REMOVAL OF TRIHALOMETHANES (THMS) VIA ULTRAFILTRATION PROCESS FROM PETROCHEMICAL WASTEWATER

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ABSTRACT

This work investigated the removal of trihalomethanes (THMs) from petrochemical wastewater through ultrafiltration (UF) process by using Polyethersulfone (PES) membrane. The present study implements filtration method to remove the THMs exist in wastewater sample. UF process has been carried out by using UHP-62 Dead-end filter cell unit with nitrogen gas. The wastewater was characterized using FTIR analysis to identify the presence of THMs. Prior the experiment, PES membrane was soaked with deionized water for 24 hours before been used to remove the particles attached on the membrane surface during their packaging and transportation. The effects of pH solution and temperature were study throughout the experiment in order to investigate the removal efficiency of the THMs by PES membranes mechanism. The operating pressure was keep constant at 1 bar and the homogeneity of the feed solution was carried out by stirring at 400 rpm, constantly. Fourier-Transform Infrared (FTIR) was used to analyze the THMs removal through IR spectrum result. The study showed that the effect of pH and temperature somehow give significantly acceptable result on THMs removal. The finding claimed that the chloroform functional group found at peaks of 771.71 cm^{-1}. At neutral and alkaline condition, it was reported that no peak of the chloroform exist in the sample after filtration, nevertheless it was identified at 717.22 cm^{-1} for acidic solution.

Keywords: Chloroform, polyethersulfone membranes, petrochemical wastewater, trihalomethanes, ultrafiltration.

INTRODUCTION

The most common THM compounds as a result of chlorination are dibromochloromethane ($CHClBr_2$), bromoform ($CHBr_3$), chloroform ($CHCl_3$), and dichlorobromomethane ($CHCl_2Br$) [1]. Subsequently, chloroform is THM which found in the highest concentrations among all. Chlorination is one of the common treatments used widely in the industrial sector which to ensure the bacteriological quality and to produce safe water due to its extremely efficient, stability and cost effective [2-4]. On common sense, people also experiences in which chlorine have develop a chlorine flavour by itself which constitutes one of the major complaints against tap water [2-4]. As regard to this concern with chlorine flavour, there are several studies reported that the existence of disinfection by-product (BDPs) is caused by chlorination of organic matter presence in fresh water, especially trihalomethanes (THM) which may affect to human health. According to Environmental Protection Agency (EPA) has established that THMs have been linked to be a cancerous diseases as well as it is responsible to reproductive problems and miscarriage and it is become a potential serious problem. In industries, water is used for numerous applications such as a cooling water, rinsing and chemical production, as a solvent, boiler feed water, purified water, water for injection also for equipment cleaning purpose and etc. However, water quality must be controlled to avoid corrosion, equipment damage and any blockage in the pipeline due to water precipitation. THMs exhibit mutagenous and carcinogenic properties due to these compound are aromatically sensible which their presence in water might be subjected to physiologically hazardous [5]. Literally, conventional water treatment plant consists of physical treatment method such as screening, sedimentation, floatation and filtration processes. In the other hand, chemical treatment involved pH adjustment, coagulation-fluctuation process, oxidation-reduction process, and adsorption process [6]. These are some of the methods that commonly used by the industries but yet it varies by dependent on the types of wastewater would be implied for the

treatment. Hence, the aim of this work is to remove THM contain in petrochemical by ultrafiltration. The influence of solution chemistry and feed temperature were investigated throughout the experiment to determine the effectiveness of the filtration process.

MATERIALS/APPARATUS AND EQUIPMENT

The experiment has been divided into three part which are sample preparation, execution of filtration process and FTIR analysis on permeated flux. The materials and apparatus used in the experiment were beaker of 50ml, 250ml and 1000ml, conical flask of 50ml, thermometer, retort stand, deionized water, water bath, wastewater sample, sodium chloride (NaOH) and hydrochloric acid (HCL). Meanwhile, the equipment used throughout the researched were UHP-62 200ml Dead-end stirred cell, hot plate, Mettler Toledo pH meter and nitrogen (N_2) gas.

Sample collection and preparation

Feed sample of filtration process is wastewater that have been collected form petrochemical sector in 4 L of plastic bottles and preserved at room temperature. Basic characteristic of the wastewater initially determined such as pH and the color appearance. The pH value measured was 1.91 and it physical observation on color was like light clear-blue color.

Experimental Methods

Prior to filtration process, the feed water had been carried out an analysis in order to determine the existence of THMs in the sample done by FTIR. PES membranes also been soaked with deionized water approximately for 24 hours. 200 mL of feed water sample was filled in the dead end filter unit and it has been pressurized by nitrogen gas to promote driving force on the solute to pass through the membrane surface. The allowable pressure is at 1 bar and constant stirring speed at 400 rpm to promote solution homogeneity [2]. Permeated flux drained from the process was collected in 50 mL of beaker for every 60 min. Hence, these permeated flux had been undergone FTIR analysis in order to investigate the removal of THMs. The same procedure was repeated to be implied for the next parameter which were the study on effect of pH and temperature of THMs removal performance. There were pH 4, 7 and 10, NaOH solutions was used for pH-adjustment of the feed solution. Next, there were temperature of 40°C, 60°C and 90°C, the water bath concept was used for temperature control during filtration took placed. After the filtration process end, every permeated flux had been undergo FTIR analysis. The THMs removal performances had been analyzed through IR spectrum result for each parameters.

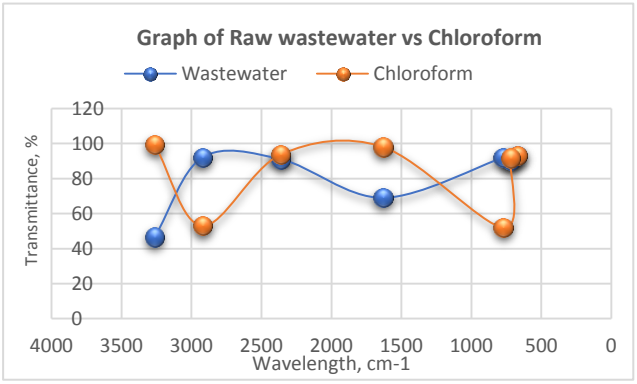
RESULTS AND DISCUSSIONS

The presence of THMs had been characterized prior to filtration process by detection of its functional group through FTIR analysis's spectrum result. THMs has been identified as a compound of alkyl halides with their general formula CHX3 where X may be indicates as any halogen or combination of halogens atom [4].

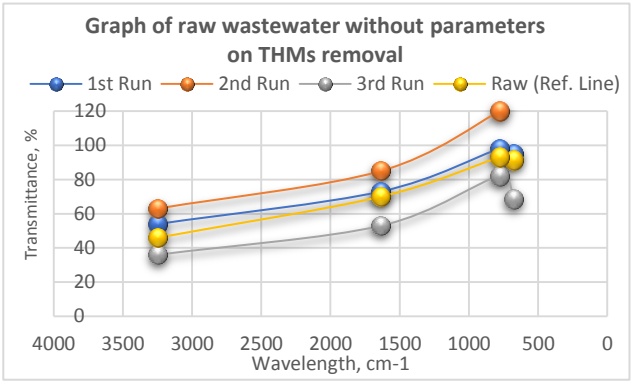
As regards to Figure 1(a), THMs was identified in finger print region at a wave number of 719.88 cm^{-1} which falls in the finger print region, range of 700-799 cm-1. By comparing the IR spectrum result of raw water sample and blank sample of chloroform, it showed that THMs regions in wastewater are corresponded to chloroform's. According to Environmental Fact Sheet of New Hampshire Department, THMs were found in highest concentration as chloroform [3]. So, chloroform was analyzed by FTIR to detect the dominant peak range that's subjected to chloroform functional groups. Hence, it found at peaks of 771.71 cm-1, which in the peak range of C-Cl_3. Thus, it has confirmed the presence of THMs in the wastewater sample was corresponded to chloroform's peak but at low absorption.

Based on the Figure 1(b), it illustrates the IR spectrum result of permeated of raw wastewater sample that has been filtered with the original initial characteristic. The experiment was repeated for three times in order to ensure a significant result for the THMs removal. For the first trial, the peaks of C-Cl_3 which responsible for THMs compound were identified in the permeated in sample 1 which found at 777.53 cm^{-1} where in sample 2 and sample 3, none of THMs peaks could be found. For the second trial, there were none of THMs peaks could be identified in sample 1 and 2 while in sample 3, the peaks of THMs could found at 783.12 cm^{-1}. Even though, some IR spectrum showed an insignificant result but yet the ultrafiltration process however was shows some decrement of the THMs in small amount even without applying any parameters or changing any characteristic of original condition. These kind of insignificant result may be due to some

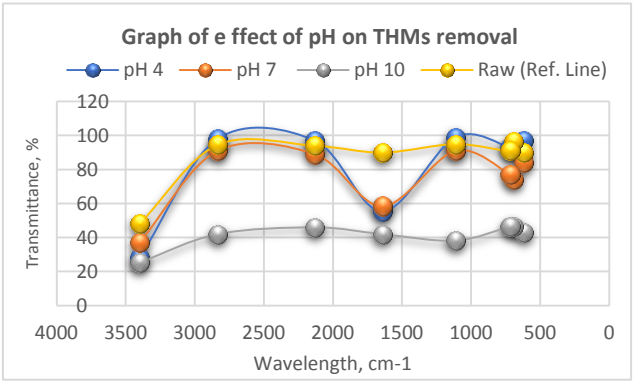
technical problems of the equipment itself. That is due to there are no significant chemical reaction either between the molecule in the solution nor the reaction on the membrane surface.



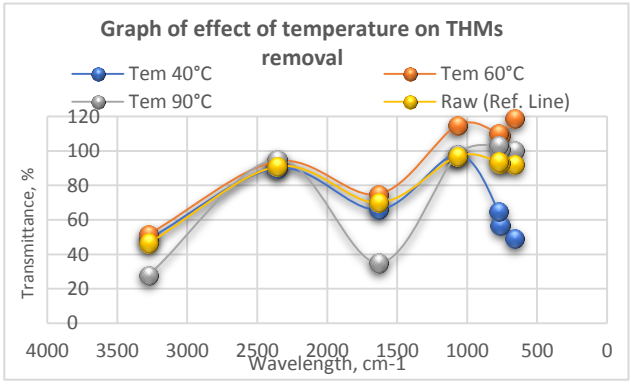
(a)



(b)



(c)



(d)

Figure 1: (a) Determination of THMs in wastewater sample; (b) THMs removal without applying any parameters; (c) Effect of pH solution on THMs removal; and (d) Effect of temperature solution on THMs removal.

Based on Figure 1(c) spectrum of pH 4, the result shows that functional groups of THMs was identified at 717.22 cm^{-1}. For neutral conditions, none of THMs functional groups could be identified but there are still have another finger regional peaks of others compound. By comparing the result pH 10, it is clearly that less or none of the compound in finger print area could be identified. Acidic solutions carry high concentration of hydrogen ion [H^+] which acid ions may acts as proton donors, therefore, reactions can be occured to ion acceptor such as OH^- to complete their chemical bonding of the compound to form other compound thus increased the molecular weight. Hence, difficult for the solute to pass through the membrane. In the other hand, in chemistry, metal salt is an ionic compound resulted from the neutralization reaction of an acid and a base. The presence of the metal salt is because the addition of NaOH into the acidic sample which regulated to increase the pH. The acidic condition carry negatively charged ions due to salt-forming anions which oxide ions, O2- is negatively charged ions in the acidic solutions. High concentration of negative charge is due to O2- ions. On top of that, the hydrophobicity of the PES membrane is a negatively charged hence there have the correlation between the membrane surface and acidic solution. Due to negatively charged of membrane and acidic solution, the membrane surface will allow the molecules to pass through the pores. This is because of the phenomenon negative and negative charged will be repuls. Therefore, the THMs could not be removed in acidic condition.

The experiment was performed at three different temperature, 40°C, 60°C and 90°C with original pH of raw feed sample. According to the IR spectrum result illustrated in Figure 1(d), THMs was found in permeated sample for temperature 40°C and 60°C at peak of 762.34 cm^{-1} and 774.08 cm^{-1}, respectively, while none of alkyl halides groups could be identified in 90°C permeated sample. In this case, the permeated could be considered as it has been contaminated during

the filtration process takes place due to technical problem of the equipment membrane has loosen up since the rubber to hold the membrane in tight position also has worn out due to the equipment has been used for so long ago without any maintenance. Thus, the wastewater inside the cell could flow to the permeated collecting area at the bottom of the filter cell unit without been filtered. The composition of permeated and unfiltered water was mixed together hence affect the result. Theoretically, a higher temperature may subjected to decreased van der waals force between the molecules. Molecules absorb heat energy and tend to vibrate vigorously as their kinetic energy increased. The kinetic energy will responsible to break the bond of weak Van der Waals force between molecules of the compound. Hence, diffusivity of the solvent through the membranes will be increase due to the low resistance for the small molecules or low molecular weight of solutes to pass through the pores membrane and retained THMs molecule on the membrane surface.

CONCLUSIONS

THMs removal performance had been investigated in the ultrafiltration process carried out through PES membrane. The result had showed some significant and insignificant THMs removal based on the temperature, pH, the nature of the solution as well as the membrane characteristics. The nature of membrane also had contributed to THMs removal worked by the mechanism of hydrophobicity of the membrane. Throughout the result of the experiment, it showed that the temperature was influenced to the viscosity and diffusivity of the feed solution. It significant with the fact which by increased of temperature, the viscosity of the fluid would be decreased. Instead of decrement of THMs in the IR spectrum, the physical observation of surface membrane also explained that there were more scattered deposition of molecule at temperature 90°C compared to 60°C and 40°C, respectively. Hence, it can be conclude that higher temperature could initiated a higher THMs removal.THMs removal, also had increased with pH. A significant filtration performance was found at pH 10 because of the spectrum result showed there were THMs reduction together with other compound could not been defined compared to lower pH of 7 and 4. At pH 7, the result showed a significant performance due to its neutral condition. Overall, it had proven that acidic condition was impossible to remove THMs in this researched study.

ACKNOWLEDGEMENT

I would like to express my deepest appreciation to all those who provided me the possibility to complete this research project. Especially, who always boost me up in completing this project is fully supported by AP. Dr. Indok Nurul Hasyimah Mohd. Amin, thank you for all of your advices, suggestions, encouragement, guidance and support throughout this work.

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