CHEMICAL MODIFICATION OF POLYMERS IN ORDER TO IMPROVE THE COMPLEXATION ABILITY OF HEAVY METAL IONS

Laurent DAMBIES\textsuperscript{2)}, Agnieszka JAWORSKA\textsuperscript{1)}, Grażyna ZAKRZEWSKA-TRZNADEL\textsuperscript{1)}

\textsuperscript{1)} Intytut Chemii i Techniki Jądrowej, Drodna 16, 03-195 Warszawa
\textsuperscript{2)} Visiting researcher in the scope of Marie Curie Transfer of Knowledge Project AMERC (MTKD-CT-2004-509226)

Abstract

Toxic heavy metals in water are global problems that create growing threat to the environment. For the removal of heavy metals from aqueous solutions it is possible to apply polymer enhanced ultrafiltration (PEUF). Strongly acidic water soluble polymers prepared from poly(vinyl alcohol) 10,000 can be used in PAUF (Polymer assisted ultrafiltration) to remove with high capacity \(\text{Co}^{2+}\) ions between pH 3 and pH 6 with the same efficiency. The retention of cobalt in polymer enhanced ultrafiltration was higher when modified polymer - sulfonated PVA as a complexing agent was applied.

1. INTRODUCTION

Membrane processes can be efficient methods for removal of metal ions, as well as radioactive species like cobalt-60, which is usually present in liquid radioactive waste in form of small ions. When ultrafiltration membranes are applied for radioactive wastes processing, the metal ions have to be formerly bound with macromolecular compound to form complexes that can be retained by the membrane.

Polymer assisted ultrafiltration (PAUF), also described as PEUF (polymer enhanced ultrafiltration), LPR (liquid phase polymer retention) or Polymer Filtration (PF) is a relatively new process of separation for purifying water containing metal ions. PAUF combines the ion exchange or chelating properties of a functionalized water soluble polymer with the sieving power of an ultrafiltration membrane.

Among soluble polymers, the most popular is polyacrylic acid used in its sodium or hydrogen form which can bind numerous metal ions such as \(\text{Zn}^{2+}, \text{Ni}^{2+}, \text{Mg}^{2+}\). Polyethyleneimine (PEI) is also quite effective in removing metal ions such as \(\text{Hg}^{2+}, \text{Cd}^{2+}, \text{Cu}^{2+}\) and \(\text{Zn}^{2+}, \text{Co}^{2+}\). Another popular polymer is polyallylamine for the removal of \(\text{Cu}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}\) [1-3].
A survey of the papers on PAUF indicates that for a large number of them, commercially available polymers are used instead of tailored polymers.

As far as the synthesis of water soluble polymers concerned, two approaches can be used which are the functionalization of an existing polymer or the synthesis of the polymer starting with the individual monomer(s) by radical polymerization.

In the present work the first method using poly(vinyl alcohol) and poly(ethylene glycol) to attach series of different ligands (sulfonic, phosphoric, EDTA) was chosen.

### 2. POLYMERS SYNTHESIS

#### 2.1. SYNTHESIS AND CHARACTERIZATION OF SULFONATED POLYMERS

For PVA polymers synthesis procedure is adapted from patent 2,531,468 [4] and is carried in three steps: pretreatment of the PVA polymer (10,000, 50,000 and 100,000 MW), preparation of the sulfonating agent and the reaction itself. 4.4 g of PVA (100 mmoles) are transferred in a 100 mL round bottom flask equipped with a condenser. 25 mL of pyridine were added and the mixture was stirred with a magnetic stirrer for 2h at 80°C then cooled down in the ice bath. 25 mL of pyridine were transferred to a 500 mL Duran bottle fitted with a small glass funnel. A stirring bar is added in the bottle and placed in an ice bath. 8 mL of chlorosulfonic acid were measured in a graduated cylinder and added drop by drop through the funnel in the pyridine solution during 30 min using a disposable glass pipet.

Sulfonating agent was redissolved in 25 mL of pyridine by warming up the bottle to 60 °C and added quite quickly to the PVA-pyridine mixture kept in the ice bath by using a disposable glass pipet. Round bottom flask was placed in an oil bath at 80 °C and reaction allowed to proceed at this temperature for 3 to 4 hours.

Sulfonates based on PVA 10,000 and 50,000 were soluble in water at room temperature whereas sulfonates based on PVA 100,000 were soluble at higher temperatures. Sulfonated PVA 10,000 had a solid yellow color while the 100,000 form had a very pale yellow color.

<table>
<thead>
<tr>
<th>PVA molecular weight</th>
<th>Acid capacity of the final polymer solution in (mmol/mL)</th>
<th>Acid capacity (mmol/g dry polymer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000</td>
<td>0.429</td>
<td>4.93</td>
</tr>
<tr>
<td>50,000</td>
<td>0.177</td>
<td>3.8</td>
</tr>
<tr>
<td>100,000</td>
<td>0.00624</td>
<td>3.60</td>
</tr>
</tbody>
</table>
2.2. PREPARATION AND CHARACTERIZATION OF PHOSPHORYLATED PVA

4 g of PVA 100,000 were added in a 100 mL round bottom flask along with 50 mL of H₃PO₄ (85 % in water). Reaction was carried out for 5 hours at 65 ºC then continued overnight at room temperature. At the end of the reaction a gold color supernatant was obtained and gummy light brown polymer (water soluble) attached in the bottom of the flask. Polymer was redissolved in water and filtered through a membrane of 10,000 MW cut off. The polymer solution obtained was titrated with 0.1 M NaOH. It had acid capacity of 0.00979 mmol/mL corresponding to 0.82 mmol/g. Acid capacity was quite low which might be related to the high molecular weight of PVA or the experimental conditions that were not optimal for this reaction.

3. Co²⁺ REMOVAL BY PAUF

The next step was ultrafiltration process coupled with complexation by water soluble polymers. Tab. 2 and Fig. 1 show results of the experiment.

The 50 mL-ultrafiltration cell Amicon was used for all experiments. In the 100 mL-volumetric flask 1 mL of cobalt stock (1 mg or 0.017 mmole) with a suitable volume of polymer solution to give 0.17 mmole of acid groups were added. Solution was completed to 100 mL with distilled water, mixed and transferred in a beaker with a magnetic stirrer. The pH was adjusted to the desired value with NaOH 0.1 M or HCl 0.1 M. Solution was agitated for at least 2 hours and pH was checked and adjusted if necessary. 50 mL of the solution were then added to the ultrafiltration cell fitted with 10,000 MW cut-off membrane (PES Millipore). The remaining solution was kept to analyse the initial cobalt concentration. Ultrafiltration cell was closed and the assembly was put under pressure of 3 bars to carry out the filtration.

Retention coefficient of the Co²⁺ ions was investigated between pH 3 and 6 for different polymers based on poly(vinyl alcohol). Commercially available poly(acrylic acids) 100,000 and 15,000 MW were chosen as benchmark for this study.

Table 2. Characteristics of acidic polymers used for PAUF

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Acid capacity (mmol/g)</th>
<th>Molar ratio H+/cobalt</th>
<th>Mass ratio Polymer/cobalt</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA-SO₃H 10,000</td>
<td>4.93</td>
<td>10</td>
<td>34.5</td>
</tr>
<tr>
<td>PVA-SO₃H 100,000</td>
<td>3.60</td>
<td>10</td>
<td>27.4</td>
</tr>
<tr>
<td>PAA 15,000 H⁺</td>
<td>12.9*</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>PAA 100,000 H⁺</td>
<td>13.2*</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>PVA-PO₄H 100000</td>
<td>0.82</td>
<td>10</td>
<td>208</td>
</tr>
</tbody>
</table>

*Theoretical acid capacity to PAA= 1000/72= 13.9 mmol/g
4. CONCLUSIONS

The retention of cobalt in polymer enhanced ultrafiltration was higher when modified polymers as complexing agents were applied.

Strongly acidic water soluble polymer prepared from poly(vinyl alcohol) 10,000 can be used in PAUF to remove with high capacity Co\(^{2+}\) between pH 3 and pH 6 with the same efficiency. Sulfonated PVA 10,000 performed very well with a rejection rate above 95\% between pH 3 and 6.

REFERENCES