Application of radiation-graft material for metal adsorbent and crosslinked natural polymer for healthcare product

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Abstract

Graft polymerization and crosslinking in radiation processing are attractive techniques for modification of the chemical and physical properties of conventional polymers. The graft polymerization and subsequent chemical treatment can introduce a chelate agent function into a conventional polymer such as polyethylene. The obtained amidoxime fibrous adsorbent was applied to the recovery of uranium from seawater. Soaking of 350 kg adsorbent 12 times in seawater led to the collection of 1 kg of uranium. Natural polymers such as derivatives of starch and cellulose were radiation-crosslinked to form hydrogels. Mats of crosslinked carboxymethyl cellulose were evaluated by 68 patients after surgical operation. No bedsore was observed in almost all patients after operation. This product was commercialized as “Non-bedsore” in Japan.

Keywords: Graft polymerization; Metal adsorbent; Crosslinking; Degradable hydrogel

1. Introduction

Graft polymerization (Kabanov et al., 1991) and crosslinking (Dole, 1972) are well known reactions in radiation processing of polymers. These reactions were initialized by high-energy irradiation of γ-ray or electron beam toward the polymer as shown in Fig. 1. Thus, the radiation-induced graft polymerization (RIGP) can be applicable to the conventional polymers having various shapes such as membrane (Choi et al., 2000), fabric (Basuki et al., 2003), and fiber (Kuraga et al., 2003). The radiation-induced crosslinking can be carried out in solid (Darwis et al., 1999) and liquid state (Rosiak and Ulaski, 1999). Polymers modified by grafting and crosslinking have been widely industrialized as battery separators, heat shrinkable materials, and wound dressing (Machi, 1996).

From the point of view of environmental preservation, fibrous adsorbents for toxic metals such as lead have been extensively developed by RIGP. The fibrous adsorbents could be synthesized by introducing a functional chelate group such as amidoxime (Shiraishi et al., 2003) and iminodiacetic acid (Konishi et al., 1996) into nonwoven fabrics. These fibrous adsorbents had high selectivity to heavy ions and revealed 100 times higher rate of the toxic metal adsorption than that of the commercial adsorbent resin in column mode experiments (Jyo et al., 2001). This high performance of the fibrous adsorbents is attractive for removal of toxic metals from streaming water.

It was found that polysaccharide derivatives such as carboxymethylcellulose (CMC) and carboxymethyl-starch could be crosslinked in the paste-like condition using high energy irradiation (Yoshii et al., 2003). The resulting hydrogel still is biodegradable and the waste hydrogel can be converted into fertilizer by degradation of bacteria in soil.

The present paper reviews two applications: Recovery of uranium from seawater by using fibrous adsorbent...
synthesized by RIGP and production of crosslinked-polysaccharide to be used as mat for prevention of bedsore.

2. Recovery of uranium from seawater by graft adsorbent

Uranium is dissolved in seawater in the concentration of only 3.3 ppb. Its total amount, however, reaches $4 \times 10^{12}$ kg which is equivalent to the 1000 times of the mine uranium. Adsorbent of the titanium oxide has been used for the recovery of uranium in seawater (Ito et al., 1992). However, the seawater should be pumped up to contact effectively with the titanium oxide adsorbent since this adsorbent sinks without any agitation. The cost of the pumping is too high to promote the industrialization of the uranium recovery from seawater. To realize the effective contact with seawater without any agitation, the screening of organic adsorbent has been carried out. The effective contact between the organic adsorbent and seawater can be realized by wave motion when the adsorbent is soaked in the seawater. This is because the density of the organic adsorbent is as same as seawater. After screening of 200 functional groups, the amidoxime group was found to be the most promising chelate agent (Schenk et al., 1982).

The fibrous adsorbent having amidoxime group was synthesized by RIGP in the following three steps (Katakai et al., 1998):

1. Irradiation of the nonwoven fabric with electron-beam or $\gamma$-ray.
2. Co-grafting of acrylonitrile (AN) and methacrylic acid (MA).
3. Conversion of cyano groups in grafted nonwoven fabric to amidoxime groups.

A nonwoven fabric made of polyethylene-coated polypropylene fibers with average diameter of 13 $\mu$m was selected as a trunk polymer for RIGP. In the first step, irradiation at 200 kGy of electron beam is necessary for obtaining the degree of grafting of 150% on the grafting condition of 2 h at 40°C. The degree of grafting was expressed by the percentage of increased weight based on the initial weight of the trunk polymer. The grafting was carried out by immersing the irradiated nonwoven fabric into 50% monomer mixture of AN and MA (4:1 in weight ratio) in dimethylsulfoxide. The co-grafting of AN with a hydrophilic monomer like MA increased the adsorption rate (Kawai et al., 2000). In the chemical reaction of the third step, hydroxylamine (NH$_2$OH) changed CN groups into amidoxime groups. The degree of grafting was determined to be 100% corresponding to 4 mmol amidoxime per g-dry adsorbent.

Uranium recovery from seawater was tested in a marine experiment from 1999 to 2001 by using RIGP amidoxime adsorbent as shown in Fig. 2. The equipment was set at the Tsugaru straits in northern Japan to collect 1 kg uranium from seawater.

Fibrous adsorbent of 6000 m$^2$ was synthesized for the marine experiment. The rolled nonwoven fabrics, 200 m long and 1.5 m wide, were irradiated with $\gamma$-ray. The irradiated roll was set in the graft chamber, 2.5 m wide, 2 m high and 4.5 m long, in which the nonwoven fabric was wound reversibly with 5 m/min through the reservoir of the 90% monomer mixture of AN and MA.
MA (4:1 in weight ratio) solution in nitrogen atmosphere.

The obtained adsorbents were cut into the size of 29 cm × 16 cm. These adsorbents of 120 sheets were alternately put with spacers to make adsorbent stacks, 29 cm × 16 cm × 29 cm. The adsorbent stacks were packed into three adsorption beds in a stainless-steel square mesh-container, 4 m in one side and 15 cm in inner height. One adsorption bed can pack 144 adsorbent stacks. Totally, 350 kg of adsorbent could be submerged into seawater in maximum. Three adsorption-beds were connected with 1.5 m ropes and submerged from a square float with one side of 8 m long into the sea at 20 m depth. After immersion for a certain number of days, the adsorption beds were pulled up as shown in Fig. 3.

The adsorbent stacks were soaked into HCl solution of two different concentrations to elute the adsorbed metals fractionally (Suzuki et al., 2000). The alkaline and the alkaline earth metals were washed out from the adsorbent with 0.01 M HCl, and uranium, nickel, and copper were eluted by 0.5 M HCl. After the fractional elution of the metals, the adsorbent can be regenerated with 0.45 M KOH solution at 80 °C for 1 h and submerged into seawater repeatedly for the recovery of uranium. The eluted uranium in HCl solution was purified by solvent extraction and precipitation.

Table 1 summarized the submersion period, submersion days, seawater temperature, number of stacks, and adsorbed uranium in the marine experiment for 3 years (Seko et al., 2003). During the submersion, the temperature of seawater and the relative flow rate between adsorbent and seawater were monitored. The total amount of the adsorbed uranium was estimated by measurements on some of the adsorbent stacks to be 1 kg in terms of ammonium diuranate, (NH₄)₂U₂O₇, after 12 experiments of the submersion.

Recovery of uranium from seawater with fibrous amidoxime adsorbent is considered to be a promising technology to secure the fuel resources for atomic power plants. It was inferred that the factors, which affect the amount of uranium adsorption were the temperature of seawater and the up-and-down motion of the adsorption bed. These results imply that the recovery of uranium from seawater with adsorbent should be carried out in areas of warm sea and high wave height which induces the needed up and down motion of the adsorption beds.

Problems to be solved from the marine experiment were the lightening of the weight of the heavy submerged parts, especially the metal bed, and the further improving the efficiency of the contact between the adsorbent and the seawater in the adsorbent stack. The solutions of these problems are important to realize of a reasonable low cost for uranium recovery from seawater.

**Table 1**

Uranium adsorption from seawater in marine experiment of the graft adsorbent

<table>
<thead>
<tr>
<th>Submersion period</th>
<th>Submersion days</th>
<th>Seawater temperature (°C)</th>
<th>Number of stacks</th>
<th>Adsorbed uranium (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1999</td>
<td>29 Sep.–20 Oct.</td>
<td>21</td>
<td>19–21</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>8 Jun.–28 Jun.</td>
<td>20</td>
<td>12–13</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>28 Jun.–8 Aug.</td>
<td>40</td>
<td>13–22</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>8 Aug.–7 Sep.</td>
<td>29</td>
<td>20–24</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>7 Sep.–28 Sep.</td>
<td>21</td>
<td>24–22</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>28 Sep.–19 Oct.</td>
<td>21</td>
<td>20–18</td>
<td>144</td>
</tr>
<tr>
<td>2000</td>
<td>15 Jun.–17 Jul.</td>
<td>32</td>
<td>13–18</td>
<td>216</td>
</tr>
<tr>
<td></td>
<td>18 Jul.–20 Aug.</td>
<td>32</td>
<td>18–20</td>
<td>216</td>
</tr>
<tr>
<td></td>
<td>15 Jun.–20 Aug.</td>
<td>65</td>
<td>13–20</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>20 Aug.–21 Sep.</td>
<td>31</td>
<td>20–19</td>
<td>216</td>
</tr>
<tr>
<td></td>
<td>18 Jul.–21 Sep.</td>
<td>63</td>
<td>18–19</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>15 Jun.–21 Sep.</td>
<td>96</td>
<td>13–19</td>
<td>72</td>
</tr>
</tbody>
</table>

Fig. 3. Pulling up of submerged adsorption beds packed with graft adsorbent stacks.
3. Crosslinked polysaccharide for surgical operation mat

Cellulose and its derivatives generally undergo degradation by high energy radiation. Radiation crosslinking, however, was observed in high concentration solution (paste-like condition) of carboxymethyl cellulose (CMC) (Fei et al., 2000). When CMC solution was irradiated with 5 kGy by electron beam, CMC of 10% solution gave 42% gel fraction. Increasing dose monotonously up to 40 kGy raised the gel fraction to 60%. A gel fraction of 70% was obtained at CMC concentration of 20% at 10 kGy. When the CMC concentration went up 50%, the gel fraction was reduced to 5%. More than 60% of CMC was not dissolved in the water. It is assumed that high degree of radiation crosslinking of CMC was induced by the increased mobility of its molecules in water and by the formation of CMC radicals after the abstraction of H atoms by the intermediate products of water radiolysis (Wach et al., 2003).

Crosslinked CMC is suitable for healthcare product such as surgical operation mats for prevention of bedsores. High viscous solution of 20% CMC was pressed into a plastic bag and irradiated with 10 kGy (γ-ray). Fig. 4 shows the CMC gel, a plastic bag containing CMC gel, and the crosslinked CMC mat in the surgical operation room. Such mats were tested by 68 patients in a hospital. No bedsores were observed in 64 patients and only red spots appeared on 4 patients immediately after surgical operation. This result reveals that the crosslinked CMC mat is extremely effective to prevent bedsores during surgical operation. This CMC gel mat is considered to disperse the body pressure and to maintain the best circulation of blood during operation. Hence, the crosslinked CMC mat was commercialized as “Non-bedsore” in Japan. The waste of this CMC gel can be converted into a fertilizer by degradation of bacteria in soil. Being biodegradable is a big advantage of this crosslinked hydrogel.

References