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# RO membrane treatment of domestic grey-water containing different detergent types

P.S. Singh*, P. Ray, J.J. Trivedi, A. Prakash Rao, K. Parashuram, A.V.R. Reddy*

*RO Division, CSIR-Central Salt and Marine Chemicals Research Institute, Bhavnagar 364002, India*
*Tel. +91 278 2566511; Fax: +91 278 2567562; emails: puyam@csmcri.org; avreddy@csmcri.org*

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## ABSTRACT

Water reclamation from grey-water containing detergent and salinity (~2,000 ppm) was carried out using indigenously developed brackish water TFC membrane module (4040 size) at 250 psi operating pressure. Reusable water with <300 ppm inorganic solutes and trace amounts of organic content of detergent origin was produced upon reverse osmosis (RO) treatment of grey-water. The RO module performance in terms of product flux was influenced by the detergent type present in the feed water. While the product flux was rather unchanged for the feed containing a commercial linear alkyl benzene-alfa olefin sulfonate-soda ash based detergent, a significant flux decline (~25%) was observed for the feed containing a commercial $C_8$–$C_{24}$ primary/secondary ethoxylates based detergent. However, the membrane selectivity in terms of salt rejection was slightly higher for the feed with detergent than that of the detergent-free feed. This can be due to the surface-active agent of the detergent which alters the surface potential of the membrane. This is in agreement with the changes observed by atomic force microscopy (AFM) and the Zeta-potential measurements.

*Keywords:* Membrane treatment; Wastewater; Grey-water; Surfactant

## 1. Introduction

Reverse osmosis (RO) membrane separation process has emerged as an effective solution for desalination of brackish and seawater into potable water [1–4]. Besides desalination to produce potable water, treatment of wastewater to obtain reusable water is one of the other major applications of RO membrane technology [5–8]. Treatment of industrial aqueous effluents or wastewaters for reuse is the most promising option to decrease groundwater consumption while protecting the environment and reducing the pollution. Effluents from industry and households contain harmful toxic chemicals, soapsuds, dirt particles, etc. Surface-active agents of detergents—most commonly known as surfactants—are main pollutants in grey-water which are difficult to remove by conventional treatment processes. These organic chemicals can greatly reduce the surface tension of water and other liquids when used in very low concentration. They are amphiphilic compounds with a hydrophilic head and hydrophobic tail and have a tendency to attract and repel water molecules respectively. The highest consumption of surfactants is in detergents and cleaners. They are also used as auxiliaries in textiles, leather and paper, in different

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*Corresponding author.

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chemical processes, food industry, and agriculture. The other areas of applications of detergents include as solubilizer for perfumes and flavors, conditioning agent in skin and hair care products, emulsifiers in creams and lotions, foaming agents for shampoo, and thus, grey-water produced from household uses generally contains organics of surfactants origin [9,10]. Today water is too valuable to be left untreated as the clean water sources are decreasing continuously worldwide and reduce, recycle, and reuse is the essential requirement for water sustainability.

In the present work, we report a study of thin-film composite (TFC) RO membrane in the treatment of domestic grey-water for obtaining reusable water. The surfactant present in the domestic grey-water can be negatively charged (anionic) or positively charged (cationic). The interaction between the surfactant and the membrane surface was investigated by atomic force microscopy (AFM) and Zeta-potential measurements in order to examine surfactant influence on membrane performance.

## 2. Experimental

### 2.1. Preparation of thin-film composite reverse osmosis (TFC RO) membrane

Thin-film composite reverse osmosis membranes were prepared in two steps using semi-automated casting and coatings units. In the first step, polysulfone microfiltration support of 1 m × 100 m size was prepared at the rate of 4 m/min according to the phase inversion process. For this purpose, polysulfone casting solution was prepared by dissolving 15 wt.% Udel P-3500 PS (Solvay, USA) in AR grade *N,N*-dimethylformamide (DMF). The resultant polymer solution was cast on a moving web of non-woven fabric and immersed in a water bath containing 2% DMF and 0.1 wt.% sodium lauryl sulfate (SLS) surfactant in order to form a porous polysulfone membrane. In the second step, the polysulfone surface was coated with an ultrathin polyamide film according to the usual interfacial polymerization technique by initially immersing the polysulfone support membrane in 2% (w/v) solution of *m*-phenylenediamine (MPD, Lancaster Chemical Co.) in water, followed by immersing into 0.1% (w/v) trimesoyl chloride (TMC, Lancaster Chemical Co.) in n-hexane solution which resulted in the formation of a thin polyamide film over the surface of polysulfone support. Spirally wound TFC RO membrane modules of 4″ (dia.) × 40″ (length) were fabricated. Further details on the membrane preparation process can be obtained from our earlier publications [11,12].

### 2.2. Characterization of the TFC RO membrane

AFM images of the TFC membrane samples were acquired using NT-MDT AFM instrument. Zeta potentials of the membrane surfaces were measured by ZETA-CAD instrument using 0.01 M aqueous KCl solution. TFC membrane sample test coupons were evaluated for permeate flux and selectivity on a batch type RO test kit comprising four cells in series. Testing was done with NaCl solution of 2,000 ppm concentration at a pressure of 250 psi. A standard digital conductivity meter (Eutech Instruments, CON 700) was used to measure the salt (NaCl) concentrations in the feed and product water for determining membrane rejection.

### 2.3. Treatment of domestic grey-water

For the treatment experiments, synthetic grey-water of 100 L having about 2,000–3,000 ppm salts (NaCl + $MgSO_4$) and 50 ppm commercial detergents, a linear alkyl benzene-alfa olefin sulfonate-soda ash based detergent, or $C_8$–$C_{24}$ primary/secondary ethoxylates based detergent was prepared. This grey-water was treated with a pilot RO plant consisting of a spirally wound 4040 TFC RO module at a feed flow rate of 13 L/min at 250 psi. The total organic contents of the feed and product were analyzed by TOC analyzer (Elementar, Liqui-TOC), HPLC (Waters-Alliance), and LC-MS (Waters-Micromass) techniques.

## 3. Results and discussion

### 3.1. Properties of the thin-film composite reverse osmosis (TFC RO) membrane

The TFC RO membrane was prepared in a semi-large scale capacity using the polysulfone casting and polyamide coating devices as reported elsewhere [11,12]. The TFC RO membrane is comprised of a three-layered structure such as top ultrathin polyamide active layer (0.015–0.02 μm thickness), middle polysulfone porous support layer (30–35 μm thickness), and the bottom reinforced polyester fabric (100–110 μm thickness). The polysulfone support on the non-woven polyester web was formed according to the usual phase inversion process. The structure of polysulfone support is of asymmetric nature which means less porous near the surface resulting due to tightly compacted sub-micron sized nodular dendritic structure and large macrovoids underneath. The ultrathin polyamide film on the top of the porous polysulfone support was obtained according to the interfacial polymerization process by initially filling the pores of nodular polysulfone structure with the diamine monomer in water and then polymerizing with a multifunctional acid chloride monomer dissolved in water immiscible organic solvent like hexane [13–15]. The polyamide film is responsible for selective transport of the solutes through the membrane. It is a dense structure formed by intergrown micrometer sized domains wherein each domain is comprised of nanometer sized blocks [16]. The pore number densities of the polyamide film are in the order of magnitude $10^{22}$ per $m^3$ and the average void radius estimated using PALS from infinite spherical potential well of radius is about 0.386 nm [17,18]. The spirally wound TFC RO modules of 4″ (dia) × 40″ (length) size were fabricated using four TFC RO membrane sheets of 1 m width × 2.3 m length, which thus gives about 8 $m^2$ active membrane area per module. These modules were explored for their applicability for water reclamation from domestic grey-water and industrial aqueous carboxylic acid effluent.

### 3.2. Water reclamation from grey-water using TFC RO membrane

Application of the TFC RO membranes for water reclamation from grey-water containing 500–2,000 ppm salts ($NaCl + MgSO_4$) and 50 ppm commercial detergents (linear alkyl benzene-alfa olefin sulfonate-soda ash or $C_8$–$C_{24}$ primary/secondary ethoxylates based) was carried out and the total organic content of the feed and product were analyzed. The linear alkyl benzene-alfa olefin sulfonate-soda ash based detergent contains a lesser amount of organic carbon of surfactant origin (~5–6 ppm) than that of $C_8$–$C_{24}$ primary/secondary ethoxylates based detergent (~23–34 ppm) for the same amount of detergent added during the experiments. It was observed that salt rejection efficiency of the RO module was enhanced in the presence of detergents. The total removal of organic of detergent origin by the RO membrane treatment was observed. The treated product water quality was similar to potable tap water. As given in Table 1, the carbon content of the product water was about 2 ppm as estimated by TOC analyzer which was similar to the carbon content (possibly from dissolved $CO_2$) of potable tap water. The membrane performance in terms of product flux was however influenced by the detergent type in the feed water. While the product flux was rather unchanged for the treatment of feed containing linear alkyl benzene-alfa olefin sulfonate-soda ash based detergent, a significant 25% flux decline was observed for the treatment of feed containing $C_8$–$C_{24}$ primary/secondary ethoxylates based detergent. This might imply that the product water flux output is dependent on the type of detergent contained in the aqueous feed. This can be due to the fact that surface active agent (surfactant) of the detergent alters the surface potential of the membrane thereby affecting the performance. The surfactant present in the detergent can be negatively charged (anionic) or positively charged (cationic) or non-ionic. The interaction between the surfactant and the membrane surface was investigated by the analysis of the membrane surface topologies using AFM.

### 3.3. Effect of surfactant in the feed on membrane performance

In order to understand the effect of surfactant–membrane interaction on membrane performance,

Table 1
Analysis of feed and product at 75% recovery from RO membrane treatment of grey water containing detergents, salinity and hardness

| | Feed (ppm) | | | Product (ppm) | | | % Salt rejection | Product rate (liters/min.) |
|---|---|---|---|---|---|---|---|---|
| | Carbon | NaCl | $MgSO_4$ | Carbon | NaCl | $MgSO_4$ | | |
| Saline water | | | | | | | | |
| (i) | 1.95 | 2,150 | 0 | 1.58 | 199 | 0 | 90.7 | 4.3 |
| (ii) | 1.90 | 1,820 | 875 | 1.42 | 151 | 95 | 90.9 | 4.2 |
| Saline water with LAB detergent[a] | | | | | | | | |
| (i) | 5.11 | 2,120 | 0 | 2.28 | 186 | 0 | 91.2 | 4.6 |
| (ii) | 5.13 | 1,820 | 830 | 1.87 | 165 | 60 | 91.5 | 4.2 |
| Saline water with ET detergent[b] | | | | | | | | |
| (i) | 34.01 | 2,000 | 0 | 2.01 | 136 | 0 | 93.2 | 2.8 |
| (ii) | 30.60 | 1,770 | 760 | 2.01 | 136 | 75 | 91.7 | 3.0 |

[a] Linear alkyl benzene-alfa olefin sulfonate-soda ash based detergent.

[b] $C_8$–$C_{24}$ primary/secondary ethoxylates based detergent.

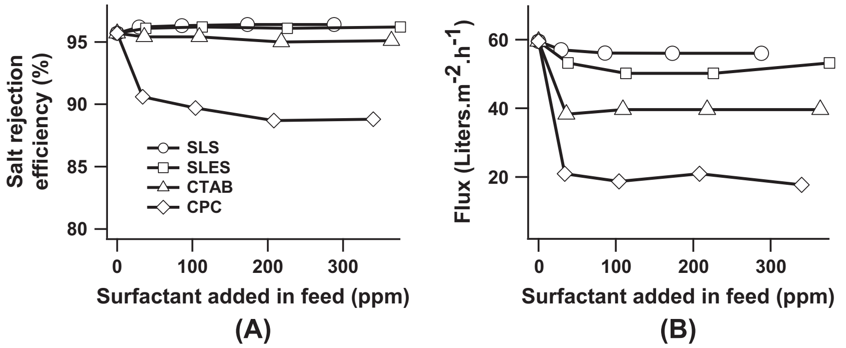

Fig. 1. Influence of trace surfactants in the feed to the performances of the membranes.

experiments were performed with membrane test coupons in a RO test kit using 2000 ppm NaCl feed solution containing a small quantity (30–380 ppm) of a surfactant. As shown in Fig. 1, addition of SLS in the feed, the membrane exhibited a slight increase in the salt rejection efficiency while the flux remained nearly the same when compared to the initial membrane performance in the absence of surfactant. The enhancement of the membrane performance in terms of product flux without decreasing the salt rejection efficiency was observed when another anionic surfactant, sodium lauryl ether sulfate (SLES) was added in the feed. However, the membrane exhibited reduction in both the salt rejection and product flux when cationic surfactant, cetyltrimethylammonium bromide (CTAB) or cetylpyridium chloride (CPC) was added in the feed. Thus, it is very clear that anionic surfactant in the feed enhanced membrane performance in salt rejection efficiency (~2–3% increase) as well as water flux. On the other hand, the cationic surfactants in the feed reduced both the product flux (~50–70% decrease) as well as the salt rejection efficiency (~2–10% decrease) significantly. Thus, the changes in the membrane performances were resulting from the changes in membrane surface charges because of surfactant–membrane interaction.

### 3.4. AFM observation of surfactant–membrane interaction

AFM is the one of best technique to obtain detailed morphological information on surface aggregates at the nanometer length scale. A small portion of flat TFC membrane was immersed in the deionized water containing ~30 ppm surfactant for 2 h, washed with water and dried in air at 25°C for the AFM observation of surfactant–membrane surface interaction. Two cationic and two anionic surfactants were used for the experiments. SLS and SLES were anionic surfactants, whereas CTAB and CPC were cationic surfactants. The AFM images of the surfactant treated membrane surfaces are shown in Fig. 2. The detailed statistical characteristics of the surfaces for the fresh membrane and the surfactant treated samples were obtained by roughness analysis of the AFM surface image scan area of 5 × 5 μm. The mean value of peak to peak distance ($S_y$), and the first moment of the distribution which is the mean value of peak to peak distance ($\mu$), the average arithmetic roughness ($S_a$), the root mean square roughness ($S_q$) are summarized in Table 2. The surface topologies for the surfactant treated samples were of typical hill–valley morphology of the $S_a$, and $S_q$ values of 43–68 nm and 53–86 nm, respectively. The fresh TFC RO membrane had the $S_a$ and $S_q$ values of about 120 and 146 nm, respectively, indicating that the average surface roughness had decreased by about 50% in the surfactant treated samples.

The distribution of grain sizes in the hill and valley regions of surface topology were analyzed from the image scan area of 5 × 5 μm for the surfactant treated samples using Windows based NT-MDT Image Analysis Software Build 3.5.0.2064 as shown in Fig. 3. Log-normal distribution curves to the data were observed. The log-normal distribution function can be expressed as:

$$\frac{df(G)}{dG} = \frac{1}{G \ln \sigma_G \sqrt{2\pi}} \exp\left[-\frac{(\ln G - \ln \mu_G)^2}{2(\ln \sigma_G)^2}\right] \tag{1}$$

where $G$ is the polymer nodule size, $\sigma_G$ is the standard deviation and $\mu_G$ is the mean nodule size

From the fits, it was clear that the median nodule sizes for all the surfactant treated samples were found to be similar, although there are some differences in the polydispersity of the sizes at the higher ranges. The median nodule sizes in the hill and valley regions of the surface topology was about 200 nm for CTAB-treated sample while all the other surfactant treated samples exhibited smaller nodular sizes with median value in the range of about 100–150 nm. The distribution of nodular sizes was in accordance with the size

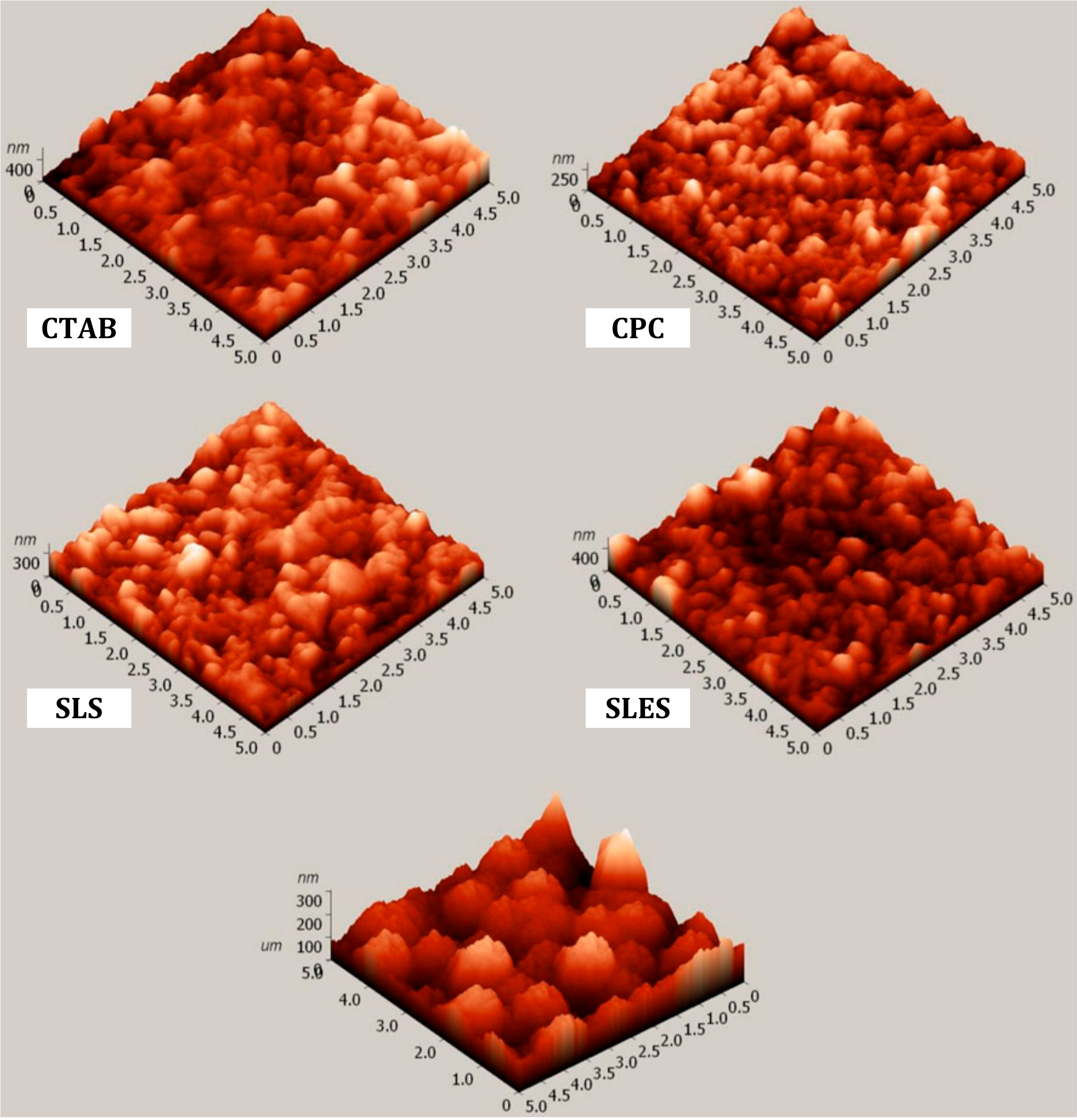

Fig. 2. The AFM images for the untreated and surfactant treated membrane surfaces.

Table 2
The peak to peak maximum distance ($S_y$), the mean value of peak to peak distance ($\mu$), the average arithmetic roughness ($S_a$), the root mean square roughness ($S_q$) for the fresh and surfactant treated membrane surfaces

| Sample | $S_y$ (nm) | $\mu$ (nm) | $S_a$ (nm) | $S_q$ (nm) |
|---|---|---|---|---|
| Fresh RO | 860 | 390 | 120 | 146 |
| SLS treated-RO | 435 | 215 | 50 | 62 |
| SLES treated-RO | 600 | 216 | 68 | 86 |
| CTAB treated-RO | 632 | 285 | 64 | 83 |
| CPC treated-RO | 344 | 158 | 43 | 53 |

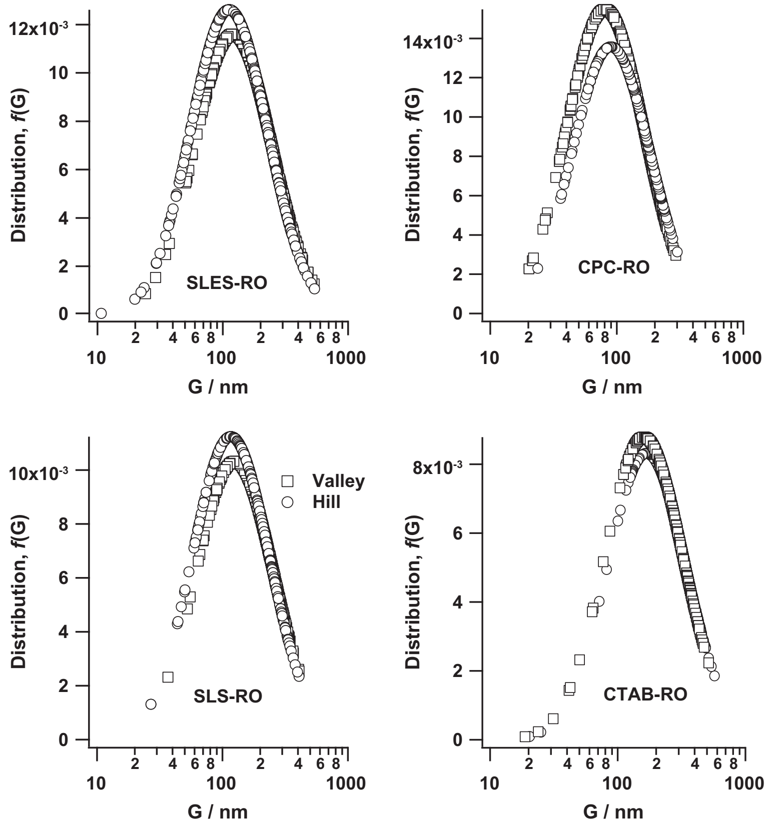

Fig. 3. Polymer nodule size distribution of hill-valley morphology of the membrane surfaces.

values of surface roughness analysis given above. It has been reported that surfactants form surface aggregates of different shapes depending on the system under investigation [19,20].

### *3.5. Zeta-potential measurements of surfactant treated membrane samples*

The membrane charge after the treatment with the water containing 0.1 mM surfactant was determined using zeta-potential measurements. The surface of the polyamide active layer that was formed by the interfacial polymerization between *m*-phenylene diamine and trimesoyl chloride monomers is usually contains amide (–CONH–) and negatively charged carboxylic acid (–COOH) [21,22]. The adsorption characteristics of the surfactant on the membrane surface depend on the molecular structure of the surfactant such as the type of polar head and structure and length of the hydrocarbon chain and thus leading to the change in membrane surface charge. Indeed, as shown in Fig. 4(A), the membrane treated with cationic surfactants (CTAB or CPC) exhibited positive zeta-potential while the membrane that was treated with anionic surfactants (SLS or SLES) exhibited negative zeta potential on the membrane surface. This may be attributed to the fact that the initial adsorption of the cationic surfactant on membrane surface occurs due to the electrostatic attraction between the negative charge of the membrane and the positively charged head of the surfactant and thus leaving the hydrophobic chain towards the bulk water. Subsequently, there will be the formation of hemimicelles or two dimensional surfactant aggregate structures by the association of the surfactant ions with each other along the hydrocarbon chain while projecting the positively charged head of the surfactant towards the bulk water in order to reduce the free energy of the system [23]. This phenomenon results in the generation of positive charge on the membrane surface. Further, the hydrophobic chains of the hemimicelle type structure may be shrunk on the polyamide active layer as the dangling of the hydrophobic chains in the aqueous bulk solution is thermodynamically not favorable conformation—and thus making the membrane more compact which results in the decrease in separation performance. The large decrease in the membrane performance with the addition of CPC may be attributed to the lengthy

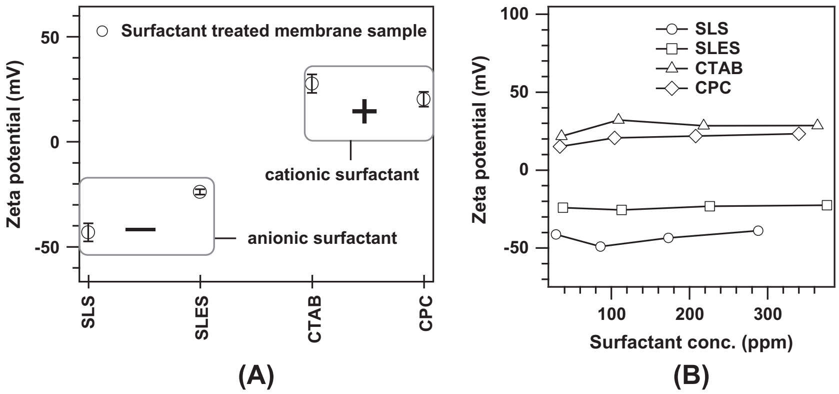

Fig. 4. Zeta-potential values of the membrane treated with cationic surfactants (A) and anionic surfactants (B).

aliphatic tail which probably tends to coil more on the polyamide surface and thus making it somewhat denser besides increasing the hydrophobic nature.

In the case of anionic surfactants, there will be electrostatic repulsions between the negatively charged membrane and the surfactant head. Hence, the initial adsorption of the anionic surfactant on the membrane surface occurs due to the hydrophobic interactions between the hydrophobic tail of the surfactant and the membrane surface and thus projecting the negatively charged head of the surfactant towards the bulk water. This results in the increase in the negative charge of the membrane surface. Further, it also appears that the surfactant chain might be in the expanded configuration due to the interaction of the negatively charged group with the feed solutes and thus improving the separation performance of the membrane. The membrane charges after the surfactant treatment with the surfactant concentration ranging from 30 to 380 ppm were nearly similar as shown in Fig. 4(B). This might indicate a trace amount (ppm level) of surfactant in the feed stream was enough to modify the membrane surfaces.

## 4. Conclusions

Application of the TFC RO membranes for water reclamation from grey-water containing 500–2,000 ppm TDS and small amounts (in ppm) of commercial detergents such as, a linear alkyl benzene-alfa olefin sulfonate-soda ash based detergent and a $C_8$–$C_{24}$ primary/secondary ethoxylates based detergent were carried out. The membrane performance was influenced by the detergent type in the feed water. This can be due to the fact that surface active agent (surfactant) of the detergent alters the surface potential of the membrane thereby affecting the performance. As observed by the AFM studies, the fresh TFC RO membrane had average surface roughness of about 116 nm which was decreased by about 50% in the surfactant treated samples. The effect of surfactant–membrane interaction on the membrane performance was clearly observed. The anionic surfactant in the feed enhanced the membrane performance with some increase (~2–3% increase) in salt rejection efficiency. On the other hand, the cationic surfactants in the feed reduced both the product flux (~50–70% decrease) and the salt rejection efficiency (~2–10% decrease) significantly. Thus, the changes in the membrane performances were attributed to the changes in membrane surface charge due to the surfactant–membrane interaction which agrees well with the membrane charge as determined by Zeta-potential measurements. The membrane treated with ~30 ppm cationic surfactants (CTAB or CPC) exhibited positive Zeta-potential on the membrane surface while the membrane treated with ~30 ppm anionic surfactants (SLS or SLES) exhibited negative zeta-potential on the surface.

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