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Attempts to capturing ppb-level elements from sea water with hydrogels

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ABSTRACT

Stable energy resource supply is an important subject from the perspective of national security. In this sense, recovering uranium from seawater is important and profitable for the countries of which the land is surrounded by sea and is not endowed with energy resources such as Japan. However, the concentration of uranium dissolved in seawater is extremely low (ppb level) but the total amount of uranium is huge because of the tremendous seawater volume on the Earth. Therefore, in order to promote the efficiency of adsorbents capturing ppb-level uranium from seawater, the authors propose the utilization of hydrogel as a new adsorbent base material. In order to demonstrate the usefulness of the hydrogel for the ppb-level element-adsorption from seawater, the authors have developed the amidoxime incorporated hydrogel and have examined their ppb-level uranium capturing efficiency in the presence of other elements. From the experimental results, a potential for this purpose has been demonstrated by considerably high adsorption functionality.

1. Introduction

Today, the uneven distributions of useful mineral resources on the lands have induced serious problems affecting the national security of some countries, especially Japan. The reason of these undesirable situations comes from the origins of the resources, the crustal movement and volcanic activity, and unfortunately the Japan island is not located in the favorable areas. In these circumstances, a lot of investigations for aquiring useful and rare elements has been intensively carrying out in various ways; and among them, the collections of valuable elements from seawater is promising from the standpoint of stable resource supply. Besides, this method is particularly profitable to Japan, which land is surrounded by sea; in spite that the concentrations of many valuable elements in seawater are at a level of ppb or ppt (Sverdrup et al., 1942; Shigematsu, 1978); detailed description on the uranium concentration distribution in the oceans is available (Owens et al., 2011), considerable amounts of these elements can be still expected because there is tremendous volume of seawater on the earth.

Among the investigations for capturing valuable rare elements from sea water, advanced studies has been done for recovering uranium. These works could contribute to stabilise the supply of energy resource by utilizing for the separation various inorganic and organic adsorbents including biomasses (Katoh et al., 1982; Vernon et al., 1982; Vernon and Shah, 1983; Saito et al., 1987a, 1988; Seko et al., 2003; Kalin et al., 2004; Sodaye et al., 2009; Rao, 2011; Vivero-Escoto et al., 2013; Khajeh and Jahanbin, 2014; Yamazaki et al., 2015). The total amount of uranium in seawater is estimated over 4 billion tons (Brin, 1979).

In Japan, the most recent large-scale demonstration experiments on the extraction of uranium from seawater were performed by the scientists of Japan Atomic Energy Research Institute (JAERI) and Japan Atomic Energy Agency (JAEA) utilizing organic adsorbents composed of μm-scale-diameter polyethylene fibers grafted with amidoxime group. Though their investigations demonstrated the effectiveness of their method by gaining a kg-order weight of uranium (Seko et al., 2004), their studies also made clear that, in practical applications, there still remain problems to be solved on adsorbent efficiency and implementation cost (Tamada et al., 2006).

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The efficiency of the whole adsorbent is determined by two factors: the adsorption efficiency of every target-capturing functional group and the functional-group density in the whole adsorbent. Corresponding thereto, two ways for improving the functionality of the adsorbent can be considered: increasing the efficiency of the functional group and implanting the functional groups more densely on base material. In the previous study, the functional group was the amidoxime group and the base material was the polyethylene fiber with a μm-scale diameter; because the amidoxime group was selected from a wide variety of candidates (Schenk et al., 1982), the authors estimate that there may be almost no room for finding other functional groups with more functionality in the condition of seawater. For this reason, the authors have been focusing on another option: setting the amidoxime groups with the higher concentration. Specifically, in the previous studies, amidoxime groups were grafted 2-dimensionally on the surface of the macro-sized substrate, μm-scale-diameter fibers; in the present paper, the authors propose another type of base materials, hydrogels, for increasing the density of the functional groups in the adsorbent. Hydrogel is a water-filled 3-dimensional polymer network with a nanometer-scale mesh size; namely, solute and solvent molecules are surrounded by network mesh with a dimension less than 100 times as their size (Tanaka, 1981; Cohen et al., 1992; Almdal et al., 1993). Because of this characteristic structure, its solid phase (polymer) and liquid phase (water) are highly intermingled with an extensive interaction area demonstrating high solvent holding capacities; the water diffusion coefficients in some hydrogels analogous to the specimens in the present study are suppressed down to ~ 20% of the values outside, even in the case of ~0.06 of network-polymer volume fraction (Muhr and Blanshard, 1982). In addition, many kinds of functional groups can be easily introduced with a molecular-scale interval by simple chemical reactions as well as γ-ray grafting.

Until these days, the authors have been investigating the hydrogel's properties for its utilization for environmental purification and resource recycling. In their studies, it was found that some functional hydrogels can capture hazardous heavy-metal ions with considerably higher efficiency than other adsorbents and that they can also release most of the adsorbed heavy metals. By combining these experimental results, the authors demonstrated a new heavy-metal recycling system utilizing hydrogel (Hara et al., 2010). The useful characteristics of the hydrogel compared with other adsorbents and treatments are as follows:

- Transportation costs can be considerably suppressed. Because the organic hydrogel is composed of light elements such as H, C, N and O, the weight ratio of captured heavy metal to the adsorbent can be set much larger than inorganic absorbents such as zeolites.
- The organic hydrogels utilized in the present study called chemical hydrogels are made of the nano-scale-mesh polymer-network cross-linked with covalent bonds, which are not easily disintegrated in a wide range of condition (such as pH 1–13) maintaining ~50 kPa of elastic modulus sufficient for the present purpose (Cohen et al., 1992; Anseth et al., 1996). With this reason, the chemical hydrogels can be used in more various situations than polymer flocculants forming flocks by the electrostatic adhesion between the flocculants and captured multivalent ions, which are fragile and easy to decay by changing the pH condition. The structural stability against pH condition is very important for desorption treatments of the captured ions because such treatments are usually executed by changing pH condition (Hara et al., 2010; in the case of sea uranium, Tamada, 2010).
- Compared with the solvent extraction method, the recovery treatment with the hydrogels can be simply done without a fear causing environmental pollution by toxic organic solvents.
- The recovery with the hydrogel does not produce any by-product. In the ordinal treatments for waste fluid, the heavy metal ions in the waste fluid are precipitated as hydroxide, which is not easy to handle.

Such a high functionality comes from the above mentioned characteristic structure of hydrogel, which can be also effective for recovering uranium from seawater. Under these circumstances, in the present study, the authors have investigated the uranium capturing functionality of the amidoxime-incorporating hydrogel from the solution containing ppb-level uranium and several other ions for examining the possibility of utilizing the hydrogel as a uranium-capturing adsorbent from seawater.

2. Experimental

2.1. Hydrogel adsorbent preparation

Together with 60 mM of *N*,*N*'-methylene-bisacrylamide (BIS), several concentration ratios of acrylamide (AAm) and acrylonitrile (AN) were dissolved into respective 10 ml of 70%(v/v) dimethyl sulfoxide (DMSO) aqueous solutions under the condition of [AAm] + [AN] = 1.0 M (Hereafter, these solutions are called as pregel solutions). After adding ammonium peroxodisalfate (APS), a reaction initiator, the pregel solutions had been kept in a 40 °C water bath for 24 h waiting for completing a radical polymerization to form the AAm/AN hydrogels with several AAm:AN ratios (Fig. 1(a)). After the syntheses, ~10 g (~10 cm^3) of cubes were cutout from the hydrogel lumps and rinsed in pure water for washing out non-reacting components for 1 day. The weight ratios of the polymer networks (composed of AAm, AN, BIS) in the hydrogels and solvent (water) were ~7% and ~93%, respectively. The chemical formula and contents of the reagents in the pregel solutions are listed in Tables 1 and 2.

Each washed AAm/AN hydrogel was cut into 10 mg pieces. They were immersed in a 3%(w/v) hydroxylamine hydrochloride (NH_2—OH·HCl) aqueous solution of which the pH was adjusted at 7 by potassium hydroxide (KOH). The temperature of the solution was increased and was kept at 77 °C for 4 h. This procedure was applied for the conversion of AN's cyano (CN) groups to amidoxime (AO) groups (Fig. 1(b)). After this amidoximation treatment, the hydrogels were taken out from the NH_2—OH·HCl solution and had been immersed in respective 80 °C 2.5%(w/v) KOH aqueous solutions for 1 h. After then, the treated hydrogels had been rinsed in pure water for 1 day; the final hydrogels swelled ~20 times as much as before due to the conversion of hydrophobic CN groups to hydrophilic AO groups by the amidoximation.

2.2. Confirmation of the conversion of acrylonitrile group to amidoxime group

Fourier transform infrared (FTIR) (FTIR 620, JASCO Co.) and ^{13}C NMR (JNM, JEOL Ltd.) spectra of the hydrogels before and after the amidoximation treatments were measured for confirming the conversion of AN group to amidoxime group. For the FTIR spectral measurements, the respective hydrogels were dried naturally for ten days, and then, were ground into powders in a mortar by grinding with the pestle. Then, each of the 1 mg of hydrogel powder was thoroughly mixed with 100 mg of powdery potassium bromide (KBr) in a simillar manner. Finally, the mixed powders were shaped into pellets with a pressure of 68,950 kPa (10,000 psi). For the ^{13}C NMR spectroscopy measurements, the hydrogels were also dried

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