



Article Sequestering Rare Earth Elements and Precious Metals from Seawater Using a Highly Efficient Polymer Adsorbent Derived from Acrylic Fiber

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Abstract: An amidoxime and carboxylate containing polymer adsorbent derived from acrylic fiber has shown extremely high efficiencies for extracting critical materials and precious metals from seawater. Among 50 extractable elements, the lanthanides, cobalt, and palladium were ranked near the top with K_D values in the order of 10^7 , about an order of magnitude higher than that of uranium. The K_D value of the lanthanides increased linearly with the atomic number indicating charge density is a factor controlling trivalent lanthanide extractability in seawater. The data given in this report provides crucial information regarding the strategies of ocean mining of critical materials and precious metals.

Keywords: lanthanides; amidoxime; adsorbent; acrylic fiber; critical materials



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1. Introduction

The idea of extracting valuable mineral resources from oceans has been proposed and pursued by many research programs [1]. These efforts reflect the demands from industries, particularly those within the advanced clean energy technologies, for critical materials which continue to increase. As a result, the land-based mineral reserves of such materials will eventually be depleted. The concentrations of many critical materials dissolved in seawater are typically very low [2,3]; however, due to the large volume of seawater, the total amounts of some critical materials in seawater are much greater than their land-based reserves [4].

Recent calculations indicated that land-based uranium reserves will be depleted by the end of this century [5]. The concentration of uranium in seawater is about 3 ppb (parts-perbillion, or micrograms per kilogram of seawater); however, the total amount of uranium available from seawater is about 1000 times greater than the land-based uranium reserves according to some estimates [1]. For this reason, developing effective sorption materials for the extraction of uranium from seawater has been a research area of considerable interest in recent years [5,6]. Among many sorption materials tested, the amidoxime and carboxylate containing fiber adsorbents appear to be most effective and selective for extracting uranium from seawater [5,6].

Amidoxime groups provide strong binding sites for uranyl ions whereas carboxylate groups make polymer fiber hydrophilic. To prepare this type of polymer fiber adsorbent, a radiation induced grafting technique is traditionally used to attach precursors of the amidoxime and carboxylate functional groups to polyethylene fibers. A recent report shows that acrylic fiber, a commonly available fabric material consisting mainly of polyacrylonitrile, can be used as the starting material for synthesizing amidoxime and carboxylate containing fiber adsorbents via a simple two-step reaction process [7]. In this process, a

part of the nitrile groups in acrylic fiber are first converted to amidoxime groups by a reaction with hydroxylamine which is followed by hydrolysis of another portion of the nitrile groups to carboxylate groups in a sodium hydroxide solution. This simple synthesis process greatly reduces the cost and time required for the preparation of the polymer fiber adsorbent. The fiber adsorbent prepared from acrylic fiber has a uranium adsorption capacity comparable to or higher than those prepared by more elaborated radiation induced grafting techniques [5,6,8,9].

In addition to extracting uranium, amidoxime/carboxylic fiber adsorbents can also extract transition metals including vanadium, copper, iron, cobalt, etc., from seawater; however, the possibility of extracting critical materials such as rare earth elements (REEs) and precious metals from seawater using this type of fiber adsorbent has not been reported in the literature. We have recently investigated the possibility of extracting REEs and precious metals from seawater utilizing the amidoxime/carboxylate fiber adsorbent derived from acrylic fiber. The marine water extraction tests were performed utilizing a circulating seawater flume system available at the PNNL–MCRL (Pacific Northwest National Lab—Marine and Coastal Research Lab) [10]. Preliminary results are presented in the current paper.

2. Materials and Methods

The textile grade acrylic fibers used in this research were provided by Kaltex consisting of 92% acrylonitrile and 8% methyl acrylate by weight. Methanol (99.9% purity), sodium hydroxide (98% purity), and hydroxylamine (50 wt.% aqueous solutions) were purchased from Thermo Fisher (Waltham, MA, USA) and used as received. The fiber adsorbent used for this study has a composition of about 45% amidoxime, 45% carboxylate, and 10% nitrile. The chemical structure of this fiber is shown in Figure 1.



Figure 1. The chemical structure of the amidoxime-carboxylate containing polymer adsorbent derived from acrylic fiber.

The detailed procedure of the adsorbent material synthesis was reported in the literature [7]. The amidoxime-based polymer adsorbents were prepared from acrylic fibers (92% acrylonitrile and 8% methyl acrylate monomers) received from Kaltex. The procedure for converting the acrylic fibers to the amidoxime–carboxylate containing polymer adsorbents involves two steps: amidoximation and alkaline hydrolysis. The identity of functional groups on fibers during synthesis and in the final product was confirmed by Fourier transform infrared (FTIR) spectra given in Figure 3 [11–13]. The FTIR spectra were acquired on dry adsorbent samples using a ThermoNicolet 6700 FTIR spectrometer Thermo Fisher, Waltham, MA, USA). FTIR measurements were made with a SplitPea attenuated total reflection (ATR) accessory (Harrick Scientific Inc., Pleasantville, NY, USA) along with a silicon internal reflection element used as a reflection medium. High resolution FTIR spectra in the range of 4000 to 700 cm⁻¹ were acquired using 500 co-added scans at a 2 cm⁻¹ resolution with a Norton–Beer "medium" apodization function. The FTIR spectra were normalized to the 1450 cm⁻¹ peak, the methylene group in-plane bending or scissoring band (δ_s CH₂), to facilitate comparison. We employed the FTIR to control the ratio amidoxime/COO⁻ based on the decrease of the -CN peak. The functionalization of the polymer adsorbent is reproducible. The standard deviation of the three braid fibers (about 10 g each) was less than 5%.

Marine tests of the fiber adsorbent were performed at the PNNL–MCRL located in Sequim, Washington. The seawater was pumped from the Sequim Bay, Washington, and filtered with 0.45-micron filters. The flow-through channel for conducting the flume experiments under controlled temperature and flow-rate conditions was developed by the MCRL scientists. The flumes were constructed of darkened acrylic material to limit biological growth. The flow rate (linear velocity) could be manipulated by using pumps with varying capacity and different flume dimensions. Controlled water flow within the flume was accomplished by recirculating the water using a centrifugal water pump with a nonmetallic pump head (Finish Thompson pump, model DB6H, Finish Thompson Inc., Erie, PA, USA) to minimize contamination concerns. A cross-sectional view of the flume illustrating the recirculation system is given in Figure 2.



Figure 2. Conceptual side-view of a flume system.

Three bundles of fibers in braid forms (about 10 g each) were mounted within the flume. Each braid had a spacing of about 0.15 m to avoid interfering with each other. An external pump was used to recirculate seawater in the flume. The linear velocity in the flume was controlled by a gate valve at the exit of the pump. The flow-rate in the recirculating water was continuously monitored by a flow meter (Omega Engineering Inc., Norwalk, CT, USA). Fresh seawater (1.5–2 L/min) was fed into the flume using the seawater delivery system. The height of the water level in the flume was controlled by the height of the overflow standpipe, which could be varied between approximately 0.20 and 0.25 m. Seawater rose in the flume to the height of the overflow tube and then spilled out at the same rate as it was introduced from the head tank. We employed a 63 L flume (length 1.22 m, width 0.20 m) and the target linear velocity was 2 cm/s in this study. The pH, salinity, temperature, trace elements, and dissolved organic carbon (DOC) of flume seawater were monitored throughout the experiment as described in previous literature [10,14-17]. Three braided adsorbent materials were mounted in the circulating seawater flume system and flowed smoothly for 56 days at 20 °C. According to our published data [7,17], the uranium adsorption capacity of the amidoxime-carboxylate containing fiber reaches near equilibrium after 56 days of exposure to seawater. Other trace metals in seawater including vanadium, iron, zinc, nickel, and cobalt follow the same trend as uranium in the seawater adsorption experiment [17]. Therefore, 56 days was selected for this rare earth and precious metals adsorption study. After that, triplicate samples (~ 100 mg per portion) were taken from each braid adsorbent using a titanium-coated scissor and digested with 50% aqua regia for an inductively coupled plasma (ICP) analysis using inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer 7300, PerkinElmer, Waltham, MA, USA) or inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific iCAP Q, Waltham, MA, USA). The standard deviation given in Table 3 was calculated from nine samples (N = 9). The adsorption capacities of different metals on the polymer fibers were calculated by the following formula:

Adsorption capacity $(mg/g \text{ or } g/kg) = C (mg/L) \times \frac{volume \text{ of digested solution (50% aqua regia), } L}{mass \text{ of absorbent, } g}$

where C represents the metal concentration in a digested solution obtained from ICP analysis.

3. Results and Discussion

After the amidoximation reaction, FTIR spectra (Figure 3) showed that about 50% of the nitrile groups (2242 cm⁻¹) of the original acrylic fibers were converted to the amidoxime groups. The presence of C=N, N–H, and N–O stretched at 1652, 1594, and 908 cm⁻¹, respectively, confirming the formation of amidoxime-type functional groups. This C=O stretch (1736 cm⁻¹) also decreased in intensity and was located as a small shoulder on a prominent iminic C=N (1652 cm⁻¹) stretching band. The alkaline solution converted the nitrile groups to the carboxylate groups as shown in the FTIR spectra in Figure 3. The majority of ester was converted to COO⁻ in the alkaline hydrolysis step, as indicated by the disappearance of the C=O stretch (1736 cm⁻¹) of ester. The final distribution of the chemical groups in the fiber adsorbent was estimated to be 45% amidoxime, 45% carboxylate, and 10% nitrile. The fiber showed some gel-like property after synthesis but became fiber-like in contact with seawater due to the salting-out effect (Hofmeister effect) [18].



Figure 3. FTIR spectra of the original acrylic fiber (black), after amidoximation (step 1, red) and after alkaline hydrolysis (step 2, blue). Conditions: step 1, NH₂OH, 70 °C, 45 min and step 2, NaOH, room temperature, 24 h.

The concentrations of the lanthanides (from atomic number Z = 57 La to Z = 71 Lu) in the surface seawater (depth 3 m) of the western Pacific Ocean are extremely low, in the order of parts per trillion (ng/L) as shown in Figure 4a [19]. Figure 4a was produced from the original data reported by a research paper published in 2017 [19]. The light lanthanides have higher concentrations in the ocean water relative to the heavy lanthanides. Among the light lanthanides, neodymium (Nd) has a higher concentration (about 1 ng per liter, or 1 ppt) in the ocean water relative to its neighboring elements. The adsorption pattern of the lanthanides from the Sequim Bay seawater by the amidoxime–carboxylate containing polymer fiber (Figure 4b) resembled the concentration distribution pattern reported for the dissolved lanthanides in the Pacific Ocean (Figure 4a). Neodymium was one of the highest adsorbed lanthanides found on the fiber after 56 days of exposure to the seawater. The concentration of Nd in the fiber was close to 20 mg per kg of the fiber, corresponding to a distribution coefficient [10] (K_D = concentration of Nd in fiber/concentration of Nd

in seawater) of $(1.80 \pm 0.31) \times 10^7$. This distribution coefficient is about an order of magnitude higher than the K_D value of uranium ($(2.17 \pm 0.01) \times 10^6$) reported by a recent uranium-from-seawater study utilizing the same fiber [7].

When the K_D values of all the extracted lanthanides are plotted in the order of increasing atomic number (Figure 4c), a reasonably linear relationship ($R^2 = 0.79$) is observed favoring the heavy lanthanides over the light lanthanides. As Figure 4c reveals, except for La (Z = 57) and Lu (Z = 71), a good linear trend ($R^2 = 0.93$) was observed between the K_D values of lanthanides and the corresponding atomic number. The two end members of the lanthanide series, i.e., La (Z = 57) and Lu (Z = 71) were somewhat off the linear relationship. It is known that the radius of the trivalent lanthanide ions (Ln^{3+}) decreases as the atomic number increases in the lanthanide series, the so-called lanthanide contraction [20]. This means the charge density of the trivalent lanthanide ions increases with an increase in Z number of the lanthanide series. Heavy trivalent lanthanides with a higher charge density typically form stronger bonds in coordination with many ligands [21]. The degree of adsorption of the trivalent lanthanides in the seawater by the fiber adsorbent correlated positively with the charge density of the lanthanide ions (Figure 4d).



Figure 4. (a) Concentrations of lanthanides in western Pacific Ocean water (depth = 3 m). The relative standard deviation (RSD) for every REE was $\leq 10\%$ [19]. (b) The lanthanides adsorption capacities after 56 days of exposure to filtered Sequim Bay seawater at 20 °C. Relation between the distribution coefficients (K_D) of lanthanides on the acrylic fiber-based adsorbent to (c) atomic numbers of the lanthanides and (d) ionic radii of the trivalent lanthanides (Lu³⁺ is on the left side in (d)). Note: The error bar was calculated from nine samples (N = 9).

The possibility of extracting precious metals including gold, silver, platinum, and palladium were also investigated. Gold in seawater is not extractable by the fiber adsorbent. No detectable amount of gold was found on the fiber after acid digestion and analysis by ICP-MS. Palladium, platinum, and silver were present on the fiber at 6 mg/kg, 0.11 mg/kg fiber, and 0.33 mg/kg fiber, respectively, according to our analysis. The relatively high adsorption of palladium is noteworthy because palladium is present in seawater at a very low concentration, about 6×10^{-2} ppt [2,3]. Oceanic abundance is calculated assuming a total ocean volume of 1.3×10^9 km³ (1.3×10^{21} L) [1]. The total amount of palladium in oceans based on this concentration should be about 8.6×10^4 tons. The distribution coefficient of Pd was very large ((9.90 ± 1.47) $\times 10^7$), comparable to those of the lanthanides (Table 2). The amount of Pd (6 mg per kg fiber) extractable from seawater is of economic significance. Palladium is widely used as a catalyst in many industrial processes, and it is more expensive than gold in the current spot market price [22].

According to this study, the metals extractable by the amidoxime–carboxylate containing polymer fiber from the Sequim Bay seawater can be roughly classified into the following groups (Tables 1 and 2) based on their concentrations found in the fiber after 56 days of seawater exposure.

Table 1. Adsorption range of different elements by the amidoxime–carboxylate containing polymer fiber in Sequim Bay seawater after 56 days of exposure at 20 °C.

Adsorption Range per kg Fiber	Elements
10–25 g	Mg, Ca
1–10 g	V, U, Fe, Ni, Zn
$10^{-1} - 10^{0}$ g	Cu, Co, Cr, Ti, Sr, Mn
$10^{-2} - 10^{-1}$ g	Y, Zr, Mo, La, Nd
10^{-3} - 10^{-2} g	Ce, Pd, Lanthanides (except La, Nd, Tb, and Lu), Sc, Ga, Sn, Cd, Nb
10^{-4} – 10^{-3} g	Tb, Lu, Tm, Li, Ag
10^{-5} - 10^{-4} g	Pt, Bi, Te, Sb, Th, Ir
$10^{-6} - 10^{-5}$ g	Rh, Ru, Re, In, Os

Table 2. The range of distribution coefficient (K_D) of different elements on the amidoxime–carboxylate containing polymer fiber in Sequim Bay seawater after 56 days of exposure at 20 °C.

Range of Distribution Coefficient (K _D)	Elements
$10^{7} - 10^{8}$	Pd, lanthanides, Ti, Co, Ir
$10^{6} - 10^{7}$	Ni, Sn, Y, V, Zr, Sc, Te, Nb, Bi, Th, U, Pt, Ga, Fe, Ru
$10^{5} - 10^{6}$	Cu, Zn, In, Os, Mn, Ag, Cr, Rh
$10^4 - 10^5$	Cd
$10^3 - 10^4$	Мо
$10^2 - 10^3$	Re, Sb
$10^{1}-10^{2}$	Ca, Mg, Sr
$< 10^{1}$	Li

Magnesium and calcium were the main elements adsorbed by the fiber in contact with seawater and their concentrations were typically in the range of 10–25 g per kg of the fiber. Vanadium, uranium, iron, nickel, and zinc were the next group of metals adsorbed by the fiber with concentrations in the range of 1–10 g per kg of the fiber. Copper, cobalt, chromium, titanium, strontium, and manganese in the seawater were extracted by the fiber in the range of 0.1–1 g per kg of the fiber. The next group in the range of 10–100 mg per kg of the fiber included the REEs, yttrium, lanthanum, and neodymium. Palladium and the other lanthanides in the seawater were extracted by the fiber in the range of 1–10 mg per kg of the fiber. The exact amounts of each element adsorbed by the fiber under the specified conditions are given in Table 3.

Elements	56-Day Adsorption Capacity (g/kg _{ads.})	Elements	56-Day Adsorption Capacity (g/kg _{ads.})
Mg	26.57 ± 1.47	Pr	$(3.65 \pm 0.68) imes 10^{-3}$
Ca	14.80 ± 0.60	Sc	$(2.27\pm 0.31) imes 10^{-3}$
V	6.38 ± 0.30	Ga	$(2.13 \pm 0.45) imes 10^{-3}$
U	6.02 ± 0.02	Sn	$(2.05\pm 0.22) imes 10^{-3}$
Fe	2.97 ± 0.08	Cd	$(2.04\pm 0.14) imes 10^{-3}$
Ni	2.95 ± 0.16	Но	$(1.56 \pm 0.27) imes 10^{-3}$
Zn	1.26 ± 0.05	Eu	$(1.22\pm 0.22) imes 10^{-3}$
Cu	0.44 ± 0.01	Nb	$(1.17\pm 0.15) imes 10^{-3}$
Co	0.27 ± 0.01	Tb	$(9.53 \pm 1.76) imes 10^{-4}$
Cr	0.22 ± 0.01	Lu	$(7.19 \pm 1.20) imes 10^{-4}$
Ti	0.155 ± 0.003	Tm	$(6.89 \pm 1.18) imes 10^{-4}$
Sr	0.13 ± 0.01	Li	$(6.15\pm 0.27) imes 10^{-4}$
Mn	0.12 ± 0.04	Ag	$(3.34\pm0.61) imes10^{-4}$
Y	$(6.69 \pm 1.12) imes 10^{-2}$	Pt	$(9.88 \pm 1.23) imes 10^{-5}$
Zr	$(5.10 \pm 0.67) imes 10^{-2}$	Bi	$(9.28 \pm 1.66) imes 10^{-5}$
Mo	$(2.75 \pm 0.35) imes 10^{-2}$	Te	$(6.41 \pm 0.29) imes 10^{-5}$
La	$(1.91\pm 0.32) imes 10^{-2}$	Sb	$(6.11\pm 0.79) imes 10^{-5}$
Nd	$(1.87 \pm 0.33) imes 10^{-2}$	Th	$(5.23\pm0.68) imes10^{-5}$
Ce	$(9.18 \pm 1.57) imes 10^{-3}$	Ir	$(4.33 \pm 0.59) imes 10^{-5}$
Dy	$(6.40 \pm 1.10) imes 10^{-3}$	Rh	$(8.51 \pm 1.01) imes 10^{-6}$
Pd	$(5.94\pm0.88) imes10^{-3}$	Ru	$(7.06 \pm 0.73) imes 10^{-6}$
Gd	$(5.22\pm 0.93) imes 10^{-3}$	Re	$(6.62 \pm 1.06) imes 10^{-6}$
Er	$(5.15\pm0.86) imes10^{-3}$	In	$(6.61 \pm 1.07) imes 10^{-6}$
Yb	$(4.57\pm0.73) imes10^{-3}$	Os	$(2.96\pm 0.24) imes 10^{-6}$
Sm	$(4.18\pm 0.74) imes 10^{-3}$	-	-

Table 3. The adsorption capacities of different elements on the amidoxime–carboxylate containing polymer fiber (Sequim Bay seawater at 20 $^{\circ}$ C, 56 days exposure).

Note: Average of 3 fiber braids (triplicate samples from each braid) about 10 g each in a circulating seawater flume at PNNL–MCRL.

In terms of distribution coefficients (K_D), palladium, titanium, cobalt, iridium, and lanthanides have K_D values in the range of $10^7 - 10^8$ (Table 2). In general, the larger the K_D value, the greater the affinity of the adsorbent to extract an element from seawater. The values of K_D > 10^4 are considered to exhibit a high affinity [23]. The amidoxime-carboxylate containing fiber obviously has very high affinities for many critical metals in seawater. The binding constants of uranyl, some transition metal ions, lanthanides, and alkaline earth metal ions with a single amidoxime molecule are known in the literature [24–27]. The data given in Table 4 indicates that the binding strength of glutarimidedioxime with some metal ions in the seawater followed the order: $V^{5+} > Fe^{3+} > UO_2^{2+} \approx Cu^{2+} > Eu^{3+} \approx Nd^{3+} > Ni^{2+} > Ca^{2+} \approx Mg^{2+}$. The K_D values of these metal ions were almost in the same order predicated by their thermodynamic binding constants except for the Eu³⁺, Nd³⁺, Cu²⁺, and Ni²⁺.

Table 4. Stability constants (β , binding constants) of the glutarimidedioxime complexes with selected metal cations [25–28].

Metal	log β
V ⁵⁺	53.00 ± 0.40
Fe ³⁺	43.94 ± 1.08
UO_2^{2+}	36.80 ± 2.10
Cu ²⁺	35.77 ± 0.11
Eu ³⁺	30.30 ± 0.30
Nd ³⁺	29.80 ± 0.70
Ni ²⁺	27.05 ± 0.10
Ca ²⁺	14.55 ± 0.08
Mg^{2+}	14.43 ± 0.12

The reuse of the fiber adsorbent depends on the elution method and seawater exposure conditions. How to elute adsorbed REEs and precious metals from the fiber and separate them from uranium is unknown at the present time. According to the literature [29–31], in simulated seawater spiked with 8 ppm of uranium, the fiber can be reused at least 4-5 times without losing its uranium adsorption capacity by either sodium bicarbonate elution [29] or potassium carbonate + hydrogen peroxide elution [30,31]. An economic analysis was published assuming a 5% reduction in uranium adsorption capacity per reuse cycle using acid elution to remove uranium from the exposed amidoxime-carboxylate containing fiber [32]. In a real seawater study, degradation of the amidoxime functional groups to carboxylate groups in the fiber was observed based on FTIR data obtained during long-term seawater exposure (from 28 to 140 days); however, the fiber was reusable even with some amidoxime degradation after 28 days of exposure but the uranium adsorption capacity started to decrease after the second reuse cycle [16]. The fiber degradation mechanism appears complicated and requires extensive investigation. Further research to develop effective elution methods for rare earth elements and precious metals from seawater exposed fiber and studies to enhance the durability of the fiber for repeated use are highly desirable.

4. Conclusions

Seawater contains vast amounts of valuable minerals, some of which are very scarce and expensive including rare earth elements, platinum group metals, lithium, copper, cobalt, silver, and gold. The amidoxime-based adsorbents derived from acrylic fiber show high affinities ($K_D > 10^4$) with these metals in seawater except for lithium and gold. These extractable metals may be considered as by-products of the ocean mining of uranium utilizing the fiber adsorbent. The starting material of this novel fiber adsorbent is easily available, and the synthesis procedure is simple and scalable. The fiber adsorbent can be mass produced for the extraction of valuable minerals from seawater. Direct seawater extraction (mining) is environmentally friendly compared to land mining and the recovery of uranium from seawater has received much attention over the past decades [5,6]. As early as 1964, the idea of extracting uranium from seawater was discussed by Davies et al. in a Nature paper [33]; however, very limited studies have been conducted on the recovery of REEs and precious metals from seawater. A few reports utilizing marine green algae and synthetic mineral particles for recovery of REEs from simulated seawater spiked with REEs are known in the literature [34,35], but these materials are not easily deployable in a seawater environment and are less efficient compared with the fiber adsorbent described in this report.

This work reports important data for the first time regarding the extraction of REEs and precious metals from seawater using a novel polymer adsorbent derive from an acrylic fiber. It is also noteworthy that the extraction of valuable metals from saline brines generated in desalination plants appears especially attractive [36,37]. The highly saline brine contains all minerals present in the ocean at nearly twice the concentrations in seawater. Mining minerals from these brines can offset part of the desalination cost as well as mitigate the brine disposal problem. Further research in this area is currently in progress.

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