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ARTICLE TYPE

Emulsified oily-waste water: An approach to the pretreatment with inorganic salts and treatment using two indigenous membrane modules

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Present study proposes the application of high sheared membrane modules in separating the oil and water from its emulsified form. Moreover, the assessment was carried out with the oil-in-water (o/w) emulsion after being treated with different electrolytes and the results from the treated feed to membrane were compared with the untreated feed to the membrane. Two high sheared modules, called turbine flow membrane module (TFMM) and radial flow membrane module (RFMM) were compared to understand the superlative performance in removing the oil from its o/w emulsion (either treated or untreated) using 25kDa polysulfone (PSf) membrane at different temperatures as well as pressures. It was observed that the permeate flux is 30-38% higher in all cases with TFMM, depending on operating temperature and pressure. Furthermore, among the electrolytes used, 15% sodium slufate (Na_2SO_4) solution shows maximum of 26% oil removal from emulsion, while TFMM shows 45% higher permeate flux compared to RFMM with this pretreated feed to the module.

Introduction

Oil is nowadays one of the acrimonious components of wastewater that is continuously polluting the water because of increased urbanisation and industrial revolution in all over the world. Furthermore, the issues with the oily wastewater manifolds, once the oil is getting mixed with the water to form a homogeneous mixture in presence of emulsifiers, called emulsion. Mainly two types of emulsion can be formed in case with the oily wastewater - one is thermodynamically stable microemulsion consisting of smaller oil droplets (radii in the range 0-100 nm) and another is kinetically stable macroemulsion having larger oil droplets (0.05-100µm)[1,2]. Several industries produce oil contaminated emulsified wastewaters include heavy metal industries, paint industries, textile industries, refineries, petrochemical industries, food industries, chemical manufacturing industries, allied industries and many others[3]. The formation of emulsion gets increased due to the presence of contaminants like silt, metal particles, emulsifiers, cleaners, soaps, solvents, and other residues. Therefore, without proper measures if this wastewater is discharged to urban sewerage system, it ultimately conveys the water to some river or sea manifesting imbalance in aquatic flora and fauna. Moreover, the drainage of such oily wastewater populates hydrocarbons in the aquatic environment and perturbs the aquatic life by attenuating the entrance of sunlight through the surface of the water. Phenols, polyaromatic hydrocarbons (PAH) and many other components of oily wastewater that ultimately accumulated in our every day's water resources, are mutagenic as well as carcinogenic for human being[4]. Hence, the discharge of such hazardous contaminants in oily wastewater needs to be prevented and taken care off.

Treatment of the oily wastewaters according to the environmental discharged standards (oil content less than 5 ppm) requires various oil treatment systems[5,6]. So far different strategies have been adopted in the treatment of oily wastewater. There are different conventional technologies adopted by several water treatment fraternities attributing to the separation of oil from oil-water emulsion. Some of these schemes are gravity separation, API oil-water separator followed by skimming, dissolved air flotation, de-emulsion coagulation and flocculation[7–9]. Gravity separation process followed by skimming is fairly effective to get rid of free oil from wastewater. API unit has been widely accepted as an effective, low cost, primary treatment step. However, these methods are not effective for removing smaller oil droplets and emulsions attributing to thermodynamically stable microemulsion. However, the oil that adheres to the surface of solid particles in contaminated oily wastewater could be effectively removed by sedimentation. Dissolved air flotation (DAF), the mostly used treatment unit for oil-water emulsion, uses air to increase the buoyancy of smaller oil droplets through continuous bubbling of air from the bottom of the tank in order to enhance the rate of oil-water separation. The influent emulsified oil of DAF is getting detached from its mixture with water, called demulsification, either chemically, or thermally, or by both together. DAF units typically employ chemicals to promote coagulation and to increase flock size to facilitate separation[6,8] apart from relying solely on the buoyancy force. All these conventional systems based on physical and chemical principles, indeed, cannot give an absolute guarantee in effective separation attributing to an improved effluent quality. However, high consumption of chemicals in coagulation makes these processes costly and even sometimes the unutilised chemicals are also found in the final wastewaters as contaminant. Hence, the eradication of such chemicals from water becomes one of the primary challenges. Moreover, the time dependent coagulation process might attain a partial demulsification, which ultimately fails to reduce the oil contaminant from the water.

In order to mitigate such limitation with the primary treatment techniques for oily waste water treatment, Hockenberry and Lieser[10] had applied membrane separation technique along with the conventional heat pretreatment to demulsify the emulsion and separating oil from water. They had applied ultrafiltration followed by the reverse osmosis process, where the separation of surfactants from oil-water interface attributes to the demulsification process. It was observed that the reverse osmosis process ultimately results almost clean oil. In the subsequent year, Salahi et al.[6] adopted similar approach, where the oily wastewater was treated using combined ultrafiltration and reverse osmosis process manifesting almost 95-100% of oil and grease content. However, one of the limitations with any membrane separation process is membrane fouling, sometimes which is irreversible and makes the process cost intensive. Especially, with the oily wastewater the primary issue is the adsorption of oil over the membrane surface that eventually reduces the performance of the membrane along with its longevity[11]. However, in presence of surfactant in case of emulsion the scenario is something different. According to Panpanit and Visvanathan[11], with an increase of bentonite clay concentration in oil in water emulsion (o/w) the resistance over the membrane initially decreases and goes through a minimum. In a recent study, same fact was supported by Kiss et al.[12], where they had seen that the increased concentration of emulsifier reduces the fouling of the membrane due to oil. Moreover, the performance of the process depends on the nature of the emulsion and the materials for the membrane selected. In 2006, Shu et al.[13] had fabricated a ceramic supported polyamide/polyvinyl alcohol thin film composite membrane for the treatment of o/w microemulsion. According to them, with this fabricated membrane the fouling of the membrane can be mitigated enormously with almost 99% oil rejection even with such stable microemulsion. However, the specialised form of membrane fabrication sometimes increases the overhead cost of the process attributing to an urge for the comparatively low cost simple approach in order to combat with the fouling. One of the commonest techniques in reducing the fouling of the membrane is an increase in the shear rate over the membrane surface that ultimately reduces the fouling after sweeping away the adsorbed oil from the surface. Li et al.[14] had studied the recovery of oil from o/w emulsion using rotary disk filtration system. According to their study, the rotation of a smooth membrane or the vane attached membrane removes the possibility of coalescence of oil droplets and resists the formation of bigger oil droplets. Therefore, the formation of secondary layer over the surface of the membrane could be eradicated completely by the shear enhanced membrane, especially with the vane attachment, attributing to better oil recovery. However, one of the key considerations with the shear enhanced membrane is the energy consideration that eventually increases the accumulated cost associated with the process. However, energy expenses involve the cost to rotate the membrane attributing to additional accessories' cost. In 2014, Putatunda et al.[15] had fabricated a high sheared membrane module, where the vanes can be rotated using the introduced feed flow energy and thus reduces the additional expenses associated with the adjoining of other machineries in order to increase shear rate over the surface.

In the present study the oily emulsified wastewater, synthesised using spent oil collected from local automobile garages amd water, has been primarily treated with four different salts, alum, sodium chloride, sodium sulphate and magnesium chloride to demulsify the oil-water emulsion. Subsequently the emulsified wastewater as well as the sodium sulphate treated wastewater, which gives better result compared to other electrolytes, has been sent to two indigenous high sheared membrane module, namely radial flow membrane module (RFMM) and turbine flow membrane module (TFMM), equipped with 25 kDa polysulfone (PSf) ultrafiltration (UF) membrane for better removal of oil with higher throughput.

Material and methods

Materials

0.025 m^3 (2.5 L) of emulsified wastewater as feedstock solution was prepared after mixing spent oil with water in the ratio of 1:200) aided by an emulsifier, home detergent (1% w/v). Detergent was procured from local grocery shop, and spent mobil has been collected from local gas stations with car wash facility. Ultrapure deionised water was collected from the Arium RO unit followed by Arium 611DI ultrapure water system (Sartorius, Göttingen, Germany). Sodium chloride (NaCl) (CAS No. 7647-14-5), sodium sulphate (Na_2SO_4) (CAS No. 7757-82-65), magneseum chloride ($MgCl_2$) (CAS No. 7791-18-6) and alum (CAS No. 7784-24-9) used as electrolytes in order to destabilize the emulsion had been procured from Merck (Mumbai, India). Sodium hypochlorite (NaOCl) (CAS No. 7681-52-9), sodium hydroxide (NaOH) (CAS No. 1310-73-2) and ethanol (CAS No. 64-17-5) were also procured from Merck (Mumbai, India).

Destabilization of emulsion and the subsequent membrane operation

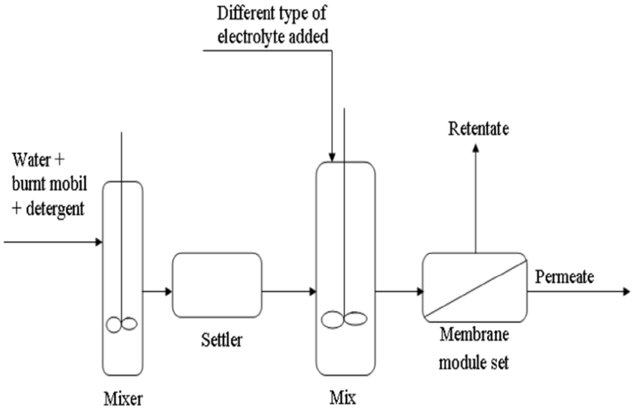

Fig. 1 Flow diagram for the treatment of oily waste water

2% (w/v), 5% (w/v), 10% (w/v) and 15% (w/v) solutions for each of the electrolytes were added to the emulsified solution at ambient temperature of around 30-35°C and the solution was stirred at 100 rpm stirrer speed for 1.5 hrs. Fig. 1 shows the schematic representation of the process for emulsified oily waste water treatment. The demulsified feed (emulsified water treated with 15% sodium sulphate solution) was introduced in turbine flow membrane module (TFMM) and radial flow membrane module (RFMM) fitted with 25 kDa polysulfone (PSf) membrane (0.041 m effective diameter, procured from Koch Membrane, USA).

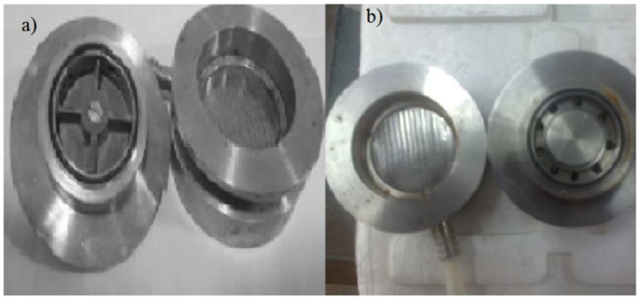

Fig. 2(a) Turbine flow membrane module (TFMM) **(b)** Radial Flow membrane module (RFMM)

Furthermore, to study the performance of the two aforesaid membrane modules in comparison to salt pretreated emulsion as a feed to the membrane module, emulsified oily wastewater without such pretreatment has been introduced in both RFMM and TFMM. However, prior to experimental runs, both the membranes were subjected to water compaction at a trans-membrane pressure (TMP) (ΔP) of 0.6 MPa, higher than that of experimental TMPs (0.3 MPa, 0.4 MPa and 0.5 MPa) in order to avoid any changes in the pores' size during the experimental runs. Compaction of the membrane was ensured after 5400 s (1.5 hrs), when the water flux became stable for a substantial period of time. Total petroleum hydrocarbon (TPH) present in emulsion has been analysed with the standard ASTM D3173-75 methods. TFMM and RFMM[15] (fabricated by Concept International Ltd, Kolkata, India), both the modules were constructed of SS316, has been shown in Fig. 2.a and 2.b. A plunger pump (Maker: American Sparing & Press Workshop Pvt. Ltd., Mumbai, 3 H.P.; Maximum Pressure: 400 psi) is attached with the module to withdraw the pretreated oily feed solution from a jacketed feed tank (Capacity: 0.005 m^3 or 5 L) and introduced it to the membrane module. During experiments the temperature of the feed solution had been maintained at 15, 20, 25 and 30°C. The pressure over the membrane was controlled using a back pressure regulator valve (BPRV) fitted in the retentate line.

The performance of the module was studied at a TMP of 0.3, 0.4 and 0.5 MPa. Fig.3. shows a schematic diagram of the experimental setup used for experiment. Once an experimental run was completed, the fouling was estimated measuring the hydraulic resistance. Membrane was washed with a solution of 10% (v/v) n-hexane in water, which resulted in at least 90-95% water flux recovery. Finally, the membrane was second washed with 1(N) NaOH and 2% (w/v) NaOCl solution in order to enhanced regaining of the flux. The primary wash with n-hexane was continued for an average duration of 2 hrs until the desired flux regain was achieved, while the secondary wash cycle was continued for 1.5 hrs on average basis. After the completion of experiment, the membrane was stored with 20% (v/v) ethanol solution for subsequent use.

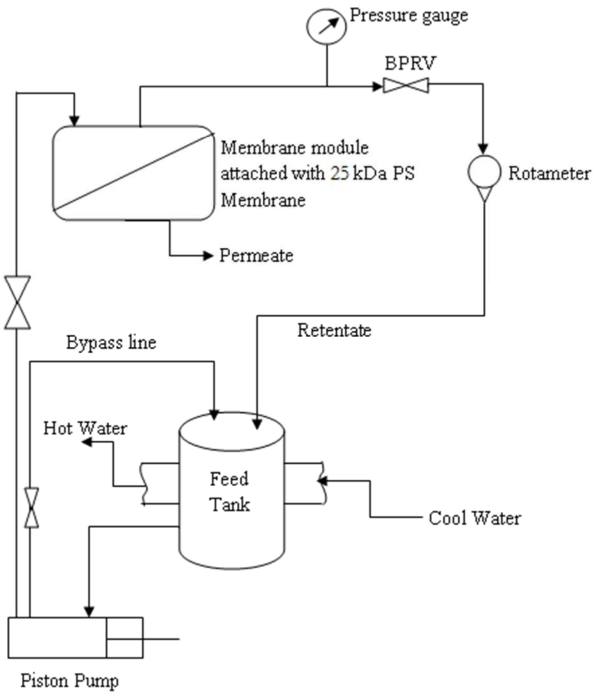

Fig. 3 Schematic diagram for the experimental setup used in this case

Result and Discussions

Effect of different salts on emulsified wastewater

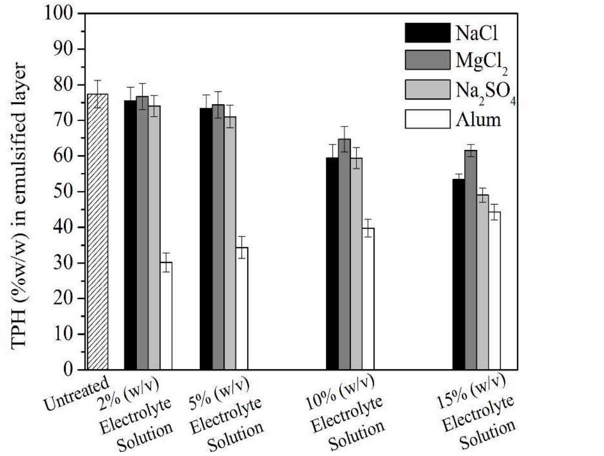

Fig.4 Percentage of TPH (with a S.D. of 5% error margin) in the organic phase collected from the separator after salt dosing. Data were collected after 72 h of salt dosing to the emulsified oily water

Fig. 4 shows the variation of total petroleum hydrocarbon (TPH) from spent fuel present in the aqueous layer after addition of different salts, such as alum, sodium chloride, sodium sulphate and magnesium chloride, as electrolytes in the emulsified oil in water system. The reduction of TPH in the aqueous layer confirms the demulsification process, leading to a formation of top oily layer. From the figure it can be seen that addition of sodium chloride, sodium sulphate and magnesium chloride decreases TPH with an increase in the salt concentration, while, alum follows an opposite trend. After keeping the emulsion in bench for 72 hr with added electrolytes, three distinct layers had been observed. The top layer consists of lighter oil, the middle layer consists of rest of the emulsified oil-in-water solution and the bottom portion was the sediment of suspended solids, mainly dirts. Continuous addition of different salts with increased concentration to the emulsion altered the height of uppermost oil layer, which had been noticed visually. One of the basic concepts with the emulsion is the idea of the charge distribution over the surface of the colloidal particle that could be explained leading to a formation of electrical double layer as explained by Helmholtz in 1850. The detergent used in the present study is the domestic caustic detergent consisting of sodium and sulfonates/sulfates group.

Addition of salts decreased the zeta potential (measured using Malvern Nano-ZS90 zeta analyzer), which ultimately leads to a coalescence of smaller oil droplets to form larger droplets. Due to increase in the droplet size, the droplets float at the top of the aqueous surface[16] as lighter oily layer according to Stoke's law (Eq. 1). Moreover, the decrease of zeta potential compressed the electrical double layer, i.e. the Debye length (Eq. 2), which can be estimated after knowing the ionic strength (Eq. 3) of the solution with added electrolytes. Table 1 shows the ionic strength of the electrolytes in the o/w emulsion.

From Fig. 4, it is evident that 15% Na_2SO_4 provides maximum reduction in TPH in residual emulsion layer beneath the top oily layer. As the oil droplets are being negatively charged, therefore, the accumulation of positive ions because of the added electrolytes might compress the electrical double layer to retain electroneutrality. This leads to an increase in the Van der Waals' (Eq. 4)[17] force of attraction between the dispersed phases and electrolytes. After the ions being adsorbed on the oppositely charged surface of the dispersed phase in an emulsion, the ionic compressibility was getting reduced[19]. More compression will produce more internal repulsive energy to ensure the stability of the emulsion. Addition of alumn will release Al^{3+} ion in the aqueous solvent, which is adsorbed over the charged surface of the colloidal particles and reduces the surface potential. As a result it reduces the potential barrier by charge neutralisation, and through Van der Waals forces dispersed phases will aggregate. According to Kudoh et al.[20], the ionic compressibility is proportional to the slope of ionic radius versus logarithm of bond strength (Z/Ɲ), and it is 0.155 x 10^{-11} m^2 N^{-1} for Al^{+3}. Moreover, with excess alumn concentration in the solvent, there is a charge reversal and the $SO4^{-2}$ ion of compressibility 5.232 x 10^{-11} m^2 N^{-1} gets attracted towards the newly formed positively charged dispersed phase. Hence, increased concentration of alumn shows less salting out destabilisation of the emulsion (Fig. 4) as it shows more compressibility (almost 50 fold) to the emulsion system compared to the other electrolytes added. At a lowest concentration of 2% (w/v), it removes almost 39% of oil from emulsified solution.

Table 1 Ionic strength of the dosed electrolytes with varied concentration in the emulsified oily waste water

Electrolytes	Concentration dosed to o/w emulsifiedwater			
	2% (w/v)	5% (w/v)	10% (w/v)	15% (w/v)
NaCl	0.34	0.86	1.71	2.57
$MgCl_2$	0.21	0.53	1.05	1.58
Na_2SO_4	0.14	0.35	0.70	1.06
Alum	0.04	0.11	0.21	0.32

On the contrary, other ions' (after addition of electrolytes NaCl, $MgCl_2$ and Na_2SO_4) effect follows the principle of double layer contraction. Fig. 5 shows the zeta potential for different electrolytes at a concentration of 15% (w/v). According to DLVO theory[17], the net potential for the interaction of the droplets is given by the summed value of Van der Waals energy of attraction and doubled layer energy of repulsion. The situation can be explained by two parameters; one, with the Debye length and the other one is the ionic radius. According to Evans and Wennerström[17], the potential for maximum interactivity occurs when for the distance of separation between two droplets in an emulsion is two times of the Debye length. In a more generic way, according to Quesada-Pérez et al.[18], the hydrated ionic radius of the salts would be more precise and overlapping of hydration zone will increase the possibility of coalescence. Eq. 5 shows the condition of interactive potential[18] along with the variation of hydrated radius for different ions. This attributes to the fact that Van der Waals attraction force becomes predominant with the first condition where the charged particles coalesce and destabilise the emulsion.

$$u_{oil} = \frac{2gr^2\left(\rho_{oil} - \rho_w\right)}{9\mu} \quad (1)$$

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_{rs} k_B T}{2000 e^2 I N_{Avogadro}}} \quad (2)$$

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2 \quad (3)$$

$$V_{VDW} = -\frac{H_{121}}{12\pi h^2} \quad (4)$$

Now if the dispersed phase radius is assumed to be unique for all the electrolytes apart from trivalent aluminium, the ratio $h/r_{hydrated}$ (Fig. 6) provides an idea of desalting operation efficiency with varied electrolytes. However, the ratio depends on how the diffuse layer is affected by the electrolytes after the addition of electrolytes, which in turn depends on the hydration energy of the electrolytes. The hydration energy of added electrolytes as given below were calculated using thermodynamic Born-Haber cycle[21]:

$MgCl_2$ (2521 kJ mol^{-1}) > Na_2SO_4 (1387.1 kJ mol^{-1}) >NaCl (771 kJ mol^{-1})

$$V_{rep} = \begin{cases} 0 : h < \left(r_{hydrated} + r_{dispersed}\right) \\ \infty : h \geq \left(r_{hydrated} + r_{dispersed}\right) \end{cases} \quad (5)$$

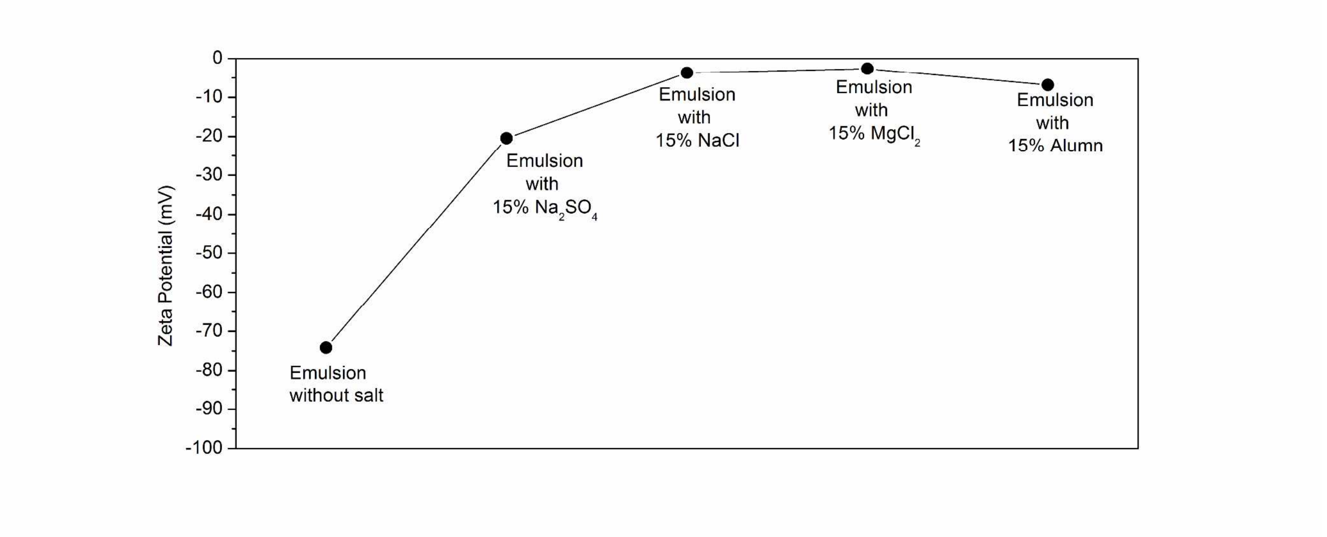

Fig. 5 Zeta potential (mV) for different electrolytes at 15% (w/v) concentration

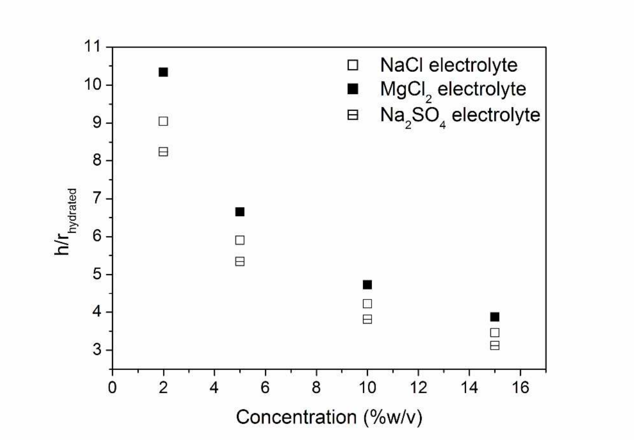

Fig. 6 Variation of $h/r_{hydraulic}$ with the electrolytes' concentration dosed in the emulsified oily wastewater

From the above series, it is well understood that NaCl will readily release ions as the hydration energy is much low compared to other electrolytes. Therefore, it apparently seems that more release of positive ions in this case after NaCl addition decrease the Debye length attributing to the destabilisation. However, according to Fig. 4, good agreement on destabilisation is shown after addition of Na_2SO_4. According to Narayan[19], one of the reasons towards the stability of lattice also depends on the ionic compressibility. Aforesaid more ionic compressibility leads to more repulsion and therefore more stable ionised condition once the electrolytes get hydrated. The compressibility of SO_4^{2-} (5.232 x 10^{-11} m^2 N^{-1}) is almost twice of Cl^- (2.952x 10^{-11} m^2 N^{-1}), which attributes to more formation of ions from Na_2SO_4. As a result it imparts a significant contribution to the decrease of double layer followed by a coalescence of thee dispersed phase. Therefore, even at low concentration of Na_2SO_4 addition shows lower percentage of oil present in the emulsified form compared to chloride salts as shown in Fig. 4. However, 15% (w/v) Na_2SO_4 removes around 26% of oil from their emulsified form. On the contrary, solvation energy of $MgCl_2$ is much higher compared to both salts (approximately 2-3 fold) that potentially reduce the ionisation and henceforth the performance of $MgCl_2$ in demulsification compared to other two salts.

Comparative study on the effect of membrane, TMP and temperature on permeate flux during ultrafiltration (UF) of emulsified oily wastewater in TFMM and RFMM

Fig. 7 and 8 shows the variation of steady state permeate flux of treated or untreated wastewater with applied TMP after 30 min run at different experimental temperatures for TFMM and RFMM module respectively. One of the primary concerns in analysing the steady state flux variation with applied TMP is to depict the pressure at which the separation shifts from pressure driven to mass transfer controlled region. Aforesaid, with membrane separation the macromolecules are getting deposited over the membrane surface that increases the concentration over the surface. Hence, reverse concentration gradient acts against the applied TMP (Eq. 6 and 7) that changes the driving force from pressure driven to mass transfer driven[22]. With TFMM the permeate flux is almost 30-38% higher compared to RFMM in all possible conditions. TMP is employed over the membrane surface with the help of a flow restrictor, which is shown (Fig. 3) as backpressure regulator valve (BPRV) fitted with the retentate line.

$$Jc = Jc_p - \left(-D\frac{dc}{dz}\right) \qquad (6)$$

$$J = \frac{\Delta P}{\mu R} \tag{7}$$

Where, J is the permeate flux, c is the bulk concentration, c_p is the permeate concentration, D is the diffusivity of the solute in the solvent, z is the distance evaluated from the membrane surface to the bulk, ΔP is the TMP, μ is the viscosity of the solution and R is the total resistance over and within the membrane.

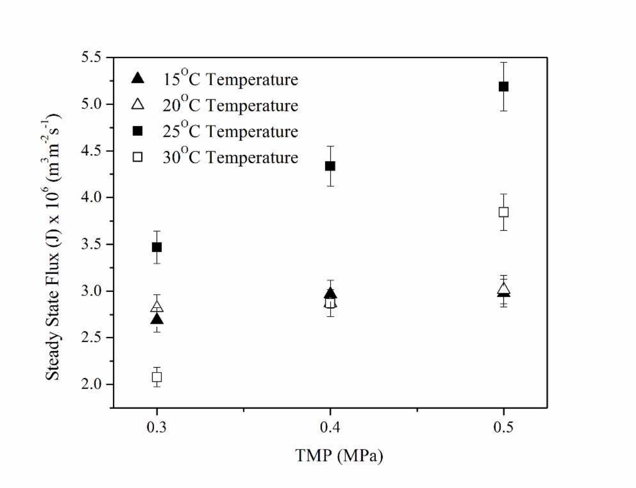

Fig. 7(a) Variation of steady state flux (<J>x 10^6 m^3 m^{-2} s^{-1}) from TFMM with varying TMP and feed temperature with the untreated emulsified wastewater

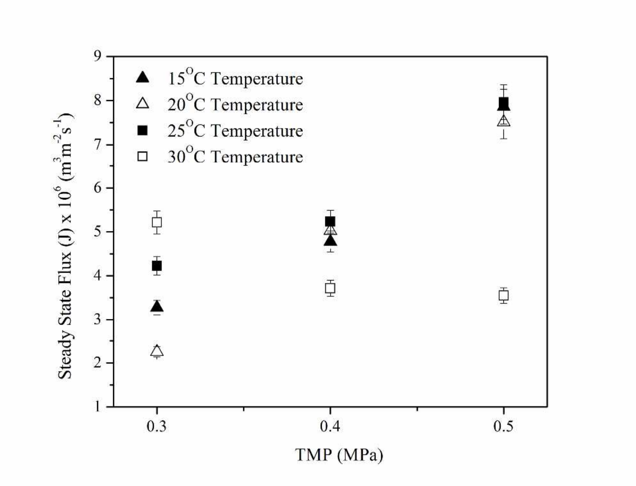

Fig. 7(b) Variation of steady state flux (<J>x 10^6 m^3 m^{-2} s^{-1}) from TFMM with varying TMP and feed temperature with the pretreated emulsified wastewater

In case of TFMM, if the applied TMP is high then it will restrict the rotation of the blades that ultimately results in reducing the sweeping action over the membrane surface and hence, less removal of the solutes from the membrane surface. Hence, increased TMP will increase the possibility for the deposition of the solutes over the surface followed by sticking of oil over the surface. The phenomenon is well understood from the contact angle measurement (using Kruss Drop Shape Analyser DSA25, Kruss GmbH, Hamburg), where it can be seen that after run the contact angle is increased by almost 1.5 fold attributing to a formation of hydrophobic surface because of sticking of oil on the surface. From Fig. 7(a) at low temperatures (15°C and 20°C), there is practically no increase in the steady state flux with the increased TMP. It is seen from the figure that only mere 8.3% increase in the steady state flux once the applied TMP increases from 0.3 MPa to 0.5 MPa. With the applied TMP the vanes are restricted to rotate and hence, the shear force over the membrane is getting reduced. Now according to Hoshyargar et al.[23], with increased shear stress the rate of shear is reduced with the emulsified o/w at 15°C-20°C. Hence, on the contrary low stress over the surface manifesting high shear rate attributes to an increased concentration over the membrane surface that imposes almost no slip condition over the surface. Therefore, at this temperature, the separation is limited by the mass transfer controlled region only instead of pressure driven process. However, the opposite effect was felt with the treated feed, where the oil is separated from water. With the oil without emulsified form the shear rate will increase with the shear force over the surface[23]. At high TMP the shear stress is reduced over the membrane attributes to a reduced shear rate and this depicts the less momentum transfer. This manifests reduced formation of gel layer over the surface and hence, the steady state flux in increased by almost 60% to 160% with the increased TMP (Fig. 7(b)).

In case of RFMM, the transport of the carried masses on retentate side occurs through eddy pockets, which eventually collapses under high pressure. Hence, the chance of formation of secondary layer by deposited oil is maximum on the membrane surface that restricts the passage of the water through the membrane. At low temperature, where the stability of emulsion is prominent attributes to a mere 15% increase at 0.5 MPa over the flux obtained at 0.3 MPa at low temperatures (Fig. 8(a)). For both of the modules, less TMP attributes to a high flow over the membrane that eventually increases the shear over the membrane surface in order to reduce the concentration polarization over the membrane.

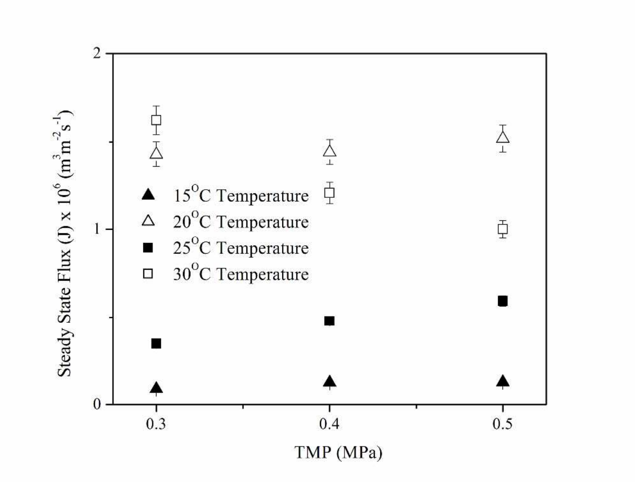

Fig. 8(a) Variation of steady state flux (<J>x 10^6 m^3 m^{-2} s^{-1}) from RFMM with varying TMP and feed temperature with the untreated emulsified wastewater

Furthermore, one of the primary concerns in any membrane separation process is the surface charge of the membrane that dictates the permeation along with other operating parameters. The membrane process here depends on primary four conditions

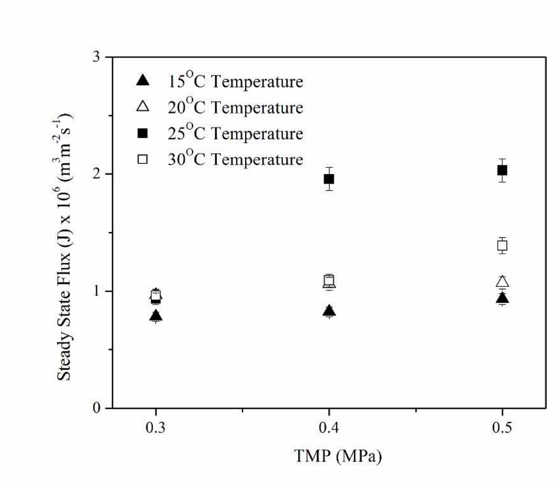

Fig.8(b) Variation of (<J>x 10^6 m^3 m^{-2} s^{-1}) from RFMM with varying TMP and feed temperature with the pretreated emulsified wastewater

that make the differences in permeation – a) membrane material b) shear environment over the membrane c) temperature of the feed and d) electrolytes' concentration. PSf membrane is hydrophobic in nature and repulses the negatively charged solutes because of the presence of strong polar sulfonated group[24]. Therefore, with the negative surface charge o/w emulsified form will be less prone to get attached with the negatively charged membrane surface. As a result, the population of counter ions gets increased over the surface. Subsequently, the osmotic pressure gradient will act in the direction away from the membrane surface to dilute the ionic strength in the mid-way between bulk and membrane surface. Hence, in case with the TFMM, at higher temperature, increase in TMP led to a substantial increase in permeation through the membrane by counteracting the reversed osmotic pressure developed. However, in case with RFMM, at high temperature (30°C) the flux gets reduced with increased pressure. With increase in temperature the electrophoretic mobility of the charged particles will increase, while there is no change with the zeta potential[25]. The charged dispersed phase with positive charges (Na^+) surrounding it (Stern layer) gets adsorbed over the negatively charged membrane surface increasing the resistance over the surface. In case of TFMM there is a tangential force over the membrane surface by the blades of the vanes that swept away the adsorbed solutes and hence reduce the polarization. While, in RFMM the mode of transport is because of the eddy transport and eddy ruptures under increased TMP. Therefore, ultimately after release, charged solutes settle down over the surface and increase the concentration polarization.

Aforesaid, with the increase in temperature, the electrophoretic mobility of the charged particle will increase while keeping zeta potential constant. This manifests more ionic concentration between bulk and membrane surfaces followed by an increase in the osmotic pressure. In this case, at 30°C and 0.3 MPa, with TFMM the steady state flux is lowest. Adsorption and hence back diffusion along with the strong upward osmotic pressure restrict the permeation. While, in case with RFMM this mobility gets disrupted because of the strong turbulence created over the membrane surface. This makes the steady state flux at this condition superior compared to the others. However, with increased TMP, this turbulence gets reduced along with the rupture of eddies and increases the mobility. In case with the TFMM highest permeate flux has been obtained for 25°C while this has been obtained at 20°C in case of RFMM. At 25°C the mobility gets increased, which might increase the osmotic pressure and at the same time the adsorbed layers' résistance, which can be taken care off by tangential shear by TFMM but not by eddies in RFMM. On the contrary, in RFMM at 25°C the steady state flux at different TMPs is lower than at 30°C with the untreated o/w emulsion. However, in this case the increased mobility is accompanied by the turbulence created within the module over the membrane. Possibly, turbulence imparts an additional force in conjunction with the inertia force due to mobility to the charged dispersed phase that is enough to overcome the repulsive force because of the double layer and ultimately helps to coalesce[26]. This coalescence results in the floatation of oil and reduces the possibilities polarization.

Comparative study on the effect of membrane, TMP and temperature on permeate flux during ultrafiltration (UF) of 15% (w/v) Na_2SO_4 treated emulsified oily wastewater in TFMM and RFMM

Fig. 7(b) and 8(b) illustrate the steady state flux after 30min run with wastewater, after being treated with 15% (w/v) Na_2SO_4, at different temperatures and TMPs using both TFMM and RFMM respectively. In case with the salt treated waste water the o/w emulsion breaks and the oil becomes free from water. Hence, colloid type charge distribution becomes neutralised that restricts the oil to stick over the membrane surface through electrostatic attraction. However, the oil shows an impermeable layer over the membrane surface that forms a secondary layer on the membrane surface. In case with RFMM, as seen with the untreated emulsion, at 25°C, the steady state flux is higher compare to the flux at 30°C attributing to an increased electrophoretic mobility leading to the adsorption of the solutes over the membrane through electrostatic attraction. However, at lower TMP the fluxes obtained at all the temperatures are equal. Here the maximum steady state flux obtained at 30°C is almost 33% higher compared to the steady state flux obtained at 15°C and 0.5 MPa TMP for untreated waste water. On the contrary, TFMM shows higher permeate flux for the treated emulsion, almost 45% higher than that of in the untreated one. One of the important observations here is that almost the same steady state flux was obtained at 30°C and 0.5 MPa pressure in case with the modules for both treated and untreated emulsified form. However, in case with the TFMM, at 30°C the steady state flux decreases with the increase in TMP. Apart from the electrophoretic mobility, one of the possible reasons might be because of less tangential shear due to increased back pressure on the blades. Hence, the secondary layer over the membrane surface due to oil can't be alleviated. This restricts the permeation through the membrane. Fig. 9 and 10 shows a comparative statement between TFMM and RFMM for the required pump energy to have 1ml of permeate collected across unit area of the membrane. According to Putatunda et al.[15] the equation for the fold increase is given by Eq. 8. It can be seen from the figures that with the untreated one (Fig. 9), RFMM required much energy compared to TFMM in order to obtain one ml of permeate across unit area of the membrane at 15°C and 0.3 MPa. However, with the increase in TMP, the energy consumption by RFMM gets reduced. On the contrary, an opposite could be observed in case with the treated feed (Fig. 10). As said before, the shear rate is decreasing with the increase in the stress in case of emulsion. Now, with the increase in TMP, as the stress component in TFMM was reduced followed by an increase in the rate, the energy requirement will be more compared to RFMM, where the energy is associated only with the eddy transport. Moreover, one of the substantial advantages with the RFMM is the rupture of the large eddies at high TMP that eventually releases energy in addition to the pump energy. Although the energy consumption is much higher in RFMM compared to TFMM with the untreated feed because of the presence of large colloidal droplets in case with the emulsion. In case with the treated feed at 30°C, due to the combined effect of less stress at 0.5 MPa TMP and the electrophoretic mobility, the energy requirement by the TFMM is much higher compared to RFMM. However, like untreated one, with the treated feed also, the energy consumption of RFMM is higher than that of TFMM manifesting TFMM's low energy consumption ability. Fig. 11 shows the FTIR spectrum for the retentate obtained after the emulsified oily water being treated with the membrane modules at 15°C and 0.5 MPa. The figure shows flattened peak in the vicinity of 3200 cm^{-1} is because of the stretching vibration in –OH due to hydrogen bonding of water with the electronegative oxygen atom in –C=O of acids. In the vicinity of 1720 cm^{-1} the peak for –C=O is observed because of the stretching vibration. However, there is a peak shift .for –C=O on the right side in the spectrum attributing to H-bonding with electronegative oxygen atom. Peak around 2840 cm^{-1} is because of stretching vibration in aldehyde's sp^3 hybridised state. Under radical environment the aldehyde groups are continuously morphed into its vinyl form attributing to a loss in such sp^3 hybridisation state[27]. Hence, the peak for such vibration is absent in case with the untreated emulsion. In the vicinity of 1100 cm^{-1} spectrum shows the peak for symmetric stretching vibration for S=O, which is primarily because of the detergent added contain SDS. However, salt treated feed to RFMM shows low transmittance compared to TFMM attributes to the more presence of SDS on the retentate side that are supposed to be permitted through the membrane because of low molecular weight.

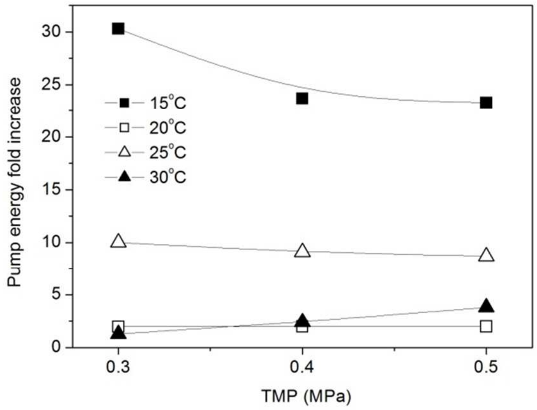

Fig. 9 Pump energy required per ml of permeate across unit area of the membrane for RFMM over TFMM at different untreated feed temperatures.

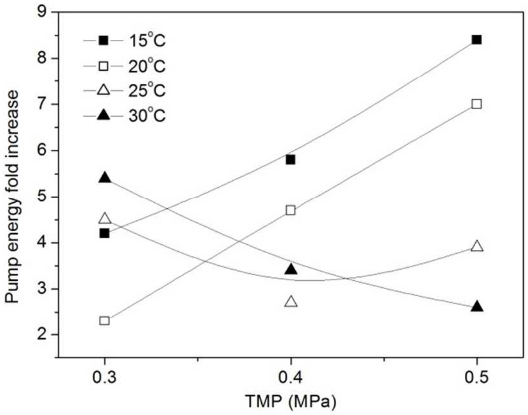

Fig. 10 Pump energy required per ml of permeate across unit area of the membrane for RFMM over TFMM at different treated feed temperatures.

$$\text{Pump energy fold increase} = \frac{E_{RFMM}}{E_{TFMM}} \qquad (8)$$

Where, E_{RFMM} is the pump energy required per ml of permeate collected across unit area of the membrane in RFMM; E_{TFMM} is the pump energy required per ml of permeate collected across unit area of the membrane in TFMM.

This manifests more secondary layer formation in case of RFMM compared to TFMM, which is at par with the steady state data obtained for both the modules. On the contrary, the band is absent in case of untreated emulsified form. The stretching vibration for S=O is sensitive to local environment changes[28]. Stretching vibration has been diminished because of its attachment with the polar aqueous environment manifesting the stable emulsion. Peaks in the range of 2300-2400 cm^{-1} are because of stretching vibration in linear coordination of CO_2[29,30]. With the untreated emulsion presence of acidic CO_2 attributes to a strong peak in this range. However, addition of Na^{+2} salt shows strong affinity for CO_3^{-2} leading to neutralisation. Hence, with the salt treated emulsified system these peaks are absent. However, in case with the untreated TFMM the absorption is more compared to RFMM manifests less neutralisation. With the emulsified form TFMM was found more productive in restricting the gel layer formation and hence, maximum salt ions can pass through the membrane. This attributes to less neutralisation showing more absorption of energy to have stretching vibration in CO_2 dissolved in the system.

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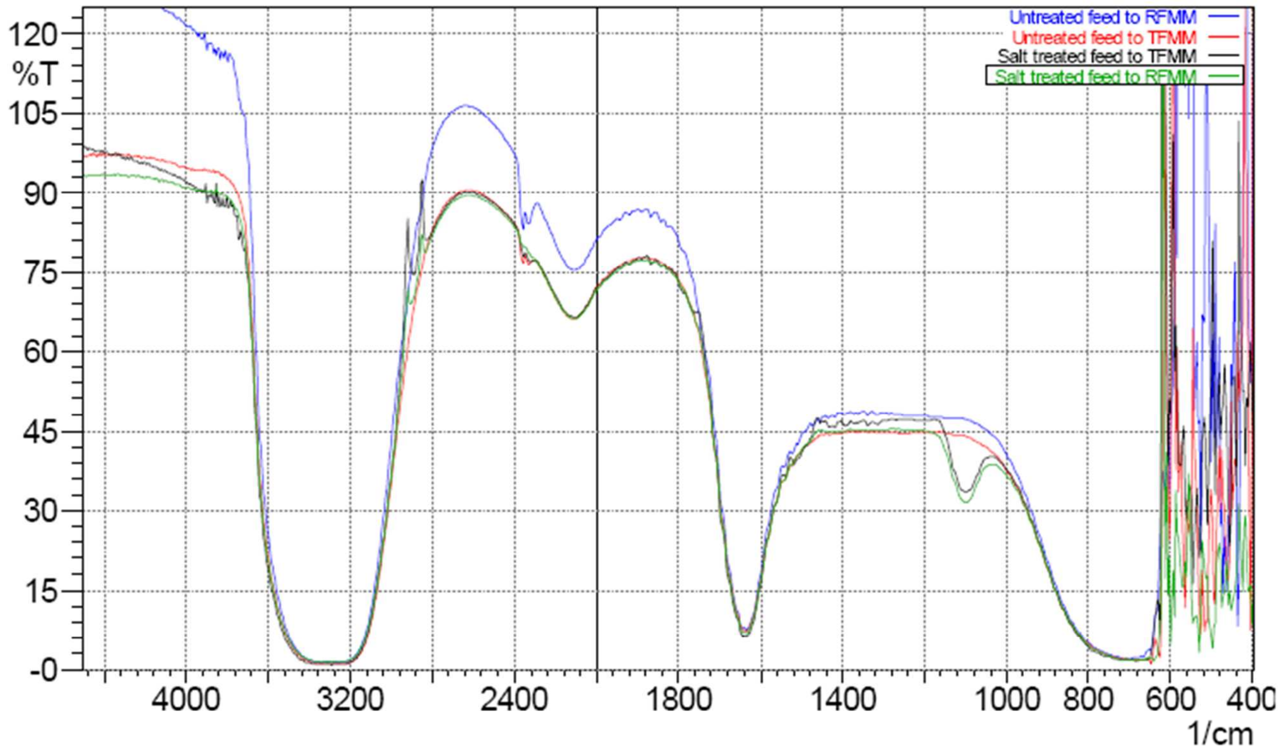

Fig. 11 FTIR chromatogram of retentate from TFMM at 15°C and 0.5 MPa

Significance test towards understanding the pretreatment of emulsified oily waste water using analysis of variance (ANOVA)

To understand the effect of salts and concentration on the demulsification procedure, a two factor ANOVA test was carried out based on null hypothesis. Table 2 shows the result of the ANOVA test. The significance test was done considering 5% confidence interval. The analysis shows that the F- value for different salts is 12.723, which is greater than the critical value with degrees of freedom 4. Therefore, it can be said that, the variation in the extent of demulsification between different salts is larger than the variation at different concentration level, for the same salts. While, on the contrary at different concentration level the variation is smaller than the variation obtained because of differences in the salts' chemical nature. From table 2 it can be seen that for the variation of salts, p-value (probability of making type-I error) is 0.001 (<0.05) that attributes to a significant effect on demulsification with the variation in salts. However, concentration of dosed salts shows p-value 0.18 (>0.05) manifesting less significant effect on demulsification. Therefore, based on the analysis it can be said that the selection of electrolytes is much crucial issue in effective demulsification compared to the variation in concentration.

Table 2ANOVA analysis on the effect of different salts and their concentration on demulsificationfollowed by separation

Source of Variation	SS	df	MS	F	P-value	F crit
Salts	2573.6	3	857.868	12.7238	0.00138	3.86255
Concentration of the salts dosed	412.499	3	137.5	2.03937	0.17889	3.86255
Error	606.802	9	67.4225			
Total	3592.91	15				

**SS: Sum squared error; df: degrees of freedom; MS: Mean square error*

Table 3 and 4 shows the significance test analyzing the effect of electrolyte treatment; temperature and TMPs on the steady state permeate flux obtained for both TFMM and RFMM respectively. In table 3(a) and 3(b), the F-values (Eq. 9 and 10) show that for RFMM the variation in the steady state flux because of different temperatures is much prominent compared to the electrolytic treatment employed to destabilize the emulsion, while effect of TMP is at par with the treatment (as the F-value is very close to the critical F-value). The later might be due to the osmotic pr-

Table 3aANOVA analysis on the effect of temperature on the salting out pretreatment and subsequent flux from TFMM at different TMPs

Source of Variation	SS	df	MS	F	P-value	F crit
Salting out treatment	19.1876	1	19.1876	2.3181	0.011	5.99
Temperature (^{O}C)	8.9178	6	1.4863	0.641	0.696	2.74
TMP (MPa)	37.0903	16	2.3181			
Total	65.1957	23				

Table 3bANOVA analysis on the effect of TMP on the salting out pretreatment and subsequent flux from TFMM at different temperatures

Source of Variation	SS	df	MS	F	P-value	F crit
Salting out treatment	19.1876	1	19.1876	3.736	0.125	7.71
TMP (MPa)	20.5459	4	5.1365	3.631	0.024	2.93
Temperature (^{O}C)	25.4622	18	1.4146			
Total	65.1957	23				

Table 4aANOVA analysis on the effect of temperature on the salting out pretreatment and subsequent flux from RFMM at different TMPs

Source of Variation	SS	df	MS	F	P-value	F crit
Salting out treatment	0.6836	1	0.6836	0.864	0.389	5.99
Temperature (^{O}C)	4.7485	6	0.7914	11.560	0.000	2.74
TMP (MPa)	1.0954	16	0.0685			
Total	6.5276	23				

Table 4bANOVA analysis on the effect of TMP on the salting out pretreatment and subsequent flux from RFMM at different temperatures

Source of Variation	SS	df	MS	F	P-value	F crit
Salting out treatment	0.6836	1	0.6836	6.391	0.065	7.71
TMP (MPa)	0.4278	4	0.1070	0.355	0.837	2.93
Temperature (^{O}C)	5.4161	18	0.3009			
Total	6.5276	23				

-essure that depends on the ionic strength of the charged dispersed phase (with positively charged stern layer) and the negative environment of the PSf membrane surface. However, in case with TFMM the treatment is much important to the flux compared to the temperature variation of the feed solution as F(=12.9)>Fcritical(=5.9) (table 4(a)). Moreover, the effect of TMP is much significant compared to the treatment of the oily water (table 4(b)). However, comparing the effect of temperature variation over the TMP variation, RFMM shows (F(=11.6)>Fcritical(=2.7)) that temperature variation is much significant to the flux compared to TFMM (F(=0.6)<Fcritical(=2.7)).

$$F = \frac{\text{Variation of the steady state flux because of the treatment of emulsified oily waste water}}{\text{Variation of the steady state flux because of the variation in temperature of emulsified oily waste water}} \quad (9)$$

$$F = \frac{\text{Variation of the steady state flux because of the treatment of emulsified oily waste water}}{\text{Variation of the steady state flux because of the variation in TMP of emulsified oily waste water}} \quad (10)$$

Conclusion

The present inspection depicts a contingent study on the application of two indigenous membrane modules RFMM and TFMM equipped with 25 kDa PSf membrane, for the treatment of emulsified oily wastewater (O/W emulsion) generated in automobile industry. One of the primary challenges with the emulsified form is the electrical double layer that may arises electrostatic adsorption of the charged phase onto the membrane surface, leading to a development of an osmotic pressure gradient and hence, repulsion. In addition, even after destabilization of the emulsion, after introducing the feed to the membrane module, the permeation depends on the presence of ions, their compressibility followed by the arrival of Van der Waals force. Here, TFMM gives around 3 fold increase in the permeate flux compared to RFMM with untreated emulsion and almost 4 fold increase with respect to the treated one. In another sense, one of the disadvantages with RFMM, especially with the treated feed is the quick shifting from pressure controlled process to mass driven process at any temperature. Hence, TFMM shows almost 53% increase in the steady state flux for treated feed over the untreated feed at 25°C. Moreover, with TFMM the maximum flux was found for the pretreated feed at 15°C, while energy requirement ratio is almost eight times for the RFMM compared to TFMM and this ensures the suitability of TFMM over RFMM in terms of lowest energy involvement to separate oil from water.

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Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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