OILY WATER TREATMENT USING CERAMIC MEMBERANE

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ABSTRACT

This research was conducted using ceramic microfiltration membrane for treatment of oily wastewater in the pilot-scale dead-end filtration system designed in the laboratory under the influence of conditions of feed flow rate 15-35 l/h, feed temperature 32-48°C, oil feed concentration 300-1200 ppm, feed solution pH 2.6-9.8. The influence of these conditions on the permeate flux rate and oil rejection percent were investigated. Experimental results indicated that when feed flow rate increased to 35 l/h permeate flux rates increased to 100 $l/m^2.h$ and oil rejection percent decreased to 70.1%, and when feed temperature increased to 48 °C permeate flux rate increased to 62 $l/m^2.h$ and oil rejection percent decreased to 56.44%. But when oil feed concentration increased to 1200 ppm permeate flux rate decreased to 17.2 $l/m^2.h$ and oil rejection percent increased to 99.7%. Also basic feed solution (pH=9.8) gave high permeate flux rate (44.51 $l/m^2.h$) and low oil rejection percent (84%) in comparison with acidic feed solution (pH=2.6) which gave low permeate flux rate (26.42 $l/m^2.h$) and high oil rejection percent (99.46%). Four classical models were investigated to flux decline and the results showed that the experimental data was consistent (R^2 = 0.9883) with the complete blocking filtration model.

الخلاصة

تم في هذا البحث أستخدام غشاء سيراميك مايكرو فلتر لمعالجة المياه الملوثة بالزيت في منظومة ترشيح مختبرية ذات النهاية المسدودة المصممة في المختبر تحت تأثير ظروف تشغيلية من معدل جريان التغذية 15-35 لتر/ساعة و درجة حرارة 32-48° م و تركيز زيت ابتدائي 300-1200 جزء بالمليون ودرجة حامضية 2.6-9.8. تم هنا دراسة تأثير هذه المتغيرات على معدل تدفق الراشح ونسبة طرح الزيت. النتائج المختبرية أثبتت أنه عند زيادة معدل جريان التغذية الى 35 لتر/ساعة يزداد معدل تدفق الراشح الى 100 لتر/متر^2.ساعة و تنخفض نسبة طرح الزيت الى %70.1 وأن زيادة درجة الحرارة الى 48° م ترفع معدل تدفق الراشح الى 62 لتر/متر^2.ساعة و تقلل نسبة طرح الزيت الى %56.44. لكن زيادة التركيز الابتدائي للزيت في التغذية الى 1200جزء بالمليون تقلل معدل تدفق الراشح الى %17.2 وترفع نسبة طرح الزيت الى %99.7. أيضا عندما يكون محلول التغذية قاعديا (pH = 9.8) فأنه يعطي معدل تدفق الراشح أعلى (44.51لتر/متر^2.ساعة) و نسبة طرح الزيت أقل (%84) بالمقارنة مع محلول التغذية الحامضي (pH = 2.6) الذي يعطي معدل تدفق الراشح أقل (26.42لتر/متر^2.ساعة) و نسبة طرح الزيت أعلى (%99.46). تم دراسة اربعة موديلات لتنبؤ بسلوك تدفق الراشح واظهرت النتائج ان النتائج العملية متطابقة (R^2 =0.9883) مع موديل انسداد المرشح التام.

INTRODUCTION

Nowadays, considerable attention has been focused on the discharge of oily wastewater and it's influence on the environment. Pollution of water by oily hydrocarbon is especially harmful to the aquatic life, as it attenuates the light and perturbs the normal oxygen transfer mechanism (Srijaroonrat et al. 1999). In the recent years, the application of vegetable oils in industries has a great attention because vegetable oils are renewable, non –toxic and environmentally friendly resource. Vegetable oils are considered to be potential candidates to substitute conventional mineral oil-based lubricating oils and synthetic esters as a result of the stringent requirement of resource conservation and environmental protection (Hua et al. 2007). The main source of vegetable oil effluent are : degumming, deacidification, deodorization steps, the blow down of the boiler and wash water from de-oiling of the bleaching earth also contribute to the effluent in small amounts (Sridhar et al. 2002).

Typical composition ranges of "Produced water" generated in the oily wastewater oil, and gas industrial processes include 50-1000 ppm of total oil and grease and 50-350 ppm of total suspended solids (TSS). Stricter environmental legislations enforce the maximum total oil and grease concentration in discharge waters to be 10-15 ppm. Major pollution in wastewater (also Known as produced water) generating from oil field is oil which may range between 100 and 1000 ppm or more depending on emulsification efficiency and crude oil nature (Abbasi et al. 2010 and Abbasi et al. 2010). The small quantity of remaining oil in water must be reduced to an acceptable limit before the water can be discharged into the sea or rivers or reinjected for water flooding. Purification of this water is urgent issue so that it can be reused to save water resources and to protect the environment (Li et al. 2006 and Abbasi et al. 2010).

In wastewater treatment plants, there exist several techniques for separation. Typical ones include gravity separation and skimming, dissolve air flotation, demulsification, coagulation and flocculation, which have several disadvantages such as low efficiency , high operation costs, corrosion and recontamination problems (Mohammadi et al. 2003 and Li et al. 2006).The emulsified oily wastewater from the processing of petroleum products (particularly in oil exploitation) was difficult to treat by using these above common methods because in addition to above reasons, those operations could create a series of problems in the application. These problems not enclosed by upsetting equipment's surface and potentially choke reservoir, but also create huge waste with the rejected wastewater containing significant amount of crude oil and lead to serious environmental pollution (Wang et al. 2009).

One of the treatment techniques used for oil separation from emulsified oily wastewater is membrane filtration (Salahi et al. 2010).Membrane separation has enjoyed great candidate since 1973 and is becoming attractive technology due to low energy consumption, no chemical additives are needed to break the emulsion, high COD removal efficiencies, and treatment facilities are quite compact and fully automated (Hua st al. 2007 and Wu et al. 2008).One troublesome problem encountered in many membrane plants is fouling which can cause a decrease in flux due to pore blocking, solute aggregation (which lead to the formation of cake, or gel layer, on the surface of the membrane) or adsorption (Brinck et al. 2000). Obtaining membranes that are capable of lowering the solutes tendency to deposit on the membrane surface will minimize fouling (Masuelli et al. 2009). Also, the development of effective membrane cleaning method is desirable for diminishing this phenomenon such as backwashing by liquid or gas (Peng and Tremblay 2008).

Ceramic membranes have been Known for years and used in many different applications depending on their numerous advantages: stability at high temperatures and pressure resistance, good chemical stability, high mechanical resistance, long life and antifouling properties (Abbasi et al. 2010). Ceramic microfiltration membranes can be made from alumina, mullite, cordierite, silica, spinel, zirconia and other refractory oxides. These membranes are very cheap because they can be prepared by extruding and calcining kaolin clay (Abbasi et al. 2010 and Abbasi et al. 2010).

Many studies focused on empirical models based on non-linear correlations for the description of permeate flux decline with time. Such these correlations that the empirical models were presented by Hermia 1982, which used to identify the fouling mechanism occurred during microfiltration process (Grenier et al. 2008, Nandi et al. 2010 and Salahi et al 2010).

The objective of this paper is to investigate oily water treatment using ceramic membrane and the influence of feed flow rate, feed temperature, oil feed concentration and feed solution pH on the permeate flux and oil rejection percent. Determination the most appropriate applicable model to the experimental data for ceramic membrane microfiltration of oily water emulsion was investigated using the empirical models presented by Hermia 1982.

THEORY

The importance of applying filtration models for flux decline to predict the variation in flux rate with time during filtration process has led to various fouling mechanisms to be proposed to better characterize the flux performance (Hu and Scott 2008 and Nandi 2010).

There are four classical filtration models were proposed by Hermia 1982 are often used to describe fouling in relations correlate the permeate flux rate with the operating time (Ohya et al. 1998, Grenier et al. 2008 and Nandi 2010). These models are:

- Complete blocking filtration assumes a seal of pores entrances and prevention of any flow through them because the large size of particles such that the particles are not superimposed one upon the other.

$$\ln(F) = \ln(F_0) - K_{comp.}t \qquad (1)$$

- Intermediate blocking filtration assumes a seal of pore entrances by a fraction of particles and some particles may settle over other.

$$1/F = 1/F_0 + K_{inter.}t \qquad (2)$$

- Standard blocking filtration (or sometimes called Gradual pore blocking) assumes an accumulation inside the pore walls of the membrane causing proportional decreasing in pore volume with filtrate volume.

$$1/F^{0.5} = 1/F_0^{0.5} + K_{standr.}t \qquad (3)$$

- Cake filtration assumes an accumulation of particles on the membrane surface forming cake layer, it thickness increases with time that adds a hydraulic resistance to filtration.

$$1/F^2 = 1/F_0^2 + K_{cake}t \qquad (4)$$

Plotting the left hand side flux function of each model verse time must be a straight line, and then plotting flux from experimental data and that is determined by these four models versus time. Often the model which best fits the experimental data is claimed to capture the fouling mechanism.

EXPERIMENTAL STUDY

Materials

The commercial tubular ceramic microfiltration membrane (0.8-0.3 µ) used in this research was made of kaolin (inside diameter: 1.5 cm, outside diameter: 4.6 cm. and length: 22 cm.). Ceramic membrane was put in the filter cartridge (100 % poly propylene). Oil-in-water emulsion (oily wastewater feed solution) was prepared by mixing edible vegetable oil (bizce oil made in Turkey, density: 910 kg/m^3 and viscosity: 4.37×10^{-2} kg/m.sec.) and tap water using homogenizer. 1M of NaOH solution (99.97% purity was purchased from BDH Chemicals Ltd) and H_2SO_4 (95.97% purity was purchased from Fluka) were used to adjust pH of feed solution.

Experimental Setup

Fig.1 shows the pilot-plant used in all the experiments. The pilot was operated in a dead-end cell. This system was consisted of a glass feed tank with a capacity of 30 l. supplied with automatic heater to heat the feed and keep it at a constant temperature and stirrer to keep the feed homogeneous. The feed was pumped through the system by means of centrifugal pump. Permeate from the system was collected in a 500 ml cylinder to determine permeate flux.

A sample of feed solution was withdrawn immediately before filtration started while sample of permeate was withdrawn periodically every 15 min. to be analyzed. The analysis of samples was attempted using ultraviolet visible light spectra photometer (Shimadzu model UV-160A) at wave length 303 nm. Periodically and after each run the membrane was regenerated physically and due to its rigidity and without any problem it was cleaned with hot water (60°C). The effectiveness of the filtration process was denoted in terms of oil rejection percent and permeate flux rate. Oil rejection percent is determined as:

$$R\,\% = (1 - C_p / C_f) \times 100 \qquad (5)$$

While permeate flux rate is determined as:

$$F = V / A.t \qquad (6)$$

RESULTS AND DISCUSSIONS

Feed Flow Rate Effect

The effect of flow rates (15, 25 and 35 l/h). on the treatment process performance were investigated with the operation conditions of feed temperature 32°C,oil feed concentration 300 ppm, and feed solution pH 6.86. Fig.2 and Fig.3 show the effect of feed flow rate on the permeate flux rate and the oil rejection percent. As shown increasing flow rate leads to increase permeate flux rate but decrease rejection percent.

This behavior may be attributed to the fact that at dead end filtration the cake/gel layer can be formed easily due to absence applied shear. Therefore increasing flow rate leads to removing the oil layer from the membrane surface. Due to extent of mixing over the membrane surface, this can reduce accumulate of oil drops which essentially acts as a dynamic membrane, as a result the oil drops on the membrane surface diffuse back to the bulk solution. The results obtained here are in good agreement with Mohammadi et al. (2003) and Wu et al. (2008).

Feed Temperature Effect

Fig. 4 and Fig.5 present the effect of temperature on the treatment efficiency at conditions of feed flow rate 15 l/h, oil feed concentration 300 ppm, and feed solution pH 6.86. While temperatures 32, 40 and 48°C was chosen for this study.

It can be observed that increasing feed temperature causes increasing in permeate flux and decreasing oil rejection percent. This can explain as at high temperatures oil/water emulsion viscosity decreases and lower viscosity eases fluid permeate through the membrane surface. These results agree with Wang etal. (2009) and Abbasi et al. (2010).

Oil Feed Concentration Effect

Oil feed concentrations of 300, 600 and 1200 ppm were investigated with the operation conditions of feed flow rate 15 l/h, feed temperature 32°C, and feed solution pH 6.86. The influence of oil feed concentrations are shown in Fig.6 and Fig.7.

According to the results the lower oil concentration the higher permeation flux of the membrane, but the oil rejection decreasing with the decreasing of oil concentration in the feed. These results are attributed to the formation of oil layer on the membrane surface with thickness increases with increasing oil feed concentration specially at dead end filtration process because there is no hydrodynamic action causes removing this layer. These results agree with Wu et al. (2008) and Abassi et al. (2010).

Feed Solution pH Effect

The effect of feed solution pH was illustrated in Fig.8 and Fig.9, at conditions of feed flow rate 15 l/h, feed temperature 32°C, and oil feed concentration 300 ppm at different feed pH of 6.86, 9.8 and 2.6. As can seen from the figure the permeate flux was increase at steady rate at the basic medium while decreased sharply at the acidic medium, but the reverse behavior can be seen for oil rejection.

This behavior was explained by former researcher as that the permeate flux under different pH was effected by the properties of the solute (droplet) in addition to the characteristics of the membrane. The stability of the oil in water emulsion was more stable at pH 4-6 than at pH of 6-10. Therefore the emulsion didn’t coagulate under stable condition and so the lower level of flux was observed at low pH. While the cake layer become more open at high pH due to the inter-droplet repulsion, and this increased the permeability, resulting in higher permeate flux. It's noticeable to mention the thickness of cake layer reduced due to the particle deposition prevented by the inter-droplet repulsion. While, corresponding to the membrane surface properties, it was found that at lower feed solution pH the membrane becomes hydrophilic and at higher feed solution pH the membrane becomes hydrophobic. Hydrophobic membrane tends to absorb foulant (oil), while leads to oil attachment on the membrane surface and therefore high oil passage. This result is agree with A-Jeshi and Nevill (2008).

Model Analysis

Models are investigated for the run with conditions of feed flow rate 15 l/h, feed temperature 32°C, oil feed concentration 300 ppm and feed solution pH 6.86, and the Fig.'s 10-14 show model prediction and experimental data for Hermia's model in different cases. The complete blocking filtration model explained the experimental data very well, as previously mentioned, the complete pore blocking happens when pore entrance blockage, which cause reduction the area to flow and leads to prevention of any flow through it. .

CONCLUSIONS

The experimental results of this work showed that using of ceramic microfiltration membrane process was effective for treatment oily water. It was obtained that F increases with increasing feed flow rate, feed temperature and feed solution pH, but decreases by increasing oil feed concentration. The results also proved that increasing oil feed concentration, acidity of the feed solution causes increasing R %, but it decreases when feed flow rate and feed temperature increase. Comparing experimental data with Hermia's model showed the best consistency corresponds to the complete blocking filtration model.

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NOMENCLATURES

A	Effective Membrane Area (m^2)
C_f	Oil Concentration in The Feed (ppm)
C_p	Oil Concentration in The Permeate (ppm)
F	Permeate Flux Ratio ($l/m^2.h$)
F_0	Initial Permeate Flux Ratio ($l/m^2.h$)
K_{cake}	Y-intercept of cake filtration model ($(m^2/l)^2$)
$K_{comp.}$	Y-intercept of complete blocking filtration model (unit less)
$K_{inter.}$	Y-intercept of intermediate blocking filtration model (m^2/l)
$K_{standr.}$	Y-intercept of standard blocking filtration model ($(m^2/l)^{0.5}$)
R	Oil Rejection
t	The Run Time (h)
V	Permeate Volume (l)

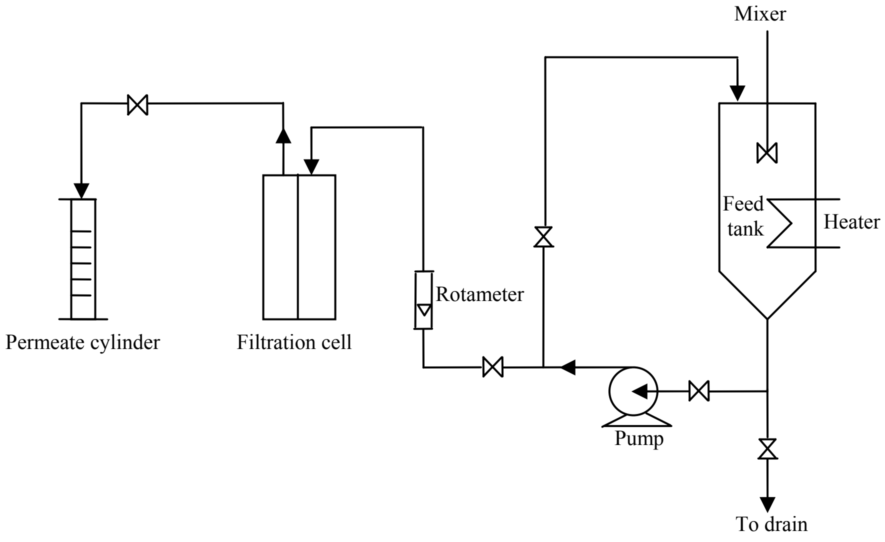

Fig.1 Experimental Set-Up

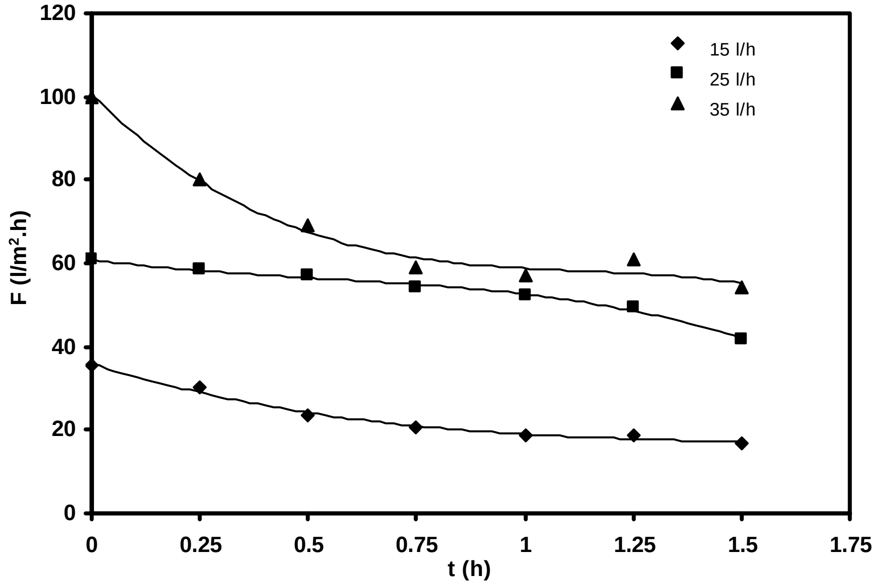

Fig.2 Time vs permeate flux rate at different feed flow rate
Feed temperature 32°C, oil feed concentration 300 ppm, and feed solution pH 6.86

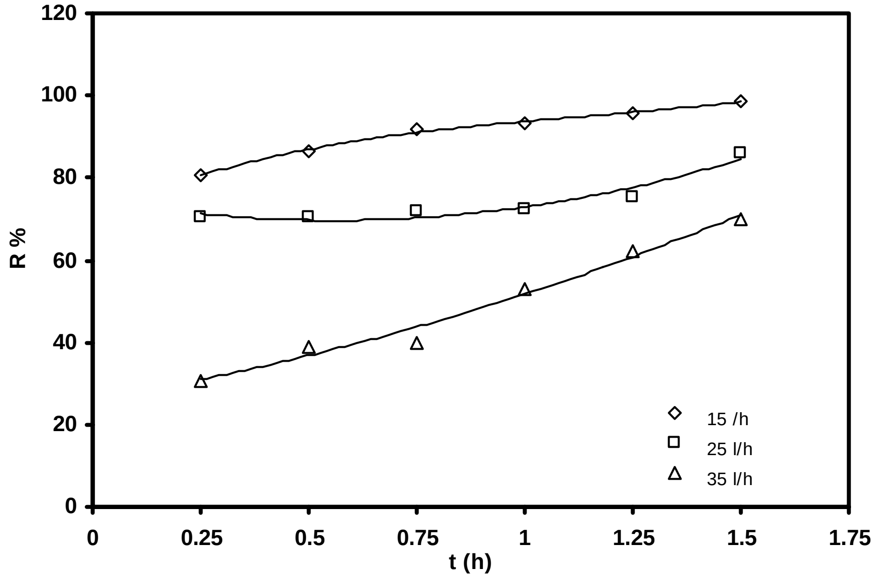

Fig.3 Time vs oil rejection percent at different feed flow rate
Feed temperature 32°C, oil feed concentration 300 ppm, and feed solution pH 6.86

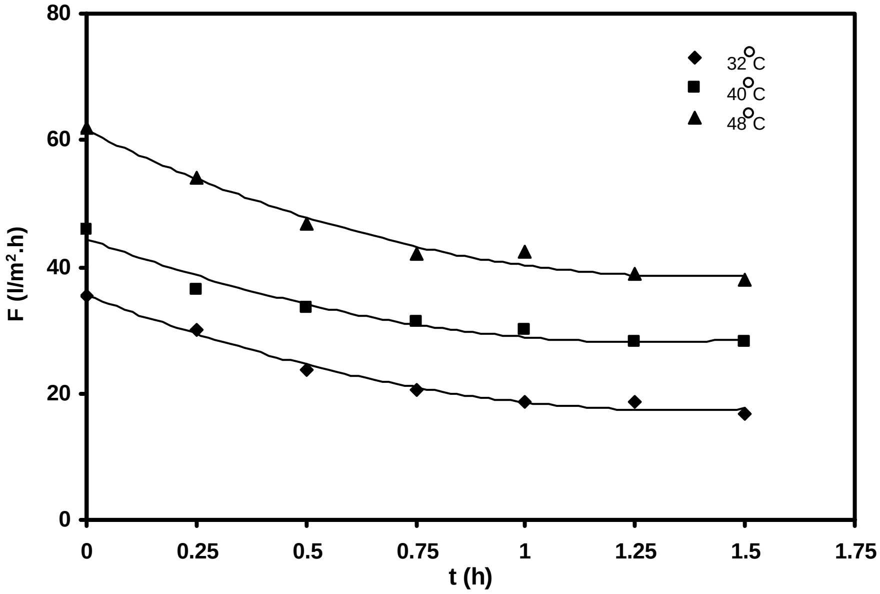

Fig.4 Time vs permeate flux rate at different feed temperature

Feed flow rate 15 l/h, oil feed concentration 300 ppm, and feed solution pH 6.86

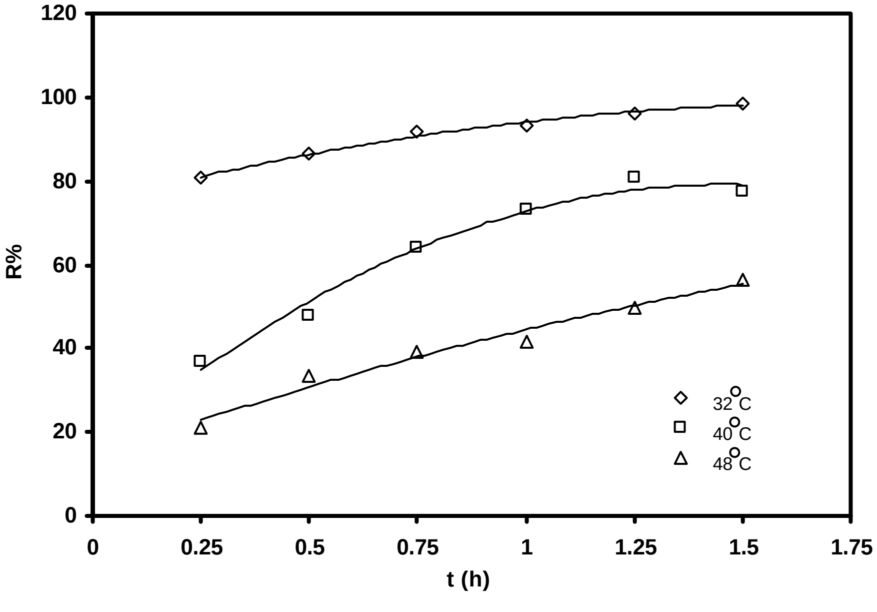

Fig.5 Time vs oil rejection percent at different feed temperature
Feed flow rate 15 l/h, oil feed concentration 300 ppm, and feed solution pH 6.86

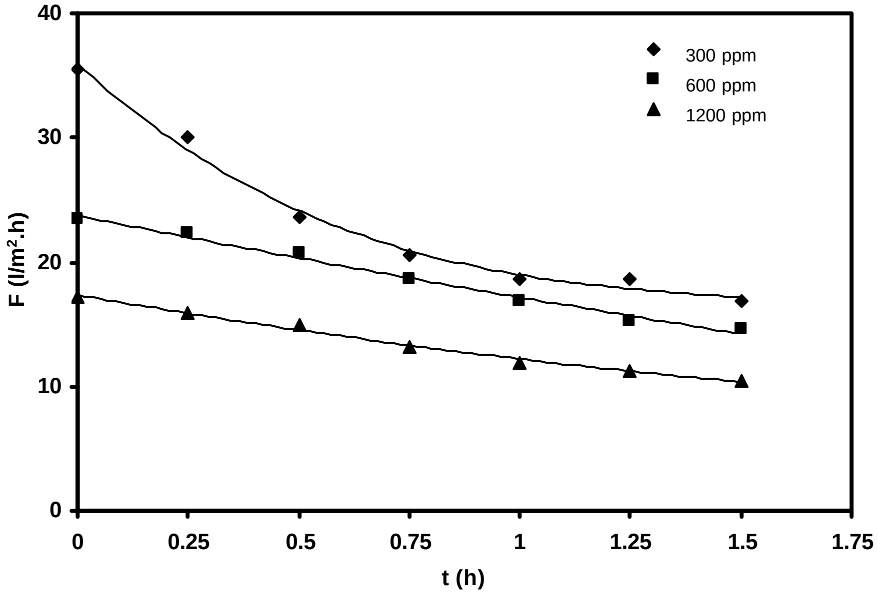

Fig.6 Time vs permeate flux rate at different oil feed concentration Feed flow rate 15 l/h, feed temperature 32°C, and feed solution pH 6.86

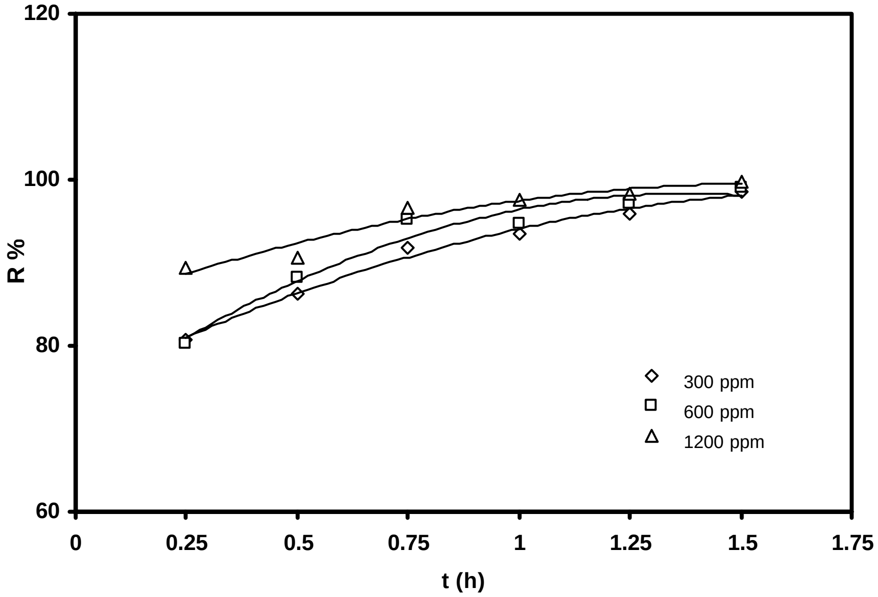

Fig.7 Time vs oil rejection percent at different oil feed concentration Feed flow rate 15 l/h, feed temperature 32°C, and feed solution pH 6.86

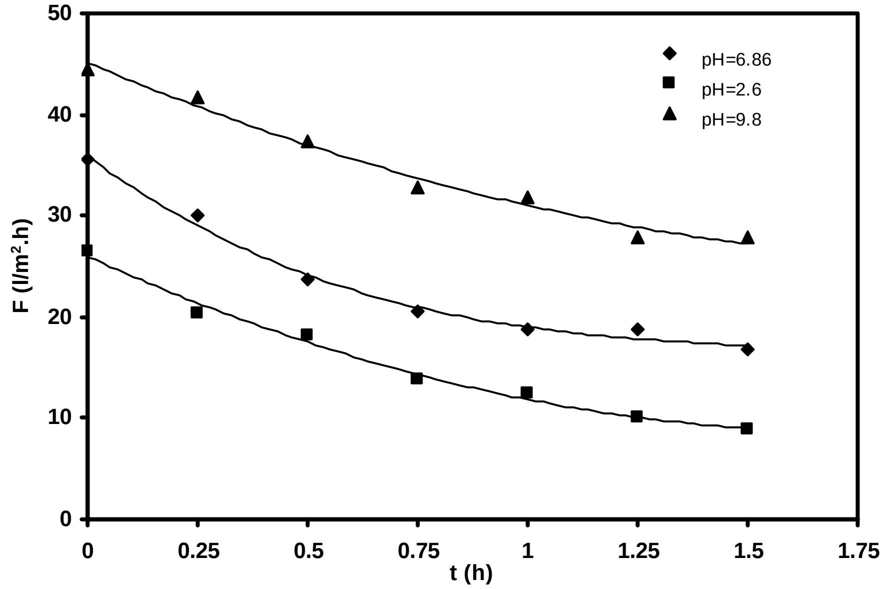

Fig.8 Time vs permeate flux rate at different feed solution pH
Feed flow rate 15 l/h, feed temperature 32°C, and oil feed concentration 300 ppm

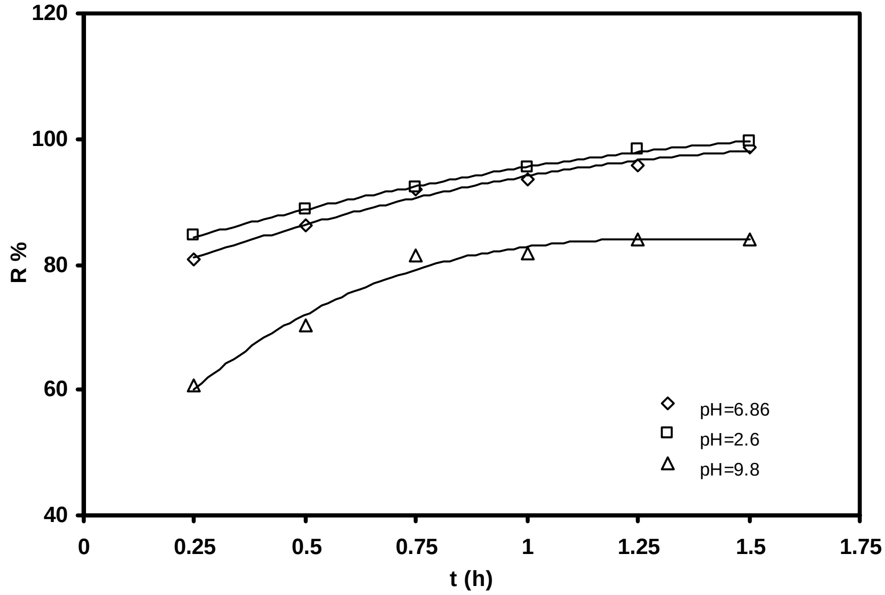

Fig.9 Time vs oil rejection percent at different feed solution pH
Feed flow rate 15 l/h, feed temperature 32°C, and oil feed concentration 300 ppm

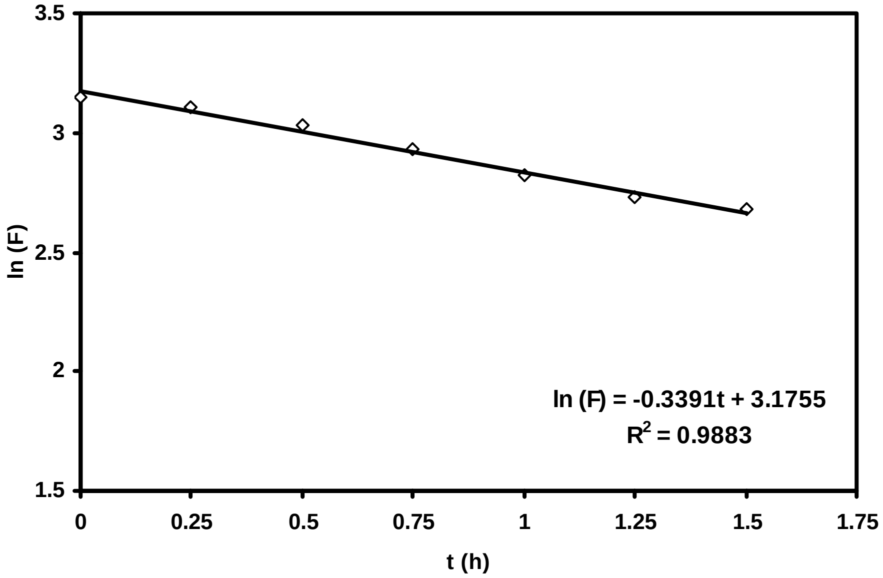

Fig.10 Complete blocking filtration model

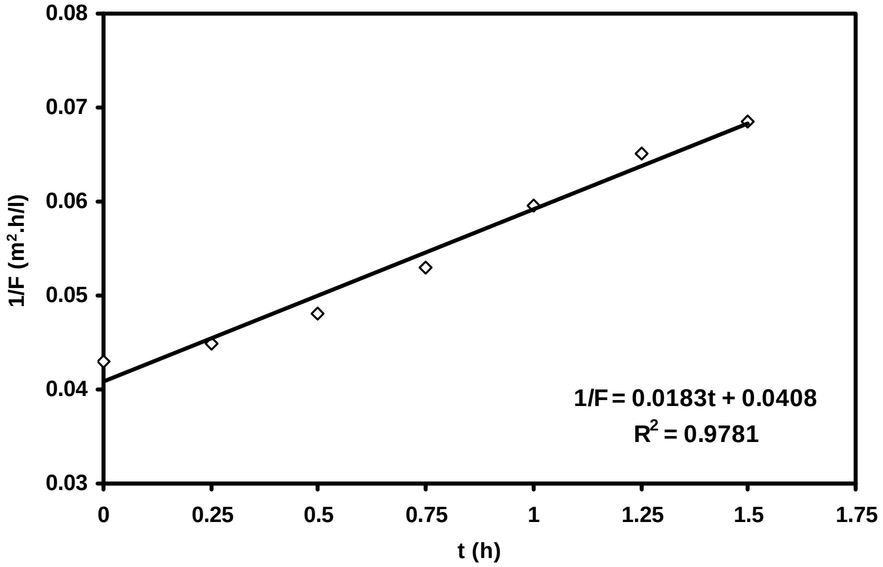

Fig.11 Intermediate blocking filtration model

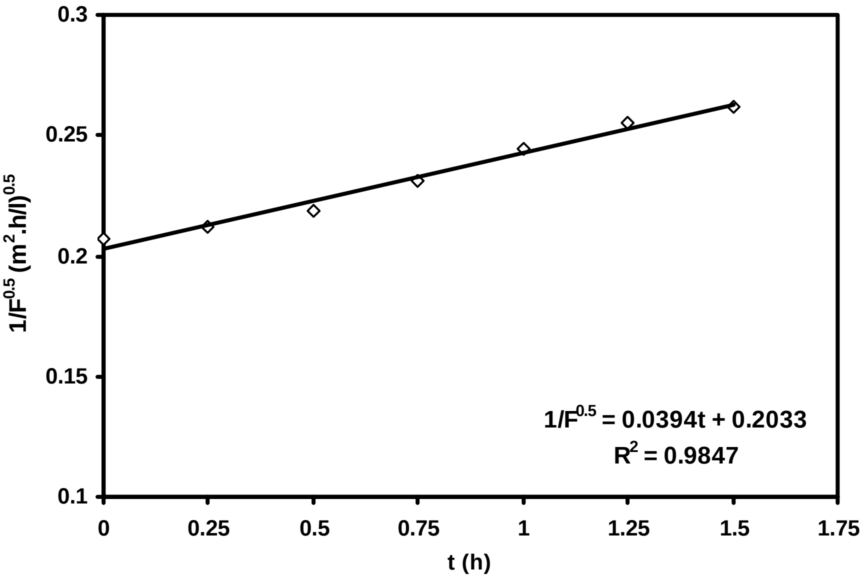

Fig.12 Standard blocking filtration model

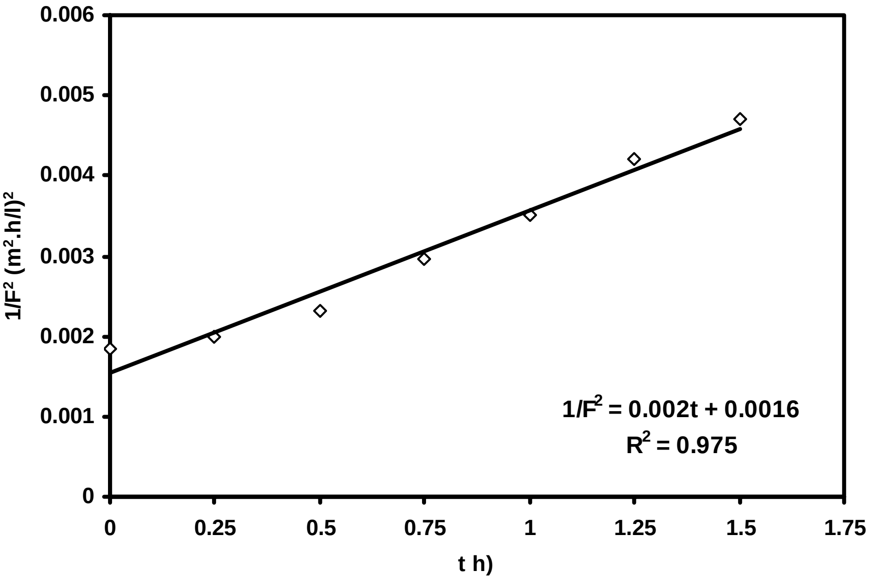

Fig.13 Cake filtration model

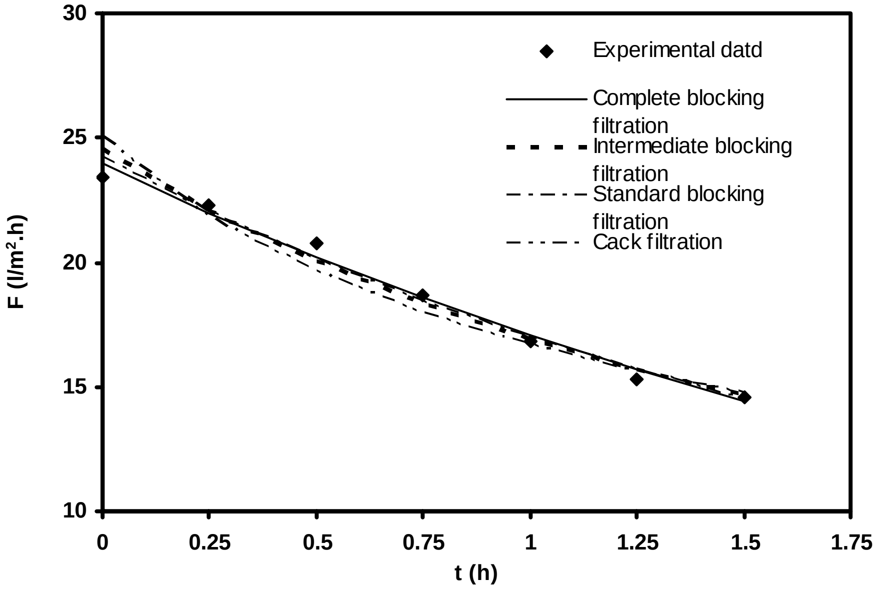

Fig.14 Comparison of experimental data with filtration model prediction