Separation of Ni^{2+}, Cu^{2+} and Cr^{6+} Metal Ions from Water by Complexation Micro Filtration Technique Using Synthetic Polymer Membranes

Elamathi Swaminathan[1], Saravanan Nagappan[2],
Padmavathi Rajangam[3],Sangeetha Dharmalingam*[4]

Department of Chemistry, Anna University, Chennai - 600 025, Tamil Nadu, India
[1]elamathe@gmail.com; [2]saravana_nagapan@yahoo.co.in; [3]padma_vathi25@yahoo.com; *[4]sangeetha@annauniv.edu

***Abstract*-Waste water from industrial areas contains many toxic heavy metal ions, which are carcinogenic and need to be removed before water recycling. In this study, complexation microfiltration technique was used to separate the metal ions. Initially, known concentrations of metal ions were complexed with polyethylene glycol (PEG) and polyacrylic acid (PAA). Polymer enhanced microfiltration process has been investigated for removal of toxic heavy metals such as Ni^{2+}, Cu^{2+} and Cr^{6+} from synthetic waste water solutions. The concentration of metal ions in the sample water was analyzed by UV–Vis spectrophotometer. The effects of pH and polymer/metal ratio using two different membranes such as nylon and cellulose nitrate (CN) were investigated. The membranes were characterized by FTIR to identify the functional groups present in the membrane matrix and SEM analysis used to find the pore size and the metal deposition present over the membrane. Among the various combinations, PAA as the complexing agent at pH ≥ 8 proved to be most effective for the removal of nickel (II) and copper (II), and pH ≤ 4 for chromium (VI) metal ions.**

***Keywords*- Micro filtration; Heavy Metalion Separation; Polymeric Membrane; Complexation Process**

I. INTRODUCTION

Waste water from various sources, contains many metal ions that concern us of occupational or residential exposure. Among the various heavy metal ions present in our environment, 23 of these are very dangerous to our body, such metal ions are antimony, arsenic, bismuth, cadmium, cerium, lead, nickel, copper, chromium, manganese, iron, silver, thallium, tellurium, tungsten, uranium, vanadium and zinc ions etc. Interestingly small amount of these elements are common in our environment and diet, which are actually necessary for our good health, but larger amount of any of them may cause allergic reactions, chronic toxicity, diarrhoea and so on. Some of the heavy metal toxicity results are: (i) short term exposure results in damaged or reduced central nervous functions, lower energy levels, damaging of blood components, lungs, kidneys, liver and other vital organs and (ii) long term exposure may result in slowly progressing physical, muscular and neurological degenerative processes that mimic cancer [1, 2].

For some heavy metals, toxic levels can be just above the background concentration naturally found in nature. Therefore it is important for us to know about the heavy metal toxicity and to take protective measures against excessive exposures. The maximum contamination levels of some heavy metal ions for safe drinking water are nickel: 2 mg/dm^3, copper: 1.3 mg/dm^3, chromium: 0.10 mg/dm^3, manganese: 0.05 mg/dm^3, iron: 0.5 mg/dm^3, arsenic: 10 $\mu g/dm^3$ and mercury: 2 $\mu g/dm^3$ [3-5].

Waste water from various industries contains toxic heavy metal ions, which must be removed before recycling or discharging directly into the surface water. The conventional processes to treat this kind of waste water are chemical precipitation, ion-exchange, adsorption or biosorption and membrane separation techniques. Nowadays membrane separation processes such as micro filtration, ultra filtration, nano filtration, reverse osmosis and electro-dialysis play a vital role in heavy metal separation from waste water [1]. In the recent years, the complexation-microfiltration technique has been shown to be a promising technique for removal of heavy metals.

Some biopolymer macroligands are able to complex with heavy metal ions [6-8]. The other group of synthetic macroligands are carboxyl methyl cellulose [9], diethylamino ethyl cellulose [10], polyvinyl ethylene imine [11, 12], polyvinyl alcohol (PVA) [13], PAA [14-16] and PEG. Such complexed heavy metal ions can be removed easily from waste water than free metal ions. So the complexation – microfiltration process is a more convenient method for separation of heavy metal ions.

In our work, micro filtration technique was used to separate some of the heavy metal ions such as Ni (II), Cu (II) and Cr (VI) from various sources. The presence of these heavy metals causes allergy and it may affect the human nervous system. So, it is essential to remove these metals from water. In this study, the commercially available membrane filters such as nylon and CN were used. Initially, the metal ions were complexed with water soluble polymers like PAA and PEG. These polymers were

selected because of their higher bonding selectivity. Metal ions formed agglomerates with polymers and easily separated under certain pH conditions. The most important parameters which could affect the influence of the separation process are properties of complexing agent and pH [5]. The present work mainly focuses on the separation of heavy metal ions using PAA complexing agent with varying pH conditions using nylon and cellulose nitrate membranes.

II. EXPERIMENTAL PROCEDURE

A. Materials

Nickel sulphate ($NiSO_4$. $6H_2O$) was purchased from G.S. Chemical testing lab and allied industries (New Delhi), Copper sulphate ($CuSO_4$. $6H_2O$) and potassium-di-chromate ($K_2Cr_2O_7$) were purchased from Qualigens fine chemicals (Navi Mumbai), pH buffer tablets of pH 4, 7 and 9.2 were purchased from Sisco research laboratories Pvt. Ltd (India), purified di-sodium hydrogen phosphate dihydrate (Na_2HPO_4. $2H_2O$), sodium di-hydrogen phosphate (NaH_2PO_4. $2H_2O$), polyethylene glycol (PEG Mw = 3500-4000 g/mole) and concentrated hydrochloric acid (HCl) were purchased from Merck limited (Mumbai). Poly acrylic acid (PAA M_w = 1800) was purchased from Sigma Aldrich (Bangalore). The membranes chosen for this study, such as nylon, and cellulose nitrate (CN) were purchased from Sartorius biolab products (Germany). The pore sizes of nylon and CN membranes are 0.2 μ. The known and unknown amounts of feed solutions were diluted by using prepared double distilled water.

B. Metal Complex Preparation and Separation

Initially, known concentrations (250, 500, 750 and 1000 ppm) of nickel sulphate, copper sulphate and potassium-di-chromate solutions were prepared separately. Complexes of nickel, copper and potassium were prepared from corresponding solutions using water soluble PAA and PEG polymers. These metal ions (using Nylon and CN membrane) and metal complexes (using Nylon membrane filter) were separated by using lab made membrane filtration unit. The membrane filtration unit consists of three main parts, (i) Input feed solution holder, (ii) Membrane holder and (iii) Output chamber. The membrane filter of 47 mm diameter was kept on the top of the membrane holder, which had a base part of output chamber. On top of the membrane holder, the input feed solution holder was placed and then it was clamped tightly, to avoid any leakage of water. Small amount (~10-20 ml) of solution was poured into the input feed solution holder. 30 mm Hg pressure was applied using vaccum pump to suck the solution from input feed solution holder and the filtrate was collected in the output chamber. The filtrate was tested and the percentage rejection of metal ions and metal complexes were determined using UV – Visible spectrophotometer. The separation of metal complexes was carried out at 2, 4, 5, 7 and 8 pH levels. pH of the solution was adjusted using di-sodium hydrogen phosphate and sodium di-hydrogen phosphate.

C. Characterization

The concentration of metal ions and metal complexes in the output solutions were tested using UV-Visible spectrophotometer (Perkin-Elmer spectrophotometer, Type: Lambda 15) to calculate the percentage rejection of metal ions. The surface morphology of membranes was characterized by scanning electron microscopy (HITACHI-S3400N), to analyse the microstructure of the membrane filters. The presence of functional groups was identified by Fourier transform infrared studies using Perkin-Elmer FTIR spectrometer in the range 4000-400 cm^{-1}.

III. RESULTS AND DISCUSSION

A. Removal of Metal Ions

The percentage rejection of metal ions with various membrane filters are shown in Figs. 1, 2 and 3. From the data, it can be seen that all the metal ions showed up to 60% rejection while using nylon and CN membranes. The reused membranes (used membranes were washed and again used for the separation process) also showed up to 60% rejection of metal ions. After washing also, the metal free membrane filter was obtained. After several use (6 times) membrane showed lower performance, still it removed more than 40% of metal ions. The results reported in this paper, were determined by the membrane permeate flux, which plays a paramount role in controlling the rate of deposition onto membrane surfaces. Membrane fouling can be reversible or irreversible. Both reversible and irreversible fouling causes permeate flux decline. The flux decline by reversible fouling can be recovered by membrane washing with deionized water, while the flux decline caused by irreversible fouling cannot be recovered unless the membrane is replaced or cleaned by chemical reagents. Reversible fouling occurred due to the formation of cake or gel layer of the foulant on the membrane surface, whereas irreversible fouling usually occurred due to strong physisorption or chemisorption of solutes onto the membrane surface.

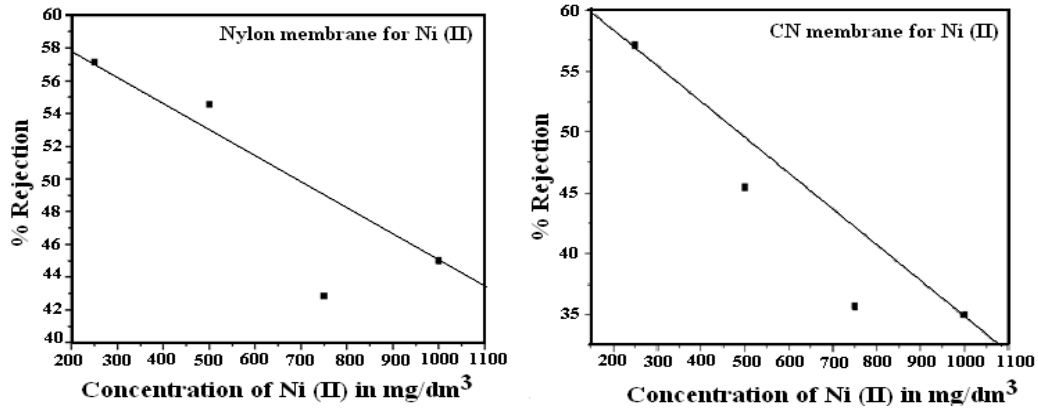

Fig. 1 Effect of membrane filters on % rejection of Ni (II) ion from aqueous solutions using a) Nylon, b) CN membrane filters

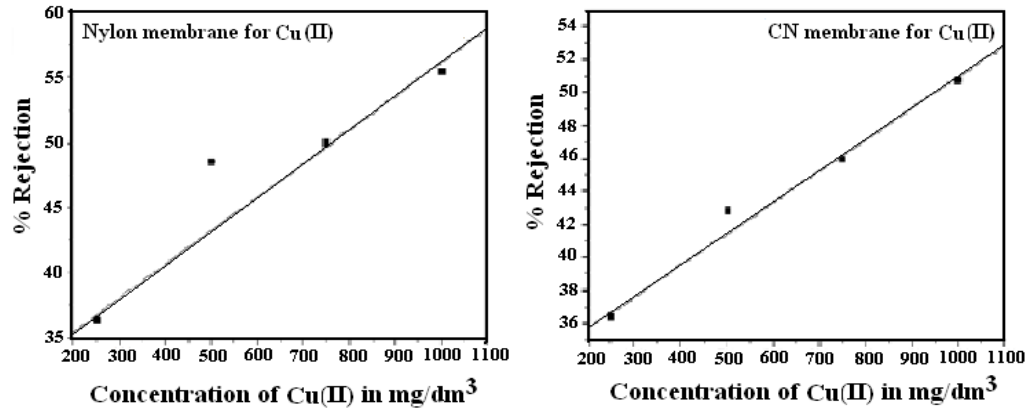

Fig. 2 Effect of membrane filters on % rejection of Cu (II) ion from aqueous solutions using a) Nylon, b) CN membrane filters

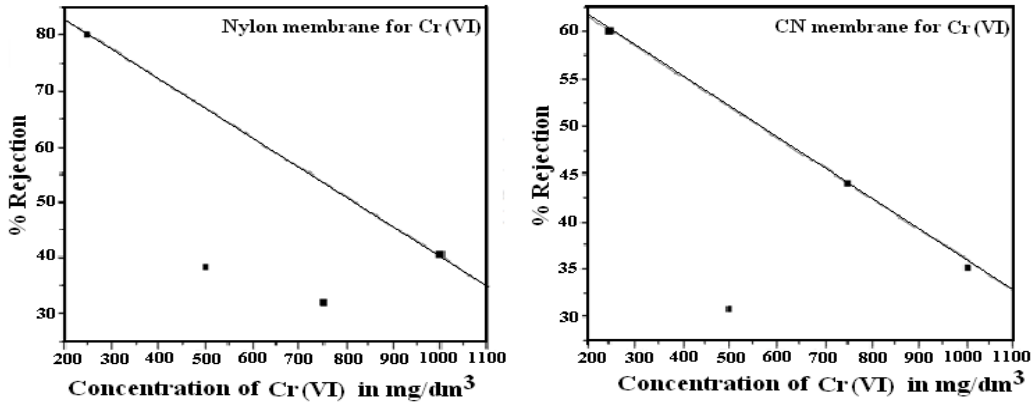

Fig. 3 Effect of membrane filters on % rejection of Cr (VI) ion from aqueous solutions using a) Nylon, b) CN membrane filters

B. Effect of pH on Complexation

Metal separation processes using nylon and CN membranes were performed for known concentrations of Ni, Cu and Cr sulphate solutions. In order to improve the percentage rejection of metal ions, the metals were complexed with water soluble PAA and PEG polymers. Initially 500 ppm of PAA and PEG was dissolved in water, then 500 ppm of metal ions was dissolved in polymer solution to obtain polymer/metal complex due to presence of reactive sites in the polymer chain. To study the effect of pH on separation, polymer/metal complex was prepared in various pH solution (Figs. 4, 5 and 6), using disodium hydrogen phosphate. Since, the OH groups in the polymer get easily complexed with metal ions at low pH, the Cr^{6+} ion easily formed complex with polymer solution at lower pH. Whereas, at high pH, the OH group in the polymer chain may react with large amount of sodium ions present in the disodium hydrogen phosphate (buffer solution) molecules and hence may prevent the complex formation resulting in decrease of percentage rejection at high pH. However, the percentage rejections are higher for metal complexes then compared to free metal ion rejection and there was only a slight difference in the percentage rejection between lower and higher pH ranges in the case of complex separation. Percentage rejection of Ni^{2+} and Cu^{2+} ion-complexes

increases with increase in pH. Moreover they form complexes easily, since these metals need only 2 reactive sites to form complex. At high pH both the metal shows more than ninety percentage rejection for all the membranes. It should be noted that a pH value in the aqueous phase may cause the metal ion to precipitate and these would hinder the penetration [17].

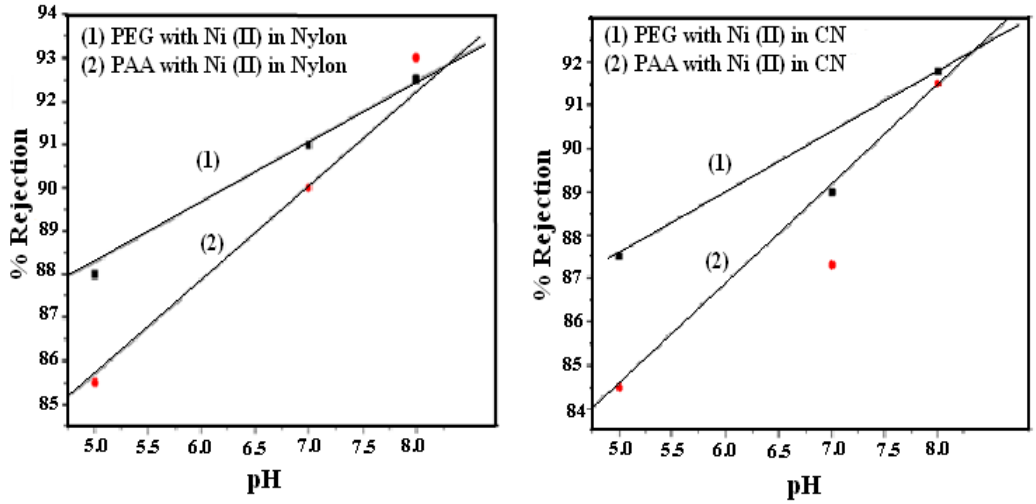

Fig. 4 Effect of pH on the % rejection of Ni complex with PEG and PAA from aqueous solutions using a) Nylon, b) CN membrane filters

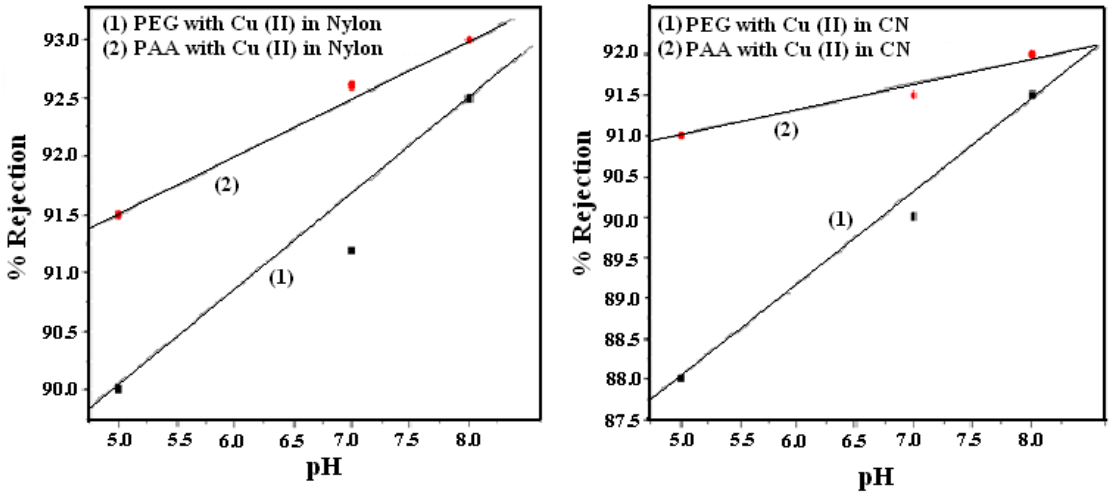

Fig. 5 Effect of pH on the % rejection of Cu complex with PEG and PAA from aqueous solutions using a) Nylon, b) CN membrane filters

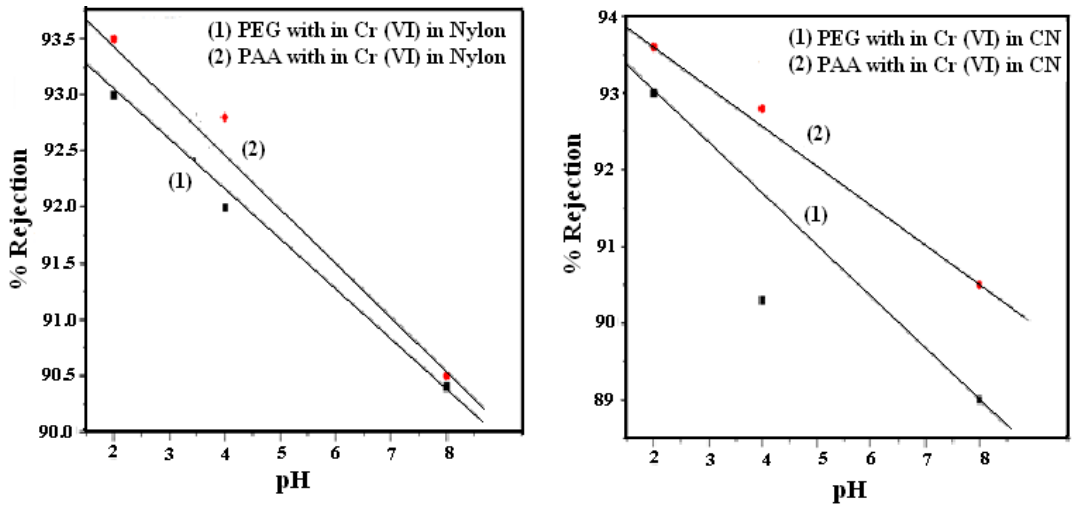

Fig. 6 Effect of pH on the % rejection of Cr complex with PEG and PAA from aqueous solutions using a) Nylon, b) CN membrane filters

The metal ions were complexed with water soluble PAA and PEG. Compared to PEG metal complex, the PAA polymer easily formed the complexes with metal ions with higher percentage rejection, due to presence of higher active OH group in the PAA than PEG. But in the case of Cr metal complex, the percentage rejection was higher at lower pH range [18-20].

It was found that Ni^{2+}, Cu^{2+} metal ions complexed well with PAA water soluble polymer at pH $\geq$ 8 and for Cr^{6+} at pH 3-4, which could be confirmed by their percentage rejection of metal ions in the water sample. The efficiency of the heavy metal ion removal by the complexation process depends on the extent of retention of polymeric ligand. The extent of retention of the polymeric ligand depends not only on the pore size and pore distribution in the filter membranes, but also on the molecular weight distribution of the polymeric ligand itself. There was more separation of Ni/PAA complex at higher pH in nylon membrane, which could be due to morphology of the membrane surface.

C. Scanning Electron Microscopy (SEM)

The surface of the fresh nylon membrane was clean and smooth and uniform pore size was observed throughout the membrane as shown in Fig. 7 (a). After the separation process, the membrane surface was found to be covered with lots of metal/complex agglomerates; their original surface structure was loosened; the entire surface of Nylon was completely covered with added mixture as shown in Fig. 7 (b, c and d). Ni (II) - PAA components appeared as tiny particles. A thick layer of deposit was clearly visible on nylon membrane in Fig. 7 (b). Fig. 7 (c) illustrates the SEM image of Cu (II) - PAA complex and Fig. 7 (d) shows the SEM image of Cr (VI) - PAA complex dispersed on nylon membrane. Some metal complex agglomerates are observed on the surface of the membrane filter. The polymer matrix showed a much lower adsorption capacity with Cu and Cr metal complexes. When compared to Cu and Cr, Ni ion readily forms metal complexes with polymer.

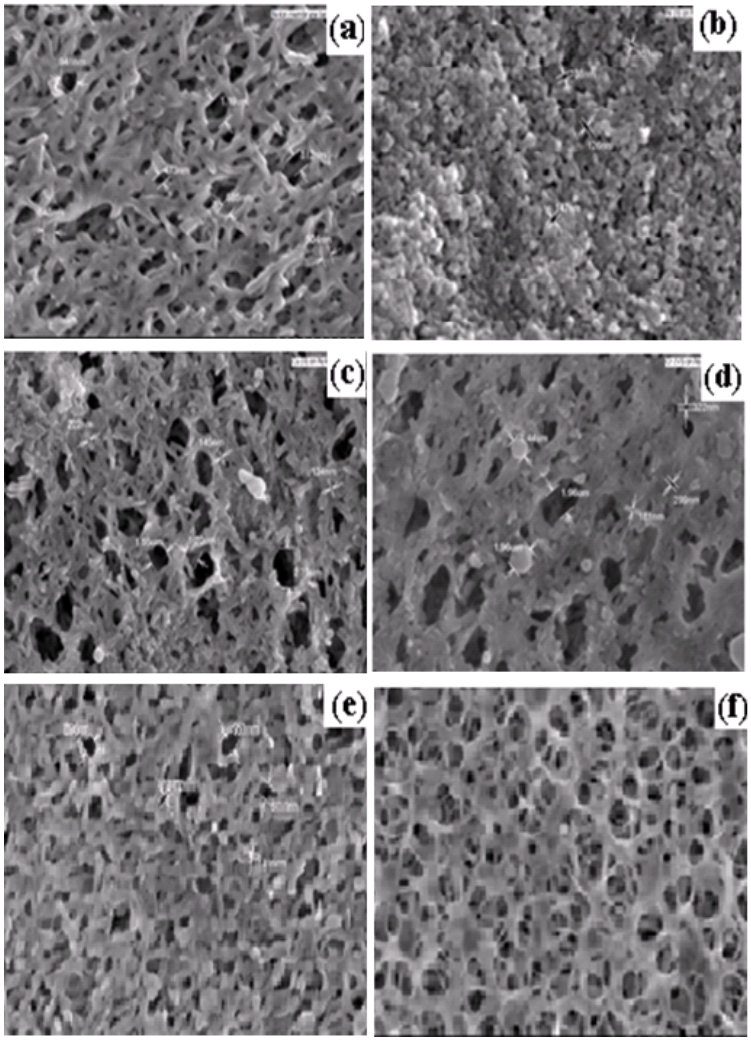

Fig. 7 SEM images of Nylon membranes (a) before use, (b), (c) and (d) are after deposition of PAA/metal complex of Ni (II), Cu (II) and Cr (VI) respectively, (e) recovered nylon membrane after washing, (f) Cellulose nitrate membrane before treatment

Fig. 7 (e) shows the SEM image of Ni(II) – PAA loaded nylon membrane after washing several times with hot water. The surface of the nylon membrane was found to be smooth and uniform once again. Hence the nylon membrane can be reused without any loss in physical properties. Surface morphology of CN is shown in Fig. 7 (f). It was observed that the membrane had regular pore size. CN membrane also showed good performance in metal rejection like nylon membrane, but different

from nylon membrane. The CN membrane showed lower retaining property after several washing. The histogram peaks of the nylon membranes before metal ions deposition and after treatment are shown in Fig. 8. The histogram peaks reveal the retaining of pores in the nylon membrane after washing. The re-usability of nylon membrane was found to be good when compared to CN membrane filter.

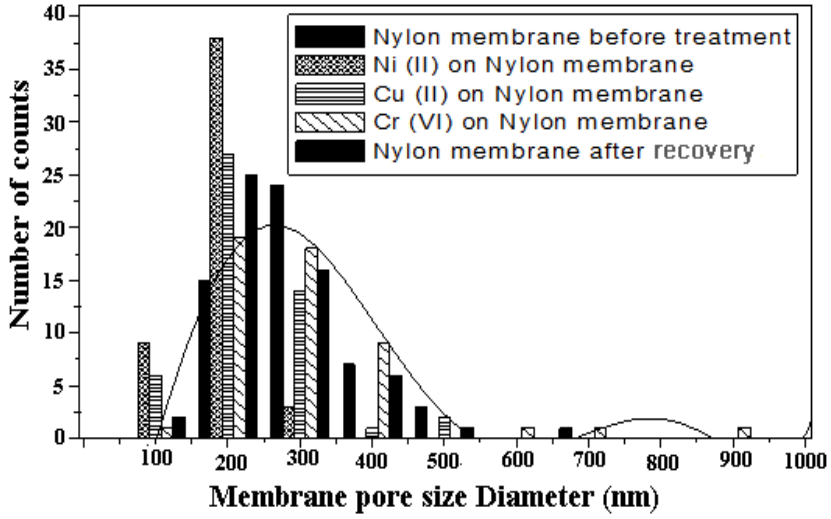

Fig. 8 Histogram peaks for Nylon membrane before and after treatment and metal ions complexed with PAA

D. Fourier Transform Infrared Spectroscopy (FTIR)

1) Nylon Membrane:

The FTIR spectra of nylon membrane before and after washing are shown in Fig. 9 (a and e). In the FTIR spectra, the CH_2 symmetric and asymmetric stretching was not clearly resolved. The broad envelop that lay at 1400 cm^{-1} includes N-H stretching and CH_2 stretching vibrations. In addition there was O-H stretching of water, which gives a broad band between 3000 and 4000 cm^{-1}. The broad peak that lies at 1750 cm^{-1} was attributed to C=O stretch of amide and CH_2 bending modes. In addition it was also due to O-H bending mode, all these vibrations are not clearly resolved. There are group of peaks below 1000 cm^{-1} that were assigned to CH_2 rocking vibrations. From these two spectra, it was to be depicted that the membrane stretches are not affected by the metal and poly acrylic acid treatment.

The FTIR spectra of nylon membrane deposited with Ni (II), Cu (II) and Cr (VI) are shown in Fig. 9 (b, c and d). The intense broad band between 3000 and 4000 cm^{-1} are due to O-H stretch of water and O-H stretch of PAA. The broadening of the band illustrates extensive hydrogen bonding. The CH_2 vibrations give their characteristic peaks below 3000 cm^{-1}, but they are also overlapped with their main band. The bonding modes of water, amide, carboxylic acid C=O stretching and CH_2 bending modes give a broad intense band at 2000 and 1000 cm^{-1}. These features are same for all the three metal acrylic acid loaded nylon membrane.

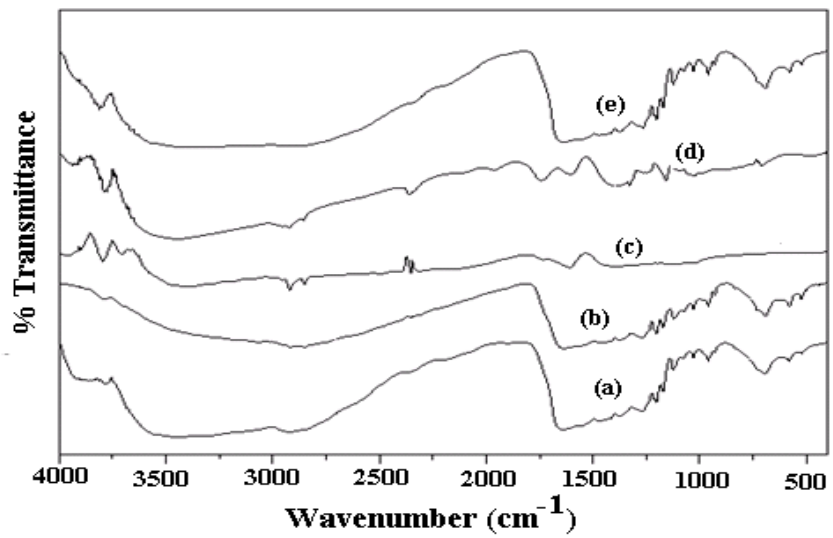

Fig. 9 FTIR spectra of Nylon membranes (a) before treatment (b) PAA loaded with Ni (II), (c) Cu (II), (d) Cr (VI) metal ions deposition on nylon membrane, (e) after recovery

2) Cellulose Nitrate Membrane (CN):

The FTIR spectra of Cellulose Nitrate membrane before and after use are shown in Fig. 10 (a and e). The peak at 3750 cm^{-1} was due to free O-H stretch of cellulose. The hydrogen bonded O-H stretching of cellulose and OH stretch of water gives an intense peak at 3490 cm^{-1}. The CH_2 vibrations were clearly seen just below 3000 cm^{-1}. The H_2O bending mode gives a sharp peak close to 1630 cm^{-1}. The CH_2 bending vibrations and C-O stretching vibrations of CN gives a broad band between 1560 cm^{-1} which was assigned to NO_2 stretching. Both the spectra display the same characteristics and hence the membrane properties are retained after metal-PAA treatment.

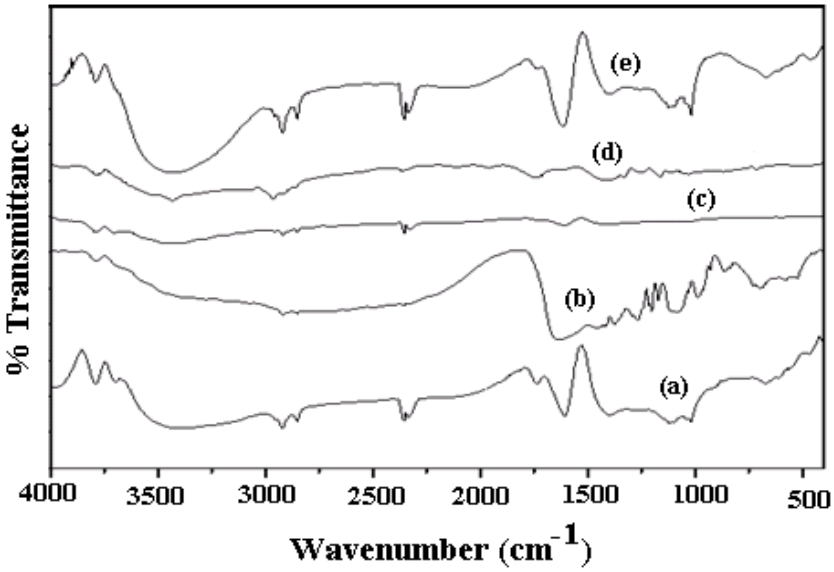

Fig. 10 FTIR spectra of Cellulose nitrate membranes (a) before treatment (b) PAA loaded with Ni (II), (c) Cu (II), (d) Cr (VI) metal ions deposition on cellulose nitrate membrane, (e) after recovery

The FTIR spectra of metal and PAA loaded CN membrane are shown in Fig. 10 (b, c and d). In all the spectra, the free O-H stretch of cellulose occurs close to 3750 cm^{-1}. The O-H stretch of cellulose, water and PAA shows intense peak at 3450 cm^{-1}. Similarly the CH_2 vibrations of CN are clearly seen just below 3000 cm^{-1}. The H_2O bending vibrations and C=O vibration of PAA gives a broad peak at 1630 cm^{-1}. The peaks between 1500 and 1400 cm^{-1} are due to the CH_2 bending modes, NO_2 vibrations, COO vibrations and C-O vibrations. But they are not clearly resolved. From the above FTIR analysis of different membranes, it could be said that the membrane characteristics are preserved after metal treatment.

IV. CONCLUSION

The present work deals with the seperation of Ni^{2+}, Cu^{2+} and Cr^{6+} ions from water sample by metal ion seperation and metal complex seperation method using commercially available nylon and cellulose nitrate membrane filters. PAA and PEG were used as metal complexing agents. The following conclusions were drawn from our study. Both the membranes showed good percentage rejection (80-90%) for all the metal complexes with PAA and PEG. It was shown that the complexation and filtration processes are pH dependent. The metal rejection was more efficient in alkaline condition than in acidic condition. The effect of metal ion separation on membrane filters showed good rejection for both nylon and cellulose nitrate membrane filters. From FT-IR study, it was concluded that there was no chemical change in the membranes after filtration. The SEM study confirmed the retaining property of the nylon membrane. After the separation process the obtained result concluded that nylon membrane was found to be more efficient even after several use. Compared to PEG, the PAA complexing agent (at pH≥ 8) proved to be more effective for the removal of the metal ions, due to bonding process which was more efficient in alkaline condition than in neutral or acidic condition.

ACKNOWLEDGEMENT

The authors would like to thank The Board of Research in Nuclear Sciences (BRNS) and CTDT, Anna University Chennai for their financial assistance to carry out the research work vide letter No. 2007/36/08 – BRNS/597 dated 27.06.2007 and CTDT – 1/RSS/2009 dated 28.06.2009 respectively. The first author acknowledges the CSIR for the Senior Research Fellowship.

REFERENCES

[1] Kurniawan T A, Chan G Y S, Lo W H and Babel S, Physico–chemical treatment techniques for wastewater laden with heavy metals, J Che. Engg., 118 (2006) 83-98.

[2] Council of European Communities, Directive 98/83. On the quality of water intended for human consumption. EC Official J. (1998)

L330.

[3] National primary and secondary drinking water regulations patent by United States environmental protection agency, EPA 816-F-09-004, May 2009.

[4] WHO. Guidelines for drinking-water quality, first addendum to third edition, vol. 1, Recommendations, 3rd ed., WHO, 2006.

[5] Borbely G and Nagy E, Removal of zinc and nickel ions by complexation–membrane filtration process from industrial wastewater, *Desalination*, 240 (2004) 218-226.

[6] Juang R S and Shiau R C, Metal removal from aqueous solutions using chitosan-enhanced membrane filtration, J Membr Sci, 165 (2000) 159-167.

[7] Cervera M L, Arnal M C and Guardia M, Removal of heavy metals by using adsorption on alumina or chitosan, Anal Bioanal Chem, 375 (2003) 820-825.

[8] Llorens J, Pujola M and Sabate J, Separation of cadmium from aqueous streams by polymer enhanced ultrafiltration: a two-phase model for complexation binding, J Membr Sci, 239 (2004) 173-181.

[9] Petrov S and Nenov V, Removal and recovery of copper from wastewater by a complexation-ultrafiltration process, Desalination, 162 (2004) 201-209.

[10] Trivunac K and Stevanovic S, Removal of heavy metal ions from water by complexation-assisted ultrafiltration, Chemosphere, 64 (2006) 486-491.

[11] Muslehiddinoglu J, Uludag Y, Ozbelge H O and Yilmaz L, Effect of operating parameters on selective separation of heavy metals from binary mixtures via polymer enhanced ultrafiltration, J Membr Sci, 140 (1998) 251-266.

[12] Canizares P, Perez A and Camarillo R, Recovery of heavy metals by means of ultrafiltration with water-soluble polymers: calculation of design parameters, Desalination, 144 (2002) 279-285.

[13] Vieira M, Tavares C R, Bergamasco R and Petrus J C C, Application of ultrafiltration-complexation process for metal removal from pulp and paper industry wastewater, J Membr Sci, 194 (2001) 273-276.

[14] Bodzek M, Korus I and Loska K, Application of the hybrid complexation-ultrafiltration process for removal of metal ions from galvanic wastewater, Desalination, 121 (1999) 117-121.

[15] Zhang Y F and Xu Zh L, Study on the Treatment of Industrial Wastewater Containing Pb2+ Ion Using a Coupling Process of Polymer Complexation-Ultrafiltration, Separ Sci Technol, 38 (2003) 1585-1596.

[16] Borbely G and Nagy E, Removal of zinc and nickel ions by complexation–membrane filtration process from industrial wastewater, Desalination, 240 (2009) 218-226.

[17] M.E. Campderrós, A. Acosta, and J. Marchese, Selective separation of copper with Lix 864 in a hollow fiber module, Talanta, 47 (1998) 19-24.

[18] Korus I, Bodzek M and Loska K, Removal of zinc and nickel ions from aqueous solutions by means of the hybrid complexation–ultrafiltration process, Sep Purif Technol, 17 (1999) 111-116.

[19] Lee J and Walker H W, Effect of Process Variables and Natural Organic Matter on Removal of Microcystin-LR by PAC−UF, J Environ Sci Technol, 40 (2006) 7336-7342.

[20] Preetha B and Viruthagiri T, Bioaccumulation of chromium(VI), copper(II) and nickel(II) ions by growing Rhizopus arrhizus, J *Biochem Eng*, 34 (2007) 131-135.