Chemical Engineering Journal 298 (2016) 125–135

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Novel poly(imide dioxime) sorbents: Development and testing for enhanced extraction of uranium from natural seawater

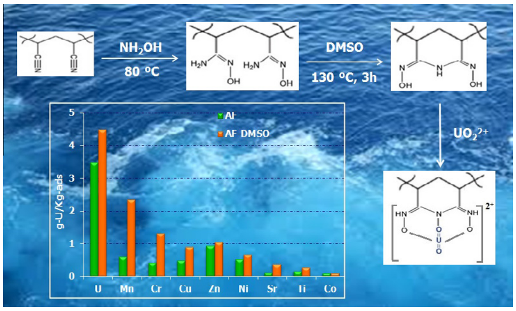
S. Das [a,*], S. Brown [b], R.T. Mayes [a], C.J. Janke [a], C. Tsouris [a], L.-J. Kuo [c], G. Gill [c], S. Dai [a,b,*]

[a] *Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6053, USA*
[b] *Department of Chemistry, University of Tennessee, TN, USA*
[c] *Marine Sciences Laboratory, Pacific Northwest National Laboratory, Sequim, WA 98382, USA*

HIGHLIGHTS

- Hydroxylamine reacts with acrylonitrile forming both amidoxime and imide dioxime.
- Formation of cyclic imide dioxime maximized by treating with DMSO at 130 °C for 3 h.
- High e$^-$ donation ability of imine N in conjugated imide dioxime strongly binds U.
- So far, highest reported U adsorption capacity in seawater with selectivity over V.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 February 2016
Received in revised form 31 March 2016
Accepted 1 April 2016
Available online 9 April 2016

Keywords:
Polymer
Grafting
Amidoxime
Imide dioxime
Uranium adsorption
Seawater

ABSTRACT

A new series of amidoxime-based polymer adsorbents were synthesized at the Oak Ridge National Laboratory (ORNL) by electron beam induced grafting of acrylonitrile and itaconic acid onto polyethylene fiber. Hydroxylamine derivatives of poly(acrylonitrile) (PAN) moiety are demonstrated to possess two kinds of functional groups: open-chain amidoxime and cyclic imide dioxime. The open-chain amidoxime is shown to convert to imide dioxime on heat treatment in the presence of an aprotic solvent, like dimethylsulfoxide (DMSO). The formation of amidoxime and imide dioxime was confirmed by ^{13}C CP-MAS spectra. The adsorbents were evaluated for uranium adsorption efficiency at ORNL with simulated seawater spiked with 8 ppm uranium and 5 gallon seawater in a batch reactor, and in flow-through columns with natural seawater at the Marine Science Laboratory (MSL) of Pacific Northwest National Laboratory (PNNL) at Sequim Bay, WA. The DMSO-heat-treated sorbents adsorbed uranium as high as 4.48 g-U/kg-ads. from seawater. Experimental evidence is presented that the poly(imide dioxime) is primarily responsible for enhanced uranium adsorption capacity from natural seawater. The conjugated system in the imide dioxime ligand possesses increased electron donation ability, which is believed to significantly enhance the uranyl coordination in seawater.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Uranium is the main nuclear fuel that undergoes nuclear fission to generate energy. With the development of advanced nuclear technologies, the demand for uranium is expected to increase. A 2011 study by the Organization for Economic Co-operation and Development estimated that at the current consumption rate, the

---

* Corresponding authors at: Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6053, USA. Tel.: +1 865 207 8078; fax: +1 865 241 5152 (S. Dai). Tel.: +1 865 403 2466; fax: +1 865 241 5152 (S. Das).

E-mail addresses: dass1@ornl.gov, amisdas@gmail.com (S. Das), dais@ornl.gov (S. Dai).

http://dx.doi.org/10.1016/j.cej.2016.04.013
1385-8947/© 2016 Elsevier B.V. All rights reserved.

global conventional reserves of uranium (7.1 million tons) could be depleted in roughly a century [1]. Therefore it is of a significant interest to look for resources of uranium other than the conventional terrestrial ores. Seawater is a major source of uranium. The total estimated quantity of uranium in seawater is around 4.5 billion tons [2]. Uranium is present in seawater in very small concentrations of about 3.3 ppb and distributed uniformly all over the world. Considering the huge amount of seawater in the world, the total amount of uranium in seawater is estimated to be $\sim$1000 times more than that available in terrestrial ores [3]. Thus, the oceans have the potential to become the most eco-friendly and a long sustainable resource for uranium. However, it is very challenging to extract uranium from seawater because of its extremely low concentration while many other elements (e.g., Na, K, Ca, Mg and some transition metals) are present in overwhelmingly higher or comparable concentrations. Therefore, the extraction process must be extremely efficient, selective and must be operated in-situ without violating the seawater eco-culture. Uranium in seawater is mainly present as complex of the anionic triscarbonato-uranate (VI) $[UO_2(CO_3)_3]^{4-}$ species. A recent study reported that the uranium (VI) species in seawater is dominated by the ternary Ca-UO_2-CO_3 and Mg-UO_2-CO_3 complexes [4], so that any extracting agent, if successful, must be able to compete with calcium, magnesium and carbonate for the complexation of U(VI).

Since the 1980's, many materials and methods have been developed for the extraction of uranium from seawater [5–15]. Among the various separation technologies employed, solid phase extraction of uranium by chelating amidoxime-based functional polymers emerged as the most promising in terms of kinetics, cost and adsorption capacity [16–20]. Marine tests by Japanese researchers with PAO-braided fiber adsorbents showed 1.5 g-U/kg-adsorbent after 30 days of exposure in the Okinawa area [10]. Inspired by this success, researchers at the Oak Ridge National Laboratory (ORNL), Pacific Northwest National Laboratory (PNNL), Lawrence Berkeley National Laboratory (LBNL), and universities in the US and other countries started investigating different factors affecting the uranium uptake from seawater.

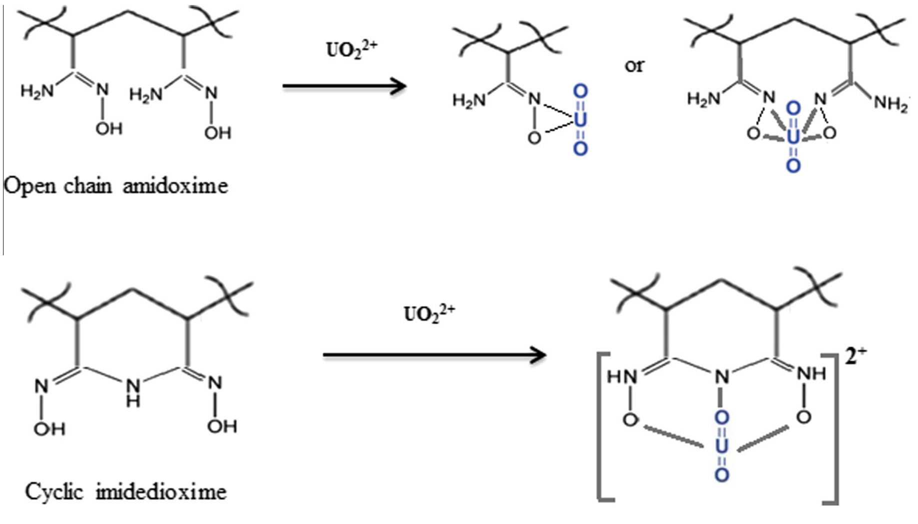
In this present work, a series of adsorbents containing acrylonitrile along with itaconic acid at different mole ratios were prepared by radiation induced graft polymerization (RIGP) onto high surface area polyethylene trunk fiber [16,17]. Conversion of polyacrylonitrile to polyamidoxime in the grafted precursor fibers was done by reacting with hydroxylamine. The reaction of hydroxylamine with polyacrylonitrile at high temperatures is reported to produce simultaneously both the open-chain diamidoxime and cyclic imide dioxime. It is believed that the two adjacent amidoxime groups in the adsorbent may form cyclic imide dioxime [18,23–25]. The imide dioxime has been claimed as the actual binding site as supported by crystallographic [26] and thermodynamic [27] studies. Open chain amidoxime is claimed to bind UO_2^{2+} in η^2 coordination through the oxygen and nitrogen of the oxime (Scheme 1). On the other hand, the cyclic imide dioxime forms a tridentate coordination for UO_2^{2+} with a higher binding constant [28]. Uranyl binding by open-chain amidoxime is not thermodynamically favorable relative to carbonate in seawater [29]. In this report, an investigation for maximum formation of cyclic imide dioxime sites leading to enhanced uranium adsorption in seawater is described.

A higher temperature of the reaction of acrylonitrile with hydroxylamine favors cyclic imide dioxime over open-chain amidoxime [23,30]. Elvidge et al. [31] reported that the open-chain form converts into cyclic form even by sublimation. Thermal cyclization is reported as an effective path for conversion of open-chain amidoxime into cyclic imide dioxime in the glutarimide dioxime [32–34]. These observations motivated us to investigate conversion of open-chain amidoxime into imide dioxime at elevated temperature using different organic solvents. Although there are several reports [23,25,26] where it was hypothesized that imide dioxime has a stronger affinity for uranyl than that of amidoxime, there is no direct evidence to support the fact that the cyclic imide dioxime indeed enhances uranium binding in natural seawater. In fact, recent work by Abney et al. suggests a lesser role for the imide dioxime than previously assumed as the uranium spectra for the seawater contacted poly(acrylamidoxime) fiber, which contained both amidoxime and cyclic imide dioxime, did not match the features observed for the uranyl-glutarimide dioxime molecular complex [35]. The current work demonstrates a significant enhancement of uranium adsorption efficiency from natural seawater by the cyclic imide dioxime loaded poly(acrylamidoxime) adsorbent.

2. Materials and methods

2.1. Materials

All chemicals were reagent-grade or higher. Acrylonitrile (AN), itaconic acid (ITA), tetrahydrofuran (THF), methanol, dimethylsulfoxide (DMSO), N, N-dimethylformamide (DMF), propylene carbonate (PC), hydroxylamine hydrochloride (HA-HCl) and



Scheme 1. Open-chain amidoxime and cyclic imide dioxime and their possible binding modes of binding with UO_2^{2+}.

Download English Version:

https://daneshyari.com/en/article/145552

Download Persian Version:

https://daneshyari.com/article/145552

Daneshyari.com