

Ultrafiltration Behaviour of Trihalomethanes (THMs) from Petrochemical Wastewater

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ABSTRACT: *This work investigated the ultrafiltration of trihalomethanes (THMs) from petrochemical wastewater by polyethersulfone (PES) membrane. The ultrafiltration process was carried out by using UHP-62 dead-end filter cell unit. The wastewater was initially characterised using Fourier transform infrared (FTIR) and gas chromatography (GC) to identify the presence and concentrations of THMs, respectively. Prior to the experiment, PES membrane was soaked overnight with deionised water before being used to remove the particles attached on the membrane surface during their packaging and transportation. The concentration of THMs in the feed was determined and the effects of solution chemistry were studied to investigate the removal efficiency of the THMs by PES membranes. The operating pressure was kept constant at 1 bar and the homogeneity of the feed solution was achieved with a constant stirring at 400 rpm. FTIR was used to analyse the THM removal through IR spectrum result. The study showed that the effect of pH somehow gave significantly acceptable results on the THM removal. The chloroform functional group was found at peak 771.71 cm^{-1} with highest concentration about $1750\text{ }\mu\text{g l}^{-1}$. At neutral and alkaline conditions, no chloroform peak was detected, whereas in acidic solution, the peak was identified at 717.22 cm^{-1} .*

Keywords: Ultrafiltration, polyethersulfone membranes, petrochemical wastewater, trihalomethanes, PES membrane

1. INTRODUCTION

The most common trihalomethane (THM) compounds formed from chlorination are dibromochloromethane (CHClBr_2), bromoform (CHBr_3), chloroform (CHCl_3) and dichlorobromomethane (CHCl_2Br).¹ Among them, CHCl_3 has the highest concentration. Chlorination is one of the common treatments used widely in the industrial sector to attain bacteriological quality and produce safe water due to its efficiency, stability and cost effectiveness.²⁻⁴ Chlorinated water develops a certain flavour and smell found in tap water which sometimes become a cause for complaint.²⁻⁷ Several studies reported the existence of disinfection by-products (DBPs) caused by chlorination of organic matters presence in the fresh water, especially THMs, which may adversely affect human health. The Environmental Protection Agency (EPA) has established that THMs have been linked to cancer-related diseases, and may result in reproductive problems, miscarriage and other potential harms.

In industries, water is used for numerous applications such as cooling water, rinsing and chemical productions, solvents, boiler feed, purified water, injection liquid as well as for equipment cleaning purpose. 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, and due to these properties, their presence in water might become physiological hazards.⁵ Conventional water treatment plant consists of physical treatment method that includes screening, sedimentation, floatation and filtration processes. On the other hand, chemical treatment involves pH adjustment, coagulation-fluctuation, oxidation-reduction and adsorption processes.⁶ These are some methods commonly used but they vary depending on the types of wastewater for the treatment. Hence, the aim of this work is to remove THM contents in petrochemical by ultrafiltration. The influence of solution chemistry was investigated throughout the experiment to determine the effectiveness of the filtration process.

2. EXPERIMENTAL

A 4-l feed wastewater sample was supplied by a local petrochemical company, Petronas Penapisan (Melaka) Sdn. Bhd., Malaysia. The pH of the sample was measured at 1.91 and the physical appearance was light clear-blue colour (Figure 1). The characteristic was adjusted with sodium chloride (NaOH) and hydrochloric acid (HCl).



Figure 1: Physical appearance of the feed solution.

2.1 Experimental Methods

Initially, the sample was characterised by using gas chromatography (GC) and Fourier-transform infrared (FTIR) to determine the concentration and presence of THMs. An amount of 200 ml of feed water sample was filled in the dead-end filter unit and pressurised with nitrogen gas. The allowable pressure was 1 bar and stirring speed at 400 rpm to promote solution homogeneity.² The permeate flux was collected in 50 ml of beaker for 60 min. Then, it was analysed to determine the THM removal. The characteristic of the feed sample was adjusted to different pH values of 4, 7 and 10.

3. RESULTS AND DISCUSSION

3.1 Determination of THMs in the Feed Sample

Figure 2 represents the functional group of THMs in the feed solution. It was found that the functional group of alkyl halides appears at wavenumber 719.88 cm^{-1} while the functional group of chloroform which is associated with C-Cl bond was found at $700\text{--}785\text{ cm}^{-1}$ region. According to Environmental Fact Sheet of New Hampshire Department, US, THMs were found in highest concentration

as chloroform.³ Alkyl halides are compounds in which C is attached to X, where X may indicate any halogen or combination of halogens atom.⁴ Another functional group of THMs which corresponds to C=C bonding appears at 1620–1680 cm^{-1} .

Figure 3 shows the concentration of THMs in the petrochemicals wastewater. It was recorded that the concentration of chloroform is the highest at 1750 $\mu\text{g l}^{-1}$, while the concentrations for bromoform, dichloromethane and bromodichloromethane vary between 70 $\mu\text{g l}^{-1}$ and 200 $\mu\text{g l}^{-1}$.

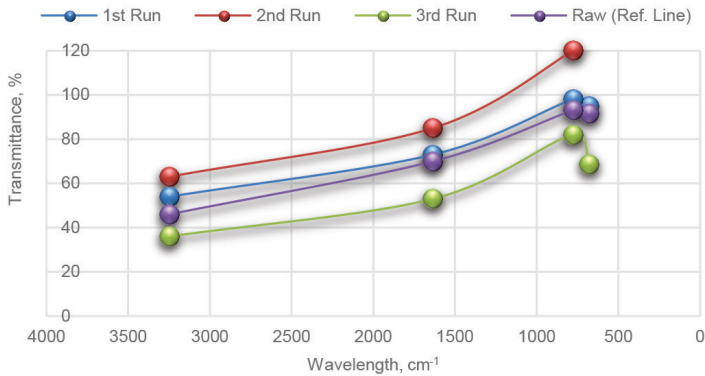


Figure 2: FTIR spectrum of feed solution.

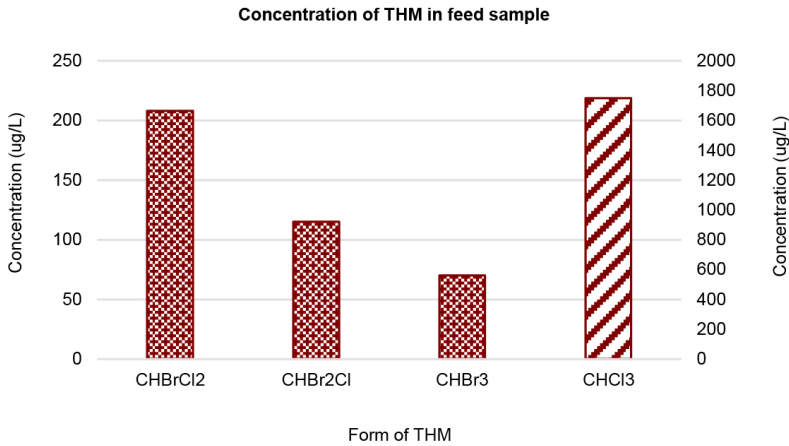


Figure 3: Concentration of THMs in feed solution.

3.2 Effect of pH on the THM Removal

Figure 4 exhibits the effect of pH on the flux behaviour during ultrafiltration of THMs from petrochemical wastewater. It was noted that the greatest flux reduction occurred in an acidic level. Generally, the pH would affect the membrane surface charge and the solute charge. It was claimed by the researchers that a sieving mechanism is responsible for the retention of uncharged solutes, while for the charged components, an electrostatic interaction takes place between the components and the membrane.⁵

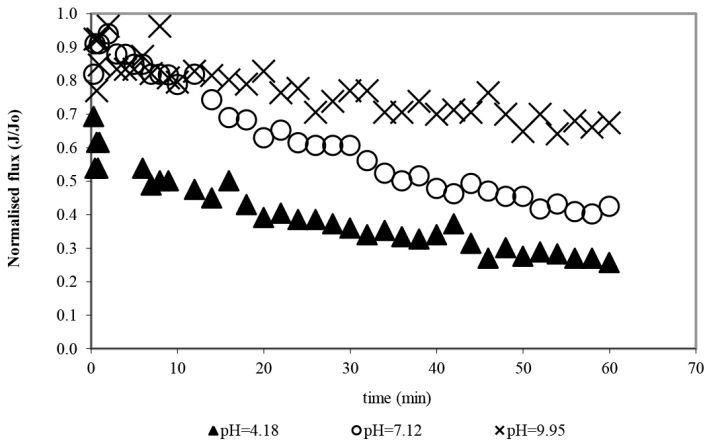


Figure 4: Effect of solution chemistry on flux decline of THMs.

Figure 5 represents the effect of pH to the THM removal. It was recorded that the concentration of bromodichloromethane is significantly reduced to about 60.0% and 89.1% in alkaline and acidic conditions, respectively. For dibromochloromethane, the concentration is reduced to about 43.48% at low pH and none was detected at high pH. For chloroform, the concentration is only reduced to 8.23% at pH 10 and can reach up to 69.00% at pH 4. Essentially, the trend of THM removal is correlated with the flux performance as previously discussed.

The possible explanation for this condition is that an acidic solution carries a high concentration of hydrogen ion $[H^+]$, in which acidic ions may act as proton donors. Therefore, reactions can occur with ion acceptors such as OH^- to complete their chemical bonding of the compound to form other compound, thus increasing the molecular weight. Hence, it is difficult for the solute to pass through the membrane. On the other hand, metal salt is an ionic compound resulted from the neutralisation reaction of an acid and a base. The presence of metal salt is due to the addition

of NaOH into the acidic sample which is regulated to increase the pH. The acidic condition carries negatively charged ions due to salt-forming anions, oxide ions (O_2^-), which are negatively charged ions in the acidic solutions. High concentration of negative charge is due to O_2^- ions. On top of that, the hydrophobicity of the PES membrane is negatively charged, hence there is a correlation between the membrane surface and the acidic solution. Due to negatively charged membrane and incomplete dissociation of THMs, the THMs would undergo higher removal in acidic level.

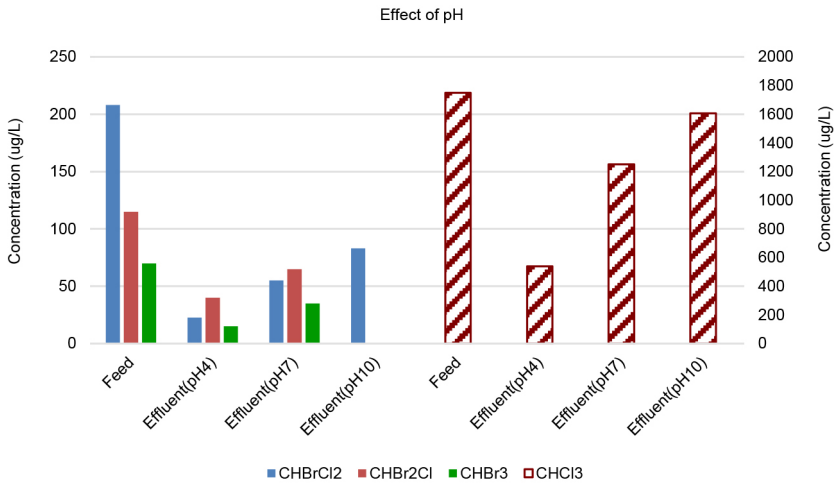


Figure 5: Effect of solution chemistry to the THM removal.

Figure 6 shows the determination of THMs at different pH values after ultrafiltration process. At low pH, the functional group of THMs was identified at 717.22 cm^{-1} . At neutral conditions, none of THM functional groups could be identified but there are still other regional peaks of other compounds. By comparing the result at pH 10, it is clear that less or none of the compound in finger print area could be identified.

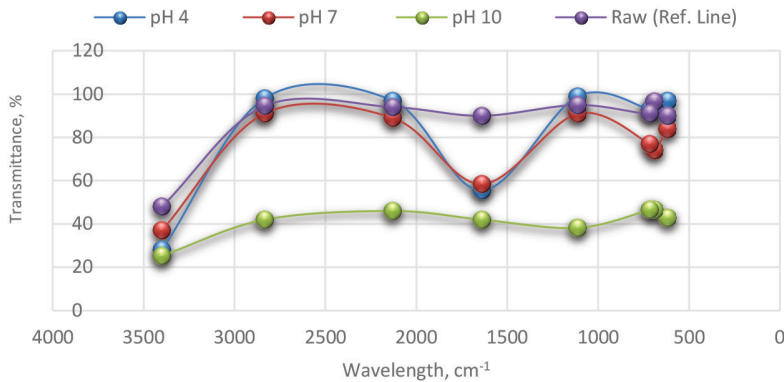


Figure 6: Effect of pH on the determination of THMs in wastewater sample.

4. CONCLUSION

Ultrafiltration process can be one of the promising technologies in removing THMs from wastewater. The characteristic of feed solution seems to play a major role in determining the permeate flux as well as flux reduction. The hydrophobicity behaviour of the membrane material and solution chemistry will influence the adhesion force between the solute and the membrane surface. The effective removal of THMs is expected occur at a low pH due to incomplete dissociation of the acid which carries a similar charge with membrane and induces repulsive force. A better filtration performance and insignificant removal of THMs was detected at high pH because of the lower reduction of concentration after the ultrafiltration. Even though there were THM reduction after treatment at both pH, the content levels were considerably high compared to the regulated limit by the Malaysia's Ministry of Health. Hence, the application of membrane separation as a potential technology enables water treatment consultants, technologists and practitioners to determine the pre-treatment requirements without conducting time-consuming and costly pilot studies.

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