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Degradation of Crude Oil Spills in Marine Waters Using Ultra Filtration Membranes and Biological Processes

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Abstract

Degradation of crude oil using ultra filtration membrane and the bioligical process is aim to get result of more effective processing. This membrane ability able to shift the ascription waste as cost becoming waste as profit. This matter gives the positive implication not only industrial party because process almost always profit, inclusive of for environment continuity which is uncared frequently. Process biologist used system aeration with the aerobic bacteria coming from seeding of waste of itself oil, environmental friendly so that. To process the ultra filtration membrane, using pressure difference, temperature and rate of flow which vary and stay in a series of reactor, so that easy to operational. Process of biologic to degraded BOD, color, paraffin, oil and grease, happened by the parameter degradation more than 50%, with the improvement DO more than 50%, while COD, phenol, ammonia, and its pH less than 50%. Process of Ultra filtration (UF) Membrane to degraded more than 50%, are: BOD, COD, Phenol, Ammonia, Paraffin, Color, Oil and Grease. The pH which at the most 50%. The result of this research, can be evaluated from excess and insufficiency from each process which can be seen from some factor, like operational factor, fund factor, and experienced factor. In this study, it was found that membrane ultra filtration was more effective in reducing the organic content in the spill of crude oil in marine waters than biological processes.

Keywords: Crude oil, degradation,ultra filtration (UF) membrane.

INTRODUCTION

The role of sea transportation has a considerable impact on the life of marine biota, one of which is due to oil spills and the former washing of ships or even in the event of a tanker accident. As a result of the oil spill, special handling is needed through seawater treatment. In physical processing will require a long time and large costs. The processing of chemicals will carry the risk of the effects of chemicals on marine life and considerable costs. But ini biological processing by utilizing bacteria or sea fungi, so that it is simpler, easier, and low risk for marine biota.

Membrane technology is one of the relatively new separation technologies, but its application has extended to various sectors including the water treatment and industrial waste sectors. Ultra filtration (UF) membranes are one of the selective membrane separators using pressure as their driving force, used to minimize and reuse waste water in other forms. So the purpose of this study is to evaluate the ability of bacteria to degrade oil spilled in marine waters. And evaluate the ability of Ultra filtration (UF) membranes to reduce petroleum spills with physical processes (Ciardelli et al., 2000; Gander et al., 2000; Tellez et al., 2002).

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And evaluate the ability of ultra filtration (UF) membranes to reduce petroleum spills with physical processes (Hartomo and Widiatmoko, 1994; Noworyta et al., 2003).

Pollution by Petroleum, from the source of oil entering sea water comes from: offshore crude oil drilling, crude oil transportation, non-petroleum activities (domestic waste, ship washing, etc. Petroleum can be shaped: gas (liquid gas) , liquid (crude oil), solid (asphalt, tar, bitumen) or as a combination of these forms: Three Main Components of Chemically Crude Oil, namely, Paraffin Hydrocarbon, Naphthenic Hydrocarbon or Aliciclic Hydrocarbon, Aromatic Hydrocarbon. , including: specific gravity or gravity type, viscosity, boiling point and flash point, color, fluoresced, odor, and calorific value.

Biological control of crude oil waste by utilizing oil-degrading microbes, crude oils is complex hydrocarbon molecules, so 1 type of microbe is unable to degrade it. Microorganisms decomposing crude oil hydrocarbons: Pseudomonas and Bacillus. Usually found in natural oils, because of the ability of bacteria to break down hydrocarbons as nutrients. Environmental factors that affect the biodegradation of (crude) oil of the earth, as growth inhibitors and accelerators: Oxygen, pH, temperature, nutrient, type of contamination and toxicity.

Applications in the Oil Industry, for Biological Processing, According to Kusmiati (1999) that Dr. Gordon Hill, a chemist from Univ. Saskatchewan has demonstrated that a process using the Pseudomonas line, can be more effective and inexpensive to eliminate contamination of the oil industry. This process has been tested further by the Saskatchewan Research Council (SRC) (Ekins et al., 2007).

The membrane is a thin layer between two phases and functions as a selective separator. The principle works based on differences in diffusion coefficient, pressure as the driving force, temperature and flow rate. The membrane is the best available technology for water treatment, because:

- Ability to make waste as profit and not cost, from the waste itself
- Increasing or decreasing the scale of the sample is not a problem with membrane module design that is simple, compact, easy to operate and does not require a lot of equipment.

This technology does not require chemicals to operate so it does not increase the amount of waste produced. In its application the membrane produces: permeate: water products that can be reused as raw water in the process and concentrate, the waste produced is reduced in terms of volume, but in terms of concentration it is much more concentrated (Reutenbach & Albrecht, 1989; Scott, 1995).

Several types of membranes and their respective characteristics are membranes commonly used are reverse Osmosis (RO), Micro filtration (MF), and Ultra filtration (UF). The average value of the permeate flow rate is expressed as flux, which is the flow rate of the unity of the membrane area unity of time (L/M2hr-1). Flux values that pass through the membrane depend on pressure, feed concentration, temperature and flow rate and turbulence in the feed channel (Wenten, 2000). The flux value will increase if the given pressure increases, the concentration of solids in the solution is low, the temperature is higher and the flow rate or turbulence increases (Stephenson et al., 2000).

At each change of operation a membrane was washed using 1% NaOH. Membrane washing was carried out by circulating 1% NaOH for 1 hour and back wash for 30 minutes. After that rinsing with water is done until the washing water reaches a neutral pH. But if the treated waste is alkaline then washing is done in the same way using 1% HCl solution.

METHODS

This research is laboratory scale which is conducted in two locations, these location are:

1. In the laboratory of Department of Environmental Engineering, University of Pembangunan Nasional "Veteran" Jawa Timur, to examined the degradation of crude oil using a biological system.
2. In the laboratory of the Biotechnology Study Center, BPPT Serpong, Banten, to examined the degradation of crude oil using Ultra Filtration Membrane.

Sampling for marine waters was used in two locations: Kenjeran-Surabaya and Ancol-Jakarta. Parameters used in biological processes and Ultra filtration (UF) Membrane, was the organic content of crude oil which includes : Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), phenol, ammonia, paraffin, color, pH, oil

and fat. Ultra filtration Membrane Processes, samples used by Ancol sea water, Jakarta, and for biological processes using Kenjeran marine waters, Surabaya.

In this research, two systems were used to degrade crude oil in seawater, biological systems and membrane ultra filtration systems. Experiments were carried out three times repetition, with the average characteristics of chemical and organic parameters of sea water presented in Table 1. In the process of ultra filtration membrane and biological, samples of crude oil, using crude oil from PT. Migas, Cepu (Table 2. Chemical Characteristics of Crude Oil in PT. Migas Cepu).

Tabel 1. Marine Waters Characteristics in Kenjeran and Ancol

Parameter	Marine Waters of Kenjeran	Marine Waters of Ancol
Biological Oxygen Demand (BOD) (mg/L)	67.96	68.13
Chemical Oxygen Demand (COD) (mg/L)	1.22	2.34
Phenol (mg/L)	0.00	0.10
Amoniak (mg/L)	0.012	1.217
Color (PtCo)	0.05	0.26
pH	7.12	7.8

Tabel 2. Chemical Characteristics of Crude Oil in PT. Migas Cepu

Parameter	Result
Biological Oxygen Demand (BOD) (mg/L)	6830
Chemical Oxygen Demand (COD) (mg/L)	15650
Phenol (mg/L)	11
Amoniak (mg/L)	18
Parafin (%)	15.84
Warna (PtCo)	14 CU
pH	6,3

1. Biological Processing

In Biological Processing, two stages are carried out, at the beginning of the growth of bacteria by seeding, it was characterized by growing microbes as expected. The next step is the process of acclimatization; this process was done to adapt the existing bacteria to wastewater that would be processed. Acclimatization was carried out at concentrations of diluted waste, with dilution of 50% to 100%. The acclimatization was stopped when obtains a final concentration value of 50% of the initial wastewater concentration.

Conditioning sea water with crude oil so that it can be mixed and become waste as expected, with a comparison as follows:

Tubes A = 1: 1 = Oil: Sea water

Tube B = 1: 0.5: 0.5 = Oil: Sea water: Aquadest

Tubes C = 1: 0.1: 0.9 = Oil: Sea water: Aquadest

The sea water that has been conditioned, was given the bacteria acclimatized and aerated for 7 days, and carried out observations and analysis of the results of the running

2. Ultra Filtration Membrane Processing

The composition of marine waters and crude oil for processing Ultrafiltration (UF) membranes is 1: 1 comparison between sea water and crude oil. With variations:

1. Pressure on Ultra filtration (UF) Membrane with variation: 1 atm; 1.7 atm; 2.4 atm; 3.5 atm
2. The flow rate used in Ultra filtration (UF) Membrane are: 1 m/scd, 2 m/scd, 3 m/scd, 4 m/scd
3. Waste temperature for Ultra filtration (UF) Membranes are: 30 oC, 40 oC, 50 oC

Sea water that has been mixed with petroleum will be inserted into the ultra filtration membrane, so that the sea water will be filtered by the UF Membrane. The same is done on distilled water as a control value of treated wastewater. Membrane washing is also carried out in the event of pore blockage by colloids. Washing is done based on the nature of the waste to be processed. For acidic crude wastewater, washing is done by using a low-grade base (1% NaOH), so that there is no too large surge so that the membrane pores become brittle and tear easily.

Below, a flow diagram of the UF process membrane is described in treating oil spills in marine waters, in Figure 1 (UF Membrane Flow Chart).

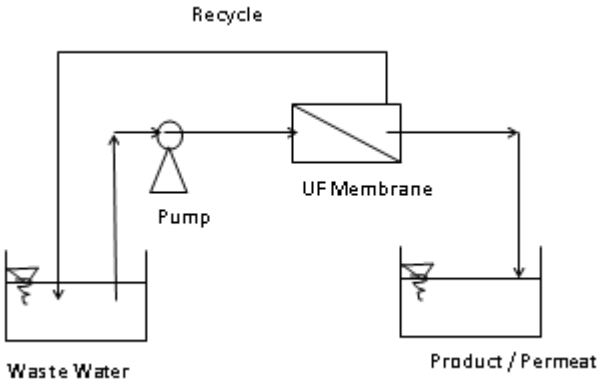


Figure 1. Unit Filtration Membrane Flow Chart

RESULT AND DISCUSSION

1. Biological Process

In this biological process, phasing is carried out to breed bacteria that are able to degrade oil spills. The three stages include seeding, which is the stage to grow bacteria, it is expected that bacteria can live in seawater waste, followed by the acclimatization stage, followed by the running stage. In this study, the seeding process for 21 days was marked by MLVSS (Mix Liquor Volatile Suspended Solid) which was formed in the range of values that were not fluctuating. Then continued acclimatization for 14 days, marked by COD content which decreases its concentration. The results of the above process, bacteria are ready to be remediated with crude oil.

The result that identified bacteria that are able to degrade crude oil, are: Pseudomonas and Bacillus. This aerobic bacterium, called Oleophilic bacteria, means being attracted to oil. These bacteria use hydrocarbons as a food source and remodel the oil. Then the bacteria convert hydrocarbons to methanol, water and CO2.

Below (Figure 3) it is explained the decrease in the parameters of organic content of crude oil waste after 7 days. And 14 days.

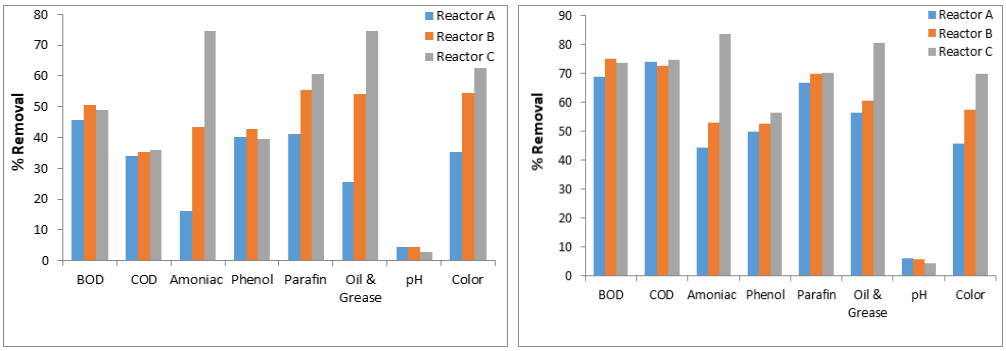


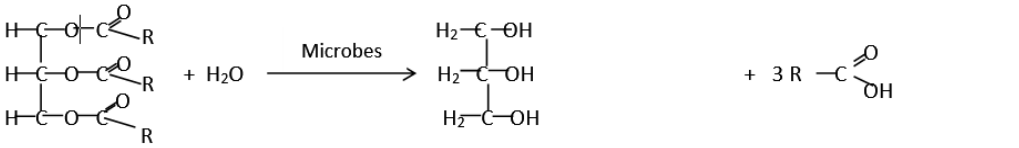
Figure 2. Decrease in Organic Crude Oil Content based on biological process at (a) 7 days, (b) 14 days

We look Figure 2, shows after 7 days biological process, decreasing BOD, color, paraffin, oil & fat, a parameter decrease of more than 50%, with an increase in DO more than 50%. COD, phenol, ammonia and pH changes are less than 50%. Bacterial work to decompose organic content in marine waters, has increased on day 14, with an average increase of around 70%.

The decrease in organic content is caused by microbial activity that destroys organic pollutants. Pollutants that are easily damaged by microbes are organic content, which changes to CO2, H2O, N2, PO4 and others. With the reaction obtained as follows:

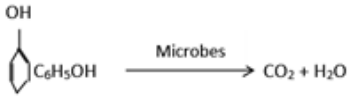
$$\text{CHONP} \xrightarrow{\text{microbes}} \text{CO2} + \text{H2O} + \text{PO4}$$

The decomposition of oil and grease, due to chemical activity in waste. Damaged oils and fats break down into glycerol and glycerol acid which dissolves in water.



There is a reaction like the one above, then the decrease in oil and fat in seawater waste due to degradation by microbes within a period of 7 days, can reduce above 50%.

Phenol compounds which are contained in wastewater tend to decrease after decomposition with microbes. The existence of several microbes capable of damaging phenols such as Pseudomonas and Bacillus, which convert phenol compounds into basic compounds, such as in the reaction as follows:



Ammonia compounds contained in waste, generally derived from the decay of microbes in waste, oil and water. Ammonia is a nitrogen compound that is widely used for plant growth in water. Besides that, ammonia is very useful for bacterial nutrition, as a source of nitrogen. Under normal conditions, ammonia is very easily oxidized by oxygen, forming a reaction as follows:

$$NH_3 + O_2 \xrightarrow{\text{microbes}} N_2 + H_2O$$

N_2 is very easily absorbed by plants and microbes. From the results of the study, ammonia tends to decrease due to microbial activity in wastewater.

The seawater which is crude oil, contains a lot of paraffin. After experiencing treatment with microbes, the amount of paraffin contained decreases. This is due to the presence of several types of microbes that require hydrocarbon compounds needed by life. Hydrocarbon compounds break down into carbon dioxide and water, like the reaction below:

$$(CnH_2n)n + O_2 \xrightarrow{\text{microbes}} CO_2 + H_2O$$

The original waste in this study has a brownish color because it comes from crude oil. In treating for seven days, the intensity of the color will decrease. This is due to organic compounds which are pollutants and which give brown color, tend to decrease due to microbial activity. The decreasing number of organic compounds, the color intensity also decreases.

Observation of pH on waste treated for 7 days, pH values tend to rise until the pH value becomes normal. Because initially the waste is acidic, which are 6.5. This is due to the presence of acid compounds derived from organic compounds, such as H2S. H2S compounds by microbes are converted into media of life. In microbial life this requires sulfur. With reduced sulfur, sulfide acid also decreases, resulting in acidity decreasing. When acidity decreases, the activity of hydrogen [H +] in the waste water will decrease and the pH will increase.

2. Ultra Filtration (UF) Membrane

Membrane ultra filtration has fine pores of mill micron size, which often clog the pores so that the membrane must be washed. For waste in this study which has acidic properties, membrane neutralization is needed to restore the performance of the membrane clogged with pores by using a base solution (1% NaOH). The way to do that is to circulate for one hour and did backwash for 30 minutes. Then rinsing with water is done until the washing water reaches normal pH. Washing is done every time a blockage is thickened.

Effect of Temperature, Pressure and Flow Rate on UF Membrane Performance

In this study, washing was carried out based on the temperature of crude oil waste. This causes the temperature to affect the specific gravity of crude oil, the higher the temperature, the lighter the density of crude oil.

Washing at a temperature of 30oC was carried out 6 times, at a temperature of 40oC washing 4 times, at a temperature of 50oC washing was done twice. This is different from the process that uses distilled water samples as a control, no washing process occurs because there is no blockage in the membrane.

The use of pure water flux as a control is intended to determine the standard value of membrane work without blockage. This processing depends on variations in temperature, pressure, and flow rate of waste, so the results obtained also vary, as in table 4 (Effect of pressure and temperature on flux).

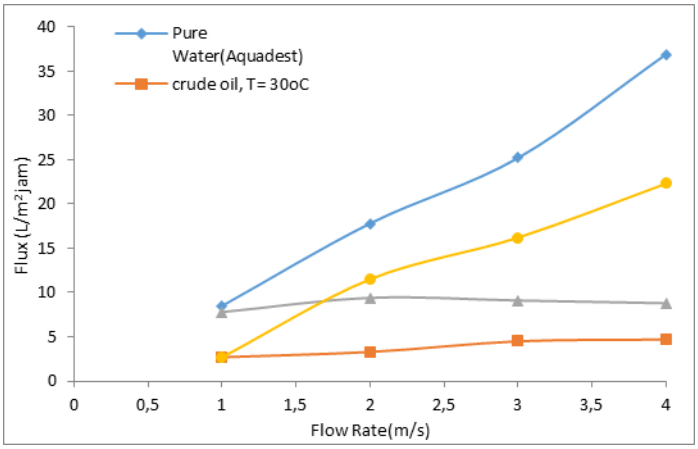


Figure 3. Effect of Pressure and Temperature on Flux

In Figure 3, the flux value of pure water tends to be constant with respect to filtration time in various conditions of different operating temperatures, because there is no blockage on the membrane, and shows that pure water can freely pass through the membrane pores. In contrast to crude oil waste which has a lot of blockage due to paraffin and other elements contained in petroleum samples. Because of the high temperature so that crude oil becomes lighter than crude oil at low temperatures, the conditions are still thick. While the influence of the water flow rate (flow velocity) which varies with the flux value can be seen in Table 5 (Effect of flow rate and temperature on flux).

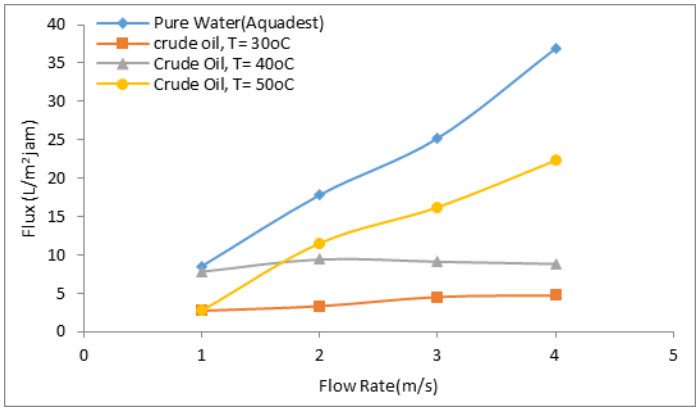


Figure 4. Effect of Flow Rate & Temperature on Flux

In Figure 4, pure water is used as a control under conditions of 50oC. Because in pure ir does not experience blockage, it produces maximum value. Whereas the waste samples often experience blockages so backwash (membrane washing) needs to be done. Pure water flow rate has no effect on differences in temperature, pressure and flow rate. Because the results to be obtained will be the same, other than that pure water does not experience colloid, unlike the samples of petroleum waste containing colloid. And the specific gravity of the oil affects the temperature, pressure and flow rate during the processing process.

Decreasing Organic Parameters on Petroleum with UF Membrane

The results of analysis of raw water (permeate) from crude oil waste water obtained from membrane ultra filtration (UF) shwon in table 1.

Table 1. Percentage of Decreasing Sea and Crude Oil Waste Water

Parameter	Influent	Effluent	Percentage (%)
BOD (mg/L)	50	25	50
COD (mg/L)	400	175	56.25
Phenol (mg/L)	0.7	0.01	98.57
Amoniac (mg/L)	5.0	0.5	90
Paraffin (mg/L)	9.6	4.3	55.21
Color (PtCo)	40	10	75
Oil&Grease (mg/L)	10	1.52	84.8
pH	4.76	6.8	42.85

The decrease in the value of BOD is 50%, COD reaches 56.25%, this is because the organic content is not soluble in water, is bound to oil, so it is rather difficult to catch by the pores of the membrane. The decrease in phenol reached 98.57% because phenol dissolves in water so that it can be easily captured in the pores of the membrane and bound by other compounds, as well as ammonia, which decreases by 90%. The paraffin, which has concentrated properties, can easily cover the surface of the pores, so that the decrease is around 50%.

From these two process can be evaluated the advantages and disadvantages of each process which can be seen from several factors, such as process time factors, technological factors, operational factors and natural factors. It was

found that membrane ultra filtration (UF) technology is more effective, although it requires more expensive costs than biological processes. In addition, using Ultra filtration (UF) membranes produces permeate which can be reused as industrial process water or returned to the sea for this process

CONCLUSION

Degradation of crude oil waste water with a biological process, identified by bacteria that play a role in reducing the organic content of crude oil waste is Pseudomonas and Bacillus. For a 14-day process for biological processes, the BOD value, color, paraffin, oil and fat a decrease of more than 70% while for COD, Phenol, Ammonia, and pH not more than 70%. Whereas in membrane Ultra filtration (UF) processing the average yield for the research parameters has decreased by more than 50%, even for phenol, ammonia, fat oil and color, decreasing above 80%, at 1 hour processing time. UF membrane used, with a pore size of 500 Daltons by varying pressure, temperature and flow rate. From the evaluation of the two processes in this study, biologically and UF membranes, in terms of process time factors, natural influences, and operations, the potential for membrane ultra filtration to treat crude oil spills in marine waters has advantages compared to biological processes.

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