

Mathematical Modelling of Zinc Removal from Wastewater by Using Nanofiltration and Reverse Osmosis Membranes

Miqat Hasan Salih¹, Ahmed Faiq Al-Alawy²

Chemical Engineering Department, College of Engineering, University of Baghdad, Iraq

Abstract: *The present work aimed to study the efficiency of nanofiltration (NF) and reverse osmosis (RO) process for treatment of heavy metals wastewater contains zinc. In this research, the salt of heavy metals were zinc chloride (ZnCl₂) used as feed solution. Nanofiltration and reverse osmosis membranes are made from polyamide as spiral wound module. The parameters studied were: operating time (0 – 70 min), feed concentrations for zinc ions (10 – 300 mg/l), operating pressure (1 – 4 bar). The theoretical results showed, flux of water through membrane decline from 19 to 10.85 LMH with time. Flux decrease from 25.84 to 10.88 LMH with the increment of feed concentration. The raise of pressure, the flux increase for NF and RO membranes. The maximum recovery was 99% and 57% for NF and RO respectively. In general, polyamide nanofiltration and reverse osmosis membranes give a high efficiency for removal of zinc. The separation efficiency of heavy metals in reverse osmosis membrane higher than nanofiltration membrane. While the water flux in NF process higher than RO process. The water flux theoretically calculated is a function of pressure, feed temperature, feed concentration, feed flow rate and time.*

Keywords: Nanofiltration, Reverse osmosis, Zinc ions, Mathematical model

1. Introduction

Water is a limited resource and vital for the sustainability of life on earth and is necessary to achieve environmental, social and economic development, which has become a rare commodity. Water scarcity occur because of water pollution, inefficient water use, lifestyle change, climate change and population growth; with extreme events such as floods and droughts. The industrial applications development and increment of world population, environmental pollution problem became important. Communities produce both solid and liquid wastes. The water supply from the society after it has been utilized in various applications is essentially the liquid waste (wastewater). Precious resource conservation and the sustainable development of water will require maximal recycling and reuse [1-3].

The mine waters and their removal and water supplies, presence of polluting and toxic heavy metals in wastewaters from industrial effluents have received much attention in recent years. Industrial wastewaters often contained a considerable amount of heavy metals that is endanger the environment and public health if they discharged without efficient treatment [4].

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 [5]. Wastewater containing heavy metals originated mainly from metal plating facilities, fertilizer industries, thermoplastics, pigment manufacture, stabilizers, paper industries and pesticides galvanizing plants, batteries, mining operations, tanneries, etc. [6].

Heavy metals are major sources of environmental contamination. Some of heavy metals can form toxic materials even in low concentration. The traditional methods for removal of organic materials are chemical and biological treatment of the toxic compounds degrades them to CO₂ and

salts. The metals are permanent and the only way to remove the metals is to change their physical and chemical states by precipitation and reduction /oxidation. There are a number of researches that studied physical and chemical treatments to reduce the concentration of heavy metals in their waste water to within safe levels [7, 8].

Some of the heavy metals toxicity results are: (i) slowly progressing neurological, muscular, and physical degenerative processes that mimic cancer if the exposure to heavy metals for a long term and (ii) lower energy levels, damaged or decreased central nervous functions, kidneys, liver, damaging of blood components, lungs and other vital organs if the exposure to heavy metals for a short term [9].

Zinc is one of the heaviest metals, which is widely used in a wallpaper, batteries, production of rubber it plays an important role as a catalyst during manufacture, protective coating on to ferrous material, electrolytic deposition from an acidic plating bath, plastics, cosmetics, printing inks and photocopier paper. The electroplating industry is an important source of zinc metal, because it is the major consumer of zinc and its materials [6, 10]. Zinc is a trace element that is important for human health. It is essential element of the physiological functions for living matter and organizes many biochemical processes. The large amount of zinc can cause health problems, such as anemia, vomiting, skin irritations, nausea and stomach cramps [11, 12]. The methods used to remove zinc from heavy metals contaminated wastewater are: electro dialysis with removal efficiency from 97.6 to 98.7% [13], adsorption with removal efficiency ranging from 90 to 95% [14], nanofiltration membrane with removal efficiency of 90% [15], low pressure reverse osmosis membrane with removal of 99% [16]. The maximum contaminant level (standards) of zinc metal in water is <10 mg/l [17].

The heavy metals existing in contaminated raw water can cause problems in the plants of water treatment. They can reduce the efficiency of the treatment plants and inhibit the biological treatment processes [18]. Thus, various technologies have been applied for the removal of heavy metals from water and wastewater, such as chemical precipitation, adsorption, coagulation-flocculation, floatation, ion exchange, electrochemical processes, and membrane filtration have been developed in the recent years for decreasing the amount of wastewater produced and to improve the quality of treated water [19]. Coagulation-flocculation and chemical precipitation have been widely utilized to treat wastewater of electroplating industry, their disadvantages like sludge production, impossibility of directly reusing heavy metals and consumption of an excessive chemicals are obvious but membrane technology has been increasingly used in the treatment of heavy metals wastewater because of their convenient operation and high efficiency. The collected heavy metals and the purified water can be reused directly if the heavy metals contained in wastewater are removed by using membranes [20].

One of the most efficient systems for wastewater and water treatment is membrane process. It is an economically feasible, compact process and has a high retention level of pollutants. Membrane process has been given an especially importance in water treatment systems due to its ability to remove chemical and physical issues in a highest purification degree [21]. The membrane systems used for heavy metals removal from wastewater are liquid membranes and pressure driven membrane systems such as reverse osmosis (RO), nanofiltration (NF), and membrane hybrid processes [22].

Nanofiltration (NF) is a cross flow, pressure driven membrane that is distinguished by a molecular weight cut off of 200 –1000 Dalton. NF is primarily utilized for the removal of low molecular weight multivalent salts and organics from water. The membrane separation system which uses thin porous membranes with pore sizes ranging from 0.5 to 2 μm is nanofiltration. NF systems operate at pressures ranging from 0.3 to 1.4 MPa. NF thus represents a process that functions between UF and RO, and is often defined 'loose reverse osmosis'. NF membranes are also called water softening membranes. Nanofiltration membranes are often negatively charged, so the anion repulsion that determines salt retention primarily [23]. Due to its low energy consumption, nanofiltration membranes are the economical desalination system for brackish water desalination. nanofiltration offers a great advantage of lower operating costs than reverse osmosis and electrodialysis [24].

Membranes with higher water permeability but with a lower rejections of dissolved components, would be a great improvement for separation process. Nanofiltration in compare with the ultrafiltration and reverse osmosis membranes, has been always a difficult system to describe. The properties of nanofiltration membrane is primarily the combination of high retentions for multivalent ions that reach to 99% e.g., calcium, magnesium, chromium, zinc, nickel, copper, sulfate, iron, arsenic, etc., with low to moderate retentions for monovalent ions ranging from 0 to 70% e.g., sodium, potassium, chloride, and the high rejection which reach to 90% for organic materials that having a molecular

weight ranging from 150-300 which is greater than the molecular weight of the membrane. Nanofiltration membranes are still a gray zone in terms of transport mechanisms and physicochemical interactions, a transition membrane with properties of both ultrafiltration and reverse osmosis, but with its own specific properties. As a result, industrialists and scientists feel reliance about what can be expected from a nanofiltration membranes, and many applications proved to be successful [25].

Because of the more open polymer structure of nanofiltration membranes the pure solvent flux is much higher than that of reverse osmosis membranes. Despite the differences in solvent flux the transport mechanism for both processes is considered the same and is generally thought to be primarily solution diffusion. Nanofiltration is also used for the production of potable water from brackish waters [26].

Reverse osmosis (RO) was the first membrane system to be widely commercialized. Reverse osmosis membranes are utilized to separate low molecular weight compounds and salts from water because they are highly permeable to water and highly impermeable to organic molecules, colloids, salts and microorganisms [27].

Initially, RO was applied for the desalination of brackish water and seawater. Increased demands on the industry to reclaim useful materials from waste streams, decrease energy consumption, conserve water and control pollution have made new applications economically attractive. Reverse osmosis membranes offer the possibility of higher retention of salts at decreased applied pressures, and decreased costs. Reverse osmosis is the best level of filtration available. The reverse osmosis membrane acts as a partition to all dissolved inorganic molecules, organic molecules and salts with a molecular weight larger than 100. Water molecules pass freely through the membrane giving a pure stream (permeate). Dissolved salts rejection is typically ranging from 95% to greater than 99%. The applications of reverse osmosis membranes are varied and numerous; including heavy metal wastewater treatment such as in electroplating industry, biomedical separations, wastewater recovery, purification of home drinking water, desalination of seawater or brackish water for drinking purposes, industrial process water and food and beverage processing. Reverse osmosis is often used in the medical and laboratory applications, power industry (boiler feed water) and production of pure water for utilize in the semiconductor industry. Operating pressures for reverse osmosis membranes typically ranging from 75 psig for brackish water to greater than 1,200 psig for sea water. Low pressure reverse osmosis membranes decrease the operating costs of reverse osmosis, by lowering the required applied pressure of the process to less than 100 psi [18, 28].

In this research, the effect of time, feed concentration and pressure on flux, recovery and feed concentration have been studied for polyamide spiral wound NF and RO membranes to remove zinc from wastewater.

2. Mathematical Modeling

The model is based on the solution diffusion model is the widely used. In the spiral wound element water passes

through the membrane element; portion of this water passes in the product stream, resulting in continuous change conditions over the length of the membrane element [29]. The transport of solute and solvent are independent of each other in the solution diffusion model. The flux of solvent, which is generally water through the membrane is linearly proportional to the pressure difference and osmotic pressure difference across the membrane [30-32]:

$$J_w = k_w (\Delta P - \Delta \pi) \quad (1)$$

Where J_w is the flux of water ($l/m^2.h$), k_w is the permeability coefficient of pure water ($l/m^2.h.bar$), ΔP is the applied pressure (bar) and $\Delta \pi$ is the osmotic pressure of the solution (bar). Solution osmotic pressure is related to its dissolved solute concentration and is predicted from Van't Hoff equation as [33]:

$$\pi = \phi i R_g T C \quad (2)$$

Where ϕ is the osmotic coefficient, i is the number of dissociated ions per molecule (Van't Hoff factor), T is the temperature (K), R_g is the universal gas constant ($l.bar/mole.K$) and C is the solute concentration (mg/l). The solute flux through the membrane is proportional to the solute concentration difference across the membrane [30]:

$$J_s = k_s \Delta C \quad (3)$$

Where J_s is the solute mass flux ($mg/m^2.h$), k_s is the permeability coefficient of salt (m/h) and ΔC is the concentration gradient across membrane (ppm). And:

$$C_p = \frac{J_s}{J_w} \quad (4)$$

Where C_p is the concentration in permeate (mg/l).

By measuring the concentrations of solute in the feed solution (C_f) and also in the permeate solution (C_p), the rejection is calculated as follows [22]:

$$R \% = \left(1 - \frac{C_p}{C_f}\right) * 100\% \quad (5)$$

Where $R\%$ is the rejection percentage of solute and C_f is the concentration in feed solution.

At steady state, the flux of solute to the membrane surface can be balanced by solute fluxes flowing away from the membrane and through the membrane as following [29]:

$$\frac{dM}{dt} = 0 = J_w C a - D_L \frac{dC}{dz} a - J_w C_p a \quad (6)$$

Where M is the solute mass (mg), t is the time (s), D_L is the solute diffusion coefficient in water (m^2/s), z is the distance perpendicular to the surface of membrane (m) and a is the surface area of membrane (m^2).

Equation 6 can be not only applied at the surface of membrane but also at any plane in the boundary layer because the net flux of solute must be constant everywhere in the boundary layer to prevent the solute accumulation in that

layer. By the integral of Equation 6 across the boundary layer thickness with the boundary conditions: $C(0) = C_M$ and $C(\delta_B) = C_{FC}$, where C_{FC} is the feed concentrate channel concentration and C_M is the membrane surface concentration.

$$D_L \int_{C_M}^{C_{FC}} \frac{dC}{C - C_p} = -J_w \int_0^{\delta_B} dz \quad (7)$$

Integrate Equation 7 as:

$$\ln \left(\frac{C_M - C_p}{C_{FC} - C_p} \right) = \frac{J_w \delta_B}{D_L} \quad (8)$$

$$\frac{C_M - C_p}{C_{FC} - C_p} = e^{\frac{J_w \delta_B}{D_L}} = e^{J_w / k_{cp}} \quad (9)$$

The solute convective flow to the surface of membrane is much greater than the diffusion of the solute back to the bulk feed solution as the water passes through the membrane, as a result; the solute concentration at the membrane wall increases [34]. Concentration polarization is defined as the ratio of the solute concentrations of membrane and feed concentrate stream as [29]:

$$\beta = \frac{C_M}{C_{FC}} \quad (10)$$

Where β is the concentration polarization factor.

Combining Equation 10 with Equations 5 and 9 gives the following expression:

$$\beta = (1 - R) + R (e^{J_w / k_{cp}}) \quad (11)$$

In the spacer filled feed channel of a spiral wound membrane element, Schock and Miquel, 1987[35] found that the mass transfer coefficient of concentration polarization could be calculated from equations below, when the calculations for the velocity in the channel and the hydraulic diameter took the presence of the spacer into account:

$$k_{cp} = 0.023 \frac{D_L}{d_H} (Re)^{0.875} (Sc)^{0.25} \quad (12)$$

$$Re = \frac{\rho v d_H}{\mu} \quad (13)$$

$$Sc = \frac{\mu}{\rho D_L} \quad (14)$$

Where $k_{cp} = D_L / \delta_B$ is the mass transfer coefficient of concentration polarization (m/h), d_H is the hydraulic diameter (m), Re is the Reynold number, Sc is the Schmidt number, v is the velocity in the feed stream (m/h), ρ is the density of feed water (kg/m^3) and μ is the dynamic viscosity of feed water ($kg/m.s$).

The water and solute fluxes are expressed by Equations 1 and 3, but the difference in concentration, difference in osmotic pressure and difference in applied pressure rely on the position in the pressure vessel [29]:

$$J_{w,z} = k_w (\Delta P_z - \Delta \pi_z) = k_w [(P_{FC,z} - P_{P,z}) - \frac{\pi M_z - \pi P_z}{z}] \quad (15)$$

$$J_{S,z} = k_S (\Delta C_z) = k_S (C_{M,z} - C_{P,z}) \quad (16) \qquad C_{P,z} = \frac{J_{S,z}}{J_{w,z}} \quad (25)$$

Where $C_{M,z}$ is the concentration at the surface of membrane, $C_{M,z} = \beta_z C_{FC,z}$ and $\pi_{M,z}$ is the osmotic pressure at the surface of membrane.

The flow of permeate and flow of mass of solute through the membrane are equal to the flux multiply by the area of membrane for the differential element. The accumulative water and solute transfer across the membrane is predicted by integrating the flow between the feed end and the position z in the pressure vessel, as:

$$Q_{P,z} = \int_0^z J_{w,z} w dz \quad (17)$$

$$M_{S,z} = \int_0^z J_{S,z} w dz \quad (18)$$

Where w is the width of feed concentrate channel (m) and $M_{S,z}$ is the solute mass transferred (mg/s). At any point in the channel the flow rate can be predicted by [29]:

$$Q_{FC,z} = Q_F - Q_{P,z} \quad (19)$$

The concentration of solute could be calculated as:

$$C_{FC,z} = \frac{Q_F C_F - M_{S,z}}{Q_{FC,z}} \quad (20)$$

The flux of water and solute are influenced by solute concentration at the membrane surface and concentration polarization. Both velocity and flux are changing, β must be determined by Equation 11:

$$\beta_z = R \left(e^{\frac{J_{w,z}}{k_{CP,z}}} \right) + (1 - R) \quad (21)$$

The velocity which mass transfer coefficient k_{CP} depends on it can be calculated from the following equation:

$$v_z = \frac{Q_{FC,z}}{hw} \quad (22)$$

Where h is the height of feed concentrate channel (m). The concentration of solute at the surface of membrane as a function of position expressed as:

$$C_{M,z} = \beta_z C_{FC,z} \quad (23)$$

The feed channel pressure drops because of the head loss, head loss changes across the length of the membrane. Turbulent conditions are maintained, so head loss in the channel is given by the expression:

$$h_L = \delta_{HL} v^2 L \quad (24)$$

Where h_L is the feed concentrate channel head loss (bar), δ_{HL} is the head loss coefficient (bar.s²/m³), v is the velocity of water in feed concentrate channel (m/s) and L is the length of the channel (m).

The concentration of product can be determined from the ratio of the fluxes of solute and water per Equation 4 as:

Membrane module unit in continuous operation consists of a tank for feed, a tank for product and the membrane element. The concentrate is recycled to the tank of feed so the properties of solution in feed tank changed with time and the permeate is separately collected in the product tank [36].

Recovery can be expressed as the volume of permeate divided by the initial volume of feed. This expression applied in batch concentrating mode. For the overall system, the expression is [37]:

$$Y\% = \frac{V_P}{V_F^0} * 100\% \quad (26)$$

Where $Y\%$ is the recovery percentage, V_P is the volume of permeate (l) and V_F^0 is the initial feed volume (l).

Material balance equation applied for the product tank as [37]:

$$Q_P C_P = \frac{d(V_P C_{Pavg})}{dt} \quad (27)$$

C_{Pavg} is the product average concentration (mg/l).

Expansion of equation 27 yields:

$$Q_P C_P = V_P \frac{dC_{Pavg}}{dt} + C_{Pavg} \frac{dV_P}{dt} \quad (28)$$

Initial conditions, at $t=0$, $V_P=0$, $C_{Pavg}=C_P=0$. The variation in the product volume corresponds to the production rate of membrane as:

$$\frac{dV_P}{dt} = Q_P \quad (29)$$

Substitution to Equation 28:

$$\frac{dC_{Pavg}}{dt} = \frac{Q_P (C_P - C_{Pavg})}{V_P} \quad (30)$$

Material balance on the membrane element gives:

$$Q_F C_F = Q_P C_P + Q_C C_C \quad (31)$$

Analogous material balance equation can be obtained around the feed tank:

$$Q_C C_C - Q_F C_F = \frac{d(V_{Ft} C_{Ft})}{dt} \quad (32)$$

Developing this equation gives:

$$-Q_P C_P = V_{Ft} \frac{dC_{Ft}}{dt} + C_{Ft} \frac{dV_{Ft}}{dt} \quad (33)$$

Where V_{Ft} is the volume in the tank of feed at a time t , with a concentration in the tank C_{Ft} . The tank of feed is assumed well mixed [37] so:

$$V_{Ft} = V_F \quad (34)$$

And:

$$C_{Ft} = C_F \quad (35)$$

The variation in the feed tank volume with time corresponds to the production rate as:

$$-\frac{dV_F}{dt} = Q_p \quad (36)$$

Integrating equation 4.36 with the initial condition: $t=0$, $V_F = V_F^o$

$$V_F = V_F^o - Q_p t \quad (37)$$

Substituting these expressions in Equation 33:

$$\frac{dC_F}{dt} = \frac{Q_p(C_F - C_P)}{(V_F^o - Q_p t)} \quad (38)$$

Knowing that the system of interest is closed, the conservation of mass reveals that the solute mass in feed tank at initial time is equal to the sum of various streams and tank:

$$V_P = \frac{V_F^o(C_F - C_F^o)}{(C_F - C_{Pavg})} \quad (39)$$

Substituting V_p by its expression in Equation 30:

$$\frac{dC_{Pavg}}{dt} = \frac{Q_p(C_P - C_{Pavg})}{V_F^o(C_F - C_F^o)} (C_F - C_{Pavg}) \quad (40)$$

Equation 38 and 40 are the outcome of material balances on the product tank, feed tank, and membrane element. The solution of this set of ordinary differential equations requires the values of C_P and Q_p . C_P and Q_p are obtained from the steady state equations 4 and 17 as initial values for the ordinary differential equations when the concentration and product rate of permeate change with position of module. The equations of the mathematical model can be solved by using MATLAB PROGRAM.

3. Results and Discussion

In this research, the water flux, recovery and feed concentration calculated theoretically for zinc chloride salt ($ZnCl_2$). The equations for calculation depends on many variables such as feed temperature, water viscosity, water density, zinc chloride concentrations, flow rate, pressure, zinc chloride diffusion coefficient, permeability coefficient for pure water, zinc chloride permeability and others parameters.

As shown in Figs.(1) and (2), the data shows a linear relationship between pure water flux and driving force (ΔP). Polyamide membrane permeability for pure water is determined from the slope of this curve, the value of k_w was obtained $13.02 \text{ l/m}^2 \cdot \text{bar} \cdot \text{h}$ for NF membrane and $6.74 \text{ l/m}^2 \cdot \text{bar} \cdot \text{h}$ for RO membrane. Figs.(3) and (4) show a linear relationship between mass flux of solute and driving force (ΔC). Membrane permeability for salt is determined from the slope of this curve, the value of k_s was obtained $1.28 \cdot 10^{-3} \text{ m/h}$ for NF membrane and $2.5 \cdot 10^{-4} \text{ m/h}$ for RO membrane.

3.1 Effect of Time for NF and RO Membranes

The permeate flux, recovery and final concentration of feed for nanofiltration and reverse osmosis unit are plotted with time (0-70 min) for zinc chloride. This is shown in Figs (5) to (7).

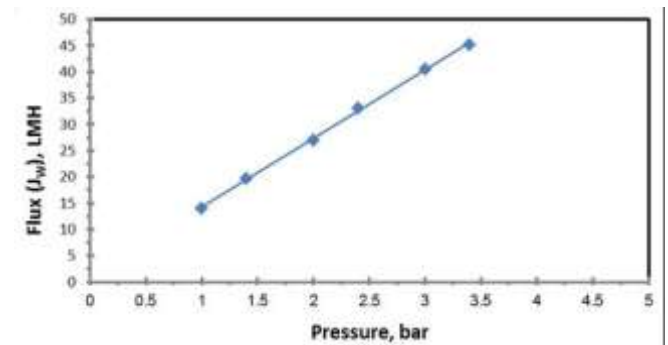


Figure 1: Pressure vs. Pure Water Flux for NF Process ($Q_F=30 \text{ l/h}$, $T=26^\circ \text{C}$, $t=10 \text{ min}$)

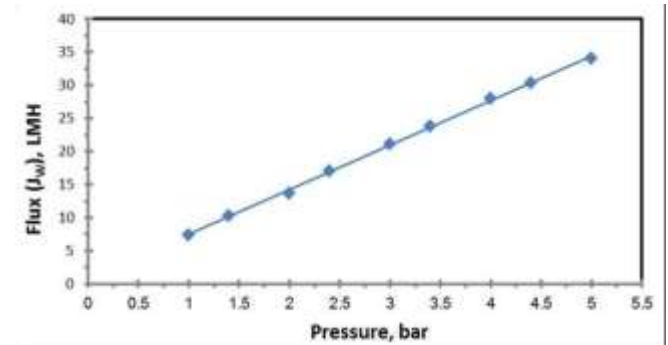


Figure 2: Pressure vs. Pure Water Flux for RO Process ($Q_F=30 \text{ l/h}$, $T=26^\circ \text{C}$, $t=10 \text{ min}$)

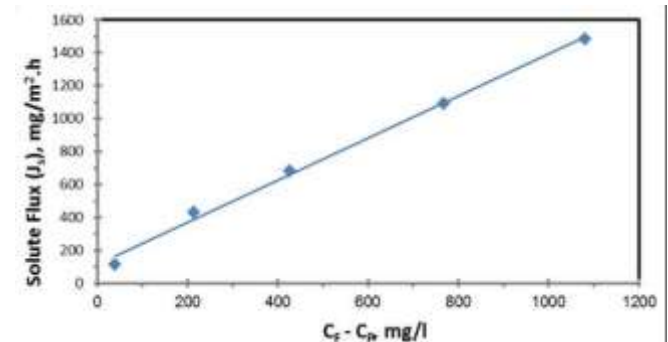


Figure 3: Concentration Difference vs. Solute Flux for NF Process ($Q_F=40 \text{ l/h}$, $T=26^\circ \text{C}$, $t=30 \text{ min}$, $P=2 \text{ bar}$)

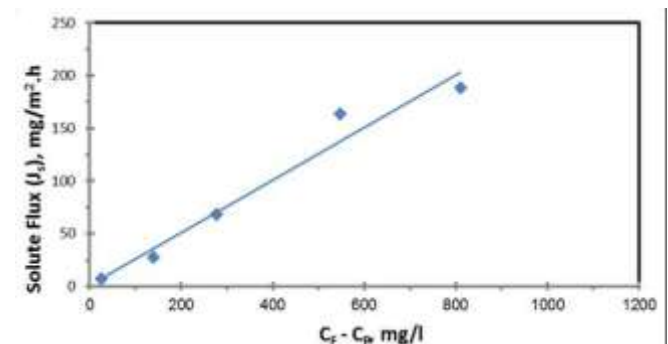


Figure 4: Concentration Difference vs. Solute Flux for RO Process ($Q_F=40 \text{ l/h}$, $T=26^\circ \text{C}$, $t=30 \text{ min}$, $P=2 \text{ bar}$)

The flux decline with increase in time. The continuous decline of the flux was mainly because of the gradual solution viscosity increment and to heavy metal deposition on the surface of the membrane; with the increasing in feed concentration and osmotic pressure gradually, which led to further membrane scaling and concentration polarization. Due to the boundary layer on the surface of the membrane formed by heavy metals the resistance against flux increased. Furthermore, increasing in osmotic pressure because of concentration polarization cause a decrease in the driving force and the flux inversely proportional to time and the increasing in time leads to increase the concentration of heavy metals in feed vessel, this leads to increase in osmotic pressure and the flux decrease as Equation 1. This behavior is agreement with [20, 38]. The increase in time from 10 to 70 min resulted in the decline of flux from 19.04 to 18.92 LMH for zinc in NF and from 10.97 to 10.85 LMH in RO.

The recovery has been increased with time, this behavior due to Equation 26 as the accumulation volume of permeate was increase with time. It can be observed that the concentration of heavy metals solution in feed vessel increase with increase in operating time. This behavior due to the recirculation mode (i.e. concentrate stream recycled to the feed stream). The increase in time to 70 min resulted in the increase of salt feed concentration from 712.77 to 76209 mg/l for zinc in NF and from 679.23 to 1420.61 mg/l in RO.

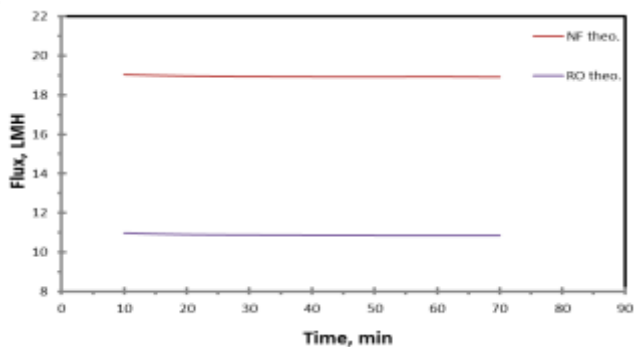


Figure 5: Flux vs. Operating Time ($Q_F=40$ l/h, $T=26$ °C, $P=2$ bar, $C_{F Zn^{+2}}=300$ mg/l)

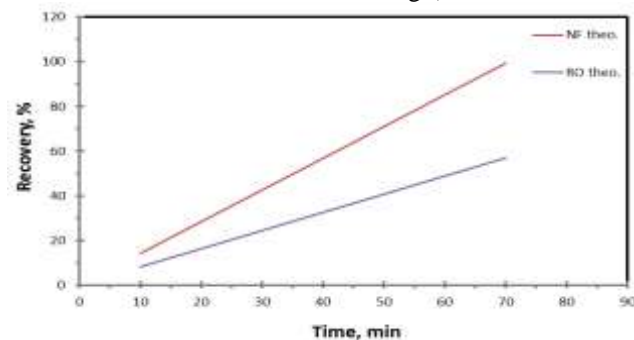


Figure 6: Recovery Percentage vs. Operating Time ($Q_F=40$ l/h, $T=26$ °C, $P=2$ bar, $C_{F Zn^{+2}}=300$ mg/l, $pH=6$)

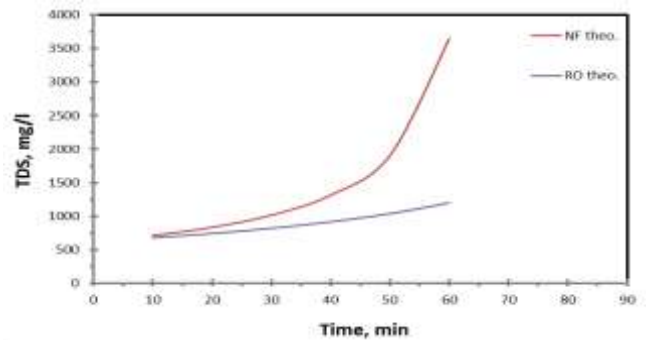


Figure 7: Feed Concentration as TDS vs. Operating Time ($Q_F=40$ l/h, $T=26$ °C, $P=2$ bar, $C_{F Zn^{+2}}=300$ mg/l, $pH=6$)

3.2 Effect of Feed Concentration for NF and RO Membranes

Figs.(8)to(10) show the effect of feed concentration on flux, recovery and the concentration of zinc chloride in feed respectively. The permeate flux has been decreased with increasing feed concentration. This behavior due to increase in osmotic pressure, decrease of the effective pore size of the membrane due to adsorption of solute on the surface of the membrane and the effect of concentration polarization. This behavior is agreement with Al-Rashdiet al., 2013[8]. The increase in feed concentration of ions from 10 to 300 mg/l resulted in the decline in flux from 25.84 to 18.94 LMH for zinc in NF and from 13.61 to 10.88 LMH in RO.

The recovery has been decreased with increase of feed concentration. The increase in feed concentration of ions from 10 to 300 mg/l resulted in the increase of salt feed concentration from 44.92 to 1014.89 mg/l for zinc in NF and from 29.72 to 820 mg/l in RO.

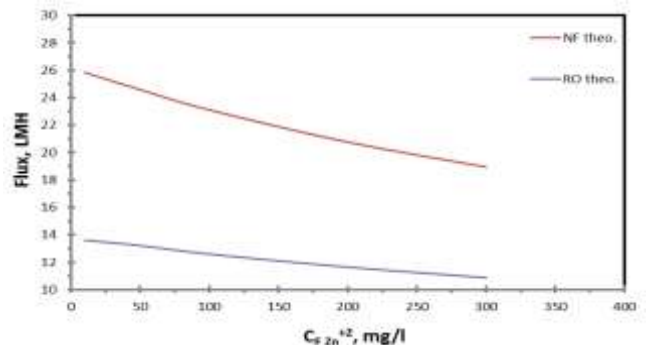


Figure 8: Flux vs. Feed Concentration of Zinc Ions ($Q_F=40$ l/h, $T=26$ °C, $P=2$ bar, $t=30$ min, $pH=6$)

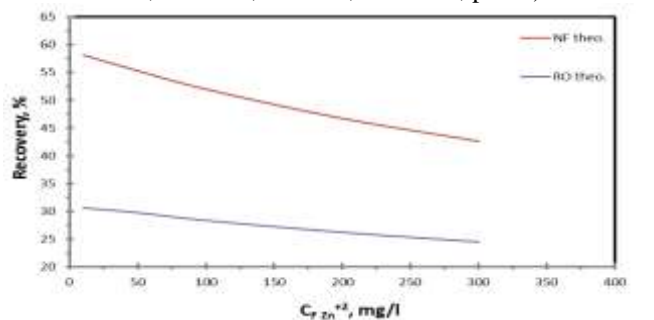


Figure 9: Recovery Percentage vs. Feed Concentration of Zinc Ions ($Q_F=40$ l/h, $T=26$ °C, $P=2$ bar, $t=30$ min, $pH=6$)

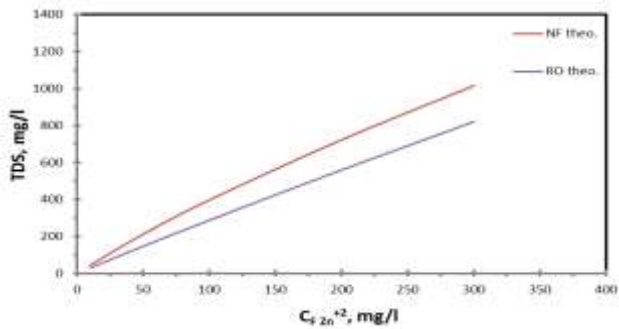


Figure 10: Feed Concentration as TDS vs. Feed Concentration of Zinc Ions ($Q_F=40$ l/h, $T=26$ °C, $P=2$ bar, $t=30$ min, $pH=6$)

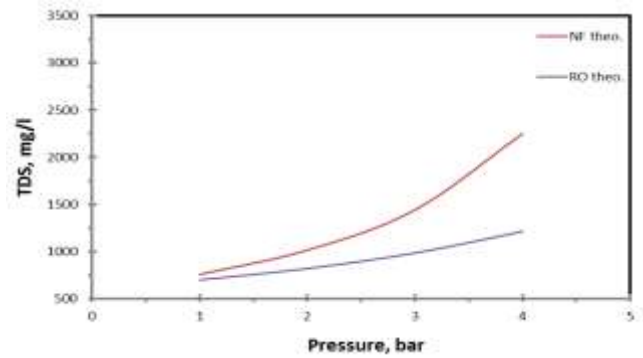


Figure 13: Feed Concentration as TDS vs. Operating Pressure ($Q_F=40$ l/h, $T=26$ °C, $t=30$ min, $C_{F Zn^{+2}}=300$ mg/l, $pH=6$)

3.3 Effect of Operating Pressure for NF and RO Membranes

The permeate flux has been increased with increasing applied pressure (see Fig.(11)), this behavior due to an increase of the preferential sorption of water at higher pressure, and thus the solvent permeability increases at high pressure compared with the solute permeability. The increase in applied pressure from 1 to 4 bar resulted in the increase in flux from 9.12 to 34.22 LMH for zinc in NF and from 4.92 to 21.94 LMH in RO. This behavior is agreement with Lee et al., 2006[38]. Fig.(12) shows the effect of pressure on recovery. The recovery has been increased with increasing applied pressure. Fig. (13) shows the effect of pressure on feed concentration. The increase in applied pressure from 1 to 4 bar resulted in the increase of heavy metal concentration in feed vessel from 756.95 to 2249.43 mg/l for zinc in NF and from 698.36 to 1212.53 mg/l in RO.

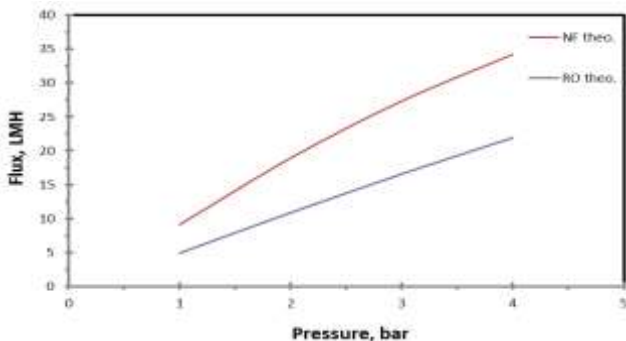


Figure 11: Flux vs. Operating Pressure ($Q_F=40$ l/h, $T=26$ °C, $t=30$ min, $C_{F Zn^{+2}}=300$ mg/l, $pH=6$)

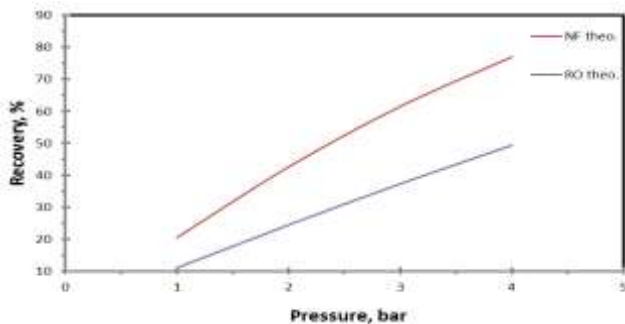


Figure 12: Recovery Percentage vs. Operating Pressure ($Q_F=40$ l/h, $T=26$ °C, $t=30$ min, $C_{F Zn^{+2}}=300$ mg/l, $pH=6$)

The flux for nanofiltration is higher than that from reverse osmosis membranes, this due to the pore size of nanofiltration membrane which is larger than that of reverse osmosis membrane as a result the permeability of pure water for nanofiltration is approximately twice that of RO. The concentration of heavy metal ions in permeate for nanofiltration is higher than that from reverse osmosis membranes. The concentration or rejection has been affected by size exclusion than other mechanisms, the rejection for RO system mainly depends on solution diffusion transport.

4. Conclusions

- 1) The polyamide nanofiltration and reverse osmosis membranes are a suitable methods for the removal of heavy metals from wastewater due to giving a pure water and allowed permeation of zinc.
- 2) The water flux for NF and RO membranes decreases with raising in feed concentration and time, increases by raising the applied pressure.
- 3) The maximum recovery percentage of water was 99% for NF and 57% for RO.
- 4) The flux for nanofiltration is higher than that from reverse osmosis membranes, The concentration of heavy metal ions in permeate for nanofiltration is higher than that from reverse osmosis membranes.
- 5) The permeability of pure water for nanofiltration membrane (AXEON NF4-1812) is approximately twice that of RO membrane (VONTRON-ULP 1812-50).

References

- [1] Alzahrani, S., Mohammad, A. W., Hilal, N., Abdullah, P., and Jaafar, O., 2013. "Comparative Study of NF and RO Membranes in the Treatment of Produced Water—Part I: Assessing Water Quality". Desalination. 315, 18–26.
- [2] Al-Alawy, R. M., 2015. "Thermo-Osmosis of Mixtures of Water and Organic Compounds through Different Membranes". Ph.D. thesis, Baghdad University.
- [3] Dannels, E., Green, T., Wettlaufer, A., Madhurnathakam, C. M. R., and Elkamel A., 2016. "Wastewater Treatment with Microbial Fuel Cells: A Design and Feasibility Study for Scale-up in Microbreweries". Journal of Bioprocessing & Biotechniques. 6, 1-6.

- [4] ERDOĞAN, D., 2005. "Removal of Heavy Metals from Wastewaters by Ion Flotation". M.Sc. thesis, İzmir Institute of Technology.
- [5] Srivastava, N. K. and Majumder, C. B., 2008. "Novel Biofiltration Methods for the Treatment of Heavy Metals from Industrial Wastewater". Journal of Hazardous Materials. 151, 1-8.
- [6] Jain, G., 2013. "Removal of Copper and Zinc from Wastewater Using Chitosan". M.Sc. thesis, National Institute of Technology, Rourkela.
- [7] Mohammad, A. W., Othaman, R. and Hilal, N., 2004. "Potential Use of Nanofiltration Membranes in Treatment of Industrial Wastewater from Ni-P Electroless Plating". Desalination. 168, 241-252.
- [8] Al-Rashdi, B. A. M., Johnson, D. J. and Hilal, N., 2013. "Removal of Heavy Metal Ions by Nanofiltration". Desalination. 315, 2-17.
- [9] Swaminathan, E., Nagappan, S., Rajangam, P. and Dharmalingam, S., 2013. "Separation of Ni²⁺, Cu²⁺ and Cr⁶⁺ Metal Ions from Water by Complexation Micro Filtration Technique Using Synthetic Polymer Membranes". Progress in Nanotechnology and Nanomaterials. 2, 47-54.
- [10] Abbar, A. H., 2015. "Removal of Heavy Metals from Wastewaters Using a Flow-by Fixed Bed Electrochemical Reactor". Ph.D. thesis, Baghdad University.
- [11] Addai, M. K., 2014. "Removal and Recovery of Heavy Metals by Nickel Smelter Slag". M.Sc. thesis, Western Ontario University.
- [12] Fu, F. and Wang, Q., 2011. "Removal of Heavy Metal Ions from Wastewaters: A Review". Journal of Environmental Management. 92, 407-418.
- [13] Mohammadi, T., Sadrzadeh, M., Moheb, A. and Razmi A., 2005. "Zinc Ion Removal from Wastewater by Electrodialysis". Ninth International Water Technology Conference. 1155-1163.
- [14] Zwain, H. M., Vakili, M. and Dahlan, I., 2014. "Waste Material Adsorbents for Zinc Removal from Wastewater: A Comprehensive Review". International Journal of Chemical Engineering. 2014, 1-13.
- [15] Frare's, N. B., Taha, S. and Dorange, G., 2005. "Influence of the Operating Conditions on the Elimination of Zinc Ions by Nanofiltration". Desalination. 185, 245-253.
- [16] Ujang, Z. and Anderson, G. K., 1996. "Application of Low-Pressure Reverse Osmosis Membrane for Zn²⁺ and Cu²⁺ Removal from Wastewater". Water Science and Technology. 34, 247-253.
- [17] Wahaab, R. A., Moawad, A. K., AbouTaleb, E., Ibrahim, H. S. and El-Nazer, H. A. H., 2010. "Combined Photocatalytic Oxidation and Chemical Coagulation for Cyanide and Heavy Metals Removal from Electroplating Wastewater". World Applied Sciences Journal. 8, 462-469.
- [18] Hamdzah, M. B., 2007. "Low Pressure Reverse Osmosis Membrane for Rejection of Heavy Metals". M.Sc. thesis, University Teknologi Malaysia.
- [19] Abhang, R. M., Wani, K. S., Patil, V. S., Pangarkar, B. L. and Parjane, S. B., 2013. "Nanofiltration for Recovery of Heavy Metal Ions from Waste Water - A Review". International Journal of Research in Environmental Science and Technology. 3, 29-34.
- [20] Wang, Z., Liu, G., Fan, Z., Yang, X., Wang, J. and Wang, S., 2007. "Experimental Study on Treatment of Electroplating Wastewater by Nanofiltration". Journal of Membrane Science. 305, 185-195.
- [21] Prados, J. C. and Cervello, G. G., 2011. "Water Purification and Management". Springer.
- [22] Gherasim, C. V. and Mikulášek, P., 2014. "Influence of Operating Variables on the Removal of Heavy Metal Ions from Aqueous Solutions by Nanofiltration". Desalination. 343, 67-74.
- [23] Madlool, J. J., 2014. "Water Treatment of Main Outfall Drain for Injection in Nasiriyah Oil Field". M.Sc. thesis, Baghdad University.
- [24] Dach, H., 2008. "Comparison of Nanofiltration and Reverse Osmosis Processes for a Selective Desalination of Brackish Water Feeds". Ph.D. thesis, University of Angers.
- [25] Li, N. N., Fane, A. G., Winston Ho, W. S. and Matsuura, T., 2008. "Advanced Membrane Technology and Applications". John Wiley & Sons, New Jersey.
- [26] Cousins, R. B., 2003. "Membrane Technology".
- [27] Sourirajan, S., 1970. "Reverse Osmosis". Academic Press, New York.
- [28] Dow Liquid Separations, FILMTEC™ Reverse Osmosis Membranes. Technical Manual.
- [29] Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe K. J. and Tchobanoglous, G., 2012. "MWH's Water Treatment Principles and Design". Third edition, John Wiley and Sons, Inc.
- [30] Kucera, J., 2010. "Reverse Osmosis Design, Processes, and Applications for Engineers". John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts.
- [31] Al-Bastaki, N. M. and Abbas, A., 1999. "Modeling an Industrial Reverse Osmosis Unit". Desalination. 126, 33-39.
- [32] Al-Alawy, A. F. and Salih, M. H., 2016. "Experimental Study and Mathematical Modelling of Zinc Removal by Reverse Osmosis Membranes". Iraqi Journal of Chemical and Petroleum Engineering. 17, 3, 57-73.
- [33] Khudair, W. N., 2011. "Reduction of Concentrating Poisonous Metallic Radicals from Industrial Wastewater by Forward and Reverse Osmosis". M.Sc. thesis, Baghdad University.
- [34] Williams, M. E., 2003. "A Review of Reverse Osmosis Theory". Corporation and Williams Engineering Services Company, Inc.
- [35] Schock, G. and Miguel, A., 1987. "Mass Transfer and Pressure Loss in Spiral Wound Modules". Desalination. 64, 339-352.
- [36] Jamal, K., Khan, M. and Kamil, M., 2004. "Mathematical Modelling of Reverse Osmosis". Desalination. 160, 29-42.
- [37] Absar, B., Kadi, S. E. L. and Belhamiti, O., 2008. "Mathematical Modeling of Reverse Osmosis Process by the Orthogonal Collocation on Finite Element Method". Asian Journal of Applied Sciences. 1, 1-18.
- [38] Lee, J. W., Kwon, T. O. and Moon, I. S., 2006. "Performance of Polyamide Reverse Osmosis Membranes for Steel Wastewater Reuse". Desalination. 189, 309-322.