MERCURY REMOVAL PETROCHEMICAL WASTEWATER USING HOLLOW FIBER EXTERNAL MEMBRANE BIOREACTOR

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ABSTRACT

Nowadays, mercury removal from Petrochemical waste by using external membrane bioreactor is becoming one of the favourite biological treatments used to preserve the environment. This treatment is conducted by using *Pseudomonas putida* as the biological sources to reduce the mercury content in the waste. Combination membrane system with bioreactor after treatment process is to remove mercury effectively The purpose hollow fiber membrane to filter out any supernatant like suspended solid, turbidity and mercury concentration that polluted the water sources Mercury removals in this study are in aerobic phase. The objective of the present study was to investigate the influence of aeration rate and agitation speed using *Pseudomonas putida.* The mercury removal process was conducted under various aeration rates is 0.5, 1.0 and 1.5 L/min and agitation speeds 100, 180 and 200 rpm respectively in external membrane bioreactor. The optimum temperature for growth of bacteria is 37°C and pH is 6-7. Parameter studied in this experiment work is agitation speed and aeration rate. Dependencies of this parameter to the growth of the bacteria are studied. The optimum aeration rate for this study is 1.0 L/min and agitation speed is 180 rpm. The other parameters significant study is total suspended solid(TSS), biological oxygen demand(BOD), chemical oxygen demand (COD) and turbidity. This parameter also to meet the requirement of Malaysia DOE, Standard (B) on Environmental Quality Act 1974. This study can be concluded that successful mercury can be conducted using *Pseudomonas putida* The scale up of bioreactor could be done for massive mercury removal from petrochemical has.

ABSTRAK

Dewasa ini,penbuangan merkuri daripada bahan buangan industi petrokimia mengunakan membran bioreactor adalah salah satu keadaan rawatan biologi untuk melindungi alam sekitar.Rawatan ini mengunakan bakteria *Pseudomonas putida* sebagai sumber biologi untuk mengurangkan kandungan merkuri didalam bahan buangan Gandingan diantara sistem membrane dengan biorektor selepas rawatan adalah cara untuk membuang kandungan merkuri dengan lebih berkesan.Tujuan mengunakan membrane hollow fiber ini adalah untuk membuang keluar sebarang bahan asing seperti jumlah pepejal terapung,kekeruhan dan kepekatan merkuri yang menjadi bahan pemcemar di dalam sumber air.Pembuangan merkuri di dalam kajian ini adalah mengunakan udara.Tujuan kajian ini dijalankan adalah menyiasat keperluan kadar udara dan kelajuan putaran menggunakan Pseudomonas putida.Proses pengurangan merkuri dijalankan dibawah pelbagai kadar udara iaitu 0.5,1.0 dan 1.5 L/min dan bagi kadar puraran pula adalah 100,180 dan 200 rpm didalam membran biorektor.Suhu optimum bagi pertumbuhan bacteria pseudomonas putida adalah 37°C dan pH adalah 6-7. Kajian parameter bagi kerja ekperimen ini adalah kadar putaran dan juga kadar udara.Kadar pergantungan pada parameter ini bagi pertumbuhan bakteria telah dikaji.Kadar udara yang optimum unutk kajian ini adalah 1.0 L/min dan kadar putaran adalah 180 rpm.Kajian yang berkaitan dengan parameter lain juga dikaji iaitu jumlah pepejal teranpung,keperluan oksigen biologi,keperluan oksigen kimia dan kekeruhan.Parameter ini juga untuk memenuhi keperluan Standart B Jabatan Alam Sekitar Malaysia berdasarkan Akta Kualiti Alam Sekitar 1974. Kajian ini boleh disimpulkan bahawa merkuri berjaya dikurangkan dengan menggunakan *Pseudomonas putida.*Skala yang besar boleh dilakukan secara besar-besaran untuk mengurangkan kandungan merkuri daripada industri petrokimia.

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LIST OF SYMBOLS/ABBREVIATIONS

DOE	-	Department of Environmental
g	-	gram
g/l	-	gram per liter
$Hg(N0_3)_2$		mercury nitrate
h	-	hour
JMR		jisim molarities reactive
l/min	-	liter per minute
M		molor
min	-	minutes
ml	-	milliliter
mg/l	-	milligram per liter
MBR		membrane bioreactor
OD	-	optical density
ppm	-	part per million
ppb		part per billion
rpm	-	rotation per minute
%	-	percentage
°C	-	degree Celsius
°F		degree of Fahrenheit
µl	-	microliter
V		volume

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CHAPTER 1

INTRODUCTION

1.1 Overview of Research

In recent years, there has been a growing need to eliminate hazardous pollutants from waters. Mercury pollution has been recognized as a primary environmental issue and public health problem (.L.I. Sweet et al,2001) Anthropogenic mercury emissions have been increasing above background levels in water and air since the beginning of the industrial period (W.F. Fitzgerald et al,1998) and it has been estimated that thousands of tons are introduced into the atmosphere every year by both emission and reemission (T.L. Leonard et al,1998).

Mercury, which is included in the list of priority pollutants of the US EPA, has been paid great attention for many years. The permitted discharge EPA limit of wastewater for total mercury is 10 ppb, and the limit for drinking water is 2 ppb (Nam et al., 2003; USEPA, 2001). Related limits established by the Ministry of the Environment of Japan are, however, 5 and 0.5 ppb Takahashi et al., 2001, respectively. Meanwhile, the Word Health Organization (WHO) recommends 1 ppb as the maximum acceptable concentration in drinking water (Forster and Wase, 1997). Mercury is carcinogenic, mutagenic, teratogenic and promotes tyrosinemia. High-concentration of mercury causes impairment of pulmonary and kidney function, chest pain and dyspnousea (Berglund and Bertin, 1969).

Mercury, ubiquitous in the environment, is consideredone of the most toxic and persistent pollutant that may accumulate in the food chain, primarily in fish (USEPA, 2001; Sloss, 2002; Clarkson, 2002; Johnsson et al., 2005; Carlos et al., 2007; Zenrihun et al., 2007). Mercury can easily enter the human body through inhalation, ingestion and other pathways, and can do harm to human health. Several important ecological accidents caused by mercury, notably between 1953 and 1956 in Minamata's bay in Japan, are very well known (Bockris, 1997; Rio and Delebarre, 2003).

Mercury and its compounds are involved in a variety of industrial uses and applications, e.g. as catalysts in the chloralkali industry, preservatives and pigments in the paint industry, pesticides, pulp and paper industry, battery production, etc. (USEPA,1999). The major sources of mercury pollution are effluents from chloralkali, pulp paper, oil refining, electrical, rubber processing and fertilizer industries (Baeyens et al., 1996). Other major source of mercury emission into the atmosphere is flue gases from coal combustors used in electricity generation (Morimoto et al., 2005; Li et al., 2003).

There are several type to remove mercury from the petrochemical waste. This type including chemical or physical separation process such as solvent extraction, ion-exchange, precipitation, membrane separation, reverse osmosis, coagulation and photoreduction (Chiarle et al., 2000; Patterson and Passono, 1990; Larson, 1992; Skubal and Meshkov, 2002).All this process can be applied for effective reducing of mercury concentrations from various aqueous solutions.

Existing techniques of mercury removal, such as precipitation or ion exchange, are expensive and not sufficiently efficient, as small but significant amounts of mercury still remain in the water. Researchers discovered that many bacteria had developed high tolerance to heavy metals, which related to the binding of these metals to proteins, e.g. metallo-thionein that binds mercury.

As naturally thriving mercury-tolerant bacteria are rare and cannot be grown easily in culture, researchers at Cornell University, Ithaca, New York, inserted the metallo-thionein gene into Escherichia coli. A sufficiently large number of genetically engineered bacteria could thus treat mercury-polluted water inside a bioreactor. The efficiency of the procedure was high, as mercury was removed from polluted water down to a few nanograms per litre. Once the bacteria died, they were incinerated to recuperate the accumulated pure mercury

Today most of this treatment process is quick expensive and required more energy and also large quantity chemical. To solve this problem, the biological treatment using *Pseudomonas putida* can be apply in industry to obtained the efficiency of remove mercury This bacteria capable to change the toxic ionic mercury to non toxic metal mercury To more effectives ,the hollow fiber membrane will combined as the secondary treatment to remove the non ionic metal mercury in the bioreactor.

Hollow Fiber Membrane is one the other hand technique for mercury removal in petrochemical wastewater. To immobilize the genetically engineered cells, a cross flow membrane bioreactor was constructed and mercury bioaccumulation was investigated. The goal of these studies is to develop a system to retain the genetically engineered cells that will remove and recover mercury on a continuous base from large quantities of contaminated wastewater or a mercury extraction solution produced in a soil or sediment cleanup process in which mercury contaminated soil or sediment is washed with a solution containing an mercury creator. At the same time, the function of hollow fiber membrane for this treatment is to remove the other parameter like turbidity, total suspended solid and also concentration of mercury after the treatment

1.2 Problem Statement

Mercury is the one of contaminant in petrochemical wastewater. In petrochemical sector and industries, the production of mercury is very large every year. Mercury is heavy metal compound, so it is very dangerous to the human and our ecosystem. The production of mercury not only dangerous to the human and ecosystem but it also give more problem to our equipment. The high level concentration of mercury also can make some of equipment in the plan easy to damaged and also will corrupt to the line when we want take some reading of equipment . Mercury in crude oil above certain limits can be problematic to refining operations. The effect of mercury is poisons catalysts and reduces the quality of refined products. For waste with mercury concentrations below 260 ppm, EPA specifies stabilization before disposal. Environmental impacts are also important because running mercury-laden crude's can produce wastewater and solid waste streams having mercury concentrations that exceed regulatory limits. Mercury originating in crude feeds can deposit in equipment and thus can become an important health and safety issue during inspection and maintenance operations.

Refiners have the need to know exactly how much mercury is in the refinery crude diet to allow blending to acceptable limits or to develop contingencies. Attaching a certain range to the concentration of mercury in a purchased crude oil is not an easy task and significant errors can be encountered that can produce negative impacts on refinery operations and profitability. Before this, the scientist show that mercury cannot be degraded either biologically or chemically, and besides, it can be converted into more toxic compounds in the environment (K. Wang et. Al, 2004). But now with the new technology, the scientist has use the microorganism like *Pseudomonas Putida* to remove mercury. This technique not only contaminate to the waste but also friendly to environment at the end of this process

1.3 Objective of Research

The objective of this undergraduate research project is to reduce mercury concentration in petrochemical wastewater using hollow fiber external membrane bioreactor in order to meet the requirement of the environmental

1.4 Scope of Research Work

Scopes of the research is to remove or reduce mercury in petrochemical wastewater by using hollow fiber membrane external bioreactor. For this process, the bioreactor and hollow fiber membrane system are constructed for the petrochemical waste water contain mercury can be removed effectively. The scopes of the research for this study are:

i) To analyze water quality the parameter base on the Environmental Quality Art 1974 before introducing to the membrane bioreactor process.

ii) To control the process in bioreactor such as temperature, pH, mixing time, propeller speed and nutrient concentration.

iii). To select the best culture condition before scaling up in membrane bioreactor.

iv). To comply the parameter base on the Environmental Quality Art 1974 at the end of the process.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Mercury

Mercury (Hg), naturally-occurring element is a silver-white liquid at room temperature. Due to this property, it is also referred to as liquid silver, hydrargyrum, and metallic mercury. The most common mineral form of mercury is the non-toxic, insoluble mercuric sulfide or cinnabar (HgS) a by-product obtained by the processing of complex ores that contain mixed sulfides, oxides, and chloride minerals . Naturally occurring Hg is released by degassing of the earth's crust, volcanoes and the evaporation from oceans

Mercury has a wide variety of uses in industry: medicine, dentistry, batteries, science, and military applications. The burning of fossil fuels and medical waste incineration accounts for more than 80% of all anthropogenic sources(Raskin, et al, 2000.) Fifty-five percent of the total consumption of mercury is by chloralkali synthesis (used in electrodes), the wood pulping industry, paint, and electrical equipment. It has been estimated that the global reservoir of atmospheric mercury has increased by a factor of 2 to 5 since the beginning of the industrial revolution . Atmospheric contamination by industry has recently decreased, but mining is still a significant contributor to the contamination of ground and surface waters.

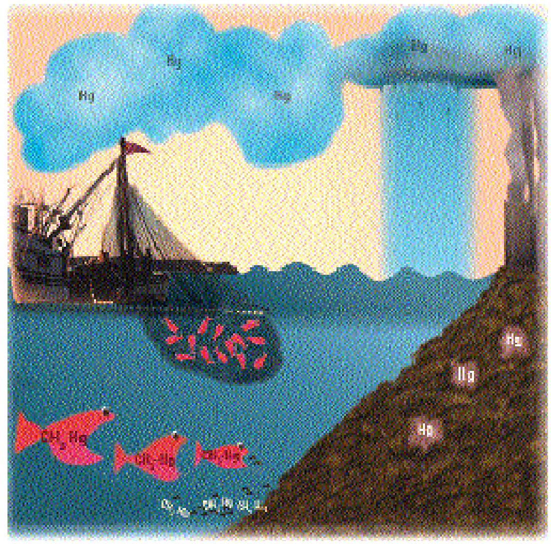

Figure 2.1 Transport and distribution of mercury within to environment

This reveals that more than half of the mercury released into the environment today is from anthropogenic sources. Mercury cannot be degraded either biologically or chemically, and besides, it can be converted into more toxic compounds in the environment (K. Wang et al, 2004). The biogeochemical cycle of mercury is well established, conversion of inorganic forms such as Hg(II) into organomercury through biomethylation being perhaps the most important transformation given the dramatic toxic effects caused by the latter to living organisms . Many international organizations have limited maximum allowable contents of mercury in water and food.

Thus, the US environmental protection agency (EPA) has limited mercury concentration in water for human consumption to 0.002 mg/L(ppm) in accordance to the primary drinking water standard (Irene Wagner-Dobler et al, 2003) while the European Community has indicated a maximum mercury concentration of 0.001 mg/L(ppm) in drinking water (Delgado S et al, 2008). Mercury is its strong absorption into biological tissues and slow elimination from them.

2.1.1 Forms of Mercury

Mercury is transported and distributed in the environment through two processes. The first involves the atmospheric circulation of elemental mercury from land and water sources, which has a global effect . Elemental mercury is initially released into the atmosphere, captured by precipitation and ultimately deposited in the sediments of lakes and oceans. This process leads to the second type of the transport and distribution of mercury. It involves the deposition of mercury in the sediments of lakes and oceans and its transformation to a methylated species by anaerobic bacteria. The amount of methyl-mercury produced by anaerobic bacteria may be decreased by demethylation reactions and volatilization of dimethylmercury

2.1.2 Health Effects of Mercury

The problem with methyl-mercury is that it is consumed by aquatic organisms, especially fish and bioaccumulates in their tissues. Biomagnification of methyl-mercury poses a serious human health risk which was first realized during the 1950 and 1960's at Minamata Bay, Japan where more than 1000 people were killed and 5000-6000 suffered irreparable neurological damage from the consumption of mercury contaminated seafood. Contamination at Minamata Bay resulted from organic mercury runoff produced by an acetylaldehyde facility

Mercury poses such a huge threat to human health because once it enters the body the destruction that occurs is usually irreversible. Symptoms associated with mercury toxicity are tremors, ataxia, paresthesia, sensory disturbances, cardiovascular collapse, severe gastrointestinal damage, irreversible damage to the brain, kidneys, and developing fetuses, and even death .Studies conducted have shown that neurological symptoms caused by methyl-mercury can continue indefinitely even after exposure from the source has ceased

2.2 Material Safety Data Sheet (MSDS) of Mercury

2.2.1 Physical and Chemical Properties

This MSDS has been prepared according to the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all of the information about physical and chemical properties of mercury, for further review ,see at Appendices C

2.3 Environmental Quality Regulation

Environmental quality is a set of properties and characteristics of the environment, either generalized or local, as they impinge on human beings and other organisms. Environmental quality is a general term which can refer to different characteristics that relate to the as well as the environment, such as air and water purity or pollution, noise and the potential effects which such characteristics may have on physical and mental health caused by human activities.

In Malaysia, we apply the environmental quality regulation to ensure that the treatment we use to removal mercury always meet the Malaysia DOE, Standard (B) on Environmental Quality Act 1974,for further review see the Appendices C

2.4 Type of Membrane

2.4.1 Membrane Bioreactor

The membrane bioreactor (MBR) is the combination of a membrane process like microfiltration or ultrafiltration with a suspended growth bioreactor, and is now widely used for municipal and industrial wastewater treatment with plant sizes up to 80,000 population equivalent

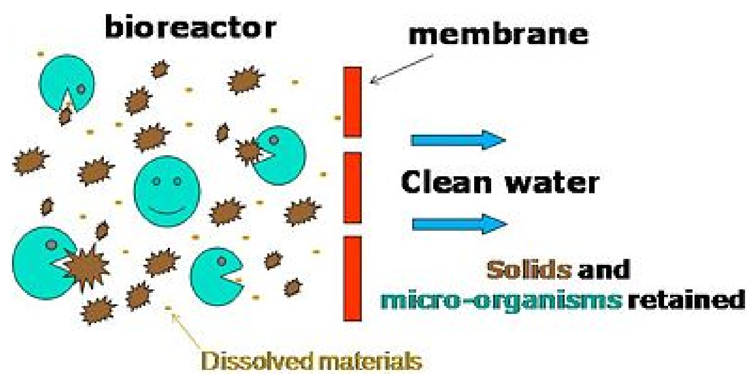

Figure 2.2 Simple schematic describing the Membrane Bioreactor process

When used with domestic wastewater, MBR processes could produce effluent of high quality enough to be discharged to coastal, surface or brackish waterways or to be reclaimed for urban irrigation. Other advantages of MBRs over conventional processes include small footprint, easy retrofit and upgrade of old wastewater treatment plants. There are two MBR configurations exist, first internal, where the membranes are immersed in and integral to the biological reactor; and second is external or side stream, where membranes are a separate unit process requiring an intermediate pumping step. The schematic are shown in the next page.

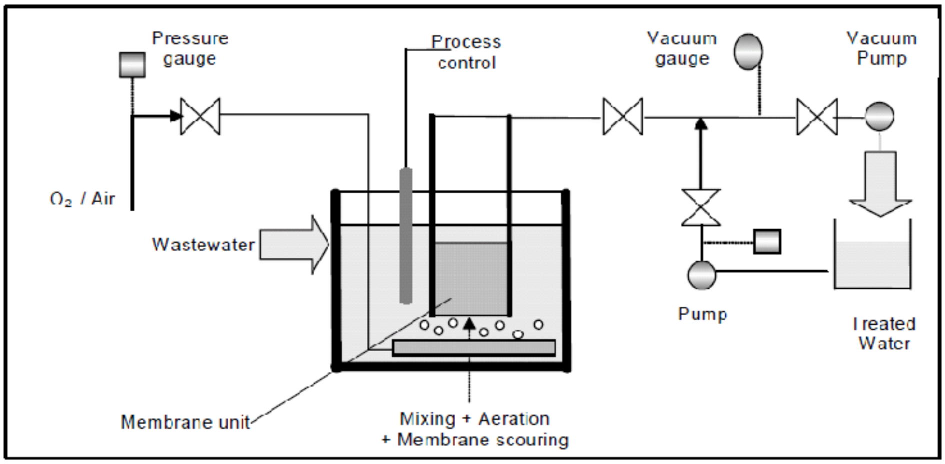

Figure 2.3 Schematic of Integrated (submerged) MBR

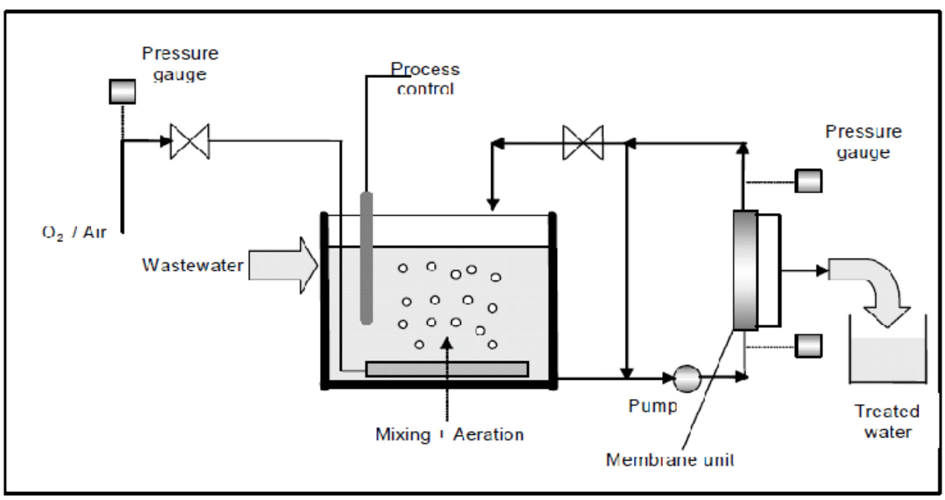

Figure 2.4 Schematic of Recirculated (external) Membrane Bioreactor

Recent technical innovation and significant membrane cost reduction have pushed membrane bioreactor to become an established process option to treat wastewaters. As a result, the membrane bioreactor process has now become an attractive option for the treatment and reuse of industrial and municipal wastewaters, as evidenced by their constantly rising numbers and capacity.

2.4.2 Cross flow Microfiltration

Cross-flow microfiltration using submerged membrane with air bubbling can provide a continuous solid-liquid separation system by simple equipment, such as a low-rate suction pump, an air blower and a vessel. In this system, the size of the separation module could be reduced by using hollow fiber membranes packed in high density. In order to apply this beneficial process to a wastewater treatment bioreactor, we constructed filtration models to design the membrane system.

Higher transmembrane pressure and lower fluidity of feed operations (eg transmembrane pressure of over 40 kPa and air-liquid two phase flow velocity of under 0.5 ms^{-1}) caused the rapid crowding of hollow-fiber membrane elements and reduced the effective membrane surface area. The hollow fiber membrane module packed in high density could be applied for solid -liquid separation.

2.4.3 Hollow Fiber Membrane

Hollow fiber membranes have been successfully employed in a wide variety of industries including food, juice, pharmaceutical, metalworking, dairy, wine and most recently municipal drinking water. Depending on the application, hollow fiber membranes can be highly practical and cost effective alternatives to conventional chemical and physical separation processes.

Hollow fiber membranes offer the unique benefits of high membrane packing densities, sanitary designs and, due to their structural integrity and construction, can withstand permeate back pressure thus allowing flexibility in system design and operation.

The Hollow Fiber geometry allows a high membrane surface area to be contained in a compact module. This means large volumes can be filtered, while utilizing minimal space, with low power consumption. Hollow fiber membranes can be designed for circulation, dead-end, and single-pass operations. Hollow fiber cartridges operate from the inside to the outside during filtration. This means that process fluid (retentate) flows through the center of the hollow fiber and permeate passes through the fiber wall to the outside of the membrane fiber.

Tangential flow can help limit membrane fouling. Other operating techniques that can be employed with hollow fiber membrane systems include back flushing with permeate and retentate reverse flow. Benefits of Hollow Fiber Membranes (inside to outside permeate flow direction)

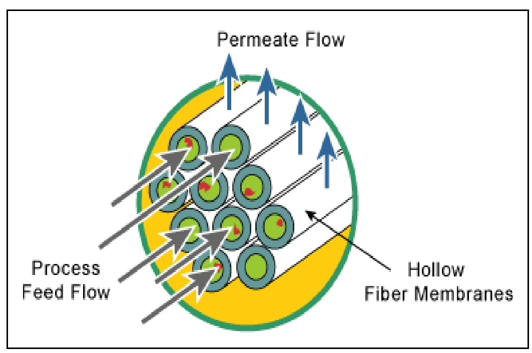

Figure 2.5 Flow of membrane

2.5 Advantages of Hollow Fiber Membrane

Hollow fiber is one of the most popular membranes used in industries. It is because of its several beneficial features that make it attractive for those industries. Among them are :

i) Modest energy requirement . In hollow fiber filtration process, no phase change is involved. Consequently, need no latent heat. This makes the hollow fiber membrane have the potential to replace some unit operation which consume heat, such as distillation or evaporation column.

ii) No waste products. Since the basic principal of hollow fiber is filtration, it does not create any waste from its operation except the unwanted component in the feed stream. This can help to decrease the cost of operation to handle the waste.

iii) Large surface per unit volume .Hollow fiber has large membrane surface per module volume. Hence, the size of hollow fiber is smaller than other type of membrane but can give higher performance.

iv) Flexible. Hollow fiber is a flexible membrane, it can carry out the filtration by 2 ways, either is "inside-out" or "outside-in".

v) Low operation cost :.Hollow fiber need low operation cost compare to other types of unit operation.