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TREATMENT OF SYNTHETIC OILY WASTEWATERS BY COAGULATION - MF HYBRID PROCESS USING MULLITE - ALUMINA CERAMIC MEMBRANES

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Abstract

In this research, effects of in-line coagulation on permeation flux (PF), flux reduction (FR) and total organic compound rejection (TOC R) of synthesized mullite-allumina MF ceramic membrane (with 50 wt % alumina content) during treatment of synthetic oily wastewater in were investigated. Four coagulants ((ferrous chloride ($FeCl_2.4H_2O$), ferrous sulphate ($FeSO_4.7H_2O$), aluminum chloride ($AlCl_3.6H_2O$) and aluminum sulphate ($Al_2(SO_4)_3.18H_2O$)) plus equal concentration of slaked lime in form of calcium hydroxide ($Ca(OH)_2$) were examined in the coagulation – MF hybrid process at different concentrations (0, 50, 100 and 200 ppm). At the best condition (200 ppm of ferrous sulphate plus slaked lime), PF increased from 118.32 to 212.55 (L m^{-2} h^{-1}), FR decreased from 58.5 % to 17.82 % and TOC R increased from 89.6 % to 92.5%.

Key words: ceramic membranes, coagulation, hybrid process, microfiltration (MF), synthetic oily wastewater treatment

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1. Introduction

Membrane separation is one of the effective technologies for treatment of oily wastewaters (Abbasi et al., 2010; Abbasi et al., 2012, Mustereţ and Teodosiu, 2007). Membrane separation processes are interest because their energy consumption is relatively low, scale up of them is simple and these processes can be controlled easily (Barjoveanu and Teodosiu, 2010; Sun et al., 2011; Zahrim et al., 2011; Zhang et al., 2008).

Membrane fouling can cause a permeation flux decline due to concentration polarization and/or deposition of macromolecules over the membrane surface and/or within the membrane pores. The concentration polarization is caused by accumulation of contaminants over the membrane surface (Konieczny et al., 2006). The fouling phenomena reduce permeation flux and membrane performance (Dascalu et al., 2016; Konieczny et al., 2009).

The fouling of membranes can be reduced using pretreatment applications. Therefore, coagulant agents are employed before membrane filtration process in order to improve oil removal efficiency with reduction of fouling (Abbasi et al., 2011; Canizares et al., 2008; Di Bella et al., 2014; El-Gohary et al., 2010; Hilal et al., 2004; Hilal et al., 2005; Hua et al., 2007; Santo et al., 2012; Yan et al., 2012; Zeng et al., 2007).

Coagulant agents aggregate particles and organic matters by limiting pore blockage of membranes and formation of a porous cake that can be easily removed by hydraulic cleaning (Hilal et al., 2004; Yan et al., 2012). "In-line" process is the technique of combining coagulation with microfiltration process. This process consists of

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batching the coagulant to the feed immediately before the membrane, omitting the stage of sedimentation, which results in reduction of the dose of the coagulant during wastewater treatment (Choi and Dempsey, 2004; Lee et al. 2009; Leikne, 2009; Konieczny et al., 2009; Rodrigues et al., 2017).

Metallic salts such as aluminum and ferric are widely employed as coagulant agents in wastewater treatment. Aluminum and ferric salts can separate impurities such as colloidal particles and dissolved organic substances from wastewater. Nearly, all colloidal impurities in wastewaters are negatively charged and maybe stable as a result of electrical repulsion. In addition, highly charged cations such as Al^{3+} and Fe^{3+} should be effective in this respect. However, over the normal range of pH values in natural waters, these cations are not found in significant concentrations, as a result of hydrolysis, which can give a range of products.

Many hydrolysis products are cationic and these can interact strongly with negative oil droplets, giving destabilization and coagulation, under the correct conditions of dosage and pH. Excess dosage can give charge reversal and restabilization of oil droplets (Duan and Gregory, 2003). Positively charged precipitated particles may deposit on impurity particles, again giving the possibility of charge neutralization and destabilization. Generally, charge neutralization with aluminum and iron salts occurs at quite low metal concentrations at around neutral pH.

A further possibility is that surface precipitation of hydroxide can occur, with similar consequences. In fact, hydroxide precipitation leads to the possibility of sweep flocculation, in which impurity particles become enmeshed in the growing precipitation and thus are effectively removed. The following hydrolysis schemes proceed from left to right as pH increases, giving first the doubly- and singly-charged cationic species and then the uncharged metal hydroxide, $Al(OH)_3$ and $Fe(OH)_3$. With further increasing pH, the soluble anionic forms, $Al(OH)_4^{-1}$) and $Fe(OH)_4^{-1}$, become dominant (Eqs. 1-2).

$$Al^{+3} \rightarrow Al(OH)^{+2} \rightarrow Al(OH)_2^{+1} \rightarrow Al(OH)_3 \rightarrow Al(OH)_4^{-1} \quad (1)$$

$$Fe^{+3} \rightarrow Fe(OH)^{+2} \rightarrow Fe(OH)_2^{+1} \rightarrow Fe(OH)_3 \rightarrow Fe(OH)_4^{-1} \quad (2)$$

It must be noted that $Fe(OH)_3$ and $Al(OH)_3$ have low solubility in water and precipitates. At high pH values, the best aluminum dosage increases because of the reduced positive charge of the adsorbed species. Using higher coagulant dosages, where extensive hydroxide precipitation occurs, giving sweep flocculation. In sweep flocculation, impurity particles are enmeshed in a growing hydroxide precipitation and are effectively removed from suspension. Sweep flocculation mechanism is generally more rapid than coagulation by charge neutralization and gives larger flocs (Duan and Gregory, 2003).

In this study, ferrous chloride ($FeCl_2.4H_2O$), ferrous sulphate ($FeSO_4.7H_2O$), aluminum chloride ($AlCl_3.6H_2O$) and aluminum sulphate ($Al_2(SO_4)_3.18H_2O$), were examined to enhance performance of hybrid coagulation – MF process for synthetic oily wastewater treatment using home-made mullite-alumina ceramic membranes.

Slaked lime has many positive effects. It adjusts the pH to the best value and retrieves decreasing pH because of consuming OH^- by metal ions in hydrolysis reactions, acts as a coagulant aid, and improves sludge settleability and stability. However, it may increase the dry solids content of the sludge (Amuda and Alade, 2006; Duan and Gregory, 2003).

There are a few papers in literature regarding enhancement of oily wastewaters treatment using MF ceramic membranes with coagulant agents. Therefore, this research is unique, because there are any researches in literature on.

2. Experimental

2.1. Preparation and characterization of membranes

Symmetric mullite-alumina (50 wt% alumina content) MF membranes were synthesized from kaolin clay and α-alumina powder. The kaolin material was obtained from the Zenooz mine in Marand, Iran. The chemical analysis of kaolin is listed in Table 1. Commercial grade of α-alumina with 99.6 wt % purity was used to prepare the mullite-alumina membranes. The powder has an average particle size of 75 μm. Tubular membranes (inner diameter: 10 mm, outer diameter: 14 mm and Length: 30 cm) were conveniently made by extruding a mixture of kaolin clay and alumina powder with distilled water using an extruder.

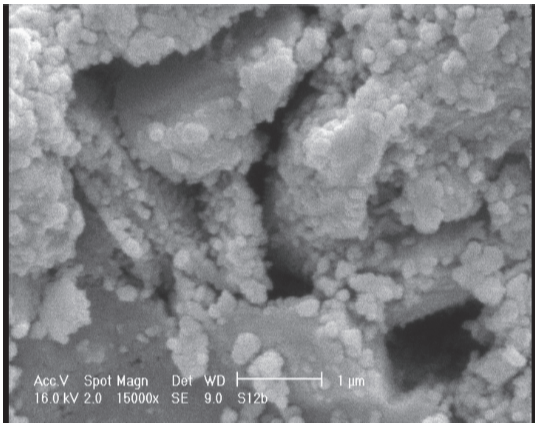
The cylindrical shaped membranes were dried at room temperature within 48 h. For improving mechanical resistance of membranes, calcinations were carried out at 1350 °C for 3 h.

Free silica removal was carried out with aqueous solutions containing 20 wt% NaOH at a temperature of 80 °C for 5 h. Removal of free silica causes micro-porous tubular ceramic membranes to be made with good porosity (Kazemimoghadam et al., 2002). The membranes were washed with distillated water for 12 h at a temperature of 80 °C in order to remove NaOH.Porosity of the membranes measured by water absorption method and was equal to 49 %. Permeation flux of the membranes at certain pressure (1 bar), temperature (25 °C) and cross flow velocity (1 m s^{-1}) for distillated water were 109 (L m^{-2} h^{-1}).

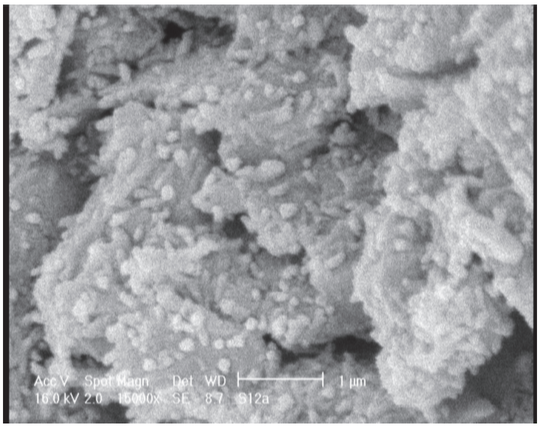
Fig. 1 shows SEM of mullite-allumina ceramic membrane with 50 wt. % alumina content. Characterization of the membranes using mercury porosimetry method showed that the average pore radius was 0.728 μm.

Table 1. Chemical analysis of the kaolin clay

Component	*Percent*	*Phases*	*Percent*
SiO_2	61.62	Kaolinite	64
TiO_2	0.4		
Al_2O_3	24-25	Illite	2.4
Fe_2O_3	0.45-0.65		
K_2O	0.4	Quartz	27
Na_2O	0.5		
L.O.I	9.5-10	Feldspar	6.6
Total	100		100



(a)



(b)

Fig. 1. SEM micrographs of the 50 wt % mullite-alumina membrane: (a) cross-section 15000 X and (b) surface 15000X

2.2. Synthetic oily wastewater

Oil-in-water emulsions (synthetic oily wastewaters) with 1000 ppm oil were prepared by mixing condensate gas from Seraje, Ghom, Iran, (C_8-C_{12}) and distilled water. Triton X-100 (0.01wt %) was added as emulsifier to the mixture to stabilize the emulsions. Triton X-100 with CAS number: 9002-93-1 was purchased from Merck Company. A blender was used to mix the emulsion at high shear rates (6000 rpm) for 30 min. The oil-in-water emulsions were highly stable for employing in the MF experiments because within 12 h, no phase separation was observed and the mean oil droplets size almost remained constant. Volumetric droplet size distribution of the emulsion (1000 ppm oil in water) is presented in Fig. 2.

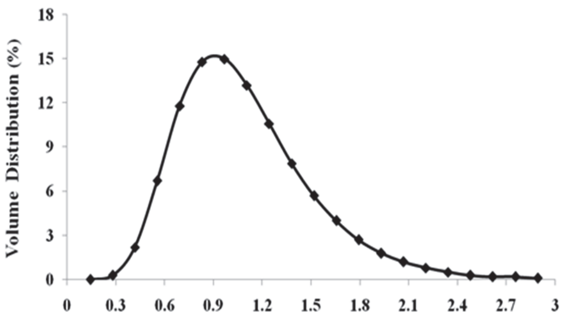


Fig. 2. Volumetric droplet size distribution of the synthetic oily wastewater

As observed, mean droplet size is 1.09 μm. Four coagulants (ferrous chloride ($FeCl_2.4H_2O$) with CAS number: 13478-10-9, ferrous sulphate ($FeSO_4.7H_2O$) with CAS number: 7782-63-0, aluminum chloride ($AlCl_3.6H_2O$) with CAS number: 7784-13-6 and aluminum sulphate ($Al_2(SO_4)_3.18H_2O$ with CAS number: 7784-31-8) plus lime in form of calcium hydroxide ($Ca(OH)_2$) with CAS number:1305-62-0 produced in Merck Company, Germany, were also used in all the coagulation – MF process experiments. It must be noted that in all experiments of coagulation-filtration method, slaked lime has been used.

2.3. Setup

In order to carry out the experiments almost close to an industrial scale, an experimental scale setup was designed. The pilot was operated in cross flow mode. The membrane surface area in contact with the feed was equal to 110 cm^2. The MF cell was installed in the plant according to Fig. 3 and all the industrial reservations were considered during the experiments. The system mentioned above had a vessel with a capacity of 10 L. This vessel had a heater to heat the wastewater and keep its temperature on a certain temperature and also a stirrer in order to keep the feed uniform. The feed temperature was controlled by a digital thermometer with an accuracy of ± 0.1 °C. A tubular heat exchanger was used to control the feed temperature. During the experiments, the process was carefully monitored to control cross flow velocity (CFV), pressure and temperature.

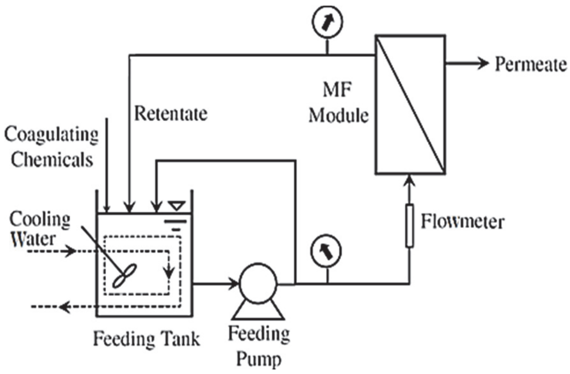


Fig. 3. Microfiltration setup

2.4. Operation

Coagulant agents (ferrous chloride ($FeCl_2.4H_2O$), ferrous sulphate ($FeSO_4.7H_2O$), aluminum chloride ($AlCl_3.6H_2O$) and aluminum sulphate ($Al_2(SO_4)_3.18H_2O$) were added with slaked lime in equal concentration to the feed tank before MF and mixed well by a mixer at 100 rpm for 5 min followed by slow mixing with 20 rpm for 30 min.

After that, pump was started and the mixture of synthetic oily wastewater and coagulant agent with slaked lime was filtrated using the MF mullite-allumina ceramic membranes. In order to avoid unsteady state conditions, the permeate data during the first 30 second of MF process was neglected. In previous work (Abbasi et al., 2010), MF treatment of synthetic oily wastewaters with 1000 ppm oil-in-water emulsion without coagulant agents was investigated. The results indicated that the best operating condition is: pressure of 3 bar, cross flow velocity of 1.5 m s^{-1} and temperature of 35 ºC. Therefore all the experiments for the coagulation – MF process were carried out at this condition for 60 min**.**

3. Method

Permeation flux (PF), flux reduction (FR) and TOC rejection (TOC R) are important parameters in design and construction of MF separation units for treatment of oily wastewaters. PF presents the amount of permeate per unit time and per unit membrane surface area. FR represents the amount of cake/gel layer formed on the membrane surface. To measure MF performance for treatment of oil-in-water emulsions, TOC R should also be evaluated.

PF is measured gravimetrically with an electronic balance via weighting permeate. PF is calculated as follows by determine the permeate volume (V) collected per unit membrane surface area (A) per unit time (t) (Eq. 1):

$$\text{PF} = \left(V/At\right) \qquad (3)$$

FR is calculated as follows (Eq. 2):

$$FR = ((PFi - PFw)/PFw) \times 100 \qquad (4)$$

where PF_i is PF of distillated water for fresh membranes and PF_w is PF of distillated water for fouled membranes. TOC R is calculated as follows (Eq. 3):

$$\text{TOC } R = \left(1 - C_p/C_f\right) \times 100 \qquad (5)$$

where: C_p represents TOC concentration in permeate and C_f is TOC concentration of feed (Abbasi et al., 2010).

4. Results and discussion

4.1. Treatment using hybrid coagulation – MF process with different coagulants

As shown in Fig. 4(a), by increasing aluminum chloride concentration up to 100 ppm, PF decline slightly decreases. This is due to sweep flocculation by formation of large flocs and the reduction of attraction energy between oily droplets and membrane surface. Another reason for this phenomenon is that during coagulation-MF process, the oil droplets become large and the cake/gel layer porosity increases (Lin et al., 2008a; 2008b). But at higher concentration of aluminum chloride, PF decreases because at high dosage of coagulant agents, charge reversal and restabilisation of oil droplets occurs. Therefore, large flocs are not formed and oil droplets fill the membrane surface and pores. Also, insoluble aluminum hydroxide with other impurities ($CaCl_2$ and $Ca(OH)_2$)) block the membrane pores and this subject causes PF to be reduced. It must be noted that at the early filtration, this phenomenon is less significant but as time increases blocking of membrane pores are raised.

Fig. 4b presents variation of PF and FR at the end of MF with coagulant agents. The results show that at the best coagulant agent concentration (100 ppm), PF increases 39.21 % and FR decreases 25.48 % compared with MF process only. The results for quality of treated synthetic wastewater (Fig. (4c)) illustrate that by increasing concentration of aluminum chloride, TOC R increases because oil droplets become larger and cannot pass through the membrane pores. Also, at high coagulant concentration, coagulant sludge blocks the membrane pores and makes a cake/gel layer on the membrane surface (Barbot et al., 2008; Lee et al., 2005; Unlu, et al., 2009). By increasing coagulant concentration up to 100 ppm, TOC R increases from 89.6 % to 91.4 %. Therefore, by considering PF as the main goal, coagulation concentration of 100 ppm can be considered as the best operating condition.

As shown in Fig. 5a, PF decline slightly decreases with increasing aluminum sulphate plus slaked lime concentration up to 50 ppm because sweep flocculation occurs and large flocs are formed a highly porous cake layer on the membrane surface by a low attractive energy.

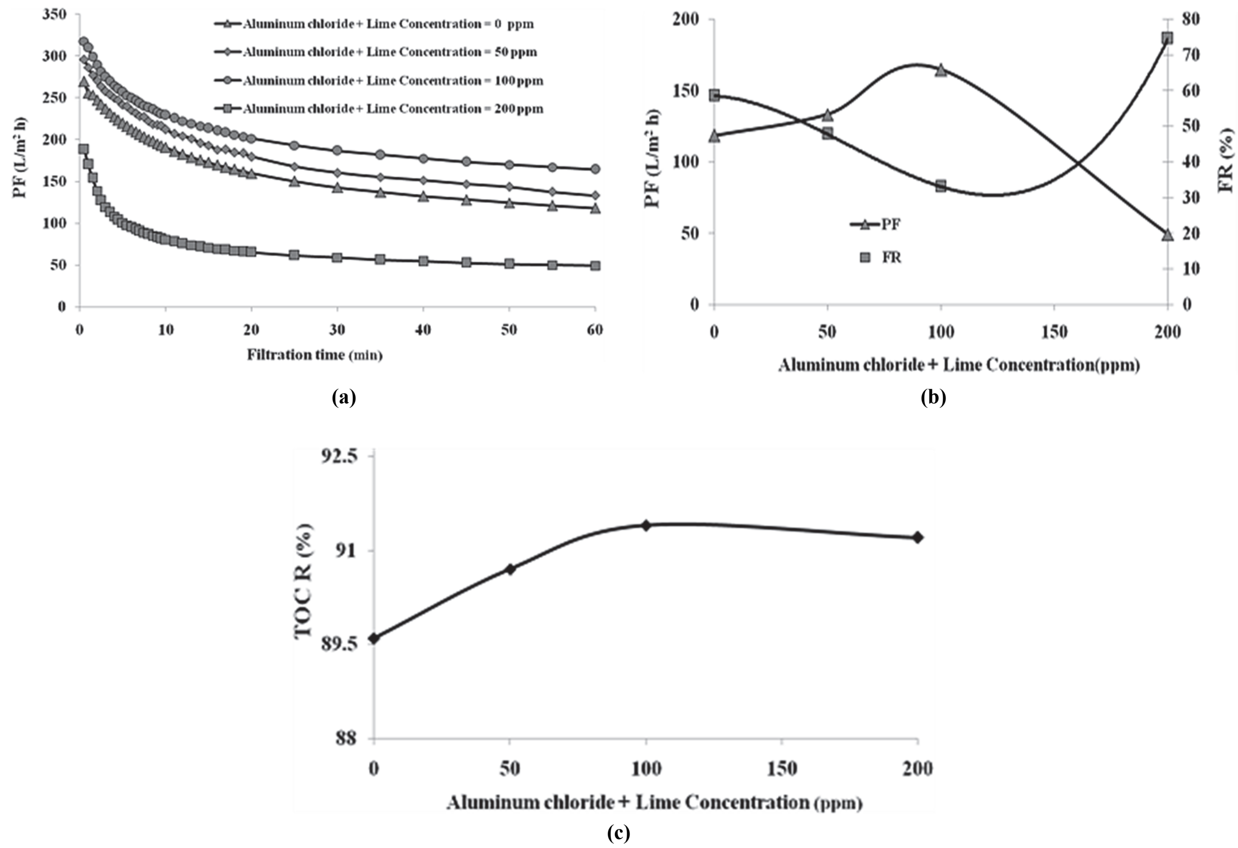


Fig. 4. Variation of: (a) PF with time , (b) PF and FR and (c) TOC R at the end of filtration with different aluminum chloride plus slaked lime concentration in hybrid coagulation – MF system using mullite-allumina ceramic membrane

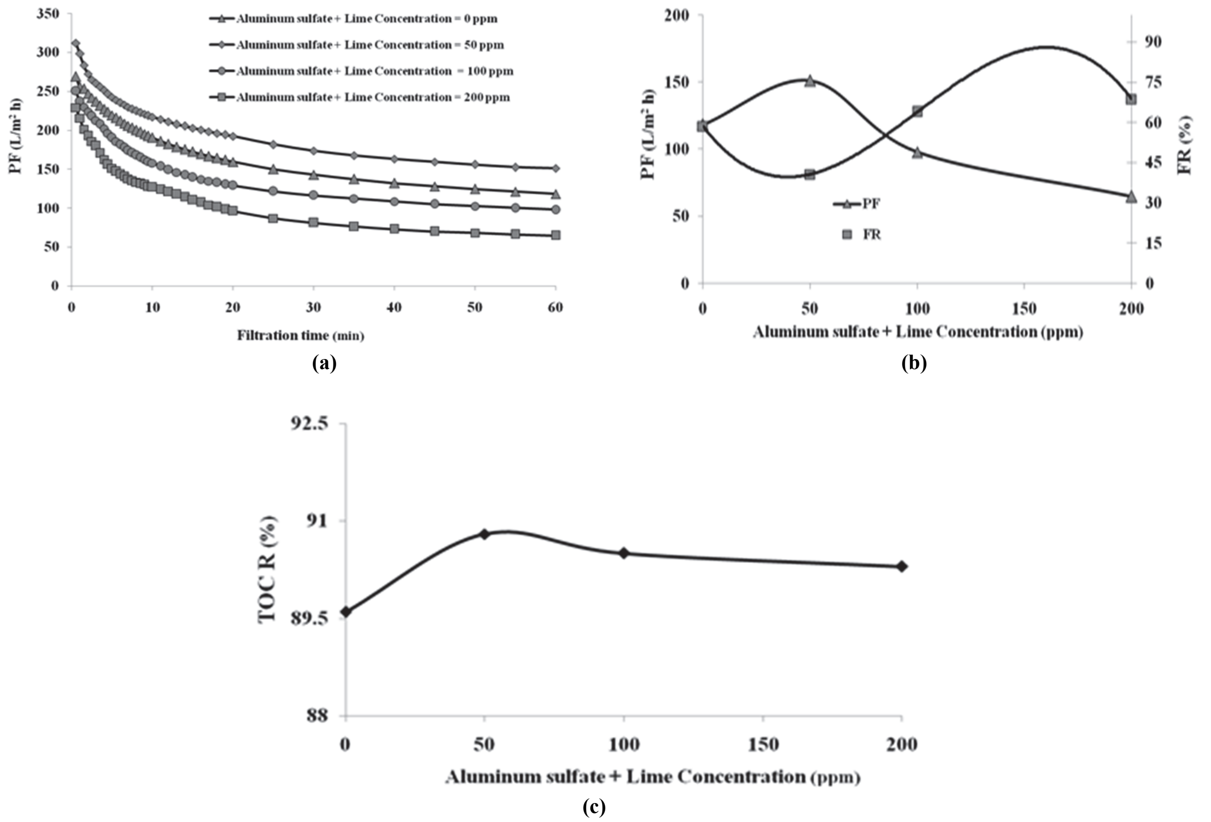


Fig. 5. Variation of: (a) PF with time , (b) PF and FR and (c) TOC R at the end of filtration with different aluminum sulfate plus slaked lime concentration in hybrid coagulation – MF system using mullite-allumina ceramic membrane

However, at higher concentration of coagulant agent, PF decline increases even compared with MF process. The reason of this phenomenon is charge reversal and restabilisation of oil droplets due to high dosage of aluminum sulphate and slaked lime. In fact, charge reversal (formation of the soluble anionic form $Al(OH)_4^{-1}$)) causes that large flocs and large oil droplets are not formed in synthetic wastewater because oil and $Al(OH)_4^{-1}$ have negative charge.

The results of Fig. 5b illustrate that the best concentration of coagulant agent is 50 ppm. At this condition, PF increases 21.74 % and FR decreases 17.87 % compared with MF process. The same reason as that of coagulation with aluminum chloride salt can be presented.

The results of TOC R as presented in Fig. 5c show that by increasing aluminum chloride concentration up to 50 ppm, TOC R increases up to 90.8 %. However, further increasing coagulant concentration from 50 to 200 ppm, decreases TOC R from 90.8 % to 90.3 %. Therefore, aluminum sulphate concentration of 50 ppm can be considered as the best operating condition. Fig. (6a) identifies reduction of PF decline by addition of coagulant agents concentration up to 200 ppm because of sweep flocculation. As shown in Fig. (6b), by increasing ferrous chloride plus slaked lime concentration from 0 to 200 ppm, FR decreases at the end of filtration from 58.5 % to 17.84%. This phenomenon indicates that complete coagulation at high concentration does proceed. In addition, high dosage of ferrous chloride plus slaked lime enhances coagulation process and large flocs are formed and FR decreas (Duan, and Gregory, 2003; Zahrim et al., 2011; Unlu et al., 2009). However at the best condition (200 ppm), PF increases 79.64 % compared with MF process at the end of filtration. The results illustrate that at high dosage of ferrous sulphate (200 ppm), charge reversal and restabilisation of oil droplets by formation of the soluble anionic form $Fe(OH)_4^{-1}$ does not occur.

Fig. 6c shows that maximum TOC R is 92.5 % at 200 ppm coagulant concentration. In fact, at the best condition (200 ppm), TOC R increases 2.9 % and at the worst condition (50 ppm), TOC R increases 1.5 % compared with MF process. As represented in Fig. 7a, PF decline decreases by increasing ferrous sulphate plus slaked lime concentration up to 50 ppm because sweep flocculation occurs and large flocs are formed a highly porous cake layer over the membrane surface by a low attractive energy.Further increasing coagulant concentration up to 200 ppm, raises PF decline because at high ferrous sulphate concentration, charge reversal of oil droplets occurs.

The best concentration of ferrous sulphate plus slaked lime is 50 ppm because as shown in Fig. 7b, at the end of filtration, PF increases 58.57 % and FR decrease 35.62 % compared with MF process.

Fig. 7c illustrates that by employing the hybrid coagulation – MF process with 50 ppm ferrous sulphate, TOC R increases from 89.6 to 92 %. The results indicate that at high dosage of ferrous sulphate (100 ppm), charge reversal and restabilisation of oil droplets by formation of the soluble anionic form $Fe(OH)_4^{-1}$ occurs.

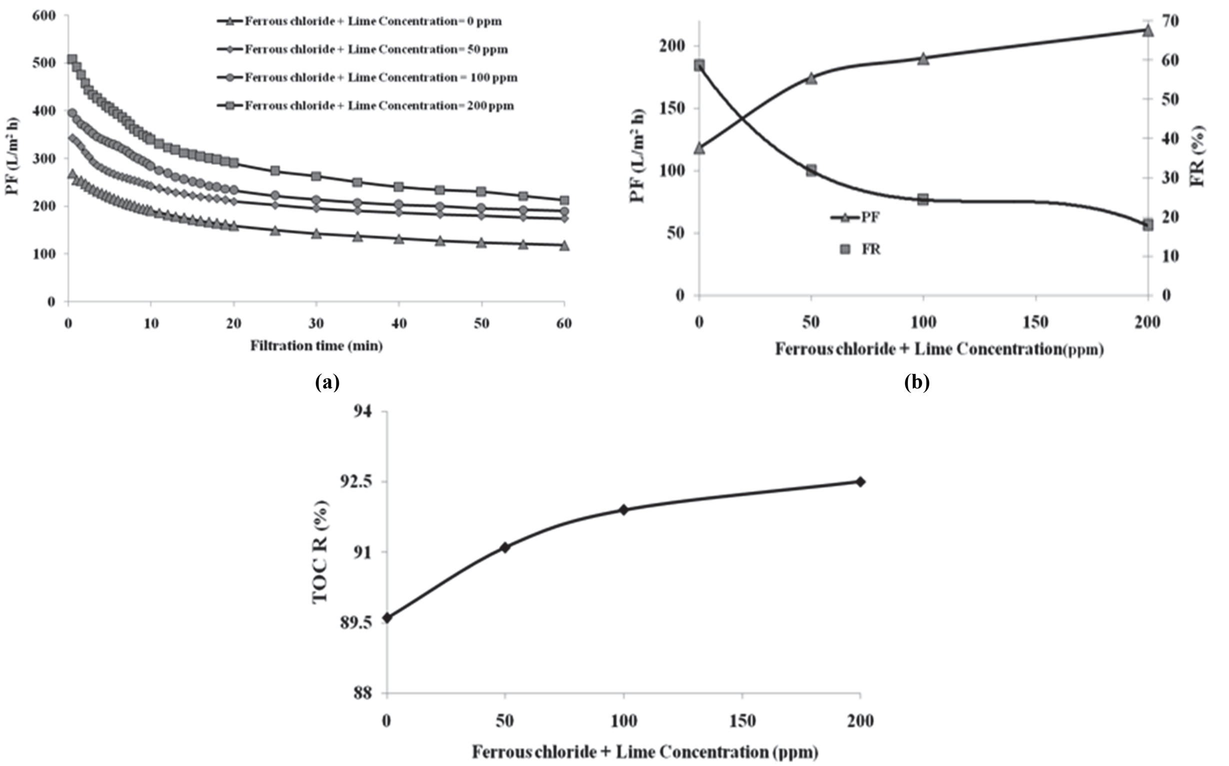


Fig.6. Variation of: (a) PF with time , (b) PF and FR and (c) TOC R at the end of filtration with different ferrous chloride plus slaked lime concentration in hybrid coagulation – MF system using mullite-allumina ceramic membrane

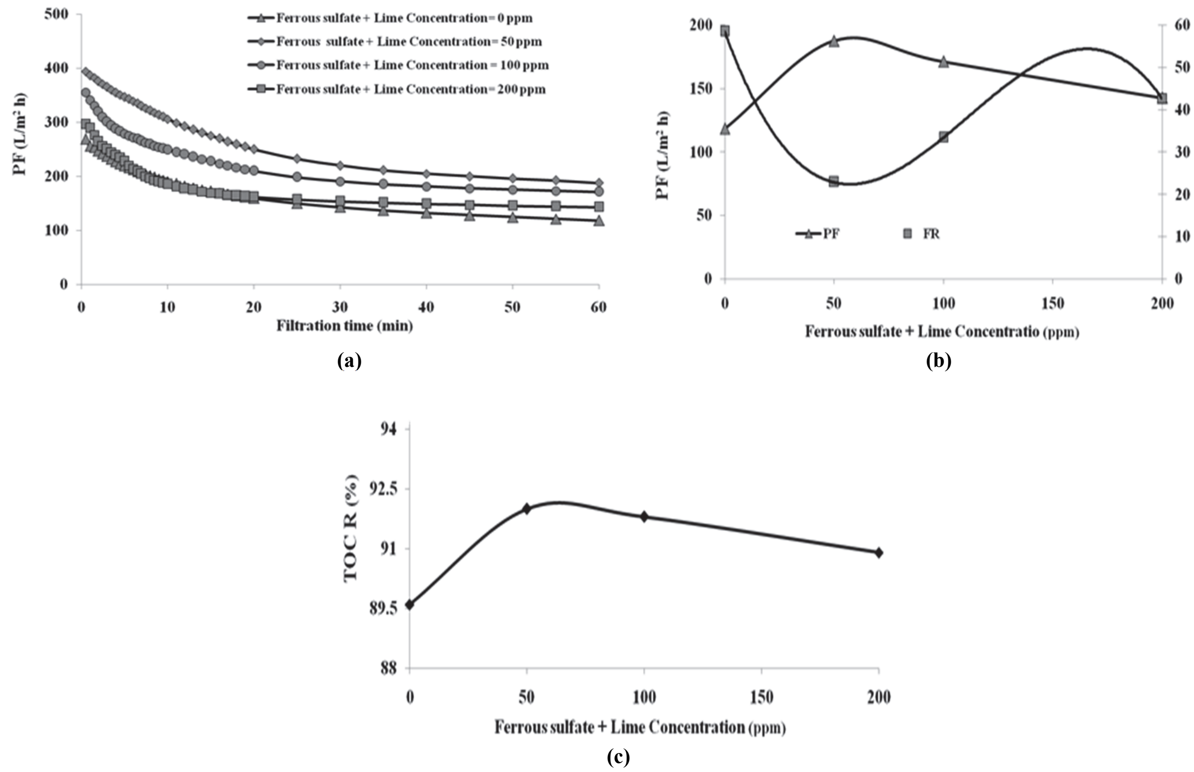


Fig.7. Variation of: (a) PF with time , (b) PF and FR and (c) TOC R at the end of filtration with different ferrous chloride plus slaked lime concentration in hybrid coagulation – MF system using mullite-allumina ceramic membrane

4.2. Analysis of results

In summary, the results of the hybrid coagulation – MF process using four coagulant agents at the best condition are listed in Table 2. These results indicated that at the best dosage of coagulant agents, sweep flocculation occurs, therefore large flocs with highly porous cake layer and low attractive energy between cake layer and membrane surface formed. In addition, large flocs do not pass through the membrane pores, therefore TOC R increases.

In final, it can be said that coagulant agents improve the membrane performance at low dosage (50 ppm) for ferrous sulphate and aluminum sulphate, mean dosage (100 ppm) for aluminum chloride, and high dosage (200 ppm) for ferrous chloride. At the best conditions in all experiments (200 ppm of Ferrous chloride), PF increases from 118.32 to 212.55 (L m^{-2} h^{-1}), FR decreases from 58.5 % to 18.72 % and TOC R increases from 89.6 % to 92.5%.

By considering low dosage of aluminum and iron salts in coagulation-MF process and significantly increasing of PF, the coagulation-MF process is economical. As an environmental protection view, the sludge of coagulation in this process, has free and complexed aluminum that could be recovered because they are toxic and can be used again. Also, for disposal of them to land or others locations, environmental regulations should be considered. On the other hand, in the coagulation process, sludge contains the suspension of inorganic and organic substances typically, hydrated aluminum oxide, and iron oxide. The recovery of the coagulant has high economic advantage and is recommended as a suitable treatment option for the disposal of wastewater sludge.

Table 2. Performance of the mullite-allumina ceramic membrane in coagulation – MF hybrid process for treatment of the synthetic wastewater at the best operating conditions

Coagulant	***PF*** ***(L m^{-2} h^{-1})***	***FR*** ***(%)***	***TOC R*** ***(%)***
No coagulant	118.32	58.5	89.6
Aluminum chloride + Lime (100 ppm)	164.59	33.02	91.4
Aluminum sulfate + Lime (50 ppm)	151.2	40.63	90.5
Ferrous chloride + Lime (200 ppm)	212.55	17.82	92.5
Ferrous sulfate + Lime (50 ppm)	187.62	22.88	92

5. Conclusions

In this work, in-line coagulating method has been employed in MF process by synthesized mullite-alumina MF membranes for treatment of synthetic oily wastewaters. Aluminum and iron salts with slaked lime have been used as coagulant agents.

All the experiments for the coagulation – MF process were carried out at this condition for 60 min: pressure of 3 bar, cross flow velocity of 1.5 m s^{-1} and temperature of 35 ºC.

Results showed that at suitable concentration of coagulant agents, due to sweep flocculation by formation of large flocs and the reduction of attraction energy between oily droplets and membrane surface, PF decline of membranes decreases. Of course, at higher concentration of coagulant agents, PF decreases because of charge reversal and restabilisation of oil droplets. Therefore, large flocs were not formed and oil droplets filled the membrane surface and pores. The results identified that iron salts have better performance compared with aluminum salts.

The best results were obtained for the hybrid coagulation – MF process with 200 ppm of ferrous chloride plus slaked lime. At this condition, PF increases 79.64 %, TOC R increases 2.9 % and FR decrease 40.68 % in comparison with MF process without coagulant agents.

The lowest performance in coagulation-MF process was observed for 50 ppm of aluminum sulfate plus slaked lime. At this condition, PF increases 27.79 %; TOC R increases only 0.9 % and FR decreases 17.87 % related to MF process.

Coagulation-MF process is economical by considering low dosage of aluminum and iron salts in coagulation-MF process and significantly increasing of PF. In addition, the recovery of the coagulants has high economic advantage and is recommended as a suitable treatment option for the disposal of wastewater sludge.

Nomenclatures

C - Concentration (mg L^{-1})
d-Internal diameter of tubular membrane (m)
FR - Flux reduction (-)
L - Tubular membrane length (m)
P - Pressure (Pa)
PF - Permeation flux (L m^{-2} h^{-1})
PFwi - permeation flux of distilled water for fresh membranes (L m^{-2} h^{-1})
PFww - permeation flux of distilled water for fouled membranes (L m^{-2} h^{-1})
R - Rejection (-)
t -Time (s)
T -Temperature (◦C)
TOC - Total Organic Carbon (mg L^{-1})
CFV - Cross-Flow Velocity (m s^{-1})
P - Pressure gradient (Pa)

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