Removal of Ni(II), Pb(II), and Cu(II) from Industrial Wastewater by Using NF Membrane

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Abstract
This article reviews the technical applicability of nanofiltration membrane process for the removal of nickel, lead, and copper ions from industrial wastewater.

Synthetic industrial wastewater samples containing Ni(II), Pb(II), and Cu(II) ions at various concentrations (50, 100, 150 and 200 ppm), under different pressures (1, 2, 3 and 4 bar), temperatures (10, 20, 30 and 40 °C), pH (2, 3, 4, 5 and 5.5), and flow rates (1, 2, 3 and 4 L/hr), were prepared and subjected treated by NF systems in the laboratory. Suitable NF membrane was chosen after testing a number of NF membranes (University of Technology-Baghdad), in terms of production and removal. NF system was capable of removing more than (85%, 78%, and 66% for Ni(II), Pb(II), and Cu(II) ions respectively). The permeate flux for all H.M ions for were ranges between (14 to 62 L/m².hr). The results showed that the NF membrane was capable of treating industrial wastewater with any concentration of heavy metals ions and reducing the ion concentration to about (15, 22, and 34 ppm) for Ni(II), Pb(II), and Cu(II) ions respectively. The low level of the heavy metals concentration in the permeate implies that water with good quality could be reclaimed for further reuse. The NF membrane is characterized by efficiently H.M. ions removal medium with high productivity and very low pressure up to 1 bar, which means very little cost for NF system.

Introduction
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 harmful effect of metal content in the returned water to the natural water sources or to land. 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.

Use of most techniques (except nanofiltration and reverse osmosis), 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. There are techniques to them effective in the removal of low concentrations of metals ions only, and be inefficient with high concentrations. As for nanofiltration system, it is effective in all concentrations even the very small ones. Many natural and synthetic adsorbents can effectively remove dissolved heavy metals; most of them show some disadvantages such as poor adsorption capacity, low efficiency, cost ratio, and ineffectiveness at high metal concentration [3].

Nanofiltration membrane processes has been selected because of many advantages of them, as high efficient, low cost, simple operation, and working with any feed concentration.

Nanofiltration (NF) is a cross flow, pressure driven process that is characterized by a membrane pore size corresponding to molecular weight cutoff of approximately 200 –1000 Dalton.

Three metals 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 was chosen the most appropriate for operating conditions that achieve less cost and best make 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, Lead acid – battery Bullets.</td>
<td>Negatively influence Plant growth.</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.</td>
<td>This toxicity possibly due to redox cycling and the generation of reactive oxygen species that damage DNA.</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.</td>
<td>Osteoporosis, Liver Cirrhosis Cardiomyopathy Arrhythmia Heart Failure Heart Attack-Hypothyroidism, Hypopituitarism -Adrenal Gland, Neurodegeneration.</td>
</tr>
<tr>
<td>Ni</td>
<td>0.02</td>
<td>Used to manufacture stainless steel, non-ferrous alloys, batteries, electronics, and aerospace applications.</td>
<td>With immoderate amounts, can become toxic. Cause liver damage, decreased body weight, heart, and skin agitation.</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.</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.</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.</td>
<td>Effects on the nervous, digestive and immune systems, and on lungs, kidneys, skin and eyes.</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.</td>
<td>Cause skin damage or problems with circulatory system, and an increased risk of getting cancer.</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, flotation, adsorption, ion-exchange, electrodialysis and membranes system [5].

These processes aim to reduce the amount and proportion of metals to the allowable limit which is not a danger to health or the environment [6].

Nanofiltration Process

Nanofiltration (NF) is a pressure driven membrane process. Hydraulic pressure is used to overcome the feed solution’s osmotic pressure and to induce diffusion of pure water (referred to as permeate) through a semi-permeable NF membrane. The residual feed stream (referred to concentrate, or reject) is concentrated by the process, and depending on water quality, may be suitable for further water recovery in additional downstream unit processes; otherwise, the residual stream requires disposal. NF is designed to achieve removal of divalent and multivalent ions (e.g., calcium, magnesium, sulfate, iron, arsenic, etc.), and is occasionally referred to as membrane softening. NF may achieve moderate to low removal of monovalent ions (e.g., sodium, potassium, chloride). NF is commonly employed to remove hardness from brackish groundwater to produce potable water. Water characterized by high concentrations of calcium or magnesium and monovalent salts may be treated with NF prior to a reverse osmosis, therefore NF is used in drinking water purification system, also in many industrial processes to remove heavy metals and coloring agents. NF seems to be very interesting in view of the high permeate capacity with a low or medium system pressure. Another factor is the matter passage; i.e. the content of solid matter in the concentrate is much lower than in the reverse osmosis. This also reduces the costs for disposal of the residues either on site or externally [7].

Advantages heavy metals removal by using of nanofiltration includes:

- Low operating costs
- Low energy costs
- Hard water softening
- Reduction of heavy metals
- No chemicals addition
- The value of pH after nanofiltration Innocuous.
- No phase change
- Simple equipment
- Effective in all concentrations even small ones.

1. NF Membranes Models

There are many models of NF membrane like spiral wound, disc and tubular. These models are shown in Figures 1, 2 and 3, respectively.

![Fig. 1: NF membrane, spiral wound module [8]](image1)

![Fig. 2: NF membrane, Disc module [8]](image2)
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The most difference between spiral wound, disc and tubular modules is the component density which is clearly highest in the spiral wound modules, that leads to less investment and operation cost [9].

2. Transport Mechanism for NF Membranes

NF process is relatively simple in design. It consists of a feed water source; feed pretreatment, high pressure pump, NF membrane. A schematic of the NF process is shown in Figure 4. This figure show three streams of the NF membrane process, the feed; the product stream called permeate, and the concentrated feed stream, called the concentrated or retentive. The water flow through the membrane is reported in terms of water Flux.

There are four types of Transport mechanism of membranes:
1- Bulk flow through membrane pores.
2- Diffusion through membrane pores.
3- Restricted diffusion through membranes pores.
4- Solution-diffusion through dense membranes.

The transport mechanism type depends on membrane type. The three first types suitable for MF, and UF membranes (microporous membranes), while the (Solution-diffusion), used for RO membrane because it is dense membrane. The behavior of NF membrane is between microporous and dense membrane.

Experimental Work

Ni(II), Cu(II) and pb(II) had been selected in this work. For every test a feed must be prepared firstly by dissolving the required quantity of heavy metal in pure water with required parameters (concentration, pressure, temperature, pH, and feed flow rate), and introduce it to the feed tank. The feed water is pumped from the feed tank and pumping it with different pressures. The change in pressure is done through the gradual closing of the valve of reject water (it should not be closed completely), with reading the feed water pressure gauge (before entering to membrane cell) to
get the pressure required for each operation.
For obtaining the required feed flow rate control valve is used after the pump and before membrane. The physical and chemical properties of Ni(II), Cu(II) and Pb(II) are listed in Table 1.

Table 1: Physical and chemical properties of H.M. [10]

<table>
<thead>
<tr>
<th>H.M. ion</th>
<th>Chemical Formula</th>
<th>M.wt (g/mol)</th>
<th>Density g/cm³</th>
<th>Solubility in water (molal)</th>
<th>Purity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(II)</td>
<td>NiSO₄.6H₂O</td>
<td>262.58</td>
<td>1.948</td>
<td>77.5 at 30°C</td>
<td>99.8</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Pb(NO₃)₂</td>
<td>331.21</td>
<td>4.53</td>
<td>52 at 20°C</td>
<td>99.5</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>CuSO₄.5H₂O</td>
<td>249.7</td>
<td>2.286</td>
<td>1.502 at 30°C</td>
<td>99.8</td>
</tr>
</tbody>
</table>

The chemicals used to adjust the pH and to clean membranes are presented in Table 2:

Table 2: physical and chemical properties of auxiliary chemicals [11]

<table>
<thead>
<tr>
<th>Material</th>
<th>M.wt (g/mol)</th>
<th>Density g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>58.44</td>
<td>2.17</td>
</tr>
<tr>
<td>HCl</td>
<td>36.46</td>
<td>1.18</td>
</tr>
<tr>
<td>NaOH</td>
<td>39.997</td>
<td>2.13</td>
</tr>
</tbody>
</table>

Three types of nanofiltration membrane have been examined (NF1, NF2 and NF3) to choose the suitable membrane. Pure water had been used first, then solution of heavy metals ions. The removal percentage and permeate flux are calculated. The pressure effects on the membrane are also tested.

Table 3 shows the specification of each type of NF membrane. The nanofiltration membrane (NF1) had been selected because of the high efficiency of the production and removal and withstands the high pressure and heat. Figures 5 and 6, show the photographic view of the NF1 membrane and its thickness.

Table 3: specification of nanofiltration membranes*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average pore Diameter</th>
<th>Dope composition (wt %)</th>
<th>Bore fluid composition NMP/water</th>
<th>Coagulation bath temperature (°C)</th>
<th>Extrusion pressure (bar)</th>
<th>Bore fluid flow rate (ml/min)</th>
<th>Air gap length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 NF1</td>
<td>63.0 nm</td>
<td>PPSU/NMP; (29:71)</td>
<td>0/100</td>
<td>36</td>
<td>3</td>
<td>3</td>
<td>3.5</td>
</tr>
<tr>
<td>2 NF2</td>
<td>47.75 nm</td>
<td>PPSU/NMP; (29:71)</td>
<td>0/100</td>
<td>36</td>
<td>1.5</td>
<td>3</td>
<td>3.5</td>
</tr>
<tr>
<td>3 NF3</td>
<td>65.74 nm</td>
<td>PPSU/NMP; (25:75)</td>
<td>0/100</td>
<td>36</td>
<td>2.5</td>
<td>1.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

*According the membrane laboratory (University of technology- Baghdad)

Fig. 5: Photographic view of the NF1 membrane (SEM MAG)

Fig. 6: Photographic view of the NF1 membrane thickness (SEM MAG)
Experimental Procedure
Figure 7 shows the schematic diagram of the NF process. 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 is left to operate for at least 3 minutes to reach steady state (the time required to reach the steady state was early calculated). In the meantime permeate and rejected water return to the feed tank for the purpose of maintaining of 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. Performance of Three Types of NF Membrane for Heavy Metals Percentage Removal and Permeate Flux
Figure 8 shows that the percentage removal of heavy metals at 1 bar were 71.2%, 68%, and 45, while the removal were 85%, 73%, and 35% at 4 bar of NF1, NF2, and NF3 respectively.

Figure 9 shows the differences among three types of NF membranes where the permeate fluxes were 15.5, 6, and 12.5 L/m².hr at 1 bar, while the fluxes were 62, 31, and 49 L/m².hr at 4 bar of NF1, NF2, and NF3 respectively.

Fig. 7: Schematic diagram of the NF process, [4]

Fig. 8: Effect of pressure on removal percentage of Ni(II) at different types of NF membrane (concentration = 100ppm, temperature=30°C, pH=5.5, flow rate=30L/hr)
2. Effect of Different Parameters on Heavy Metal Removal and Permeate Flux for Membrane System

2.1. Effect of the Concentration of Feed
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.

For NF system, the Figure 10 shows that increasing of concentration for Nickel (II), Lead (II), and Copper (II) leads to decrease of removal percentage, with fixed parameters (pressure 3 bar, pH 5.5 and temperature 30 °C); At 50 ppm concentration of heavy metals, the percentage of removal was 73%, 69%, and 54% for Nickel (II), Lead (II), and Copper (II) respectively; and at 200 ppm concentration of heavy metals, the removal decreased to 67%, 61%, and 45% for Nickel (II), Lead (II), and Copper (II) respectively. Figure 11 shows the effect of the concentration on flux, where increasing in the concentration for Nickel (II), Lead (II), and Copper (II) led to decrease in flux. The flux was 15.4 L/m².hr at 50 ppm concentration and it was 14.9 L/m².hr at 200 ppm.

This decrease in removal and flux for NF systems is because the increase in feed concentration leads to turbulence in flow at boundary layer that's leads to obstruction the pass ions across the pores, causing to decrease the removal and flux [12]. There is another explanation: the increasing in feed concentration leads to increase in the concentration of the negatively charged ions at the membrane surface, thus increasing shielding of negatively charged of the membrane. This results leads to reduce the repulsion forces on the positively charged ions and thus decreasing removal and flux [13].
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The flux of polybenzimidazole (PBI) nanofiltration hollow fiber membrane to CuSO₄ decrease with an increasing in metal ion concentration, [12], and with Daniel James Johnson, (2015) who has used NF270 membrane with 1000 mg/L concentration, pressure =4 bar, and pH = 1.5 ± 0.2. They reported the removal of copper ions is 90% at low concentrations, and decreased to 58% at the high concentration, while the removal was 99%, 89%, and 74% for cadmium, manganese, and lead respectively.

2.2. Effect of Pressure
Pressure is a very important parameter to operate the NF membrane. The membrane system has certain pressure difference, depending on the type of material that must be removed.

Figure 12 shows the effect of pressure on the removal of Nickel (II), Lead (II), and Copper (II) ions. The initial concentration was fixed as 100 mg/L, initial pH was adjusted at 5.5, and temperature was 30 ºC. From this figure it can be seen that the removal of metals increased from 71.2% ,67%, and 51 % of Ni(II), pb(II) and Cu(II) respectively at 1 bar, to 85%, 78%, and 66 % of Ni, pb and Cu respectively at 4 bar.

These results may be because the membranes incompletely prevent H.M. ions to be dissolved in feed water, therefore some H.M. passed through the membrane. When feed pressure is increased, these H.M. ions pass increased as water is pumped through the membrane at a high rate than H.M. can be transported. There is a certain limit and point on the curve which represents the increase in removals as pressure is increased.

Figure 13 shows that permeate flux increase linearly nearly from 15.2, 13, and 14 L/m².hr at 1 bar, to 62, 57, and 60 L/m².hr at 4 bar, for Ni(II), pb(II), and Cu(II) with constant parameters (concentration 100 mg/L, temperature 30 ºC, pH 5.5, , and feed flow 30 L/hr).

2.3. Effect of Temperature
Figure 14, shows the effect of temperature on Nickel (II), Lead (II), and Copper (II) removal from aqueous solution by NF system.

The effect of temperature of NF seen in the figure shows that the removal has been 66.5%, 64%, and 49% for Nickel (II), Lead (II), and Copper (II) respectively at 10 ºC, and 72%, 68%, and 51% for Nickel (II), Lead (II), and Copper (II) respectively at 40 ºC.

Figure 15, shows the effect of temperature on permeate flux.
values of permeate also increased clearly from 7, 7.5, and 6.8 L/m².hr at 10°C, to 21, 20, and 21.5 L/m².hr at 40°C, for Ni(II), pb(II), and Cu(II) respectively.

The flux of permeate is increase with temperature increase, because the diffusivity of water increases and its viscosity decreases. The increasing of temperature caused an increase in pore size of the polymeric membrane [14].

The highest value of permeate flux was 15.2, 14.9, and 15 L/m².hr at pH 5.5, and the lowest value was 14.2, 14, and 14.3 L/m².hr at pH 2, for Ni(II), pb(II), and Cu(II) respectively, as it was shown in Figure 17. The increase in removal 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 electro neutrality of the permeate solution, the removal of the Ni(II), pb(II), and Cu(II) ions increases, and the permeate flux increase also, [15], [16].

2.4. Effect of pH
Removal of H.M. (Ni(II), pb(II), and Cu(II)) at different pH (2 – 5.5) is presented in Figure 16. It can be noticed from the figure that the H.M. removal values increased from 54%, 51%, and 34% at pH 2, to 71.2%, 67%, and 51% at pH 5.5 for Ni(II), pb(II), and Cu(II) ions respectively.
Laura A. Richards et al. (2010) reported that the removal of nickel ions across NF membrane is dependent on pH, where increasing the concentration of sodium sulphate in the feed solution lead to increase the pH of the feed solution [17]. 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.

2.5. Effect of Feed Flow Rate

The increase in feed flow rate leads to increase the flux and more removal of heavy metals, because of removal of fouling layer from the surface of membrane, provided that it does not exceed a certain extent because values more than the limit lead to a lack of capacity of the filter membrane and possibly damage the membrane. This depends on construction and the mechanical strength of the membrane.

Figures 18 shows increasing feed flow rate led to decrease in permeate concentration, for H.M across NF membrane. The removal percentage were 71.2%, 67%, and 51% at feed flow rate 1 L/hr, which increased to 73.4%, 69.9%, and 56.5% at feed flow rate 4 L/hr for Nickel (II), Lead (II), and Copper (II) respectively.

Figure 19, shows the effect of increasing of feed flow rate on permeates flux for all metals, the permeate fluxes are 15.2, 15.1, and 15.1 L/m².hr at feed flow rate 1 L/hr. It increased to 41, 39, and 37 L/m².hr at feed flow rate 4 L/hr for Nickel (II), Lead (II), and Copper (II) respectively. 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 [18], [19], [20].

These results are in close agreement with J. Fernandez, (2010), who noticed the permeate flow will increase with increase in the feed flow rate or the cross flow velocity. That is when cross flow velocity is 0.2 cm/s, the permeate flux is $0.80 \times 10^{-6}$ m³/s·m²; and when cross flow velocity changes to 0.7 and 1.7 cm/s, the permeate flux is 1.08 and $1.39 \times 10^{-6}$ 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 $0.80 \times 10^{-6}$ m³/s·m² [21].

Conclusions

The conclusions drawn from this work are:

1. The NF membranes are very efficient to remove heavy metals
from industrial wastewater which produced for many industries.

2. H.M ions removal from industrial wastewater and permeability flux by NF membrane is proportional to applied pressure, pH, solution temperature and feed flow rate, but it is inversely proportional to feed concentration.

**Recommendations for Future Work**
The following recommendations can be helpful for future work:

1. Present work can be extended to study other conditions such as adding some chemical materials that help to extend the life of the membrane.

2. The study of new types of NF membrane for the purpose of improving the efficiency of the membrane in terms of production and removal.

3. This work can be extended to study the removal of other types of pollutants such as organic, inorganic and macroscopic contaminants from industrial waste water by NF membrane.

4. This work can be extended to study a comparative between the RO and NF membranes in terms of energy consumption.

**References**


