Treatment of chromium wastewater using membrane separation processes

Pavel Kocurek, Karel Kolomazník and Michaela Bařinová

Abstract—This paper deals with the application of membrane separation processes for chromium wastewater treatment. It describes the rejection of trivalent chromium using a commercial membrane for reverse osmosis (RO98pH). Separation experiments were performed with model solutions of chromium. The effects of feed pH, chromium concentration and temperature were investigated. The results showed that pH of the feed solution has influence on the stability of dissolved particles with negative impact on membrane fouling. Prepared feed solutions were stable till pH=6, over this value floccules sedimentation occurred. RO98pH rejected almost 100% Cr(III) at various pH values using 100 mg.L\(^{-1}\) concentration level, operating pressure 1.5 MPa and at temperature 20°C. Similar results showed separation experiments using various Cr(III) concentration from 10 till 560 mg.L\(^{-1}\) and pH=5.5±0.2. Increase of operating temperature causes higher permeate flux and has no significant influence on the rejection level of Cr(III). Obtained results show application possibility of reverse osmosis for chromium removal in wastewaters.

Keywords—chromium, membrane separation, reverse osmosis, wastewater treatment, leather industry.

I. INTRODUCTION

Wide spectrum of physical-chemical and biological treatment methods and their combination is commonly used for treatment of various wastewater. With development of new methods and with focus on higher environmental protection, some technologies no longer meet current requirements. For this purpose, membrane separation processes, especially pressure-driven membrane separation processes, have found wide use abroad [1]. Membrane separation provides many advantages and versatility of usage. These processes have enforced in these areas of human activity where the other technologies dominate nowadays. We can regard them like clean, environmentally-friendly and efficient alternative to traditional processes.

This work was supported in part by the European Social Fund and by Czech Republic’s state budget under Grant OP VK CZ.1.07/2.3.00/30.0035.

P. Kocurek is with the Tomas Bata University in Zlin, Faculty of Applied Informatics, Department of Automation and Control Technologies, Zlin, 76005, Czech Republic (phone: +420576035628; e-mail: kocurek@fai.utb.cz).

K. Kolomazník is with the Tomas Bata University in Zlin, Faculty of Applied Informatics, Department of Automation and Control Technologies, Zlin, 76005, Czech Republic (e-mail: kolomaznik@fai.utb.cz).

M. Bařinová is with the Tomas Bata University in Zlin, Faculty of Applied Informatics, Department of Automation and Control Technologies, Zlin, 76005, Czech Republic (e-mail: barinova@fai.utb.cz).

Chromium wastewaters occur in various industries and there is need of their treatment or of recycling of reagents. Leather industry belongs given to its size and the amount of produced waste to these industries with large negative impact on the environment. It produces big volume of wastewaters with different composition and some of them contain chromium. Many studies have been performed focusing on the recycling of reagents [2] and waste utilization [3]. From 1 tonne of wet-salted hide is manufactured approximately 200 kg of leather. Concurrently is generated more than 600 kg of solid waste during tanning process and the volume 30-35 m\(^3\) of wastewater is discharged into environment in leather industry [4]. In these wastewaters we can expect several concentrations of chromium - basic chromium sulphate is the most popular tanning reagent. Besides high concentrations of chromium, sulphates, chlorides and organic substances wastewaters from chromium tanning are characterized by low pH value and high temperature. But according to these facts, membrane separation can find its place in treatment schema [5], for example to improve the quality of the recycled chromium. Metals, lipidic substances and other impurities could presence in recovered chromium using traditional method combining alkaline precipitation of chromium and dissolution of Cr(OH)\(_3\) in sulphuric acid [6].

II. MEMBRANE SEPARATION

Membrane processes are used in general to separate homogeneous or heterogeneous liquid solutions and mixtures, gaseous mixtures, and suspensions of solid particles of microscopic dimensions (less then ca. 1x10\(^{-5}\) m) in liquids. A common feature of membrane separation is high separation efficiency. The separation selectivity depends on the particular membrane process and on the membrane type. Because membrane separations take place at ambient temperatures, there is no damage to thermo-labile substances. The membrane units may be operated remotely using modern control systems that reduce the cost of labour. Membrane processes are relatively extended abroad. The technique may be applied in low-volume batch equipment or in a continuous large capacity treatment plant.

Membrane processes are based on the separation of the solution into two different streams using a semipermeable membrane. Permeate contains solvent and the particles which passed through the membrane. The remaining particles which were captured by membrane form the concentrate. The
difference across the membrane of pressure, concentration, electrical potential, or temperature serves as the driving force.

Focus of this work is usage of pressure-driven membrane separation processes for wastewater treatment. Operating conditions of these processes are mentioned in Table I.

<table>
<thead>
<tr>
<th>separation process</th>
<th>particle size</th>
<th>operating pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>microfiltration</td>
<td>&gt;0.1 μm</td>
<td>&lt;500 kPa</td>
</tr>
<tr>
<td>ultrafiltration</td>
<td>10-100 nm</td>
<td>500-1000 kPa</td>
</tr>
<tr>
<td>nanofiltration</td>
<td>1-10 nm</td>
<td>1-4 MPa</td>
</tr>
<tr>
<td>reverse osmosis</td>
<td>0.1-1 nm</td>
<td>3-10 MPa</td>
</tr>
</tbody>
</table>

Microfiltration and ultrafiltration are most similar to the classical filtration. They are suitable for the removal of suspended particles, colloids, bacteria and viruses, high-molecular substances etc. The separation is based on the sieve-effect. These processes are commonly used like pre-treatment.

The principle of nanofiltration and reverse osmosis is the same. But the separation ability of nanofiltration is usually considerably lower. This separation technology can separate especially monovalent ions with lower efficiency than reverse osmosis, separation level of polyvalent ions is comparable. The mechanism is not based on the sieve-effect but on the diffusion.

In the case of reverse osmosis the separation proceeds on the ionic level. Mono- and polyvalent ions and low-molecular organic substances are separated. Reverse osmosis technology can be installed in industry for dissolved matter reduction, especially inorganic salts removal (chlorides, nitrates, sulphates, ammonia nitrogen). This is related to the need to use the relatively compact and non-porous membranes. The higher is the concentration of dissolved salts in feed, the higher is the osmotic pressure of feed and the higher operating pressure of device must be applied. Solvent pass through the membrane and dissolved matter is caught by membrane.

Nanofiltration and reverse osmosis are used like the main technologies for wastewater treatment. Pre-treatment is necessary in most installations, post-treatment could be included too, but in most cases is not needed. It depends on the type of wastewater, on the applied separation process and on the desired level permeate (actual need of operator). Both can remove common cations and anions, organic matter and heavy metals with high efficiency, but not limited to.

Osmotic pressure plays significant role in the description of reverse osmosis. It is generated by a semipermeable membrane which separates ions and solvent passes therethrough.

Osmotic pressure \( \pi \) is described in osmotic equilibrium. The following formula is valid for electrolyte solutions.

\[
\pi = RTc\left[1 + \alpha(v'_c + v'_A - 1)\right] \\
C_{v'_c}A_{v'_A} \leftrightarrow v'_cC + v'_A A
\]  

(1)

\( T \) is thermodynamic temperature, \( R \) is molar gas constant, \( c \) is concentration of solutes, \( \alpha \) is the degree of dissociation, \( C \) and \( A \) mean cation and anion and \( v \) refers to quantity. So concentration of solutes and temperature have main influence on the osmotic pressure of feed solution, subsequently on the operating condition of separation process. However, that formula is only valid for very diluted and simple solutions.

Among other factors that affect reverse osmosis belong rejection \( R \), volume reduction factor and permeate flux. Rejection indicates the separation efficiency of component or total. For calculation serve concentration values in feed \( c_F \) and in permeate \( c_P \) or conductivity values \( \kappa \) can be used.

\[
R = \frac{c_F - c_P}{c_F} \geq \frac{K_F - K_P}{K_F} 
\]

(2)

Volume reduction factor is defined like ratio between feed volume and concentrate volume. Permeate flux is hourly flux of permeate through the membrane with area 1 m\(^2\). Its values are different for setup of operating conditions of separation process and can indicate membrane fouling. For final comparison of separation experiments its necessary to hold the same operating temperature because permeate flux is increasing with temperature.

### III. Chromium and its Occurrence

The anthropogenic sources of chromium are wastewaters from metallurgy, metal coatings, leather industry and textile industry. Wastewater from chromium tanning can contain up to 4100 mg.L\(^{-1}\) of Cr(III) [6].

Chromium occurs in waters most often in two oxidation states Cr(III) and Cr(VI). Chromium can be bonded to organic matter. The most stable form of occurrence is Cr(III); Cr(VI) compounds are strong oxidative reagents. Under normal conditions is hexavalent chromium simply reduced into trivalent chromium. But under some conditions opposite reaction occurs and toxic hexavalent chromium is formed [9]. Hexavalent chromium is classified as a carcinogen. Technical legislation of chromium wastewater treatment is strict from this purpose and is based on the probability of presence hexavalent chromium.

### IV. Materials and Methods

Behaviour simulation of Cr(III) solution on membrane was performed under various conditions. The influence of pH, concentration and temperature was studied. For this experiments the membrane typed RO98pH (Alfa Laval, Sweden) for reverse osmosis was chosen. The rejection of NaCl solution of this composite membrane is higher than 97% (NaCl 2 g.L\(^{-1}\), 1.6 MPa, 25°C). Operation conditions: pH range 2-11, typical operating pressure range: 1.5-4.2 MPa, maximum operating pressure: 55 MPa, temperature 5-60°C [10]. Hexavalent chromium is oxidation reagent and can destroy the membrane, so this solution wasn’t used.
For this purpose the feed solution was prepared using CrCl$_3$•6H$_2$O (Lach-Ner) and distilled water. Solution of NaOH (Roana) was used for the pH adjustment of feed.

Feed solution 100 mg.L$^{-1}$ of Cr(III) was prepared under various pH values within 3-6. After that membrane separation was applied. Separation experiments were performed under these parameters: operation pressure 1.5 MPa, temperature 20°C and value of achieved volume reduction factor 4. After this group of experiments one pH value was chosen and other separation experiments were performed under the same operating conditions using feed solutions 10, 100 and 560 mg.L$^{-1}$ of Cr(III). Finally, the influence of temperature on the separation of Cr(III) was investigated. Stability of membrane process, Cr(III) rejection, pH values of streams and permeate flux were measured during every experiment.

After every separation experiment analysis of all streams were performed. Chromium concentration was measured on AAS SensAA (GBC Scientific Equipment, Australia), conductivity on conductivity-meter GMH3430 and pH values on pH-meter GMH3530 (Greisinger Electronic, Germany).

All separation experiments were performed on membrane separation unit LAB-M20 (Alfa Laval, Sweden) in laboratory scale. The equipment was customized for batch processing. The volume of the feed tank was ca. 12 L. The actual separation takes place on a plate-and-frame module DSS equipped with 36 membranes with total membrane area 0.63 m$^2$. A Rannie piston pump with maximum operating pressure of 6.0 MPa was used. A separate water supply was used to maintain the pistons of the pump moist. A flow liquid-liquid heat exchanger cooled the membrane module. Water from the faucet served as the cooling agent.

V. RESULTS AND DISCUSSION

A. Influence of pH

pH of solution is important factor influencing the stability of prepared Cr(III) solution. Solutions with pH values within 3-6 were stable; increasing pH over 6 flocculation occurred and floccules fallen to the bottom of the vessel. For the membrane separation only Cr(III) solutions with pH values 3.3 (RUN1), 5 (RUN2) and 5.5 (RUN3) were used.

![Fig. 1](image1.png)

Fig. 1 dependence of rejection on volume reduction factor under different pH values (100 mg.L$^{-1}$ Cr(III))

![Fig. 2](image2.png)

Fig. 2 dependence of rejection on volume reduction factor under different Cr(III) concentrations and pH=5

![Fig. 3](image3.png)

Fig. 3 dependence of permeate flux on volume reduction factor under different Cr(III) concentrations and pH=5

Using operating pressure 1.5 MPa we can observe changes of permeate flux comprising different feed concentrations. Permeate flux is the highest in experiment RUN4. Values for experiments RUN2 and RUN5 are comparable. There is no significant decrease of permeate flux in time but it could differ.
using real wastewater sample. Only in the case of experiment RUN5 we can see a slight decrease of permeate flux because Cr(III) concentration of feed water was considerably higher.

C. Influence of Temperature

Temperature influences the following parameters of separation process - osmotic pressure and permeate flux. Feed solution was prepared under the same conditions like in the case of experiment RUN2. The operating temperature was increased in range 15-26°C and the influence of temperature on permeate flux and rejection was observed.

![Fig. 4 dependence of permeate flux on temperature](image)

In Fig. 4 we can see strictly linear trend of experimental values of permeate flux. Increasing the temperature by 1°C will increase the permeate flux of 3.6%. The effect of the chromium concentration in permeate is negligible. It is showed in Fig. 5. Concentration of chromium may be affected by small measurement error. These values are essentially comparable.

![Fig. 5 dependence of Cr(III) concentration in permeate on temperature](image)

In Fig. 4 we can see strictly linear trend of experimental values of permeate flux. Increasing the temperature by 1°C will increase the permeate flux of 3.6%. The effect of the chromium concentration in permeate is negligible. It is showed in Fig. 5. Concentration of chromium may be affected by small measurement error. These values are essentially comparable.

Table II comprises composition of the feed and permeate in all separation experiments. Rejection of Cr(III) achieves in all case high values near 100%. Due to the size of Cr$^{3+}$ reverse osmosis provides sufficient reserve in rejection. Nanofiltration in general separates these ions with similar efficiency but rejection of monovalent ions could not be sufficient.

VI. CONCLUSION

In this study membrane separation of chromium by reverse osmosis using various operating conditions was performed. Separation experiments with Cr(III) solutions provided very good results given to high rejection values. The results showed that pH of feed solution has influence on the stability of dissolved particles with negative impact on membrane fouling. Prepared feed solutions were stable till pH=6, over this value floccules sedimentation occurred. RO98pHt rejected almost 100% Cr(III) at various pH values using 100 mg.L$^{-1}$ concentration level, operating pressure 1.5 MPa, volume reduction factor 4 and at temperature 20°C. Similar results showed separation experiments using various Cr(III) concentration from 10 till 560 mg.L$^{-1}$ and pH=5±0.2. Increase of operating temperature causes higher permeate flux and has no significant influence on the rejection.

These results have positive impact on the application of membrane separation processes in leather industry. But in the case of real wastewater from chromium tanning treatment, laboratory and pilot-plant experiments including appropriately pre-treatment for separation process optimization are needed.

REFERENCES


