Effect of Zeta Potential and Concentration on the Rejection Behavior of Calcium Carbonate by Ceramic Titanium Dioxide Nanofiltration Membrane

Amer Naji Ahmed Al-Naemi
PhD, Senior Chief of Engineers
Ministry of Science and Technology-Directorate of Environment and Water Treatment
amer.alnaemi@yahoo.com
Ahmed Faiq Hassan Al-Alawy
Professor
Chemical Engineering Department - College of Engineering -University of Baghdad
ahmedalalawy@yahoo.com
Mudhaffar Yacoub Hussein
Instructor
Oil Engineering Department - College of Engineering - University of Misan
mudhhussein@yahoo.com

Abstract

The rejection of calcium carbonate salt ($CaCO_3$) was investigated by using a ceramic titanium dioxide (TiO_2)-Alumina layered (Al_2O_3) nanofiltration membrane possessing a normal pore size of 0.9 nm.

The membrane was operated in the cross flow method. Measurements were conducted using several concentrations of salt (5.0 ppm and 10.0 ppm as under saturation), (13.0 ppm at saturation) and (50.0 ppm as above saturation), over different values of pH (3.0, 6.0 and 9.0), and at applied transmembrane pressure (TMP) changing from 1.0 to 15.0 bar. The feed solution at a flow velocities (1.0 and 2.0 m/s).

At constant pH (6.0) and velocity 1 m/s the rejection increases with increased pressure and reaches the highest value (61.0%) at (TMP), 6.0 bar with concentration (5.0 ppm), and then begins to decline with increasing pressure. Increasing both pH value and flow velocity increases rejection. Increased flow velocity from (1.0 m/s to 2.0 m/s), increases the rejection up to 6% at pH (6.0) and concentration 10.0 ppm. Maximum rejection was found equal to (70%) at (TMP) of 6.0 bar, concentration 5.0 ppm, pH 9.0 and velocity 2.0 m/s.

In the case of saturation, 50.0 ppm the rejection from the beginning decreases with increasing pressure. The monitored rejection characteristics were compared with zeta potentials of fine particles of the membrane were measured from electrophoretic (estimated by using electrophoresis method) material. The isoelectric point (i.e.p.) was at a pH 3.6. The TiO_2 membrane was negatively charged at pH higher than (i.e.p.) and positively charged at pH lower than (i.e.p.).

Keywords: Zeta potential, Salt rejection, Nanofiltration, Microelectrophoresis potential.

1. Introduction

The more widespread components of scale in applications of membrane are calcium carbonate ($CaCO_3$), calcium sulphate ($CaSO_4.2H_2O$), and silica, [11,23]. Together the nucleation and the development of crystal steps of the fouling or operation of scale formation based mostly on the ratio of supersaturation in the concentrate (saline solution feed) of a mineral salt. In operation, providers of membrane counseled not to exceed the product of solubility of each probable combination of scale formation compounds or to put some type of pretreatment of water. The more common process, other than limitations of water recovery (that in most situations is unfavorable), are adjustment of pH value by addition of acid and the use of antiscalants (inhibitors of scale). Commonly together techniques are used with each other for brackish waters treatment [12,1].

The capability to predict scaling is a significant factor in controlling its appearance. The applied technique in membrane plants of water treatment is based on determination of degree of supersaturation that is explained as the activity product of ion of the salt divided by its product of solubility. In specific cases, but, with different moderately soluble salts ($CaCO_3$, CaF_2, $BaSO_4$) supersaturation with regarding to a mineral salt does not substantially denote which scaling would take place [3,2]. In fact, when the ratio of supersaturation, much more than one (see Eq. 2), formation of scale happens [2].

The growth of a scale is a multistep process, of that adhesion of the scaling or fouling agents to the surface is a main stage. Water quality, flow velocity and temperature are some of factors influencing scaling.

In areas of geographical where ground water and rain water come into touch with bearing rock of carbonate, particularly, chalk and limestone, chemical weathering can happen. Weathering may share up to (50%) of the bicarbonate and carbonate salts existent in natural water. In other areas of non-carbonate rocks the bicarbonate and carbonate originate completely from the soil carbon dioxide and atmosphere carbon dioxide.

Concentrations of calcium carbonate in natural waters are normally lower than (15 ppm), however for waters related with loaded rocks of carbonate, concentrations may attain (30 to 100) ppm [6].

The possibility for calcium carbonate scaling occurs in most types of feed water, inclusive surface, brackish or well waters. $CaCO_3$ creates a dense, highly adherent precipitation and its deposit in a nanofiltration (NF) or reverse osmoses (RO) factory must be obviated. It is the almost popular kinds of scaling in many systems, containing oil or gas production systems or cooling installation of water. In systems of nanofilration (NF) and reverse osmoses (RO) it shows that the maximum danger of calcium carbonate scaling (as with another salt) occurs in the stream of concentrate at the ends of pores of the of the membrane system.

Fouling is a main problem in processes of nanofiltration (NF) and reverse osmosis (RO), putting critical limitations of performance to installations of membrane. An investigation of types, mechanisms and major species concerned of scaling in nanofiltration membrane can be sited in Ref. [26].

Fouling (or scaling of precipitation) products from the raised concentration of fouling species higher than their limits of solubility and leads to deposition on to the membrane. A raised concentration of the fouling creating species in the bulk because withdrawal of permeate, that is further increased in the zone next to the surface of membrane by the influence of the imbricated of concentration polarization, in fact, as water permeates across the NF and RO membranes, the concentration of retained ions in the boundary layer (BL) close to the surface of membrane becomes extremely more than which prevailing in the bulk of electrolyte solution. This impact is higher announced at great fluxes of permeate and less flow velocity. As in other kinds of scaling, fouling tends to decrease flow of permeate and raise pressure drop through the element and affects the efficiency of the performance of the (NF) and (R.O) membranes and reduces rejection. Furthermore, scaling may usually result in physical harm of the membrane because the irreversible pore plugging and to hardness of scale elimination. For that reasons, reduction of fouling or scaling is a significant consideration in the process of generality nanofiltration (NF) and reverse osmoses (RO) operation.

Researches on calcium carbonate scale formation in systems of membrane are finite. Drack et all. [9] depict a laboratory operation for description of the calcium carbonate scaling tendency reverse osmoses (RO) waters feed for estimating antiscalant performance. Whereas finite experimental data on calcium carbonate scaling on surfaces of membrane by determining flux decline of permeate can be found in the literature [5,14].

The aim of this work is to study for the first time the rejection behavior of calcium carbonate salt ($CaCO_3$) for nanofiltration titanium dioxide ceramic membrane in relation to its zeta potential at different electrolyte concentration, (below saturation, saturation and above saturation), pH, the transmembrane pressure/ permeate flux and two different cross flow velocities.

2. Theory

The driving force of thermodynamic for $CaCO_3$ crystallization, either on surface of membrane or in the bulk (formation of scale), is demonstrated as the variance of Gibbs free energy between the equilibrium state and supersaturated.

$$\Delta G = -RT\, ln[\frac{(Ca^{2+})(CO_3{}^{2-})}{K_{sp}}]^{\frac{1}{2}} \qquad (1)$$

Here (K_{sp}) is constant (or the solubility product of thermodynamic) of the prevailing polymorph, (T) is the absolute temperature and (R) is the constant of ideal gas. Amounts in parentheses indicated activities of the conformable ions. The expression in brackets is the ratio of supersaturation of the crystalline deposit, explained as [21,22]:

$$S = [\frac{(Ca^{2+})(CO_3{}^{2-})}{K_{sp}}]^{\frac{1}{2}} \qquad (2)$$

Bicarbonate (hydrogen carbonate HCO^-) and carbonate (CO_3^{2-}) are salts originated from carbonic acid (H_2CO_3). Hydrogen carbonate (H_2CO_3) is an extremely weak acid created when little quantities of (CO_2) dissolve in water, it is not mostly stable and splits up nearly instantly on forming.

The acid salt bicarbonate is formed when half the acidic hydrogen is exchanged by metal e.g. calcium. Carbonates are created when together the acidic hydrogen ions are replaced for a metal. The relative quantities of (CO_3^{2-}, HCO_3^- and H_2CO_3), in water are correlated to the pH. The process of weathering combined with the pH of water includes that the anion of bicarbonate is dominant in surface waters. Its concentration in waters of surface are mostly lower than 500 ppm and commonly lower than 25 ppm [6].

The zeta potentials (ζ) of the fine particles were measured (microelectrophoresis method) using equation of Helmhots-Smoluchowski:

$$\zeta = \frac{\mu U}{\varepsilon \varepsilon_o} \qquad (3)$$

Where:

- μ is the viscosity of solution (pa.s)
- $U = (\frac{u}{E})$ is the electrokintic mobility of the particle $(\frac{m/s}{V/cm})$
- u is the velocity of particle in electrical field (m/s)
- E is the strength of electrical field (V/cm)
- ε_o is the permittivity of free space (8.854×10^{-12} C/V.m)
- ε is the dielectric constant (75.8) [7,10].

3. Materials and Methods

3.1 Membrane

Circular tube a NF TiO_2 ceramic membrane (Inopor® single channel, produced by GmbH Veilsdrof – Germany) was chosen to carry out the experimental work of the present research. Tubular ceramic TiO_2 membrane having a normal pore size of

0.9 nm. The active membrane surface layer is formed of (TiO_2) with three supported layers of (Al_2O_3). The membrane pieces area is approximately 41.8 cm^2 (Inside diameter = 0.7 cm, outside diameter = 1 cm and length = 19 cm).

3.2 Experimental procedure

Experiments of membrane rejection were carried out in a laboratory cross flow membrane filtration unit with tubular ceramic nanofiltration dioxide membrane. Fig. 1 represents a schematic diagram of the experimental set up.

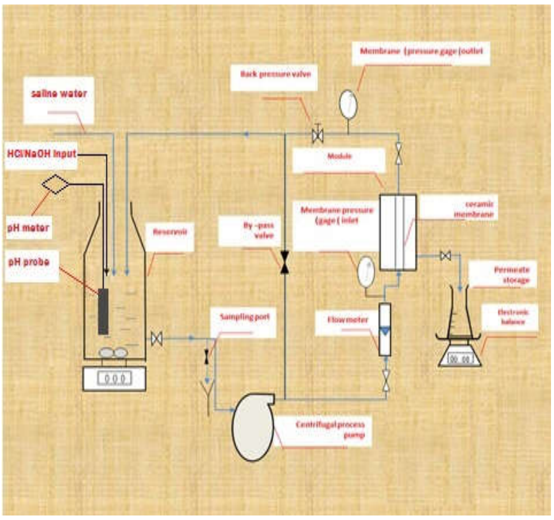


Fig. 1. A Schematic diagram of titanium dioxide nanofiltration membrane set up.

The feed solution, at flow rates of 2.3 L/min and 4.6 L/min, is lead up to the tubular ceramic membrane by means of a centrifugal pump (BALDOR. RELIANCE, Super-E Motor. CAT.No.CEM 3354, SPEC 35AOIZPBOZGI U.S.A) able to achieve required pressures reach to 15 bar.

The above flow rates equivalent to 1 m/s and 2 m/s respectively. Pressure is observed and controlled by using two globe valves at two ends of the membrane section (the entrance and the exit), it is thus preserved steady during the run. Permeate flow is observed continuously, flow rate of the permeate determined by using measuring cylinder fixed on top an analytical balance (Sartorius weighing Technology GmbH, Goettingen, Germany AZ 214, 28103699), glass containers (10 liter), a magnetic stirrer (Model No.HS-30, Human Lab Instrument Co. Korea), reinforced PVC 1.25 cm flexible piping (Germany) and different fittings. The tubular ceramic membrane was mounted in uPVC (see-through) module house that was held vertically, different pieces of piping, valves (st:st 316 L), connectors and a stop clock, complete the system. Salt ($CaCO_3$) (BDH chemicals Ltd pool England) were used as a solutions in the rejection experiments. Deionized water (BOECO, Filter Cartridge BOE80910 type : 50136990, Thermo Fisher, Germany) with conductivity 0.05 µs/cm was used in the preparation of salt solution. Further, the concentration of ions in the flux of permeate were observed. In this work each experiment of filtration was repeated twice to obtain good reproducibility. Rig of filtration was worked using on transmembrane pressure TMP (1-15) bar for rejection experiments. The transmembrane pressure (TMP) was monitored using two gauges pressure (WIKA Germany) at two ends of the nanofiltration membrane and controlled using a valve to produce the need backpressure. The concentration of cations in the permeate were estimated using inductive coupled plasma-optical emission spectrometry (ICP-OES) (Model: Agilent Technology 700 Series ICP-OES simultaneous ICP-AES, U.S.A).

3.3 Membrane Characterization

A piece of ceramic membrane was cut to an extent of two mm to achieve investigation of the NF TiO_2 surface of membrane by using SEM : Scanning electron microscope (FEI QUANTA 200, purge, Czeh Republic) turned on at an accelerating voltage (20 – 30 KV). Add to that, analysis of an elemental was determined by using (EDXS : an energy dispersive X-ray spectrometer). The zeta potential of (TiO_2) membrane was evaluated. A pieces of (TiO_2) membrane were crushed by using mortar. The effective diameter of the fine particles is approximately equal to (500 nm) as show in **Fig. 2** using (Zeta plus, Zeta potential and particle size, Analyzer, 21521, Brookhaven Instruments, U.S.A.).

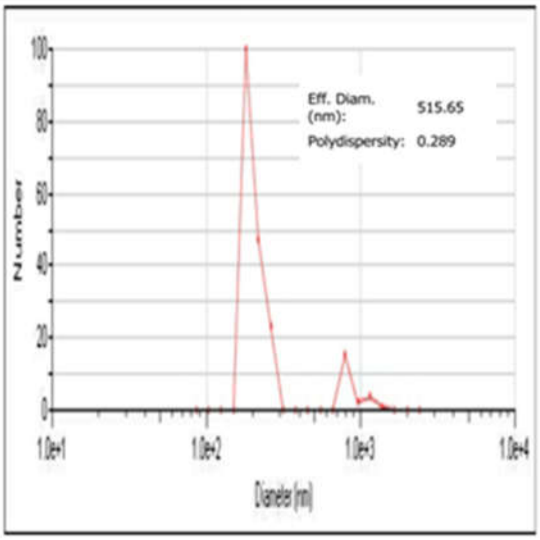


Fig. 2. Represents the effective diameter measurement of the tubular titanium dioxide nanofiltration membrane particles with Eff. Diam. : 515.65 nm.

4. Result and discussion

4.1 SEM image and spectrums EDXS of NF membrane.

The (SEM) cross section image of NF TiO_2 membrane is shown in **Fig. 3**. The tubular NF TiO_2 used in this work is a asymmetric membrane having effective side surface that is formed from a thin layer of TiO_2 and Al_2O_3 which can be seen distinctly. A typical ceramic membrane pore was fixed and (3.0) various membrane support layers the outer of that is formed of sintered Al_2O_3 are shown. **Fig. 4** represents the indicated spectrums of the TiO_2 effective surface of membrane gained by using (EDXS). It can be seen that the ceramic TiO_2 NF membrane used in this inspector contains the main elements, titanium, T, oxygen, O, aluminum, Al.

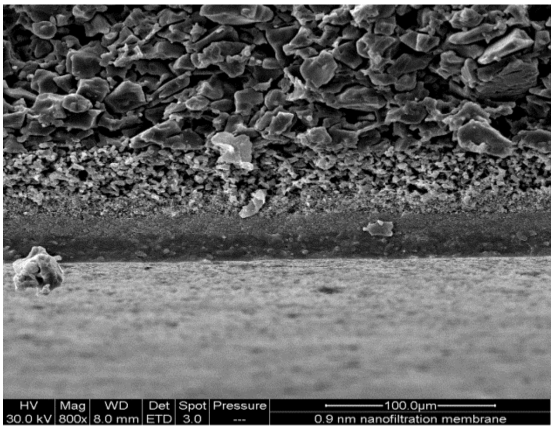


Fig. 3. The (SEM) image of cross-section of TiO_2 nanofiltration membrane

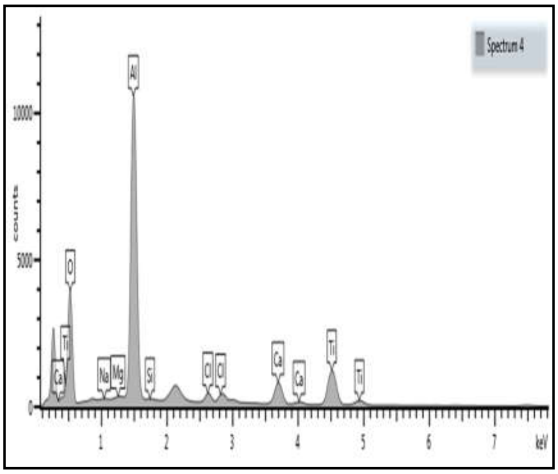
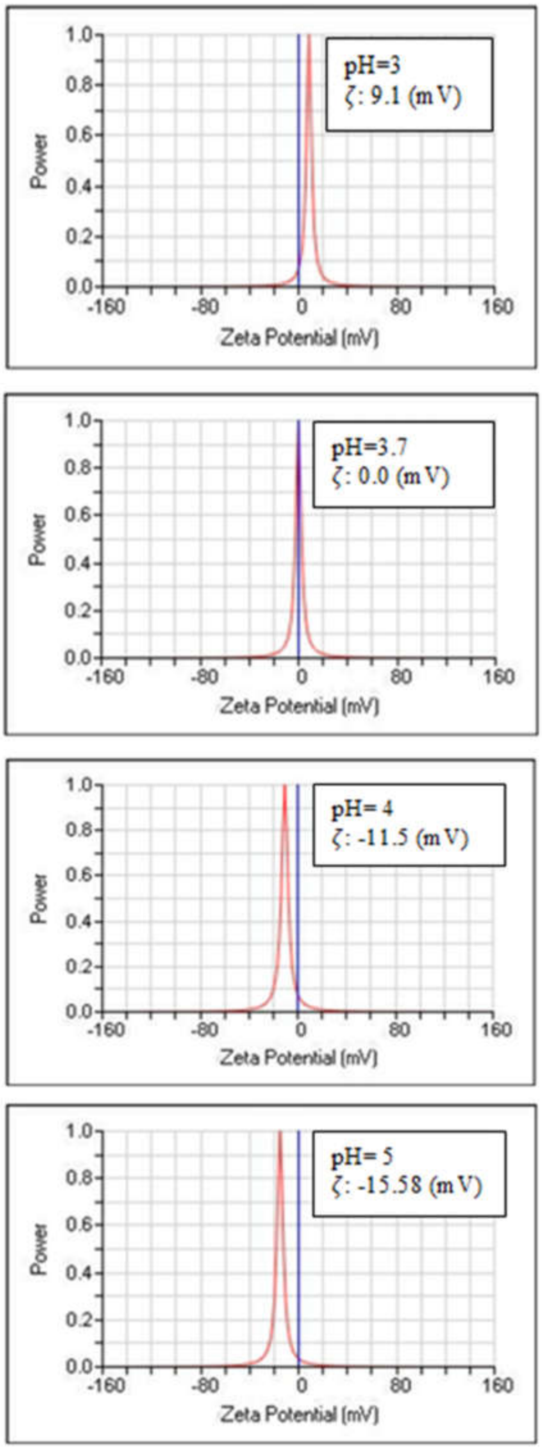


Fig. 4. EDXS spectrum of TiO_2 nanofiltration membrane.

4.2 Impact of electrolyte concentration and pH on the zeta potentials of TiO_2 NF membrane.

The electrophoretic mobility of the finely ground particles was estimated using (Zeta plus, Zeta potential and particle size, Analyzer, 21521, Brookhaven Instruments, U.S.A.) at two different concentrations of $CaCO_3$ (5 and 10 ppm) and pH values (3-9) as shown in **Fig. 5** and **Fig. 6** respectively.



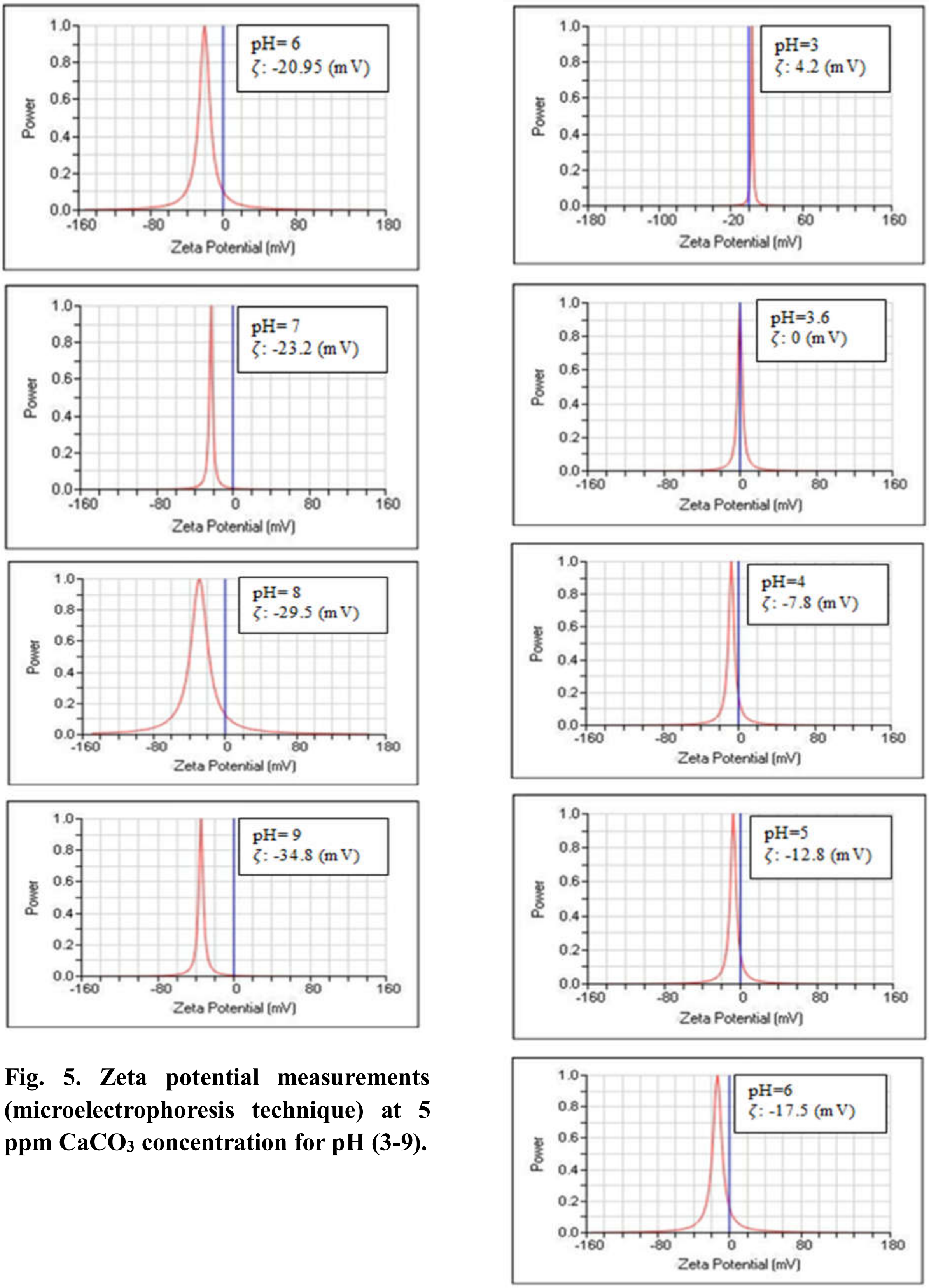


Fig. 5. Zeta potential measurements (microelectrophoresis technique) at 5 ppm $CaCO_3$ concentration for pH (3-9).

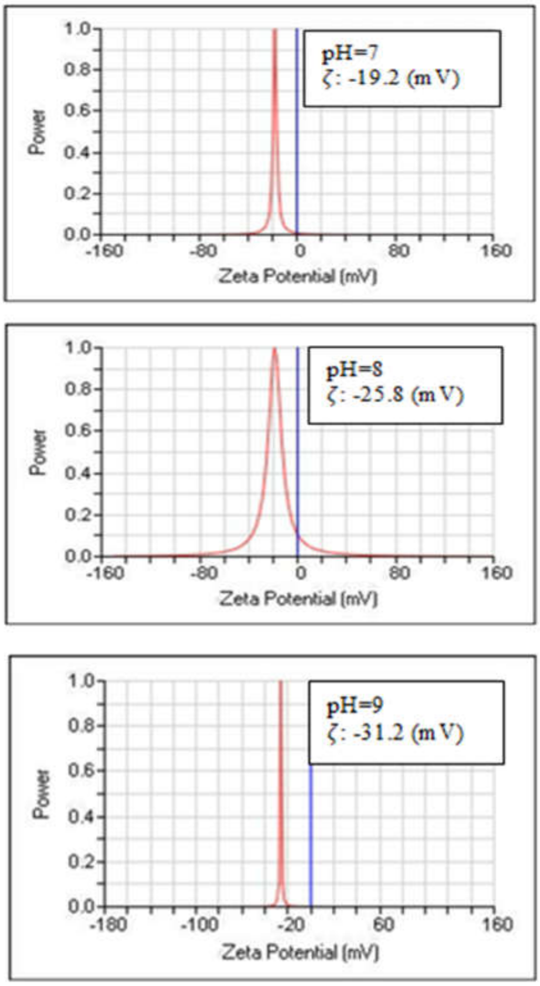


Fig. 6. Zeta potential measurments (microelectrophoresis technique) at 10 ppm $CaCO_3$ concentration for pH (3-9)

Fig. 7 shows a plot of the estimate zeta potential (microelectrophoresis technique) across a range of pH (3-9) using 5 and 10 ppm $CaCO_3$ as a background electrolyte. In order to keep the concentration fixed, the pH of the ceramic oxide suspensions was adjusted in the extent of (pH 3 to pH of 9) by using (0.1 M NaOH or HCl) and the electrokinetic potentials of the fine particles were estimated.

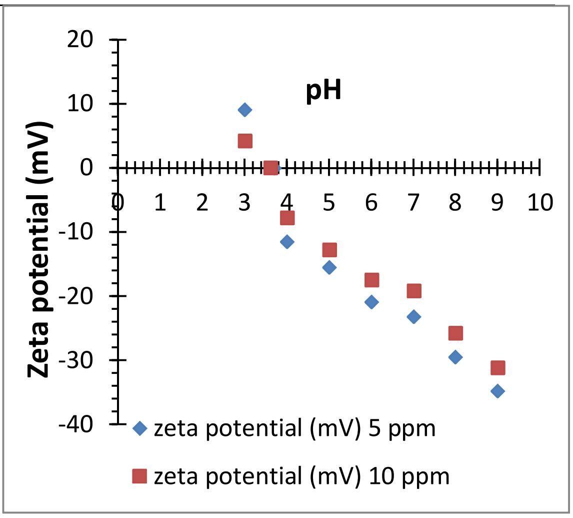


Fig. 7. Effect of pH on zeta potential.

The results of experiments showed that the electrokinetic potentials of the NF membrane used in this investigate is positive charged at pH of 3 being (9.1 and 4.2 mV) for (5 and 10 ppm) respectively. The (i.e.p.) is found between pH value of (3.7 and 3.6) respectively. Some investigator [20,15] have imputed changes in the isoelectric point to the adsorption of (cations and anions) of electrolyte solution on the surface of membrane. As the value of pH was increased the electrokinetic potential become higher negative, with the highest values were found at pH 9 (-34.8 and -31.2) mV for 5 and 10 ppm calcium carbonate, respectively. From those outcomes, it was shown that when fixing calcium carbonate concentration, the sign of the electrokinetic potential (zeta) could be considerably changed by changing pH, whilst the fixed value of pH, the changes in concentration of salt do not have such a big influence can be significantly obtained in the zeta potential values compared with the changes in zeta potential values with pH values changes.

This investigation is in agreement with other workers [19] who inspected the zeta potential of asymmetric ceramic membrane (TiO_2, Al_2O_3 and silica). And illustrated this behavior in terms of the proportion equilibrium which take place at the surface of membrane. The mean value of zeta potential reductions as the concentration of electrolyte solution rises, a result that may be interpreted by reduction in active thickness of diffuse layer as the concentration raises.

4.3 Effect of electrolyte concentration and (TMP) on the rejection of $CaCO_3$ at constant pH

The impact of concentration and (TMP) on the rejection of calcium carbonate as a single electrolyte in the 0.9 nm circular tube has been investigated experimentally. The experiments of rejection were carried out at fifteen different feed pressures in the extent from 1.0 to 15.0 bar with solute feed concentrations of 5 ppm, 10 ppm (below saturation), 13 ppm (saturation) and 50 ppm supersaturation concentration at constant pH (6.0).

Fig. 8 shows that the retention of calcium carbonate at 5, 10 and 13 as a function of applied transmembrane pressure (TMP) at pH (6.0) and velocity 1 m/s. It can be deduced, from this figure that the rejections of calcium carbonate was increased with increasing (TMP) in a noticeable jump when increasing the (TMP) from 1.0 bar to 2.0 bar. After that, the increase of rejection is gradually and slightly with increasing pressure until it reaches the highest rejection by a certain pressure and according to the concentration. The highest rejection of the calcium carbonate at constant pH (6.0) were obtained at applied transmembrane pressures (6,4 and 2 bar), were (61.2%, 56.8% and 50%) for $CaCO_3$ feed concentration of 5 ppm, 10 ppm and 13 ppm M respectively.

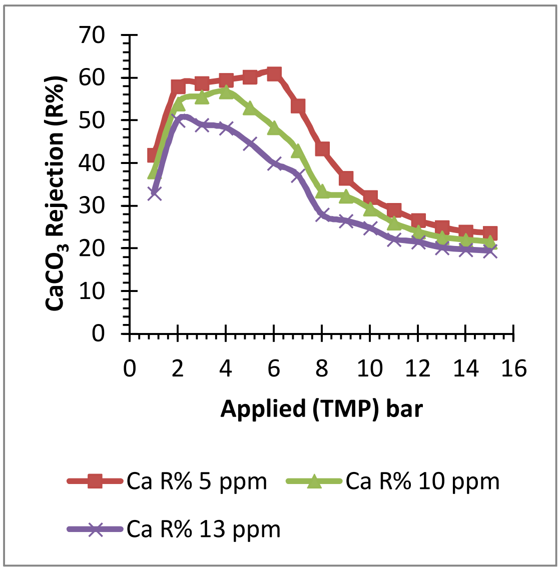


Fig. 8. Effect of concentration on $CaCO_3$ rejection.

After pressures 6,4 and 2 bar the rejections of calcium carbonate gradually decreases to the lowest rejection of (23.7%, 22% and 20%) for feed concentration (5, 10 and 13 ppm) respectively, at 15 bar.

The rejection behavior of salt solutions of calcium carbonate is rare and differs from other salts. Although calcium carbonate salt ($CaCO_3$) has very low solubility in water (13-15 ppm at 25° C), but its solubility increase with increasing pressure. All waters in contact with atmosphere absorb carbon dioxide. However, with increased applied transmembrane pressure (TMP), the pressure in the small nanopores of membrane will increase. Thus, the ratio of carbon dioxide solubility increased, carbonated water is formed by dissolving CO_2, reacts with lime stone calcium carbonate ($CaCO_3$) to form soluble calcium carbonate ($Ca(HCO_3)_2$) [12], as shown in the following chemical equations.

$$CaCO_3 + H_2O + CO_2 \rightarrow H_2CO_3 \qquad (4)$$

$$H_2CO_3 + CaCO_3 \rightarrow Ca(HCO_3)_2 \qquad (5)$$

The first reaction produces carbonic acid and the second reaction produces calcium bicarbonate.

An demonstration for the empirically estimated rejection order can be found by matching the coefficients of diffusion of the two different ions (CO_3^{-2} and HCO_3^-). The diffusion coefficient of HCO_3^- ion (1.19×10^{-9} m^2/s) is greater than CO_3^- ion (0.92×10^{-9} m^2/s) [18,24]. It is supposed that the coefficients of diffusion in the membrane can be similar by those in electrolyte solutions. The rejection of salts does not depend on the coefficient of diffusion of the salt, but on the ratio of coefficients of diffusion for the co-ions (HCO_3^- and CO_3^{-2}) and counter ion (Ca^{+2}) as previously fixed for another salts by Dresner [17] in explanation the perfect exclusion theory. Rejection raises with lowering coefficient of diffusion of the salt if the ratio of diffusion coefficients of the ions is fixed [4]. Based on those theories diffusion coefficient of ($Ca(HCO_3)_2$) is higher than the diffusion coefficient of ($CaCO_3$) and decreases the rejection with rising diffusion coefficient of the co-ion (HCO_3^-) and increases with rising coefficient of diffusion of counter-ion (Ca^{+2}). The order of the rejection sequence is inversely reflected in diffusion coefficients, so that diffusion shown to be a significant transport mechanism [16].

Solubility of calcium carbonate ($CaCO_3$) increases due to the formation of more soluble calcium bicarbonate. This explains why the rejection is reduced with increased pressure to a certain rang, based on the calcium carbonate concentration.

Fig. 9 shows that the rejection calcium carbonate at 50 ppm (supersaturation) as a function of applied (TMP). Form this figure it can deduced that the rejections of calcium carbonate were decreased as the applied (TMP) increased.

The rejection of the calcium carbonate at applied (TMP) 1.0 bar was (34 %) for $CaCO_3$ concentration 50 ppm while the rejection at 10.0 bar was (-37.6 %). This is explained by the reasons mentioned above in the case of concentrations 13 ppm and less. Add to that precipitation (or scaling) outcomes from the raised concentration of fouling forming species behind their limits of solubility and their scaling onto the membrane. A raised concentration of scale creating species in the bulk distinctly happens because withdrawal of permeate, that is further enhanced in the zone next to the permeate surface by superimposed influence of concentration polarization: in fact, as permeate of water through the membrane increased, the concentration of retentions ions in a layer of boundary near the membrane becomes significantly higher than which prevailing in the bulk. This impact is more pronounced at high fluxes of permeate and at low cross flow velocities [11,23]. The growth of the crystal stages of the scale creation process and the nucleation based mainly on the ratio of supersaturation of a salt in the concentrate.

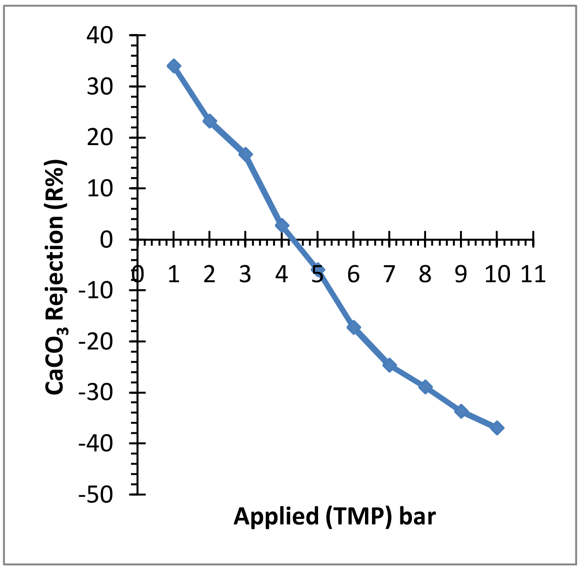


Fig. 9. Calcium carbonate rejection at supersaturation concentration (50 ppm $CaCO_3$).

4.4 Relation between zeta (electrokinetic) potentials and salt ($CaCO_3$) rejection.

The charge of material surface, that depends on the values of pH of the electrolyte solution, is an essential measurable factor inquiring the efficiency of a tubular ceramic NF membrane separation process. It should be saved in memory that the Ca^{+2} cation has a lesser ionic radius (0.099) nm [13] than the CO_3^{-2} anion (0.178) nm [8] and which either of them are smallest than the pore radius of NF membrane used 0.9 nm. Therefore, since the radius of ceramic NF membrane pore is great related to the radii of ionic, the rejection of electrolyte solution is not dominated by the influence of pore radius and the essential mechanism accountable for the retention of the salt is the interaction of the electrokinetic (zeta) potential that are connected to its charge of surface can be a helpful designation of a membrane`s propensity for rejection of salt.

The refusal of calcium carbonate at different pH (3,6 and 9) as a function of applied TMP is equal to (58%, 61% and 70%) respectively, for zeta potential (9.1, -20.95 and -34.8 mV) respectively at fixed concentration 5 ppm and velocity 1 m/s as shown in **Fig. 10**. It is shown that, for asymmetric titanium dioxide (TiO_2)/ Alumina (Al_2O_3) membrane used in the present research, the surface of membrane has positive charge at a value of pH lower than the pH value of isoelectric point (3.6 – 3.7), so that the cations adsorption, at least the ions of (H^+) from electrolyte solution must be taken into considerable and this may help to raise the rate of rejection and in addition the rate of rejection of the neutral salts combining a divalent cation and an anion could be predicted to reduction when the a values of pH rises to the (i.e.p) and then increase the percentage of rejection with increased pH values [25].

However, one of the essential parameters governing rejection of ions by the ceramic NF membrane is the repulsion of electrostatic between TiO_2 membrane and ions and thus alters in the zeta potential should be reflected by alters in rejection of salt. In this search, zeta potential is seen to be functions of pH values and concentration of salt. Increased concentration of salt decreased the electrokinetic (zeta) potential by reducing thickness of the electrical double layer (E.D.L) whereas alter in values of pH changes the zeta potential of amphoteric titanium dioxide nanofiltration ceramic membrane through reaction of the kind.

$$MOH + H^+ \rightleftharpoons MOH_2^+ \rightleftharpoons M^+ + H_2O \qquad (6)$$

$$MOH + OH^- \rightleftharpoons M(OH)_2^- \rightleftharpoons MO^- + H_2O \ (7)$$

The first reaction produces positively charged surface and the second reaction produces negatively charged surface, respectively, thus the isoelectricpoint agrees to the degree where there is no net (zero) charge on the surface of ceramic TiO_2 membrane. In addition to separate from the amphoteric oxide surface dissociation hydronium (H^+) and hydroxyl (OH^-) groups may also physically adsorbed thus changing the charge of surface membrane. As there is no repulsion of electrostatic between ions and surface of membrane when there is no charge a membrane will be most inactive at its isoelectric point and this will be noticed as less in rejection of salt. In the existent search the isoelectric point is about pH of (3.6 – 3.7) (electrophoresis), thus a lower value in the rejection of salt is predicted between pH of (3.5 – 4). **Fig. 10** shows the calcium carbonate ($CaCO_3$) rejection as a function of (TMP/permeate flux) at pH of (3,6 and 9) for concentration (5 ppm) calcium carbonate respectively, this represents the sequence of zeta potential interactions created between the membrane surface charge and the ions.

The least in rejection of salt was found at pH of (3.0) equals to (58%) that is broadly in correspond with the determined of rejection by using streaming potential method by Jacobasch [15].

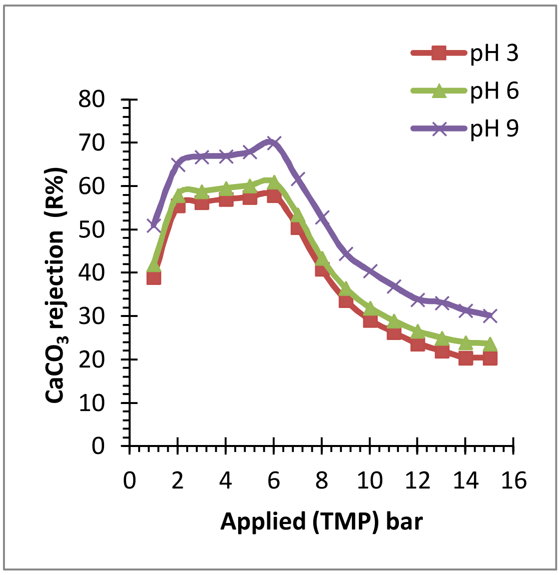


Fig. 10. Effect of pH on $CaCO_3$ rejection.

4.5 Effect of velocity on the rejection of salt ($CaCO_3$).

The effect of a cross flow velocity on the rejection of ($CaCO_3$) as a function of (TMP) / flux of permeate has been studied. The experiments of rejection were conducted at average of feed pressures (1-15 bar) with solute feed concentration of 10 ppm and pH (6.0). **Fig. 11** shows that the rejection of ($CaCO_3$) was increased with increasing cross flow velocity as the maximum rejection (56.8 %) at 1 m/s has become (60.7 %) at 2 m/s and increase ratio was approximately (6%) and interpretation of the result is that increased across flow velocity leads to minimize concentration polarization [11,23,16].

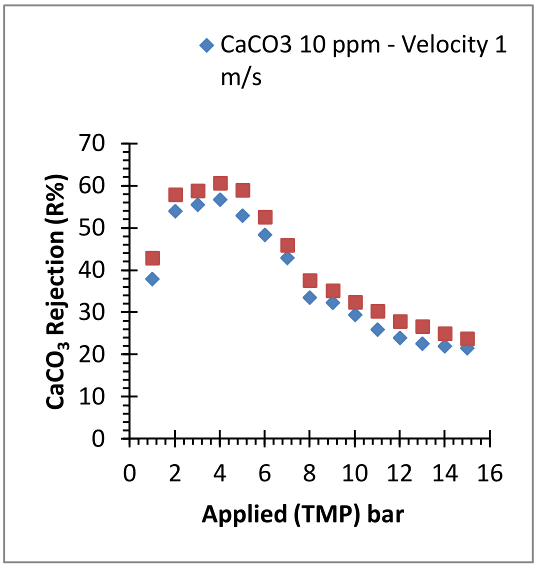


Fig. 11. Effect of velocity on the rejection of $CaCO_3$.

5. Conclusions.

The analysis result by using images of (SEM) and a spectrum analyzer of (EDXS) used to estimate the structure and composition of the tubular ceramic titanium dioxide NF membrane is of asymmetric building and is included an effective surface prepared of titanium dioxide (TiO_2) supported by (3.0) layers of alumina (Al_2O_3) each of various thickness. In the existence of low concentrations of electrolyte solution ($CaCO_3$), the rejection varies with concentration, pH values and transmembrane pressure (TMP) / permeate flux, although at above saturation concentration of $CaCO_3$ the rejection was always decline with increasing pressure. The rejection increased with increased cross flow velocity, pH value and decreased with increased concentration.

The electrokinetic (zeta) potential alters with values of (pH) and was shown to be positive at little (pH) lower than (pH) of 3.6 – 3.7 (i.e.p.) and negative at (pH) higher than (i.e.p.), Zeta potential reduce with increasing calcium carbonate concentration due to the decreasing the thickness of double electrical layer (diffusion layer).

Observed as a sequence, the rate of rejection of salt reduces continually with rising concentrations of calcium carbonate at each pH, a lower in calcium carbonate rejection was found at pH of 3.0 for the asymmetric ceramic titanium dioxide membrane, that was closest to the pH of the isoelectric point of the membrane.

Nomenclature

K_{sp} is the solubility product.

R is the universal gas constant (8.314 $J.mol^{-1}.K^{-1}$).

T is the temperature (K°).

ζ is the zeta potential (V).

μ is the viscosity of the medium (0.89×10^{-3} pa.s).

ε_o is the permittivity of free space (8.854×10^{-12} C/V.m).

ε is the Dielectric constant (75.8).

U is the electrophoretic mobility ($\frac{u}{E}$).

u is the velocity of particle in electrical field (m/s)

E is the strength of electrical field (V/cm)

References:

1. Amjad, Z., 1996, Scale inhibition in desalination applications—an overview, in: Proceedings of the Corrosion '96, NACE Conference, Paper 230, p.

2. Andritsos, N., Kontopoulou, M., Karabelas, A.J., Koutsoukos, P.G., (1996), $CaCO_3$ deposit formation under isothermal conditions, Can. J. Chem. Eng. 74, 911–919.

3. Boerlage, S.F.E., Kennedy, M.D., Bremere, I., Witkamp, G.J., van der Hoek, J.P., Schippers, J.C., (2000), Stable barium sulphate supersaturation in reverse osmosis, J. Membr. Sci. 179, 53–68.

4. Bowen, W.R. , Mohammad, A.W., Hilal, N., (1997), Charac- terisation of nanofiltration membranes for predictive purposes-use of salts, uncharged solutes and atomic force microscopy, J. Membr. Sci. 126, 91-105.

5. Brusilovsky, M., Borden, J., Hasson, D., (1992), Flux decline due to gypsumprecip-itation on RO membranes, Desalination 86 , 187–222.

6. Chapman D (Ed.) (1992), Water Quality Assessments, A Guideto the Use of Biota, Sediments & Water in Environmental Monitoring. Chapman Hall, UK.

7. Chiu, T.Y., James, A.E., (2006), Electrokinetic haracterization of cleaned non-circular multi-channelled membranes, Desalination 189, 13–20.

8. Dasent, (1979) p. 78; H.D.B. Jenkins and K.P. Thakur, J. Chem. Educ., 56, 576.

9. Drak, A., Glucina, K., Busch, M., Hasson, D., Laˆıne, J.-M., Semiat, R., (2000), Lab-oratory technique for predicting the scaling propensity of RO feed waters, Desalination 132, 233–242.

10. Ernst, M., Bismarck, A., Springer, J., Jekel, M., (2000), Zeta-potential and rejection rate of a polyethersulfone

nanofiltration membrane in single salt solution, J. Membr. Sci. 165, 251–259.

11. Faller, K.A. (Technical Editor), 1999, AWWA Manual M46—Reverse Osmosis and Nanofiltration, AWWA.

12. Gill, J.S., 1996, Development of scale inhibitors, in: Proceedings of the Corrosion '96, NACE Conference, Paper 229, p. 18.

13. Hassan, A., Ali, N., Abdull, N. and Ismail, A., 2007, A theoretical approach on membrane characterization: the deduction of fine structural details of asymmetric nanofiltration membranes. Desalination, 206(1): p. 107-126.

14. Hasson, D., Semiat, R., Bramson, D., Busch, M., Limoni-Relis, B., (1998), Suppres- sion of CaCO scale deposition by anti-scalants, Desalination 118 285–296.

15. Jacobasch, H.J., Simon, F., Werner, C., Bellmann, C., (1996), Technisches Messen. 63 439–446.

16. Johan Schaep, (1998) , Bart Van der Bruggen, Carlo Vandecasteele, Dirk Wilms, Influence of ion size and charge in nanofiltration, Separation and Purification Technology 14, 155–162.

17. L. Dresner, (1972), Some remarks on the integration of the extended Nernst-Planck equations in the hyperfiltration of multicomponent solutions, Desalination 10, 27-46.

18. Li Y.-H. and Gregory S. (1974) Diffusion of ions in sea water and in deep-sea sediments. Geochim. Cosmochim. Acta 38, 703–714.

19. Moritz, T., Benfer, S., Arki, P., Tomandl, G., (2001) , Influence of the surface charge on the permeate flux in the dead-end filtration with ceramic membranes, Sep. Purif. Technol. 25, 501–508.

20. Mullet, M., Fievet, P., Reggiani, J.C., Pagetti, J., (1997), Surface electrochemical properties of mixed oxide ceramic membrane: zeta potential and surface charge density, J. Membr. Sci. 123, 255–265.

21. Papelis, C., Hayes, K.F., Leckie, J.O., 1988, HYDRAQL, Technical Report No. 306, Stanford University, Stanford, CA.

22. Plummer, L.N., Busenberg, E., (1982), The solubilities of calcite, aragonite and vaterite in CO_2 –H_2O solutions between 0 and 90°C, Geochim. Cos- mochim. Acta 46 1011–1040.

23. Rautenbach, R., Albrecht, T., 1989, Membrane Processes, John Wiley & Sons, New York.

24. Robinson R. A. and Stokes R. H. (1959) Electrolyte Solutions, second ed. Butterworth's, London, p. 559.

25. Santos, L.R.B., Santilli, C.V. , Larbot, A., Persin, M., Pulcinelli, S.H., (2001), Influence of membrane-solution interface on the selectivity of SnO_2 ultrafiltration membranes, Sep. Purif. Technol. 22–23 , 17- 22.

26. Schafer, A., Andritsos, N., Karabelas, A.J., Hoek, E.M.V., Scheider, R., Nystrom, M., 2004, Fouling in nanofiltration, in: A. Sch¨ afer, D. Waite, A. Fane (Eds.), Nanofiltration—Principles and Applications, Elsevier, Oxford, UK, pp. 169–239.

تأثير جهد زيتا والتركيز في سلوك رفض $CaCO_3$ باستخدام غشاء الترشيح السيراميكي النانوي TiO_2.

عامر ناجي احمد

دكتوراه- خبير- رئيس مهندسين

وزارة العلوم والتكنولوجيا – دائرة البيئة ومعالجة المياه

الأستاذ احمد فائق حسن العلوي

قسم الهندسة الكيمياوية - كلية الهندسة - جامعة بغداد

المدرس مظفر يعقوب حسين

قسم هندسة النفط - كلية الهندسة - جامعة ميسان

الخلاصة :

تم دراسة ازالة (رفض : *rejection*) ملح كاربونات الكالسيوم ($CaCO_3$) باستخدام غشاء ثاني اوكسيد التيتانيوم (TiO_2) السيراميكي النانوي المدعوم بطبقات من الالومينا (Al_2O_3).

غشاء الترشيح يمتلك حجم قطر اولي *0.9* نانو متر. اعتماداً على ذوبانية ($CaCO_3$) تم اجراء قياسات ازالة الملح من الماء (رفض : *rejection*) باستخدام عدة تراكيز من الملح (*5* و *10* ملغم/لتر) تحت نسبة التشبع, (*13* ملغم/لتر) نسبة التشبع و (*50* ملغم/لتر) فوق التشبع وبدوال حامضية *pH* مختلفة (*3* , *6* و *9*) وبضغط مرور عبر الغشاء *(TMP)* من *1.0* الى *15* بار.

تم استخدام سرعتين لجريان المحلول الداخل (*1* م/ثا) و (*2* م/ثا). في دالة حامضية *pH* ثابتة *(6)* وسرعة (*1* م/ثا) تزداد الازالة مع زيادة الضغط وتصل الى اعلى قيمة *(61%)* في ضغط (*6* بار) وبتركيز (*5* ملغم/لتر) وبعد ذلك تبدأ بالنزول مع زيادة الضغط. زيادة كل من الدالة الحامضية *pH* وسرعة الجريان تؤدي الى زيادة نسبة الازالة. عند زيادة السرعة من (*1* م/ثا) الى (*2* م/ثا) تزداد نسبة الازالة الى حدود *(6%)* في دالة حامضية *pH (6.0)* وتركيز (*10* ملغم/لتر). اعلى نسبة ازالة وجدت *(70%)* في ضغط *(6.0)* بار, ودالة حامضية *pH (9.0)* وسرعة (*2* م/ثا), في حالة التشبع (*50* ملغم/لتر) الازالة من البداية تنقص مع زيادة الضغط.

نتائج الازالة الحاصلة تم مقارنتها مع جهد زيتا المقاس بواسطة طريقة الترحيل الكهربائي *(microelectrophoresis potential method)*. نقطة التعادل الكهربائي للغشاء حصلت في *pH (3.6)*. وضحت النتائج بأن الازالة تزداد مع زيادة جهد زيتا. غشاء TiO_2 شحنته سالبة في قيم *pH* اعلى من *(3.6)* وموجبة في قيم *pH* اقل من *(3.6)*.

الكلمات المفتاحية: جهد زيتا, رفض الملح, الترشيح النانوي, جهد الترحيل الكهربائي.