes
FAs	Fulvic acids
HS	Humic substances
NOM	Natural organic matter
OM	Organic matter
DBPs	Disinfectant by-products
TMP	Trans-membrane pressure
THMs	Trihalomethanes
HAAs	Haloacetic acids
MCL	Maximum contaminant level
UF	Ultrafiltration
RO	Reverse osmosis
MF	Microfiltration
NF	Nanofiltration
SDI	Silt density index
MWCO	Molecular weight cut off

CHAPTER 1

INTRODUCTION

1.1 Background

A membrane or, more properly saying, a semipermeable membrane, is a thin layer of material that is capable of separating materials as a function of their physical and chemical properties when a driving force is applied across the membrane. Membranes can be classified by the range of materials separated and the driving forces employed. For one of the membrane process to be study on is ultrafiltration (UF) membrane process. Historically, by the 1930s, polymer ultrafiltration membrane with pores of various sizes had been developed; important work was done by William Elford, who cast membranes of cellulose acetate and of cellulose nitrate and who also elucidated most of the principles of UF (Mallevialle et al., 1996). Since the development of this membrane, interest in membrane processes for water treatment has grown steadily, and this technology are now become of the objectives of substantial international research, development, commercial activity, and full scale operation. This relatively recent global increase in use of the membranes can provide better treatment for water and reduce the water scarcity due to recent world population rapid growth and continuing industrialization (Jolly, 2000).

However, this future promising technology faces a fouling problem. The contribution to the fouling problem is foulants. In membrane process, the foulant is humic acids (HAs) where it is one of the components in natural organic matters (NOM) where it can be found in soil. It is a very important organic substance in producing fertile soil. These organic matters play a direct part as they are the sources of plant nutrients which are liberated in available forms during mineralization (Senn & Kingman, 1973). Besides being a source of nutrients for the plant, organic matters also have a fundamental effect on the physical properties of the soil such as water holding capacity and contribute in the structure formation. It is also determines to a large degree such physico-chemical properties as the exchange capacity and buffering properties; these properties are of great importance, not only in controlling the uptake of nutrients by the plant and their retention in the soil, but also in suppressing the deleterious effect of soil acidity. Besides that, there is also conclusive evidence from past researched like Burdick in 1965 supported that small amounts of certain organic substances that highly dispersed humic acids will have a definite, positive effect on the growth and development of the plant.

As mentions, these organic matters especially humic acids (HAs) become the main fouling problem on the membrane filtration method. The fouling can be characterized into reversible and irreversible. The decisive difference between reversible and irreversible fouling is back washable or non-backwashable (Wenshan et al., 2012). The irreversible type is the humic acids (HAs) which cause blockage of membrane pore and thus will lead to declination of the permeate flux and efficiency of the filtration. Apart from that, based on the research done by Susanto & Ulbricht (2005), the feeding water characteristic and the operation parameter of the membrane such as pH value, operating time, transmembrane pressure and the concentration of calcium ion will also influence the fouling index of humic acid on the membrane. It is well known and recognized that calcium is an important environmental component, and its complexation by humic acid. Calcium ions will implicate in the fouling of hydrophobic membrane (Schnitzer & Khan, 1972).

1.2 Motivation and statement of problems

Fresh water sources are the fundamental need for the people to maintain health, agricultural production, economic activity as well as the aquatic environment. It can be said that it is a vital and irreplaceable basic necessity for mankind to live on. However, the world is facing water scarcity which means that there are limited water supplies for meeting prevailing or projected water demand at a specific location (Coping with Water Scarcity, 2006). According to UN-Water, by 2025, 1800 million people will be living in countries or regions with absolute water scarcity, and two-thirds of the world population could be under stress conditions. The situation will be exacerbated as rapidly growing urban areas place heavy pressure on neighbouring water resources. Usually, the roots lead to water shortage in the arid and semiarid regions is affected by droughts and wide climate variability, combined with population growth and economic development, that the problems of water scarcity are most acute. This phenomenon brings an important message that the clean water source will become limited in future (Prisciandaro et al., 2001).

In Malaysia, river water contributes as the main water source for the people and predominant for the environment. Malaysia is using traditional wastewater treatment method which is chlorination. Though the chlorine that dissolve in the water can kill bacteria and viruses; however the huge problem is the occurrence of reaction between the chlorine and humic acid where the reaction will produce carcinogenic by-product, trihalomethane and haloacetic acid which are very hazardous to human. The water is not safe to consume for a long term (Wei & Zydney, 2000). On the other hand, the membrane technology to treat water is not yet widely applied in the Malaysia neither in the industrial field nor the agricultural field due to several factors such as high cost of membrane, exposure to membrane technology and some are high energy consumption. Hence, the membrane technology could have a huge potential to be utilize in the nationwide in order to enhance the water quality and ensure the water to be treated correctly instead of the conventional treatment method to provide clean and drinkable water.

Among the membrane process, ultrafiltration membrane has been chosen as one of the best filtration membrane. Past researched done by Katsoufidou et al., (2005) show that UF membrane could be done at low pressure, energy and also has higher permeated flux after filtration. Moreover, UF membrane also have superior and stable permeate quality even under conditions of variable feed-water characteristics. But, the efficiency of the membrane is affect by fouling where one of the fouling agents is humic acids (HAs) (Jun et al., 2005). This fouling agent could induce the membrane to be fouled due to blockage of the membrane pore. In spite of that, the fouling index of humic acids (HAs) could be driven by other aspect such as pH of the feed solution as well as the presence of the calcium ions. Nevertheless, until today, studies that done on this parameter associated with this particular membrane has been in scarcity when it comes to the river in Malaysia as well as the studies on this parameter on ultrafiltration membrane (ChanHyuk et al., 2006). This is because for different area it will have different concentration of humic acids (HAs) in the river water.

1.3 Objectives

The research’s aim is to study on the fouling index of humic acids (HAs) removal by polyethersulfone UF membrane under different pH of the feed solution and the impact of the pH value on the formation on membrane fouling.

1.4 Scope

In this research, the first scope is to study on the pure water permeability under different membrane pressure, trans-membrane pressure (TMP) on the polyethersulfone UF membrane.

The pressure of the membrane will be tests from 1 bar to 5 bar for the experiment. A constant volume will be collected and the time will be recorded when the desired volume of the solution is achieved. The permeate flux will be calculated by using flux formula. Results obtained will then undergo a simple excel simulation in order to produce a clear data make a confirmation that the membrane applied is UF membrane.

Next, the second scope is to examine on a different pH of the feed humic solution that will be treating by the membrane under constant pressure, 4 bar. The pH will be examine is pH 3, pH 7 and pH 9 which represent acidic, neutral and alkali condition. The volume to be collected is set and the time to achieve the desired volume will be recorded. Hence, the permeate flux can be calculated as it will shows the fouling index of humic acids (HAs) on the polyethersulfone UF membrane. A graph of flux vs pH will be plotted to study the fouling behavior of UF membrane under different pH.

Furthermore, the third scope is to study on the effect of calcium ion on the fouling index of the membrane. Calcium chloride anhydrate will be add into humic acid solution with three different pH; pH 3, 6, and 9. The desired volume will be collected corresponding with the time will be recorded as well. Then, there will be calculation on the permeate flux and the solute rejection.

Lastly, the scope is to study the solute rejection of the membrane. After the filtration of humic acid solution with and without addition of calcium chloride anhydride, the solute rejection of the membrane will be study as well. The rejection can be determined by examine the final concentration of humic acid in the solvent after the ultrafiltration process. Thus, by using initial and final concentration of humic acid, the rejection of the membrane can be calculated.

1.5 Organization of the thesis

Chapter 2 provides a description on the humic substances and its main components are humic acids (HAs), fulvic acids (FAs) and humins. Besides, a review will be done on the impact of chlorination of humic acid as well. Then, a brief discussion also provided on four types of membrane processes: ultrafiltration (UF), microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO). Nonetheless, there is also discussion on the fouling behavior of the membrane which is the main study for the research.

Chapter 3 will be having the discussion on material and methodology. A detail list of material and equipment that need in the experimental study will be present in that particular chapter. After that, methodology of the experiment study will be discussed in that chapter as well. This includes the determination of pure water permeability under different transmembrane pressure and the filtration of the humic acids (HAs) solution representing synthetic river water condition under different pH value treated by the membrane and hence, the fouling index of the humic acids (HAs) will be studied.

Chapter 4 will present result and discussion. The result that obtained is the permeability of pure water. The graph plotted will be study and compare with past researched. The result will be discussed in this chapter in order to have a better understanding. Besides, it is also consist of fouling index, permeate flux and solute rejection of the membrane. All of these results will be further discussed in that particular chapter and compared with past researched so the it is relevant and validate.

Chapter 5 will present the conlusion and recommendation. The objectives and purpose of this research study will be conclude and some recommendations or suggestions will be suggested so that this research data could contribute to other research in the future.

CHAPTER 2

LITERATURE REVIEW

2.1 Chapter Overview

In this chapter, a detail review will be done on the humic acids and ultrafiltration membrane processes which is main the focus in this research study. Besides that, a review on the humic acid origin substance, humic substances and other elements in the humic acids (HAs) such as fulvic acid (FAs) and humins will be done as well. This chapter also includes the effect of chlorination of humic acids. As for the membrane processes, 4 types of membrane processes: microfiltration (MF), nanofiltration (NF), reverse osomosis (RO) and ultrafiltration (UF) will be review on their characteristics and specifications. Another part will be review in this chapter is the membrane fouling.

2.2 Humic substances

In soil, natural organic matter (NOM) or soil organic matter (SOM) is a basic component of the agro-ecosystem and acts as an essential link among the various chemical, physical and biological soil properties. Normally, it functions as a medium to prevent soil erosion and desertification and also a driving variable in environment changes since it acts both as a source and as reservoir for carbon. This is because in recent years, organic amendments have been chosen over than traditional manure, due to its efficiency for the improvement and/or restoration of NOM (Hyun-Chul & Dempsey, 2013). Several organic residues and wastes produced by anthropic activities are potential candidates for recycling as soil amendment after appropriate treatments, which should be adequate to sanitation and reduction of metal and organic contaminants in the substrate, and transform the initial fresh organic matter (OM) into stabilized organic forms. These prerequisites are considered essential for any waste to be safely, conveniently and efficiently used as soil amendment in order to avoid or, at least, limit any hazard for chemical and biological soil properties, crop production and water quality. However, organic waste materials are seldom applied to soil in the fresh or raw state. Generally, they are properly processed previous to soil application, in order to obtain an amendment possessing beneficial rather than adverse effects on soil fertility and agricultural production.

The most common treatment of organic raw materials is the composting process, which consists basically of a controlled biological transformation of raw OM operated by aerobic micro-organisms. During composting, a large part of the original OM is mineralized and the residual OM is transformed into new organic materials, in which the humification processes typically occurring under natural soil condition have started and proceeded to some degree, producing “humic-like substances” (Campitelli et. al., 2006). The composting makes the compost organic matter similar to natural organic matter which mainly consists of humic substance (HS).

According to Saiz-Jimenez & Dee Leeuw (1986), humic substances (HS), the major organic constituents of soils and recent sediments, are widely distributed over the earth's surface and very abundant in almost all terrestrial and aquatic environments. Soil humic substances are basically arise from or left over after the chemical and biological degradation of plants and animal residues by microorganisms, stable than their precursor.

Humic substances have a large molecular size. According to Piccolo (2001), the apparently large molecular size of humic substances is actually a supramolecular structure of small bio-organic molecules of a molecular mass smaller than 1000 Da, held together by weak forces, such as Van der Waals force. Apart from that, based on Kononova’s research back in 1961, the classical definitions of HS are operational only and are based on solubility properties in the aqueous solutions used as soil extractants. The generalized terms humic acids (HAs), fulvic acids (FAs), and humins cover the major fractions still used to describe HS components where humic acids (HAs) is the major constituent can be found in the humic substances.

In figure 2.1, it shows that the general precipitation method to precipitate or extract out the component such as for humins, it has to be alkaline precipitation to precipitate it out from the main molecule whereas through acidic precipitation the humic acids (HAs) will be remove as insoluble residue meanwhile fulvic acids (FAs) is the soluble residue in this method. Generally, this figure is showing the relationship of humic acid (HAs), fulvic acids (FAs) and humins and categorize under humic substance.

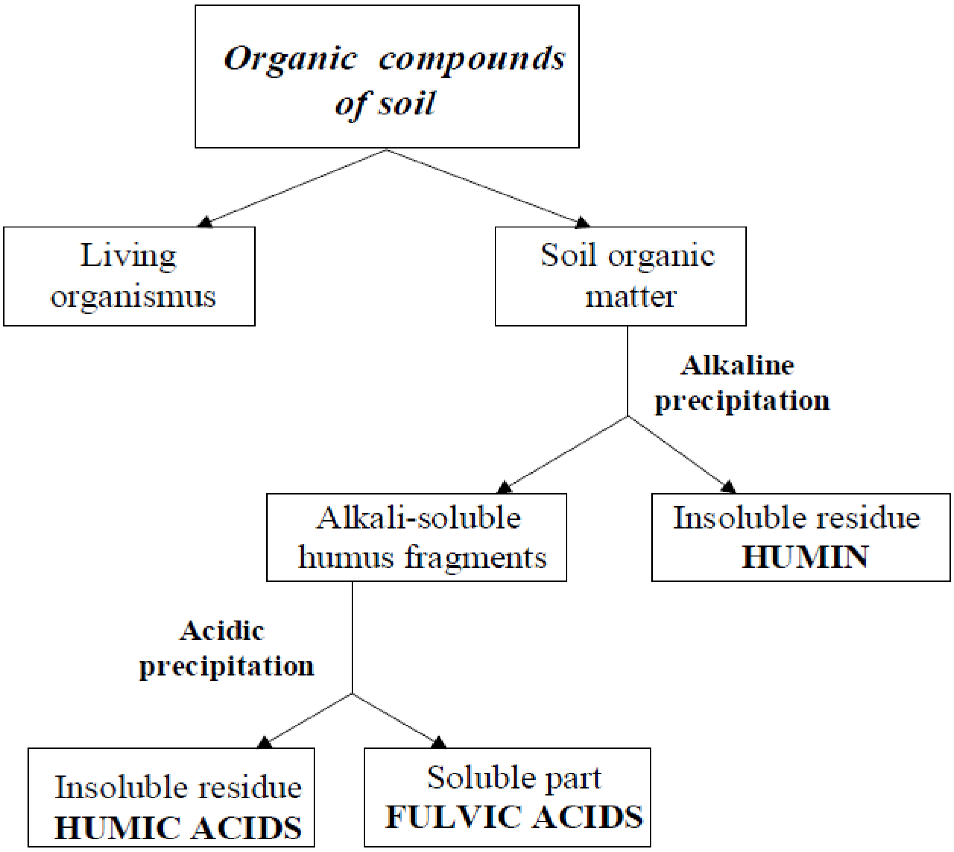

Figure 2-1: Scheme of division of humic substances in dependence of their solubility (Pena-Mendez et. al., 2005).

2.2.1 Humic Acid

Humic acids (HAs), basically are carbon-rich materials with various characteristic and a fairly constant 3 mmol/g HA carboxylic acid contents but consists of variable phenol contents and total acidity (Davies & Ghabbour, 2001). They are termed polydisperse because of their variable chemical features. From a three dimensional aspect, these complex carbon containing compounds are considered to be flexible linear polymers that exist as random coils with cross-linked bonds. The elemental composition of different humic acid (HAs) shown that the major elements in their composition are C, H, O, N, and S regardless the origin place they found (Gajdosova et al., 2001). On average 35% of the humic acids (HAs) molecules are aromatic (carbon rings), while the remaining compounds are in the form of aliphatic (carbon chains) molecules (Pettit, 2006). Based on the early work of Flaig & Beutelspacher (1968), the molecular sizes of humic acids (HAs) are range from approximately 10,000 to 100,000. This is further proven by Stevenson (1994), molecular sizes of humic acids (HAs) is in the range of 30,000 to 60,000 shows that the size of the humic acid is in that particular range.

Besides that, humic acid (HAs) is having remarkably similar empirical formula though it exists at varies place such as forest litter and grasslands (Paciolla et al., 1998).

Apart from that, humic acids (HAs) consist of different types of functional groups which also include alcohol, amine, amide, carbonyl, and quinone. But, humic acids (HAs) usually present in a phenol and long carboxylic acid dominated group in the chemical structure (Domany et al., 2002). Moreover, according to Pena-Mendez (2005), humic acids (HAs) contain 400-870mmol/100g acidic nature functional groups and most of the acidity in the humic acids (HAs) is due to the carboxylic, phenolic-OH and/or phenolic groups which dissociate to develop negative charges. The imides groups (NH_2), secondary and even tertiary amines, among others, can be protonated to develop positive charges when it is at very low pH.

River water mainly is the place where humic acids (HAs) can be found. This is because through the rain water, it will run-off from the surrounding land into the water surface. Therefore, the concentration of humic acids (HAs) in water surface will be varies during the raining season which means high concentration of humic acids (HAs) will be present in the wet season while lower concentration of humic acids (HAs) will exist in the dry season (Lowe & Hossain, 2008). In spite of that, each river at different place will have different concentration of humic acids (HAs). Some rivers are severely contaminated by the humic acids (HAs) in contrary some rivers just merely consists of humic acids (HAs).

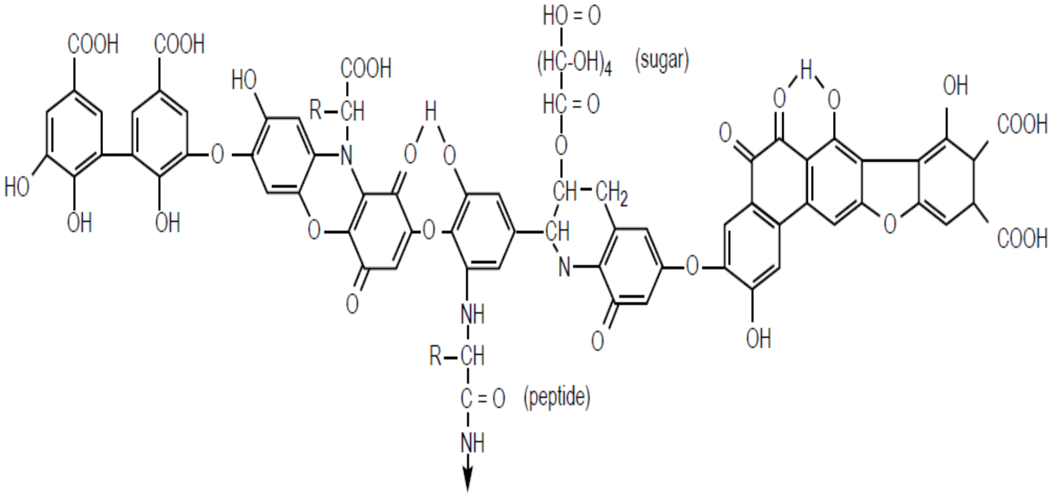

Figure 2-2: Model structure of humic acid (Stevenson, 1982)

2.2.2 Characteristics of humic acids (HAs)

The characteristics of humic acids (HAs) make it is a very useful material in agricultural field and plantation field. It plays an important role in improving quality of soil, especially in soil with low organic matters (Pettit, 2002). Acoording to Senn and Kingman (1973), humic acid has been used in enhancing crop productivity and soil fertility. Humic acids (HAs) help break up clay and compacted soils, decomposing rocks and minerals, assist in transferring micronutrients from soil to plants, enhance water retention, increase seed germination rates, and stimulate the development of microflora populations in soils. It is also promote conversion of a number of elements into forms that are available to plants such as the effect of humic acids (HAs) on the conversion of iron into available forms, protecting plants from chlorosis which is already experimented by Dekock in 1955. Relatively, humic acids (HAs) and their derivatives also increase the permeability of plant membranes, so promoting the uptake of nutrients by the plant.

Apart from that, humic acids (HAs) also slow down water evaporation from soils. This is especially important in soils where clay is present at low concentration or not at all, either in arid areas, or in sandy soils that are without the capability to hold water. Humic acids also provide sites for microflora to colonize. Bacteria secrete enzymes which act as catalysts, liberating calcium and phosphorous from insoluble calcium phosphate, as well as iron and phosphorous from insoluble iron phosphate (Pena-Mendez et al., 2005). In 1951, Khristeva researched that if the humic acids (HAs) enter the plant early stages of development are a supplementary source of polyphenols, which function as respiratory catalysts. This results in an increase in the living activity of the plant: enzyme systems are intensified, cell division is accelerated, root systems show greater development and, ultimately, the yield of dry matter increases.

2.2.3 Conventional treatment method and chlorination of humic acids (HAs)

In Malaysia, the water treatment industry is still applying conventional treatment method which is chlorination where a specific amount of chlorine is added into water to treat it. There are many methods like sedimentation, ozonization, coagulation, adsorption and flocculation to treat water but these methods do not always satisfy the continuing tightening of drinking water standards (Siyanytsya et al., 2008). Sedimentation and filtration normally imply together to remove the flocs and other neutralized particles, including pathogens. On the other hand, coagulation is the neutralization process where the change on the surface of the particles will be neutralized. Besides that, the adsorption of HA on activated coals depends essentially on composition and admixtures of surface water, thus a choice of an optimal sorbent is needed for treatment of the each specific type of surface water (Mc Creary & Snoeyink, 1980). Ozonation of aqueous solutions of HA leads to formation and accumulation of low molecular weight organic compounds such as alcohols, aldehydes and acids that are highly stable to molecular ozone (Meijers, 1976).

Although these processes can remove 99 to 99.9% of pathogens, but yet disinfection is still a critical process to protect the public from contracting waterborne diseases. Therefore, chlorination becomes one of the methods that can be used to disinfect water and sterilize the microbes that exist in the water (Yuefeng, 2003). This method was first used over a century ago, and is still used today. It is a chemical disinfection method that uses various types of chlorine or chlorine-containing substances, which includes chlorine gas, hypochlorite solutions, ozone, chlorine dioxide and other chlorine compound in solid and liquid form for the oxidation and disinfection of what will be the potable water source (Agency, 1999).

In contrast, this chlorination process may cause the formation of organic-halides by the reaction of free chlorine with organic matter especially humic acids (HAs) in the water which will produce disinfection by-products (DBPs) (Junsung et al., 2002). Disinfection by-products (DBPs) comprise of several organic and inorganic compounds that are formed by reactions between chlorine, naturally occurring organic matter (NOM), major humic substances, and bromide in drinking water (Minear & Amy, 1996).

$$\text{NOM} + \text{chlorine} + \text{bromide} \longrightarrow \text{THMs}$$

This equation shows that addition of chlorine in water treatment process will cause the production of THMs. It is a complex reaction between chlorine and humic substances lead to production of THMs, HAAs, HANs and cyanogen halides. Table 2.1 shows the major species of DBPs that are commonly identified from chlorine treatment that are trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitrile (HANs), cyanogen halides, and halopicrins.

Through various testing and experimental study, researchers found that trihalomethanes (THMs) and haloacetic acids (HAAs) are the two major classes of DBPs commonly found in waters disinfected with chlorine. The amount of the disinfectant by-products is depending heavily on the concentration of humic acids (HAs). Besides, there are also some early studies mainly focused on the formation of THMs and HAAs.

Chemical class	Chemical compound
Trihalomethanes (THM)	Chloroform
	Bromodichloromethane
	Dibromochloromethane
	Bromoform
Haloacetic acids (HAAs)	Monochloracetic acid (MCAA)
	Dichloroacetic acid (DCAA)
	Trichloroacetic acid (TCAA)
	Monobromoacetic acid (MBAA)
	Dibromoacetic acid (DBAA)
	Tribromoacetic acid (TBAA)
	Bromochloroacetic acid (BCAA)
	Bromodichloroacetic acid (BDCAA)
	Chlorodibromoacetic acid (CDBAA)
Haloacetonitrile (HANs)	Dichloroacetonitrile
	Trichloroacetonitrile
	Dibromoacetonitrile
	Bromochloroacetonitrile
Cyanogen halides	Cyanogen chloride

Table 2-1: Major species of DBPs

From the table 2.1, there are some examples of trihalomethanes (THMs) and haloacetic acids (HAAs) model strucuture such as trichloromethane (chloroform), bromodichloromethane, dichloroacetic acid and trichloroacetic acid. These few chemical compounds are the DBPs that form after chlorination treatment.

trichloromethane bromodichloromethane

dichloroacetic acid trichloroacetic acid

Figure 2-3: Model structure of trichloromethane, bromodichloromethane, dichloroacetic acid and trichloroacetic acid.

These compounds are classified as probable or possible human carcinogens by the US Environment Protection Agency (US EPA) (Agency, 1999). Their presence in drinking water has given rise to health risk concerns. According to the US EPA guidelines, originally, the maximum contaminant level (MCL) of 100 µg.l^{-1} has been set for total THMs. Then in 1999, USEPA has set the new MCL of the disinfection in stage 1 at 80 µg.l^{-1} under disinfection by-product, DBP's rule. In addition to these standards, a MCL for HAAs of 60 µg.l^{-1} was proposed in the stage 1 rule as well. Meanwhile, for stage 2 of the D/DBP Rule may lower the MCLs for THMs and HAAs to 40 µg.l^{-1} and 30 µg.l^{-1}, respectively. Hence, techniques to rapidly determine the problematic organic fractions most responsible for DBP formation within NOM are important for the minimization of DBP formation in water treatment systems (Grunwald et al., 2002).

2.2.4 Health effect of THMs on human body

According to Grunwald et al. (2002), THMs and HAAs will cause serious health effect like cancer through different types of entry pathway to human body. For instance, Trichloromethane or chloroform may be absorbed into the body through ingestion, inhalation, and through the skin. The largest source of human exposure to THMs in the U.S. is from the consumption of chlorinated drinking water. Besides consuming water, other water uses in the home may contribute significantly to total chloroform exposure both from breathing in chloroform vaporized into the air and from it passing through the skin during bathing. Swimming in chlorinated pools will also contribute to the total exposure from the same exposure paths. There are also have one study observed that a greater percentage of chloroform passed through the skin when bathing water temperatures were increased. However another fact is chloroform does not concentrate in plants; therefore, the contribution from food to total chloroform exposure is small.

Furthermore, the health effect cause by chlorinated halogens such as THMs and HAAs has been an issue for public concerns (Reckhow et al., 1990). THMs like chloroform's acute effects on humans have been obtained primarily during its past use as an inhalation anesthetic. In addition to central nervous system effects, chloroform anesthesia was associated with cardiac arrhythmias and abnormalities of the liver and kidneys. Inhalation exposure experiments with animals revealed that high levels are toxic to the liver and secondarily to the kidneys. Skin contact with undiluted chloroform may cause a burning sensation, redness, and blistering. However, acute effects of exposure to the other THMs are not documented in the literature, but are expected to be similar to chloroform.

Nonetheless, there are also studies on the chronic effect of chloroform. Chronic oral exposure of humans to chloroform at high doses results in adverse effects on the central nervous system, liver, kidneys and heart. To determine the similar effect that will happen on human body, several animal studies has been conducted have shown decreased body weights in rats and mice given chloroform at high oral doses and an increased incidence of respiratory disease at higher doses. At still higher doses given orally, liver abnormalities and decreased size of the reproductive organs were observed in rats. In animal studies investigating effects of chronic exposure to each of the other THMS, liver toxicity was observed. BDCM also caused kidney toxicity (Meier et al., 1986).

The most crucial factor is the THMs could have carcinogenic effect on human. Thus, chloroform has been demonstrated by several studies to produce kidney and liver tumors in rats and mice when given orally. In studies of human populations using chlorinated drinking water in which chloroform is the predominant THM, small increases in the incidence of rectal, colon and bladder cancer have been consistently observed, with evidence strongest for bladder cancer. However, the evidence to support chloroform as the main cause for cancer is not firm because of other possible carcinogens was found in this water. It is impossible to identify chloroform as the sole carcinogenic agent. Therefore, chloroform has been classified by the U.S. Environmental Protection Agency (EPA) as "probable human carcinogen," based on sufficient animal evidence and inadequate human evidence of carcinogenicity. Evidence from animal studies now strongly indicates that chloroform exposure causes cancer only after first producing sustained cell toxicity. The research shows that only at a certain threshold level of exposure is necessary to cause cell toxicity, cancer from chloroform exposure can only occur if that threshold level is exceeded (Klaassen, 2001).

2.2.5 Fulvic acids (FAs)

Fulvic acids (FAs) are one of the components can be found in humic substances. They are a mixture of weak aliphatic and aromatic organic acids which capable to soluble in water at all pH conditions (acidic, neutral and alkaline). Their composition and shape is quite variable. In terms of size, fulvic acids (FAs) are smaller than humic acids (HAs), with a molecular weights range from approximately 1,000 to 10,000. However, fulvic acids (FAs) have oxygen content twice that of humic acids (HAs) (Domany et al., 2002). Due to the existence of many carboxyl (-COOH) and hydroxyl (-COH) groups in fulvic acid (FAs), thus they are much more chemically reactive which means that the exchange capacity of fulvic acids (FAs) is more than double that of humic acids (HAs). This is because exchange capacity is due to the total number of carboxyl (- COOH) groups present. The number of carboxyl groups present in fulvic acids (FAs) ranges from 520 to 1120 cmol (H+)/kg. According to Hutchinson (1992), fulvic acids that analyzed, relatively show small amount and no evidence of existence of methoxy (-CH3) groups, they are low in phenols, as well as are less aromatic compared to humic acids from the same sources.