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CHEMICALLY CLEANING OF UF MEMBRANES FOULED BY OILY WASTE WATER

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Abstract-The Ultra filtration membranes are used for treatment and reused of oily waste waters. The fouling of the ultra filtration membranes is caused due to inorganic and organic materials present in waste water that adhere to the surface and pores of the membranes and resulted in fouling and deterioration perforformance with increase in cost of energy and membranes replacement. In this experiment, Ultra filtration membranes fouling and cleaning were performed with oily waste water and selecting cleaning agents using laboratory scale cross flow membrane test unit. The result showed that the combination of cleaning agent that is metal chelating agent (Ethylene diamine tetraactetic acid) and an surfactant (sodium dodecyl sulfate (SDS) and sodium hydroxide were able to clean fouled membranes very effectively than the individual cleaning agent. The flux recovery percentage was found to improve with increasing cross flow velocity, temperature, pH and concentration of the cleaning solutions.

Keywords-ultrafiltration; fouling; cleaning; surfactant; oily waste water.

I. INTRODUCTION

The fouling of membranes is typically caused by inorganic and organic materials that adhere to the surface and pores of the membrane and result in deterioration of performance (reduce flux of the membrane) with consequent increase in costs of energy and membrane replacement.

A. Fundamental of Separation

The forces of interaction between the membrane surface and particles in the solution are important in understanding the fouling phenomena. The normal basis for quantifying particle surface interaction is DLVO theory where the particle surface interactions in aqueous environments could be predicted by the summation of van der Waals and electrostatic double layer forces. Reducing the interaction between the particles and the membranes as much possible can reduce the fouling phenomena. This can be achieved when the critical value (flux and pressure) arises as a balance between the hydrodynamic force driving solute towards the pore and electrostatic forces opposing the motion. Critical flux stems from the concept that the higher the flux the stronger is the drag force towards the membranes. The stronger concentration polarization and higher the compaction of particles. Critical flux is defined as the limiting flux value below which a flux decline over time does not occur.(1).the number of parameter influenced this critical flux have been discussed in detail can be found(2).It is maintained that if one operates below the critical flux the fouling can be avoided or minimized. The fouling is common to all types of membrane separation.

B. Fouling

Membranes fouling are an extremely complex phenomenon that has not been defined precisely. In general the term used to describe the undesirable formation of deposits on membrane surfaces. This occurs when rejected particles are not transported from the surface of the membrane back to the bulk stream. The foul ant are typically colloidal materials of one types or another and their properties and interaction with membranes dominant fouling /cleaning processes. Colloids are defined as fine suspended particles in the size range of few nanometers to few micrometers. Examples of common colloids sizes foulant includes inorganic(clay, silica salt and metal

oxides),organic natural and synthetic organics, biological(bacteria and other micro-organism) .The fouling of membrane can be divided into external surface fouling build –up of a cake/gel like layer on the upstream face of the membrane and pore blocking fouling(3).In dead end filtration system, the latter is divided into three types complete pore blocking (blocking a pore by a particle with approximately the same as the pore size),incomplete pore blocking(intermediate fouling) and standard pore blocking (gradual pore narrowing and constriction by particle that is much smaller than the pore size (4).
The fouling are classified in to three types on basis of fouling materials (5-8)
1, Inorganic fouling due to deposition on membrane surface of inorganic scales (mainly Baso4, caso4, CaCO3)
2, Organic fouling are due to natural organic material found in the process stream, proteins, carbohydrates, and humic acid.
3, Biofoulig due to microbial attachment to the membrane surface followed thereafter by their growth and multiplication in presence of adequate supply of nutrients that deposited on membrane surfaces.

C. Inorganic fouling

The term membrane scaling is commonly used in the precipitate formed is a hard scale on the surface of the membranes. Scaling usually refers to the formation of deposits of inverse-solubility salt such as caco3, CaCO3,, Silica and calcium phosphate. Inorganic scale formation can even lead to physical damage of the membranes, and it is difficult to restore membranes performance due to the difficulties of scale removal and irreversible membrane pore plugging (9)

D. Organic fouling

Organic fouling could cause either reversible or irreversible flux decline. The reversible flux decline, due to NOM Fouling, can be restored partially or fully by chemical cleaning (10)whereas the reversible flux decline cannot be restored at all even by rigorous chemical cleaning is applied to remove NOM.Membrane fouling in presence of NOM .Membrane fouling in presence of NOM can be influenced by membrane characteristics (8,11-14),including surface structure as well as surface chemical properties, chemistry of feed solution including ionic strength (15),Ph, the divalent ions, the properties of NOM,including molecular weight and concentration of monovalent ions and divalent ions(16,17),the properties of NOM,including molecular weight and polarity (8,13,18-19) pressure, concentration polarization and mass transfer properties of fluid boundary layer, These factors either increased or decrease the fouling rate as shown in Table 1.

	Value	NOM Fouling rate	Causes
Ionic strength concentration	Increased	Increased	Electrostatic repulsion
pH	High pH Low pH	Increased Increased	Hydrophobic forces Electrostatic repulsion
Divalent cations	Presence	increased	hydrophobicity
NOM Fraction	Hydrophobic Hydrophilic	Increased decreased	hydrophobicity
Surface morphology	Higher	increased	Valley blocking
Permeate flux(High recovery)	Higher	increased	hydrophobicity
Pressure	Higher	increased	compaction

Humic substance in aquatic environment are considered to be the major fraction of NOM, are refractory anionic macromolecules of low to moderate molecular weight,humic substance contains both aromatic functional groups (20).In addition, while studying the effect of NOM properties on fouling of NOM fouling of membranes ,they fractionized NOM into hydrophilic and hydrophobic components. They found that the hydrophobic fraction was the major factor causing permeate flux decline while the hydrophilic fraction had relatively small effect (21).

E. Biofouling

Biofouling is dynamic process of microbial colonization and growth, which results in the formation of microbial biofilms.Biofilm formation invariably, precedes biofouling, which becomes an issue only when biofilms reach thickness and surface coverage that may cause problems such as decline normalized flux.

Biofouling can be controlled by1) removal of degradable components from feed.
2) Ensuring the relative purity of the chemicals dosed
3) Performing effective cleaning procedures.

Developing strategies for fouling control has always been a major challenge in membrane research. However, despite the many preventive strategies, fouling is inevitable. A long term solution would be to remove the foulant deposited on membrane surfaces via chemical cleaning (22). Membrane cleaning is performed when there is a significant drop in permeate flux or salt rejection, or when there is a need to increase the TMP significantly to maintain the desired water flux (22,23).There are two strategies that are usually employed to minimize the effect of fouling.

The first group includes minimizing fouling by using adequate feed pretreatment, membrane treatment and membrane modification. The second group involves membrane remediation by chemical cleaning which is carried out to restore membrane fluxes (24, 25).

This study was performed on flat sheet membranes which fouled with oily waste water, the fouled membranes were washed with chemical agents such as alkali, SDS and EDTA.the effect of the concentration of each cleaning agent and combination of cleaning agent on membranes flux is evaluated. The effect parameter like pH, temperature, and concentration of the cleaning agents on the efficiency of the membranes is evaluated.

II. EXPERIMENTAL SET UP

Fabrication of module and development of module

For experimentation, membrane module are fabricated, it consist stainless still plate of diameter 120mm.The module is fabricated using various mechanical accessories as follows

Feed plate: Feed plate is circular plate and it has diameter of 120 mm.it made up materials of stainless steel. The plate has three holes of diameter 0.25 inches. The purpose of these holes is to
1) Rejection removal. 2) Feed entrance 3) connection for pressure gauge.

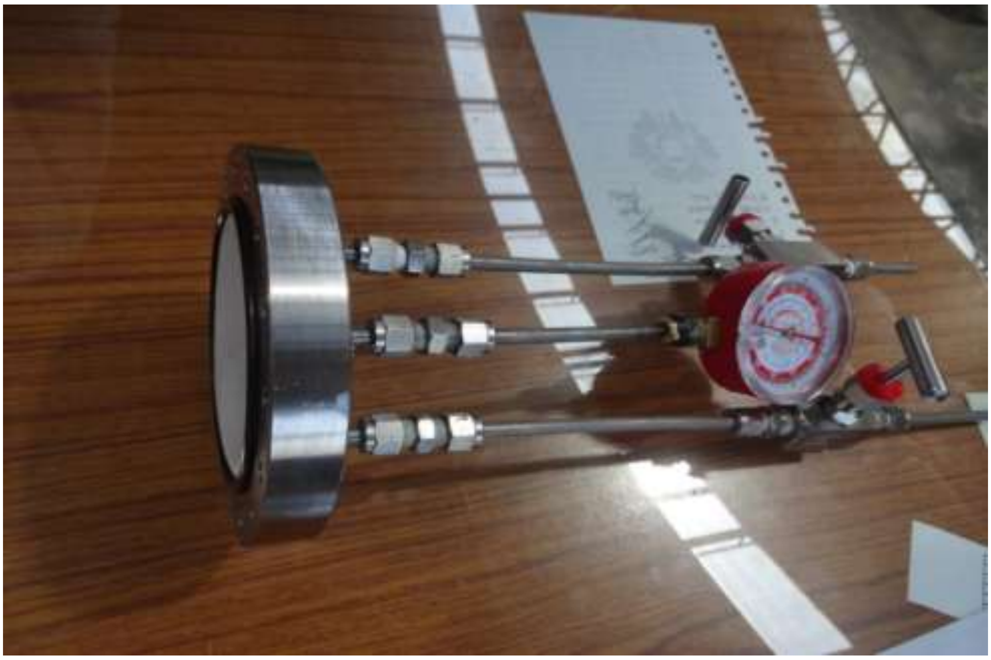

Fig1. Feed plate

Fig.2.Permeate plate

A. Permeate plate

The Permeate plate is a circular plate and made-up of stainless-steel materials. The plate has diameter of 120mm.The plate is provided with one hole having diameter 0.25 inch. The hole is provided to removal of permeate.

Process: The ultra filtration membranes is cleaned using various cleaning agents like sodium hydroxide,ethylenediamine tetra acetic acid, sodium dodecyl sulfate and combination of cleaning agents with different concentration. The membrane flux is evaluated for 5%, 10%,15% and 20%concentration of cleaning agents**.**1000 ml cleaning agent solution is taken and pumped by peristaltic pump and passed to the membrane module through the feed line having needle valve. This valve regulates the flow rate of the feed solution which enters in a module. The rejected line was closed till the pressure reaches the value of 10 psi. At this pressure permeate started coming out from the permeate line. Then the pressure maintained at 10 psi. The process was continuous for 1 hour and tap water is used to evaluate the flux of the membranes and the results were recorded.

III. RESULT AND DISCUSSION

This section is focused on the types of Membrane fouling processes that lead to deterioration of the plant performance and their subsequent recovery using membrane cleaning processes. Different types of inorganic and organic fouling have been addressed in this study. Fouling problems lead to higher operation costs, higher energy demand, reduce the lifetime of the membrane and increase the cleaning frequency. Our work also reveals that it regenerates the membrane performance, even though some cleaning methods have potential limitations the success of chemical cleaning methods depends on many factors such as the nature of the foulant, type of cleaning agents, pH, and the concentration of the cleaning chemicals. These factors affect the outcome of the cleaning procedure and therefore need thorough investigation in order to establish the cleaning system.

A. Effect of concentration

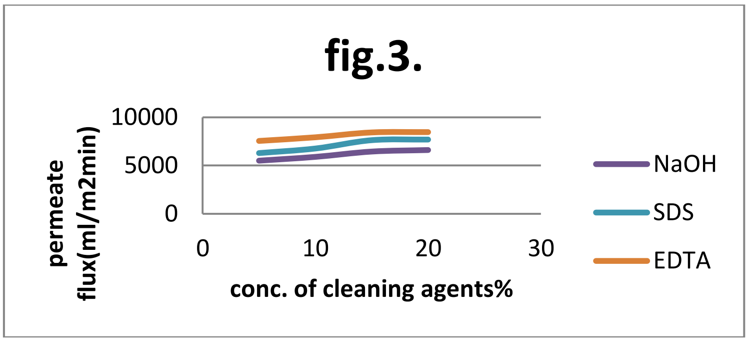

Fig3. Effect of individual conc. of cleaning agent vs. permeate flux of membrane

Fouling of UF membranes due to oily wastewater is mostly due to the precipitation of oil and grease, suspended solids, colloidal materials and minerals on the membrane surfaces. Based on feed conditions three types of cleaning agent's alkali, surfactant and metal chelating agent are used. Figure.3.shows the concentration of individual cleaning agent effect on permeates flux of the membrane. With increased in concentration of cleaning agents permeate flux of the membrane increased. The highest permeate flux is found for EDTA as a cleaning agent whereas lowest permeate flux found for alkali (sodium hydroxide) as a cleaning agent.SDS have higher permeate flux compare to alkali (sodium hydroxide). Because alkali has a moderate effect, while EDTA, which is a chelating agent, has a good ability to combine with metals. It is used in special soaps to remove metallic Concentration. The effect of SDS (surfactant) can be attributed to the cleaning strength of emulsifiers due to altering the interfacial tension of water. This result gives better separation of fouling materials from the membrane surface.

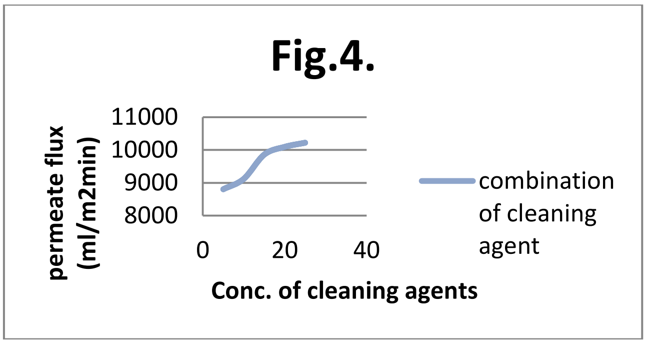

Fig.4.Effect of combination of cleaning agent {alkali surfactant and chelating agent] on flux of membranes

Figure.4. shows the effect of combination of three cleaning agent (alkali, surfactant and chelating agent) on membranes flux. Cleaning experiments were performed using cleaning agent solutions containing different concentrations of SDS, alkali and EDTA.The results clearly show that cleaning efficiency using SDS, alkali and EDTA increases with increasing the cleaning agent Concentration. The cleaning with a combination of EDTA, alkali and SDS is relatively more effective. This is due to the fact that SDS has both hydrophobic and hydrophilic groups, and is semi soluble in both organic and aqueous solvents. Surfactants can solubilize macromolecules by forming micelles around them, and help to remove the precipitated materials from the membrane Surface. Also, EDTA can remove divalent cations from complex organic molecules and improve the cleaning efficiency of the fouled membrane. Generally, SDS is more responsible for removing oil and grease, while EDTA removes minerals from the membrane surface. NaOH changes the pH of the solution and provides a better condition for the highest removal of foulants with EDTA and SDS.

B. Effect of CFV

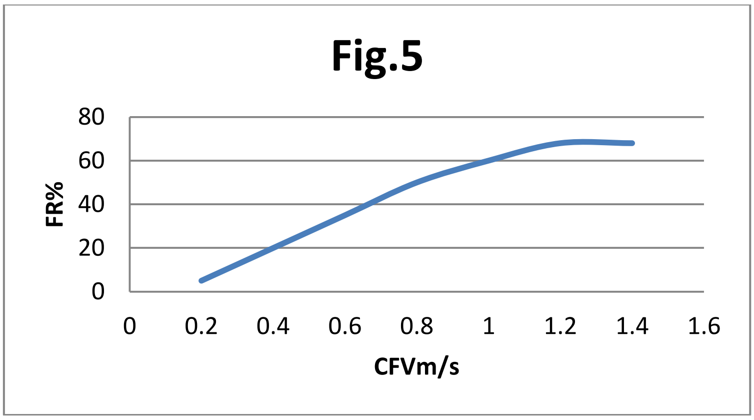

Fig.5.CFV vs. FR percentage

CFV play an important role in membrane flux rate. Madaeni reported that in an experiment carried out using a fouled UF membrane cleaned with caustic cleaning at low and high CFV, it was found that the cleaning efficiency increased at high CFV compared to low CFV. The effect of CFV on cleaning efficiency was also investigated, as shown in Fig.5.The cleaning efficiency increases with increasing CFV till 1.20 m/s, and then remains almost constant. Increasing CFV, which causes higher shear rates, enhances the mass transfer of the cleaning agent through the deposited materials on the membrane surface, thus increasing the cleaning efficiency. The cleaning efficiency increased with increasing CFV only when the chemical reaction between the foulant and the cleaning agents was high enough to produce a favorable reaction. Otherwise, an increase in CFV which results in an increase in the shear rate does not enhance the mass transfer of foulant in the fouling layer to the bulk solution. It can be calculated that the chemical reaction between the cleaning agents with deposited fouled and associated mass transfer phenomena are quite important in membrane cleaning.

C. Effect of pH.

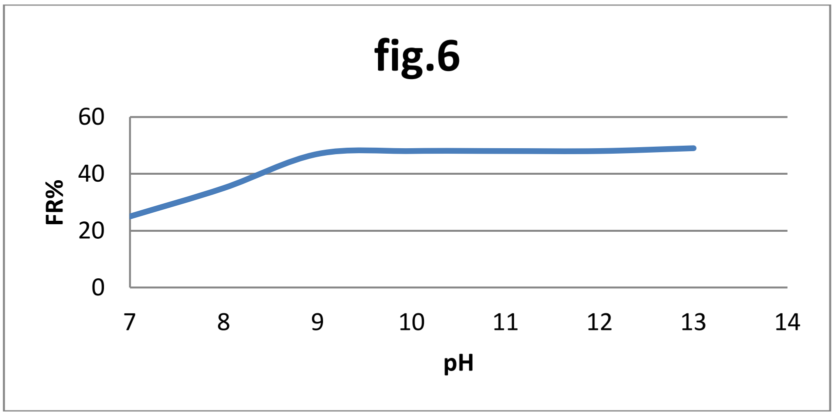

Fig.6.pH vs. FR percentage

Li et al. [26] reported that the cleaning efficiency of EDTA depends on the pH of the solution as a result of deprotonation of functional groups.Mohammadi and Kazemimoghadam [27] reported that the influence of solution pH on EDTA cleaning efficiency had a remarkable effect. The effect of pH on the cleaning efficiency of the Cleaning agent (combination of SDS and EDTA) is illustrated in Fig.6. It is shown that cleaning efficiency increases with increasing pH from 7 to 11. The higher chelating ability of EDTA with increasing pH results in a more effective ligand-exchange reaction between ETDA and alginate-metals complexes within the alginate cake layer. Consequently, the alginate cake layer is broken down relatively more easily, resulting in a higher cleaning efficiency. It was concluded that the cleaning solution pH is a governing factor affecting the chemical reaction between deposited fouled and EDTA, whereas the chemical reaction between deposited foulant and SDS is less influenced by cleaning solution pH. The best pH should be selected according to the higher cleaning efficiency and greater chemical stability. Thus, a pH of 9 can be an optimum value

D. Effect of temperature.

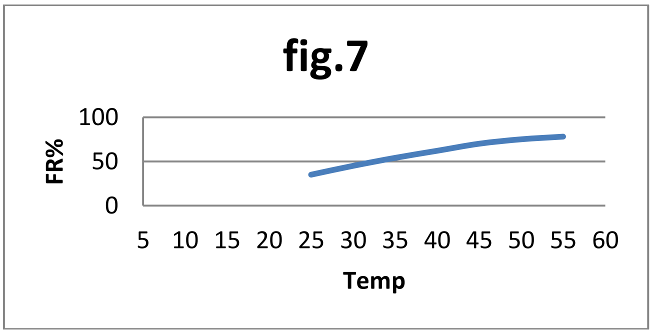

Fig 7. Temperature vs. FR percentage

The temperature plays a very important role in cleaning membranes. Increased in temperature increased cleaning efficiency, due to increase in transport process and solubility of the material. Generally membranes are sensitive for very high temperature. Membranes manufacturers recommend that chemical cleaning be carried out at a temperature lower than 450c. and Li et al. [17] reported that preheating the cleaning solution up to about 40_{o}C had a significant impact on increased FR compared to 25^{0}C, where the increased cleaning temperature was favorable for the desorption of deposits from the membrane surface. The figure.7. Shows the effect of a combination of cleaning agent (EDTA and SDS) solution at various temperatures on FR% of the membranes. The cleaning efficiency increases with increasing temperature. This is due to the fact that both the rate of the chemical reaction between the cleaning agent and the deposited materials and the rate of diffusive transport of the deposited materials from the cake/gel layer back to the bulk solution increase as the temperature increases. A cleaning temperature of 40°C can be recommended for the cleaning. Therefore, both the rate of the chemical reaction of EDTA with deposited fouled and the diffusive transport of foulant from the fouling layer to the bulk solution increased as the temperature was increased.

IV. CONCLUSION

The best cleaning agent to enhance the cleaning efficiency of the fouled UF membrane was found to be a combination of SDS, alkali and EDTA. A combination of SDS (as a surfactant) alkali and EDTA (as a chelating agent) as a powerful cleaning agent performed very effectively. EDTA is able to combine with metals. The effect of SDS can be attributed to the cleaning strength of emulsifiers due to their ability to alter the interfacial tension of the water. NaOH changes the pH of the solution and provides a better condition for the highest removal of foulants with EDTA and SDS. The cleaning efficiency of the recommended cleaning agent was further improved by optimizing the cleaning condition. The effectiveness of chemical cleaning in terms of chemical reactivity depends on the type of foulant, cleaning solution pH, the cleaning chemicals concentration and temperature.

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