

Studies on Fiber Adsorbent of Uranium from Seawater

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Abstract

Structural analysis of "so-called" amidoxime polymer has been undertaken and elucidated the imidedioxime structure as a significant component. On the basis of structural informations, a highly efficient uranyl adsorbent was successfully developed.

1,3,5-Tricyanopentane was chosen as a model compound of polyacrylonitrile and its reaction with hydroxylamine was examined by using characteristic chemical shifts of amidoxime and imidedioxime carbons at 155 and 145 ppm, respectively. With use of excess hydroxylamine toward the total cyano content, the reaction course was dependent on the relative ratio $\text{NH}_2\text{OH-HCl/KOH}$, i.e., the acidic condition lead to the formation of imidedioxime, while the basic favored amidoxime. Under the condition of the use of less amount of hydroxylamine, the relative tendency was similar to the above, but the $\text{EtOH/H}_2\text{O}(1:1)$ solvent accelerated the conversion rate of amidoxime to imidedioxime than MeOH.

Polymer structure was analyzed through a ^{13}C NMR spectra under the Cross Polarization-Magic Angle Spin condition. Contrary to the control of reaction pathways observed for the model compounds, the choice of solvent determined the structure of fibrous polymer. Irrespective of acidic and basic conditions, MeOH solvent gave predominantly the amidoxime structure, while $\text{EtOH-H}_2\text{O}(1:1)$ favored the formation of the imideoxime.

Since imidedioxime has already been proved by the author to possess a higher coordinating ability than amidoxime, polyacrylonitrile fiber was treated first with hydroxylamine in $\text{EtOH-H}_2\text{O}(1:1)$ followed by the alkaline treatment. The resulting polymer gave an adsorption rate as high as $650 \mu\text{gU/g}$ adsorbent after one day contact with natural seawater. This value is much higher than the value $150\text{-}200 \mu\text{gU/g}$ adsorbent, obtainable by the conventional amidoxime polymer.