Iraqi Journal of Chemical and Petroleum Engineering
Vol.17 No.2 (June 2016) 53- 68
ISSN: 1997-4884

University of Baghdad
College of Engineering

Thermal Osmosis of Mixtures of Water and Organic Compounds through Different Membranes

Ahmed Faiq Al-Alawy[*] **and Ramy Mohamed Al – Alawy**[**]
[*]*University of Baghdad – Chemical Engineering Department*
(E-mail: ahmedalalawy@yahoo.com)
[**]*University of Baghdad – Chemical Engineering Department*
(E-mail: rami_mo80@yahoo.com)

Abstract

The present work aimed to study the efficiency of thermal osmosis process for recovery of water from organic wastewater solution and study the factors affecting the performance of the osmosis cell. The driving force in the thermo osmosis cell is provided by a difference in temperature across the membrane sides between the draw and feed solution. In this research used a cellulose triacetate (CTA), as flat sheet membranes for treatment of organic wastewater under orientation membrane of active layer facing feed solution (FS) and draw solution (DS) is placed against the support layer. The organic materials were phenol, toluene, xylene and BTX (benzene, toluene, and xylene) used as feed solution. The osmotic agent in draw solution was sodium chloride salt. The membranes have high rejection percentage for NaCl and organic materials. In this research, the operating conditions that have been studied are: temperature of draw and feed solution (18 – 45 °C) and the operating time of process was (0 – 3) hours. It was found that water flux in thermal osmosis process increases with increasing temperature of draw and feed solution (by average ratio 1:2), and decreases with increasing operating time.

Key Words: thermal osmosis, wastewater solution

Introduction

Due to fast depletion of the freshwater resources, the world is facing crisis of fresh water all over the world. The industrial and domestic activities have polluted the surface water as well as ground water up to a greater extent [1]. Hence the cost of removal of organic pollutants from water has been increased remarkably in last few years. There are several technologies for treating wastewaters. And this poses a great challenge to chemical engineer’s to develop low cost effective and environmentally safe disposal and treatment methods. Organic compounds in water derive from three major sources: (1) the breakdown of naturally occurring organic materials, (2) man-made chemicals from domestic and commercial activities, and (3) treatment additives and chemicals formed during reactions that occur during water treatment and transmission [2].

The health effects of organic compounds can vary greatly according to the compound, which can range from being highly toxic to having no known health effects. The health effects of organic compounds will depend on the nature of the organic compound, the level of exposure, and the length of exposure. For example, long-term exposure to volatile organic compounds can cause damage to the liver, kidneys, and central nervous system. Short-term exposure to volatile organic compounds can cause eye and respiratory tract irritation, headaches, dizziness, visual disorders, fatigue, loss of coordination, allergic skin reactions, nausea, and memory impairment [3]. Several treatment methods are available for treating the organic wastewater includes adsorption and membranes separation, anaerobic processes, and combined applications of flotation and coagulation processes, stripping and oxidation. All of these are used for treating organic and inorganic waste. Most of these methods suffer from some drawbacks, such as high capital and operational cost, regeneration cost, and problem of residual disposal [2]. In recent decades various membrane separation processes have been developed and utilized in the field of potable water purification, and more recently in the treatment of various process and waste liquors. Some of the membrane processes are capable of removing both dissolved and particulate contaminants.

A wide variety of membrane separation processes exist. These differ from one another in the model and configuration of the membrane, the mechanism of trans-membrane transport for various water solution components, the nature of the process driving force and other features. Membrane separation processes may be classified and categorized by a number of criteria.

A basic distinction between the individual methods is the process driving force used to purify or concentrate a solution, which may be a pressure gradient, concentration gradient, electrical potential gradient or temperature gradient. In some instances, and specifically in some processes under development, more than one driving force may be used. Membrane processes can be classified with respect to the process driving force such as pressure gradient, electrical potential, concentration gradient, temperature gradient, and combined driving forces [4].

Nanofiltration (NF) membranes reject organic compounds with a molecular weight of 200 – 500 or above. Nanofiltration has been used industrially in water softening applications, removal of dissolved organic substances and fractionation of low and high molecular weight organic substances [5]. Colloids, suspended solids and high molecular weight organic molecules do not pass through the ultrafiltration (UF) membrane with water. They are rejected and remain in the concentrate stream. Reverse osmosis typically removes 95 – 99.5% of total dissolved inorganic solids and 95 – 97% of dissolved organic solids. The microfiltration (MF) membrane rejects particles and dissolved macromolecules larger than 0.1 µm.

Despite more recent technology advancements, membranes systems, by definition, still need to provide enough driving force to overcome the intrinsic osmotic pressure in brackish or seawater. A more energy efficient way is to harness the force of nature, osmotic pressure, the natural pressure that drives water molecules to the saltier side across a semipermeable membrane. Forward osmosis (FO) does just that.

The process itself is not new. Forward (or Direct) osmosis is an isothermal process that refers to the diffusion of water through a semipermeable membrane (i.e. dense and water selective membrane, hydrophilic membrane such as cellulose triacetate) from a higher water concentration side to the osmotic agent side. The advantage comes when the salt in the draw solution (DS) can be removed efficiently and cheaply.

The process is a simple two-part process. A draw solution with salt content higher than the water to be purified is used to draw water across a semipermeable membrane. Water comes to the draw solution without external energy or pressure. After water is drawn to the saltier side, the draw solution is processed to remove the salts. The salts are subsequently recovered and reused. An FO system with its low energy operation, close to zero liquid discharge operation, ingredients safe to handle and completely recoverable, low capital, maintenance and replacement cost, and the possibility to be completely off the grid makes it an ideal choice for remote and small operations.

The development of a suitable FO membrane became the most critical piece for realizing the potential of the FO technology [6]. In this research, study the efficiency of thermal osmosis process as a new application for recovery of pure water from organic solution. Sodium chloride was used as draw solution (DS), and organic compounds such as phenol, toluene, BTX, and xylene in water were used as feed solution (FS). Used three types of membranes are cellulose triacetate (CTA), cellulose acetate (CA), and thin film composite (TFC) in the thermo osmosis to achieve high recovery percentage.

Theoretical Thermal Osmosis

Thermo-osmosis is a phenomenon in which matter is driven through a membrane or an orifice from one chamber to another on account of the temperature difference between the two chambers. This can occur for a single fluid or a mixture of fluids. In a system without a membrane or a barrier, temperature gradient can give rise to concentration gradient and this phenomenon is called thermal diffusion. Thermo-osmosis was the first non-equilibrium phenomenon which was extensively studied from experimental and theoretical angles, both for the case of liquids, gases and gaseous mixtures. There are a number of factors, which govern the occurrence of the phenomenon of thermo-osmosis. It is essential to choose a system such that the dimensions of the pores of the membrane are comparable to the mean free path of the permeating molecules.

The deficiency is more serious in case of liquids. In case of gases, appreciable difference of pressure has been observed as a result of them-osmosis through natural rubber membranes [7]. Thermo-osmosis of water through a cellophane membrane has been reported by Rastogi, Blokhra and Agrawal. Experimental studies on thermo-osmosis of liquids (methanol and water) across Du Pont 600 cellophane were reported for the first time by Rastogi and Singh. Studies on thermo-osmosis of water through cellulose acetate membrane support predictions by Rastogi and Singh based on correlation between the existence of thermo-osmosis and the membrane pore size. Extensive studies on thermo-osmosis have been carried out using various hydrophobic and hydrophilic membranes [8].

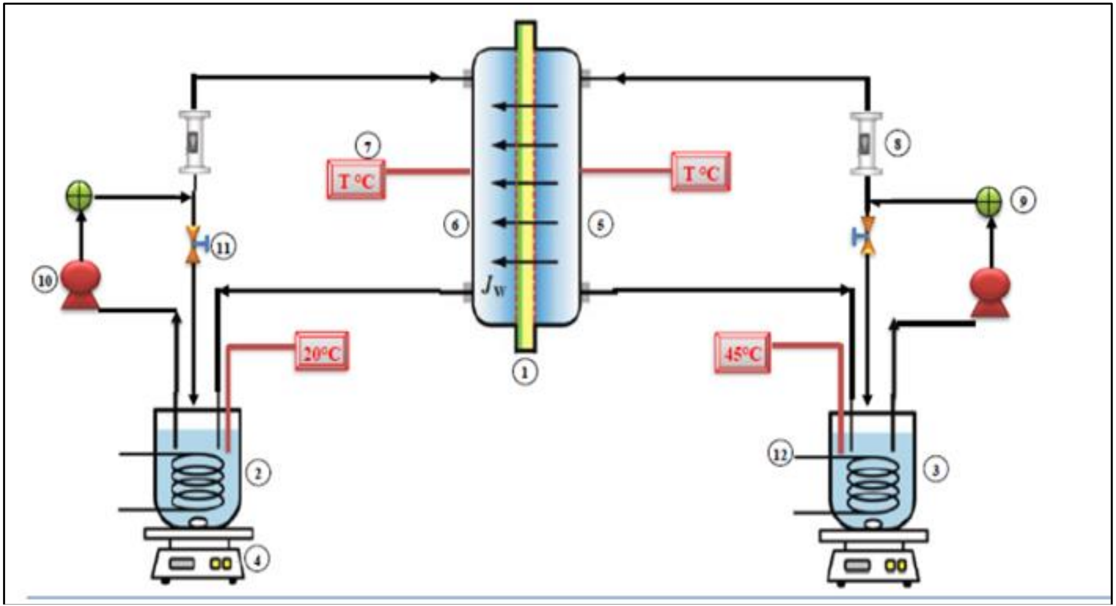
Water transfer through various hydrophilic and hydrophobic polymer membranes was observed under a temperature gradient and analyzed by a theory based on non-equilibrium thermodynamics. Water is transferred through hydrophilic polymer membranes from the cold side to the hot side because the transported entropy of water in the membrane is smaller than the molar entropy of water in the external free solutions. In contrast, water is transferred through hydrophobic polymer membranes from the hot side to the cold side because the transported entropy of water in the membrane is larger than the molar entropy of water in the external free solutions [9].

Experimental Setup and Procedure

Two types of solutions have been prepared to conduct experiments on the forward osmosis process (see Figure1). The first was the draw solution (NaCl – H2O), which was prepared in the glass vessels by dissolving the NaCl salt in 2 liter of tap water. The second solution was the feed solution, which is prepared in the glass vessels by dissolving organic substance, these substances were toluene, phenol, xylene, and BTX to obtain different concentrations of one organics substances in 2 liter of tap water.

Draw solution was pumped to one side of the membrane, and feed solution (organic solution) was pumped to the other side of the membrane by diaphragm booster pumps. The osmosis cell was designed so that both the draw solution flow and feed solution flow tangent to the membrane in the same direction (i.e. co-current flow). To change the temperature of feed and draw solutions submersible spiral copper tube (i.e. coil) was used in the vessel. The hot or cold water was pumped through the spiral tube, the temperature of feed and draw solutions controlled by microcomputer temperature controller.

Water flux was determined by measuring of the weight difference in the draw solution or feed solution per unit of time and per unit of membrane area. The concentrations of the NaCl solution, organic solution were measured by the conductivity meter and spectrophotometer respectively.



1 - FO Membrane	2 - DS reservoir	3 - FS reservoir	4 - Digital Balance	5 - FS Chamber	6 - DS Chamber
7 - Temperature Control	8 - Flow Meter	9 - Pressure Gauge	10 - Diaphragm Pump	11 - Valve	12 - Spiral tube Heater or Cooler

Fig. 1, (a) Schematic Diagram

Fig. 1, (b) Experimental Picture of Osmosis Process System

Results and Discussion

The experiments conducted in the presence of temperature difference at various types of feed solution and membranes explained the mechanisms of temperature effect on water transport across the membrane. Figures 2 to 9 show the effect of operating temperature of feed and draw solutions on water flux for different organic materials (toluene, phenol, BTX, and xylene) as feed solutions. These figures indicate that the water flux across the CTA membrane increasing when the operating temperature for DS and FS increased. The increase of the water fluxes with the rise of feed and draw solutions temperatures can be explained by several factors: fluid viscosity, concentration polarization, water permeability, mass transfer coefficient, heat transfer coefficient, and solute resistivity of membrane.

The increase of DS temperature in the range 18 - 45 °C (FS temperature constant at 45 °C) resulted in the net increase of water flux of 34.5 % in the case of toluene as feed solution, 58.8 % (phenol FS), 21.3 % (BTX FS) and 38.9 % (xylene FS). The temperature elevation in DS side from 18 to 45 °C led to an increase in DS osmotic pressure by 6.9 % as calculated from van’t Hoff law.

The increase of osmotic pressure (i.e. the driving force for water flux) due to temperature elevation in DS side, it is one of the responsible factors for such enhancement in water flux. On the other hand, the increase of DS temperature from 18 – 45 °C increased the draw solute diffusivity and water molecular diffusion coefficient, and decreased viscosity of draw solution. While, the increase in FS temperature in the range of 18 – 45 °C (DS temperature = 45 °C) was shown to produce a much more noteworthy water flux increase by 135.8 % (toluene FS), 145 % (phenol FS), 88.5 % (BTX FS) and 81.2 % (xylene FS). Increasing FS temperature vessel from 18 to 45 °C led to decrease of FS kinematic viscosity from 9.6843 x 10-7 to 6.2945 x 10-7 m2/s. In other words, the percentage of decrease in kinematic viscosity is equal to 35.1%, which corresponded to an increase of diffusivity from 1.526 x 10-9 to 2.4532 x 10-9 m2/s (i.e. 60.69 %). This behavior is in agreement with [10].

Therefore, if the temperature of DS was constant and increase in the temperature of the FS occurred from 18 to 45 °C, the water flux was more than if the DS temperature was increased from 18 to 45 °C at constant FS temperature.

This was because in the osmosis cell the feed solution was against the active layer of the membrane and the pure water transferred from organic solution (FS) to sodium chloride solution (DS). The change in the FS temperature affected the physical properties of feed solution, and these properties have a positive impact on the water flux through membrane.

The figures 10 to 13 show the effect of temperature in the feed vessel (TD and TF) and the temperature across both sides of the membrane (TDc and TFc) on water flux for different feed solution. The influence of the difference in temperature on the water flux was not the difference in temperature between the draw and the feed solution in the vessels, but the real difference in temperature for thermo osmosis process was on both sides of the membrane in the cell. The temperature in the feed vessel was different from the temperature in the cell (across the membrane). This depends on the temperature on the other side of membrane and recirculation the FS and DS between vessel and osmosis cell. Therefore, sometimes the temperatures in the cell caused higher or lower than the vessel temperature. In these figures, higher water flux was obtained when the feed - draw temperature is equal to 45 – 45 °C for different organic materials and at constant time (t = 3 h). While, lower water flux was acquired when the feed - draw temperature is equal to 18 – 18 °C.

Figures 14 and 15 show the effect of the organic materials types on the flux for CTA membrane. Figure 14 show the difference in water flux which was slightly for four organic materials (toluene, phenol, BTX, and xylene) when they used as feed solutions. This is due to the little difference in the molecular weights, in other words, nearly the same osmotic pressure of feed solution for these substances. At the same conditions, toluene has a higher flux of the other organics component, the order of the water flux was toluene > phenol > BTX> xylene. This behavior can be explained by theories of osmosis and the mechanisms for solute rejection [11] and [12]. In this research, the study of different types of membranes (CTA, CA, and TFC) to illustrate the effect of operating temperature on both sides of the membrane in the thermo osmosis process. The effect of temperature on water flux was the same behavior in the three osmosis membranes which used in the FO process. Figures 16 and 17 show the water flux with time and draw – feed temperature respectively for different membranes. Obviously, the CTA membrane has the highest water flux than CA and TFC membranes. The majority of common TFC reverse osmosis membranes are typically composed of three layers (ultrathin top, inter-support, and a thicker).

These layers are necessary for mechanical strength in high hydraulic pressure, but it considerably reduces flux based on internal concentration polarization in FO cell, which operating at very low hydraulic pressure. While, support layer in cellulose triacetate (CTA FO) membrane was allow to minimize internal concentration polarization to increase water flux. These results for CTA and TFC membranes are consistent with [13].

In the thermo osmosis process when the organic solution faces the active layer of the membrane and NaCl – H2O solution facing the support layer of the membrane, the flux decreased with operating time. The value of flux is decreased especially during two hour.

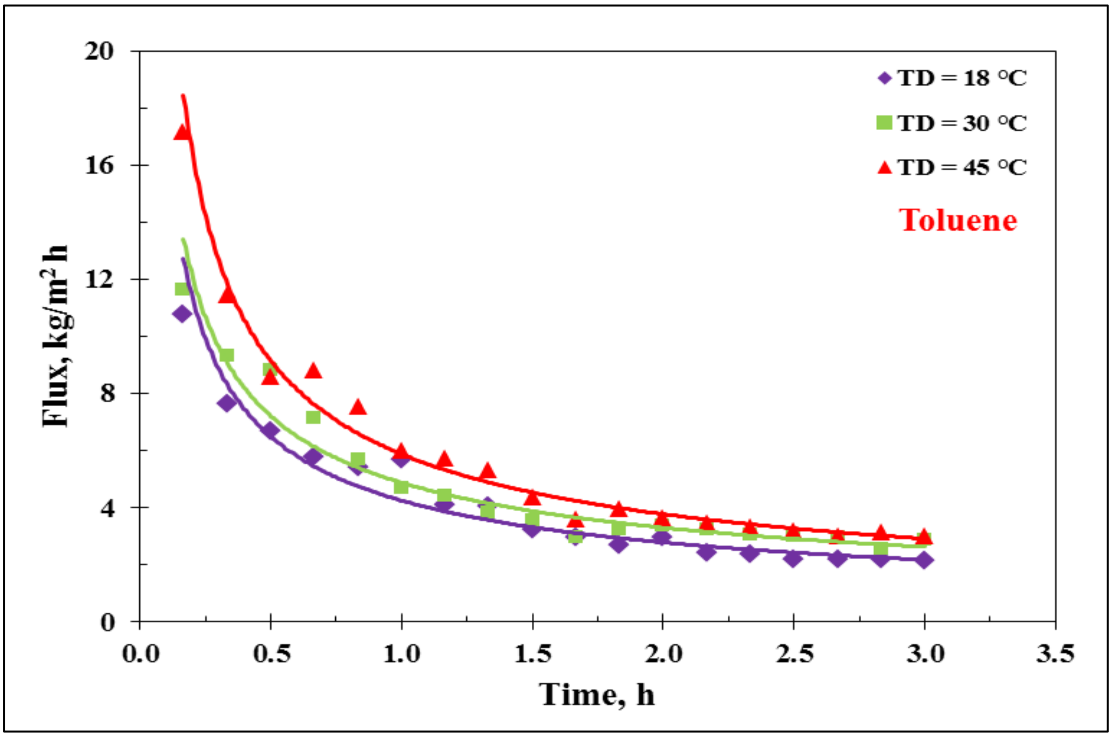


Fig. 2, Flux vs. Time at Different Draw Temperature (CTA membrane, TF = 45 ^{o} C, $Q_F = Q_D$ = 12 l/h, C_F = 50 ppm, C_D = 35 g/l and Toluene)

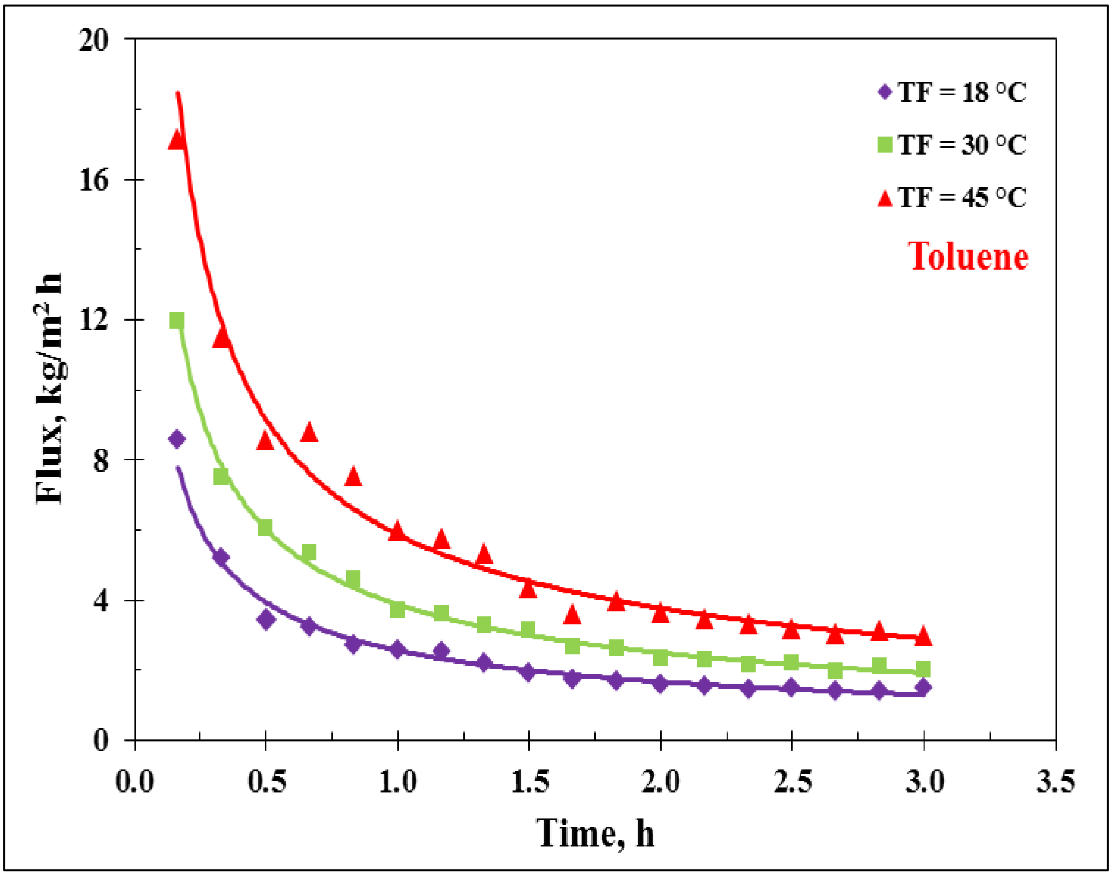


Fig. 3, Flux vs. Time at Different Feed Temperature (CTA membrane, TD = 45 ^{o} C, $Q_F = Q_D$ = 12 l/h, C_F = 50 ppm, C_D = 35 g/l and Toluene)

The water flux takes a downward slightly after the two hour of operating time.

The reason of this behavior was that the pure water transfer from the FS through the membrane to the DS, thus led to reduce the concentration of DS (i.e. reduced the osmotic pressure) which represents a driving force for permeate flux. It must be explained as follows by increasing the operating time, the organic fouling rate (concentration polarization) was increased on the surface of membrane, and led to diminish the rate of the solvent through the membranes.

The results of this declined in water flux with increased time compatible with both Jeffery et al., (2005), [14] and [15].

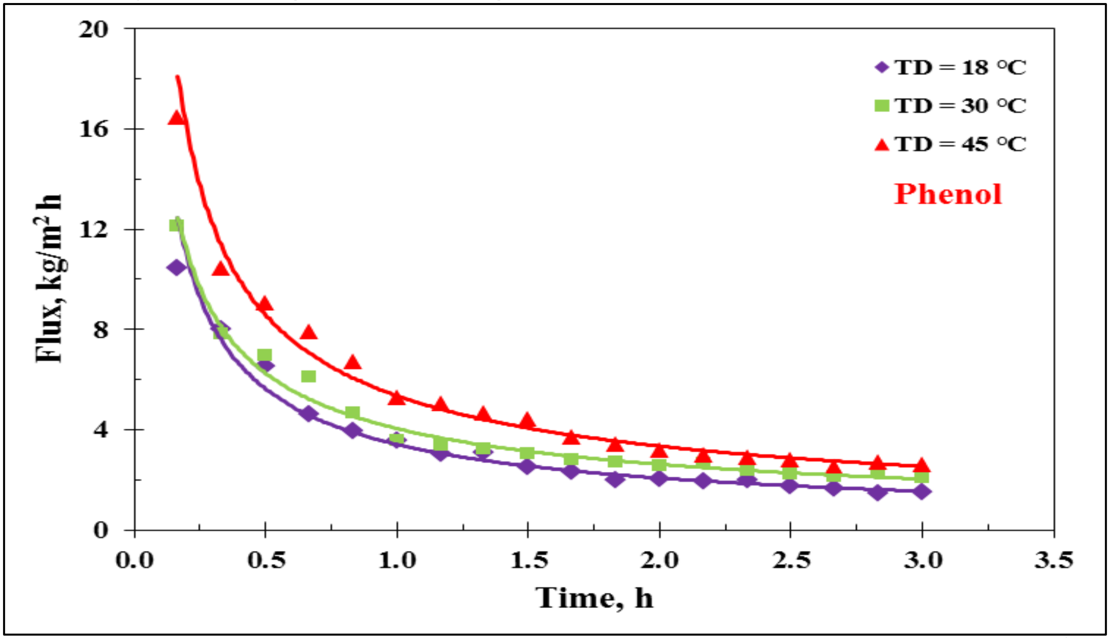


Fig. 4, Flux vs. Time at Different Draw Temperature (CTA membrane, TF = 45 ^{o} C, $Q_F = Q_D$ = 12 l/h, C_F = 50 ppm, C_D = 35 g/l and Phenol)

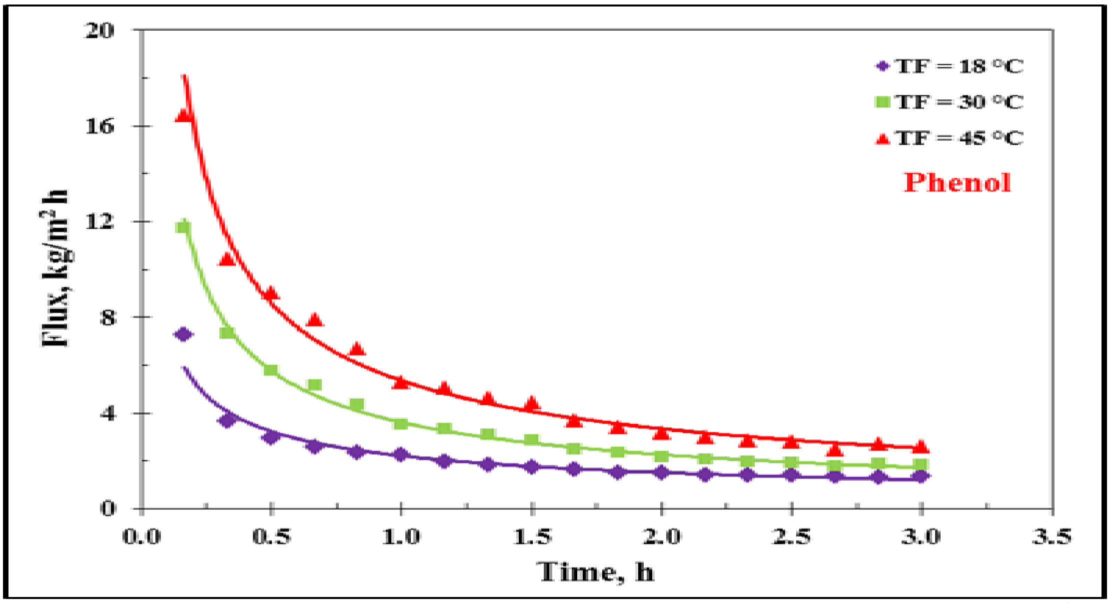


Fig. 5, Flux vs. Time at Different Feed Temperature (CTA membrane, TD = 45 ^{o} C, $Q_F = Q_D$ = 12 l/h, C_F = 50 ppm, C_D = 35 g/l and Phenol)

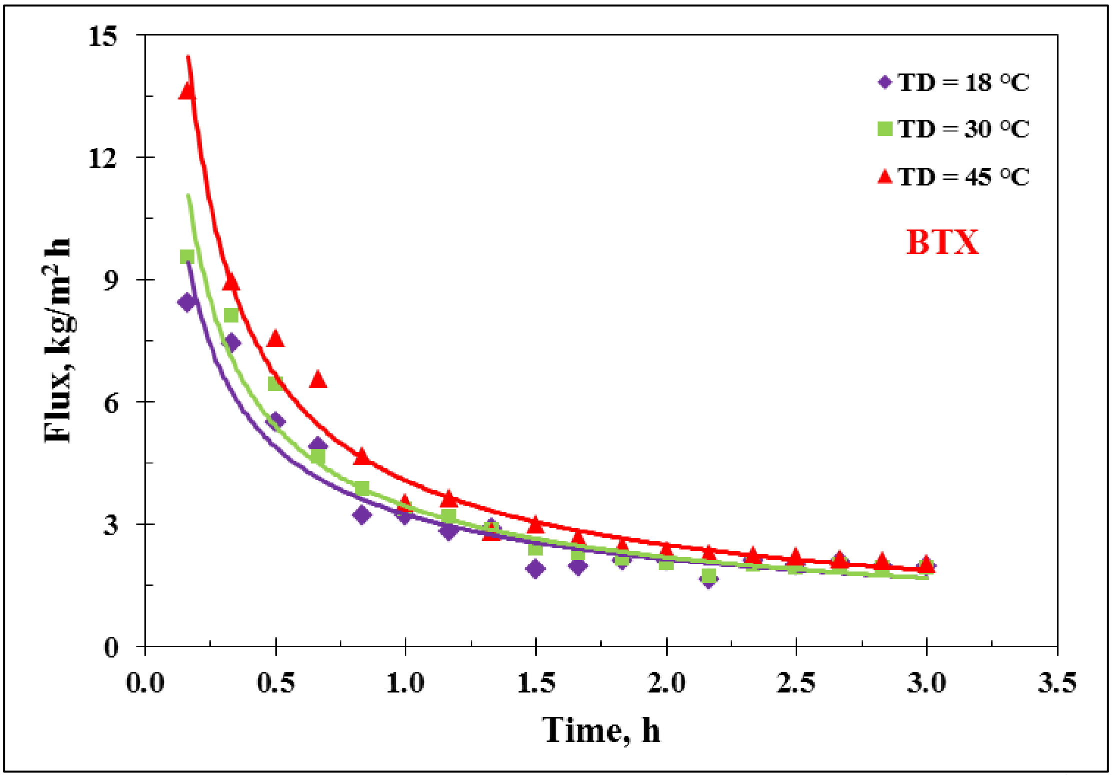


Fig. 6, Flux vs. Time at Different Draw Temperature (CTA membrane, TF = 45 ^{o} C, $Q_F = Q_D = 12$ l/h, $C_F = 50$ ppm, $C_D = 35$ g/l and BTX)

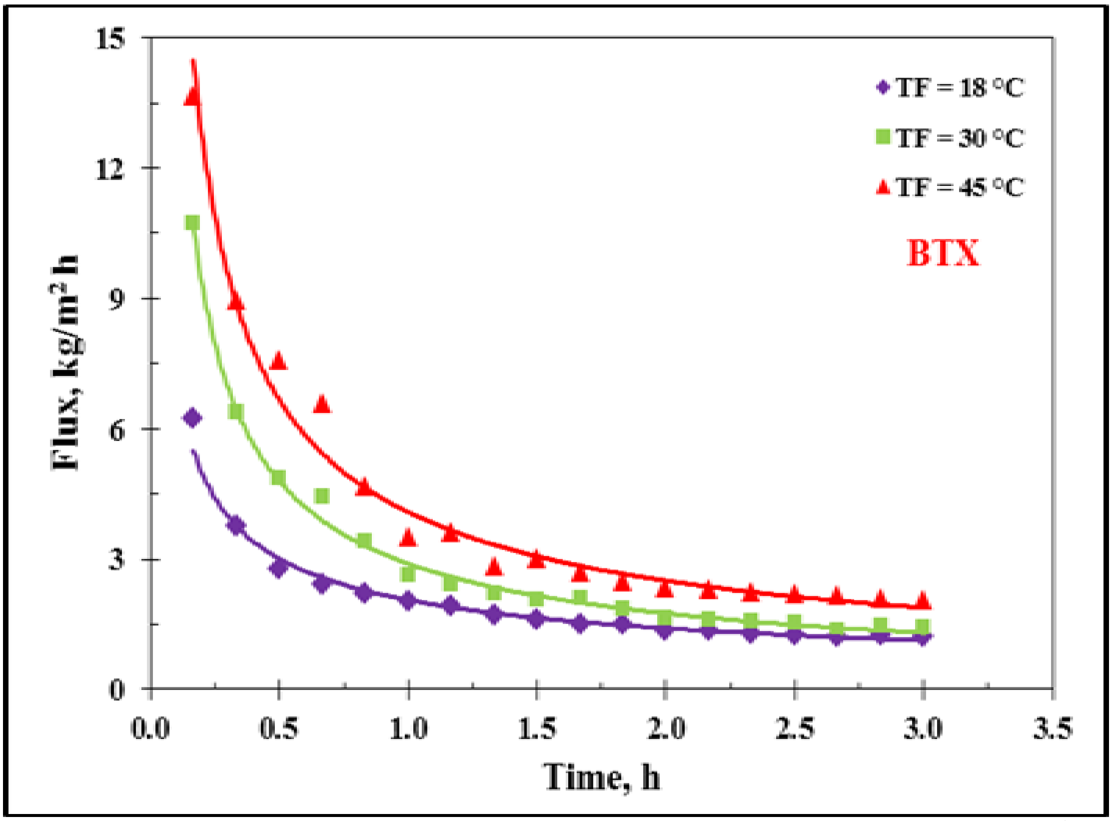


Fig. 7, Flux vs. Time at Different Feed Temperature (CTA membrane, TD = 45 ^{o} C, $Q_F = Q_D = 12$ l/h, $C_F = 50$ ppm, $C_D = 35$ g/l and BTX)

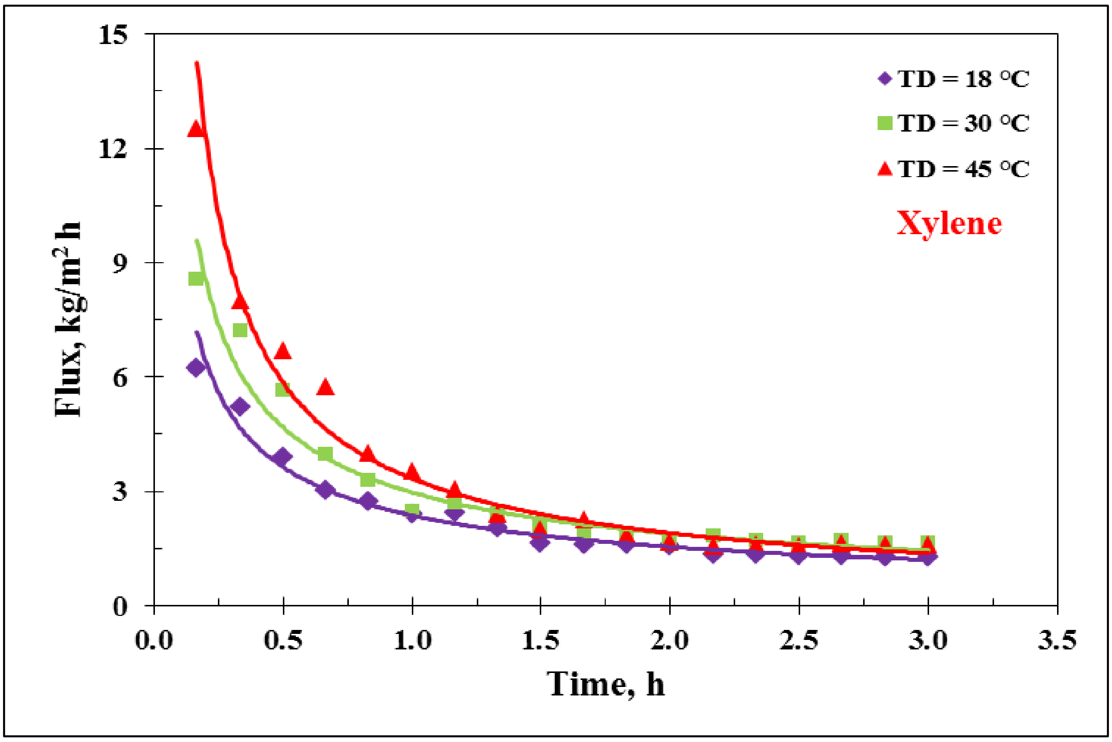


Fig. 8, Flux vs. Time at Different Draw Temperature (CTA membrane, TF = 45 °C, $Q_F = Q_D = 12$ l/h, $C_F = 50$ ppm, $C_D = 35$ g/l and Xylene)

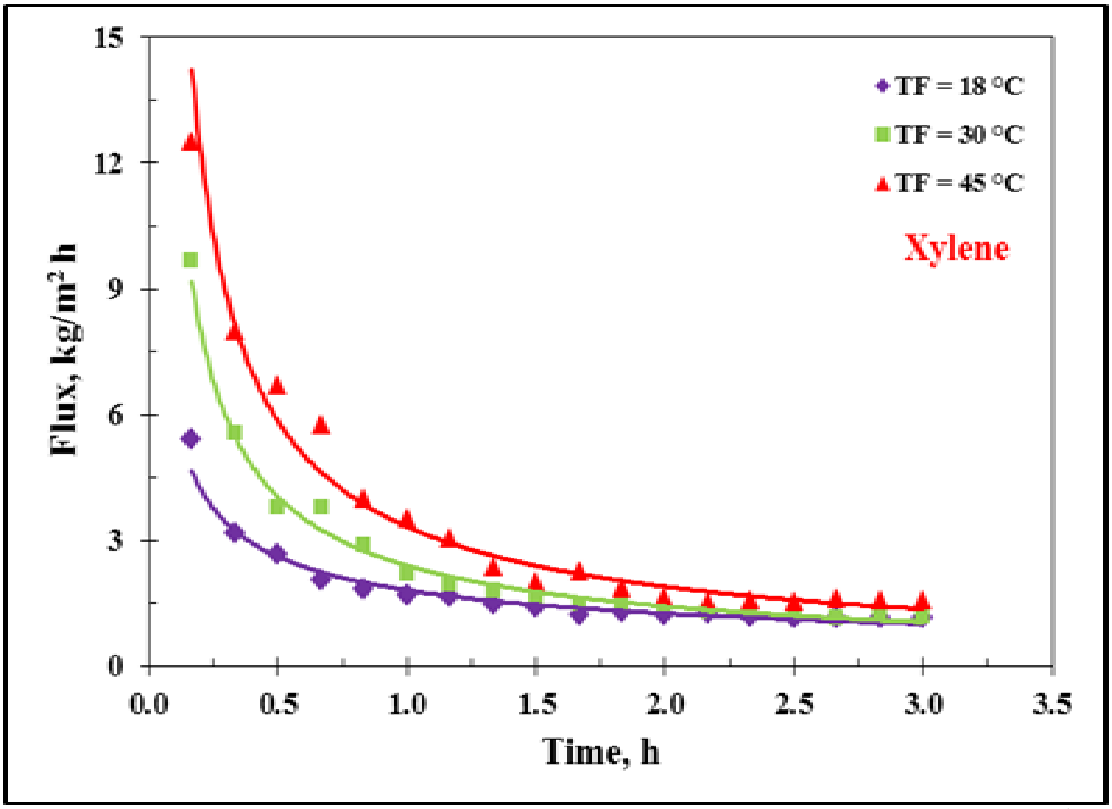


Fig. 9, Flux vs. Time at Different Feed Temperature (CTA membrane, TD = 45 °C, $Q_F = Q_D = 12$ l/h, $C_F = 50$ppm, $C_D = 35$ g/l and Xylene)

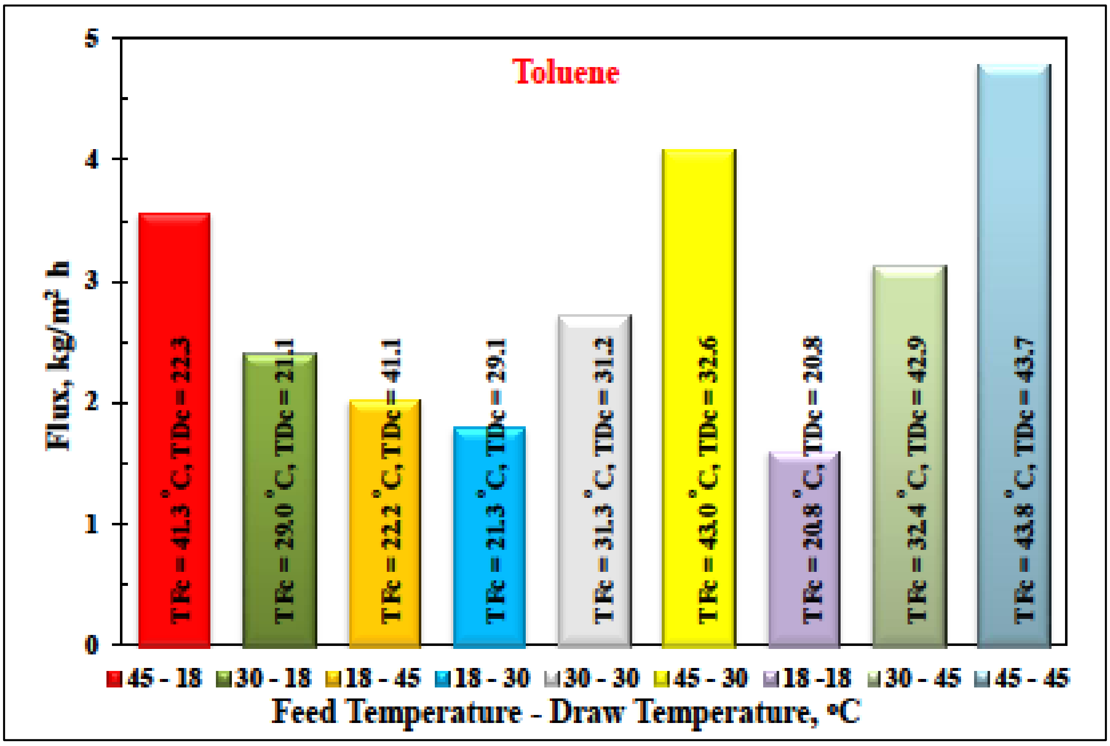


Fig. 10, Flux vs. Different Feed - Draw Temperature (CTA membrane, $Q_F = Q_D = 12$ l/h, $C_F = 50$ ppm, $C_D = 35$ g/l and Toluene)

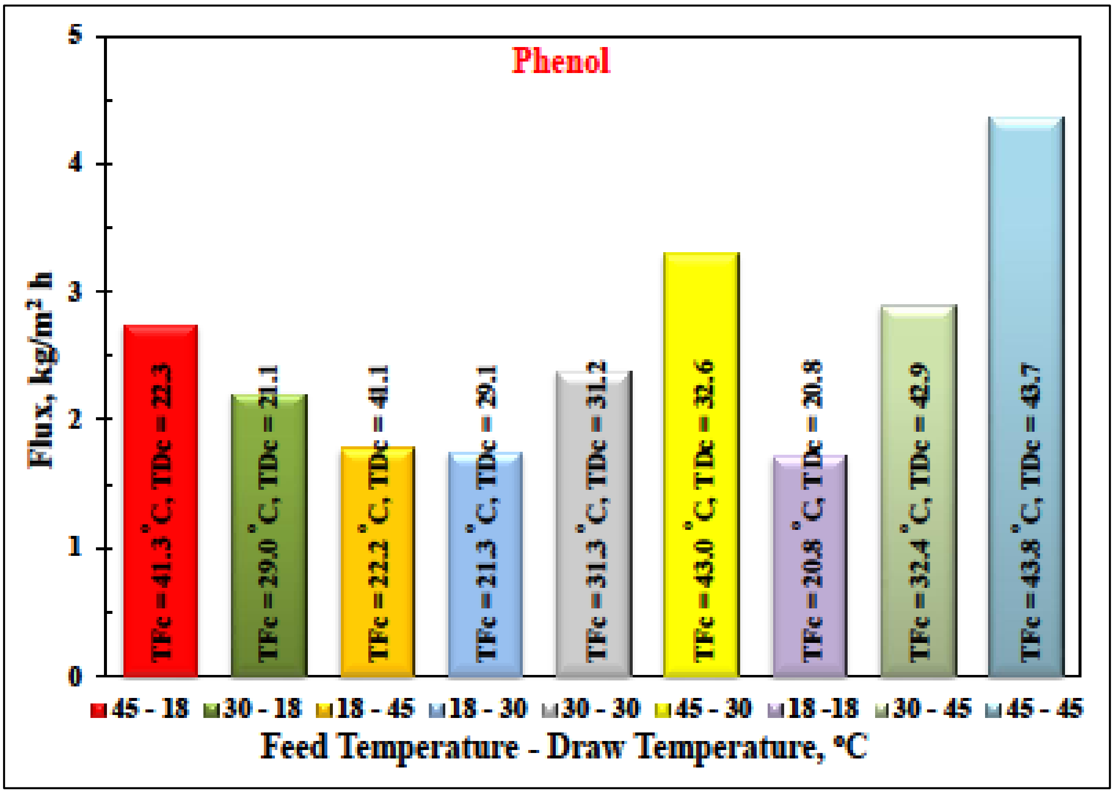


Fig. 11, Flux vs. Different Feed - Draw Temperature (CTA membrane, $Q_F = Q_D = 12$ l/h, $C_F = 50$ ppm, $C_D = 35$ g/l and Phenol)

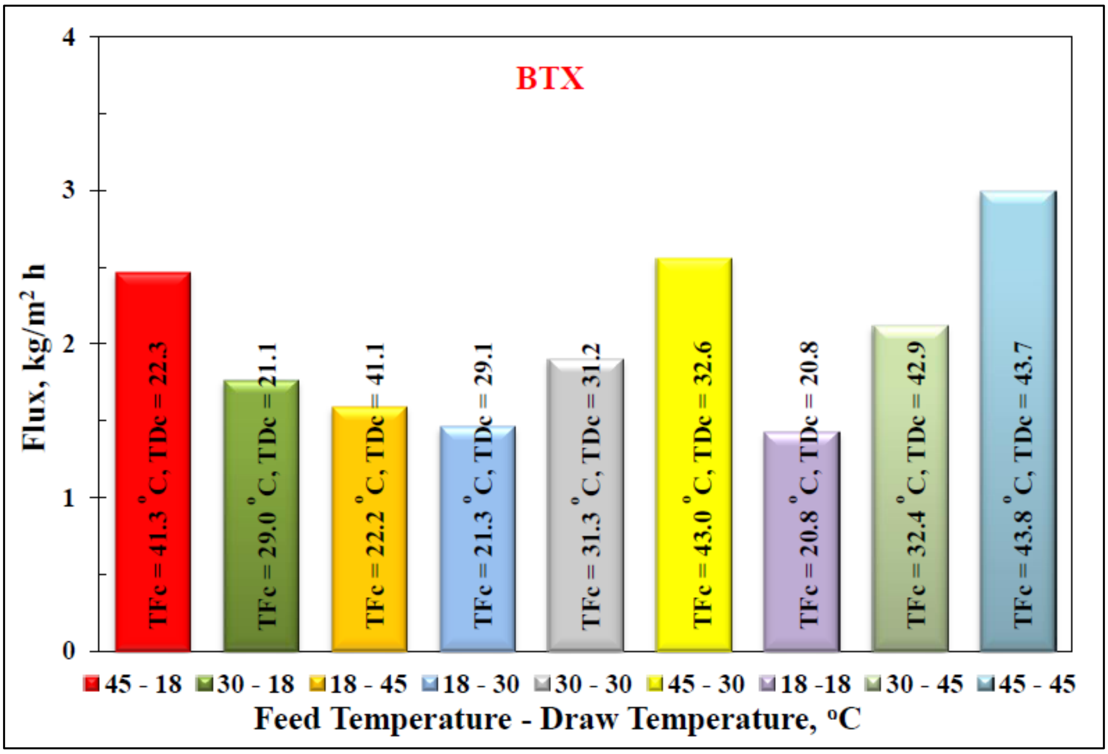


Fig. 12, Flux vs. Different Feed - Draw Temperature (CTA membrane, Q_F = Q_D = 12 l/h, C_F = 50 ppm, C_D = 35 g/l and BTX)

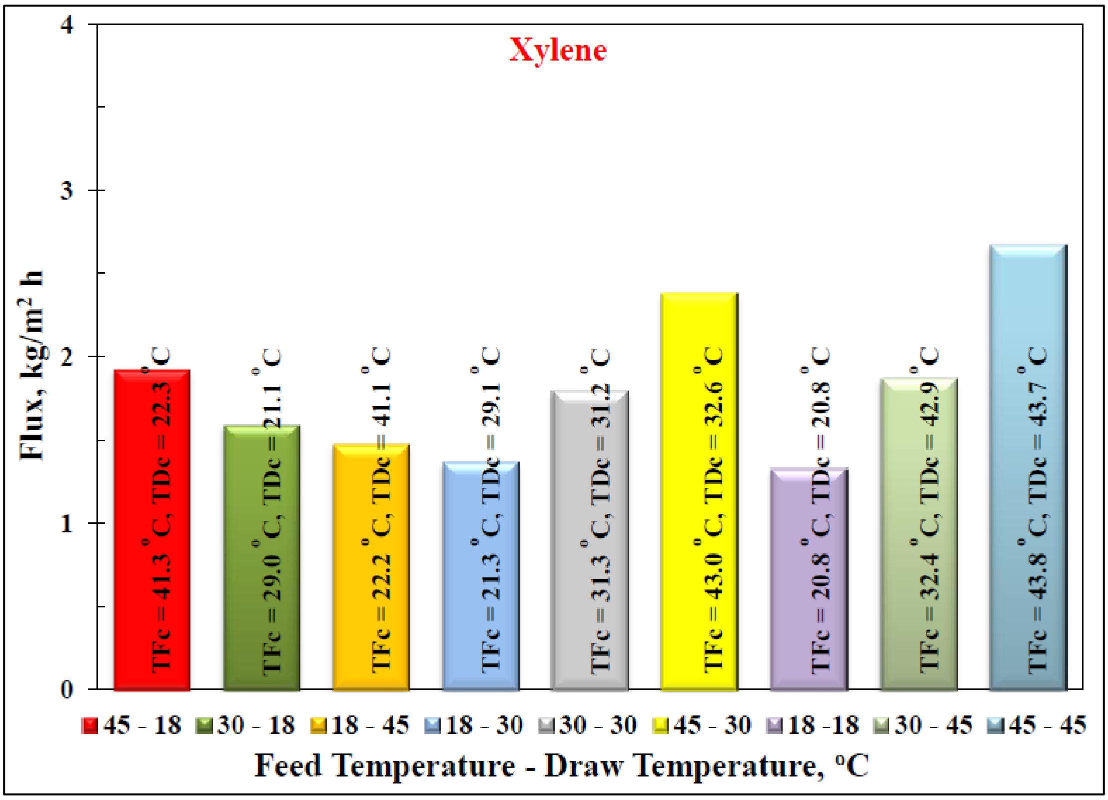


Fig. 13, Flux vs. Different Feed - Draw Temperature (CTA membrane, Q_F = Q_D = 12 l/h, C_F = 50 ppm, C_D = 35 g/l and Xylene)

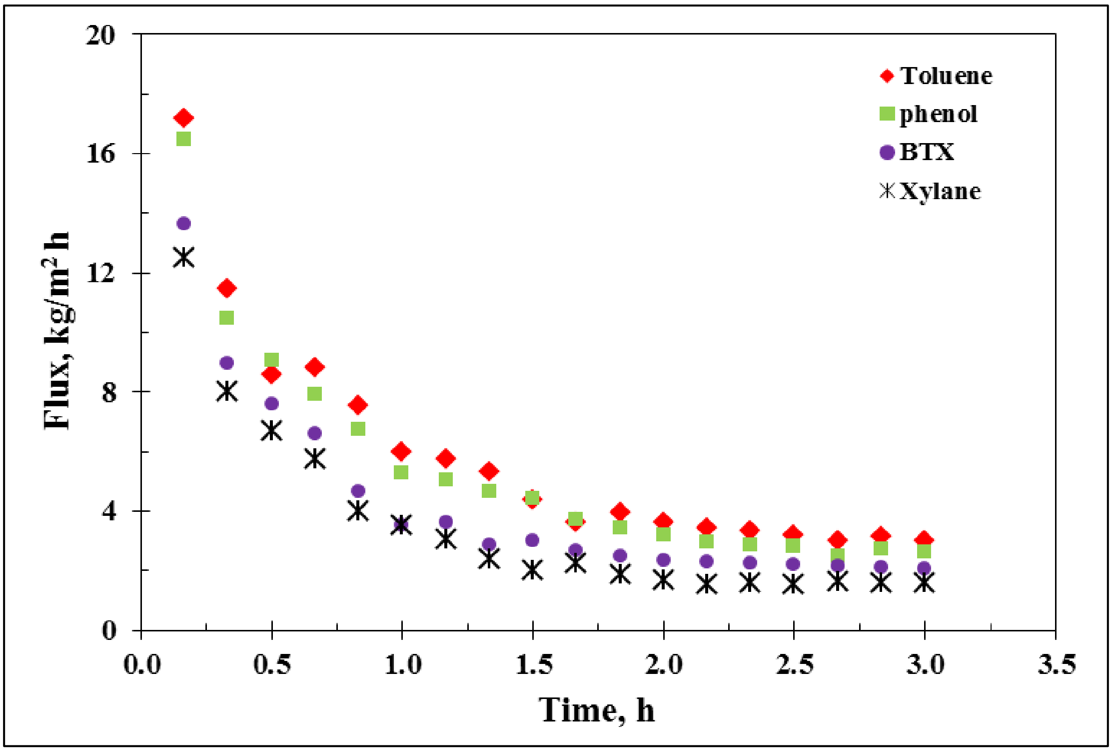


Fig. 14, Flux vs. Time at Different Types of Organic (CTA membrane, TD = 45 ^{o} C, TF = 45 ^{o} C, $Q_F = Q_D$ = 12 l/h, C_F = 50 ppm and C_D = 35 g/l)

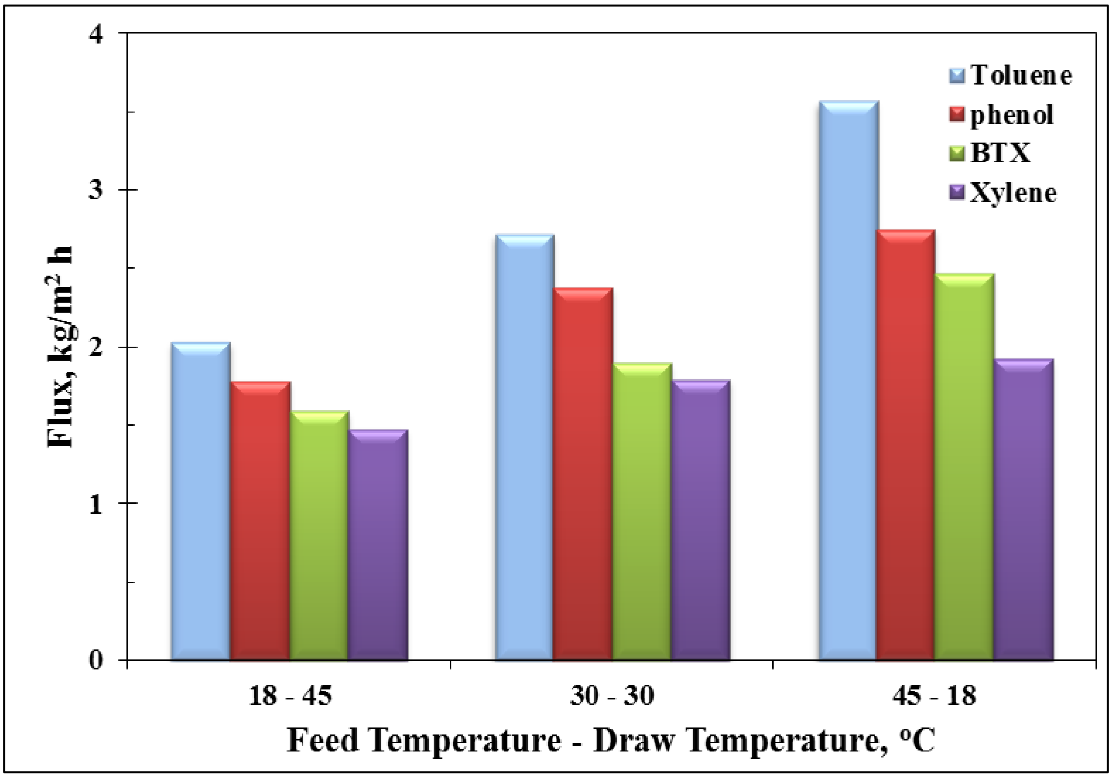


Fig. 15, Flux vs. Different Feed - Draw Temperature (CTA membrane, $Q_F = Q_D$ = 12 l/h, C_F = 50 ppm and C_D = 35 g/l)

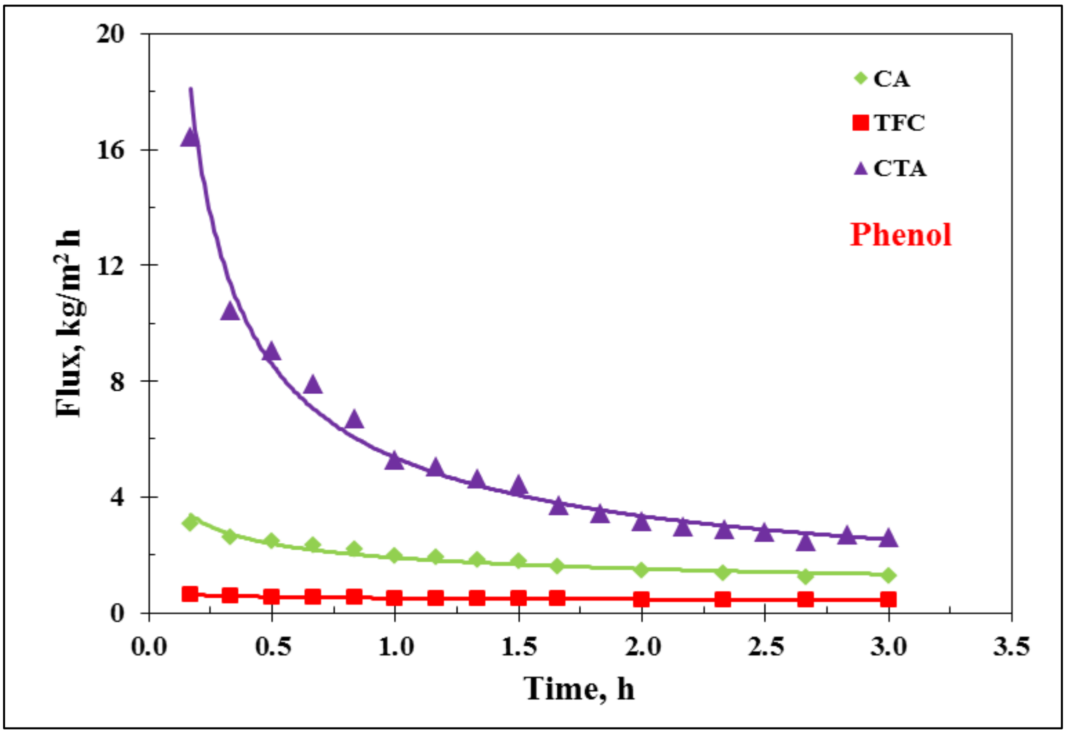


Fig. 16, Flux vs. Time at Different Types of Membranes (TF = 45°C and TD = 45°C, $Q_F = Q_D$ = 12 l/h, C_F = 50 ppm, C_D = 35 g/l and Phenol)

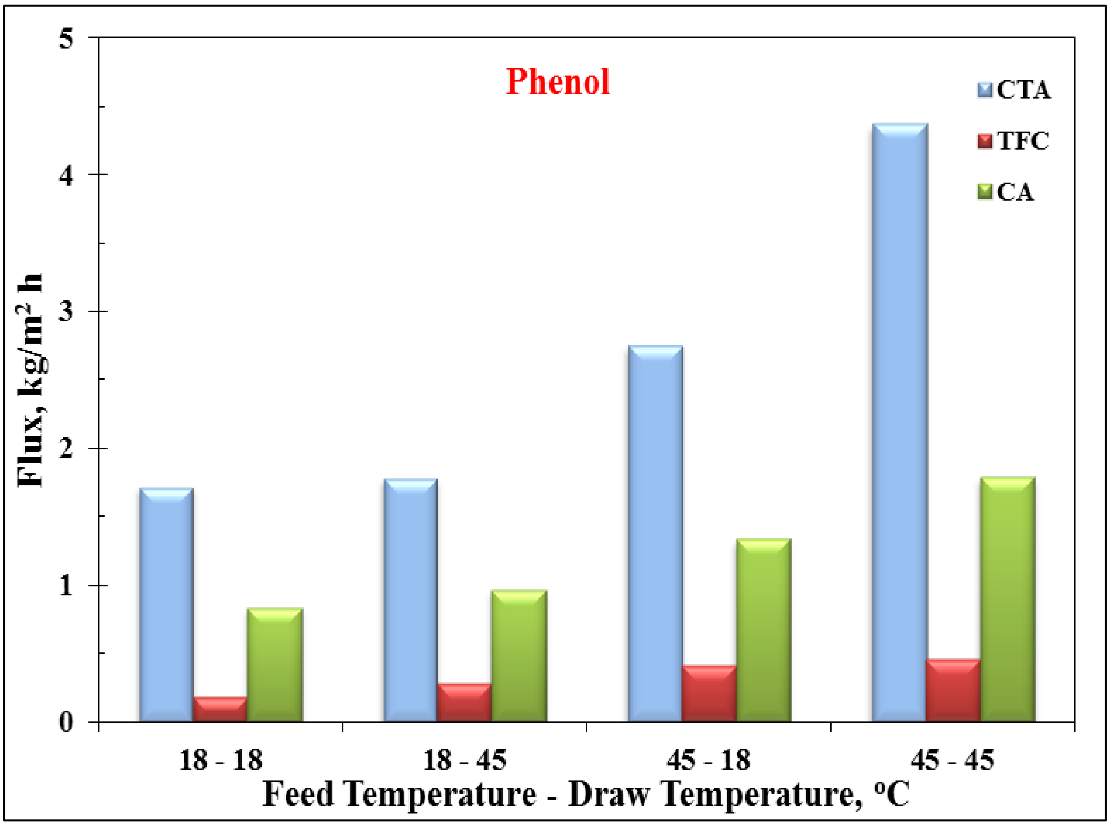


Fig. 17, flux vs. different feed - draw temperature at different types of membranes. ($Q_F = Q_D$ = 12 l/h, C_F = 50 ppm, C_D = 35 g/l, time = 3 h and Phenol)

Conclusion

Thermo osmosis process can be used for recovery of water from organic solution. It may be used a suitable alternative to other processes as lower cost. The real impact of the driving force in thermo osmosis process was temperature on both side of the membrane in the cell, not in the feed vessel. The water flux produced from the osmosis cell increase by increasing the temperature of draw solutions and feed solution. The effect of feed temperature on water flux was higher than of draw temperature. For different types of membranes with the same conditions, the order of water flux was given by CTA > CA > TFC. The averages ration increase in water flux for cellulose triacetate is about 1: 2.1 than cellulose acetate and 1: 5.9 than thin film composite. CTA, CA and TFC membranes may be considered suitable for the thermo osmosis process. The difference in flux through the membrane was slightly with different types of organic materials (phenol, toluene, xylene and BTX).

The difference in flux through the membrane was slightly with different types of organic materials. The water flux decreases with operating time due to the decrease in driving force. The water flux in the osmosis cell increased with increasing concentration of draw solutions (NaCl – H_2O) and decreasing concentration of feed solution (organic solution). While, the flux increases by increasing the flow rate of feed solution and decreases by increasing the flow rate of draw solutions. The recovery percentage of water increased with increasing operating time and temperature of osmosis cell.

References

1- Armour, M. A., 1991. Hazardous Laboratory Chemicals Disposal Guide. CRC Press, Boca Raton.

2- Bouchelta, C., Medjram, Md. S., Bertrand, O. and Bellat, J. P., 2008. Preparation and characterization of activated carbon from date stones by physical activation with steam. Journal of Analytical and Applied Pyrolysis. 82, 70-77.

3- Edzwald, J. K., 1999. Water Quality and Treatment A handbook on Drinking Water sixth Edition

4- Jinxing, Ma and Zhiwei, W., 2013. Organic matter recovery from municipal wastewater by using dynamic membrane separation process. Chemical Engineering Journal. 219, 190–199.

5- Rautenbach A. R. and Grqschl A., 1990. Separation potential of NF membranes. Desalination. 77, 73–84.

6- Gebreyohannes, A. Y., Curcio, E., Poerio, T. and Mazzei R., 2015. Treatment of Olive Mill Wastewater by Forward Osmosis. Separation and Purification Technology.147, 292–302.

7- Soowhan K. and Mench M.M., 2009. Investigation of temperature-driven water transport in polymer electrolyte fuel cell: Thermo-osmosis in membranes Journal of Membrane Science. 328, 113–120

8- Villaluenga J.P.G, Seoane B., Barragán V.M. and Ruiz-Bauzá C., 2006. Thermo-osmosis of mixtures of water and methanol through a Nafion membrane. Journal of Membrane Science, 274, 116–122.

9- Simonič M. and Lobnik A., 2011. The efficiency of a hybrid flocculation/UF process for a real dye-house effluent using hydrophilic and hydrophobic membranes. Desalination. 271, 219–224

10- McCutcheon J. R. and Elimelech M., 2006. Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis.

Journal of Membrane Science. 284, 237–247.

11- Slein M.W., Sansone E.B., 1980. Degradation of Chemical Carcinogens, Van Nostrand Reinhold, New York.

12- Zarrin E., Mahmoud E. and Hosseini M. S., 2011. Optimization of a novel method for determination of benzene, toluene, ethylbenzene, and xylenes in hair and waste water samples by carbon nanotubes reinforced sol–gel based hollow fiber solid phase microextraction and gas chromatography using factorial experimental design, Journal of Chromatography A. 1218, 3400–3406

13- Muhammad Q., 2013. Performance of forward osmosis using various membranes. M.Sc. thesis, American University of Sharjah.

14- Ge, Z. and He, Z., 2012. Effect of draw solutions and membrane conditions on electricity generation and water flux in osmotic microbial fuel cells. Bioresource Technology. 109, 70-76.

15- Abdulhakeem, A. A., James, A. M., Stuart, J. K., William, E. P., Long, D. N. and Menachem, E., 2013. Removal of trace organic contaminants by the forward osmosis process. Separation and Purification Technology.103, 258–266.