

**STUDIES ON CHROMIUM SEPARATION BY  
NANOFILTRATION MEMBRANE**

by

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Submitted

in fulfillment of the requirement of degree of

**DOCTOR OF PHILOSOPHY**

to the



**INDIAN INSTITUTE OF TECHNOLOGY, DELHI**

**APRIL - 2007**

Dedicated  
to  
my Parents

## CERTIFICATE

This is to certify that the thesis entitled “**Studies on Chromium Separation by Nanofiltration Membrane**” submitted by **Mr. Muthukrishnan. M**, to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy, as a bonafide record of research work carried out by him under my supervision and in accordance to the guidelines, rules and regulations of this Institute. The research report and results embodied in this thesis have not been submitted for any other degree or diploma in any other University or Institute.



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## ACKNOWLEDGEMENT

*I wish to express my sincere gratitude and respect to my supervisor Prof. B. K. Guha for his guidance and support throughout the research work. I am thankful for his valuable suggestions, encouragement and help to achieve my goals. His motivation, industrial exposure and moral supports are most appreciated which renders this effective research completion.*

*I wish to express my sincere thanks to my Co-supervisor Dr. Anupam Shukla for his valuable ideas and suggestion during this study and his guidance, moral support and motivation are most appreciated.*

*I am extremely thankful to Dr. (Mrs.) Rita Guha, for her constant encouragement and help during this study.*

*I wish to express my gratitude to Prof. D. Subbarao, Prof. S. K. Gupta and Prof. G. P. Agrawal, who are associated with IIT Delhi for their encouragement during the completion of this thesis.*

*I wish to express my sincere thanks to Prof. Dhingra, Prof. A. N. Baskarwar and Dr. Rajesh khanna for their valuable discussions and ideas.*

*I am indebted to my Uncle Mr. P. Kumaresan & Sister Mrs. M. Dhanam and family who have provided basic needs during this research, I thank them for their supports, motivation and help during this course of study.*

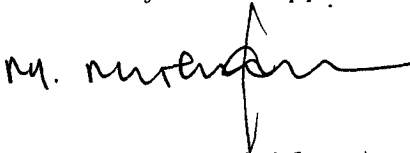
*I am also indebted to the Lab staffs Mr. Chandan Singh, Mr. Biswanath, Mr. Brahm Prakash, Mr. Lalit Kumar and Mr. Ashwani Kumar for their valuable support during this study.*

*I express my sincere thanks to my friends Mr. Anwar Ali Khan, Mr. P.V. K. K. Varma, Mr. Umesh Kumar Rai, Mr. Apoorva Prabakar, Mr. Debabaibhab Das, Mr. Vikas Mittal and Mr. Solomon Workneh for their precious help and support.*

*I thank my Father Late. Mr. R. Murugesan and Mother Mrs. M. Adi Lakshmi, Brothers Mr. Kuppuswamy, Mr. Anbazhagan and Mr. Ramakrishnan for their support, guidance and encouragement for my education and social support in life. Without their support and encouragement this thesis would not have seen the light of the day.*

*I express my sincere thanks to Chemical Engineering Department and IIT D for their support during this course.*

April 2007  
IIT Delhi

  
(M. Muthukrishnan)

## ABSTRACT

Recycle of water and chemical from wastewater stream has acquired a new dimension in the Wastewater Treatment Technology and Research areas. In this membrane separation processes have provided the most important breakthrough and are now considered as the most important modern tool. Nanofiltration membrane operation is being considered as the best separating tool for different components from solvents as applied to industrial purification as well as for wastewater treatment operation. This is mostly due to relatively milder process operating conditions of lower pressure of operation and high solvent flux and percent separation obtainable from such membrane system.

Chromium has been found many applications in industries because of its high mechanical strength, decorative and non corrosive nature. Other than its usage in metallurgical and mechanical industries in the metal form, large quantities are also used in chemical compound from (trivalent,  $\text{Cr}^{+3}$  and hexavalent,  $\text{Cr}^{+6}$ ) in leather and electroplating industries.  $\text{Cr}^{+6}$  is a highly toxic and hazardous substance. Even a relatively small amount can cause cancer, kidney and DNA damage etc. Therefore it needs extensive treatment to remove the toxic metal from wastewater before discharging the same. Further it is also a very costly metal/compound and hence its recovery is highly desirable from economic and environment point of view.

The electroplating industries are the major user of  $\text{Cr}^{+6}$  compounds and the resultant effluent discharged contains high concentration of  $\text{Cr}^{+6}$ . The effluent is usually released after the conventional treatment method of reduction and precipitation techniques. All the chromium finally ending up in landfill sites (some secured with lining and others unsecured) as hazardous sludge. This process has no potential for reuse of treated water and recovery of

chromium. Further the treated wastewater becomes more contaminated because of the incorporation of other chemical components.

The present study is directed to finding a single step solution for both the problems. The application of nanofiltration membrane has been considered because of the specific advantages mentioned above.

Spiral wound nanofiltration membrane module was used for experimental studies; experiments were carried out mostly with synthetic chrome solution prepared in the lab with specific composition for the desired feed condition. Few experiments were carried out with chrome plating trade effluent collected from an operating electroplating unit. The real plant effluent contains many chemical components other than chromium. Surfactants and polyelectrolytes out of these chemicals have the potential to alter the interfacial surface phenomenon and in turn influence the separation behavior of the metal component. Hence special effort have been made to study the effect of surfactants, polyelectrolyte and other solutes for the separation  $\text{Cr}^{+3}$  and  $\text{Cr}^{+6}$  under different operating conditions of pressure, feed flow rate, initial chromium concentration, temperature etc. Three different surfactants with different charge properties were used in this study. Two different polyelectrolytes with separate charge behavior were considered for study to the chromium removal.

The nanofiltration membranes are charged membrane. The surfactants are adsorbed on the membrane surface due to charge difference during the filtration operations. This adsorbed layer forms secondary membrane over the charged polymeric membrane layer. The charged nature of the membrane implies that ionic behavior of the solutes which depends on the pH of solution would have strong effect on the transport properties. The effect of charged

nanofiltration membrane with surfactants and polyelectrolytes has been observed at three different pH conditions in terms of chromium rejection and permeate flux.

Chromium separation by the nanofiltration system was found to be in the range of 98-99.8% for  $\text{Cr}^{+6}$  and 99-99.9% for  $\text{Cr}^{+3}$  respectively at different operating conditions. The results showed that  $\text{Cr}^{+6}$  removal is much better in the alkaline range compared to that in acidic range. Further the effect of pH on the permeate flux was found to be quite insignificant. The chromium concentration in the feed stream plays significant role for  $\text{Cr}^{+6}$  compared to that of  $\text{Cr}^{+3}$  and shows reduction in removal at high concentrations due to concentration polarization and effect of Donnan exclusion. The phenomenon of relative behavior of  $\text{Cr}^{+6}$  separation at different pH of the solution was established by carrying out special experiments using UV-Vis spectrophotometer with the permeate stream to establish the ionic behavior of the transporting component. It was observed that at acidic condition ( $\text{pH} < 6$ ) the prevailing ionic component was monovalent  $\text{HCrO}_4^-$  whereas at  $\text{pH} > 6$  it was bivalent  $\text{CrO}_4^{2-} / \text{Cr}_2\text{O}_7^{2-}$ . This resulted in high separation at  $\text{pH} > 6$  compared to that at  $\text{pH} < 6$  since monovalent ion transmission through NF membrane is higher compared to that of bivalent ions.

Higher temperature shows increase in permeates flux and marginal changes in chromium rejection for  $\text{Cr}^{+3}$  and  $\text{Cr}^{+6}$ . The increase in feed circulation rate shows high rejection rate and permeate flux for both  $\text{Cr}^{+3}$  and  $\text{Cr}^{+6}$ . Effect of the presence of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  on  $\text{Cr}^{+6}$  rejections were studied for wide range of concentrations. The addition of chloride was found to reduce the chromium rejection. In the case of  $\text{SO}_4^{2-}$ , its addition also was found to cause high reduction in separation efficiency.

Surfactants and Polyelectrolytes were found to act as charge modifier on the membrane surface. Adsorption and repulsion behavior on the membrane was observed for different surfactants. It was observed that the anionic and non ionic surfactants enhanced the hexavalent chromium separation. Cationic surfactants also enhanced separation but to a lesser extent. The effect of pH on the surfactants was found to be quite significant with respect to chromium rejection as well as permeate flux. The enhanced separation of chromium was also observed in  $\text{Cr}^{+3}$  separations. The effect of polyelectrolyte has been found to be similar to that of surfactants but the effect of pH shows different behavior for chromium rejection and permeates flux.

The experimental data were successfully analyzed by the application of Spiegler-Kedem model. The experimental results were simulated with the predicted data under similar condition of operation and it shows good fit with experimental data. Present investigation was extended to study the separation behavior of the real life plant effluent, containing many mixed compounds. The results showed a similar behavior as to the studies conducted with synthetic effluents.

The experimental investigation indicates that the treatment of chrome plating effluent by nanofiltration is technically feasible and environmentally desirable as it solves the pollution problem as well as recovers the solute and solvent water simultaneously.

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