Removal of Heavy Metals from Industrial Wastewater by Using RO Membrane

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Abstract
Industrial wastewater containing nickel, lead, and copper can be produced by many industries. The reverse osmosis (RO) membrane technologies are very efficient for the treatment of industrial wastewater containing nickel, lead, and copper ions to reduce water consumption and preserving the environment. Synthetic industrial wastewater samples containing Ni(II), Pb(II), and Cu(II) ions at various concentrations (50 to 200 ppm), pressures (1 to 4 bar), temperatures (10 to 40 °C), pH (2 to 5.5), and flow rates (10 to 40 L/hr), were prepared and subjected to treatment by RO system in the laboratory. The results showed that high removal efficiency of the heavy metals could be achieved by RO process (98.5%, 97.5% and 96% for Ni(II), Pb(II) and Cu(II) ions respectively). The permeate flux for all H.M ions was ranged between (10 to 56 L/m².hr). The low level of the heavy metals concentration in the permeate implies that water with good quality could be reclaimed for further reuse. The RO membrane is characterized by very high efficiency as the H.M. ions removal of up to (97%) with good productivity and medium pressure that means a medium cost of the RO system.

Introduction
Decreased water resources and increased uses have required a worldwide campaign for innovative water management practices. The use of effective technologies, such as membranes, for wastewater treatment containing heavy metals ions will allow the implementation of water recycling systems in industrial facilities [1], as well as reduce harming the environment. As a result, wastewater discharge cost and freshwater supply payments will decrease, and reduce environmental risks. The World Health Organization (WHO) has identified heavy metals allowed for drinking water, as well as the appropriate levels for agriculture and soil and marine and other district level [2].

Table 1 shows the minerals that can be contained in industrial water, and the highest allowable limit for drinking water, according to the World Health Organization. For removal of heavy metals from wastewater, wide types of water treatment techniques are available such as adsorption, electrodialysis, complexation-ultrafiltration process,
reverse osmosis, and nanofiltration system.

The selection of a particular treatment depends on a number of factors, for example, waste type, contaminant concentration, level of cleanup required and economics. Use of most techniques (except reverse osmosis and nanofiltration), can be practical and cost-effective only with concentrated wastewater (contain high concentration of heavy metal ions), but they will be ineffective when applied to low concentration wastewater that contain heavy ions less than 100 ppm, while there are techniques to be effective in the removal of low concentrations of metals ions only, and be inefficient with high concentrations. As for reverse osmosis system, it is effective in all concentrations even the very low values. Many natural and synthetic adsorbents can effectively remove dissolved heavy metals; most of them show some disadvantages such as poor adsorption capacity, a low efficiency, cost ratio, and ineffectiveness at high metal concentration [3].

In this research the reverse osmosis processes because of its many advantages such as high efficient, low cost, simple operation, and work with any feed concentration.

Three metal ions were selected for a search (nickel, lead, and copper) ions, as they represent different industries and scattered, with different parameters; concentration, pressure, temperature, pH, and flow rate, the values of parameters were chosen as the most appropriate for operating conditions that achieve less cost and best production.

<table>
<thead>
<tr>
<th>H.M</th>
<th>#level of H.M./ppm</th>
<th>Uses</th>
<th>Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.01</td>
<td>Building construction</td>
<td>Negatively influence Plant growth [5].</td>
</tr>
<tr>
<td>Cu</td>
<td>0.1</td>
<td>used as a conductor of heat and electricity, building material, Tharanitharan Venkatesan, 2014 Various alloys [6].</td>
<td>This toxicity is possibly due to redox cycling and the generation of reactive oxygen species that damage DNA [7].</td>
</tr>
<tr>
<td>Fe</td>
<td>0.3</td>
<td>Found in most industries that use equipment and iron pipes plating shops, wire drawing operations steel mills, and chemical milling [4].</td>
<td>Osteoporosis, Liver Cirrhosis Cardiomyopathy Arrhythmia Heart Failure Heart Attack, Hypothyroidism, Hypopituitarism, Adrenal Gland Neurodegeneration [7].</td>
</tr>
<tr>
<td>Ni</td>
<td>0.02</td>
<td>Used to manufacture stainless steel, non-ferrous alloys, batteries, electronics, and aerospace applications [8].</td>
<td>With immoderate amounts, can become toxic. Cause liver damage, decreased body weight, heart, and skin agitation [9].</td>
</tr>
<tr>
<td>Zn</td>
<td>3</td>
<td>Used for galvanizing iron, more than 50% of metallic zinc goes into galvanizing steel, also in the preparation of certain alloys, building construction, roofing and gutters, the negative plates in some electric batteries [10].</td>
<td>Zinc increase in the blood leads to a sense of bitterness or bitterness mouth food generally, vomiting, nausea and stomach pain, and these symptoms are similar to symptoms of poisoning [10].</td>
</tr>
<tr>
<td>Hg</td>
<td>0.002</td>
<td>Used in equipment (e.g. switches, gauges, thermometers, manometer) and in chemicals (e.g. Phenyl mercuric acetate, caustic soda [11].</td>
<td>Effects on the nervous, digestive and immune systems, and on lungs, kidneys, skin and eyes [12].</td>
</tr>
<tr>
<td>As</td>
<td>0.01</td>
<td>Used in paints, dyes, soaps, metals, and semiconductors, mining, Agriculture, also as wood preservative [1].</td>
<td>Cause skin damage or problems with circulatory system, and an increased risk of getting cancer [6].</td>
</tr>
</tbody>
</table>
Removal Processes of Heavy Metals

There are many processes for removing heavy metals ions from wastewater like chemical precipitation, coagulation-flocculation, adsorption, ion-exchange, electro dialysis and membranes system [13].

These processes aim to reduce the amount and proportion of metals to the allowable limit and what is not a danger to health or the environment [14].

Reverse Osmosis Process

Reverse Osmosis membrane needs pressure. The aim of RO membrane to separate the H.M. ions, salts and other contents from water using a selective membrane. The membrane is designed to allow water to pass through while retaining solutes. When the feed water is pressurized, pure water passes through the membrane into the permeate stream. The pressure of feed water depends of contents of water whenever a large concentration of water inside, need greater pressure. The concentrate water that does not permeate the membrane leaves the system as reject. RO system block diagram is shown in Figure 1.

In order to understand the mechanism of reverse osmosis process natural osmosis mechanism must be understood. Osmosis is a special kind of diffusion; the diffusion of water molecules across a permeable membrane from low solute concentration to high solute concentration like the plant absorbs the water from the soil by its root.

Figure 2 shows that using a semi-permeable membrane to divide the container into two parts, full one part with a high salt concentration, will see the water begin transfer across the membrane from lower salt concentration towards the water container with the higher salt concentration, then the rate of water flow will gradually reduce to a final stop when concentration on both sides became almost equal and the system be in equilibrium [16].

Whereas osmosis occurs naturally without pressure applied required, when reverse the process of osmosis need to apply pressure to the system. That’s mean reverse osmosis process, is osmosis process in reverse. Figure 3 shows the process of reverse osmosis.
Advantages heavy metals removal by using of Reverse Osmosis includes [15]:

- Operating costs are medium.
- Energy costs are medium.
- Hard water softening.
- Remove salts and other ions in a large percent.
- Remove the heavy metals in a large percent.
- No chemicals addition.
- The value of pH does not change much.
- No phase change.
- Simple equipment.
- Effective in all concentrations even the very few.

**Experimental Work**

In this work, three types of H.M. solutions [Ni(II), Cu(II) and pb(II)] had been selected. Table 2 shows the H.M. ions and its specifications. The specification of RO membrane cells had been used shows in Table 3.

Table 2: specifications of H.M. ions

<table>
<thead>
<tr>
<th>H.M. ion</th>
<th>M.wt (g/mol)</th>
<th>Density g/cm³</th>
<th>Solubility in water (molal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(II) NiSO₄·6H₂O</td>
<td>262.58</td>
<td>1.948</td>
<td>77.5 at 30°C</td>
</tr>
<tr>
<td>Pb(II) Pb(NO₃)₂</td>
<td>331.21</td>
<td>4.53</td>
<td>52 at 20°C</td>
</tr>
<tr>
<td>Cu(II) CuSO₄·5H₂O</td>
<td>249.7</td>
<td>2.286</td>
<td>1.502 at 30°C</td>
</tr>
</tbody>
</table>

Table 3: specification of RO membrane cells

<table>
<thead>
<tr>
<th>Type of membrane</th>
<th>RO membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material module</td>
<td>spiral wound</td>
</tr>
<tr>
<td>Size (ID, length), mm</td>
<td>100x1000</td>
</tr>
<tr>
<td>Activated area, m²</td>
<td>7.9</td>
</tr>
<tr>
<td>Maximum operating temperature, °C</td>
<td>45</td>
</tr>
<tr>
<td>Maximum applied pressure, bar</td>
<td>5.5</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>FILMTEC company</td>
</tr>
<tr>
<td>Feed water pH range</td>
<td>2-10</td>
</tr>
<tr>
<td>Maximum feed water turbidity</td>
<td>1.0</td>
</tr>
<tr>
<td>Maximum feed flow SDI (15 min)</td>
<td>5</td>
</tr>
</tbody>
</table>

**Experimental Procedure**

Three types of heavy metals were used, with five different parameters. For every test the feed must be prepared first by dissolving the required quantity of heavy metal in pure water with required parameters and the feed tank was filled with in. Water from the feed tank was pumped it with different pressures, where change the pressure through the gradual closing of the valve of reject water (it should not be closed completely). The reading of feed water pressure gauge (before entering to membrane cell) to get the pressure required for each operation. Figure 4 shows the schematic diagram of the RO process.

To obtain the required feed flow rate it must controlled by the valve after the pump and before entering the membrane.

The pure water was used in the process for the purpose of measuring the flux coefficient and for cleaning before and after every test.

After water preparation according to the required specifications and regulating the pressure, flow rate and other parameters as stated, the system was to operate for at least 3 minutes to reach steady state. In the meantime the permeate and rejected water return to the feed tank for the purpose of maintaining the water concentration. After that time permeate water was collected in flask to test the amount of heavy metals to calculate the membrane rejection and determine the permeate flow rate to calculate the membrane flux.
Results and Discussion

1. Steady State Time

Figure 5, shows the change of removal ratio of Ni(II) ion, with time, until steady state is reached. Initially the removal starts from 30%, 45%, 48%, and 50%. Then the removal begin to increase significantly till it was fixed at 98.5%, 98.2%, 97.5%, and 97.2% after 30 minutes for Ni(II) ion concentrations 50 ppm, 100 ppm, 150 ppm, and 200 ppm respectively.

Dow Company reported that the steady state time for reverse osmosis membrane is 45 to 60 minutes [17].

Figure 6 shows effect of time on permeate flux of Ni(II) ion. The permeate flux increase from 8 and 10 L/m².hr. It has taken 30 minutes to reach to study state at 42.5, and 40.5 L/m².hr for pure water and Ni(II) ion concentrate 200 ppm respectively. That means every change in cross flow velocity; the process needs a few minutes to reach steady state.

This period was necessary to obtain the stabilization of the polarization layer after changing the cross flow velocity. As a result, the removal and permeate flux reached a steady value after a few minutes [18].
2. Effect of Operating Parameters on Removal Percentage

2.1. Effect of the Feed Concentration

The feed concentrations (50, 100, 150, 200 ppm) are chosen for all metals because almost these concentrations are present in most of the industrial wastewater and that the removal process is influenced by variables more high concentrations.

Figure 7 shows the increase in concentration for all H.M leads to decrease of removal percentage, with fixing all other parameters (pressure 3 bar, pH 5.5, feed flow rate 30 L/h, and temperature 30 °C). At 50 ppm concentration of heavy metals, the percentage of removal was 98.5%, 97.5% and 96.1% for Nickel (II), Lead (II) and Copper (II) respectively. And at 200 ppm concentration of heavy metals, the removal decreased to 97.2%, 96.1% and 94.2 for Nickel (II), Lead (II) and Copper (II) respectively.

Figure 8 shows the effect of the concentration on flux of RO, where increase in the concentration for all H.M led to little decreasing in flux. Initial value of permeate flux was 42.5 L/m².hr, decrease to 40.5, 40.3, 40.6 L/m².hr at concentration 200 ppm for Ni(II), pb(II) and Cu(II), respectively.

These decreasing in removal and permeate flux for RO system because the increasing in feed concentration leads to turbulence in flow at boundary layer. This leads to obstruction in the pass of the ions across the pores, causing to decrease the removal and flux [19]. There is another explanation that the increasing in feed concentration leads to increase in the concentration of the negatively charged ions at the membrane surface, resulting in increasing shield of negatively charged membrane. This results lead to reduce the repulsion forces on the positively charged ions and thus decreasing removal and flux.

Kai Yu Wang, 2007, reported the removals and permeates flux of polybenzimidazole (PBI) nanofiltration hollow fiber membrane to CuSO₄ decrease with an increasing in metal ion concentration [20].

Fig. 7: Effect of Concentration on H.M. ions removal for RO (Pressure=3 bar, Temperature=30 °C, pH=5.5, Feed flow rate =30 L/hr)

Fig. 8: effect of Conc. on permeate flux for RO (Pressure=3 bar, Temperature=30 °C, pH=5.5, Feed flow rate=30 L/hr)

2.2. Effect of Pressure

Pressure is very important parameter to operate the RO membrane, the membrane system have certain pressure difference depending on the type of material that must be removed.

Figure 9 shows the effect of pressure on the removal of Nickel (II), Lead (II), and Copper (II) ions for RO system, the initial concentration was fixed as 100 mg/L, and initial pH was adjusted at 5.5, feed flow rate was 30 L/h, and temperature was 30 °C. From this figure it can be seen that the removal of metals increase from 92%,
93% and 91.4 % of Ni(II), Pb(II) and Cu(II) respectively at 1 bar, to 98.4%, 97.1% and 95.4 % of Ni(II), Pb(II) and Cu(II), respectively at 4 bar. This behavior was because that membrane incompletely prevents dissolving H.M. ions in feed water, therefore some H.M. passage through the membrane are present. When feed pressure is increased, these H.M. ions passage is increasingly overcome as water is pumped through the membrane at a high rate than H.M. can be transported. The increasing in the curve which represents the removal percentages will stop at certain limit even when increasing the pressure.

As was mentioned earlier these results are in agreement with the finding of Gao Jie 2014 [21]. The effect of pressure on permeate flux is Great influence significantly.

Figure 10 show that permeate flux increase linearly from 13, 11.5 and 12.5 L/m²·hr at 1 bar, to 56, 52 and 54.5 L/m²·hr at 4 bar, for Ni(II), Pb(II) and Cu(II), with constant other parameters (concentration 100 mg/L, temperature 30 °C pH 5.5, and feed flow rate 30 L/h).

These results agree with Dow-filmtec membranes manufacturer company (2012), were it was reported that the increasing in feed pressure, due to increase the removal of salts and heavy metals and the permeate flux will increase also, with other parameters constant.

2.3. Effect of Temperature

The effect of temperature on Nickel (II), Lead (II) and Copper (II), removal from aqueous solution by reverse osmosis system was studied by varying the temperature between 10 to 40 °C. The results are shown in Figure 11.

Figure shows the removal of Nickel (II), Lead (II) and Copper (II) ions as function of the temperature. The initial concentration was fixed as 100 mg/L, and initial pH was adjusted at 5.5. It can be seen that the removal percentage increased with increasing in temperature for all heavy metals. Nickel has the highest rate of removal then lead and finally copper. It also shows that these increasing has stopped after 30 °C and started to decrease. This is due to that membrane perfect work is at range of temperature from 20 to 30 °C and its material building at these conditions. Any increasing in temperature in these range leads to an imbalance in the membrane and to the expansion of the pores which allowing the transit of a large amount of ions to the product, which reduces the efficiency of the removal process. Finally the large increase in temperature (more than 30 °C) leads to decrease in the H.M. removal, because high temperatures lead to a change in the material membrane and holes expansion allowing the entry of minerals and salts.
dramatically with pure water evenly lower membrane efficiency and less removal process, then the large increase in temperature leads to membrane damage [22].

These results are in a good agreement with those obtained for Dow-filmtec membranes manufacturer company (2006), which reported, that the removal of heavy metals and the permeate flux; will increase, when the temperature increases.

Figure 12, shows the effect of temperature on permeate flux for RO membrane, the values of permeate will increase clearly and large from 16, 14 and 15.6 L/m².hr at 10 °C, to 55, 52 and 53 L/m².hr at 40 °C, for Ni(II), Pb(II) and Cu(II) respectively.

2.4. Effect of pH

Figure 13 shows that removal of heavy metals for RO system increases from 96.5%, 96.3% and 91.2% to values 98.2%, 97% and 95.3% for Ni(II), Pb(II) and Cu(II) ions respectively when the feed pH increases from 2 to 5.5.

Figure 14 shows that the highest value of permeate flux is 42, 41 and 41.5 L/m².hr when the value of the pH between is (5-6) for RO membrane, and that it starts to decrease slightly with decrease in the value of the pH until it reached to 41, 40 and 40 L/m².hr at pH 2 value for Ni(II), Pb(II) and Cu(II) respectively.

The increase in H.M. ions removal and slightly increase in permeate flux of RO membrane can be attributed to the fact that the membrane is positively charged at pH < 7.0, but the positive charge decreases with increasing pH value, resulting in a low permeate of the anions; therefore in order to maintain the electroneutrality of the permeate solution, the removal of the Ni(II), Pb(II) and Cu(II) ions increases, and also the permeate flux increased [23], [24].

Richards et al. (2011) reported that the removal of nickel ions across RO membrane is dependent on pH. Increasing concentration of sodium sulphate in the feed solution leads to increase the pH of the feed solution. The positive charges force on the membrane will be lower as the pH increases towards the surface of the membrane, this leads to low Nickel removal. GaoJie (2014) reported that the solution pH has slightly influenced the removal of this heavy metal ion if the value of pH is less than 8. The highest removal of Pb(NO₃)₂ was obtained as high as 91.05 %, by using the PEI cross-linked membranes.
and 92% at feed flow rate 10 L/hr, it increased to 98.4%, 98.2% and 95.9% at feed flow rate 40 L/hr for nickel (II), lead (II) and copper (II) respectively.

Figure 16, shows the effect of increasing of feed flow rate on permeates flux for all metals. The permeate fluxes are 33, 32 and 32.5 L/m²/hr at feed flow rate 10 L/hr, it increase to 44, 42.5 and 43.5 L/m²/hr at feed flow rate 40 L/hr for nickel (II), lead (II) and copper (II) respectively. From this figure, it was noted that increasing the feed flow rate prevents the concentration buildup in the solution at the vicinity of the membrane surface, and results in increasing of driving force. The greater shear generated at the surface due to a higher turbulence in membrane enhanced the rate of back-transport of polarized solute into the bulk of the solution, this could be a major reason for the decrease of permeate concentration [25].

The increase in the feed flow rate reduces concentration polarization value due to increase in turbulence near the membrane resulting in decreasing in the boundary layer thickness and solute concentration [26], [27], [28].

These results are in close agreement with J. Fernandez, (2010), who that the permeate flow will increase with increase in the feed flow rate or the cross flow velocity. When cross flow velocity is 0.2 cm/s, the permeate flux is 0.80 x 10⁻⁶ m³/s·m²; when cross flow velocity changes to 0.7 and 1.7 cm/s, the permeate flux is 1.08 and 1.39 x 10⁻⁶ m³/s·m², respectively. At the end of the run, when velocity returns to the initial value (0.2 cm/s), permeate flux returns to 0.80 x 10⁻⁶ m³/s·m².

2.5. Effect of Feed Flow Rate

Increased feed flow rate leads to increase the flux. Heavy metals are removed to a large extent because of removal of fouling layer from the surface of membrane, provided that is does not exceed a certain extent. This is because exceeding the limit leads to a lack of capacity of the filter membrane and possibly damage to the membrane. This depends on construction and the mechanical strength of the membrane.

Figures 15 shows the increasing of feed flow rate which led to decrease in permeate concentration. For H.M, the removal percentage are 95%, 93%
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Fig. 15: Effect of feed flow rate on flux for RO (concentration= 100 ppm, pressure= 3 bar, Temperature = 30 °C, pH=5.5)

Fig. 16: Effect of feed flow rate on flux for RO membrane (concentration=100 ppm, pressure= 3 bar, Temperature=30 °C, and pH=5.5)

Conclusions
From the present work the following conclusions can be drawn:
1. The RO membrane is very efficient to remove heavy metals from industrial wastewater which are produced in many industries.
2. H.M ions removal from industrial wastewater and permeability flux by RO is linearly proportional to applied pressure, pH, solution temperature and feed flow rate, but it is inversely proportional to feed concentration.
3. Less pressure was used for the purpose of removing the H.M. ions from the industrial waste water, which meant less possible cost.

References
27. Barakat M.A. "Removal of Cu (II), Ni (II) and Cr (III) Ions from Wastewater Using Complexation-Ultrafiltration Technique", Journal of Environmental Science and...