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OILY WASTEWATER TREATMENT USING POLYTETRAFLUOROETHYLENE (PTFE) HYDROPHOBIC MEMBRANES

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ABSTRACT

In this paper, effect of influential factors on separation of oil from oily wastewater was investigated. PTFE hydrophobic membranes with 0.45 μm pore size were used to run the experiments. Gas oil and distilled water were selected as dispersed and continuous phases, respectively. Taguchi experimental design was used to plan a minimum number of experiments. A L_9 orthogonal array (Four factors in three levels) was employed to evaluate effect of feed characteristics (gas oil content in feed), operating pressure, operating temperature and feed flow rate on the response (permeate flux and water content in permeate). Preliminary experiments were carried out to identify level of parameters. It was found that increasing flow rate to its upper limit causes permeate flux to increase and it is the most effective parameter on the response. Fouling was also found to be very effective on the response and must be controlled. It was also found that, contrary to other microfiltration processes, temperature is a very effective parameter on the response.

Keywords: oily wastewater, microfiltration, Taguchi experimental design, hydrophobic membrane.

1. INTRODUCTION

Emulsions of water, oil and solids are formed in a number of industries where immiscible organic and aqueous phases are in contact with each other [1]. A large amount of liquid waste in forms of oil in water (o/w) or water in oil (w/o) emulsions is generated in process industries such as petrochemical, metallurgical and transportational industries. Only a few papers describe separation of emulsions [2]. Demulsification becomes one of the most critical processes associated with the industries. Thus, separation of oil from o/w emulsions is important in industries involving treating liquid waste such as food processing, metal fabricating and plating, mining and textile [3].

The o/w emulsion serves the purposes of lubrication, cooling, surface cleaning and corrosion prevention in manufacturing processes. Depending on specific applications, the oil emulsion can consist of up to 97% water, the rest being a complex aqueous mixture which comprises different kinds of oils (mineral, animal, vegetable and synthetic), alcohols, sequestrants and surfactants. Even for the same application, proprietary composition of the complex aqueous mixture can vary widely among different suppliers. The temperature of o/w emulsion is usually maintained in the range between 30°C to 90°C in the process because of heat removal from the metal surfaces. Hence, some organic components of the complex aqueous mixture can become degraded after a certain period of use. Metal ions and other inorganic contaminants can enter the o/w emulsion during the manufacturing process. Moreover, a serious anaerobic biological growth often occurs in the emulsion. Therefore, the waste o/w emulsion needs to be regularly replaced several times every year. A large amount of the waste o/w emulsion is thus generated in this fashion worldwide every year by many industries [4].

Typical demulsification methods are addition of demulsifying agents; pH adjustment; gravity or centrifugal settling; filter coalescers; heater treaters; electrostatic coalescers and membrane processes. There are advantages and disadvantages to each of these demulsification techniques. In processes using additives, there are additional problems of additive disposal and recovered oil or water contamination. Adjustment of pH can sometimes be used to break some emulsions, but it has some limitations [1]. A standard method for treatment of emulsions is chemical demulsification followed by gravity settling. This process requires a variety of chemicals and the recovered water phase needs secondary purification. This therefore entails additional energy requirements and hence higher cost [5]. Gravity settling, centrifuging or heating can also break some emulsions. Centrifuges are efficient for some emulsions, but are capital intensive and extensive to run and maintain. Electric field methods are used to demulsify w/o emulsions and electrostatic coalescers are widely used in petroleum industry. Extremely high voltages (10 – 20 kV) are required to cause droplet coalescence.

Membrane technology can be an inexpensive and efficient alternative method for separation of emulsions [2]. Development of membrane technologies has most recently embodied applications in processing of emulsions. Several studies were reported that crossflow membrane microfiltration (CFMF) and ultrafiltration (CFUF) are effective processes in concentrating o/w emulsions [5 – 10].

Membrane modules for demulsification are compact and can be run continuously. Advantages of splitting emulsions by membrane processes in contrast to other processes are:

- Low energy cost, especially with microfiltration membranes that operate at low pressures
- No moving parts
- No degradation due to heating
- No extra safety considerations as in high voltage demulsification [1].

To optimize design of an existing process, it is necessary to identify which factors have the greatest influence and which values produce the most consistent performance. Experimenting with design variables –one at a time or by trial and error –until a first feasible design is found is a common approach to process optimization. However, this approach can lead to a very long and expensive time span for completing the design process. A technique for laying out the experiments when multiple factors are involved is popularly known as the factorial design of experiments. This method helps researchers to determine possible combinations of factors and to identify the best combination. Since it is extremely costly to run a number of experiments to test all combinations, application of a full factorial design of experiments is restricted when many factors and levels are studied. A commonly applied statistical method, Taguchi experimental design and analysis of variance (ANOVA), can be used to analyze results of the experiments on the response and to determine how much variation quality influencing factors contribute. In this research, to achieve low content of water in permeate and high permeate flux, effects of three operating parameters (pressure, temperature, and feed flow rate or residence time) in a microfiltration cell were studied using Taguchi experimental design [11 – 16].

2. MATERIALS AND METHODS

2.1. Membrane and module

PTFE membranes with 0.45 μm pore size manufactured by Schleicher & Schull were tested for separation and demulsification of o/w emulsions. A crossflow membrane module made from Teflon was used in the experiments. Effective area of the membrane in the module was 11.34 cm^2. To be sure entirely contact of the emulsion with the membrane surface and also better mixing of the emulsion, three exhausts were designed and fabricated as shown in Figure 1 for retentate flow.

2.2. Emulsions and emulsifier

The o/w emulsions were made using gas oil and distilled water as dispersed and continuous phases, respectively. Since stirring a mixture of small amount of oil in water creates an emulsion which is stable for a long time, emulsifier was not used. The mixture of oil and distilled water was blended for 10 min using a Pitched Curved Blade blender (with 6 fins).

2.3. Experimental setup and procedure

Separation of o/w emulsions was carried out using an experimental setup as shown in Figure 2. The setup consists of a feed tank equipped with cooling water coil, a centrifugal pump (Pentax, type PM 80, 2800 rpm, 0.77 kW), a self-designed MF cell, a Fischer Porter flow meter (0 –300 l/h) and two pressure gauges. One important consideration in the setup is that the bypass flow has a significant influence in feed temperature and high bypass flow rates cause foam formation in the feed tank. The feed (emulsion) was pumped from the feed tank through the MF cell and the retentate was returned to the feed tank. The permeate side was open to the atmosphere and transmembrane pressure drop was controlled manually using a valve on the retentate side.

2.4. Analytical method

The water content of permeate flux was measured by volumetric Karl Fischer titrator TIM 550 (manufactured with Titralab, France).

3. RESULTS AND DISCUSSION

Taguchi experimental design was used to run a minimum number of experiments. According to Taguchi parameter design methodology, one experimental design should be selected for controllable factors. A L_9 orthogonal array (that accommodates four factors in three levels each in 9 runs) was employed [12]. In the present work, three factors were studied using a L_9 orthogonal array as can be seen in Table 1.

Preliminary experiments were carried out to identify feed critical conditions as well as levels of factors. Critical conditions are those at which separation exhibits the worst results. After determining these conditions, experiments were carried out to study effects of operating parameters on separation of o/w emulsions. The worst results are minimum permeate flux and maximum water content in permeate.

Since gas oil concentration in oily wastewater (the feed) is quite low, break through pressure is low and consequently, at higher pressures water passes through the membranes. Therefore, for microfiltration of oily wastewaters with hydrophobic membranes, pressure must be lower than 1 bar based on qualitative experiments. Since, gas oil and water are evaporated at high temperatures and low temperatures can not be adjusted easily, three levels of 30, 40 and 50 °C were selected for temperature. Three levels of flow rate (30, 40 and 50 l/h) were selected based on setup limitations in controlling the flow rate. Hence, levels of the factors are as follows: Pressure (0.25, 0.5 and 0.75 bar); temperature (30, 40 and 50 °C) and flow rate (30, 40 and 50 l/h).

3.1. Effect of pressure

In Figures 3 and 4, Effect of pressure on permeate flux and water content in permeate was illustrated at different flow rates and temperatures. In these Figures the third factor is set to its moderate value. As shown in these figures, increasing pressure increases permeate flux and water content in permeate. At higher pressures, pressure, as the driving force of microfiltration process, overcomes hydrophobia property of the membrane and water droplets pass through the membrane. Regarding water content in permeate, permeate flux increases as a result of water permeation through the membrane.

3.2. Effect of temperature

Effect of temperature on permeate flux and water content in permeate at different flow rates and temperatures was depicted in Figures 5 and 6. As can be seen in these figures, increasing temperature increases permeate flux and water content in permeate. Since the permeate is mainly gas oil, its viscosity dramatically decreases with increasing temperature, and as a result, its permeation through the membrane becomes easier. This enhances permeate flux. Increasing temperature also increases water content in permeate. This phenomenon can be attributed to solubility of water in hydrocarbons, hydrophobic-hydrophilic forces in emulsions and interaction of membranes and emulsions.

Increasing temperature decreases water and oil viscosity in one hand which increases permeate flux as mentioned before and intensifies fouling and concentration polarization phenomena on the other hand which decrease permeate flux. Fouling and concentration polarization are mainly due to precipitation of the gas oil colloid particles on the membrane surface and formation of water boundary layer. However, due to the large pore sizes of the applied PTFE membranes (0.45 μm), fouling and concentration polarization phenomena seem to be negligible. Hence, no flux decline was observed at higher temperatures.

3.3. Effect of flow rate

As shown in Figures 7 and 8, increasing feed flow rate decreases water content in permeate and increases permeate flux. This can be due to the membrane fouling at lower flow rates. High feed flow rate (small residence time) causes mixing and prevents micelle accumulation on the membrane surface. Decreasing water content in permeate with increasing flow rate can also be due to accumulation of oil droplets at the membrane surface and this diminishes the effect of concentration polarization.

3.4. Optimum conditions

Since in microfiltration process, maximum permeate flux with minimum water content in permeate is sought, in order to acquire optimum conditions, economic aspects should be taken into account. In microfiltration of oily wastewater using PTFE membrane with almost large pore size, permeate flux and water content in permeate increase with increasing pressure, noticeably. Obviously, the importance of water content in permeate is less than permeate flux, in the oily wastewater treatment. Hence, considering economical aspects, moderate pressure is recommended for this type of membrane.

The same analysis can be used for selection of the optimum temperature. Increasing temperature increases permeate flux and water content in permeate. For this reason, moderate temperature (40°C) is considered as an optimum temperature.
At higher flow rates permeate flux increases while water content in permeate decreases. Therefore, optimum flow rate is found out to be the maximum onete (50 l/h).

4. CONCLUSION

In the present work, effect of operating parameters on treatment of oily wastewater was studied. Taguchi experimental design was used to plan a minimum number of experiments. Preliminary experiments were carried out to identify the levels of factors applied in a L_9 orthogonal array. PTFE hydrophobic membranes were applied in all experiments. It was found that increasing temperature, pressure and flow rate increases permeate flux. Due to the large pore size of the applied PTFE membrane, fouling was observed to be insignificant. Water content in permeate increased with temperature and pressure and decreased with flow rate. Moderate temperature and pressure and maximum flow rate was recommended to achieve an optimum separation.

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Table 1- Taguchi L_9 orthogonal array

Experiment No.	Temperature (°C)	Pressure (bar)	Flow rate (l/h)
1	30	0.25	50
2	30	0.5	40
3	30	0.75	30
4	40	0.25	40
5	40	0.5	30
6	40	0.75	50
7	50	0.25	30
8	50	0.5	50
9	50	0.75	40

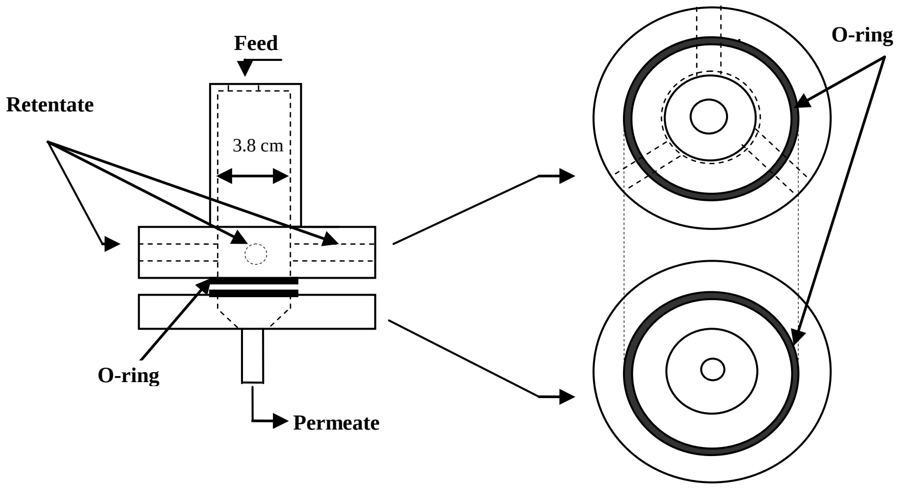

Figure 1 Membrane module

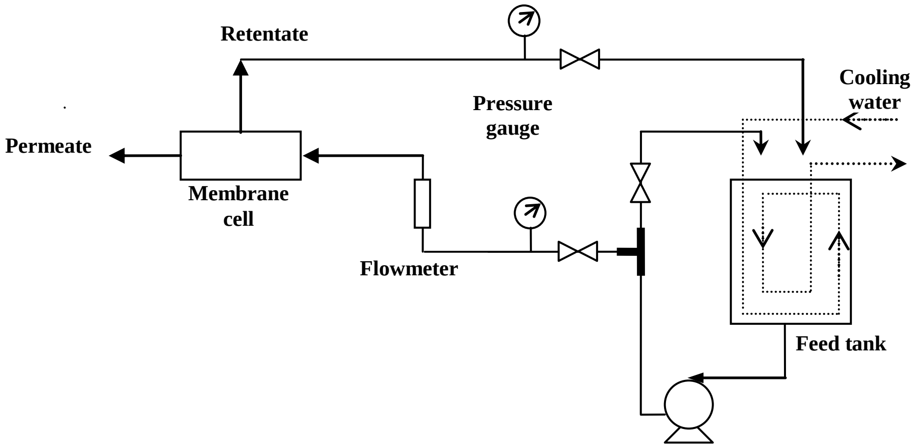

Figure 2 Schematic view of experimental setup

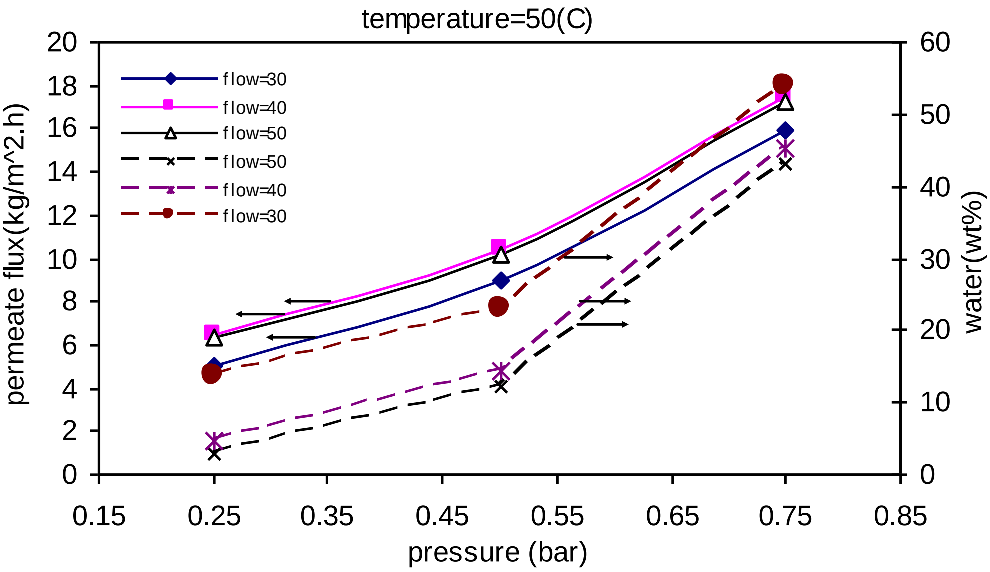

Figure 3 Effect of pressure on permeate flux and water content at different flow rates

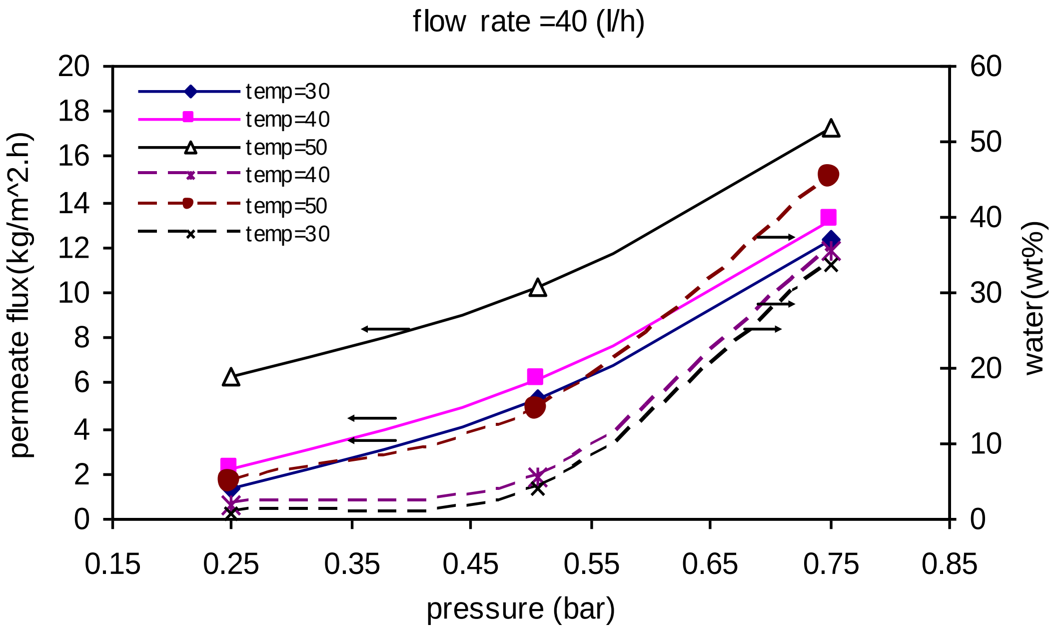

Figure 4 Effect of pressure on permeate flux and water content at different temperatures

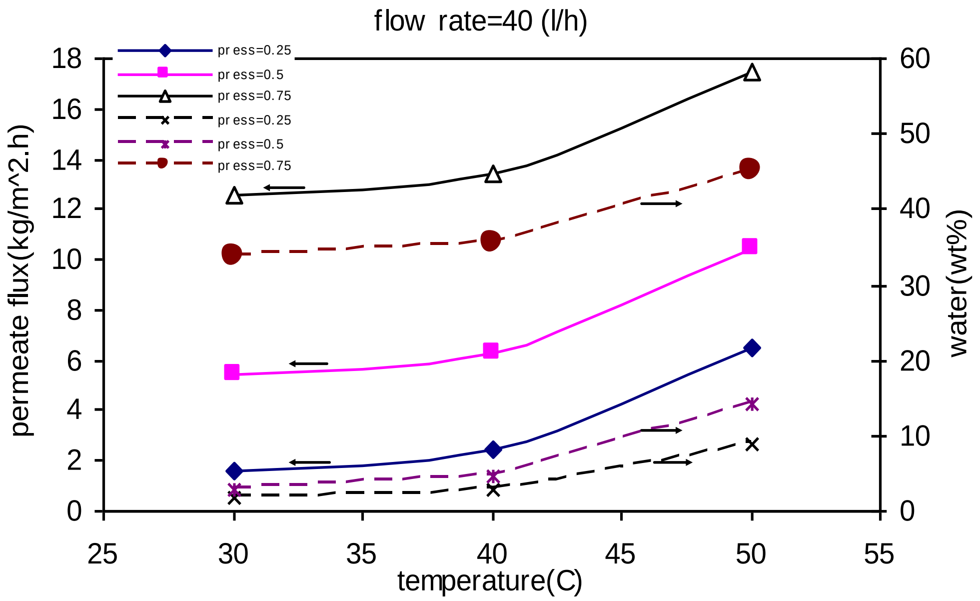

Figure 5 Effect of temperature on permeate flux and water content at different pressures

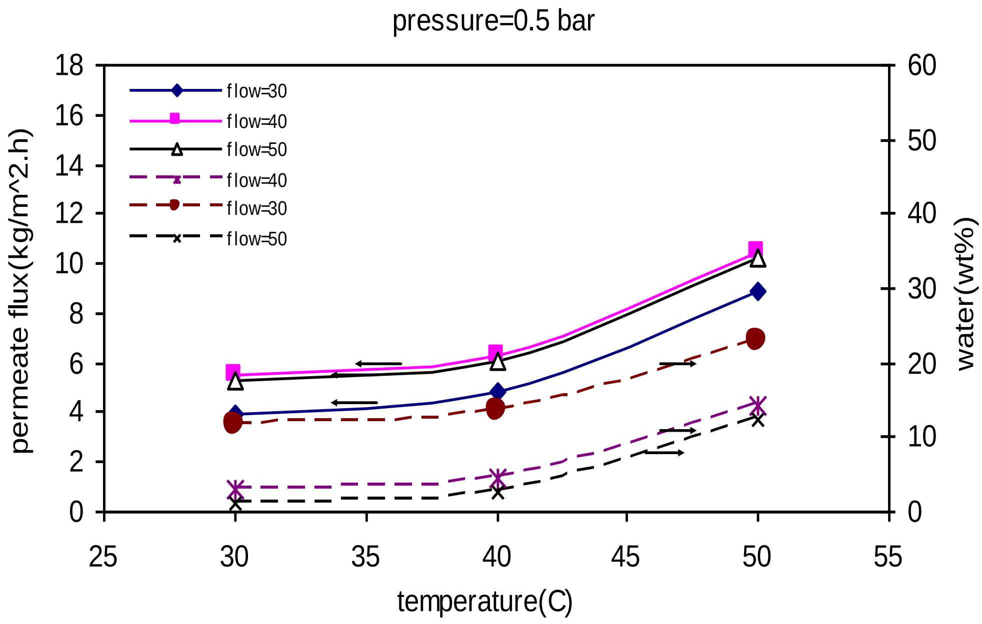

Figure 6 Effect of temperature on permeate flux and water content at different flow rates

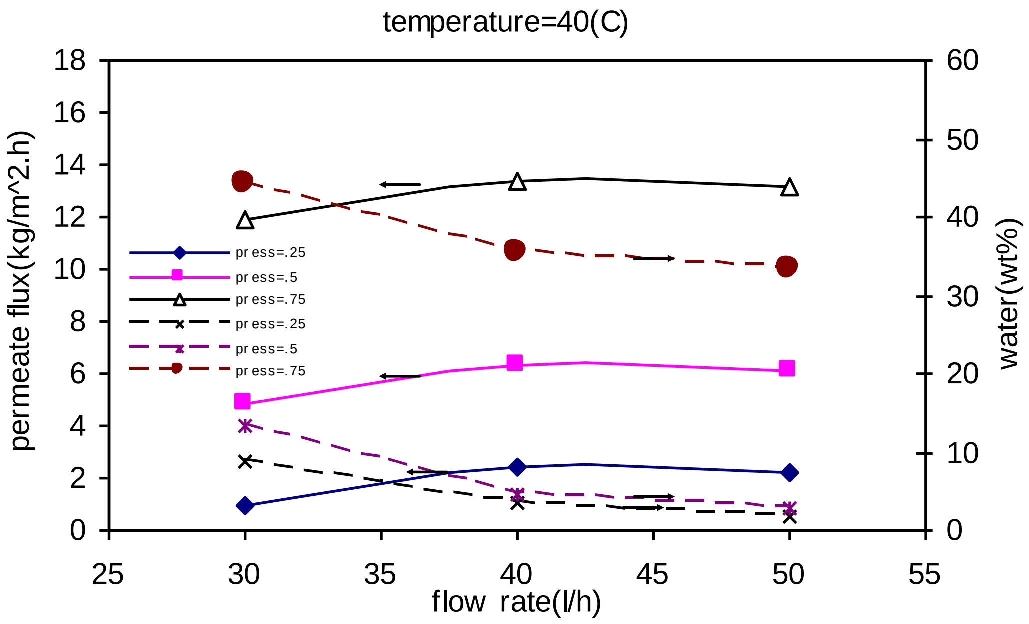

Figure 7 Effect of flow rate on permeate flux and water content at different pressures

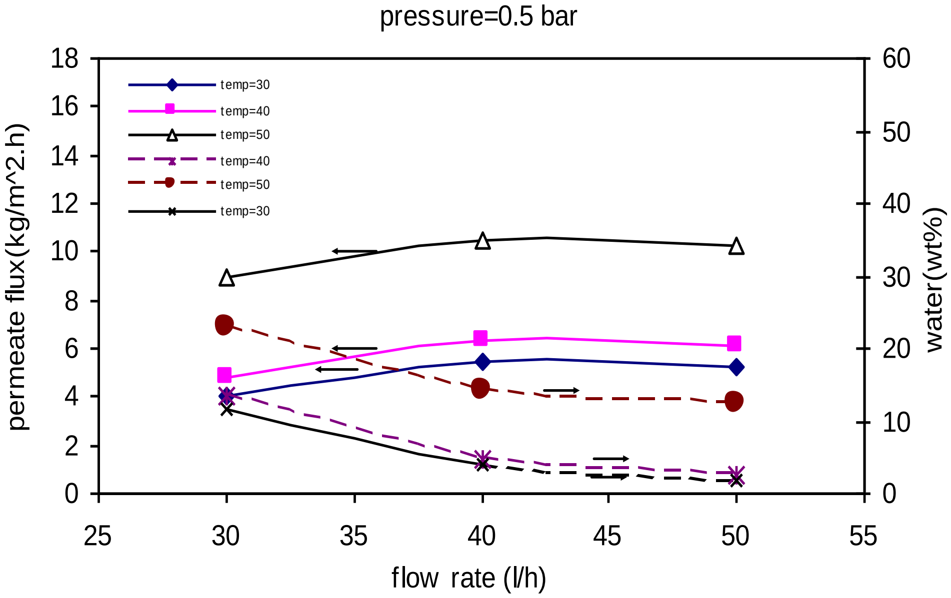

Figure 8 Effect of flow rate on permeate flux and water content at different temperatures