



## Measuring zeta potential of ceramic TiO<sub>2</sub> NF membrane for different salts by filtration potential technique using innovated silver electrodes

Mudhaffar Yacoub Hussein<sup>a,\*</sup>, Amer Naji Ahmed Al-Naemi<sup>b</sup>,  
Ahmed Faiq Hassan Al-Alawy<sup>c</sup>, Faten Hameed Kamil<sup>d</sup>

<sup>a</sup>*Oil Engineering Department, College of Engineering, University of Misan, Misan, Iraq, Tel. +9647801857780, email: mudhhussein@yahoo.com (M.Y. Hussein)*

<sup>b</sup>*Environment and Water Research Directorate, Ministry of Science and Technology, Baghdad, Iraq, Tel. +9647721779647, email: bamer.alnaemi@yahoo.com (A.N.A. Al-Naemi)*

<sup>c</sup>*Chemical Engineering Department, College of Engineering, University of Baghdad, Baghdad, Iraq, Tel. +9647901205905, email: cahmedalalawy@yahoo.com (A.F.H. Al-Alawy)*

<sup>d</sup>*Chemical and Petrochemical Research Center, Corporation of Research and Industrial Development, Ministry of Industry and Minerals, Baghdad, Iraq, Tel. +9647732405709, email: dfaten\_kamil@yahoo.com (F.H. Kamil)*

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### ABSTRACT

Nanofiltration (NF) and zeta potential are being increasingly used in water, wastewater, and pharmaceutical applications. In this study, the zeta potential behaviors of eight different 0.01 M salts (NaCl, KCl, NaHCO<sub>3</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, and MgSO<sub>4</sub>) for 0.9 nm tubular ceramic titanium dioxide NF membrane were measured for the first time using a filtration potential technique by conducting in-situ two electrodes made from a composite material that consisted of pure silver and 4% gauge 21 gold. The measurements were conducted under pH 3–9 at an applied transmembrane pressure (TMP) of 0.25–1.5 bar. Experimental results showed that the membranes of the salts were negatively charged at neutral pH and had an isoelectric point (IEP) of pH 3.4–3.8. Membrane zeta potential results were compared and justified using the electrophoresis method for the same membrane. The powder dispersions of the pulverized membrane in this measuring technique were a suspension at a certain salt concentration. Experimental results from the electrophoresis method agreed with those of the filtration potential method, whose IEP was at pH 3.3–3.5. The rejection experiments of the reference solutions (0.1 and 0.01 M NaCl) were conducted at a constant applied TMP of 12 bar. Rejection results showed that both NaCl concentrations were a function of pH. The low rejections were 17% and 21% at pH 3.8 for 0.01 and 0.001 M NaCl, respectively, and the high rejections were 34.2% and 38% at pH 9. This work also investigated the effects of the measured membrane zeta potential on the ion rejection of the standard solution of NaCl (0.01 and 0.001 M) using a similar pH range.

*Keywords:* Nanofiltration; Salt rejection; Zeta potential; Filtration potential

### 1. Introduction

The electrostatic interaction among ions in the water to be desalinated and the surface charge of the membrane plays an important role in separating ions. The impact of membrane charge on the transport of ions has been demonstrated by Donnan [1]. The widely used Donnan exclusion

is often applied to quantitatively interpret the rejection of ions [2]. Nanofiltration (NF) membranes have been rapidly developed for water flux and salt rejection because of its capability to maintain high performance levels at operating pressures that are lower than those of its predecessors [3]. NF and RO show similar rejection performances for polluting metals. NF has high fluxes at low pressures and therefore has been suggested as a good treatment that results in low capital costs of operation and maintenance

\*Corresponding author.

[4]. The separation mechanism is usually demonstrated in terms of size and charge effects [2]. The transmission of uncharged solutes is obtained by diffusion due to a gradual difference in concentration and by convection due to a pressure difference across the membrane. A sieving mechanism is reliable for the retention of uncharged solutes. An electrostatic reciprocal action (influence) happens between the membrane and charged components because most NF membranes are charged (foremost negatively).

The surface of a ceramic membrane acquires a charge when brought into contact with an aqueous medium. This charge affects the distribution of ions at the interface of the membrane and the solution, and equilibrium happens between the solution and the membrane. The ionic concentrations in the solution are not equal to those in the membrane because of the fixed membrane charge. The opposite sign of the charge to the fixed charge of the membrane (counter ion) concentration is lower in the bulk solution phase than in the membrane phase. The same sign of charge as the fixed membrane charge (coion) concentration is higher in the solution phase than in the membrane phase. A potential difference known as the Donnan potential is created in the interphase and prevents the transmission of ions of opposite charges to the solution phase and ions of the same charge to the membrane phase.

The basis of all the models of the double layer is the concept of the surface of the shear (slipping) plane. This plane surface separates the moving part of the electrical double layer (EDL) from the fixed part. The electrical potential at the shear plane is called the electrokinetic or zeta potential and is important to surface and colloids science because the surface potential itself cannot be specified experimentally. Determining the zeta potential from the membrane surface is important for membrane fouling research. However, this property is generally ignored to determine optimal operating conditions for many types of membrane separation processes. The zeta potential can be determined from one of the following electrokinetic measurements: filtration potential, electrophoresis, electroosmosis, and sedimentation potential [5]. Filtration potential and electrophoresis are the basis for most common methods, and other methods may seldom be used [6].

The filtration potential is the best experimental technique for the electrokinetic characterization of flat and tubular membrane surfaces [5] and involve the measurement of the electrical potential across the membrane under flow conditions. When the electrolyte solution is forced through the pores by the pressure gradient, the charges in the moving part of the double electrical layer move toward the ends of the pores; their accumulation creates an electrical field and a potential difference per pressure gradient that is usually known as filtration potential [7]. The performances of NF ceramic membranes in removing salinity from water are based on the complexity and concentration of the ions in the solution to be filtered and the kind of membrane material. Moreover, ceramic membranes made of metal oxides ( $\text{TiO}_2/\text{Al}_2\text{O}_3$  on the surface support in alumina) usually exhibit an amphoteric behavior; consequently, the electrical surface charge relies on the pH of the solution to be treated. Thus, attraction or repulsion happens between the charged membrane and the ionic species in the solution. In this situation, the separation of the NF membrane in the processing of the

ionic solution can be demonstrated by the summation of the size and charge influences.

The membrane charge relies on the pH of the solution and the IEP of the membrane [8]. Many studies on the filtration potential measurement of ultrafiltration (UF) membranes have been shown in the literature [9,10]. For UF membranes, these measurements reflect the filtration potential of the pores instead of the surface of the membrane. The pore filtration potential is an induced potential that occurs when the electrolyte solution flows through the membrane, whereas the surface filtration potential (for NF and RO) is an induction potential that occurs when the electrolyte solution flows tangentially to the membrane. Few studies have explored the measurement of filtration potential for NF membranes. Most of these works are limited in scope and concern soft electrolytes.

Inspection surface charge as a function of pH is important for the comprehension base, the acid characteristics of membrane surface active groups. Zeta (electrokinetic) potential was studied as a function of ionic strength and pH. However, only a limited extent of membrane types and solution chemistries were estimated. Certain complex solution chemistries pertinent to the NF processing of wastewater and natural water were not considered. Data obtained with soft salt solutions are incapable of supplying sufficient information about the various ranges of ion adsorption that may occur in the broad extent of salts in the industrial process of membrane separation [10].

The aim of this study is to systematically measure the zeta (surface charge) potential of tubular ceramic  $\text{TiO}_2$  NF membrane using filtration potential technique (utilizing two electrodes of composite silver and 4% gold to be used as alternative to platinum electrodes) under a wide range of solution chemistries (different type of salts) and investigate the performance (solute rejection) of NF membrane during a filtration of NaCl solution as a single salt to relate the performance of membrane to its charge (zeta potential) characteristics. The charge properties were estimated at different solution chemistries as a function of pH and performance was estimated at NaCl solution as a function of pH, concentration and transmembrane pressure.

The measured value of filtration potential proposed as mean values a verged on the membrane length. In addition, tangential measurements, which are usually used to overcome the tangential filtration potential which (created because of pressure drop that induced by the flow within the membrane module) could be also difficult to interpret due to the contribution to conduction current of the solution within pores.

The cost of the only raw material necessary for the manufacture of platinum electrodes is close to \$7000, and the cost of raw materials and the manufacture of alternative electrodes do not exceed \$150. Moreover, the manufacturing process of silver is easy because of the melting point of silver ( $961.78^\circ\text{C}$ ), which is considerably lower than that of platinum ( $1768.3^\circ\text{C}$ ). Silver (Ag) + 4% gold (Au) electrodes used in measuring of filtration potential, as alternative of platinum electrodes because it was cheaper and easier to use than Ag/AgCl electrodes since Ag/AgCl electrodes need to prepare coating cell [11].

The impact of solution chemical composition on the properties of the surface charge of the modern NF ceramic

membrane is studied. Furthermore, this work explores the ions that commonly exist in wastewater and natural water. The influences of solution pH, nonchalant monovalent ions ( $\text{Cl}^-$  and  $\text{Na}^+$ ), divalent anions ( $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$ ), and divalent hardness cations ( $\text{Mg}^{+2}$  and  $\text{Ca}^{+2}$ ) are involved. Surface charge mechanism procurement using the NF membrane in the existence of these solution chemistries are designed and discussed. The relations between zeta and filtration potentials (electrokinetic potential) are inspected for the NF ceramic membrane at various electrolyte concentrations and pH because the connection between membrane selectivity in terms of salt retention and zeta potential represents a linear way of correlating the electrostatic characteristics of membrane surface with its retention properties.

## 2 Materials and methods

### 2.1. Membrane

A tubular NF ceramic membrane (Inopor® single-channel, GmbH Veilsdorf, Germany) was used to perform the experimental work of this study. A tubular membrane with a nominal pore size of 0.9 nm was selected and categorized as the NF membrane. The effective inner surface layer (where the real separation occurred) was made of titanium dioxide ( $\text{TiO}_2$ ) with three alumina support layers. The total dimensions of the membranes were 7 mm inner diameter, 10 mm outer diameter, and 190 mm length. The permeate area for every tubular membrane tube was nearly  $4.18 \times 10^{-3} \text{ m}^2$ .

### 2.2. Filtration experiments

Eight salt solutions ( $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{NaHCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{MgSO}_4$ ) (BDH Chemicals Ltd., Poole, England) were used as the background electrolytes in the zeta potential measurements. A sodium chloride solution

was used in the rejection measurements. The salt solution was prepared using ultra-pure water (BOECO, Filter Cartridge BOE80910 type: 50136990, Thermo Fisher, Germany) with a resistivity of  $18 \text{ M}\Omega \text{ cm}^{-1}$ . In the feed solution,  $\text{NaCl}$  was prepared at two concentrations ( $10^{-1}$  and  $10^{-2} \text{ M}$ ) and the other salts ( $\text{KCl}$ ,  $\text{NaHCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$ ) were prepared at  $10^{-2} \text{ M}$  and used in the cross flow.

The NF membrane system is schematically shown in Fig. 1. The major parts were glass containers (5 L), a magnetic stirrer (Model No.HS-30, HumanLab Instrument Co., Korea), centrifugal pump (BALDOR.RELIANCE, Super-E Motor. CAT.No.CEM3354, SPEC35AOIZPBOZGI USA), 12.7 mm reinforced flexible PVC pipe (Germany), and various fittings. The membrane was mounted on a transparent uPVC module house, which was positioned vertically. The flow rate of the permeate was fixed using a measuring cylinder on an analytical balance (Sartorius Weighing Technology GmbH, Goettingen, Germany AZ 214, 28103699) and a stopwatch. Different pieces of connectors, pipings, and valves (st:st 316L) and a flow meter (GemüGebrMüller, Germany) completed the instruments.

Moreover, the concentrations of chloride and sodium ions in the permeate were observed. In this study, every filtration experiment was repeated at least twice to ensure reproducibility. The rig of the filtration worked at a cross flow velocity of  $1.0 \text{ m s}^{-1}$  at 0.25–1.5 bar TMP for the zeta potential experiments and 1–15 bar TMP for the rejection experiments. The TMP was observed using two pressure gauges (WIKA Germany) at each end of the membrane and controlled using a valve to produce the desired back pressure. The concentration of cations in the permeate was determined using inductive coupled plasma–optical emission spectrometry (ICP-OES) (Model: Agilent Technology 700 Series ICP-OES simultaneous ICP-AES, U.S.A). The concentration of anions was measured using IC (881 Compact IC pro- $\Omega$  Metrohm, 863 Compact Autosampler). It is important to mention that the collected permeate flux was returned to the main glass container after any step.

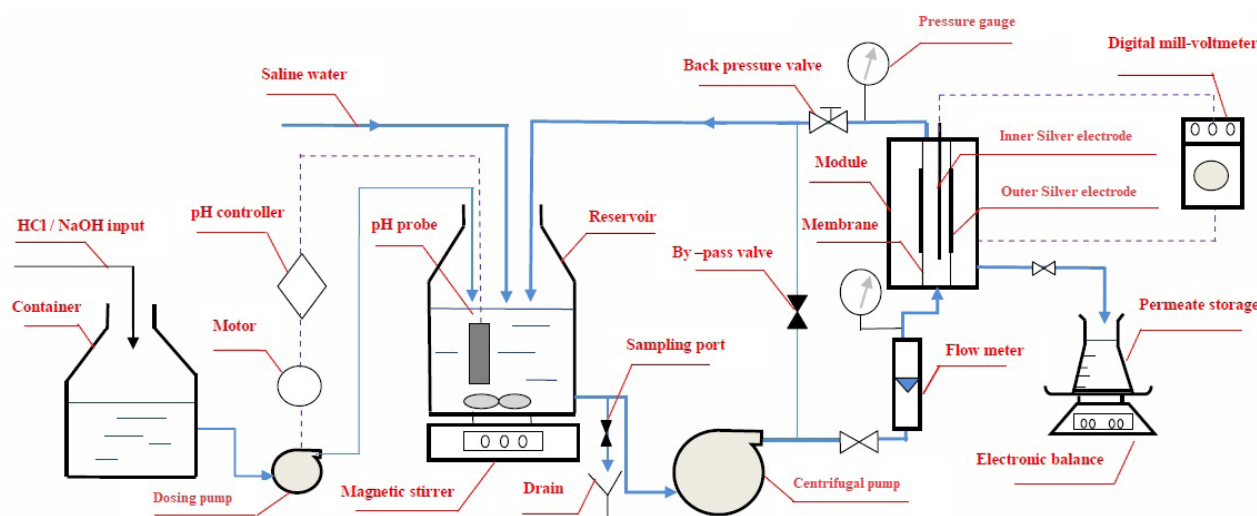


Fig. 1. Schematic diagram of tubular ceramic titanium dioxide NF membrane filtration flux rejection and zeta potential fouling installation.

### 2.3. Membrane characterization

A sample of the membrane was cut to a length of 3 mm to enable the inspection of the membrane surface using a scanning electron microscope (SEM) (FEI QUANTA 200, purge, Czech Republic) at an accelerating voltage of 20–30 kV. Moreover, elemental analysis was conducted using an energy-dispersive X-ray spectrometer (EDXS). The filtration and zeta potentials were measured. Part of the membrane was cut and crushed using a mortar. The effective diameter of the powder particles (516 nm) is shown in Fig. 2 (Zeta plus, Zeta potential, and particle size, Analyzer, 21521, Brookhaven Instruments, USA). The electrophoretic mobility of the powder particles was measured (Zeta plus, Zeta potential, and particle size, Analyzer, 21521, Brookhaven Instruments, USA) at two different ionic strengths of NaCl ( $10^{-1}$  and  $10^{-2}$  M). To maintain stable ionic strength, the pH of the particle (oxide) suspensions was adjusted to pH 3–9 using 0.1 M NaOH or HCl (where convenient). The main assumption, which is the fact that the contribution of the diffusive potential on the overall filtration potential was neglected, and the potential was assumed to be equivalent to a streaming potential. In this case, using Helmholtz-Smoluchowski equation to estimate an equivalent zeta potential.

The Velocity of a particle in an electric field is usually referred to as its electrophoretic mobility. With this information we can get the zeta potential of the particle by using the Henry equation.

$$U = \frac{2\varepsilon_r \varepsilon_0 \zeta f(k_a)}{3\mu} \quad (1)$$

$f(k_a)$  is Henry's function.

Determinations of zeta potential from electrophoretic are most generally made in moderate electrolyte concentration and aqueous media. In this case  $f(k_a)$  is 1.5, and is referred to as the Smoluchowski approximation [Eq. (2)] [12,13].

$$\zeta = \frac{3\mu U_E}{2\varepsilon_r \varepsilon_0 z f(k_a)} = \frac{3\mu U_E}{2\varepsilon_r \varepsilon_0 \times 1.5} = \frac{3\mu U_E}{3\varepsilon_r \varepsilon_0} = \frac{\mu U_E}{\varepsilon_r \varepsilon_0} \quad (2)$$

where  $\mu$  is the viscosity of the liquid (pa·s),  $\varepsilon$  is the dielectric constant of water (78.5),  $\varepsilon_0$  is the permittivity of free space ( $8.854 \times 10^{-12}$  C/V·m),  $U$  is the electrokinetic mobility ( $\frac{u}{E}$ ), and  $u$  is the particle velocity (m/s) in the electrical field of strength  $E$  (V/m).

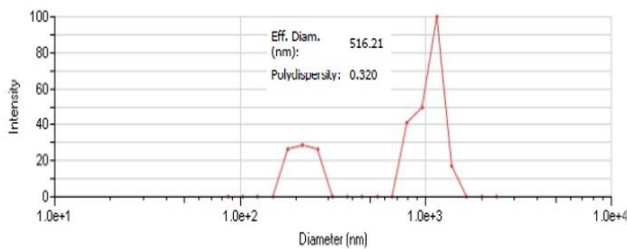


Fig. 2. Represents the effective diameter measurement of the tubular ceramic TiO<sub>2</sub> membrane powder with Eff. Diam.: 516 nm.

Despite limiting conditions, the zeta potential may be measured from the filtration potential using a suitable theory, but this transformation is not necessary if the aim is only to determine the IEP of the system. Microelectrophoresis measurements require particles of the membrane material, which can often only be obtained by destroying the membrane. The filtration potential represents the direct contact between the active surface layer of the charged membrane and the electrolyte solution (in-situ method). In this investigation, the filtration potential was measured on the membrane under a pH range of 3–9 using two concentrations of NaCl as reference salt ( $10^{-1}$  and  $10^{-2}$  M) and the other salts (KCl, NaHCO<sub>3</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, and MgSO<sub>4</sub>) ( $10^{-2}$  M).

The electric potential variance through a range of pressure driving forces ( $0 \leq \text{TMP} \leq 1.5 \text{ bar}$ ) was determined using a pair of electrodes made from a composite material, which consisted of silver and 4% gauge 21 gold, as an alternative to platinum electrodes [13] (Alfa Aesar, JohnsonMatthey Chemical, UK) and connected to a high-impedance millivoltmeter (Fluk corporation, 179 TRUERMS MULTIMETER, USA). The first electrode was wrapped around the outer wall of the tubular ceramic membrane, and the second was placed along the central line of the tubular membrane. The electrodes were linked to a voltmeter, which recorded the potential variance created by the electrolyte flow. A detailed flow diagram showing the main components of the cell for filtration potential is shown in Fig. 3. Fig. 1 illustrates the filtration rig installation used to study the zeta potential using the filtration potential method. The filtration potential used in this work was the immediate potential variance

per unit variance of the applied pressure ( $\frac{\Delta E}{\Delta \text{TMP}}$ ). This potential was selected because of the rapid experimental potential variations caused by the polarization of the electrode when measured continuously and without completely reversible electrodes; the use of immediate potentials provides a suitable means of measuring the filtration potential and achieves perfect reproducibility [14].

The composite material used in the manufacture of the two electrodes was analyzed through X-ray fluorescence (SPECTRO Analytical Instruments, model: XEPOS, Type 76004814 mbH Germany), which works using different reagents, each of which determines a set of elements. The results of the analysis are shown in Table 1.



Fig. 3a. Virgin ceramic titanium dioxide NF membrane with pore size of 0.9 nm, length = 19 cm, ID = 7 mm, OD = 10 mm.



Fig. 3b. Represents the inside electrode form, it was made from composite, length = 50 cm, D = 4 mm which passed in the center line of membrane as shown in Fig. 3a.



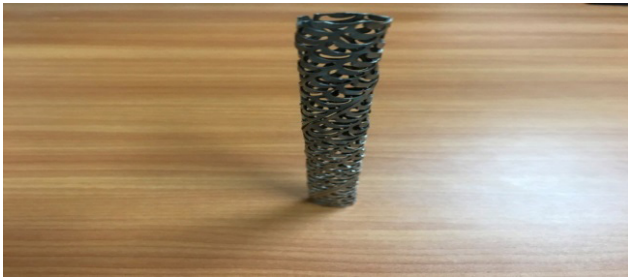


Fig. 3c. Represent the outside electrode form, it was made from the composite (silver and 4% gold), length = 14 cm, ID = 10 mm, OD = 11.3 mm.



Fig. 3d. Represents ceramic membrane as shown in Fig. 3a and the outside electrode as shown in Fig. 3b was warped around the outer wall of tubular ceramic membrane.

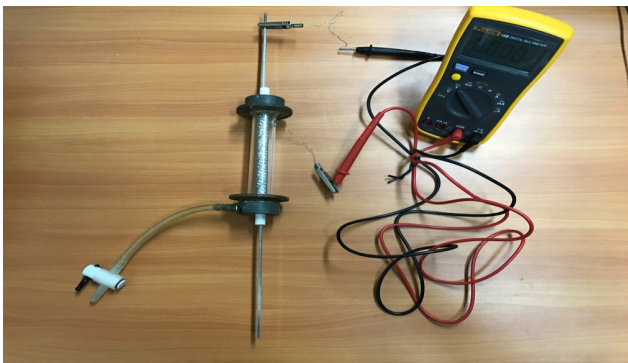


Fig. 3e. Represents the basic cell which used in the measurement of zeta potential, consist of the ceramic membrane was mounted in transparent uPVC module house, outside electrode and inside electrode were connected to high impedance milli-voltmeter.

The Helmholtz–Smoluchowski equation [Eq. (3)] was used to calculate the zeta potential from the filtration potential [15].

$$\zeta = \frac{\Delta E_s}{\Delta TMP} \frac{\mu K}{\epsilon \epsilon_0} \quad (3)$$

where  $\zeta$  is the zeta potential (mV),  $E_s$  is the filtration potential (mV),  $P$  is the applied pressure (bar),  $(\frac{\Delta E_s}{\Delta P})$  is the slope of the filtration potential versus the applied pressure curve ( $\frac{mV}{pa}$ ),  $\mu$  is the dynamic viscosity of the solution (pa·s),  $\epsilon_0$  is the permittivity of free space ( $8.854 \times 10^{-12} C/V \cdot m$ ),  $\epsilon$  is the permittivity of the solution (78.5), and  $K$  is the solution conductivity (S/m).

The growth of a net charge at a ceramic NF membrane surface impacts the distribution of cations and anions on

Table 1

Represents the results of the X-ray fluorescence test for two electrodes

Symbol	Element	Concentration
Ag	Silver	94.06 %
Au	Gold	4.2 %
Mg	Magnesium	0.041 %
Al	Aluminum	0.0069 %
Si	Silicon	0.0027 %
P	Phosphorus	0.14 %
S	Sulfur	0.00044 %
Ti	Titanium	0.0013 %
V	Vanadium	0.0014 %
Cr	Chromium	0.015 %
Mn	Manganese	0.0098 %
Fe	Iron	0.0241 %
Co	Cobalt	0.0048 %
Ni	Nickel	0.0054 %
Cu	Copper	0.3002 %
Zn	Zinc	0.0085 %
As	Arsenic	0.00051 %
Zr	Zirconium	0.050 %
Nb	Niobium	0.018 %
Mo	Molybdenum	0.134 %
Cd	Cadmium	0.0838 %
Sn	Tin	0.077 %
Sb	Antimony	0.0063 %
W	Tungsten	0.0172 %
Pb	Lead	0.0021 %

the surrounding interfacial zone, which produces accretion concentration counter ions close to the NF membrane surface. The layer of the liquid enclosure of the surface consists of the inner zone (stern layer) and the outer zone (diffuse layer). The ionic strength is determined using Eq. (4).

$$\left[ I = \frac{\sum Z_i^2 C_i}{2} \right] \quad (4)$$

where  $Z_i$  is the valency and  $C_i$  is the concentration of the ion. An increase in the ionic strength of the salt solution reduces the thickness of the EDL and leads to a reduction in the zeta potential. The EDL thickness (Debye screening length,  $K^{-1}$ ) is determined from Eq. (5) [16].

$$K^{-1} = \left[ \frac{\epsilon_0 \epsilon_r K_B T}{2000 e^2 I N} \right]^{0.5} \quad (5)$$

where  $\epsilon_r$  is the dielectric constant of the liquid (78.5, dimensionless),  $\epsilon_0$  is the dielectric constant of free space ( $8.85 \times 10^{-12} C/V \cdot m$ ),  $T$  is the absolute temperature (298 K),  $K_B$  is the Boltzmann's constant ( $1.38 \times 10^{-23} J/K$ ),  $e$  is the magnitude of electron charge ( $1.6022 \times 10^{-19} C$ ),  $I$  is the ionic strength (M), and  $N$  is Avogadro's number ( $6.02 \times 10^{23} / mol$ ).

### 3. Results and discussion

#### 3.1 SEM and EDXS results of 0.9 nm tubular ceramic NF membrane

Across-sectional SEM image of the 0.9 nm NF membrane surface is shown in Fig. 4. The tubular ceramic membrane used in this research was a composite membrane with an active side surface made from the visible thin layer of  $\text{TiO}_2$ . A membrane pore is shown. Three changed membranes served as support layers, the outermost of which was made of sintered  $\text{Al}_2\text{O}_3$ . Fig. 5 shows the specific spectra of the effective surface of the ceramic membrane determined using EDXS. The 0.9 nm NF membrane used in this research consisted of seven elements, namely, titanium (Ti), oxygen (O), aluminum (Al), carbon (C), zirconium (Zr), potassium (K), and Iron (Fe). C, Zr, K, and Fe were low-level contaminants that were created from either the membrane section that was cutoff or the construction process.

#### 3.2. Influence of anion on zeta potential of $\text{TiO}_2$ NF membrane

The measurement of zeta potential using Eq. (3) depended on the filtration potential estimations.

Fig. 6 shows a sample of the filtration potential as a function of applied TMP increment (0.25–1.5 bar) for NaCl, which was used as reference salt solution, at 0.01 M concentration and pH values of 3–9. The estimation of filtration potential is linear with TMP but the curves do not cross the origin, perhaps due to the measurement of a filtration potential (filtration and membrane potential) and not a real filtration potential. This observation is in agreement with other workers [17] who investigated the zeta potential of synthetic nanomembranes by the filtration potential method.

Figs. 7 and 8 show a sample of zeta potential measurements (mV) and mobility through microelectrophoresis over a range of pH values for background electrolyte constants of 0.01 and 0.1 M NaCl, respectively.

Fig. 9 shows a plot of the measured zeta potential (microelectrophoresis method) over a pH range of 3–9 using 0.01 and 0.1 M NaCl as background electrolytes. In this study the results of experiments were designed to test the quantitative accuracy of the electrokinetics classical model of the charged pores with ratio  $(a/k^{-1})$  in the range 0.1–10. The aqueous solutions of NaCl in the concentration range  $10^{-2}$ – $10^{-1}$  M and another salts in the concentration  $10^{-1}$  M.

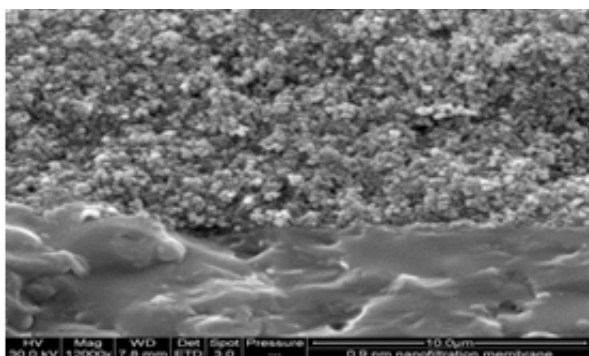


Fig. 4. SEM cross-section images of 0.9 nm titanium dioxide NF membrane.

In aqueous solution of 0.01 and 0.1 M NaCl  $k^{-1}$  (measured by using Eq. (5)) are equal to 3.04 nm and 0.96 nm respectively, so nanoporous medial ( $a = 0.9$  nm) are susceptible to electrokinetic coupling,  $(0.9/3.04 = 0.29 < 10$  and  $0.9/0.96 = 0.937 < 10$ ), whereas this ratio must be much higher than 10 to neglect EDL overlapping. That is why tangential measurements were developed to characterize nanoporous membranes. This explanation can be applied for another salts at 0.01 M concentration.

Fig. 10 shows a plot of the measured zeta potential (filtration potential and electrophoresis method) over a pH range of 3–9 for a background electrolyte of 0.01 M NaCl.

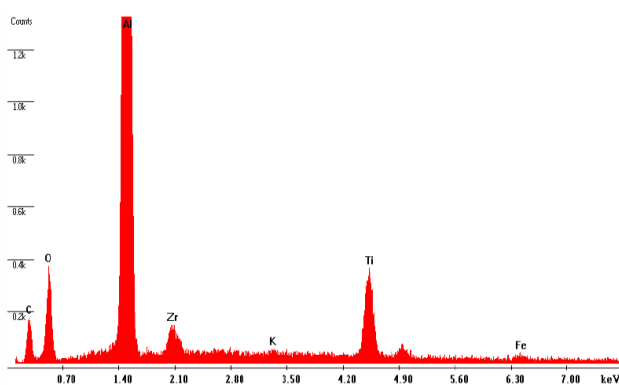


Fig. 5. EDXS spectrum of 0.9 nm titanium dioxide NF membrane.

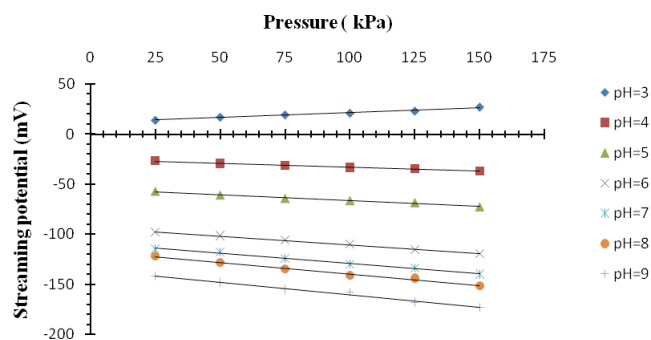
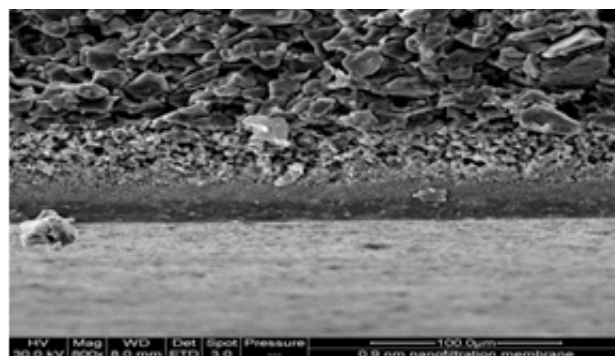


Fig. 6. Filtration potential measurements for NaCl 0.01 M versus applied pressure increment at pH = (3–9).



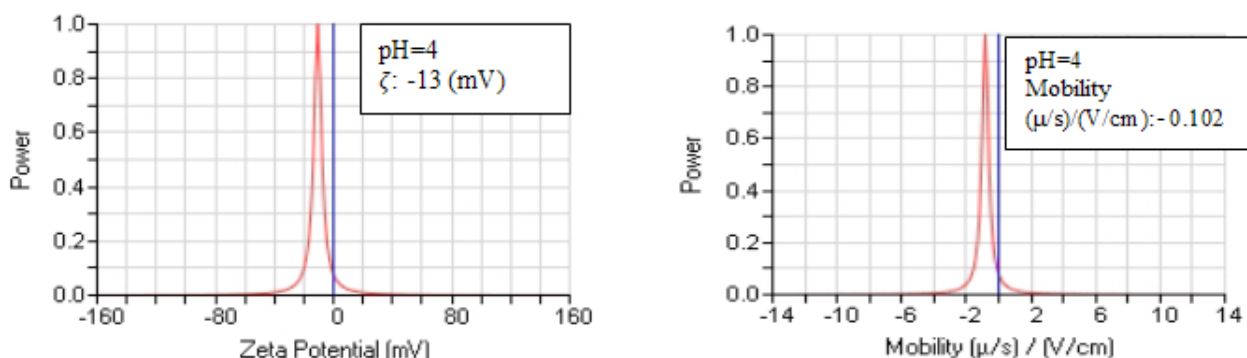


Fig. 7. Sample of zeta potential measurements at 0.01 M NaCl for pH 4.

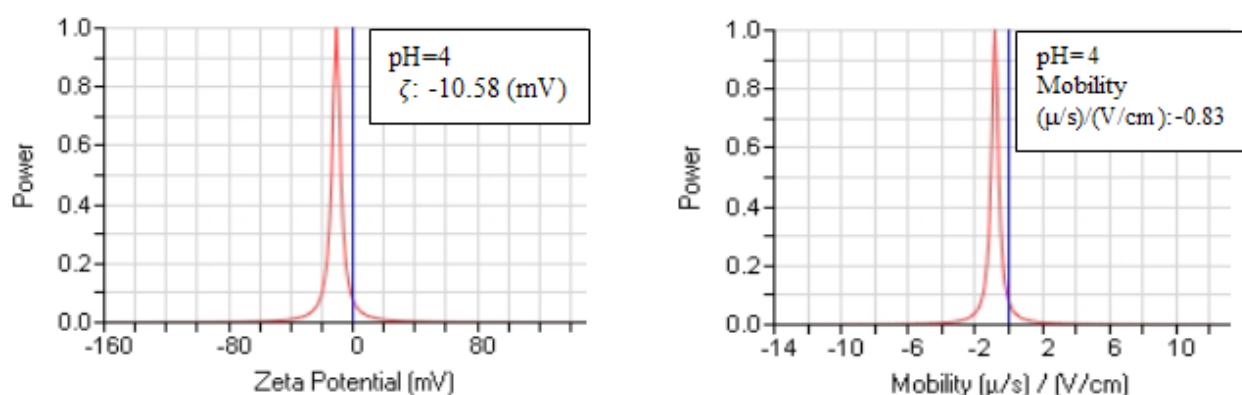


Fig. 8. Sample of zeta potential measurements at 0.1 M NaCl for pH 4.

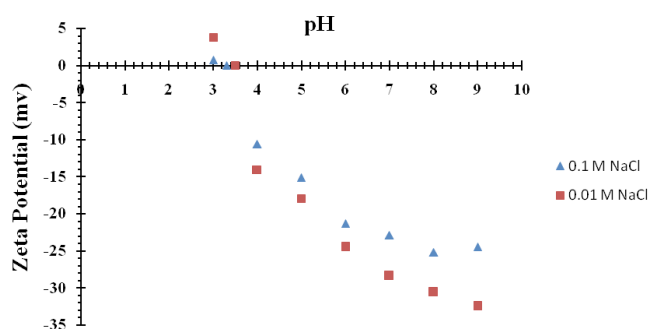


Fig. 9. The zeta potential of 0.9 nm titanium dioxide NF membrane determined from microelectrophoresis potential plotted against pH for background electrolyte of sodium chloride 0.1 M and 0.01 M NaCl with i.e. p. of 3.3 and 3.5 respectively.

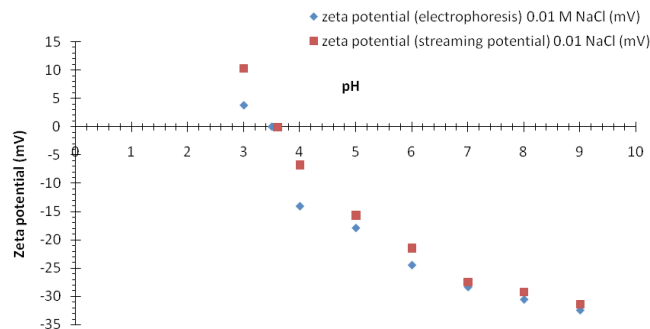


Fig. 10. The zeta potential of 0.9 nm ceramic titanium dioxide nanofiltration membrane determined from filtration potential and microelectrophoresis potential techniques plotted against pH for background electrolyte fixed at 0.01 M NaCl.

The zeta potential variations of the  $\text{TiO}_2$  NF membrane in salt solutions ( $\text{NaCl}$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{Na}_2\text{SO}_4$ ) as a function of pH magnitude are shown in Fig. 11. In the experiments using the filtration potential technique, the salt solutions were prepared at a concentration of 0.01 M, whereas those in the experiments using microelectrophoresis were prepared at concentrations of 0.1 and 0.01 M NaCl as reference solution. The  $\text{TiO}_2$  NF membrane produced an IEP, which was the pH magnitude at the zeta potential of the  $\text{TiO}_2$  membrane, which was determined by microelectrophoresis to be zero at pH values 3.3 and 3.5 for the

reference solutions of 0.1 and 0.01 M NaCl, respectively, as shown in Fig. 9. The IEP of 0.01 M NaCl was 3.6 according to the filtration potential method and 3.5 through microelectrophoresis, as shown in Fig. 10. Given the increasing pH value, the zeta potentials of the  $\text{TiO}_2$  NF membrane slightly increased to pH values of approximately 7, 8, and 9 for the  $\text{Cl}^-$  anion at 0.01 M NaCl for both techniques, as shown in Figs. 9 and 10. At a pH value lower than 7, the relation between the zeta potentials and pH magnitudes exhibited an exponential behavior for the  $\text{Cl}^-$  anion. The zeta potential of the  $\text{TiO}_2$  NF membrane changed nearly

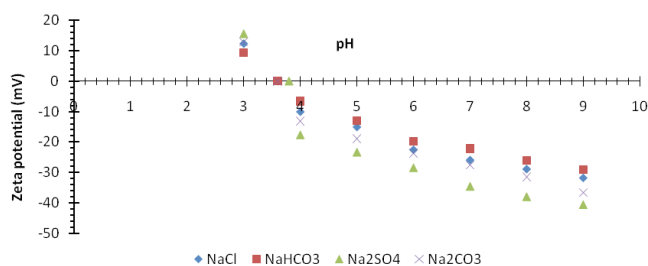


Fig. 11. The zeta potential of 0.9 nm ceramic titanium dioxide nanofiltration membrane determined from filtration potential plotted against pH for background electrolyte fixed at 0.01 M (NaCl, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub>).

linearly with the solution at pH values ranging from 6 to 9 for the Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> anions as shown in Fig. 11. The absolute zeta potential of the TiO<sub>2</sub> NF membrane was decreased in the following order: SO<sub>4</sub><sup>2-</sup> > CO<sub>3</sub><sup>2-</sup> > Cl<sup>-</sup> > HCO<sub>3</sub><sup>-</sup>, that is, the SO<sub>4</sub><sup>2-</sup> anion was more active than the other anions and had more zeta potential with the studied pH extent. The absolute zeta potentials of the TiO<sub>2</sub> NF membrane were monitored with monovalent cations and divalent anions (1:2) and were more than which monitored with monovalent cations and anions (1:1).

All salt solutions had a concentration of 0.01 M (electrolyte). The determined ionic strength using Eq. (4) for the monovalent cation and monovalent anion electrolyte solutions was 0.01 M, and that for monovalent cation and divalent anion electrolyte solutions was 0.03 M. An increase in the ionic strength of the electrolyte solution reduces EDL thickness, which decreases the zeta potential. The EDL thicknesses determined using Eq. (5) were 3.02 and 1.72 nm for 0.01 and 0.03 M ionic strengths, respectively. The potential of TiO<sub>2</sub> NF membrane had more divalent anion electrolyte solution (SO<sub>4</sub><sup>2-</sup>) with more ionic strength contrasted with those in classical EDL theories. The increase in zeta potential for the divalent anion (SO<sub>4</sub><sup>2-</sup>) was possible because of the particular anion adsorption on the ceramic membrane. The performance was similar to that reported by Zhao et al. [18].

The adsorption of anions to the TiO<sub>2</sub> NF surface of the membrane caused the negative zeta potential measured using filtration potential and microelectrophoresis potential. Anions imposed a powerful effect on the TiO<sub>2</sub> NF membrane zeta potential from a pH range of 4–9. The low pH value of 4 was monitored, and the adsorption of the Na<sup>+</sup> cation as a counter ion was increased. Thus, a low negative zeta potential was obtained, and IEP appeared at pH 3.6–3.8. Furthermore, a reduced pH value of 3.6–3.8 positive zeta potential was gained.

### 3.3 Influence of cation on zeta potential of TiO<sub>2</sub> NF membrane

To study the influence of different cations on the zeta potential of the TiO<sub>2</sub> NF membrane, chloride salts (NaCl, KCl, MgCl<sub>2</sub>, and CaCl<sub>2</sub>) were used in the experiments of filtration potential. In Fig. 12, plotted changes in zeta potential for the TiO<sub>2</sub> NF membrane at the 0.01 M salt solutions existed as a function of pH values of 3–9 in the NaCl, KCl, MgCl<sub>2</sub>, and CaCl<sub>2</sub> salt solutions. The TiO<sub>2</sub> NF membrane produced negative zeta potential magnitudes under the investigated pH extent. For the Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> cat-

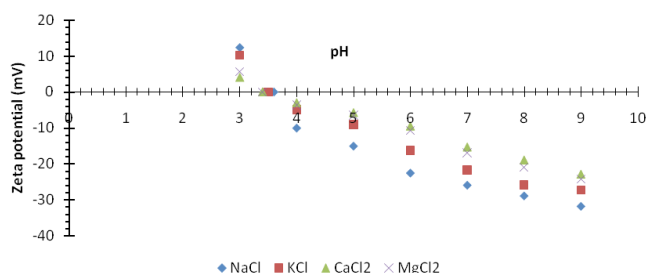


Fig. 12. The zeta potential of 0.9 nm ceramic titanium dioxide nanofiltration membrane determined from filtration potential plotted against pH for background electrolyte fixed at 0.01 M (NaCl, KCl, MgCl<sub>2</sub>, and CaCl<sub>2</sub>).

ion electrolyte solutions, the zeta potential of the TiO<sub>2</sub> NF membrane was reduced with the decreased pH values, the adsorption of monovalent and divalent cation electrolyte solutions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) increased. Thus, a low negative surface charge was obtained. IEP appeared at pH 3.4–3.6, and a reduced pH value less than 3.4–3.6 positive zeta potential was obtained.

From pH 3.0 to 9.0, the TiO<sub>2</sub> NF membrane zeta potential was compatible and agreed with EDL theory. The zeta potential of the TiO<sub>2</sub> NF membrane showed an increase with reduced ionic strength (0.01 M) for NaCl and KCl and a decrease with increased ionic strength (0.03 M) for MgCl<sub>2</sub> and CaCl<sub>2</sub>. Similar results were gained by Zeng et al. [19] in their investigation of polysulfone ultrafiltration membranes under various ionic strengths. This reduction in zeta potential with the rise in ionic strength could be demonstrated by the compression or reduction in EDL. This inspection has been mentioned in many studies [7,8].

The absolute zeta potential reductions were in the following order: Na<sup>+</sup> > K<sup>+</sup> > Mg<sup>2+</sup> > Ca<sup>2+</sup> within pH 3–9. The adsorption of cations on the TiO<sub>2</sub> NF membrane surface became highly significant in gaining a high positive zeta potential at a low pH range for the monovalent and divalent cations. MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> were used in the experiments of filtration potential to study the influence of two cations (Mg<sup>2+</sup> and Na<sup>+</sup>) on the zeta potential of the ceramic NF membrane salts. Fig. 13 plots the changes in the ceramic TiO<sub>2</sub> NF membrane in the 0.01 M salt solutions as a function of pH. The NF TiO<sub>2</sub> membrane in the MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> solutions produced IEP at pH 3.7 and 3.8, respectively. The zeta potential of the TiO<sub>2</sub> membrane changed linearly with the electrolyte solution under a pH range of 4–9 for the Na<sup>+</sup> and Mg<sup>2+</sup> cations. Positive zeta potentials were gained at pH values less than 3.7 and 3.8. The zeta potential of the TiO<sub>2</sub> NF membrane was decreased in this order Na<sup>+</sup> > Mg<sup>2+</sup> because the thicknesses of the EDL that were determined using Eq. (5) were 1.72 and 1.51 nm for concentrations of 0.03 and 0.04 M, respectively.

### 3.4 Impact of electrolyte concentration (ionic strength) and pH on zeta potentials of 0.9 nm NF ceramic membrane

The influence of pH on the zeta potential of the 0.9 nm NF TiO<sub>2</sub> membrane particles as a function of the increasing electrolyte concentration of NaCl and pH is shown in Fig. 9 for the two NaCl concentrations (10<sup>-2</sup> and 10<sup>-1</sup> M). The zeta



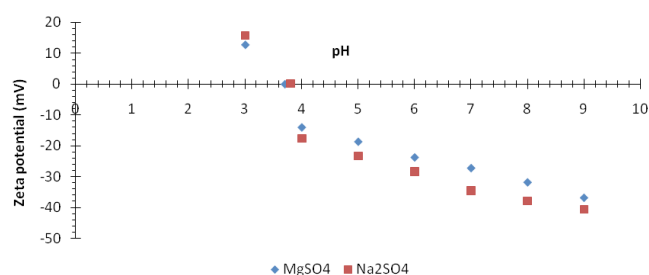


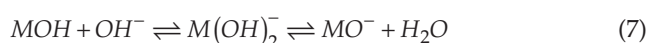
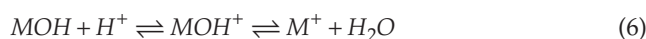
Fig. 13. The zeta potential of 0.9 nm  $\text{TiO}_2$  NF membrane determined from filtration potential plotted against pH for background electrolyte fixed at 0.01 M ( $\text{MgSO}_4$  and  $\text{Na}_2\text{SO}_4$ ).

potential of the 0.9 nm NF membrane used in this research was positive at pH 3, which was equal to 3.79 and 0.77 mV for  $10^{-2}$  and  $10^{-1}$  M NaCl, respectively. IEP was found between pH 3.3 and 3.5; several researchers [20] observed related shifts in the IEP to the adsorption of cations and anions on the membrane surface.

When pH was increased, the zeta potentials became nearly negative. The highest magnitudes, which were found at pH 9, were  $-24.46$  and  $-32.5$  mV for  $10^{-1}$  and  $10^{-2}$  M NaCl, respectively. These outcomes showed that the sign of the zeta potential could be considerably altered by changing the pH at constant NaCl concentration, whereas the variations in the concentration of salt did not have excessive influence under a fixed pH. This finding agreed with those of other researchers [21], who investigated the zeta potential of composite ceramic membranes ( $\text{TiO}_2$ , titanium oxide,  $\text{Al}_2\text{O}_3$ , aluminum oxide, and silica) and demonstrated this behavior in terms of proportion equilibrium that occurs on the surface of the ceramic membrane. The usual magnitude of zeta potential decreased as the concentration of electrolyte increased; the result showed a reduction in the active thickness of the diffused layer as the electrolyte concentration (ionic strength) increased; thus, NaCl served in this system as an indifferent electrolyte, as recorded by Chiu and James [22]. For the NaCl solution (1:1), the value of ionic strength was equal to its concentration. The thicknesses of the active layer were 0.95 and 3.02 nm under 0.1 and 0.01 M ionic strengths, respectively [18]. The filtration potential was an in-situ (direct surface membrane) measurement that was helpful in detecting the sign of membranes' electrokinetic (zeta) potential and the IEP. The zeta potential could be measured using the filtration potential method, which was not essential because both potentials were zero at the IEP, which could readily be determined from filtration potential data. Fig. 10 shows the zeta potential measurements by filtration potential and microelectrophoresis with pH for  $10^{-2}$  M NaCl. When pH was raised, zeta potentials became highly negative, and a high quantity was found at pH 9 ( $-31.35$  mV) for  $10^{-2}$  and  $10^{-1}$  M NaCl. The IEP for the filtration and electrophoresis potentials depended on the electrolyte (ionic strength) concentration and changed slightly between 3.5–3.6 and 3.3–3.5, respectively for  $10^{-2}$  and  $10^{-1}$  M NaCl. The decrease in IEP with increasing salt concentration was demonstrated clearly in terms of the particular adsorption of weakly hydrated chlorine ( $\text{Cl}^-$ ) ions [13], and the reduction in the thickness of the effective layer (diffuse layer) as the concentration increased.

### 3.5. Relationship between zeta potentials and salt (NaCl) rejection

The surface charge of the ceramic membrane, which relies on the pH of the solution, is a significant parameter that indicates the performance efficiency of a membrane separation process when eliminating ionic species. The  $\text{Na}^+$  cation had a smaller diameter 0.098 nm [23] than the  $\text{Cl}^-$  anion (0.181 nm) [1], and either was smaller than the ceramic membrane used (0.9 nm). The rejection of the electrolyte was not predominated by the impact of size and the major mechanism responsible for the rejection of salt was the electrostatic influence between the ceramic membrane surface and the ions because the radius of the ceramic membrane pore was large in comparison with the ionic radii. The zeta potentials connected to its surface charge could significantly improve the ceramic membrane's tendency for salt rejection. The surface of the composite ceramic membrane ( $\text{TiO}_2/\text{Al}_2\text{O}_3$ ) had a charge with a positive sign at low pH 3; the adsorption of the  $\text{H}^+$  ions from water must be considered and may assist the excessive rejection rate [24]. One of the operators that governed ion rejection using the NF ceramic membrane was the electrostatic repulsion between the membrane and the ions, which consequently changed during filtration potential, and the zeta potential must be reflected by differences in salt rejection. The zeta potential and the related filtration potential in this work were functions of salt concentration (ionic strength) and pH. The raised salt concentration decreased the zeta potential by EDL compression in fixed pH and changed the zeta potential of amphoteric metal oxide (ceramic membranes) using the reactions of the type [25].



The first and second reactions produced positively and negatively charged surfaces, respectively. Therefore, the IEP reached the point where no net charge (zero) existed on the membrane surface. Separating from the dissociation amphoteric oxide surface, hydronium groups may also be physically adsorbed, which would change the membrane surface charge. As theirs, no electrostatic repulsion existed between the ions and the ceramic membrane surface when there is no surface charge a membrane will be most inactive at its IEP and these will be observed in a lower in rejection of salt. In this research, the IEP was approximately pH 3.3–3.5 (microelectrophoresis) at concentrations of 0.1 and 0.01 M NaCl and pH 3.6 for the filtration potential method at 0.01 M NaCl. Thus, low salt rejection was predicted between pH 3.5 and 4. Fig. 14 shows the rejection of NaCl as a function of pH at the two concentrations of NaCl. This finding explained the succession of the electrokinetic interaction between the ions and the ceramic membrane charge. The lowest salt rejection was found at approximately pH 3.8, and this observation agreed with the IEP fixed using filtration potentials. The IEP found in situ from the filtration potentials was the best predictor of the pH of low rejection in the NF ceramic membrane. The repulsion of electrostatic may not be the only mechanism included because low rejection remained approximately 17%, which was close to the IEP.

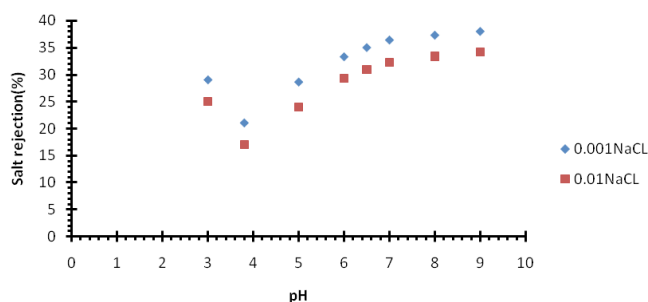


Fig. 14. Percentage of salt (sodium chloride) rejection versus pH in two concentrations (■, 0.01 M NaCl; ◆, 0.001 M NaCl), (pressure 12 bar).

#### 4. Conclusions

The outcomes of the Energy dispersive x-ray spectroscopy (EDXS) and Scanning electron microscopy (SEM) images used to determine the construction and composition of the NF ceramic membrane, emphasized that the membrane is of composite structure and is comprises an effective surface made of titanium dioxide ( $\text{TiO}_2$ ) supported by three layers of alumina ( $\text{Al}_2\text{O}_3$ ) each of various thickness. Filtration potential and electrophoresis potential measurements could be efficiently used to investigate the impact of the chemical composition of a solution on the NF ceramic membrane surface charge. The chemistry of the solution had a remarkable effect on the surface charge qualities of the ceramic membrane. Given an incurious (1:1) electrolyte (NaCl) of low concentrations (0.01 M) used to preserve steady ionic strength, the zeta potential changed with pH and was positive at less than pH 3.5 and negative at more than pH 3.5 under microelectrophoresis.

The IEP was found at approximately pH 3.5. The filtration potential changed in a similar pattern, and the IEP appeared at pH 3.6. The filtration and microelectrophoresis potentials decreased with the rising concentration of NaCl because of the increased adsorption of the  $\text{Cl}^-$  ions. The increase in sodium chloride concentration with decreasing salt rejection rate was continuous at each pH value. A low NaCl rejection was seen at pH 3.8 of the composite  $\text{TiO}_2$  membrane, which agreed with the pH of the IEP of the ceramic membrane. For such a modest electrolyte as NaCl, the rate of salt rejection depended on the electrostatic mutual actions, which were governed by the surface charge created on the ceramic membrane. By searching the zeta potential field, we obtained results that provide valuable reference to membrane fouling and its relationship to applications. A detailed database of zeta potential for membranes in different ionic solutions will improve process control in industrial, pharmaceutical, and medical membrane applications.

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