Study on The Removal of Iron (III) and Chromium (III) from Aqueous Streams Using Inorganic Nanofiltration Membrane.

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Abstract: Iron and chromium are common water pollutants which are frequently encountered together in many industrial wastewaters. This study investigates the influence of operating parameters such as cross-flow velocity, transmembrane pressure (TMP), initial metal concentration and solution pH on the rejection of Fe(III) and Cr(III) from synthetic aqueous streams by inorganic nanofiltration membrane at room temperature. The results show that the rejection is 61-98% and 86-98% for Fe(III) and Cr(III) respectively. The results also show that the increase of the metal concentration in the feed solution decreases the metal rejection, but the increase in TMP increases the metal rejection. The rejection mechanism can be discussed in the light of the effect of pH on the separation of Fe(III) & Cr(III) from water streams. At pH 2.96 and 5.7 for Fe(III) and Cr(III) respectively, water soluble metal hydroxides are formed in the solution. The interaction of these hydroxides with the membrane material leads to a cake layer accumulation on the membrane surface that acts as a new membrane.
This study reflects that the nanofiltrtaion could be a promising technology for the rejection of iron and chromium from the industrial wastewater.

Key words: rejection, ceramic membrane, pH, cake layer, Iron, Chromium.

INTRODUCTION

Although industrialization is considered the cornerstone of the development strategies due to its significant contribution to the economic growth and hence human welfare, however, in most developing countries it led to series of environmental problems. The earnest intentions are now not only targeting the qualitative and quantitative treatment of the industrial wastes but also attempting to avert their hazards to human health and restoring the quality of environment (Abdel-Shafy and Aly, 2002).

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. iron, chromium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources. The pollution sources of these metals in water are the industrial activities, such as automotive industries, metal finishing, electroplating, battery manufacturing, mining, and textile industries which release various concentrations of heavy metals. Iron and chromium are common pollutants which are frequently encountered together in many industrial wastewaters (Silva et al., 2008). Iron, in trace level concentration, is an essential nutrient for living organisms. Deficiencies in this element cause anemia but an excess can be toxic, especially in humans. For example: the accumulation of iron in the brain causes hemochromatosis, which has been associated with diseases such as Parkinson's, Alzheimer's and other genetic disorders (Crichton et al., 2002).

Chemical precipitation (Mirbagheri et al., 2005), ion exchange (Àlvarez-Ayuso et al., 2003), adsorption (Kongsuwan et al., 2009) and flotation processes such as ion flotation, precipitation flotation, and electroflotation etc (Medina et al., 2005; Belkacem et al., 2008; Capponi et al., 2006) are traditional processes for treatment of wastewater that laden with heavy metal.

Although these techniques were employed for heavy metal removal, industries are looking for competing technologies which may overcome some disadvantages of these techniques, like for instance incomplete removal high energy requirements, and production of toxic sludge (Eccles, 1999).

Recently Membrane separation systems such as Ultrafiltration UF, Nanofiltration NF and Reverse Osmosis RO have become important wastewater treatment technologies, facilitating the removal and recovery of pollutants and solvent i.e. water. For separation of heavy metals, membrane treatment is the most promising method to meet the discharge criteria by pollution control board with recovery and recycle.

NF has unique properties between UF and RO. Its separation mechanism involves steric (sieving) and electrical (Donnan) effects. A Donnan potential is created between the charged anions in the NF membrane and the co-ions in

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the effluent to reject the latter (Bruggen and Vandecasteele, 2003). The significance of this membrane lies in its small pores and membrane surface charge, which allows charged solutes smaller than the membrane pores to be rejected along with the bigger neutral solutes and salts.

Specific adsorption, reduced dielectric permittivity and hydration are additional membrane phenomena that may also affect membrane performance. Several commercial NF membranes are currently available and their separation performance is quite different from one another (Tanninen *et al.,* 2006; Wang *et al.,* 2006; Chaabane *et al.,* 2006; Artu and Hapke 2006; Fatin-Rouge *et al.,* 2006).

NF is a promising technology for the rejection of heavy metal ions such as nickel (Murthy and Chaudhari, 2008), zinc (Belkhouche *et al.,* 2009; Frarés *et al.,* 2005), copper (Cséfalvay *et al.,* 2009; Ahmad and Ooi, 2010) arsenic (Nguyen *et al.,* 2009; Figoli 2010) and chromium (Taleb-Ahmed *et al.,* 2002, Wang *et al.,* 2007) from wastewater.

In the present study, recovery of iron and chromium using 1 kDa MWCO nanofiltration membrane would be investigated. The effect of cross-flow velocity, transmembrane pressure, solution pH and metal concentration on permeate flux and metal retention would also be studied.

MATERIALS AND METHODS

2.1. Membrane:

The membrane was a tubular inorganic (ceramic) membrane manufactured by (Rhodia Orelis, Miribel, France) with a 1 kDa MWCO. Membrane module consists of 19 channels in stainless-steel housing. Its active layer was titanium and aluminum oxides supported on ceramic material. Its external diameter was 25 mm, being the total length 1178 mm. The hydraulic diameter of each membrane was 3.5 mm and the total available filtration area was 0.245 m^2.

2.2. Chemicals and Reagents:

All reagents used were of the highest pure grade. Synthetic samples of wastewater are prepared by adding required amounts of Iron (III) chloride hexahydrate, (Riedel-de Häen), Chromium (III) chloride hexahydrate, (Fluka) to Bidistilled water. The feed solutions are prepared with different concentrations of iron chloride and chromium chloride ranged from 0.1 to 2.27mM. The pH of the solutions is adjusted from 2 to 8 for Fe(III) solution, and from 3 to 8 for Cr(III) solution using 2M solution of NaOH and or HCl.

2.3. Apparatus, Experimental Methods and Analysis:

The nanofiltration consisted of a 50 L stainless-steel 316L storage tank, air compressor model HAC200/380 Haggar industrial Egypt, metal teflon-fitted feed pump (diaphragm pump) model P.025, wilden U.S.A, equalizer for adapting the entrance of air to diaphragm pump, cartridge filter, digital flow meter model SITRANS F M MAG 6000L SIEMENS Japan, multi stage centrifugal pump PANDA00.00 HILGE S.A.R.L, Germany (for recirculation of liquid inside membrane module and decreasing the fouling phenomena on the surface of membrane), a tube-in-shell heat exchanger, two pressure transducers (0–10 bar) located at the inlet and outlet of the membrane module, temperature sensor and control panel.

During filtration tests, both permeate and retentate were recycled to the feed tank in order to operate in batch recycle mode at room temperature. The transmembrane pressure was fixed by fitting a pressure valve located in the retentate stream. Permeate was kept at atmospheric pressure. Fig. 1 shows the described experimental set-up. A typical test started by filling up the feed tank with 20 L of solution to be tested. Then, the pump was switched on, transmembrane pressure was set to 1bar and the filtration was started.

About 10 mL samples of permeate were taken and the permeate fluxes were periodically measured during filtration runs. Once the steady state achieved, the transmembrane pressure was changed to a higher pressure. The aforementioned procedure was repeated for transmembrane pressures of 2, 3, 4, and 5 bar. Before and after filtration runs, pure water flux (J_w) was measured at 1, 2, 3, 4, and 5 bar using distilled water in order to know the permeate flux decrease and membrane fouling due to filtration. After that, membrane was cleaned with 10 g/L oxalic acid solution at 50°C for 1 h. Later, the membrane was rinsed with distilled water until assuring a neutral pH in both permeate and retentate. Then, the distilled water flux was measured in order to assure a complete removal of all species deposited over the membrane. Once completely cleaned, the membrane was submerged in distilled water in order to maintain its hydration state.

Metal in the feed and permeate (samples was analyzed by atomic absorption spectrometry (Perkin Elimer, model A analyst 100) in order to determine metal concentration and, subsequently metal rejection. Metal rejections (R) were evaluated from initial feed concentration (C_f) and permeate concentration (C_p) as follows:

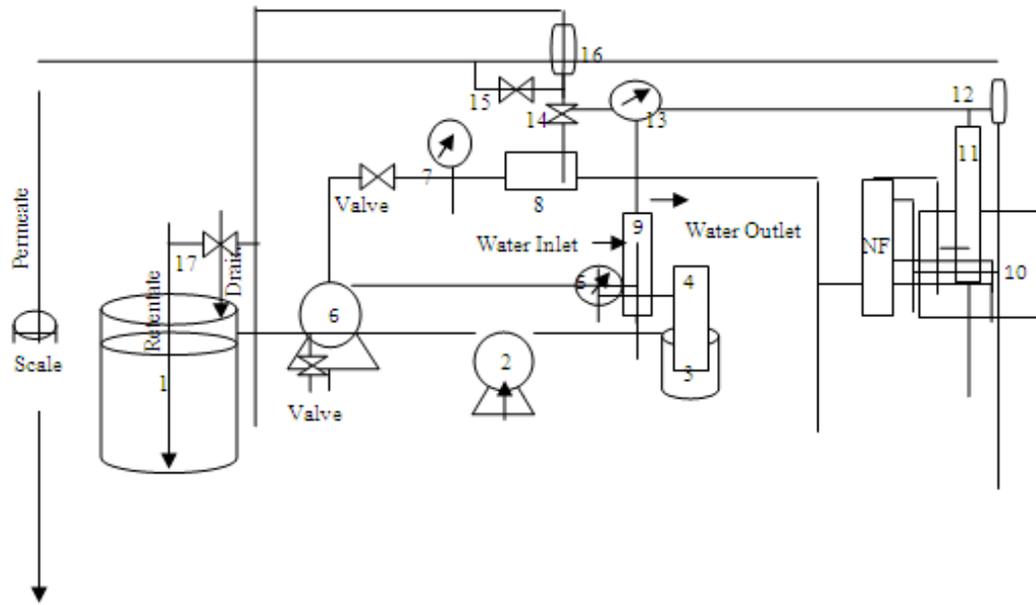$$R\% = 1 - \frac{c_P}{c_F} \times 100 \qquad (1)$$

Fig. 1: Filtration experimental set-up. 1-Feed tank 2-Diaphragm pump 3-Equlizer 4-Certridge filter 5, 7- Pressure gauge 6-Centerifugal pump 8-Digetal flowmeter 9-Heat Exchanger 10-conteral panel 11- Electric Heater 12, 16- Float flowmeter 13-Temerature gauge 14- pressure valve 15, 17-two way valve.

RESULTS AND DISCUSSION

3.1. Water Permeability:

The plot of the pure water permeates flux (J_w) at different TMP values (1-5 bar) is illustrated in Fig. 2. A linear relationship between the pure water flux and applied pressure across the membrane is obtained. The average pure water permeability of the NF membrane is 15.31L/h.m^2.bar at room temperature.
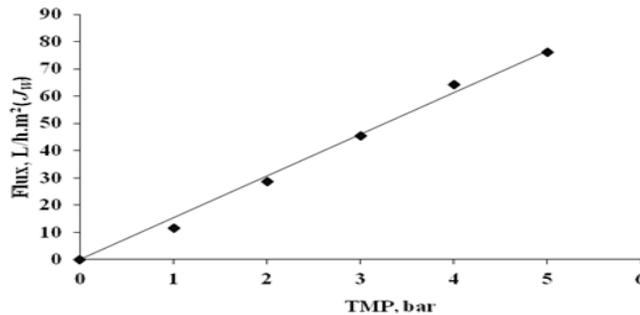
Fig. 2: Water flux change with TMP for NF membrane.

3.2. Effect of cross-flow Velocity:

The relation between the Flux and TMP at different velocities (1, 0.5and 0.27m/sec) is indicated in Fig.3. At velocity= 0.27 m/sec a plateau is obtained when TMP is greater than 2bar, this is due to formation of the cake layer. This layer decreases by increasing the velocity.

At highest cross-flow velocity, 88% of the mass carries by convection to the membrane surface is swept away by the tangential flow. The high shear tangential to the membrane surface sweeps deposited particles away thus the cake layer on the surface of the membrane is reduced (Hamachi and M.-Peuchot, 2002).
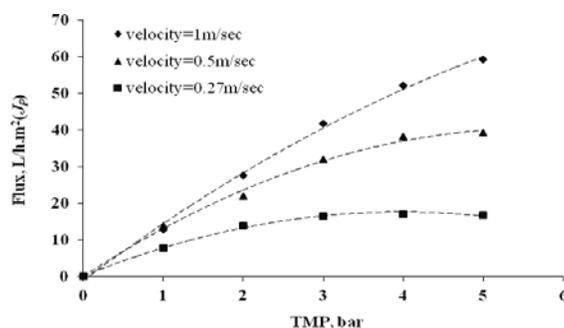
Fig. 3: Flux vs. Pressure at different cross-flow velocity of Fe^{3+}. Fe^{3+}= 0.57mM, pH=2.96.

3.3. Effect of Transmembrane Pressure (TMP):

The behavior of permeate flux (J_P) with the time at different TMP is illustrated in Fig. 4 for Fe(III) and Cr(III) solutions. The figure shows that the J_P rises with TMP and decreases along the time. The flux decline occurred during the first Twenty minutes of filtration after which steady-state is reached beyond this point. Fig. 4 also shows that, on increasing the TMP after the steady-state is achieved, J_P is temporarily increased regardless the experimental conditions. However, as long as the filtration is carried out, J_P decreases again achieving the steady-state. Generally, there is a limiting flux beyond which an increase of pressure does not cause a gain on the J_P. Thus, flux is limited by fouling and a TMP increase is reflecting either on compacting the cake layer and/or increasing its thickness.

The cake layer formation is due to a combination between size exclusion, charge repulsion and adsorption of soluble metal hydroxide species on the membrane surface (Bernat *et al.*, 2009).

The charge of ceramic membrane is a function of the pH. This can be explained by the dissociation equilibrium of the metal oxides forming the membrane (Moritz *et al.*, 2001).When metal oxides are exposed to an aqueous media, the amphoteric surface groups (MOH) may dissociate. Thus, the reactions shown in Eq. (2) and (3) can take place at acidic or basic conditions, respectively.

$$MOH + H^+ \rightarrow MOH_2^+ \leftrightarrow M^+ + H_2O \tag{2}$$

$$MOH + OH^- \rightarrow M(OH)_2^- \leftrightarrow MO^- + H_2O \tag{3}$$
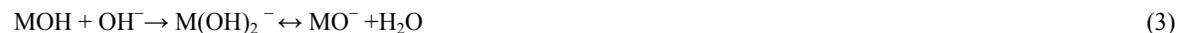
As it can be deduced from Eq. (2) and (3), the dissociation of MOH surface groups is strongly related to the pH in the vicinity of the membrane surface. In addition, if the particles have no charge or when they have the same number of positive and negative charges, the surface charge becomes zero. Out of this discussion we can understand that ceramic membranes have positive charge at low pH and negative at high pH (Bernat *et al.*, 2009).

At pH 2.96 and 5.7 for iron and chromium respectively, the metal species resulting in solution are soluble positive charged hydroxides. These charged hydroxides present in solution occur as a result of the hydrolysis process. The hydrolysis process of iron and chromium ions in aqueous media is classically explained by the following reactions:

$$2[M(H_2O)_6]^{3+} \leftrightarrow \text{polynuclear species} \leftrightarrow M_2O_3 + 9H_2O + 6H^+ \tag{4}$$
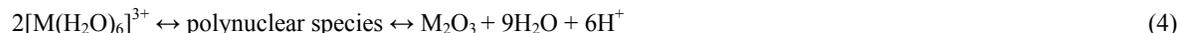
In acidic solutions, taking into account water as a weak ligands, iron ion exists as the hexaaquo ion, $Fe(H_2O)_6^{3+}$ (*M*= 163.93 g/mol) (Blesa, 1989). Accordingly, $FeOH^{2+}$ and $Fe(OH)_2^+$ are present as $Fe(OH)(H_2O)_5^{2+}$ (*M*= 162.93 g/mol) and $Fe(OH)_2(H_2O)^{4+}$ (*M*= 161.92 g/mol), respectively.

Iron and chromium hydrolysis has been considered as a polymerization process because of the formation of polynuclear species in aqueous solution, where $M(H_2O)_6^{3+}$ can be taken as the monomer (Blesa, 1989).Thus, mononuclear and polynuclear species resulting in solution could actually contribute to the rejection in the filtration process, through the adsorption on the membrane material, forming a stable layer of these species on the membrane.

After the Fe(III), Cr(III) species adsorption, the rejection may be even enhanced by charge repulsions between these positively charged hydrolysed metal species adsorbed onto the membrane and the positively charged species present in the bulk solution. In addition, the trend shown by the rejection at several TMP may suggest that, at the steady-state, a size effect could be decisive on the rejection of metal species by ceramic membrane.

3.4. Effect of pH:

The effect of pH on Fe (III) and Cr (III) rejection is represented in Fig.5. pH is studied from 2 to 8 and 3.7 to 8 for Fe (III) and Cr (III) solutions respectively. As shown from the figure, as the pH increases, rejection increases. The rejection reaches maximum at pH 4 for iron and at pH 6 for chromium. The rejection is 47% at pH 2 for iron and 36% at pH 3.7 for chromium. This is because no metal hydroxide species are formed in the solution. At pH 2.96 and 5.7 the rejection is 98.77% and 95.55% for Fe(III) and Cr(III) respectively, this is due to the formation of cake

layer of metal hydroxides. However at pH from 5 to 8 for iron and 6 to 8 for chromium the rejection is 99%, this is due to the precipitation of metal hydroxides. At this pH range no interaction between the hydroxide species and membrane is formed, therefore no membrane fouling is observed.
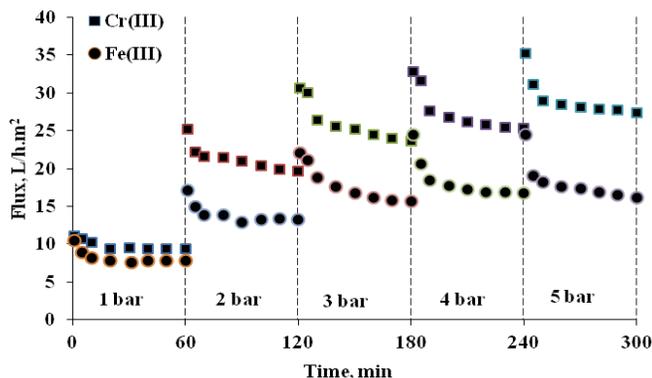

Fig. 4: Flux vs. time at different pressure of Fe^{3+} and Cr^{3+}. $M^{3+} = 0.57$mM, pH=2.96, 5.7 for Fe^{3+} and Cr^{3+} and cross-flow velocity=0.27m/sec.

The flux decline with TMP at different pH is shown at Fig 6, 7, the permeate flux decline is expressed by the ratio between the permeate flux (J_P) at steady state and the initial pure water permeate flux (J_W).

Fig 6 presents that the maximum reduction in the J_P for iron was at pH 2.96 but the lower or the higher pH have no significant effect on the flux reduction. Fig 7shows the same phenomenon for chromium, the maximum flux reduction was attained at pH 5.7 and there were no real effect of the other pH values on the flux reduction. The high flux decline at this specific pH for iron and chromium may be due to concentration polarization and stable cake layer formation on the NF membrane.
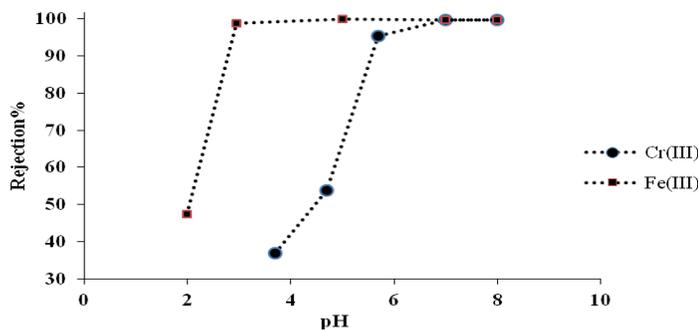

Fig. 5: Effect of pH on the rejection of Fe^{3+} and Cr^{3+}. $M^{3+} = 0.57$mM, TMP 3bar and cross-flow velocity=0.27m/sec.

3.5. Effect of Concentration:

The concentration of metal has a great effect on the flux and the metal rejection. The used Iron and Chromium concentrations were (0.1, 0.57, 1.15 and 2.27 mM) at pH 2.96 for iron and at pH 5.7 for chromium. The rejection of iron and chromium are shown in Fig 8, 9. It can be indicated from the two figures that as the concentration increase the rejection decreases. Increasing the concentration of solutions increases metal ions near the membrane, consequently increases the resistance of the formed layer. This layer resistance overcomes the membrane resistance and allows some the metal ions to pass through the pores of the membrane. It can also be indicated from the figures that increasing TMP leads to rejection increasing. When pressure is raised, water flux through the membrane increases while solute flux essentially remains unchanged as it depends largely on concentration difference across the membrane although ion transport due to convection becomes more significant compared with diffusion. A high diffusive transport of metal through the membrane compared to convective transport may be the reason for low rejection at low pressure and high feed concentration (Mehiguene *et al.*, 1999).
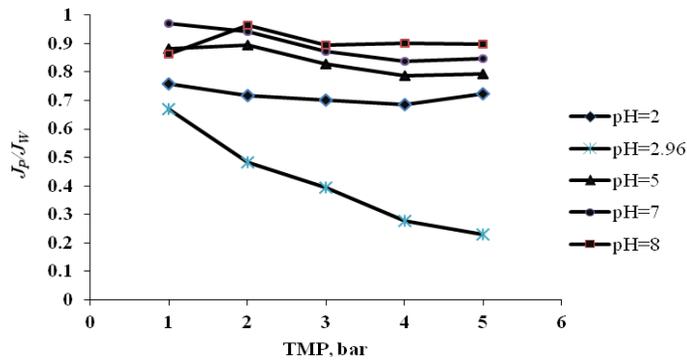
Fig. 6: Effect of the pH of Fe^{3+} solution using NF membrane on the permeate flux decrease. Fe^{3+} = 0.57mM, TMP 3bar and cross-flow velocity=0.27m/sec.
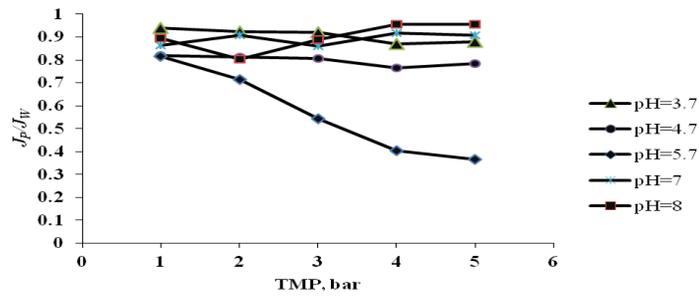

Fig. 7: Effect of the pH of Cr^{3+} solution using NF membrane on the permeate flux decrease. Cr^{3+} = 0.57mM, TMP 3bar and cross-flow velocity=0.27m/sec.
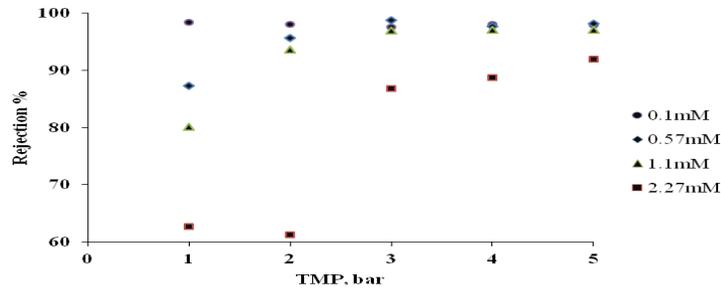

Fig. 8: Effect of pressure on the rejection of Fe^{3+} using NF membrane at different concentration. pH 2.96 and cross-flow velocity=0.27m/sec.
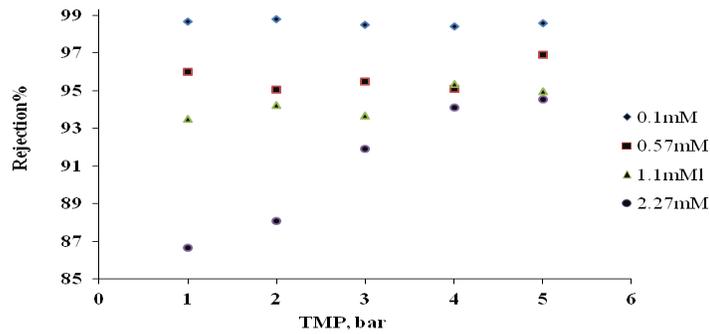

Fig. 9: Effect of pressure on the rejection of Cr^{3+} using NF membrane at different concentration pH 5.7 and cross-flow velocity=0.27m/sec.

Conclusion:

Out of this study we can demonstrate the importance of the operating parameters on the rejection of Fe(III) and Cr(III) using 1KDa ceramic nanofiltration membrane. The gained results indicate that the pH is the main parameter that affects Fe(III) and Cr(III) rejection. The rejection reaches its maximum at pH 4 for iron and pH 6 for chromium. It is suggested that the rejection mechanism based on the formation of stable layer of water soluble positive charged hydrolysed species adsorbed on membrane surface. Low cross-flow velocity could enhance the formation of this stable layer. Additionally when metal concentration in the feed solution increases, metal rejection decreases, unlike when TMP increases, rejection increases. The results shows the rejection is 61-98% for iron(III) and 86-98% for chromium(III).

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