The Role of Operating Parameters on the Rejection of Copper in Nanofiltration Process

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Abstract

Copper is one of the important sources of environmental pollution and is non-degradable, and therefore, continues to exist in water. Separation of copper ions from aqueous solutions by membrane technology is shown to be a feasible process to accomplish an effective copper removal over a broad operational range. This paper aims at the effect of operating pressure, pH and TDS on the rejection of copper ion and permeation flux in different feed concentrations by nanofiltration. Experiments were performed with synthetic solution using N90-4040 nanofiltration membrane. Isotherm experiments were carried out. Permeate flux, pH and copper concentration in permeate were measured to determine the membrane characteristics and performance. Experimental results indicated that the rejection of copper ions increases with increasing of operating pressure, pH and TDS of the solution. The rejection efficiency varied from 94% to approximately 99.9% in different operating conditions. In addition, the permeate flux increased with increase in operating pressure in four different feed concentrations. On the other hand, increasing pH and TDS resulted in decline in permeate flux.

Keywords: Nanofiltration, Copper rejection, Membrane process, Permeate flux, Applied pressure

1. Introduction

Copper is frequently found in environment, especially water, at significant quantities. To protect the public health, it is necessary to remove copper from water and effluents. Membrane methods have been introduced to recover or remove heavy metals (including copper) from the effluents or water. Nanofiltration (NF), as a membrane method, is one of the promising technologies in retention of medium sized molecules such as inorganic salts [28, 1, 14] and industrial effluents [30]. NF was also used to remove viruses from water [21]. NF is a membrane process based on molecules separation by means of a pressure gradient. Due to the restrictions on molecular weight cut-off (MWCO) ranges (200-1000 g/mol.) and the membrane average pore diameter (2nm), this process occurs in between reverse osmosis and ultrafiltration [23, 18, 10]. The applicability of membrane processes is certainly determined by physio-chemical properties of wastewater [6, 7, 3]. Many studies have been carried out to reduce the initial setup cost and membrane fouling such as optimization of chemical and operational conditions (e.g. pH, recovery ratio and modification of membrane surface), hydrodynamic cleaning with high cross-flow velocity and pretreatment of feed [15, 16, 19, 20, 32]. The application of NF to remove pesticides and other micropollutants was carried out by Berg et al. Their study revealed that at neutral pH values, complete rejection of polar organics is possible with NF [5]. Del Re and Giacomo coupled NF and supercritical water oxidation to remove and destroy toxic micropolluting organic compounds from wastewater. They claimed that such coupling reduces both the investment and the operating costs of removing toxic and dangerous micropollutants present in the wastewater and produces water of high level of purity [11]. Manis et al. showed a copper retention of 96-98% can be achieved by NF, also in case of acidic environment [22]. Chaabane et al. used NF for Cu^{2+} and other heavy metal cations removal in laboratory studies and in industrial practices as well. They studied a removal of copper by a negatively charged microporous NF membrane. The treatment of synthetic solutions and the wastewater of electric cable factory were studied. $CuCl_2$ rejection of about 47-66% depending on transmembrane pressure (1-3 bars) is reported [9]. Tanninen et al. reported 60-95% Cu^{2+} rejection of various flat-sheet NF membranes. The experiments were held in very acidic conditions [29]. Synthetic wastewater treatment containing Cu^{2+} and Cd^{2+} ions by spiral-wound RO and NF membrane modules was investigated by Qdaisa and Moussab. NF rejection of about 82-97% for copper ions was demonstrated depending on the concentration in feed water [26]. The on-site pilot testing of NF at the electro deposition plant was reported to increase the recovery of 99.8% of copper sulfate comparing to 55% recovery with traditional ion exchange [8]. Murthy and Chaudhari investigated the rejection of two different salts of Nickel and Cadmium. Rejection of about 75-98% depending on solution's pH and operating pressure was reported [24].

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In this paper, copper ion rejection by NF membrane is investigated with copper containing synthetic solutions. The effects of operating pressure, pH and TDS on permeate flux and copper removal are studied.

2 Materials and Methods
2.1 Experimental Apparatus
All experiments were carried out on a laboratory-scale membrane apparatus. The pilot is shown schematically in Fig. 1. The feed solution was kept at constant temperature in a tank. In order to supply the driving force of the membrane filtration, gauge pressure was used on the feed side of the membrane. Two cartridge filters (activated carbon and microfilter for fine particles retention) and two flowmeters (for concentrate and permeate flow measurement) were used in membrane filtration unit. The FILMTECTM™ NF90-4040 membrane with 7.6 m^2 nominal active surface area was used in the experiments. The membrane has a wide pH range of 2-12 for service. For the NF90-4040, manufacturer gives the 97% nominal salt rejection, measured at 2000 ppm MgSO$_4$ at 25C° and 4.8 bars.

1. Feed tank
2. Pressure pump
3. Valve
4. Pressure gauge
5. Microfilter (5μ & 1μ)
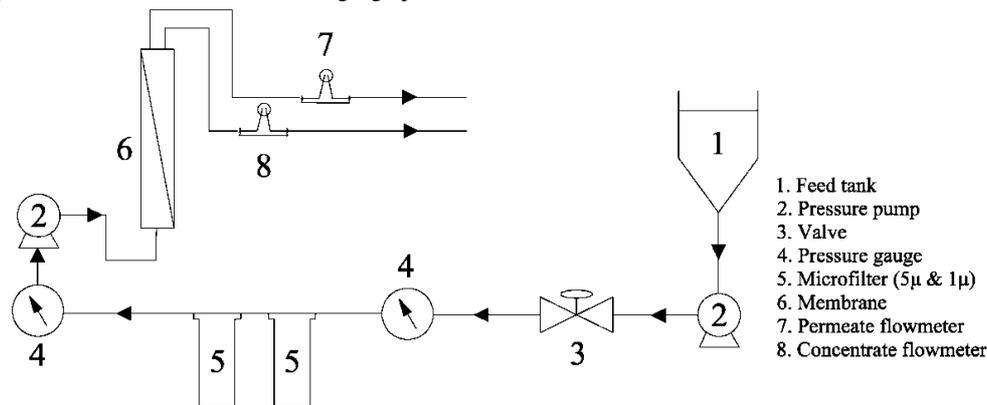6. Membrane
7. Permeate flowmeter
8. Concentrate flowmeter

Fig. 1 Schematic diagram of nanofiltration pilot setup

2.2 Experimental Procedure
Copper rejection was investigated in three different operating conditions. Operating pressures varied (2, 4, 6 bars) in four different feed concentrations (i.e. 20, 60, 100 and 140 mg/L). In addition, copper rejection of NF membrane was experimented in feed concentrations of 20 and 60 mg/L in a broad pH range, between pH 3-11. TDS (Total Dissolved Solids) of the solution was increased by adding sodium chloride (NaCl) up to 2400 mg/L. In order to prevent membrane fouling (especially after feeding high concentrated solution, i.e. 100 and 140 mg/L of copper) CIP (Clean-in-place) method was applied. 4% Citric acid solution (4 Kg of Citric acid in 100 L of water) was circulated in the membrane unit for 30 minutes. Application time for each experiment was 20 minutes. Extra time for each experiment did not raise copper rejection and could lead to membrane fouling.

2.3 Synthetic Wastewater Preparation
Copper sulphate was synthesized in four different concentrations of 20, 60, 100 and 140 mg/L by mixing in tap water. In order to investigate the Total Dissolved Solids (TDS) on copper rejection and permeate flux, sodium chloride was added to the solution to reach the TDS of 800, 1300, 2000 and 2400 mg/L. For evaluating the effect of pH, H2SO4 and NaOH were added to reach the acidic and basic pH of 3 to 11.

2.4 Chemicals and Analyses
Analytical grade CuSO$_4$ was used for the preparation of synthetic solutions. Analytical grade H$_2$SO$_4$ and NaOH were used for pH adjustment. The pH of samples was measured by Horiba pH meter. Aqualytic® copper reagent tablets were used to determine the copper concentration in permeate flow. Samples analysis was carried out by Lovibond® PC Spectro Spectrophotometer. Percentage of rejection was obtained with the following equation:

$$R\% = (1 - \frac{Cp}{Cf}) \times 100 \qquad (1)$$

Where R is the percentage of copper rejection, CP is the concentration of permeate (mg/L) and Cf is the concentration of feed (mg/L).

3 Results and Discussion
3.1 Influence of Applied Pressure
Experiments were carried out to study the effect of pressure ranging from 2 to 6 bars at pH 6.5 for copper rejection. The effect of operating pressure on the copper rejection, permeate concentration and permeate flux at fixed pH are presented in Fig. 2, 3 and 4. As shown in Fig. 2, it can be seen that the rejection performance for copper by NF90 increased as the operating pressure was increased. On the other hand, Fig. 3 shows that copper concentration in permeate decreased as pressure was increased. As Van der Horst et al. mentioned, a high diffusive transport of salts through the membrane compared to convective transport is the reason for low retention at lower pressure. With increasing pressure, convective transport becomes more important and retention will therefore also increase. However,

concentration polarization will also increase with increasing pressure, which results in a decrease in retention. The counteracting contributions of increased convective transport and increased concentration polarization result in a constant retention in higher pressures [31]. The influence of applied pressure on permeate flux is reported in Fig. 4. It can be seen that the permeate flux decreases by the increment of feed concentration in a constant pressure. This decline in flux is due to membrane fouling (which acts as a hindrance to the passage of permeate solute) in high feed concentrations (i.e. 100 and 140 mg/L).
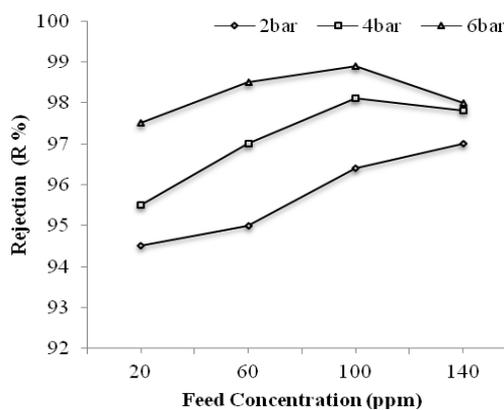

Fig. 2 Influence of applied pressure on the retention of copper in different feed concentrations
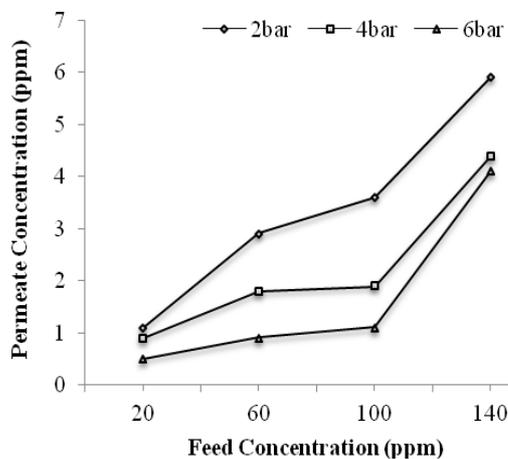

Fig. 3 Influence of applied pressure on the permeate concentration of copper in different feed concentrations

3.2 Effect of pH

The effect of the initial solution's pH on the copper rejection at fixed operating pressure (i.e. 6 bars) and two different feed concentrations of 20 and 60 mg/L are presented in Fig. 5. From the figures, it can be seen that the rejection performance for copper by NF90 increased as the pH was increased. Puasa reported that the polyamide thin-film composite membrane have charge characteristics that influence the separation capabilities, which can be altered by the solution's pH and it was

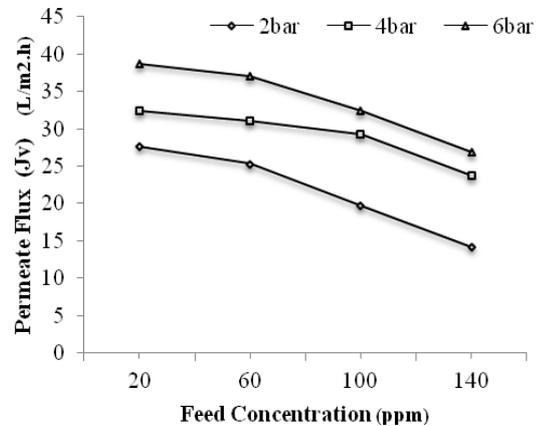reported that the isoelectric point of polyamide membrane is generally between 4 and 5.

Fig. 4 Influence of applied pressure on the permeate flux in different feed concentrations

The occurrence of an isoelectric point means that the membrane is positively charged at lower pH than the isoelectric point and vice-versa. Hence, in the case of polymeric membranes, surface membrane charge is typically negative at high pH values, it increases as the pH decreases and switches to positive values at low pH's [4, 25] Therefore, it is deduced that the trend of copper rejection obtained in this experiment was due to the changes of the membrane structures caused by the solution's pH. Freger et al. reported that at low pH, acidic hydrolysis disrupted the chemical bonds in the membrane polymer matrix.
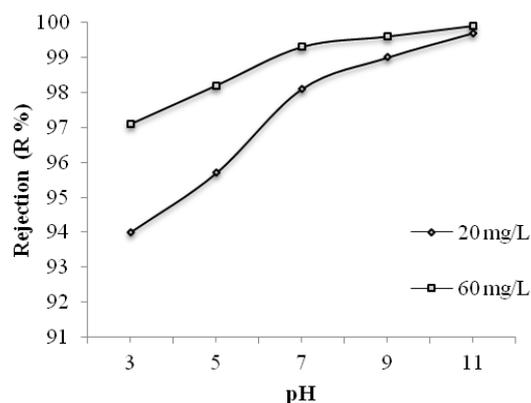

Fig. 5 Effect of pH on the rejection of copper in different feed concentrations

This condition reduced the degree of crosslinking (i.e. rigidity) of the polymer matrix which eventually caused the decrease of rejection. At the same time, acidic hydrolysis also caused the increase of the hydrophilic sites at the membrane (Freger et al., 2005). The increase of hydrophilic sites would cause the increase of permeate flux. On the other hand, the increase of copper rejection at high pH could be caused by the hydration swelling of the membrane skin layer [13]. This could result in

shrinking of membrane pore size, and thus, reduced the permeation of solute through the pores of the membrane. Meanwhile, it is believed that NF90 was rather chemical-resistant as it showed somewhat consistent performance regardless of the solution's pH. There was about 6% of increase in the rejection performance for NF90.

The effect of initial solution's pH on the permeate flux during rejection of copper at fixed operating pressure (i.e. 6 bars) and two different feed concentrations of 20 and 60 mg/L are presented in Fig. 6. As the acidic hydrolysis at low pH or swelling of membrane skin layer at high pH, as explained previously, is believed to be responsible for the increase or decrease in copper rejection. It is expected that the permeate flux would be as much affected by solution's pH as copper rejection performance due to acidic hydrolysis and hydration swelling. However, the effect of solution's pH seemed not to be as much on permeate flux if compared to the degree of changes seen in the rejection performance.
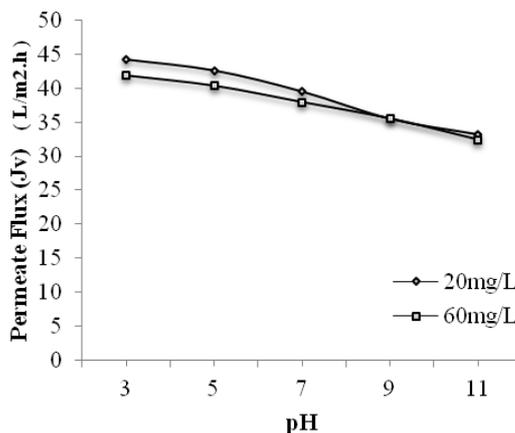

Fig. 6 Effect of pH on the permeate flux in different feed concentrations

3.3 Effect of TDS

Fig. 7 shows the effect of TDS on the rejection of copper by NF90. The experiments were carried out in four different TDS's (i.e. 800, 1300, 2000 and 2400 mg/L) and two different initial copper concentrations (i.e. 20 and 60 mg/L) at a fixed pH and operating pressure of bars. The membrane material, feed concentration and solution's pH are the parameters that can affect the copper rejection in different TDS's. As shown in Fig. 7, increasing the salt concentration resulted in the higher rejection performance of copper. This is due to the concentration polarization layer formed by salt which acts as an additional filter to the passage of the copper ions and concentration polarization layer formed by copper ions on the membrane surface [2]. The effect of TDS on the permeate flux is presented in Fig. 8. This Figure shows that with increasing the TDS permeate flux declines. As mentioned by Koyuncu et al., permeate flux is directly related to the operating and osmotic pressure differences. Osmotic pressure increases with increasing salt concentration that results in the decrease of the permeate flux. Permeate flux decline is due to the low solubility of copper in high salt concentrations which

results in the forming of polarization layer on the membrane that acts as a barrier to the passage of permeate solute [17].
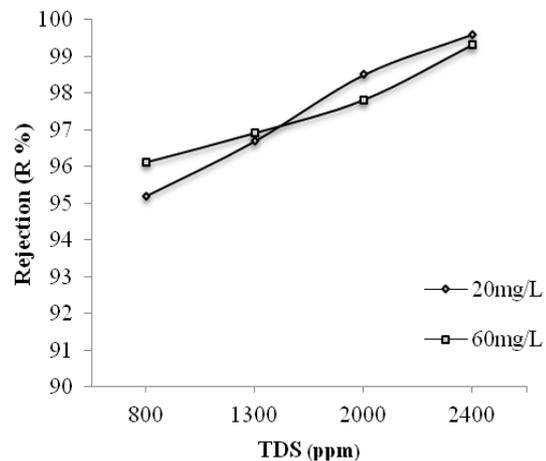

Fig. 7 Effect of TDS on the copper rejection performance in different feed concentrations of 20 and 60 mg/L
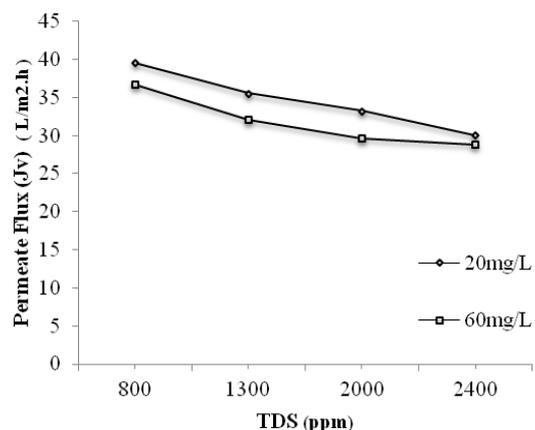

Fig. 8 Effect of TDS on the permeate flux in different feed concentrations of 20 and 60 mg/L

4 Conclusions

Copper ion rejection by means of nanofiltration process in three different operating conditions was studied. The copper rejection was found to be influenced by the applied pressure, solution's pH and TDS. These parameters also affected the permeate flux of the membrane. The rejection was found to be in the range of 94 to 99.9% for different operating conditions.

From the viewpoint of the environmental protection, it seems that under given operating conditions, nanofiltration can be considered as an efficient process to remove heavy metals from water, as illustrated by the experimental results reported in this paper.

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