Radiation Syntheses of Molecularly Imprinted Polymer for Metal Ion Selective Separation

H. Kamal, H.A. Abd El-Rehim, Y.F. Al-Qudah and E.A. Hegazy

National Centre for Radiation Research and Technology. P.O. Box 29, Nasr City, Cairo, Egypt.

ABSTRACT

The copolymer metal complexes in the form of imprinted polymers were prepared from Poly (vinyl alcohol) (PVA), Acrylic acid (AAc), Acrylamide (AAm) and 2-Acrylamido-2-methyl propane sulfonic acid (AMPS) monomers irradiated in presence of different metal ions and crosslinking agent. Characteristics and some properties of the prepared imprinted and grafted polymers were investigated. Also the possibility of their applications in various fields can be determined using atomic absorption (AA), inductive coupled plasma (ICP), X-ray fluorescence (XRF) and UV- spectrophotometer.

Keywords: Radiation, Imprinted polymer, metal ions, selective separation

1-INTRODUCTION

The synthesis of highly specific molecular imprinted polymers has been the goal of many research groups in the past decade [1-5]. Molecular imprinting is becoming recognized as a technique for ready preparation of polymeric materials containing recognition sites of predetermined specificity. This technique allows the formation of specific recognition sites in macromolecules by the use of molecule templates which include drugs [6], hormones[7], pesticides[8], proteins[9], amino acids[10], peptides[11], carbohydrates[12], coenzymes[13], nucleotides[14], nucleotide bases[15], steroids[16], dyes[17], and metal ions[18]. The application that promises to be of greatest industrial significance in the immediate future is that of molecular recognition materials for biosensors, highly specific catalysts, antibody for quantitative assay and molecular recognition, drug delivery and tailor-made separation materials [19].

Molecular imprinting in polymers is achieved by incorporating a template, or imprint molecule into a highly crosslinked polymer matrix. The imprinted molecule is identical or similar, in both size and functionality, to the target molecule. The template molecule is bonded to a polymerizable functional monomer or a polymer side group prior to crosslinking. The bond between the template and the functional monomer or a polymer can be either covalent or non-covalent. Studies have shown successful results in the area of molecular imprinting via non-covalent interaction between template and functional monomer [20] as well as via covalent interactions [21]. The non-covalent imprinting approach seems to hold more potential for the future of molecular imprinting due to the vast number of compounds, including biological compounds, which are capable of non-covalent interactions with polymerizable monomers. These non-covalent interactions are easily reversed, usually by wash in aqueous solution of an acid, a base or methanol, thus facilitating the removal of the template molecule from the network after polymerization.

In this respect, metal ion-imprinted polymers were prepared by radiation technique using Co-60 gamma rays. PVA, AAc, AAm and AMPS in unitary and binary systems, metal ion and N,N?-methylene bisacrylamide crosslinker (N,N-MBAAm), were used as the matrix for preparing imprinted molecule. After extraction of the metal ions, the imprinted polymers were used for selectively separation of different heavy and rare earth elements from unitary or binary mixture solution, which detected either by UV and/or ICP techniques. Preparation conditions of metal imprinted polymers including, the nature of the polymer or monomer, metal ion concentration, monomer-polymer composition and crosslinking degree of imprinted polymers, which may influence polymer affinity and/or selectivity towards metal ions at different pH values were investigated.
2-EXPERIMENTAL

1. Materials

Acrylamide (AAm) and Poly vinyl alcohol (PVA); M.wt 14,000 g/mol (S.d.finechem. LTD, BOSISAR); Acrylic acid (AAc), and 2-Acrylamido-2-methyl propane sulfonic acid (AMPS); M.wt. 207.25 g/mol, purity 99 % (Merck). The organic solvents, inorganic salts and the other chemical reagents were of pure grade and used without further purification.

2. Preparation of the Imprinted Polymers

In order to prepare different types of imprinted polymers, 1 ml of (20 wt%) (PVA) solution, 1 ml of (20 wt %) monomer solution, 0.1g of N,N’-MBAAm as crosslinker, 0.05 ml polyethylene glycol (PEG) and 0.5 ml of (20%) metal soluble in de-ionized water mixtures, were subjected to gamma rays at total dose of 40 kGy. Co-60 gamma rays of dose rate that ranged from 0.7 to 1.2 Gy/s were used in this study. After exposure to Gamma Rays, the irradiated composite was immersed in 0.5 M solution of HCl to extract the metals used for imprinted polymer. The imprinted polymer was thoroughly washed with water to remove the residual metal hydroxide and the excess HCl then dried at 35°C for 24h.

3. Characterization and Some Properties of the Imprinted Polymers

Scanning Electron Microscope (SEM)

The surface topography of non-imp. Poly (AMPS), La- imp. Poly (AMPS) (without extracting La-ion) and La- imp. Poly (AMPS) (after extracting La-ion) was studied using Jeol Sem-25 scanning electron microscope, (Japan). Prior to examination, the polymer films were dried under sputter-coated gold.

Swelling Measurements

The dry and weighed non-imprinted and imprinted polymers were immersed in bi-distilled water at room temperature ~25°C at different pH values using Jenway 3310 pH meter for different time intervals. Then, the polymer films were removed and blotted quickly with absorbent paper to remove water attached on its surface, and weighed quickly. The degree of swelling was determined as follows:

\[ \text{Swelling} (\%) = \left( \frac{W_s - W_o}{W_o} \right) \times 100 \]

Where \( W_o \) and \( W_s \) represent the weights of dry and swelled polymers, respectively.

4. Uptake of Heavy Metals and Rare Elements Separations by Imprinted Polymers:

(Ni\(^{2+}\), Co\(^{2+}\), La\(^{3+}\) and Uranyl ions)-imprinted polymers, or non-imprinted polymers were used for heavy metal ion (Ni\(^{2+}\), Co\(^{2+}\), Uranyl ions and Cu\(^{2+}\)) and rare element (La\(^{3+}\)) uptake and/or separations.

UV Visible Spectrophotometer.

The instrument with the double beam UV visible spectrophotometer, Milton Roy Spectronic (1201), wave length ranges from 200-600ºA was used. For determining the amount of metal ions adsorbed by imprinted polymer. The heavy metal ion element/ Arsenazo III complex prepared with different volumes of (Ni\(^{2+}\), Co\(^{2+}\), La\(^{3+}\) or Uranyl ions) solutions in the presence of 1.0 ml (0.5 wt%) Arsenazo III as indicator and 3 ml of (3%) gelatin solution then fill it up to 50 cm\(^3\) of measuring flask with (2N HCl), was prepared in order to calibrate the amount of metals adsorbed by imprinted polymers. The imprinted polymers, after extract ion of metal ions, were socked in 10 ml of different
metal solutions of concentration (600 ppm) for 4h. After removing the polymer, the remaining metals in the solution was determined by measuring the intensity of its line spectrum at wave lengths of the metal ion.

**Inductively Coupled Plasma (ICP)**

Jobin, Yvon, Ultima (ICP-AES). Atomic Emission Spectrometer, France; Frequency 40.68 MHZ, Power output 0.5-1.5 KW, Wavelength range 120-770 nm and Resolution band 10 pm (first order) and 5 pm (second order), was used in the present work. It is an instrument analysis technique based on atomic emission spectrometry. Emission phenomena occur in plasma. Plasma is a gas that has been ionized to a high degree and is electrically ionic equilibrium. The gas used is argon which is easily ionized, a good electrical conductor and is reasonable in cost. The relationship between emitted intensity from alien and the concentration of the associated element must be calculated and this determines the line’s calibration curve.

In this work the imprinted polymers (after extraction of ion of metal ions) were soaked in 10 ml of different metal ion solutions of concentration 100 ppm for 4h. After removing the polymer, the remaining metal in the solution was determined by measuring the intensity of its line spectrum at wave lengths of 367.007 nM for UO$_2$, 228.616 nM for Co, 221.647 nM for Ni, for 224.700 nM Cu and 492.097 for La.

### 3-RESULTS & DISCUSSION

1. **Selectivity and Affinity of PVA Polymer towards Co and Ni.**

   A study was made to investigate the capability of PVA to adsorb Co and Ni ions from their solutions. The metal adsorbed by PVA was determined to find out that PVA could adsorb 4 and 8 mg metal per gm PVA polymer for Co and Ni, respectively, Fig. (1). Since the adsorption capacity of PVA towards Ni or Co is poor, trials were made to increase its affinity and selectivity towards such metals. It is expected that PVA adsorption capacity and selectivity could be improve presumably through preparation of metal imprinted PVA and/or by the interaction between the functionalities of different monomers and PVA.

   Co or Ni-imprinted PVA was prepared and the affinity of such imprinted polymers towards Co and Ni individually was investigated and shown in Fig. (1). It is clear that, the affinity of Ni or Co-imprinted PVA towards Co increases compared with that for non-imprinted PVA. The affinity of Ni-imprinted PVA towards Co is slightly higher than that for Co-imprinted PVA; meanwhile, imprinting of PVA with Ni increases the affinity towards Ni to remarkable degree. However, Co-imprinted PVA shows low affinity towards Ni. From this result it can be concluded that, imprinting of PVA by using Co or Ni metals improves its affinity towards such metals, however, the selectivity towards these metals is not clear.

2. **Adsorption Capacity of PVA Interacted with Different Functional Monomers**

   On the basis of the affinities information of acrylic acid, acrylamide, or 2-acrylamido methyl propane sulfonic acid, these monomers were chosen as ligands combined with PVA, for Co and Ni complexation [18,19]. Therefore, copolymerization of acrylic acid, acrylamide, or 2-acrylamido methyl propane sulfonic acid with PVA was carried out to improve its selectivity and/or affinity towards these metal ions and the data are shown in (Fig. 2). It can be seen that the affinity of PVA towards Co or Ni was greatly enhanced by mixing it with these monomers. Such affinity is in the order; PVA/AAm < PVA/AAc < PVA/AMPS. The adsorbed amount of Co and Ni by PVA-functional copolymer immersed in individual Co or Ni feed solution is almost the same. The selectivity of PVA/AMPS and PVA/AAc of copolymer composition (1:1wt %) towards Co and Ni when they exist in a mixture is also investigated and the results are shown in (Fig. 3). It is observed that, the affinity of PVA/AMPS or PVA/AAc copolymer towards Co and Ni metals is fair and the selectivity towards them is not clear.

-81-
3. Selectivity Improvement of PVA Interacted with Different Functional Monomers by Imprinting Technique

The preparation and evaluation of imprinted polymer based on copolymer prepared from Poly (vinyl alcohol) and functional monomers in presence of N,N'-methylene bis acrylamide to give multiple recognition sites for Co and Ni ions, were investigated and shown in Fig. (4). It was found that, PVA/AAm imprinted with Co or Ni has a good affinity towards Co metal compared with that...
prepared in absence of such metals. Furthermore, the polymer imprinted with Ni shows high affinity towards Ni rather than Co and so does the co-imprinted polymers. The affinity of Ni-imprinted PVA/AAm towards Co or Ni is higher than that for non-imprinted one.

Figure (5) shows that the affinity of Co-imprinted PVA/AMPS towards Co is higher than that towards Ni, meanwhile, Ni-imprinted polymer shows high affinity towards both Co and Ni. This is probably due to the strong ionic interaction between PVA and AMPS which may increases the stability of the complex formed. The same behavior was observed for Co-imprinted PVA/AAc however, the selectivity is enhanced (Fig. 6). It is clear that, non-imp. and Ni-imp. PVA/AAc prefers Ni to complex with. Meanwhile, Co-imprinted PVA/AAc has a great affinity towards Co (~ four times higher than Ni). However, for Co or Ni-imprinted PVA/AAm and PVA/AMPS such selectivity is not pronounced.

---

**Fig (4):** Metal uptake using metal imprinted and non-imprinted PVA/AAm.

**Fig. (5):** Metal uptake using metal imprinted and non-imprinted PVA/AMPS of composition (1:1wt%).
Fig (6): Metal uptake using metal-imprinted and non-imprinted PVA / AAc of composition (1:1 wt%).

A comparative study was made for the different types of prepared copolymers imprinted with Ni or Co to show the effect of imprinted molecule on the selectivity when Co and Ni metals exist in the same solution was studied and the data are shown in Figs. (7, 8). It can be seen that for Ni-imprinted of PVA and PVA/AAm, the affinity towards Ni is higher than that towards Co. However, Ni-imprinted PVA/AAc copolymer possesses higher affinity towards Co than Ni. Although, the selectivity of Ni-PVA/AMPS towards Ni or Co is not clear. On the other hand, the selectivity of Co-imprinted PVA/AAc towards Co is clear Fig. (8), meanwhile, the affinity of Co-imprinted PVA, PVA/AAm and PVA/AMPS towards Ni is predominated.

Fig. (7): Co and Ni uptake from their mixture solutions, by using Ni-imprinted PVA and its copolymers with AAm, AAc and AMPS.
Fig. (8): Co and Ni uptake from their mixture solutions, by using Co-imprinted PVA and its copolymers with AAm, AAc and AMPS.

4. Effect of Different PVA/PAAc Compositions on the Selectivity towards Co and Ni in a Mixture:

The effect of different compositions of non-imprinted and imprinted polymers on the affinity and selectivity towards Co and Ni was studied and shown in Figs. (9-11). It was found that, as AAc content increases in the copolymer, the selectivity towards Co increases, meanwhile, the selectivity towards Ni decreases. The data shows also that by increasing the AAc content in the copolymer the affinity of polymer towards Ni decreases. The affinity as well as the selectivity of Co-imprinted polymer increase with increasing P(AAc) content in the copolymer compared with that obtained for non-imprinted or Ni-imprinted polymer. However, the selectivity and affinity for Co and Ni-imprinted polymer towards Co is higher than that for non-imprinted ones. The affinity of Ni towards Ni-imprinted polymers is higher than that of Co-imprinted.

Fig. (9): Metal uptake from their mixture solutions, using non-imprinted PVA/AAc of different compositions.
5. The affinity and selectivity of PVA/AMPS copolymer of different compositions towards Co and Ni in a Mixture:

Metal uptake using Co and Ni-imprinted PVA/AMPS of different compositions is investigated and shown in Figs. (12, 13). The affinity of the prepared copolymer towards Ni or Co increases by imprinting the polymer with Co or Ni metals and also, by increasing AMPS content in the copolymer. From the above mentioned results, it is assumed that AAc and AMPS affect the affinity and selectivity of PVA towards Co and Ni ions. To investigate the affinity of these monomers towards such metals, copolymerization of AMPS and AAc in the presence and absence of Co or Ni was investigated, for selective separation of the two metal ions from their mixture solution.
Fig. (12): Co-uptake by Co-imprinted and non-imprinted PVA/AMPS of different compositions.

Fig. (13): Ni-uptake using Ni-imprinted and non-imprinted PVA/AMPS of different compositions.
Table (1) shows that, the non-imprinted P(AMPS/AAc) has a greater affinity towards Cu rather than Co, however, Ni or Co imprinted polymer show high affinity towards Co if compared with non-imprinted one.

**Table (1):** Metal uptake by imprinted and non-imprinted copolymer of (AMPS/AAc) of composition (1/1wt%).

<table>
<thead>
<tr>
<th>Polymer P(AMPS/AAc)</th>
<th>Metal uptake (mg/g)</th>
<th>Ni: Co mixture (1:1)</th>
<th>Co: Cu mixture (1:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Co</td>
<td>Co</td>
</tr>
<tr>
<td>Non-imp.</td>
<td>30</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>Co- imp.</td>
<td>40</td>
<td>40</td>
<td>9</td>
</tr>
<tr>
<td>Ni- imp.</td>
<td>36</td>
<td>46</td>
<td>10</td>
</tr>
</tbody>
</table>

6. Some Factors Affecting the Affinity and Selectivity of Poly-functional Monomers:

The recognition ability of molecular imprinted polymers is largely governed by factors such as polymerization conditions, nature of crosslinking agent and degree of crosslinking.

**Degree of Crosslinking**

The degree of crosslinking was governed by irradiation dose as well as the type of crosslinking monomer used. The irradiation doses suitable for creating imprinted polymer of highly crosslinking level was determined by measuring the polymer gel content and swelling ratios of systems exposed to gamma rays for various irradiation doses (Table 2). It was observed that the appropriate dose for high crosslinking level is 40 kGy for almost all systems used, where, the gel content reaches to about more than 60%. From Table 2, it can be seen also that, the gel content in Co-imprinted polymer is lower than that of non-imprinted ones. The gel content for the different crosslinking monomers follows the order; PVA/AAc > PVA/AMPS > PVA/AAm > PVA. This means that the crosslinking content increases in the presence of AAc and this reveals the high selectivity of such copolymer towards Co. This is because at relatively high crosslinking level, the enforcement of the retention of the cavity memory upon the removal of such metal occurs.
Table (2): Degree of gelation (%) of the non-imprinted and Co-imprinted polymers as a function of irradiation dose and type of crosslinking monomer

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degree of gelation (%)</th>
<th>Total Dose (kGy)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Non-imprinted</td>
</tr>
<tr>
<td>PVA</td>
<td></td>
<td>43</td>
</tr>
<tr>
<td>PVA/AAm</td>
<td></td>
<td>60.5</td>
</tr>
<tr>
<td>PVA/AAc</td>
<td></td>
<td>79.5</td>
</tr>
<tr>
<td>PVA/AMPS</td>
<td></td>
<td>62</td>
</tr>
</tbody>
</table>
7. Swelling Behavior of Metal Imprinted Polymers for Different Copolymer Compositions:

It is well known that there is a relationship between polymer swelling property and the metal affinity. Fig. (14) shows the swelling of Co or Ni-imprinted polymers after metal extraction as well as non-imprinted ones at different compositions. It is obvious that, for metal imprinted or non-imprinted PVA/AAc, as the AAc content in the copolymer increases, the swelling property decreases. As the AAc content in the PVA/AAc copolymer increases, the crosslinking content increases. It is also the water uptake for Ni-imprinted polymer is higher than that for Co-imprinted and non-imprinted ones at the same corresponding compositions. The data obtained leads one to believe that metal uptake is not only governed by the swelling property but also size of the cavities, the stability of the formed complex and the size of the hydrated metal ion to be extracted. It can be conclude that the polymer swelling is not the sole factor to determine its metal affinity. The uptake of metal especially Co depends on the functional groups of the polymer mainly COOH.

![Graph showing swelling behavior of metal imprinted polymers](image)

**Fig. (14):** Effect of PVA/AAc composition on the degree of swelling for the imprinted and non-imprinted forms.

8. Adsorption and Selective Separation of Heavy and Rare Earth Metals using Poly (AMPS)

The high affinity of poly (AMPS) towards different metals encourages the author to use it in separation of other metals such as La and UO$_2$ which usually engaged with Ni or Co in the radioactive medium level wastewater. In this respect, AMPS was polymerized by using gamma rays in the presence of such metals and N,N?-methylene bisacrylamide as crosslinking agent. The affinity of non-imprinted and metal imprinted poly (AMPS) towards Ni, Co, La or Uranyl ions was studied and the data are shown in Table (3). It was found that, poly (AMPS) has a great affinity towards the metals under investigation and this affinity of non-imprinted poly (AMPS) towards such metals follows the order; La> Ni>UO$_2$>Co.
Table (3): Metal uptake by imprinted and non-imprinted Poly (AMPS).

<table>
<thead>
<tr>
<th>Imprinted Metals</th>
<th>Replaced Metal</th>
<th>Metal uptake (mg/g)</th>
<th>Non-imp.</th>
<th>Imp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Co</td>
<td>58</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>Ni</td>
<td>81</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>La</td>
<td>85</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>UO$_2$</td>
<td>UO$_2$</td>
<td>73</td>
<td>64</td>
<td></td>
</tr>
</tbody>
</table>

The lower Ni-uptake of the imprinted polymers may be due to the cavities and their fixed structure, which formed during polymerization of AMPS in the presence of metals, which restrict the reorientation of the chains to be suitable to freely complex with other metals.

The above results suggested the study of metal uptake for poly (AMPS) imprinted with Co, Ni, La and Uranyl ions in order to understand their affinity towards such metals and the results are shown in Figs. (15-17). It is observed that, the affinity of polymer imprinted with metal of small size toward metal of large sizes such as La decreases (Fig.15). It is also observed that, for example the affinity of Uranyl ions or La-imprinted poly (AMPS) towards Ni is reduced by about 45% referred to Ni-imprinted one. The decrease in affinity may be due to the larger size of imprinted cavity results from La or UO$_2$ compared with Ni atomic radius. Consequently, the cavity size resulted from metal imprinted poly (AMPS) has great effect on the metal affinity towards another metals, if the cavity is small the polymer affinity towards metals of large radius is reduced and vice versa.

Co or Ni uptake by imprinted poly (AMPS) with different metals of different sizes was studied, Figs. (16, 17) to find out that as the metal size that used for imprinting process increases, the affinity of polymers towards Co or Ni decreases. The results showed that, the large or small cavity size restricts the functional groups to react and form stable complex.

![Fig(15): La-uptake using poly (AMPS) imprinted with different metals.](image-url)
To support this idea, the swelling behavior of poly (AMPS) imprinted with different metals of various sizes was investigated and shown in Table (4). It was observed that the swelling of polymer imprinted
with metal of large size is higher than that imprinted with small one i.e. the larger the cavities the higher the polymer swelling is obtained.

Table (4): Effect of different imprinted metals on the degree of swelling (%), at pH 5.

<table>
<thead>
<tr>
<th>Poly (AMPS)</th>
<th>Swelling (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-imp.</td>
<td>264</td>
</tr>
<tr>
<td>Co-imp.</td>
<td>216</td>
</tr>
<tr>
<td>Ni-imp.</td>
<td>247</td>
</tr>
<tr>
<td>La-imp.</td>
<td>300</td>
</tr>
<tr>
<td>UO$_2$-imp.</td>
<td>302</td>
</tr>
</tbody>
</table>

9. Effect of pH on the Uranyl ions and La uptake

The effect of different pH values on the uptake of UO$_2$ and La by poly (AMPS) was studied and shown in Fig. (18). It can be seen that, as the pH values increase La and Uranyl ions uptake increases to reach a maximum at pH~ 3.5 and 4.5 for Uranyl ions and La, respectively. From these results, it is expected that it is possible to separate La from Uranyl ions in solution containing mixture of them. Therefore, a trail was made to separate Uranyl ions from La in their solutions mixture at low pH value and the results are shown in Table (5). It was observed that poly (AMPS) adsorb large amount of UO$_2$ in comparing with that of La in the concentrated acidic media. This means that poly (AMPS) may be used to separate Uranyl ions from La when they exist in a mixture of high acidic media.

![Fig. (18): Metal uptake as a function of PH, for non-imprinted poly (AMPS).](image-url)
Table (5): Effect of pH on the selectivity of non-imprinted poly (AMPS) towards La and Uranyl ions in a mixture.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Metal uptake (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Con. acidic solution</td>
</tr>
<tr>
<td>La</td>
<td>7</td>
</tr>
<tr>
<td>Uranyl</td>
<td>38</td>
</tr>
</tbody>
</table>

10. Selectivity of poly (AMPS) towards Co, Ni, Uranyl ions and La in Binary Mixtures.

The selectivity and affinity of poly (AMPS) towards Co, Ni, Uranyl ions and La ions in binary mixtures was investigated and shown in Table (6). It was observed that, the presence of metals in a mixture enhances the affinity of poly (AMPS) towards such metals.

Table (6): Metal uptake of UO$_2$, Co, Ni and La from binary mixture solutions (1:1) using UO$_2$, Co and La- imp. and non-imp. Poly (AMPS)

For example, the metal uptake of Co-imprinted polymer towards Co or La in unitary solution is 57 and 42 mg/g, respectively, Fig. (16), however, in binary system the affinity of the two metals is 143 mg/g. The selectivity for the poly (AMPS) towards the metals in binary system is not clear except for La-imprinted polymer. The polymer imprinted with La has promising selectivity towards La rather than Co or Ni when immersed in solution containing mixture of (La+Co) or (La+ Ni). The selectivity may be due to the configuration structure stability of La-imprinted polymer.

11. Morphological Structure of Imprinted Polymer.

As can be seen from Fig. (19), the non-imprinted polymer posses homogenous distribution structure, however, the metal imprinted polymer (La) have heterogeneous cracked, rough surfaces. The cracks and heterogenous surfaces dose not altered after extraction the metal from imprinted polymer.

-94-
Fig (19) Micrographs for:

a) Non-imp. Poly (AMPS).
b) La- imp. Poly (AMPS) (without extracting La-ion)
c) La- imp. Poly (AMPS) (after extracting La-ion).

4-CONCLUSIONS

It can be included that the affinity and selectivity of PVA towards Co and Ni ions was improved by imprinting of PVA using Co or Ni and also by mixing PVA with AAc or AMPs. The affinity as well as the selectivity of co-imprinted polymer increase with increasing PAAc or PAMPs content. The increase in the crosslinking content increases the selectivity of such co-polymers because at relatively high crosslinking level, the enforcement of the retention of the cavity memory upon the removal of such metal occurs. The metal uptake is not only governed by the swelling property but also size of the cavities, the stability of the formed complex and size of the hydrated metal ion to be extracted. The uptake of metal depends also on the functional groups of the polymer. The poly AMPs imprinted with La has promising selectivity towards La rather than Co or Ni when immersed in solution containing mixture of (La +Co) or (La+Ni)

5-REFERENCES