STUDIES ON CHROMIUM SEPARATION BY NANOFILTRATION MEMBRANE

by

MUTHUKRISHNAN. M

DEPARTMENT OF CHEMICAL ENGINEERING

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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.

Barun Kumar Guha

Professor

Anupam Shukla

Assistant Professor

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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, Cr^{+3} and hexavalent, Cr^{+6}) in leather and electroplating industries. 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 Cr^{+6} compounds and the resultant effluent discharged contains high concentration of 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 Cr^{+3} and 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 Cr^{+6} and 99-99.9% for Cr^{+3} respectively at different operating conditions. The results showed that Cr^{+6} removal is much better in the alkaline range compared to that in acidic rage. 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 Cr^{+6} compared to that of 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 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 (pH <6) the prevailing ionic component was monovalent $HCrO_4^-$ where as at pH >6 it was bivalent $CrO_4^{2-}/Cr_2O_7^{2-}$. This resulted in high separation at pH>6 compared to that at 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 Cr^{+3} and Cr^{+6}. The increase in feed circulation rate shows high rejection rate and permeate flux for both Cr^{+3} and Cr^{+6}. Effect of the presence of Cl^- and SO_4^{2-} on 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 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 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 nanofitration 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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