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Size Enhanced Ultrafiltration: A Novel Hybrid Membrane Process for the Removal and Recovery of Heavy Metal Contaminants.

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ABSTRACT

Copper and nickel metals have a diversity of applications in industries, and these metals are not a waste to be disposed of through effluents, but the wealth to be recovered for reuse. Moreover, their presence in water bodies causes adverse health impacts to living organisms. The present study utilizes ultrafiltration set up equipped with a 50,000Da polyethersulfone (PES) membrane for the separation and recovery of Cu(II) and Ni(II) from aqueous solutions. Water soluble polymers such as carboxymethyl cellulose (CMC), polyethylenimine (PEI), polyacrylic acid (PAA) are used as size enhancing agents. The experiments were conducted to analyze the effect of pH, polymer to metal loading ratio, and removal of metal. Mechanism of metal-polymer interaction is discussed in detail. The characteristics of complexing species before and after complexation were studied using EDX, SEM, and FTIR.
Keywords: Cu(II), Heavy metals, Ni(II), Size enhanced ultrafiltration, Ultrafiltration.

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INTRODUCTION

On a global scale, only a part of the wastewater is treated for reuse. The wastewater, from various process industries contains the valuable components which are just disposed of after the treatment. The major and unique toxic elements present in wastewater are copper, nickel, zinc, cadmium, chromium, etc. Copper finds its usage mostly in the manufacture of alloys, paints, ceramics and pesticides. Also, it is used in the electroplating industry. Nickel is mainly used to make stainless steel. Also, nickel found applications in food processing and dyeing industries. The recovery of heavy metals such as Cu(II) and Ni(II) from industrial effluents is important not only in the aspect of recovering the metal and also to prevent its adverse effect on living organisms. In accordance with World Health Organization, the maximum permissible limit of copper and nickel in drinking water is 0.05 and 0.01 mg/L respectively [1].

The existing conventional processes such as chemical precipitation, coagulation, adsorption, ion exchange are not adequate to address this problem because of the limitations like sludge disposal, higher cost/energy, and significant space requirements. In recent years, size enhanced ultrafiltration (SEUF) established as a promising approach to focus selective removal and recovery of pollutants such as heavy metals. It also ensures the reuse of water. SEUF is an alternative approach to precipitation, coagulation, ion exchange and adsorption process for the removal of Cu(II) and Ni(II) ions because of its following advantages: (i) The entire functional groups present in the ligands could be utilized, (ii) the contact time required is less and (iii) large volume water could be treated within a short period of time.

Cellulose [2-3], PES [4-5], polyvinylidene fluoride (PVDF) [6] and ceramic membranes [7] are the widely used ultrafiltration membranes for the size enhanced ultrafiltration technique. The different combinations of membrane/complexing agent have been reported for the removal of copper and nickel from wastewater. PES (10,000 and 30,000 Da)/PEI [8], acryl - nitryl copolymer (10,000 Da)/CMC [9], PES (10,000 Da)/CMC [10], PES (30,000 Da)/sodium polyacrylate [11], PES (30,000 Da)/PEI [11], Iris (10,000 and 30,000 Da)/PEI [12] are some of the combinations of membranes (with various molecular weight cut-off) and complexing agents reported in the literature for the removal and recovery of Cu(II) or Ni(II).

The present study utilized 50,000 Da PES membrane for the removal of Cu(II) and Ni(II) ions. The polymers used as complexing agents were CMC, PEI and PAA. The Continuous process ultrafiltration experiments were conducted to analyze the effect of pH, polymer to metal loading ratio, and the removal of metal. The characteristics of polymer before and after complexation were studied using EDX, SEM, and FTIR. Mechanism of complexation between metal and polymer were discussed in detail.

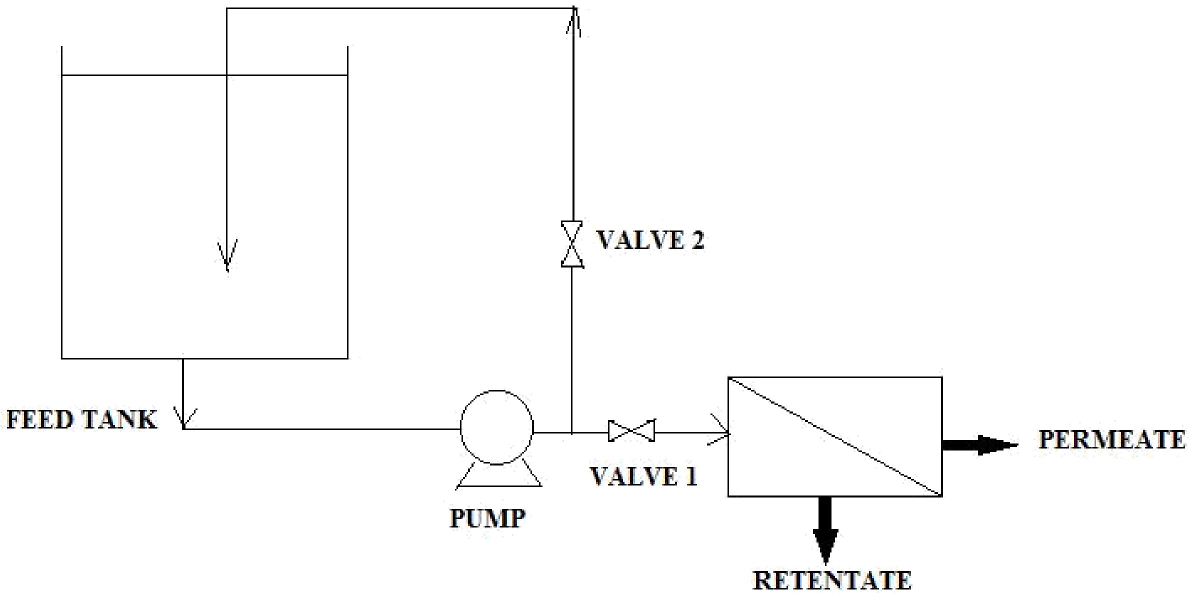
MATERIALS AND METHODS

Materials

$CuSO_4.5H_2O$ and $NiSO_4.6H_2O$ were used to prepare stock solutions (1000 mg/L) of Cu(II) and Ni(II) respectively. The Cu(II) and Ni(II) solutions used in the experiments were prepared using the requisite volume of the stock solution. The Size enhanced ulltrafiltration experiments were carried out with CMC (supplied by RANKEM, molecular weight is 90,000 – 250,000) , PEI (supplied by HIMEDIA, molecular weight is 50,000-1,00,000) and PAA (supplied by Alfa Aesar, molecular weight is 130,000 – 30,00,000). Capillary membrane elements of MWCO 50,000Da polyethersulfone UF modules were procured from M/s Davey Products, Chennai and cylindrically coated domestic polyethersulfone UF membrane from M/s Rupali Industries, Mumbai. All the chemicals used were of analytical grade. All the experimental runs were done using RO purified water.

Experimental set up

The experimental scheme used is shown in Scheme 1. It consisted of an ultrafiltration system, to which feed of desired concentration mixed with the complexing agent was pumped in. Permeate from the membrane was collected separately. The flow rate of permeate and retentate were measured manually. The cylindrically coated domestic PES ultrafiltration (UF) membrane with a diameter of 0.054 m, a length of 0.27 m and membrane area of 0.5 m^2 was used. The experiments were carried out at a pumping pressure of 0.2 MPa and the feed flow rate was manipulated to provide the desired flow rate to the UF system.



Scheme 1: The Schematic diagram of experimental setup

Experimental procedure

A series of 5 L of aqueous solutions with metal and polymer ratio of 1,2,4,6 (weight ratio) were prepared and taken in the feed tank. pH of the solution was adjusted to 4,6,8 and 10 using 0.1 M NaOH and 0.1 M HCl. The experiments were carried out at a pressure of 0.2 MPa. After circulating the solution for 10 min, the permeate sample was collected and analyzed using Atomic Absorption Spectrophotometer (AAS).

The rejection rate *R* is calculated using the given Eqn. 1.

$$\%R = \left(1 - \frac{C_p}{C_f}\right) x100 \qquad (1)$$

where C_f = feed concentration, C_p = permeate concentration

The rejection rate is the measure to find out the separation capability of a membrane.

Loading ratio (L) is calculated by Eqn. 2 to indicate the concentration ratio of polymer to metal ion [11].

$$L = C_{Polymer} / C_f \qquad (2)$$

where $C_{polymer}$ = polymer concentration

RESULTS AND DISCUSSION

The Effect of pH

The most important factor in the interaction of the metal ion with the polymer is pH. The stability of the metal complex depends on pH. The pH influence on the interaction of metal – polymer varies significantly from metal to metal. This can be utilized for the selective separation of metals.

The Effect of pH on the retention of metal using CMC

Cu(II) and Ni(II) removal using CMC were carried out by varying the pH of solutions. A series of aqueous solutions (5 L) with CMC/Cu(II) loading ratio (weight ratio) of 2, 4 and 6 were prepared. For each ratio, pH of the solution was adjusted as 4, 6, 8 and 10. The solution was passed through a PES ultrafiltration membrane at a pumping pressure of 0.2 MPa. As a whole, 12 samples of Cu(II)/CMC solutions were pumped. Permeate was collected to analyze the Cu(II) ion concentration using AAS. To study the effect of pH on Ni(II) removal, a series of aqueous solutions (5 L) with a CMC/Ni(II) loading ratio (weight ratio) of 1, 2 and 4 were prepared, and pH of the solutions was adjusted as 4, 6, 8 and 10. Ultrafiltration experiments were carried out using Ni(II)/CMC solutions as explained for Cu(II) removal studies. The effect of pH on the rejection of Cu(II) from aqueous solutions using CMC is shown in Figure 1 and the rejection of Ni(II) is shown in Figure 2. From the results, it was observed that the rejection rate was increased with the increase in pH and the optimum pH was found to be 8. At acidic pH, the carboxymethyl end could exist more as $–CH_2–COOH$. But at pH 8 and above, the carboxymethyl end present in CMC could exist more as $–CH_2–COO^–$ and results in more ionic interaction between the metal ion and CMC. At optimum pH of 8, the Cu(II) rejection was 99% irrespective of CMC/Cu(II) loading ratio. Similarly, at pH 8, Ni(II) rejection was 93% in all the studied CMC/Ni(II) ratio. This proves the ionic interaction of metal ions with CMC. Though CMC concentration is high, the available $–CH_2–COO^–$ influences maximum rejection.

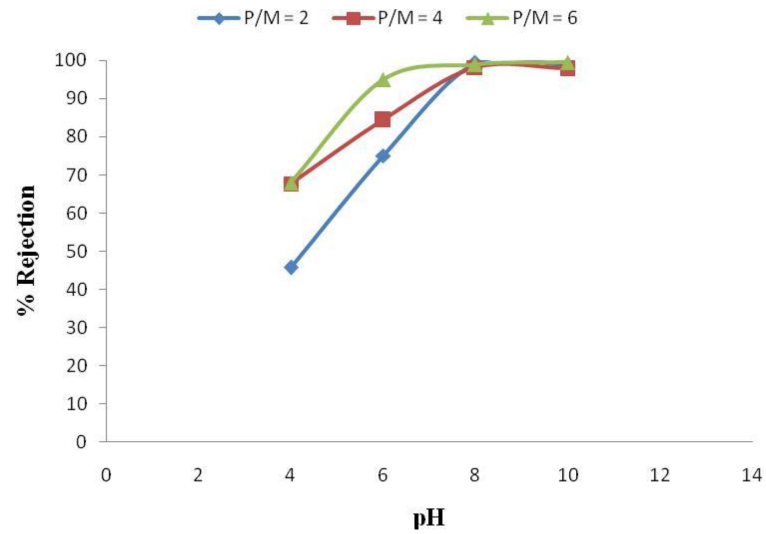


Figure 1: Rejection of Cu(II) with CMC complex

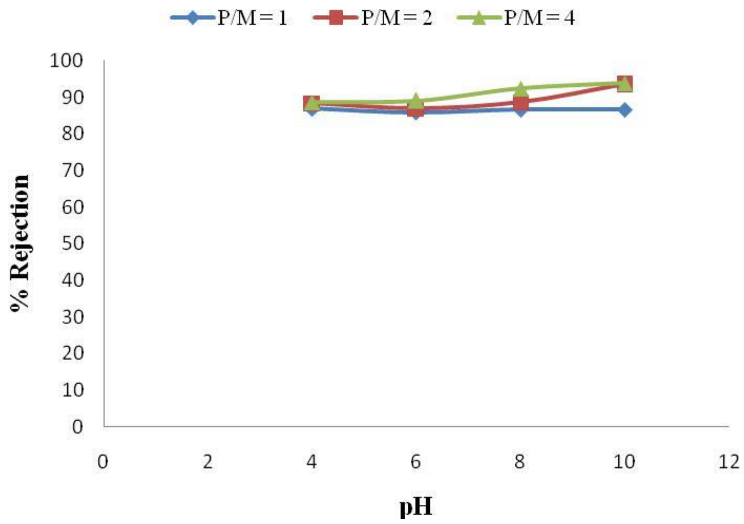


Figure 2: Rejection of Ni(II) with CMC complex

The Effect of solution pH on the retention of metal using PEI

The effect of pH on the rejection of Cu(II) from aqueous solutions using PEI is shown in Figure 3 and Ni(II) is shown in Figure 4. The maximum Cu(II) rejection observed using PEI was 96% at the optimum pH 8 with a PEI/Cu(II) loading ratio of 6. The maximum Ni(II) rejection was 87% at the optimum pH of 8 with a PEI/Ni(II) loading ratio of 4. This is different from what we observed using CMC. PEI is able to form a complex with metal ions easily due to the presence of –NH. As the concentration of PEI increases, the availability of chelation site increases. At acidic pH, the possibility of protonation of –NH is high which reduces the possibility of chelation with metals. At higher pH, –NH is readily available without getting protonated, and therefore increases the metal coordination sites.

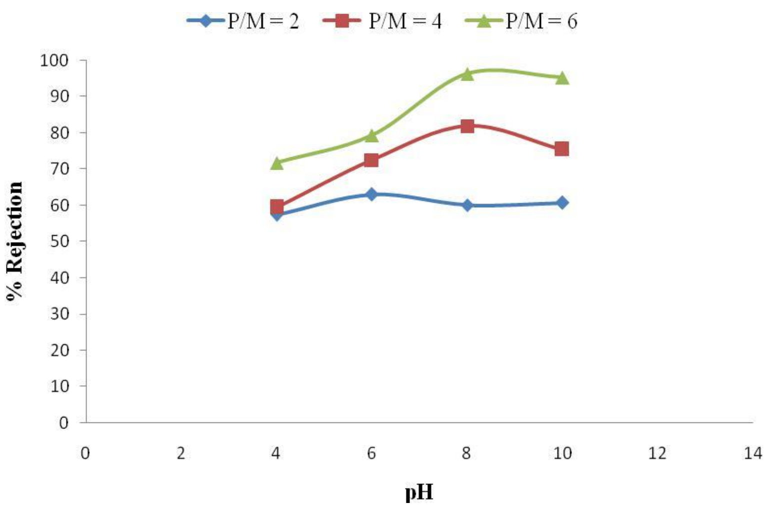


Figure 3: Rejection of Cu(II) with PEI complex

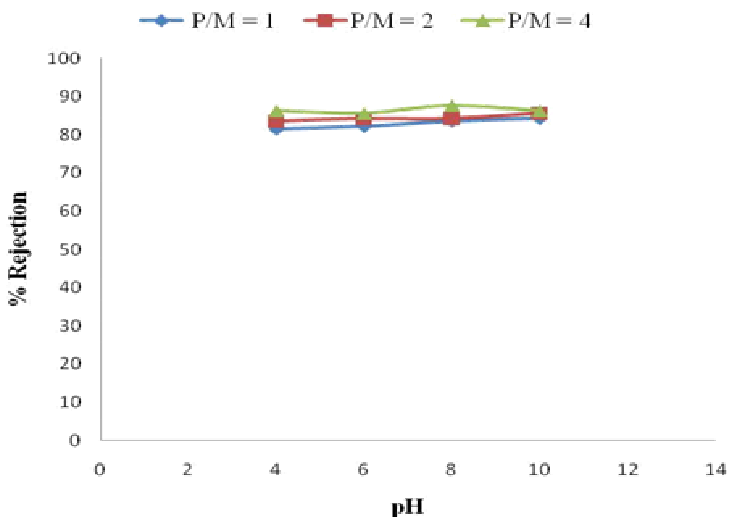


Figure 4: Rejection of Ni(II) with PEI complex

The Effect of solution pH on the retention of metal using PAA

The effect of pH on the rejection of Ni(II) from aqueous solutions using PAA is shown in Figure 5. It was observed that the % rejection was increased with the increase in pH. As the pH increases, the availability of carboxylate ion present in PAA increases. So, PAA could retain metal ions more at higher basic pH.

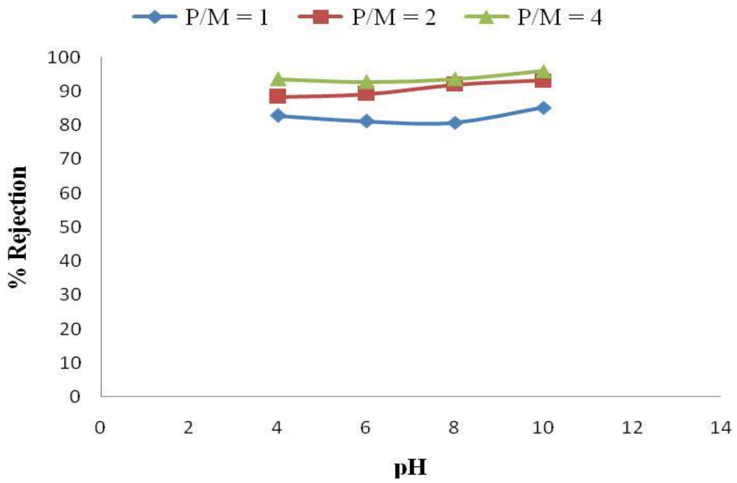


Figure 5: Rejection of Ni(II) with PAA complex

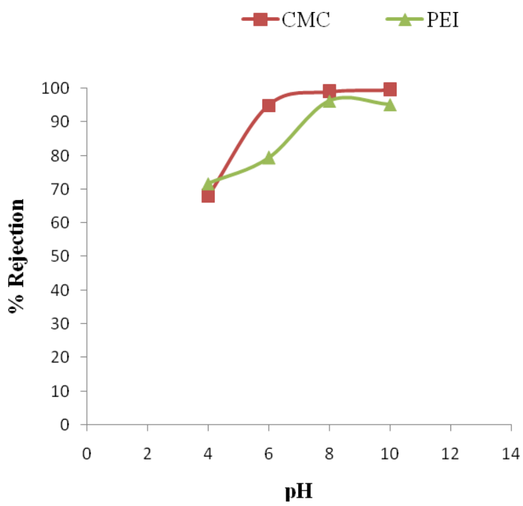


Figure 6: The Rejection of Cu(II) with CMC and PEI at a optimum loading ratio

The Effect of metal/polymer ratio on complexation ultrafiltration

It was observed that, with increase in the loading ratio the rejection rate increases. The stability of the metal-polymer complex depends on metal concentration and polymer concentration. As the polymer to metal ratio increases, the rejection capacity also increases. The complex formation reaction can be written as

$$[M(H_2O)_n] + L \leftrightarrow [M(H_2O)_{n-1}L] + H_2O \quad (3)$$

The complex formation depends upon the stability constant. The stability of the complex is more for higher values of the stability constant. The stability constant k is given by the following Eqn. 4

$$k = \frac{[M(H_2O)_{n-1}L][H_2O]}{[M(H_2O)_n][L]} \quad (4)$$

The maximum rejection of 99.5% was achieved by using CMC for Cu(II) at a loading ratio 6 as shown in Figure 1 and the maximum rejection of 93.7% was obtained for Ni(II) at a loading ratio 4 as illustrated in Figure

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2. The maximum rejection of 96% was obtained by PEI for Cu(II) at a loading ratio 6 as illustrated in Figure 3 and the maximum rejection of 86.3% was achieved for Ni(II) at a loading ratio 4 as shown in Figure 4. The loading ratio of PAA/Ni(II) required to attain the maximum rejection of 96% for Ni(II) was 4 as shown in Figure 5. Based on the literature, the maximum rejection was obtained by using the lower molecular weight cut-off membrane with higher loading rate as shown in Table 1. In this study, it was observed that using the PES membrane (50,000 Da), maximum rejection was obtained with CMC at a loading rate of 6. The rejection of Cu(II) using CMC and PEI at an optimum loading ratio is shown in Figure 6 and Ni(II) using CMC,PEI, and PAA is illustrated in Figure 7.

Table 1: Size enhanced metal removal studies using different ultrafiltration membranes

Polymer	Metal (Concentration)	Membrane	Molecular weight cut-off, Da	Loading rate	% rejection	Reference
PEI	Ni(II) (50 mg/L)	Iris	10,000	3	97.82	[12]
PEI	Cu(II) (50 mg/L)	Iris	10,000	3	96.72	
PEI	Ni(II) (50 mg/L)	Iris	30,000	3	100	
PEI	Cu(II) (50 mg/L)	Iris	30,000	3	94.39	
CMC	Cu(II) (10 mg/L)	PES	10,000	100	97.6	[10]
CMC	Ni(II) (10 mg/L)	PES	10,000	100	99.1	
CMC	Cu(II) (10 mg/L)	UF – 10PAN	10,000	6	97.1	[9]
CMC	Ni(II) (10 mg/L)	UF – 10PAN	10,000	6	92.1	
PAA	Cu(II) (100 mg/L)	-	5000	3	99.9	[3]

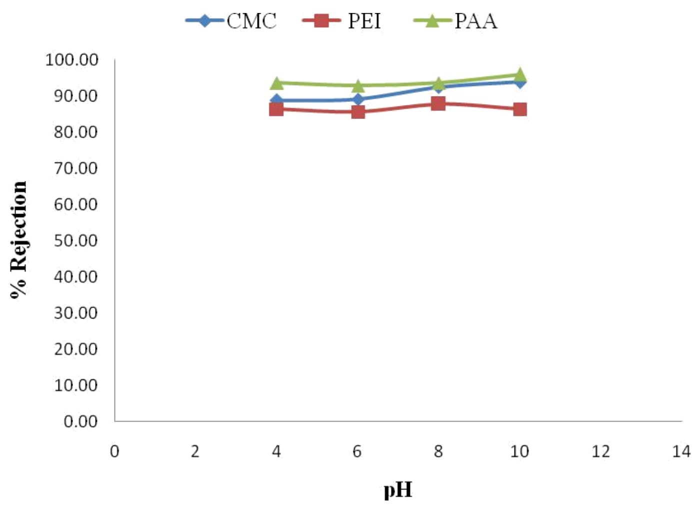

Figure 7: The Rejection of Ni(II) with CMC, PEI and PAA at a optimum loading ratio

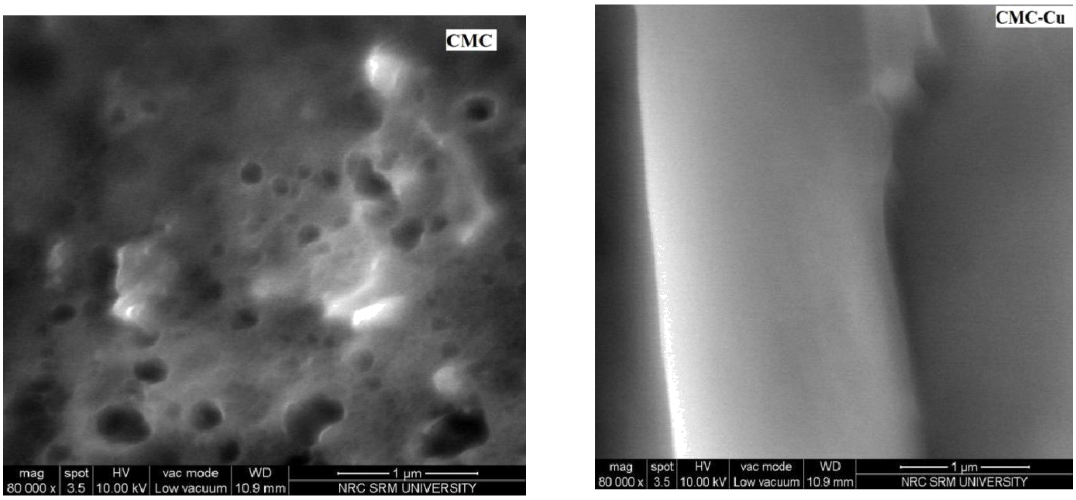

Figure 8: (a) SEM Image of CMC and (b) CMC-Cu(II)

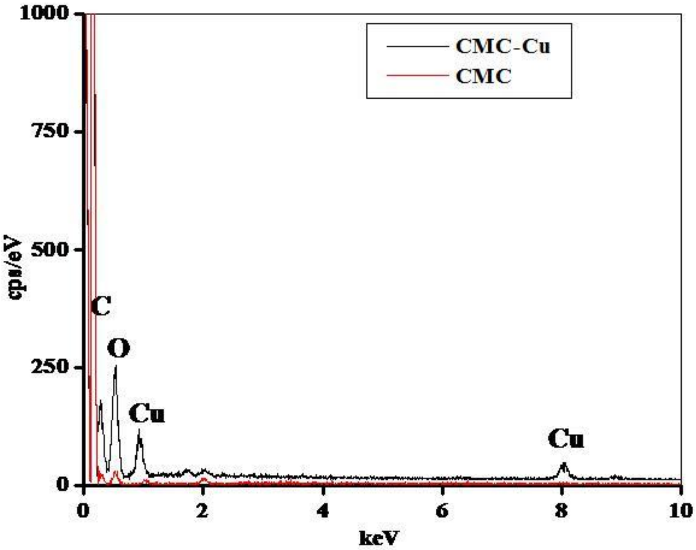

Figure 9: EDX spectra of CMC and CMC/Cu(II)

Surface morphology

The morphology of CMC before and after making the complex with Cu(II) was analyzed by scanning electron microscope (SEM) with field emission operating at 10kV. The CMC-Cu complex deposited on the surface of a PES membrane was collected and dried at room temperature. The SEM image of CMC and CMC-Cu(II) complex is shown in the Figure 8 a and b. SEM image of CMC indicates that the surface is porous in nature. After complexation with Cu(II), morphology was entirely modified, and it is illustrated in the SEM image of CMC-Cu.

EDX Analysis

EDX spectra of CMC before and after complexation with Cu(II) ion is shown in Figure 9 The EDX spectra of CMC gives the peaks specific to C, O and N elements. It was also observed that Cu peak appeared after complexation with Cu(II) ions.

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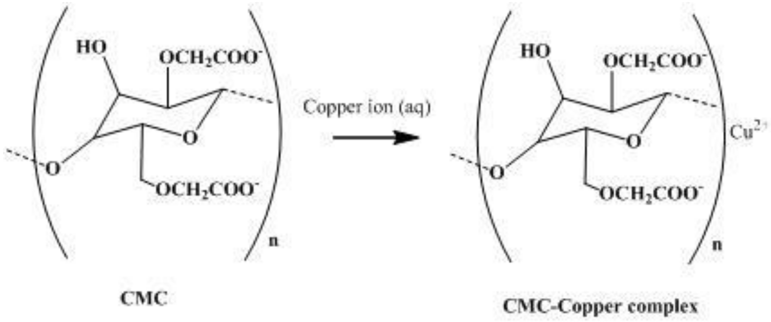
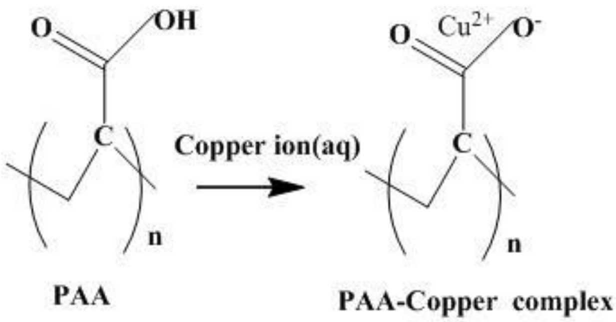
Mechanism of polymer-metal interaction

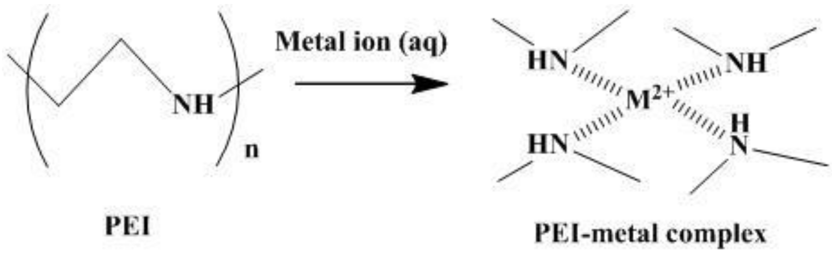
Cu(II) and Ni(II) are bonded to polymers CMC, PEI and PAA strongly through ionic interaction as well as chelation. CMC and PAA consist of –COOH group (–COONa in its salt form). The free $–COO^{-}$ sites strongly bind with the metal ions in the pH ranges studied (pH 4 to 10). This polymer-metal interaction enables the separation and recovery of metal by ultrafiltration. The schematic representations of CMC and PAA interaction with Cu(II) are given in Scheme 2 and 3 respectively.



Scheme 2: Separation mechanism of Cu(II) using CMC



Scheme 3: Separation mechanism of Cu(II) using PAA



Scheme 4: Separation mechanism of metal using PEI

The interaction between PEI and Cu(II) or Ni(II) is through chelation. The imine consists of – NH– in its structure. The possible PEI-metal chelation is depicted in Scheme 4.

CONCLUSIONS

Cu(II) and Ni(II) ion retention studies were carried out using 50,000 Da PES membrane. Water soluble polymers viz CMC, PEI, and PAA were used as the complexing agent. CMC and PAA bound to the metals through ionic interactions. PEI forms a complex with the metals. The maximum Cu(II) removal was observed as 99.5% using CMC with a loading ratio of 6. The maximum Ni(II) removal of 96% was attained using PAA in a loading ratio of 4. SEM images of polymer surface before and after complexation were analyzed. It had shown the entire physical change of polymer after the complexation-filtration process. Further studies are in progress to separate the metal from the retained polymer and to regain the polymer.

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