

Experimental Study and Mathematical Modeling for the Removal of Lead and Cadmium Ions from Wastewater by Reverse Osmosis and Nanofiltration Membranes

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Abstract

Many industrial wastewaters that contain heavy metals (HM) lead, cadmium, chromium, and cobalt ions can be produced as toxic pollutants that affect human and animal health. The industrial wastewater ions are treated efficiently with reverse osmosis (RO) membrane and nanofiltration (NF) system technologies so that water consumption can be minimized as well as environmental conservation. Industrial wastewater samples containing Cd^{+2} Pb^{+2} HMs ions at varying concentrations of 10 ppm to 500 ppm using distilled water at different pressures of (3-11) bar and a common room temperature of 25 °C and at different pHs of 4, 5, & 7. Many of the water purifiers in use today use RO and NF in the purification process as one of the efficient methods. According to the results, the RO method was one of the best methods to remove heavy metal ions from industrial water, as its efficiency (%R) reached more than 98%. The results revealed that the Rejection efficiency (%R) of the system in removing Pb^{+2} ions reached 98.548%, and Cd^{+2} 97.974 under these operational conditions: pH = 6 ± 0.2 , the pressure of 11 bar, concentration=10 - 500 ppm, time= 90 min, and T=25 °C, so it is higher efficiency Removal (%R) of Pb^{+2} , then Cd^{+2} . In the nanofiltration NF system, the highest removal %R of the Pb^{+2} ion reached 93.17%, and the Cd^{+2} ion reached 92.594%. These results were under operational conditions: pH= 6 ± 0.2 , pressure= 11, concentration= 10-500 ppm, time= 90 min, and T=25 °C. The CFSD model is good for representing the value of the experiment because it has a higher $R^2 = (97 \pm 2) \%$. A satisfactory experimental data fit is again achieved using the film theory/Spiegler-Kedem (CFSK) model. The Combined–Film Theory / Finely Porous model (CFFP) model has higher coefficients of determination, as shown in Figures 5.13 and 5.14 for RO and NF, respectively, the CFFP model is suitable to represent the experimental results. The Peclet number is used to see the separation mechanism because of diffusion; diffusion in the boundary layer cannot control the convective flow through the membrane, and the concentration polarization will be high. When the Peclet number is small ($J < K$), then the convective flow will easily be tamed by diffusion at the boundary layer.

Keywords: Membrane technology; Reduce heavy metal HM ions; reverse osmosis RO—Nanofiltration NF system; the combined film theory.

1. Introduction

A potential scarcity of water on a worldwide scale is a pressing problem that people are working hard to address right now. Due to the worldwide population expansion, more enterprises will require water to produce

manufactured goods to meet the increasing demand. The water contamination endangers human health and technological advancement [1]. Conventional secondary treatment technologies cannot adequately treat many industrial effluents because of the stringent requirements to remove certain hazardous chemicals and resistant organic compounds. Consequently, cutting-edge methods for wastewater treatment are necessary [2]. Fif fundamental physical and chemical characteristics were used to establish the human consumption water quality index. Among these features are sodium ions, chloride, sulfate, total alkalinity, pH, dissolved oxygen, and electrochemical conductivity [3].

Heavy metals HMs pollution is one of the most hazardous inorganic pollutions [4] because of the tendency to accumulate in the environment and the inability of most organisms to degrade these metals [5]. It has been estimated that many dangerous chemicals and toxic heavy metals are being discharged into rivers globally, thanks to the increasing world population and the development of industries and agriculture [6]. Water quality in the rivers is also affected since raw industrial and domestic waste is chucked into these rivers, resulting in an increased concentration of heavy metals in the water [7].

HMs are those elements that have specific density characteristics and are frequently present in industrial settings. Lead, nickel, copper, cadmium, cobalt, and zinc are naturally occurring metals and are vital in the body when taken in small quantities. Nevertheless, when taken in higher concentrations, they result in acute or chronic toxicity. There are many ways employed to minimize the concentration of HMs ions, which include phytoextraction, ion exchange, eruptive flotation, electrochemical, biosorption, phytoremediation, bio-removal, adsorption, electrocoagulation, and membrane technologies like RO and NF. Membrane processes have gained popularity in industrial applications since the late 1960s and provide acceptable methods for conventional distillation, evaporation, and extraction practices. The advantages of the membrane technology over other methods are as follows: (a) energy effectiveness, (b) absence of phase transition, (c) high selectivity, (d) easy scalability and operation, and (e) eco-friendliness. Hollow fiber membranes are helpful for the recovery of metal ions from dilute aqueous solutions and have been found to meet WHO guidelines on chemicals used in drinking water from industrial and urban settings. [8,9].

Introducing dangerous compounds into our water system, such as medications and heavy metals, might have disastrous consequences. When heavy metals like cadmium (Cd(II)) infiltrate food supplies, they pose a threat not just to aquatic life but also to human health. Moxifloxacin (MFX) and other antibiotics are present in high concentrations in polluted water treatment effluent, which poses risks to humans and promotes the development of antibiotic-resistant bacteria [10].

The effectiveness of a membrane is determined mainly by the chemical composition and physical properties of the contaminants [11]. Both membrane technologies, RO and NF, have become essential in water and wastewater treatment, so modeling such processes appears necessary. Thus, if the modeling of these processes had not been properly applied, such success would not have been attained. The enhanced models should be tailored to the current requirements, and by gaining the advantages of modified models, they can achieve better information for the enhancement of membrane performance by designing the right equipment, defining the right inputs, such as pressures and temperatures to be applied, and minimizing the cost of desalination of different salts. It may give some strategies through which membrane manufacturers can enhance the management of membrane processes effectively. This work also shows a method of estimating the parameters of the SK model, merging the SK model with the film theory (SKCF), comparing the SKCF model with the SK model, and proving that the SK model yields better estimates [12].

Sustainability and environmental protection have become one of the main goals of the United Nations' plans for the year 2030 [12]. Also, for the Sustainable Development Goals (SDGs), a clean water environment cannot be protected because of water pollution with industrial waste that releases effluents with toxic HMs [13]. The cause of severe water pollution is the limited performance of appropriate water treatment techniques that reduce the pollution rate to environmentally acceptable limits for HMs. Accordingly, the treated water does not meet the

environmental specifications of drinking water, and about 2 billion people worldwide still don't have access to pure drinking water [14].

The nanofiltration (NF) is a pressure-flowing nanomembrane with a molecular weight cut-off of 200 to 1000 Daltons. NF mainly eliminates multivalent dissolved salts and low molecular weight organic substances dissolved in water. Nanofiltration is a membrane separation system that employs thin and nanoporous membranes. These NF systems work at pressures as low as 0.3 to 1.4 MPa. Therefore, NF is located between ultrafiltration UF and RO and can be described as "bulk reverse osmosis." The most used nanofiltration membranes are negatively charged; therefore, anions (negative ions) are rejected. The low energy-consuming nature of the nanofiltration membranes makes it a cheap method of desalination of salt water. The operating and maintenance costs of nanofiltration are relatively lower than those of reverse osmosis and electrolysis [15,16]. In the RO system, Zn concentration in the permeate increased with time from 0 to 70 min, and the water flux in the RO membrane also slowly declined with time. The Zn concentrations of HMs in the permeate were enhanced as the Zn concentration in the feed was raised to between 10 and 300 ppm, whereas the flux was reduced as the feed concentration was raised. As the pressure was raised from 1-4 bar, the Zn concentration was reduced, and the flux was increased. The highest recovery rate was 54 percent. Likewise, the highest removal efficiency %RE of RO elements was 56%, and the lowest rejection %R of Zn was 99.49%. The present experimental findings demonstrated that Zn ion concentrations in the permeate were under legal standards (i.e., < 10 ppm). One mathematical model was analyzed, and the MATLAB program found the solution. The theoretical results were about 90% accurate with the experimental results [17].

They are considered the water supply of M'rirt, a small Moroccan mountain town situated 1113 m above sea level and drawing water from the Oum Errabia River. Still, it would be essential to point out that the water source has a salinity value of 1.6 g. L⁻¹ and sodium ion content are higher than Moroccan and WHO standards. It is also crucial to admit that sodium consumption in excess could also pose acute health risks in addition to chronic ones. Though diseases associated with sodium deficiency in men are rare, it is equally important to note that too much sodium is unhealthy. To lower the Na⁺ concentration and increase the overall salinity of M'rirt water supply, the present study aimed to present the technical and ecological assessment of NF and RO processes since they are two viable technologies [18].

This study seeks to generate environmentally sustainable water by employing a pilot-scale pressure-driven membrane system to filter two categories of pollutants, HMs, such as Pb and Cd, which are toxic pollutants from industrial wastewater effluents. The following specific objectives can achieve this:

The following specific objectives can achieve this:

- 1) Compare the efficiency of two types of membrane systems, reverse osmosis (RO) and nanofiltration (NF), in rejecting pollutants using synthetic wastewater under various operating factors such as feed concentration and time for Pb and Cd ions and heavy metals.
- 2) We are determining the membrane transport parameters and mass transfer coefficient employing the film theory. And solution-diffusion models.

2. Mathematical Modeling and Theoretical Analysis

This section deals mainly with the theoretical analysis of the practical experiments with RO and NF membranes for removing HM ions (Pb and Cadmium) and other important considerations. These approaches are generally accompanied by various theoretical mathematical models for assessing the transmission coefficient, whereby basic diffusion-convection differential equations are solved further under specific prerequisites and assumptions. The models that predict removal (rejection) properties also limit the experiments that may be constructed to explain particular systems. CFSD, compact film theory/Spiegler-Kedem model (CFSK), compact film theory/micropore model (CFFP), and Peclet number (Pe) of the film were used for the evaluation of the theoretical and experimental data of the heavy metal removal processes by using both [19].

2.1 Film Theory

The solute moves from convection through the boundary layer and back to the overall solution by diffusion traced with the concentration gradient mechanism. This is illustrated in Figure 1, which maps the solute transport across membranes through concentration polarization, which increases osmotic pressure and forms a thin gel layer at the membrane surface due to particles [19].

$$J \cdot C - J \cdot C_p = D \frac{dc}{dx} \quad (1)$$

$$\frac{dc}{c - c_p} = \frac{J}{D} dx \quad (2)$$

- D: coefficient for diffusion solute
- C: concentration of solute in the boundary layer
- x: distance from the film layer
- C_p: concentration solute in the permeable side

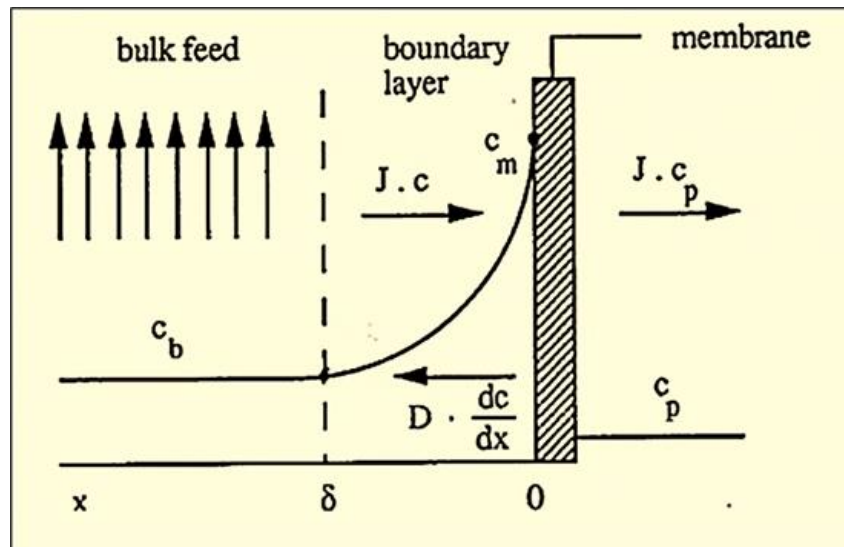


Figure 1: Concentration polarization diagram [19].

Equation (2) can be performed over the following conditions:

$$C = C_m \quad \text{at } x = 0$$

$$C = C_b \quad \text{at } x = \delta$$

- C_m: concentration solute at the membrane surface or water, which is the solvent, interface
- C_b: bulk solute
- δ: thickness of boundary layer

Yields:

$$\ln(C_m - C_p) - \ln(C_b - C_p) = \frac{J}{D_{ab}} (0 - \delta) \quad (3)$$

$$\ln \frac{C_m - C_p}{C_b - C_p} = \frac{\delta}{D_{ab}} J \quad (4)$$

- D_{ab} = diffusivity of solute an in solvent b (cm²/sec)
- $D_{ab}/\delta = K$ = coefficient for mass transfer

By rearranging equation (4):

$$J = K \ln \left(\frac{C_m - C_p}{C_b - C_p} \right) \quad (5)$$

The observed rejection %R of RO and the true solute R can be expressed below [20]:

$$R_o = \frac{C_b - C_p}{C_b} \quad (6)$$

$$R = \frac{C_m - C_p}{C_m} \quad (7)$$

Using equations (6) and (7), equation (5) becomes [21]:

$$\frac{C_m}{C_b} = (1 - R_o) + R_o \exp \left(\frac{J}{K} \right) \quad (8)$$

$$\frac{R_o}{1 - R_o} = \left[\frac{R}{1 - R} \right] \exp \frac{-J}{K} \quad (9)$$

$$\ln \frac{R_o}{1 - R_o} = \frac{J}{K} \ln \left[\frac{R}{1 - R} \right] \quad (10)$$

$$\text{Let } \frac{R}{1 - R} = P_s$$

$$\ln \frac{R_o}{1 - R_o} = \frac{J}{K} \ln P_s \quad (11)$$

When plotted $\ln \frac{R_o}{1 - R_o}$ Against J from the experimental results (Equation 11). We can estimate the total permeability coefficient (P_s) and the coefficient for mass transfer (K) from the point of intersection and the slope of the straight line.

2.2 Combined –Film /Solution-Diffusion model (CFSD)

The discussed model uses a transport mechanism whereby the solute exits the intercellular fluid into the layer of the surface membrane, which is not a barrier to the transport of molecules. The fundamental mathematical equations for this model are [22]:

$$J = L_w (\Delta P - \Delta \pi) \quad (12)$$

$$J_s = \left(\frac{D_{am} K}{\delta} \right) (C_m - C_p) \quad (13)$$

Where:

- L_w is the solvent permeability coefficient and is calculated from pure water permeability measurements ($l/m^2 \cdot s$)
- $(D_{am} K/\delta)$ is a single coefficient.

Combining Equations (7), (12), and (13), as shown by (Chaudhari and Murthy, 2008) [23] yields:

$$\frac{1}{R} = \left(\frac{D_{am} K}{\delta} \right) \left(\frac{1}{J} \right) \quad (14)$$

$$\frac{R}{1-R} = \frac{J}{D_{am}} \times \frac{\delta}{K} \quad (15)$$

$$\frac{R_o}{1-R_o} = \left[\frac{J}{D_{am}} \times \frac{\delta}{K} \right] \left[\exp \frac{-J}{K} \right] \quad (16)$$

By plotting the following:

- RO results versus J
- $(D_{am} K/\delta)$ parameter
- coefficient mass transfer (K)

all of the above can be evaluated numerically by slope-intersection of the straight line.

2.3 Combined –film theory /Spiegler –Kedem model (CFSK)

The ST description of a specific solute's movement can be accomplished using the IT model if the solute-membrane electrostatic interaction is absent. It uses convective flux in which a pressure difference (ΔP) at the membrane surface and a second mechanical molecular transport known as the pure diffusive flux, a function of the concentration gradient. This model considers the parameters of the membrane's structural lattice and the solution medium's nature. The Spiegler-Kedem nonlinear model equation is shown below (Kedem and Spiegler, 1966 [24]):

$$J = h_p(\Delta P - \sigma \Delta \pi) \quad (17)$$

$$J_s = L_s \left(\frac{dC_s}{dx} \right) + (1 - \sigma) C_s J \quad (18)$$

$$J_s = C_s J \quad (19)$$

$$L_s \left(\frac{dC_s}{dx} \right) + [(1 - \sigma) C_s - C_p] J = 0 \quad (20)$$

By integrating the equation numbered (3.20) with limits of boundary conditions:

- $x=0, C_s = C_p$ and $x=\Delta x, C_s = C_m$

$$\int_{C_p}^{C_m} \frac{dC_s}{(1 - \sigma) C_s - C_p} + \int_0^{\Delta x} \frac{J dx}{L_s} = 0 \quad (21)$$

$$\frac{C_p - C_m(1 - \sigma)}{\sigma C_p} = \exp\left(-\frac{J(1 - \sigma)}{P_s}\right) \quad (22)$$

$$P_s = \frac{L_s}{\Delta x} \quad (23)$$

$$R = \frac{\sigma(1 - F)}{1 - \sigma F} \quad (24)$$

$$F = \exp[-J a_2] \quad (25)$$

$$a_2 = \frac{1 - \sigma}{P_s} \quad (26)$$

- σ : coefficient for reflection
- P_s : coefficient for overall permeability
- F : parameter of flow
- L_s : permeability of local solute
- hp : coefficient for hydraulic permeability of the membrane

So, we can rearrange equation (24), which yields:

$$\frac{R}{1 - R} = a_1 (1 - F) \quad (27)$$

And:

$$a_1 = \frac{\sigma}{1 - \sigma} \quad (28)$$

Then, replace equation (27) with equation (9); this gives:

$$\frac{R_o}{1 - R_o} = a_1 [1 - \exp(-J a_2)] \left[\exp\left(\frac{-J}{K}\right) \right] \quad (29)$$

Therefore, the CFSK model is depicted by equation (29), whose full name is the model complex film theory/Spiegler-Kedem. Thus, we can determine the following parameters σ , P_s , and K by using a method called "the estimation of nonlinear parameter" (**Murthy and Chaudhari [25] suggest using Excel 2021**)).

2.4 Combined –Film theory / Finely Porous model (CFFP)

The following model considers the interaction between the membrane pore wall and solid particles: friction. To describe such a case, the b factor is included to take care of frictional forces. The working equation is provided below (**Vaidya et al., 2001 [26]**):

$$\frac{1}{1-R} = \left(\frac{b_f \varepsilon}{K} \right) + \left(\frac{k - b_f \varepsilon}{K} \right) \exp \left(-J \frac{\tau \varepsilon}{\varepsilon D_{ab}} \right) \quad (30)$$

- (b_f) : friction factor in a micropore model
- (ε) : void fraction (in membrane)
- (τ) : membrane tortuosity

Substituting equation (30) into equation (3.9) gives the equation shown below:

$$\frac{R_o}{1-R_o} = \left(\frac{b_f \varepsilon}{K} - 1 \right) \left[1 - \exp \left(-J \frac{\tau \delta}{\varepsilon D_{ab}} \right) \right] \exp \left(-\frac{J}{K} \right) \quad (31)$$

The CFFP model-based composite membrane/microporous is represented by the given equation (31). Membrane parameters and K can be approximated using the nonlinear parameter estimation method, and for this, (**Excel 2021 can be used**).

2.5 Determine Peclet number (Pe)

Péclet number, or Pe , is essential for assessing transport processes in the flowing fluid. It outlines how a physical property is convectively transported through the flow by (J) to diffusive transport ($K = D_{ab}/\delta$) of the same property, driven by an appropriate gradient. This dimensionless ratio is referred to as the Péclet, in contrast with the Péclet temperature described previously in this article. Péclet number can be written as:

$$P_e = \frac{\text{advective transport rate}}{\text{diffusive transport rate}}$$

$$P_e = \frac{J}{K} \quad (34)$$

K is the coefficient for mass transfer from the CFSK model (**Murthy and Chaudhari, 2009 [25]**).

3. Materials, Equipment, and Apparatus

3.1. Heavy Metals

This work selected two types of HMs solutions, Cd(II) and Pb(II). These polluting ions exist as nitrate; when dissolved in water, they turn into water-polluting ions. Table. One shows the pollutants used in this work.

Table 1: Heavy metals chemicals

HMs ions	Nitrates	M.wt g/mol	Company
Pb⁺²	Pb(NO ₃) ₂	331.2	HIMEDIA
Cd⁺²	Cd(NO ₃) ₂	236.42	CDH

3.2. Auxiliary Chemicals:

Table 2 shows the chemicals used to modify clean membranes, the pH

Table 2: The auxiliary chemicals

Chemicals	Purity %	M.wt g/mol
HCl	37%	36.46
HNO ₃	68%	63.01
NaOH	99.9	39.997

3.3. Preparation of heavy metal solutions

In deionized water, a lead ion solution can be prepared by dissolving lead nitrate, Pb(NO₃)₂. To get the desired concentration of lead ions, 1.6 g of lead nitrate is dissolved in tap water to make a 1000 ppm (mg/l) lead solution. This is done using chemical equations of stoichiometry, and the same method can be used to prepare another ion in solution.

4. Experimental Work

The industrial wastewater with the concentrations of Pb²⁺ and Cd²⁺ was simulated by dissolving the required amounts of Pb(NO₃)₂ and Cd(NO₃)₂ in tap water. The pH of the solution was then made to the required level by either adding 0.5 M nitric acid (HNO₃) or 1 M sodium hydroxide (NaOH). Figure 2 presents the flow diagram of the pilot plant for RO and NF systems utilized in these experiments. The feed solution was stored in a tank, with the operating pressure monitored using a pressure gauge varying from 0-25 bar along the feed line. The feed solution was taken from the feed vessel by a low-pressure pump, and the feed solution was further purified by filtering it through microfilters before it was pumped into the RO or NF membranes by a high-pressure pump. In Figure 2 and Table 3, the feed flow rate was regulated with a flow meter ranging from 2-150 L/min, and the treated water was channeled through a pipe. The concentrated waste stream was returned to the feed hopper and combined with the feed tank. Table 3 describes the specifications of the RO membrane (Vontron Membrane Technology Co., Ltd.) and the NF membrane (The Dow Chemical Company).

The concentrations of heavy metal ions were determined by an atomic absorption spectrophotometer (Model: AA-7000, made by Shimadzu, Japan). After obtaining the results, the solution was released via a valve, and the system was rinsed with deionized water.

The solute removal efficiency was calculated using equation 1, based on the solute concentrations in the feed solution (CF) and the permeate solution (CP). The removal efficiency (%) is defined as The removal efficiency (%) is expressed in equation 1:

CF represents the solute concentration in the feed solution (in ppm), and CP represents the solute concentration in the permeate (in ppm). [27]

$$R\% = \frac{C_F - C_P}{C_F} \times 100 \quad (35)$$

A low-pH solution, usually an acidic solution like hydrochloric acid, is used to clean the metal scales on the membrane surface, and the pH is controlled. This cleaning solution is pumped through the RO membranes and

recirculated as it cleans them several times. In the end, the system is washed with tap water several times. The cleaning process is carried on till the electrical conductivity of the product stream becomes close to the value of feed water [28].

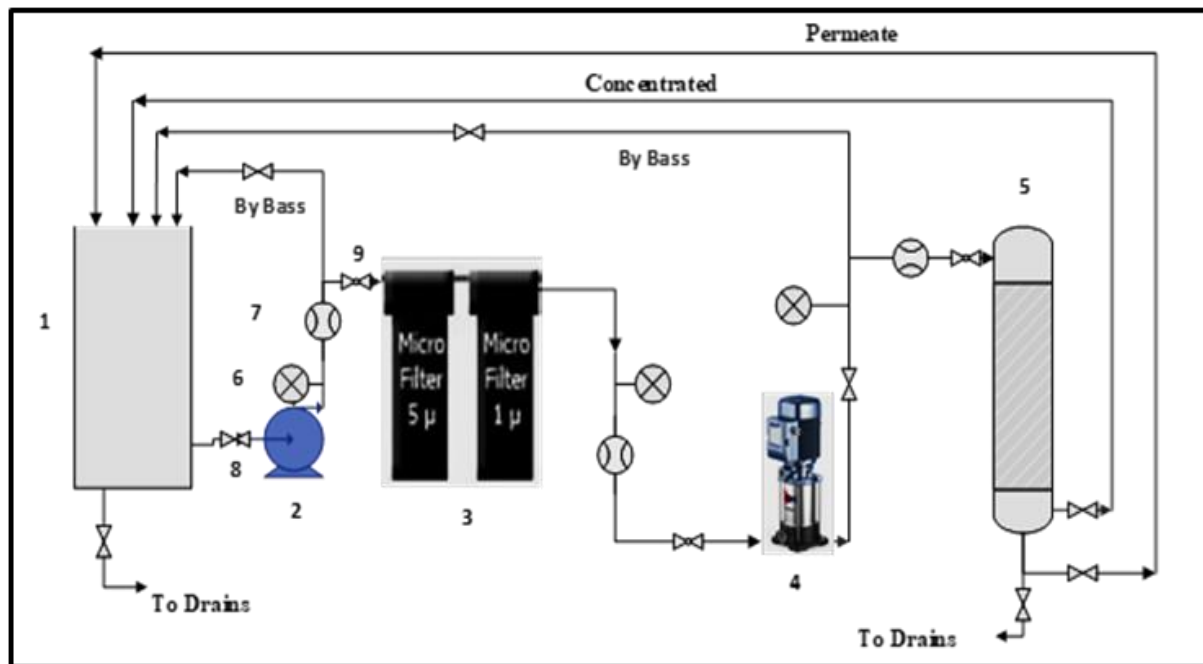


Figure 2: Schematic illustration of a RO and NF Pilot plant system 1-Feedtank, 2- Low-pressure pump, 3- Microfilter, 4- High-pressure pumps, 5-RO or NF, 6-Pressure gauges, 7- Flow meters, 8- Get valve, 9- Glob valve.

Table 3: The specifications of various equipment used in this system.

Equipment	Characteristics
pump with Low-pressure (Feed pump)	• pump category is Pentax / INOX 100/50 (Italy) • $Q = (5 - 45) \text{ l/min}$ • $H(m) = 25 - 46$ • $HP = 1$ • $P = 0.74 \text{ kw}$ • $V = 230 \text{ volt}$ • $A = 4.6 \text{ Ampere}$ • $I_p = 44$ • $T_{\text{max}} = 50 \text{ }^{\circ}\text{C}$ • $Hz = 50$ • One Phase continuous duty
pump with high-pressure	• pump category is Pentax US-200/7 (Italy) • $Q = (30 - 140) \text{ l/min}$ • $H(m) = 12.5 - 73.6$ • $HP = 2$ • $V = 230$ • $A = 9$ • $T_{\text{max}} = 50 \text{ }^{\circ}\text{C}$ • $I_p = 44$

	• Hz =50 • P= 1.65 kw • The continuous duty is one Phase
Holding Tank	the category is polyethylene with a 200L capacity
Flow meters	2 - 150 l / min, Germany
Pressure Gauges	0 - 25 bar, Germany

Table 4: Specifications of the reverse osmosis (RO) and nanofiltration (NF) membranes.

Type of membrane	RO	NF
Model	ESPA1-4040	NF-4040
Material	Composite polyamide	Composite polyamide
Module	Spiral wound	Spiral wound
Size (ID, length) (inch)	(4x40) inch	(4x40) inch
Effective area (m ²)	7.9	7.6
Max operating temp (°C)	45	45
Max pressure (bar)	41.4	41
pH range of water	2-10	3-10

5. Results and Discussion

5.1 RO System

5.1.1. Effect of HMs Concentrations on Removal Percentage

Different times and concentrations of Pb²⁺ and Cd²⁺ ions were taken and treated in the RO system, and the results are in Figures (3. a, b) and. This showed that the treatment time and the lead ion concentration affected the efficiency of the removal process. Consequently, with the increase in the concentration of lead ions, it was observed that % R increased. The removal and water purification rate increases when the lead ion concentration increases from 10 to 500 ppm. At a concentration of 500 ppm and 90 minutes, the removal rate is 98.55%, the best lead removal rate %R. With the same concentration and time, the best removal %R and purification for cadmium is 97.97%. Under conditions, feed flow rate Q_F=25 l/min, T=25 °C, P=11 bar, pH=6±0.2, (10-500 ppm). The change was less after 80 to 90 minutes, meaning the effect of time began to decrease. Therefore, the optimal performance for removing ions occurs after 80 minutes; the most appropriate is 90 minutes. It was noted that the removal sequence depends on the size of the dissolved ions (the atom's mass) when an atom with a high mass, such as in Pb²⁺, leads to a high %R, and the same applies to the rest of the ions. It was noted that increasing the feed concentration, C_F, leads to increased removal, as the efficiency of R gives High removal. C_p decreases at high concentrations greater than 300 ppm, and accordingly, the percentage of removal increases, which is in agreement with [29], which are as follows: Pb²⁺>Cd²⁺. After 80-90 minutes, it was observed after 80 minutes that the change in rejection became less due to the increase in positive charge across the membrane in the RO, which constitutes an obstacle to blocking ions. Therefore, there is little increase in the passage of ions through the membrane. Therefore, the change of removal rate decreases after 90 minutes and becomes uneconomical, and the appropriate time is 90 minutes, which agrees with [30, 31].

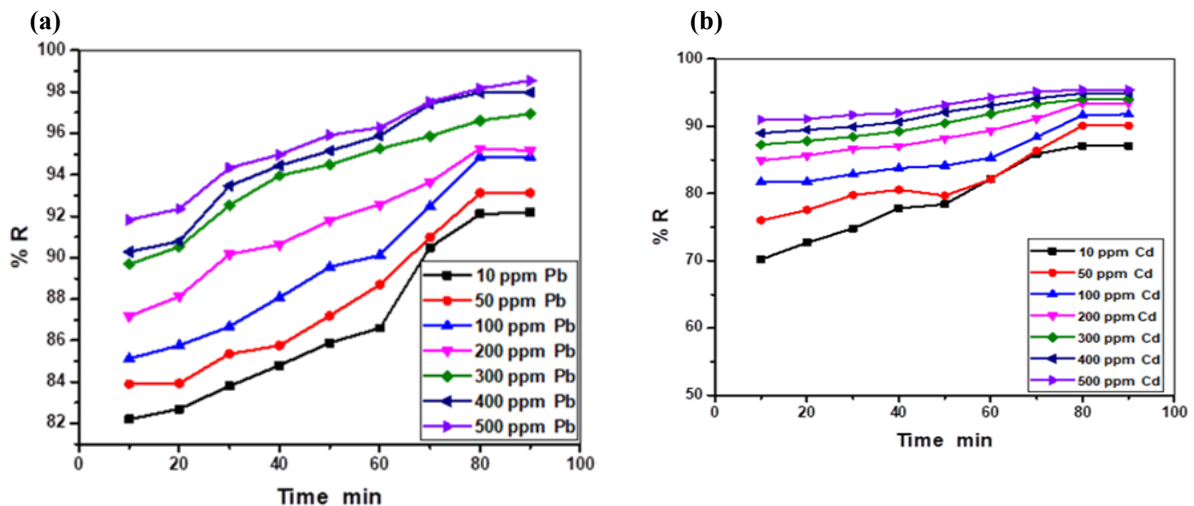


Figure 3. Effect of time with (a) Pb and (b) Cd ion concentration on the rejection rate of HMs for the reverse osmosis process (Operation conditions $Q_F=25$ l/min, $T=25$ °C, $P=11$ bar, $pH=6\pm0.2$)

5.1.2. Effect of Pressure on Removal Percentage

The effect of pressure on the efficiency of the RO system is significant because increasing the efficiency of RO requires increasing the pressure to the permissible limit. In this regard, it was pointed out that the impact of pressure is positive, as the increase in pressure from 3 to 11 bar results in an increase in the percentage removal (%R) for the best %R: 98.55% for Pb^{+2} , 97.97 % for Cd^{+2} , as shown in Figure 4, (Operation conditions $Q_F=25$ l/min, $T=25\pm2$ °C, $P=11$ bar, $pH=6\pm0.2$, operation time=90 min, and 500ppm ion concentration), the best pressure is 11 bar. The noticeable increase in removing HMs ions began after the 9 to 11 bar pressure. The reason is that the effect of the pressure is positive. However, increasing the pressure excessively is impossible because the reverse osmosis membrane becomes saturated, and the effect becomes negative. Therefore, the optimal pressure performance was 11 bar. The removal percentage increases as pressure rises; this suggests that the dynamic force enhances with increased operational pressure, reducing the resistance through the RO membrane. Such a pressure increase also reduces the boundary layer thickness of the membrane, causing membrane compaction. The actual thickness of the film δ is calculated. From Fig. 4, it can be seen that the removal efficiency is over 98% at 11 bar. This result is similar to the findings of [32, 33].

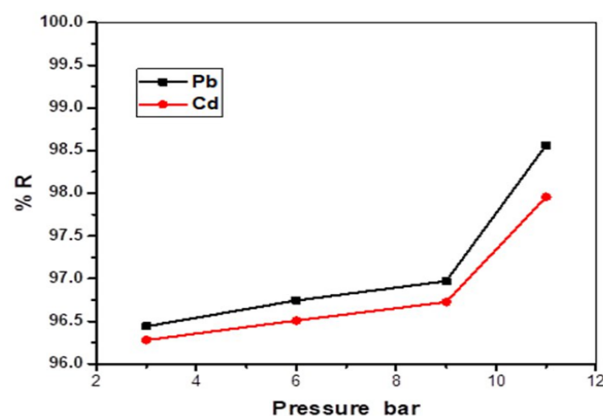


Figure 4. This shows the rejection rate of heavy metals (Pb and Cd) increases with the increase in pressure during the reverse osmosis (RO) process. The operational conditions were as follows: Flow rate (Q_F) = 25 L/min, temperature (T) = 25°C, pressure (P) = 3-11 bar, $pH \approx 6 \pm 0.2$, lead concentration = 500 ppm, and operation time = 90 minutes.

5.2 Nanofiltration NF System

5.2.1. Effect of HMs Concentrations on Removal Percentage

At a concentration of 500 and a time of 90 minutes, the removal rate is 94.172% Pb^{+2} , which is the best lead ions removal rate %R. With the same concentration and time, the best removal %R and purification for HMs Cd^{+2} is 92.594. Under the conditions, feed flow rate $Q_F=25$ l/min, $T=25$ °C, $P=11$ bar, operation time=90 min, and $\text{pH}=6\pm0.2$, as shown in Figure 5, a, b. From these results, the change was less after 80 to 90 min, which means that the effect of time began to decrease; therefore, the optimal performance for removing ions is after the time of 80 min, and the most appropriate is 90 min. It was noted in Figure 5.3 that the removal sequence depends on the dissolved ions, which are as follows: $\text{Pb}^{+2}>\text{Cd}^{+2}$, but less than RO. As illustrated in section 5.1.1.

5.2.2. Effect of Pressure on Removal Percentage

Pressure has a profound impact on the efficiency of nanofiltration (NF) systems, where an increase in pressure to the permissible limit increases the system's efficiency. The analysis showed that with the pressure increase from 3 to 11 bar, the removal percentage of heavy metals increased, and the highest value of 94.75% for Pb^{2+} was achieved with the removal of Cd^{2+} reaching 94.476%, as illustrated in Figure 6 below. It was found that the best pressure that gave the best performance was 11 bars. The reason is that the pressure effect is positive, but the pressure cannot be increased excessively because the NF membrane saturates, and the effect becomes negative. Therefore, the optimal pressure performance was 11 bar. But less than RO. As illustrated in section 5.1.2.

Comparison table between RO and NF with some references with similar practical conditions to this work. It was found that the optimal performance of RO is the best for various pollutants and better than NF.

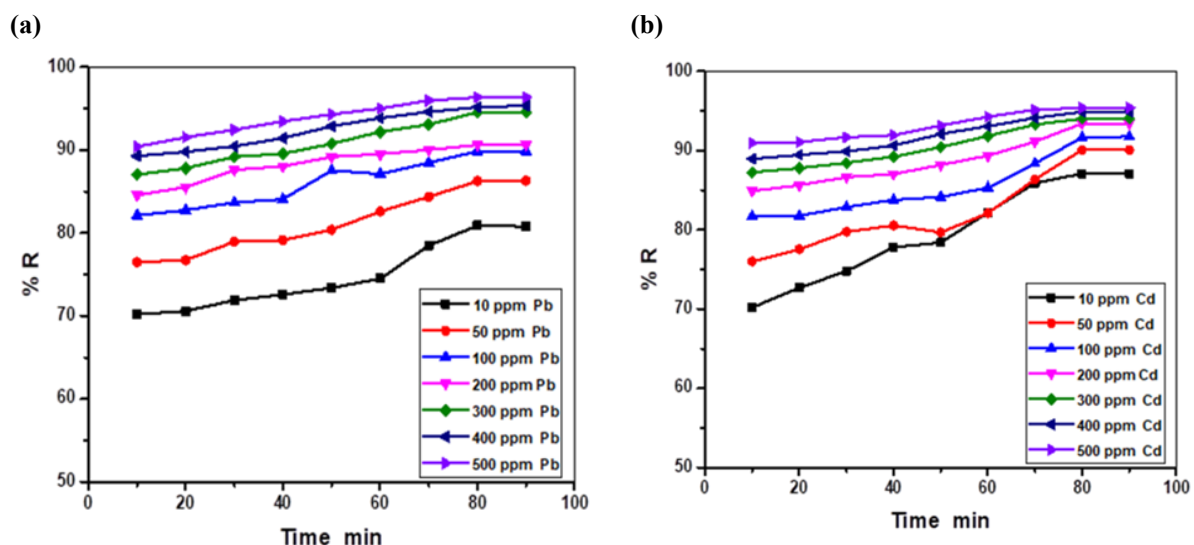


Figure 5. illustrates the NF process's rejection rate with time and increasing concentrations of Pb^{2+} and Cd^{2+} ions. Conditions: Flow rate = 35 L/min, temperature = 25°C, pressure = 11 bar, $\text{pH} \approx 6$, and concentrations range 10-500 ppm.

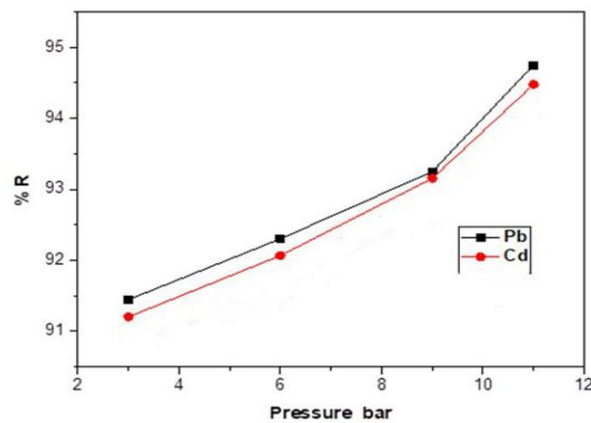


Figure 6. Effect of pressure on the rejection rate of HMs (Pb and Cd) for the NF process (Operation conditions $Q_F=25$ l/min, $T=25$ °C, $P=3-11$ bar, $pH=6\pm0.2$, 500ppm, operation time=90.

5.3 Calculation Parameters for the Membrane and Mass Transfer Coefficient

5.3.1 The Combined-Film solution-diffusion model (CFSD)

The CFSD model is suitable for representing the value of the experiment because it has a higher R^2 , as shown in Figures (7 and 8) for RO and NF, respectively. δ can be calculated using the spread of Pb and Cd as HMs and was calculated using equation (36) (Al-Moussawi, 2012 [34]).

$$D_m = 2.74 \times 10^{-9} (\text{Mwt})^{-1/3} \quad (36)$$

- D_m : coefficient for diffusion (cm^2/s)
- Mwt: molecular weight of the (Pb and Cd) HMs (grams/mol)

The value of δ increases with increasing concentration of HMs in the solution, while on the other hand, the value of K decreases with increasing concentration.

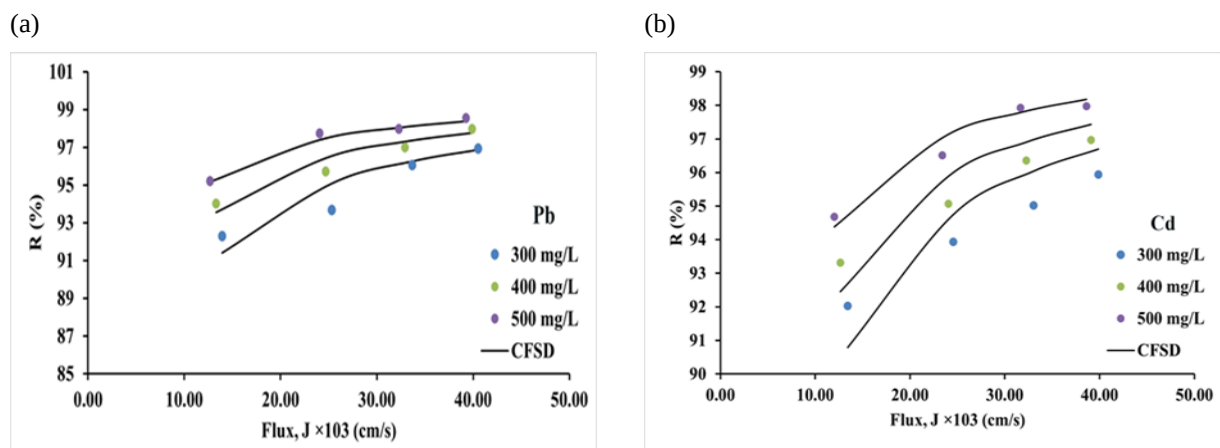


Figure 7 illustrates the results of the CFSD model for the data set of RO membrane for (a) Pb and (b) Cd as HMs

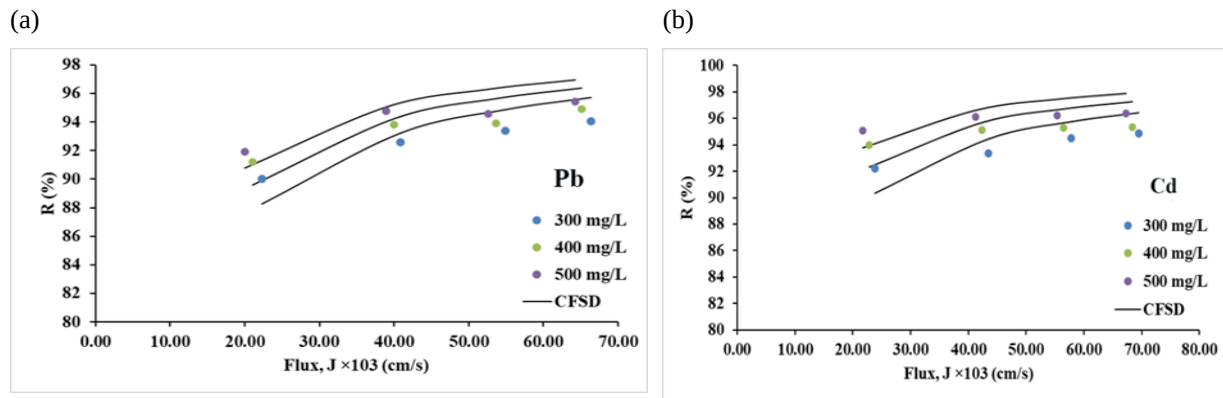


Figure 8 illustrates the results of the CFSD model for the data set of NF membrane for (a) Pb and (b) Cd as HMs

5.3.2 The combined film theory/Spiegler-Kedem (CFSK) model

The experimental data shows good agreement and trends with the results obtained from Equation 29 for all initial concentrations and membrane types, as observed in Figures 9 and 10 for RO and NF, respectively. In the case of the present study, the parameters change with the difference in the initial concentration of heavy metals. In particular, P_s is inversely related to the initial concentration: as the latter increases, less solute passes through the membrane; at the same time, σ grows because the efficiency of solute removal rises. The same observation was made by (Al-Zoubi et al. (2007) [35]).

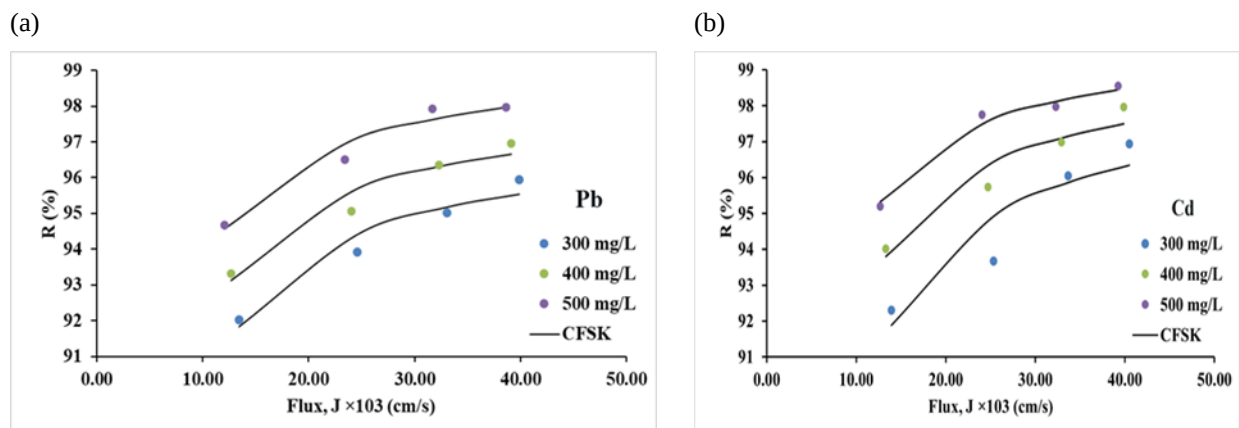


Figure 9: Results of the CFSK model for the data set of RO membrane for (a) Pb and (b) Cd of HMs

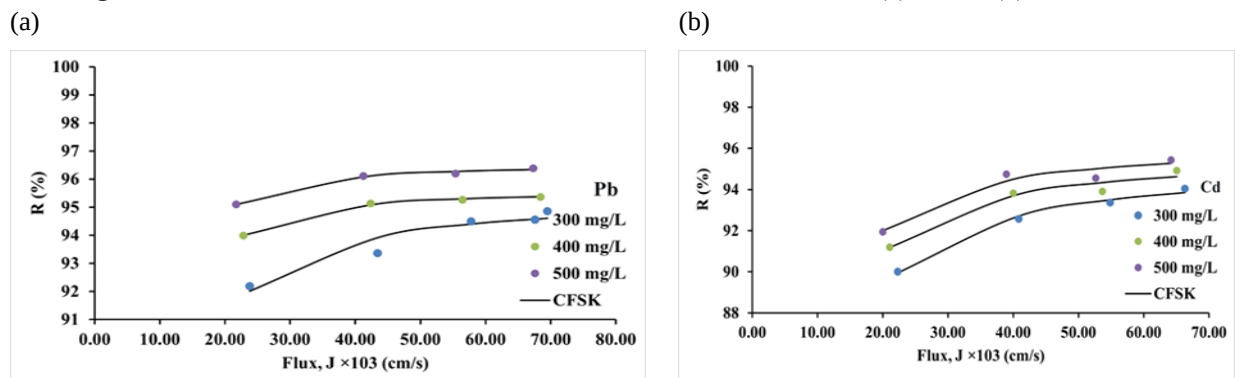


Figure 10: Results of the CFSK model for the data set of NF membrane for (a) Pb and (b) Cd of HMs

5.3.3 The Combined –Film Theory / Finely Porous model (CFFP) model

Since it has higher coefficients of determination as shown in Figures 11 and 12 for RO and NF respectively, the CFFP model is suitable to represent the experimental results which match the results of Eq. 31. The adequate thickness of the film δ can be known from the coefficient for the average value of (b2), if we assume that the film vacuum friction (ε) and tortuosity (τ) are 0.165 and 3, respectively (Soltanieh, 1981 [36]). Therefore, the average adequate thickness of the film δ for NF can be calculated as 0.86 and 0.82 cm for Pb and Cd, respectively. On the other hand, RO, 0.85, and 0.836 for Pb and Cd as HMs. A study conducted by (Vaidya et al. (2001 [26])) also produced similar findings.

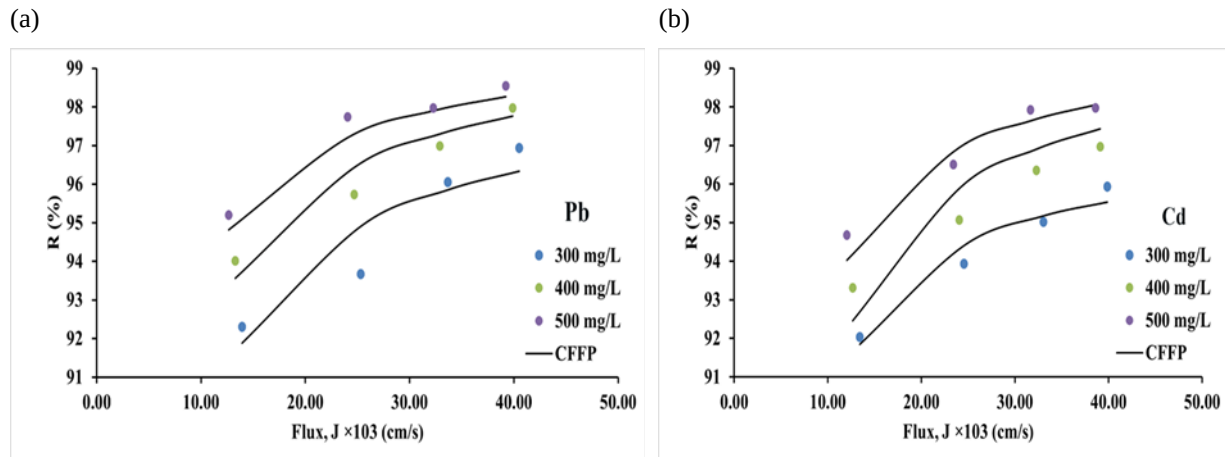


Figure 11 illustrates the results of the CFFP model for the data set of RO membrane for Pb and Cd of HMs

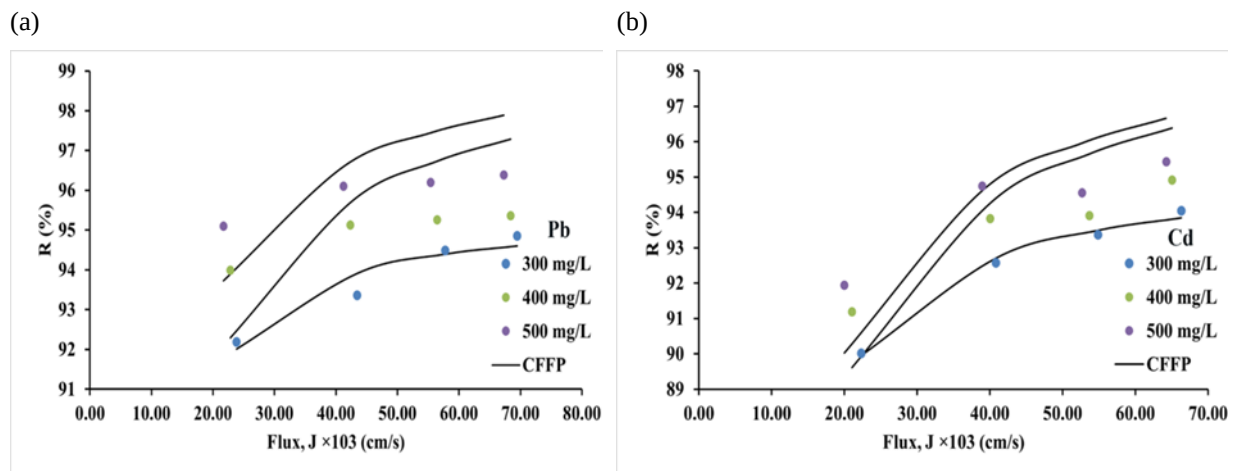


Figure 12 illustrates the results of the CFFP model for the data set of NF membrane for (a) Pb and (b) Cd of HMs

5.3.4 Dimensionless Peclet Number (Pe) Determine

As illustrated in Table 4, the Péclet number (Pe) of 20 ppm Pb and Cd as HMs has been computed using Equation 34, and this Pe increases with the increase of the flux (Murthy Chaudhari, 2009 [25]). At a high Péclet number ($J \gg K$), the stabilizing effect of the solute diffusion through the boundary layer on convective flow through the membrane gets suppressed, and the concentration polarization is conspicuous. On the other hand, When the Péclet number is low ($J \ll K$), the convective flow is readily offset by diffusion within the

boundary layer, resulting in minimal concentration polarization (**Baker, 2004 [37]**). The Péclet number is a critical factor in determining the separation mechanism driven by diffusion. Similar findings have been reported in the literature (**Chaudhari and Murthy, 2008 [23]**).

FTable 4. Determine Peclet number (Pe) for 500 ppm (Pb and Cd as HMs)

	NF		RO	
	<i>J</i>	<i>Pe</i>	<i>J</i>	<i>Pe</i>
Pb	21.71	1.115352	12.65823	0.648439
	41.25	2.119169	24.05063	1.232034
	55.39	2.845838	32.27848	1.65352
	67.30	3.457592	39.24051	2.010161
Cd	20	1.027479	12.02532	0.617814
	38.94737	2.00088	23.41772	1.203111
	52.63158	2.703891	31.64557	1.625826
	64.21053	3.298747	38.60759	1.983508

6. Conclusions

- The RO and NF membranes employed in this study have proven helpful in removing some of the HMs, including lead (Pb) and cadmium (Cd), in treated wastewater effluent.
- The maximum removal efficiency was 98.548% for the Pb²⁺ ions, and for Cd²⁺ ions, it was 97.974% using RO. In the NF system, the highest removal efficiency of Pb²⁺ ions was 93.17%. These results were achieved under the following operational conditions: pH $\approx$ 6, pressure $\approx$ 11 bar, concentration $\approx$ 500 ppm, time $\approx$ 90 min, and temperature = 25 $\pm$ 2 °C. Based on the specified conditions, the performance efficiency of the RO system was higher than that of the NF system. The treated water obtained was within the permissible limit on the mixture of heavy metals in industrial wastewater. However, the removal rate starts to decline after 90 minutes, so any further treatment is not economical, and therefore 90 minutes is the most appropriate time.
- The membranes were characterized using several models, such as film theory, combined-film theory/Spiegler-Kedem (CFSK), combined-film theory/solution diffusion model (CFSD), and combined-film theory/finely porous model (CFFP). These methods were used in determining the boundary layer thicknesses, the membrane transport parameters, and the Péclet number [Pe]. It was observed that there is a strong alignment between the theoretical predictions and the experimental results for the membrane systems.
- Further, the operating conditions, such as the pressure of 6, 9, and 11 bar, the lead concentration of 500 ppm, pH = 6, and the temperature of 25 °C, were identified to be the best. From the experimental results, it can be concluded that both membranes showed a very high optimal performance when the flux was altered with pressures of 6, 9, and 11 bar and rejection ratio, and they were both very efficient in lead removal. However, the reverse osmosis membrane has proved to perform the best in its optimal efficiency limit.

References

- [1] Jasim, N.; Ebrahim, Sh.; Ammar, S., (2023) A comprehensive review on photocatalytic degradation of organic pollutants and microbial inactivation using Ag/AgVO₃ with metal ferrites based on magnetic nanocomposites, *Cogent Engineering*, 10:1, 2228069.
- [2] Mohammed, Risalah, Maryam Jawad Abdulhasan, Shahad A. Raheem, Abeer I. Alwared, Noor A. Mohammed, Rand Fadhil Kadhim, Alaa Dhari Jawad Al-Bayati. (2023). Optimization of Response Surface Methodology for Removal of Cadmium Ions from Wastewater using Low-Cost Materials. *Journal of Ecological Engineering*, 2299–8993, 24(8), 146–156.
- [3] Glena, Ali Mahmood; Farhad, Hassan Aziz. Water Quality Assessment of Smaqli Dam- Erbil for Drinking, Irrigation and Fish Farming, *Baghdad Science Journal*, (2024) 21(4): 1147-1161.
- [4] Balassa, G.C.; Souza, D.C. And Lime, S.B.2010. Evaluation of the potential of *Pontederia Paviflora* Alexander in The Absorption of Copper (Cu) and Its Effects on Tissues. *Acta Scientiarum. Biological Sciences*, 32(3): (2010)- 311-316.
- [5] Lone, M.I.; Hi, Z., Stoffella, P.J.; Yang, X. Phytoremediation of heavy metals polluted soils and water: Progresses and perspective. *Journal of Zhejiang University Science B*, 2008. 9(3): 210-220.
- [6] Islam, M.S.; S. Han and S. Masunaga .2014. Assessment of trace metal contamination in water and sediment of some rivers in Bangladesh. *J. Water Environ. Technol.* 12, 109-121.
- [7] Raid SH. Jarallah and Nihad A. Abbas. (2019). The Effect of Sulfur and Phosphate Fertilizers Application on the Dissolved Phosphorus Amount in Rhizosphere of Zea Maize L.". *Al-Qadisiyah Journal For Agriculture Sciences*, 9(2), 233-239.
- [8] M. Jamil, M.S. Zia, M. Qasim, Contamination of agroecosystem and human health hazards from wastewater used for irrigation, *J. Chem. Soc. Pak.* 32 (2010) 370–378.
- [9] A. Singh, R.K. Sharma, M. Agrawal, F.M. Marshall, Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India, *Food Chem. Toxicol.* 48 (2010) 611–619.
- [10] Naji, A.; Abd Ali, Z., (2024). Fabrication of immobilized magnetic nanoparticles for removal of cadmium and moxifloxacin from aqueous solutions using green approach: Batch and continuous study, *Case Studies in Chemical and Environmental Engineering*, 9, 100771, 2666-0164.
- [11] Ebrahim, A.; Ebrahim, S.E., (2021). REMOVAL OF TETRACYCLINE FROM INDUSTRIAL WASTEWATER USING REVERSE OSMOSIS TECHNOLOGY. *Plant Archives*, 21, 1108-1113.
- [12] Mohammad Hadiana, Mahdie Hadianb. Comparison of Spiegler–Kedem combined with film theory model and original SK model, *Desalination and Water Treatment* 272(2022)1–5.
- [13] Kurniawan, TA; Sillanpää, M. Nano adsorbents for remediation of aquatic environment: Local and practical solutions for global water pollution problems. *Crit. Rev. Environ. Sci. Technol.* 2012, 42, 1233–1295. [[CrossRef](#)]
- [14] Liang, X.; Kurniawan, T.A.; Goh, H.H.; Zhang, D.; Dai, W.; Liu, H.; Goh, K.C.; Othman, M.H.D. Conversion of landfilled waste-to-electricity (WTE) for energy efficiency improvement in Shenzhen (China): A strategy to contribute to resource recovery of unused methane for generating renewable energy on-site. *J. Clean. Prod.* 2022, 369, 133078. [[CrossRef](#)]
- [15] Madloul, J. J., "Water Treatment of Main Outfall Drain for Injection in Nasiriyah Oil Field". 2014. M.Sc. thesis, Baghdad University.
- [16] Dach, H., "Comparison of Nanofiltration and Reverse Osmosis Processes for a Selective Desalination of Brackish Water Feeds". 2008. Ph.D. thesis, University of Angers.
- [17] Ahmed Faiq Al-Alawy and Miqat Hasan Salih. Experimental Study and Mathematical Modelling of Zinc Removal by Reverse Osmosis Membranes, *Iraqi Journal of Chemical and Petroleum Engineering*, September (2016). Vol.17 No.3. 57- 73.
- [18] Nouredine Zouhria, Fatima Zahra Addar, Mustapha Tahaikt, Mahacine Elamrani, Azzedine ELmidaoui, Mohamed Taky. Techno-economic study and optimization of the performance of nanofiltration and reverse osmosis membranes in reducing the salinity of M'rirt water city (Morocco). *Desalination and Water Treatment* 317 (2024) 100042.
- [19] Bird, R.B., Stewart, W.E., Lightfoot, E.N., (2002). *Transport Phenomena*. Book 2nd ed., John Wiley & Sons, Inc.: New York.
- [20] Lee, S., Amy, G., Cho, J., Applicability of Sherwood Correlations for Natural Organic Matter (NOM) Transport in Nanofiltration (NF) Membranes. *Journal of Membrane Science*, (2004). 240 49-65.
- [21] Hajarar, R. A., The use of Nanofiltration Membrane in Desalinating Brackish Water. Ph.D. Thesis, School of Chemical Engineering and Analytical Science, University of Manchester (2010).

- [22] Desai, K. R., Murthy, Z.V.P., Removal of Ag (I) and Cr (VI) by Complexation Ultrafiltration and Characterization of the Membrane by CFSK Model. *Separation Science and Technology*, (2014). 49 2620–2629.
- [23] Chaudhari, L.B., Murthy, Z.V.P., Application of Nanofiltration for the Rejection of Nickel ions from Aqueous Solutions and Estimation of Membrane Transport Parameters. *Journal of Hazardous Materials*, (2008). 160(1) 70–77.
- [24] Kedem, O., K. Spiegler, Thermodynamics of Hyperfiltration (Reverse Osmosis): Criteria for Efficient Membrane. *Desalination*, (1966). 1 311-326.
- [25] Murthy, Z.V.P., Chaudhari, L.B., Separation of Binary Heavy Metals from Aqueous Solutions by Nanofiltration and Characterization of the Membrane using Spiegler–Kedem Model. *Chemical Engineering Journal*, (2009). 150 181–187.
- [26] Vaidya, S.Y., Simaria, A.V., Murthy, Z.V.P., Reverse osmosis transport models evaluation: A new approach. *Indian Journal of Chemical Technology*, (2001). 8 335-343.
- [27] Hassani, A.H., Mirzayee, R., Nasser, S., Borghei, M., Gholami, M., Torabifar, B., Nanofiltration Process on Dye Removal from Simulated Textile Waste Water. *Environmental Science Technology*, 2008, 5(3) 401-408.
- [28] Xu J., Xu Z-L., Poly (vinyl chloride) (PVC) hollow fiber ultrafiltration membranes prepared from PVC/additives/solvent. *Journal of Membrane Science*, 2002, 208 203-211.
- [29] Abu Qdais, H., and Moussa, H., Removal of Heavy Metals from Wastewater by Membrane Processes: A Comparative Study, *Desalination*, 2004, Vol. 164, PP. 105-110.
- [30] Bera, A., Trivedi, J. S., Kumar, S. B., Chandel, A. K. S., Halder, S., and Jewrajka, S. K. Anti-organic fouling and anti-biofouling poly(piperazine amide) thin film nanocomposite membranes for low-pressure removal of heavy metal ions. *J. Hazard. Mater.* (2018). 343, 86–97. ISSN 0304-3894. doi:10.1016/j.jhazmat.2017.09.016.
- [31] Vercus Lumami Kapepula, and Patricia Luis. Removal of heavy metals from wastewater using reverse osmosis. *Frontiers in Chemical Engineering*. 2024. 10.3389/fceng.1334816.
- [32] Gao Jie, "Nanofiltration membrane for Lead removal, "A thesis of MSc. engineering National- University of Singapore, (2014).
- [33] Ebrahim Shahlai Esmail, Mohammed Thamer J., Oleiwi Hasanain Owaid. Removal of Acid Blue Dye from Industrial Wastewater by using Reverse Osmosis Technology. *Association of Arab Universities Journal of Engineering Sciences*, (2018). NO.3. Volume. 25.
- [34] Al-Musawi, T.J., (2012). Multicomponent Biosorption of Heavy Metals Using Fluidized Algal Biomass Bed. Ph.D. Thesis, University of Baghdad, College of Engineering, Environmental Engineering Department.
- [35] Al-Zoubi, H., Hilal, N., Darwish, N.A., Mohammad, A.W., (2007). Rejection and Modeling of Sulphate and Potassium Salts by Nanofiltration Membranes: Neural Network and Spiegler –Kedem Model. *Desalination*, 206 42– 60.
- [36] Soltanieh, M., Gill, W.N., (1981). Review of Reverse Osmosis Membranes and Transport Models. *Chem. Eng. Commun*, 12 279- 363.
- [37] Baker, R. W. "Membrane Technology and Applications", 2nd P P ed.; John Wiley & Sons, Ltd.: Chichester,(2004).