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# Synthesis and Characterization of Polymer Metal Complexes of Cu (II) and Zn (II) with NNMBA Cross-Linked Polyacrylamide Supported L-Aspartic Acid and L-Lysine

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**Abstract**

Crosslinked polymers with specific properties are widely used as catalyst supports as they are inert, non toxic and non volatile and offer advantageous features of heterogeneous catalysis such as thermal stability, selectivity and recyclability to homogeneous system. The ease of separation from the reaction products lead to operational flexibility. Moreover the amount of metal present on the surface of such catalyst is very small which is of economic significance in the case of expensive metals. Metal ion binding properties of transition metal ions Cu (II) and Zn (II) with amino acids L-Aspartic acid (L-Asp) and L-Lysine (L-Lys) supported 2 mol % N,N'-methylene bisacrylamide (NNMBA) crosslinked polyacrylamide have been studied. The swelling studies reveal that they are highly hydrophilic polymeric ligands. The characterization of the polymer, transamidated polymer, and the polymer metal complexes were done by Infra Red (IR), Ultra Violet (UV) and Scanning Electron Microscope (SEM) analysis. From carboxyl capacity measurements, SEM analysis and swelling studies it was established that the more complexation of the metal ion is found with the ligand L-Aspartic acid

**Key words:** polymer - metal complex, polyacrylamide, L-Aspartic acid, L-Lysine, metal-ion binding.

## 1. INTRODUCTION

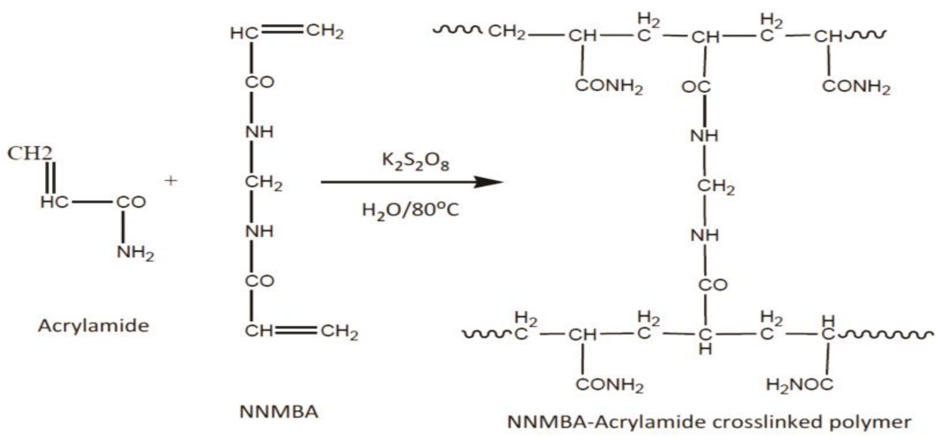
Crosslinked polymers with specific properties are widely used as catalyst supports as they are inert, non toxic and non volatile and offer advantageous features of heterogeneous catalysis such as thermal stability, selectivity and recyclability to homogeneous system[1-3] .The ease of separation from the reaction products leads to operational flexibility[4-7]. Moreover the amount of metal present on the surface of such catalyst is very small which is of economic significance in the case of expensive metals[8].The applications of polymer metal complexes in the field of catalysis have been widely investigated [9-13]. The interaction of transition metal ions with biologically active molecules is of utmost interest[14-16]. Many studies have been devoted with the interaction of metal ions with amino acids[17]. Amino acids are good chelating agents and can coordinate to transition metal ions through their amino or carboxyl groups. The present paper reports the metal ion binding properties of Cu (II) and Zn (II) ions with L-Aspartic acid and L-Lysine complexed 2 mol % NNMBA crosslinked polyacrylamide. Swelling studies of cross linked polymer, ligand attached polymer and metal attached polymer were also described.

## 2. MATERIALS AND METHODS

All reagents were provided by sigma Aldrich Company. The UV-vis spectra were recorded on a Shimadzu 160-A spectrometer. The FTIR spectra were recorded on a Bruker IFS-55 spectrometer using KBr pellets. SEM photographs were taken using a Hitachi S- 2400 instrument.

**Synthesis of 2 mol % NNMBA crosslinked polyacrylamide**

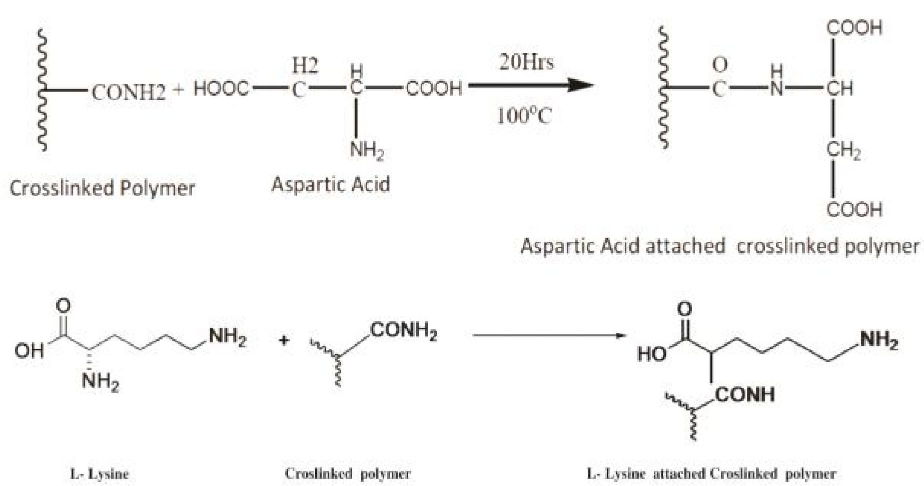
2 mol % NNMBA crosslinked polymers were obtained by dissolving acrylamide (14.0g) and NNMBA (0.6g) in 100 ml water. Potassium persulphate (100.0mg) was added and the mixture was heated at $80^0$C with stirring until the polymer precipitated. 80 ml water was added and the mixture was again heated at $80^0$ C for 30 min. The lumps were powdered, washed with water, ethanol and methanol and dried at $70^0$c. The yield of the crosslinked polymer obtained was 14.36 g.




**Scheme 1:** Polymerisation reaction between acrylamide and NNMBA

**Transamidation of NNMBA cross-linked polyacrylamide with sodium salt of amino acids**

2.5g polyacrylamide was heated with sodium salt of amino acid (L-Aspartic acid/L-Lysine 5.0g and NaOH 2.66g in 50 ml water) at $100^0$c for 20 hrs. The reaction mixture was poured in to water containing crushed ice. The functionalized polymers were collected by filtration, soxhleted using methanol and acetone, and dried at $50^0$c.




**Scheme 2:** Transamidation of cross-linked polymer

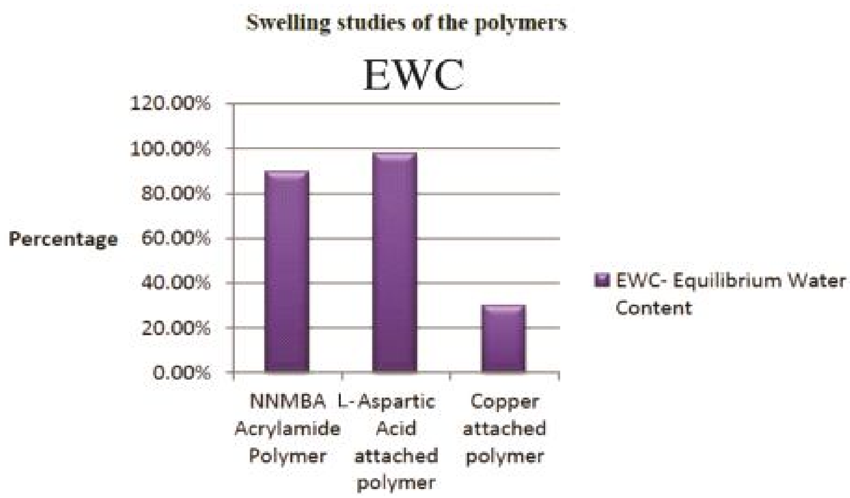
**Estimation of carboxyl capacity**
The carboxylate polymers (100mg) were equilibrated with HCl (0.2N, 10 ml) by stirring for 24 hrs. The resin samples were filtered and the filtrate was titrated against NaOH (0.2N) to a phenolphthalein end point
.

**Complexation of metal ions with 2 mol % NNMBA crosslinked poly acryl amide supported amino acid.**
Stirr the cross-linked carboxylate polymer (100.0mg) with metal salt solution $CuSO_4$ /$ZnSO_4$ (0.05N, 50ml) for 24 hrs. The complexed resins were collected by filtration, washed with distilled water to remove uncomplexed metal ions and dried.

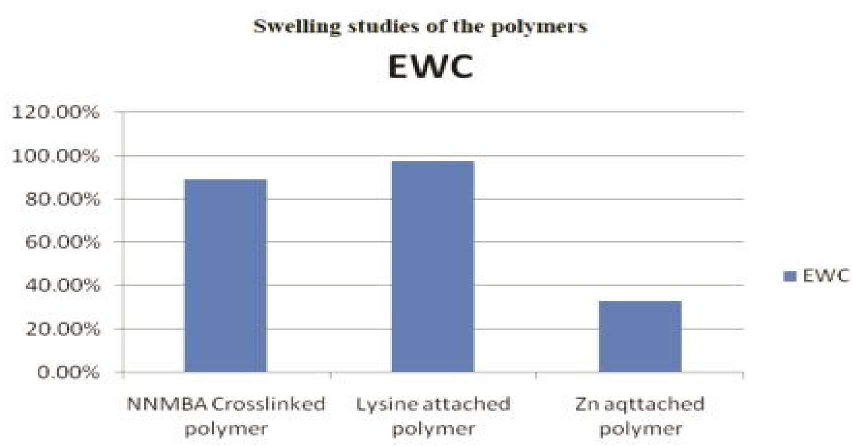
**Swelling studies**
Each of the different polymers (100 mg) was equilibrated with 50 ml distilled water for 48 hrs. The swollen resins were collected by filtration and weight was determined. The samples were dried in vacuum and weighed. From the swollen and the dry weights of the samples the equilibrium water content (EWC) was calculated using the expression

EWC =Wt. of wet resin–Wt. of dry resin X100/ Wt. of wet resin

The swelling studies are given in the Graph 1 & 2. The swellings of the complexed resins are lower than those of the uncomplexed resins. This reduction arises from crosslinking by complexation with metal ions, resulting in decreased intake of the solvent [18].




**Graph 1:**




**Graph 2:**

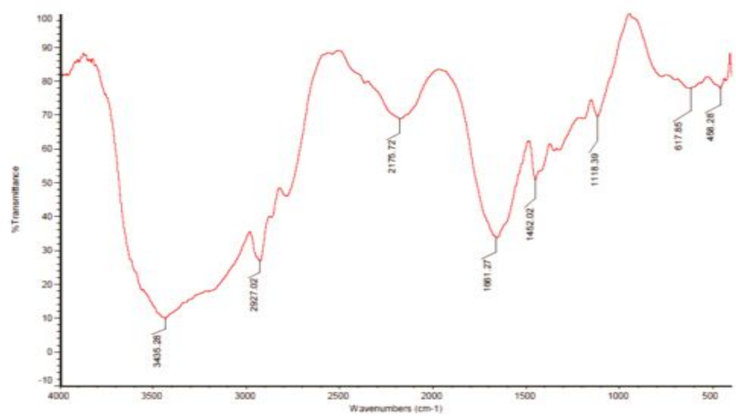
## 3. RESULTS AND DISCUSSION

The polymerization reaction is depicted in scheme 1. Amino functions were introduced in to 2 mol % NNMBA crosslinked polyacrylamide by transamidation with L-Aspartic acid /L-L Lysine. It is represented in scheme 2. The carboxyl capacity of 2 mol % NNMBA crosslinked transamidated polymers were obtained by alkali titration and was found to be 4.25 and 3.08 mmol/g for the L-Aspartic acid and L-Lysine attached polymers respectively. The less rigidity and polarity of the NNMBA crosslinking favours the polar transamidation with the sodium salt of L-Aspartic acid and L-Lysine. The metal ion complexation of the L-Aspartic acid and L-Lysine functions in different structural environments were investigated towards Cu (II) and Zn (II) ions.

### Characterization

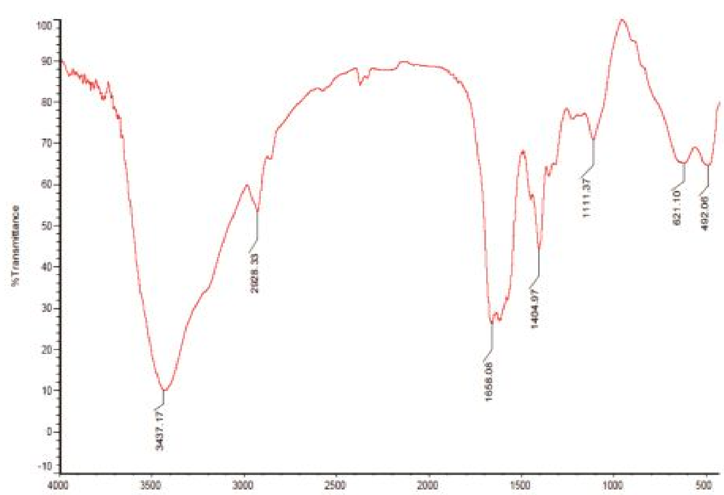
### FTIR spectra

The IR spectra of NNMBA cross linked polyacrylamide showed absorptions characteristics of the amide NH and C=O at 3453 $cm^{-1}$ and 1661$cm^{-1}$(Figure1) respectively. In the functionalized polymer, the Aspartic acid attached polymer absorbs strongly at 1658 $cm^{-1}$and Lysine attached polymer absorbs at 1564 $cm^{-1}$ (Figure 2&4) respectively. During complexation, the carboxylate group shift to 1566$cm^{-1}$and 1576$cm^{-1}$ (Figure3&5) indicating complexation with the metal ions Cu (II) and Zn (II) respectively.



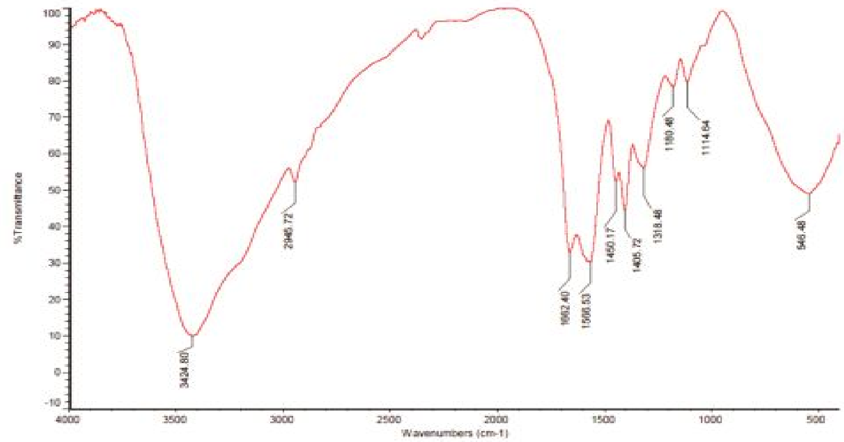

IR spectra of 2 mol % NNMBA crosslinked poly acryl amaide

**Figure 1:**



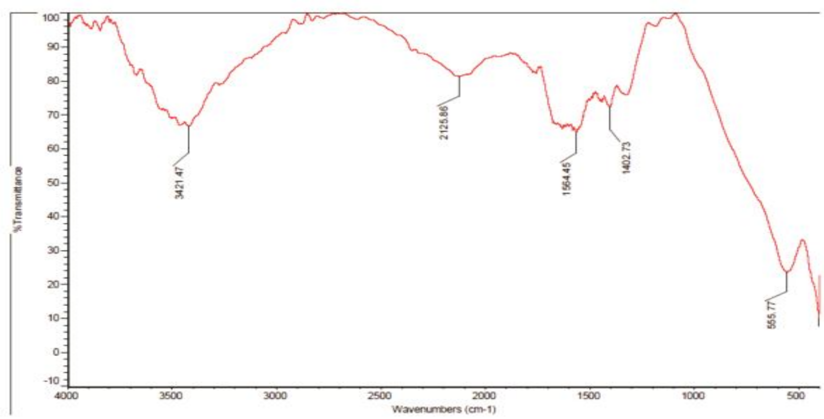

IR spectra of L-aspartic acid functionalised crosslinked polymer

**Figure 2:**



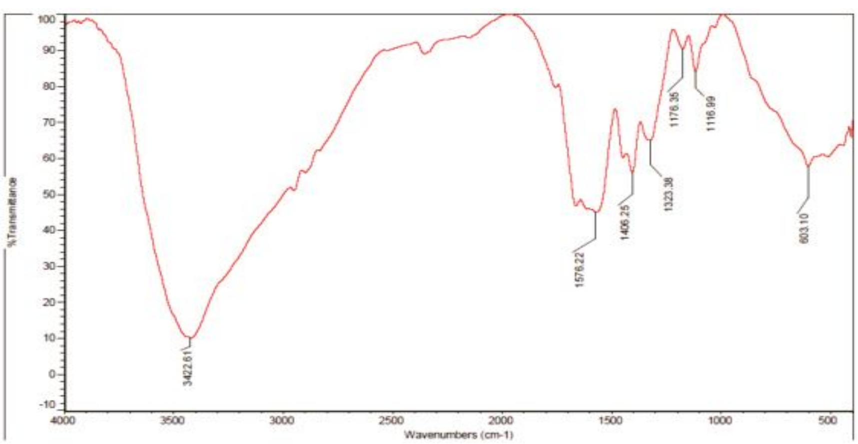

IR spectra of Cu (II) ion Complexed polymer

**Figure 3:**




IR spectra of L-Lysine functionalised crosslinked polymer

**Figure 4:**

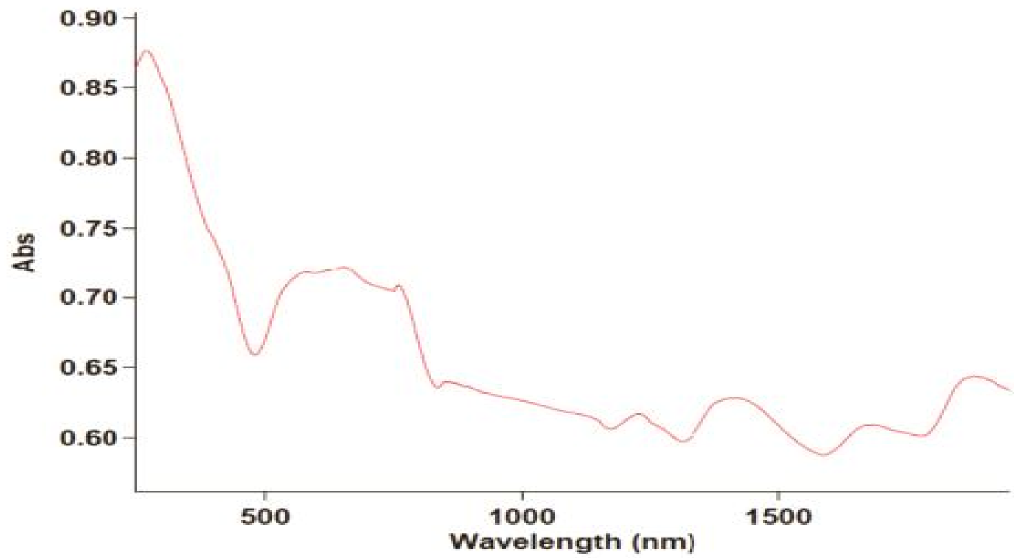



IR spectra of Zn(II) Complexed polymer

**Figure 5:**

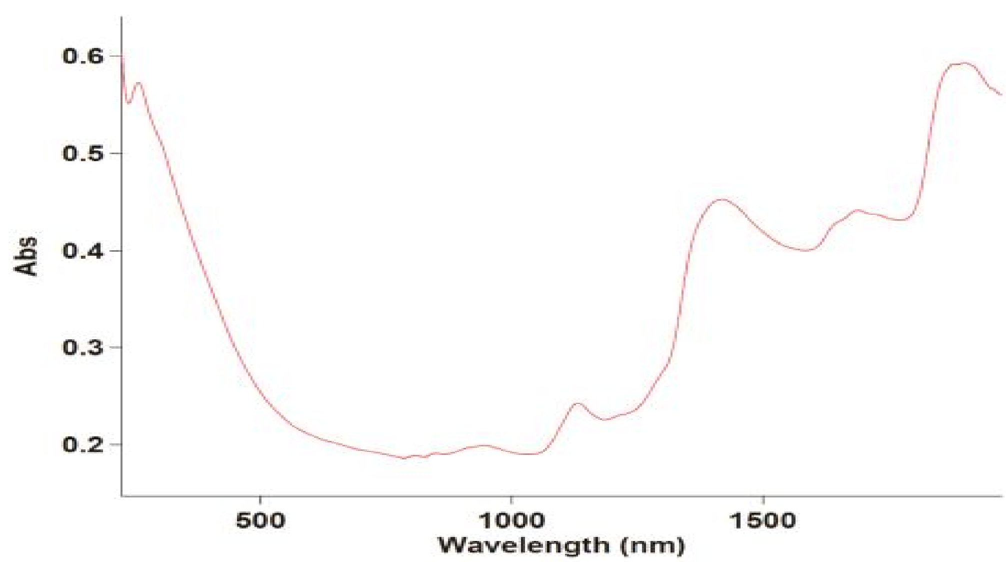
**UV-vis spectra**

The UV-vis spectra of the Cu (II) and Zn (II) complexes of 2 mol % NNMBA cross linked polyacrylamide supported Aspartic acid and Lysine are given in Figure 6 & 7. The peaks in the range 274 nm and 257 nm indicate the attachment of Cu (II) and Zn (II) with the polymeric ligand.




UV- visible spectra of copper complexed polymer

**Figure 6:**

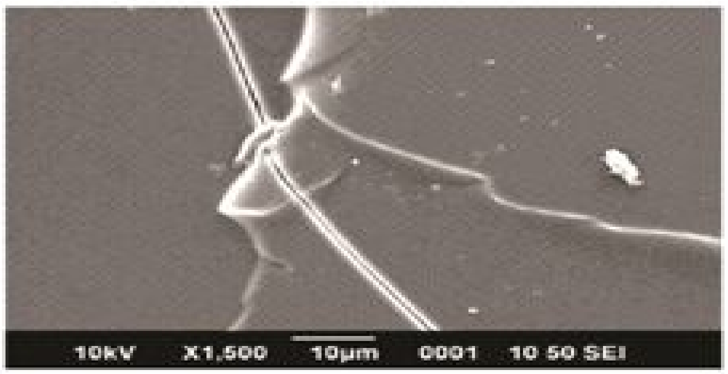



UV- visible spectra of Zinc complexed polymer

**Figure 7:**

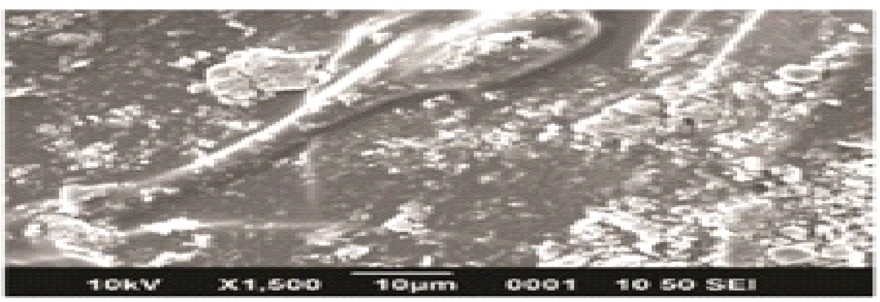
**SEM**

SEM is the most widely used technique to study the shape, size, morphology, and porosity of polymers[19]. The change in the surface morphology of the polymeric ligands on metal ion complexation was investigated using this technique. In the present work SEM was used to probe the change in morphological features of the NNMBA crosslinked polyacrylamide supported Aspartic acid and Lysine. The SEM of uncomplexed resins has smooth surfaces (Figure 8, 9&11). In the complexed resin, surface become rough and rigid[20] (Figure 10&12).This is from the contraction of the polymer matrix by the cooperative contribution of the ligands for complexation with the Cu (II) /Zn (II) ion.



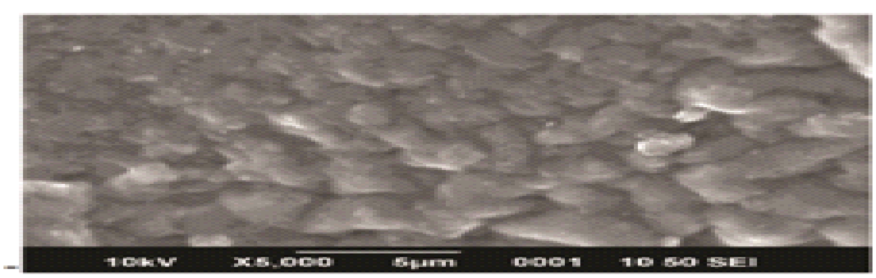

SEM of Acrylamide - NNMBA Polymer

**Figure 8:**



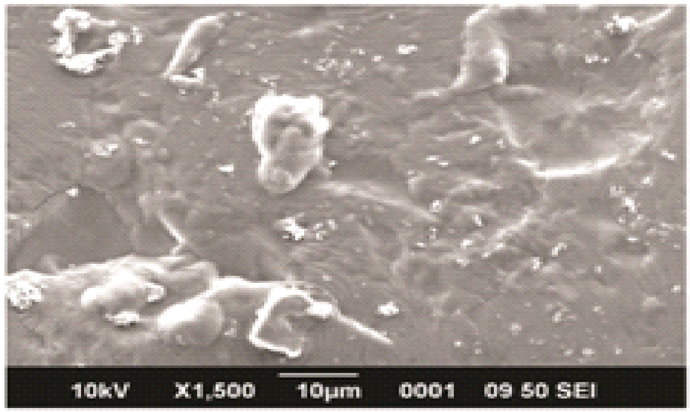

SEM of Aspartic Acid Attached Acrylamide – NNMBA Polymer

**Figure 9:**



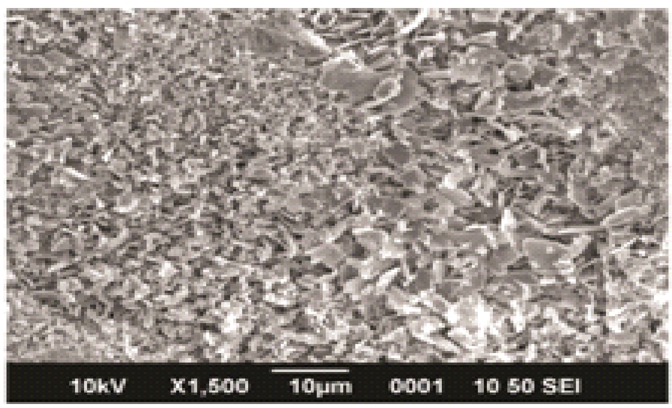

SEM of NNMBA cross linked L-aspartic acid functionalised Cu(II) attached polymer

**Figure 10:**




SEM of NNMBA cross linked Lysine functionalised polymer

**Figure 11:**




SEM of NNMBA cross linked L-Lysine functionalised Zn(II) attached polymer

**Figure 12:**

## 4. CONCLUSION

Two percentage NNMBA crosslinked polyacrylamide has been synthesized. Ligand functions were introduced into crosslinked polymer by transamidation with L-Aspartic acid and L-Lysine. The metal ion complexation of the L-Aspartic acid and L-Lysine functions were investigated towards Cu (II) and Zn (II) ions. The interaction of transition metal ions with biologically active molecules like amino acids is of utmost interest because they can be used as representative model systems to understand the metal-protein interaction in biological systems. Amino acids are good chelating agents and can coordinate to transition metal ions through their amino or carboxyl groups. Swelling studies, characterization and morphological studies of the crosslinked polymer, transamidated polymer and the Cu (II) / Zn (II) complexed polymers were carried out. The decrease in degree of swelling of metal complexed polymer establishes an effective complexation of metal ion with the ligands. From SEM analysis it is clear that the surface of complexed resin becomes more rough and rigid compared to uncomplexed resin. We have obtained greater carboxyl capacity value for Aspartic acid than Lysine attached polymer, indicating more complexation associated with the ligand Aspartic acid. From swelling studies and SEM analysis also it was established that the more complexation of the metal ion is found with the ligand L-Aspartic acid.

## 5. ACKNOWLEDGEMENT

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