

Electrokinetic Characterization of the Fouled PP Membrane in the Separation of Oily Wastes

Hyonseung Dho¹⁾, Soojung Suh¹⁾, Jae-won Lee²⁾, Kune-woo Lee²⁾

¹⁾Chongju University, Korea

²⁾Korea Atomic Energy Research Institute, Korea

The work was initiated to investigate the electrokinetic properties of a MF membrane using streaming potential measurement when oil emulsion was separated. The original and the surface modified PP membrane were examined by using flux and streaming potentials for the characterization of fouling phenomena of the PP membrane. The membrane surface was modified by a radiation grafting technique. The streaming potentials of the PP membranes were varied the charge distribution modifying by changing the pH, ionic strength, and concentrations the surfactants in oil emulsion. The shiftness to the more positive values of isoelectric point of the PP membrane was significant especially in the presence of surfactants or the surface modification.

Introduction

Wastewater containing oil must not be discharged to the receiving stream due to the adverse effects to the environments. The formation of an oily film on the water surface has potential for creating a hygienical problems. Several emerging technologies are currently available for separating oil from wastewaters. The choice for oil removal techniques are dependent on the formation and the nature of oil that they can remove. Oily wastewater, especially containing chemically emulsified oil, is particularly hard to separate oil from waste water. The best choice for current technology condering by efficiency and effectiveness is filtration technique.

Membrane separations are classified into 4 catagories; microfiltration, ultrafiltration, reverse osmosis and nanofiltration as the

pore size and the size of filterable materials.

The MF membrane separation technique is becoming increasingly more important in treating oily waste waters in the industrial uses. It is a physical separation for removing free oil and emulsified oil and finely dispersed solids from wastestream by forcing the water through a membrane under low pressure⁽¹⁾.

Membrane fouling which may become by the build up of oil or suspended solids at the membrane surface, reduces the permeate flux by creating a hydrodynamic resistance. The separation process, however, is difficult for continuing to proceed if the fouling is occured. The fouling should be avoided for economic reasons. It has been known in the protein system⁽²⁾ that hydrophobic membranes foul more rapidly than hydrophillic

membranes. The hydrophobic membranes are characterized by a flux decline that is caused by fouling due to solute adsorption and pore blocking. The characterization methods for cleaned and fouled membranes mostly focus on relating the flux of the membrane to another measurable parameter. The membrane surface has mostly been studied by using, FTIR, and streaming potential methods⁽²⁻³⁾.

Streaming potential arises when a pressure difference is applied across a membrane, causing the double layer to shear due to the flow of fluid which displaces the electric charge of the diffuse part of the double layer. The Zeta potential is an important tool for measuring oil emulsion-emulsion and emulsion-membrane interactions. These interactions have been shown to be of importance for membrane performance. There must be a correlation between the amount of fouling and the surface potentials.

For the current study, the investigation was to focus the fouling characterization of the membrane by the method of streaming potentials in the separation process of oil emulsion. Flux measurements was also made simultaneously. The measurements were mostly made at different pH, concentration of the oil emulsions, and operating time with original and the surface modified membrane.

Experiment

Reagents

A variety of oil/water mixtures was prepared with different oils and surfactants. Dodecane was selected as oil due to a pure compound. The three types of surfactants (anionic, cationic, and nonionic) were used. The anionic surfactant, sodium dodecyl sulfate(SDS) was supplied by Junsei

Chemical Co. The cationic surfactant, Cetylpyridium Chloride(CPC, BDH chemicals Ltd) and nonionic surfactants, Polyethylene glycol tert octylphenylether(Triton X-100; Shinyo Pure (Hemical Co.) surfactants were also prepared. The hydrophobic polypropylene membrane was supplied from AKZO NOVEL Co, and it was a sheet type with an area of 21.24cm². The demineralized water was filtered again by a UF membrane prior to the experiments. The KCl was used for adjusting ionic strength. The solution pH was precisely adjusted by adding HCl or NaOH.

Methods

A variety of oil/water mixtures are tested with different concentration of oil and surfactants for the flux and streaming potential measurement. The oil emulsion was prepared by an ultrasonic homogenizer for 150 seconds prior to the experiment.

A membrane was first immersed in a methanol for 24 hrs. The zeta potential of the oil emulsion was measured by Zeta Plus(Brookhaven Instrument Co.) the streaming potential and the flux were measured simultaneously by the home-made module. The flat sheet module was made with polycarbonate. The electrode plugs and some supports were made from polyvinyl chloride. The porous supports were made from polyethylene. The Ag/AgCl electrodes was placed in each compartment of the membrane module and the electrodes were connected to a voltmeter. The detailed can be shown elsewhere⁽⁴⁾. The Ag/AgCl electrodes was prepared with anodic deposition of chloride on silver from 0.1M HCl solution with a current density of 10 mA/cm².

The size of oil in the droplet in the

emulsion was controlled by measuring coulter current.

The streaming potential measurements were performed with a 10^{-3} M KCl solution. At below pH 3 the large developed conductivity disturbed the measurements and at pH above 8 the electrodes were damaged. The streaming, therefore, potential could only measure above pH 3 to below pH 8. Fig. 1 shows a schematic diagram of the experimental apparatus used in this study.

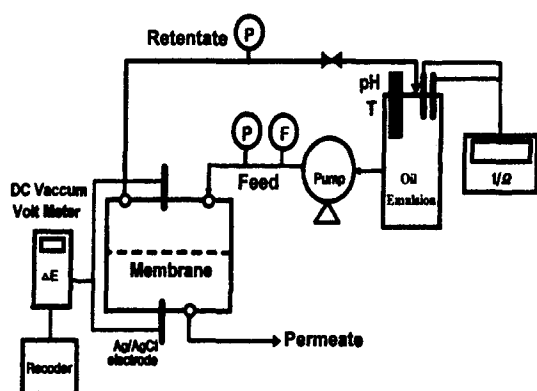


Fig 1. Schematic Diagram of the Microfiltration Apparatus

The zeta potentials of 2500ppm oil emulsion were measured in the absence were obtained by calculation from the results of streaming potentials using single Smolchowski equation⁽⁴⁾.

Results and Discussion

The zeta potentials of 2500ppm oil emulsion were measured in the absence and in the presence of 2500ppm SDS concentration, as shown in Fig. 2. The zeta potential of oil droplet was -20mV at pH 2 and decreased rapidly to -85mV at pH 6 to pH 9. The potential was then remained constant above pH 6. The zeta potential in

the presence of 2500ppm SDS concentration showed the constant values ranging from -80mV to -100mV. The results of the zeta potentials showed that the SDS had an effect on the zeta potentials of oil droplets at the acid pH ranges. The SDS made oil emulsion stable at the whole pH ranges.

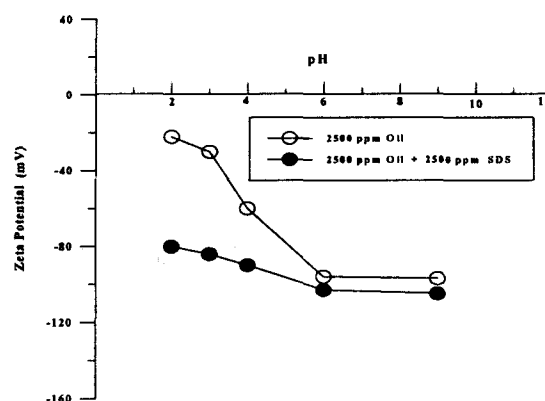


Fig 2. Zeta Potentials of Oil Emulsion as a function of pH

Fig. 3 shows the zeta potentials of oil emulsions as a function of SDS concentrations. The results showed that the zeta potential values for oil emulsion were affected by the increasing SDS concentration only for the low ranges of concentration. Above 1500ppm SDS concentrations the zeta potentials were remained -100mV. It is noted that the theoretical values of Critical Micelle Concentration(CMC) for SDS is around 1500ppm. Above the CMC, any addition of SDS will aggregate to form micelles rather than migrate to an interface and therefore change the zeta potentials.

Two sets of filtration experiments in the separation of oil emulsions were conducted for measuring the streaming potential as well as flux at the same time. The optimum

operating conditions such as flowrate, pressure, time, oil concentrations were obtained by the preliminary experimental results. During the experiment, the oil permeate was continuously recycled to the oil-water reservoir to maintain a constant oil concentration.

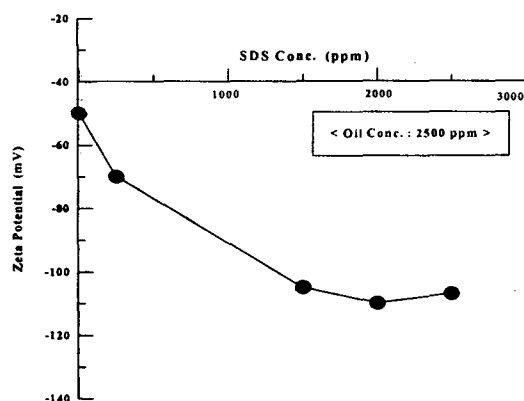


Fig 3. Zeta Potentials of Oil Emulsion in terms of SDS Concentration

The flux results shown in Figure 4 indicate that both fluxes at pH 3 and 7, respectively, were declined with increasing operating time. The steep decline can be observed until 60 minutes and was reached constant to 150minutes. The permeate flux, however, tended to decrease with increasing time. This may be due to the membrane compaction occurred with increasing time and this would tend to reduce the membrane porosity. The flux at the pH 7 was lower than that of pH 3.

The streaming potential results showed that both results were located in the negative ranges and the potentials were almost constant over the entire running time. The streaming potentials at pH 3 were almost -20mV which indicate that the i.e.p of the

membrane potentials was close. When pH of the oil emulsion was raised to 7, the potentials were more negative values to almost -160mV. The similar phenomena can be observed with the zeta potentials of oil emulsion, as shown in Fig. 2.

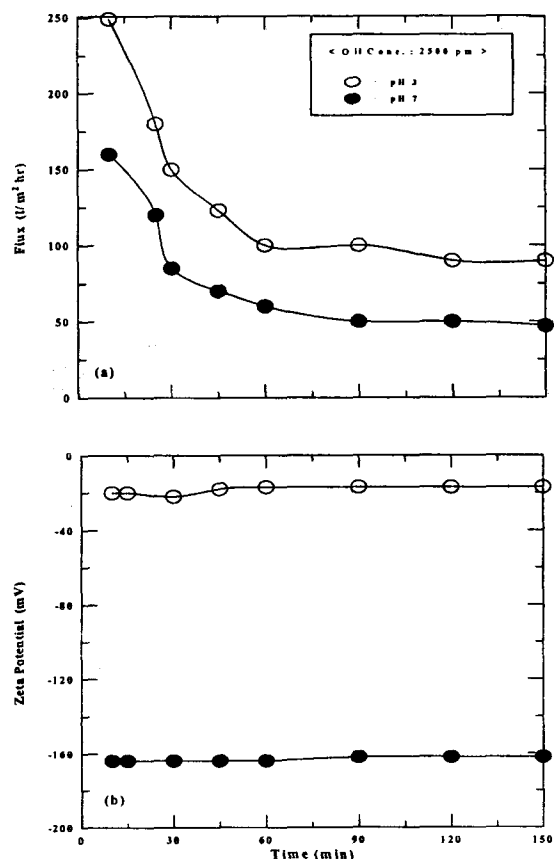


Fig 4. (a) Flux & (b) Streaming Potential of Original PP Membrane on 2500 ppm Oil Emulsion at pH 3 and 7

The zeta potentials of both oil emulsion and the membranes were affected by pH.

Fig. 5 shows a plot of fluxes and zeta potentials versus time in the absence and presence of three types of surfactants (anionic, cationic, nonionic) at pH 5.5. In the absence of surfactant, the flux of the oil emulsion

solution was smoothly declined with time and remained relatively constant for above 60 minutes. The fluxes in the presence of surfactants reached steady state in the early stages of operating time. The cationic surfactant, CPC, showed the highest flux. On the other hand, the nonionic surfactant, Triton X-100 the lowest flux. In the absence of surfactant, the zeta potentials was -115mV at 10 minutes and shifted to i.e.p direction gradually until 90 minutes and was remained constant to -40mV above 90 minutes.

The average zeta potential of PP membrane in the presence of SDS at pH 5.5 was unexpectedly almost -5mV . The zeta potential of the oil droplet at the same condition as shown in Fig. 2, was -90mV . This discrepancy might be explained by the size and stability of oil emulsion and the size of the SDS. The SDS may affect the attachment of oil droplets by lowering the interfacial tension which the oil droplets. This well dispersed and deformable oil emulsion may affect the surface potential of the membrane.

The most likely explanation for the lack of correlation between the change in permeate flux and zeta potential in the presence of SDS concentration is that some of the SDS migrates to the membrane surface and oppose the transport of oil. The electrostatic interaction between oil droplets, surfactants, and the membrane surface was significant. The membrane had a slightly negative zeta potential on the other hand, oil droplets showed highly negative zeta potentials. The cationic surfactants, CPC, affected the electrostatic interaction by adsorbing into both the droplets and the membrane surface.

Fig. 6 shows the fluxes and zeta potentials

with a fouled MF membrane with three different kinds of surfactants at 2500ppm oil. The fouled membrane was prepared by dipping into surfactants with 10,000ppm concentration for 12 hours. The result shows that the fouled membranes apparently had a higher permeate flux and therefore a dramatic decline of flux compared to Fig. 5.

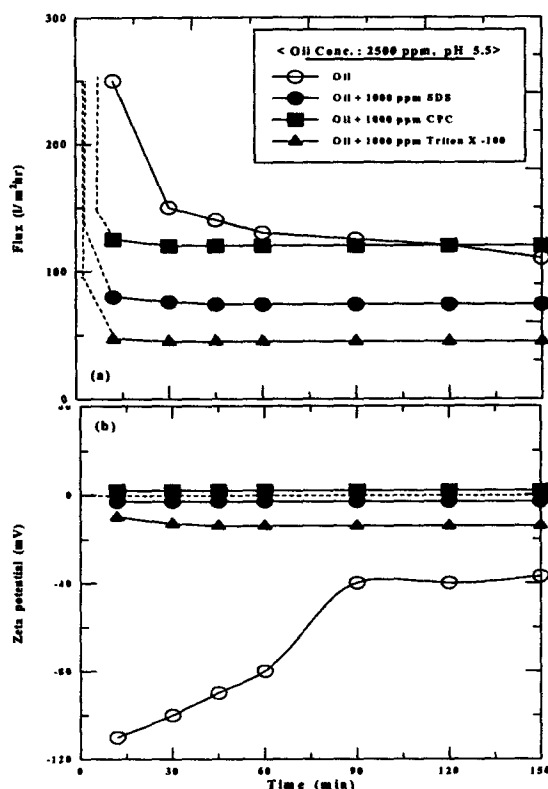


Fig. 5 (a) Flux & (b) Zeta Potentials of original PP Membrane as a function of Operating time in terms of three kinds of Surfactants at pH 5.5

As the PP membranes are already negatively charged an accumulation of an SDS at the surface should result in an even stronger negative charge. The zeta potential were -150mV . This values imply

that the highly negative SDS adsorbed membrane block the transport of oil across the membrane by increasing the electrical repulsion between the oil droplets themselves and/or between the droplets and membranes.

The removal process of oil emulsion was adversely affected by the presence of any of kinds the ionic and nonionic surfactants. The amount of concentrations of surfactants may affect the flux as well as membrane potentials. The presence of surfactants greatly reduced the coalescence efficiency⁽⁵⁾ and modified the electrical properties of the oil emulsion and the membrane.

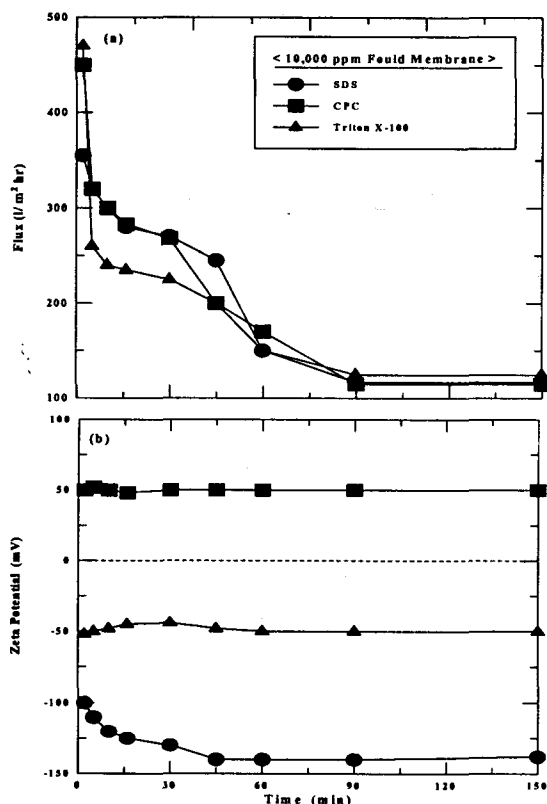


Fig 6. Flux (a) & Zeta Potential (b) of the fouled Membrane as a Function of fouled Surfactant types

Fig. 7 shows the results of zeta potentials

for the original PP membrane and the fouled membrane by 2500ppm oil emulsion. Both membranes became more negatively charged with increasing pH. The i.e.p of the original membrane was located at around pH 2. The fouled membrane, however, made i.e.p shift to more positive value to pH 3. The fouled membrane may be lost its negative membrane potential. The i.e.p may be shifted to the more positive direction.

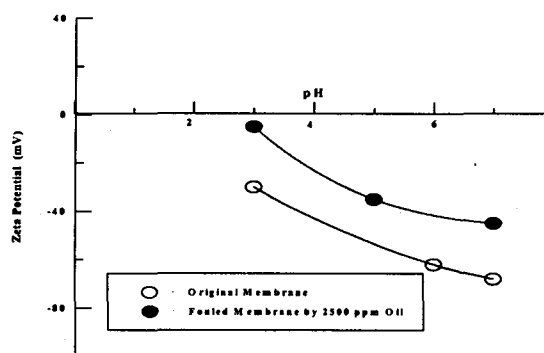


Fig 7. Comparison for Zeta Potential between Original Membrane and Fouled PP Membrane in terms of pH

The same phenomena was reported^(5,6) that the fouled membrane by UV also shift i.e.p to the more positive values.

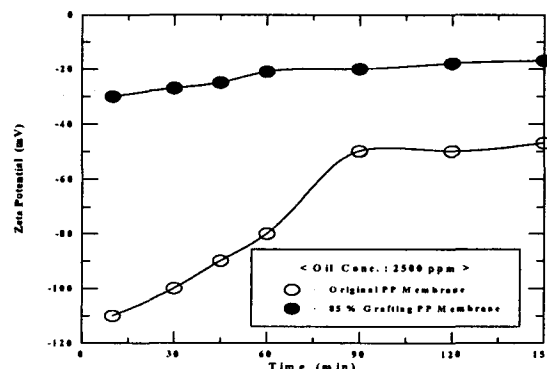


Fig 8. Zeta Potentials of 85% HEMA-g-PP Membrane

Fig. 8 shows the results of zeta potentials for 85% HEMA-g-PP membrane. The membrane was modified by radiating induced grafting of 2-hydroxyethyl methacrylate (HEMA).

The grafting rate was 85%. The zeta potentials of the surface modified membrane in the presence of 2500ppm oil emulsion was measured and compared with the original PP membrane at pH 5.5.

Here again, the zeta potentials were shifted to the positive values: This shiftness may imply the fouling phenomena of membrane.

Conclusions

The following conclusions were drawn from this study on the characterization of the separation oily wastes.

1. The average zeta potential of the oil emulsion was located at -50mV. When the SDS was added to the oil emulsion, the zeta potential drop to -100mV.
2. The permeate fluxes of the anionic, nonionic, and cationic surfactants for the oil emulsion were reached steady state extremely fast. The overall fluxes, therefore, were decreased in the presence of the three surfactants. The surfactants may have deleterious effect on oil removal process.
3. The zeta potentials of membranes containing oil emulsion in the presence of surfactants may affect oil removal by altering the electrical properties of the oil droplets and the membranes.
4. The fouled membranes by the surfactants play an important role in the separation process for the oil emulsion. The potentials at the interface was remarkably different between the original and the fouled membrane. Repulsive electrostatic interactions

between the negatively charged oil and the membrane which is already highly negative charged by the SDS hinder droplet approach and attachment.

5. The fouled membrane caused the shift of i.e.p of the original membrane to the more positive values. The surface modified by radiating technique also caused the shift of the i.e.p the original membrane to the more positive values.

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