

Optimisation of the Hydrophilic Conditioning of Amidoximated Polymers and Evaluation of their Uranium Adsorption Capability

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SUMMARY

- Polyacrylonitrile (Poly-AN) was modified using two-step conditioning: 1) amidoxime chelation and 2) conversion to carboxylic groups using sodium hydroxide (NaOH).
- Design of experiments (DOE) used to predict trends in uranium adsorption capability with changing factors of second step conditioning.
- Conditioning temperatures above 50 °C and NaOH concentrations >0.5 M are optimum to achieve highest possible uranium adsorption capacity.
- Despite an abundance of other cations, no statistical difference was observed between uptake of uranium from real seawater compared to laboratory prepared simulants and deionised water using bi-functionalised Poly-AN.

1. INTRODUCTION

The availability and cost of uranium for nuclear fuel are critical factors in the future viability of the nuclear power industry. Currently, uranium is extracted from solid ore deposits of the mineral uraninite. However, such deposits are relatively finite and the mining of uranium from underground deposits, in particular, can have many negative health effects for workers. Interestingly, while found at considerably higher concentrations in solid ore deposits, dissolved uranium is also present in seawater at lower concentrations (3 ppb). Accounting for the total volume of the oceans yields an estimated oceanic aqueous uranium mass of 4×10^{12} kg, which is equivalent to 1000 times the mass of uranium traditionally mined to date. Thus, the ocean represents a vast untapped reservoir of uranium.

However, the use of uranium from seawater pre-supposes that said aqueous deposits can be extracted economically. To meet this goal there is a requirement to produce a high-performance extraction method that can compete economically with existing mining technologies. The key to any seawater extraction technology is that it must be selective (i.e. other metal ions in seawater must not be extracted) and be able to be deployed on a large scale to maximize the concentration of the relatively tiny fraction of uranium found in seawater. Consequently, the design and synthesis of suitably functionalised adsorbents to selectively adsorb uranyl ions from multi-component seawater solutions have become an important area of international chemical research since the original suggestion of seawater extraction in the early 1970s [1].

With regards to producing a suitable uranium absorbent, in the last ten years, amidoximated polymers have been shown to enhance selectivity and increase uptake of uranium from seawater over other organic compounds, in particular in comparison with unmodified polymers [2]. The reaction of the polyacrylonitrile (Poly(AN)) with hydroxylamine in the presence of a base introduces the desired uranium selective amidoxime functionality, Poly(AN-AO), shown in Figure 1.

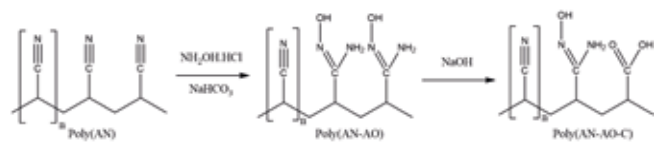


FIGURE 1: Functionalization of polyacrylonitrile (Poly(AN)) with hydroxylamine, and subsequent conversion with sodium hydroxide.

It is crucial that the base is carefully selected in this initial amidoximation functionalisation step. A weak base such as sodium hydrogen carbonate (NaHCO₃) limits the formation of carboxylate groups that will occur if a strong base is used, said carboxylic groups uncontrollably replacing amidoxime sites on the polymer and subsequently leading to a significant decrease in uranium chelation ability [3, 4].

Within the last five years, there have been reports in the literature that controllably increasing the degree of hydrophilicity of an amidoximated polymer adsorbent increases metal ion uptake above that of amidoximation alone [5, 6]. This must be carried out in a second base exposure step to enable careful control of the amount of carboxylic groups introduced so as not to

deteriorate overall uranium adsorption performance through the removal of too many amidoxime sites (*vide supra*). While various methods to increase hydrophilicity have been outlined in the literature, one of the most promising and simplistic is the use of potassium hydroxide or sodium hydroxide to convert amidoxime moieties into carboxylic moieties, as shown in step 2 of Figure 1.

However, while promising results have been reported in carboxylic functionalisation of Poly(AN-AO), there has hitherto been no concise effort to optimize and determine the key preparation factors that may influence the improved uranium adsorption capacity offered by the carboxylic functionalisation in the second conditioning step of Figure 1. Furthermore, a compounding factor in the future development of these materials is the lack of an existing method that would allow factorial dependent experiments to be followed, reproduced, and subsequently improved.

The primary aim of the work reported here is to address this by using design of experiments (DOE) software to optimise experimental design across three key physical factors: (i) NaOH concentration, (ii) conditioning time, and (iii) conditioning temperature.

In this instance, we use a reduced combinatorial method to generate suggested experimental test conditions for a wide variety of modified polymers. Said polymers are then used to absorb uranium from three different solution environments in a static absorption system to determine maximum uranium uptake. This is measured using post-addition of hydrochloric acid of appropriate molarity (around 0.5-1 M) via an elution process, with the filtrate from the adsorption and elution (the eluate) analysed using Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) to determine total uranium capacity. The output from these tests is statistically analysed in the same DOE software through mapping of the full parameter space to identify trends in conditioning and solution composition. Finally, determination of the degree of error of the generated predictive model for each physical condition is used to confirm whether qualitatively observed trends are statistically significant. Note, although a dynamic system is more representative of the suggested industrial application due to the infinite replenishment of uranium allowed in seawater (and therefore constant concentration), this work represents initial screening to ascertain optimal synthesis conditions, and thus static batch tests were preferred.

Seawater is a complex aqueous matrix of salts, ranging over several orders of magnitude in concentration. Since the intended use of the polymer adsorbents is to extract uranium from seawater, the effect of competing metal ions and their effect on adsorption capacity must be carefully studied. However, many previous studies of the uranium adsorption of amidoxime-functionalised Poly(AN) materials have only used ultrapure or refined chemical compositions to prepare seawater simulants, with relatively few studies performed in actual seawater [2, 7-9]. As a result, it is unclear as to what differences, if any, exist between the use of different water types and consequently whether studies in ultrapure or refined chemical compositions are wholly or partially exportable to uranium extraction in real seawater.

Thus, using the DOE method outlined above, the secondary aim of the work reported here has been to examine the adsorption of uranium from real seawater by functionalised Poly(AN) materials

and compare uptake with both a seawater simulant containing sodium chloride and magnesium chloride, as well as an ultrapure deionized water uranium solution.

2. MATERIALS AND METHODS

2.1. Materials

Polyacrylonitrile (Poly-AN) was purchased from MP Biomedical, LLC (product code 0521753805). The seawater (2L) was collected off the coast of the Wirral in the Northwest of England in March 2018 and was used in the experiments without any pre-treatment. The Water Purification System used was a Millipore Elix 3 (resistivity specification >5 M Ω ·cm at 25 °C).

2.2. Polyacrylonitrile functionalisation

A stirrer bar was added to a beaker (2 L). Sodium hydrogen carbonate (120 g) was then added, followed by deionised water (1 L), and stirred at 500 rpm. The solution was neutralized to ~pH 6 by gradual addition of hydroxylamine hydrochloride (100 g) in order to avoid a rapid evolution of gas. The pH evolution was monitored using litmus paper. Poly(AN) powder (5 g) was then added, and the suspension was stirred at 500 rpm at 50 °C for 1 hr. The modified Poly(AN) was vacuum filtered, washed repeatedly with deionised water, and dried in an oven at 60 °C for 24 hrs. This method was repeated seven times to produce a stock of Poly(AN AO) (~35 g) for use in section 2.3.

2.3. Conditioning of Amidoximated Polyacrylonitrile

The poly(AN-AO) was conditioned in the second step to give poly(AN-AO-C) under varying temperature conditions, reaction times, and NaOH concentrations (with constant volume). Experiments were designed using the DOE software MODDE from Umetrics. Table 1 gives a design of experiments for the variable conditioning parameters selected using the reduced combinatorial method within the software.

A stirrer bar was again added to a beaker (2 L). Sodium hydroxide (6, 12, or 18 g) was added depending on the desired concentration from Table 1, followed by the addition of deionised

Exp No.	Product Name	Mass (g) of Poly(AN-AO)	NaOH		Temp (°C)	Time (hrs)
			Mass (g)	Conc (M)		
1	Poly(AN-AO-C1)	1	6	0.15	25	0.5
2	Poly(AN-AO-C2)	1	12	0.30	25	1.0
3	Poly(AN-AO-C3)	1	18	0.45	25	2.0
4	Poly(AN-AO-C4)	1	6	0.15	40	1.0
5	Poly(AN-AO-C5)	1	12	0.30	40	1.0
6	Poly(AN-AO-C6)	1	12	0.30	40	1.0
7	Poly(AN-AO-C7)	1	12	0.30	40	2.0
8	Poly(AN-AO-C8)	1	18	0.45	40	0.5
9	Poly(AN-AO-C9)	1	6	0.15	50	2.0
10	Poly(AN-AO-C10)	1	12	0.30	50	0.5
11	Poly(AN-AO-C11)	1	18	0.45	50	1.0

TABLE 1: Suggested experimental conditioning parameters determined using MODDE DOE software.

water (1 L) and subsequent stirring at 200 rpm. Poly(AN-AO) (1 g) was added, and the suspension was further stirred at 200 rpm for the specified temperature and specified time based on Table 1. The so conditioned material was vacuum filtered, washed with deionised water, and dried in an oven at 60 °C for 24 hrs.

2.4. Adsorption of Metal Ions

Each of the polymer adsorbents, poly(AN), poly(AN-AO), and poly(AN-AO-C#) were tested for uranium adsorption performance against a uranium solution, a seawater simulant solution, and a real seawater solution as detailed in Table 2.

Solution name	Bulk solvent	Metal/Salt Concentration (ppm)				Solute
		U	NaCl	MgCl ₂	NaHCO ₃	
U – aqueous solution	DI H ₂ O	10	-	-	193	DI H ₂ O
U – seawater simulant	DI H ₂ O	10	15000	2000	193	DI H ₂ O
U – seawater	Seawater	10	15000	2000	193	Seawater

TABLE 2: Initial solution composition for adsorption experiments.

The solution pH was adjusted to ~8 using sodium hydrogen carbonate. 15 mg of adsorbent was added to 10 mL of U solution in a 15 mL sample vial and then placed on a shaker table at 120 min⁻¹ for 24 hrs before the vial contents were separated via vacuum filtration. The filtrate was set aside for analysis while the adsorbent was rinsed with deionised water prior to elution/desorption experiments.

2.5. Elution/desorption of Uranium Ions

For elution, each metal-loaded adsorbent was transferred to a new sample vial (15 mL) containing hydrochloric acid (1.0 M, 10 mL), and placed on a shaker table at 120 min⁻¹ for 24 hrs. The vial contents were vacuum filtered, and the filtered eluate set aside for ICP-MS analysis.

2.6. Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS)

ICP-MS was performed using a Perkin Elmer Elan DRC-e. Each adsorption and elution cycle was diluted by a factor of 10 for each polymer adsorbent and metal solution combination. The total adsorption capacity was then calculated using:

$$\begin{aligned}
 \text{Adsorption Capacity} & \left(\frac{\text{g}[\text{metal}]}{\text{kg}[\text{adsorbent}]} \right) \\
 & = [\text{metal}] \text{ in acid wash} \left(\frac{\text{g}}{\text{L}} \right) \\
 & \times \text{acid wash to adsorbent ratio} \left(\frac{\text{L}}{\text{kg}} \right)
 \end{aligned}$$

3. RESULTS

As described in section 2.3. the influence of three factors for converting amidoxime functionality into carboxylic acid groups was methodically investigated using a design of experiment matrix (L9 orthogonal array) within MODDE. The limits of the factors,

Factor	Minimum	Median	Maximum	Units
Concentration	0.15	0.30	0.45	M
Temperature	25	40	50	°C
Duration	0.5	1.0	2.0	h

TABLE 3: Conditioning parameter constraints used.

shown in Table 3, were chosen to allow the entire parameter space to be mapped efficiently and to show factor-factor interactions.

The calculated adsorption capacity taken from the results of the ICP-MS analysis for the unmodified Poly(AN), amidoxime modified Poly(AN-OA), and bi-functionalised Poly(AN-OA-C#) conditioned materials (the latter listed in Entries 1-11) are given in Table 4.

Entry	Product Name	Conditioning			U adsorbed (g.kg ⁻¹)		
		[NaOH] (M)	Temp (°C)	Time (hrs)	U aq	U sim	U sea
C1	Poly(AN)	0.00	25	0.0	0.006	0.033	0.048
C2	Poly(AN-AO)	0.00	25	0.0	0.174	0.130	0.123
1	Poly(AN-AO-C1)	0.15	25	0.5	0.213	0.068	0.144
2	Poly(AN-AO-C2)	0.30	25	1.0	0.172	0.029	0.213
3	Poly(AN-AO-C3)	0.45	25	2.0	0.223	0.033	0.155
4	Poly(AN-AO-C4)	0.15	40	1.0	0.149	0.033	0.164
5	Poly(AN-AO-C5)	0.30	40	1.0	0.362	0.065	0.210
6	Poly(AN-AO-C6)	0.30	40	1.0	0.267	0.224	0.276
7	Poly(AN-AO-C7)	0.30	40	2.0	0.297	0.353	0.305
8	Poly(AN-AO-C8)	0.45	40	0.5	0.319	0.315	0.306
9	Poly(AN-AO-C9)	0.15	50	2.0	0.308	0.423	0.264
10	Poly(AN-AO-C10)	0.30	50	0.5	0.358	0.343	0.184
11	Poly(AN-AO-C11)	0.45	50	1.0	0.366	0.416	0.354

TABLE 4: Uranium adsorption for unmodified, amidoxime modified and bi-functionalised polyacrylonitrile adsorbents prepared under a range of conditioning parameters.

From Table 4 it can be seen that, as expected, the amidoxime modified Poly(AN-AO) and bi-functionalised Poly(AN-OA-C#) samples all show increased sorption of uranium over the unmodified Poly(AN).

Using the dataset in Table 4, the design of experiment software MODDE was used to produce a Multiple Linear Regression model in order to predict the behaviour of each parameter with regards to uranium adsorption (concentration of NaOH, conditioning temperature, conditioning time, and water composition). The coefficient of determination (R², also reported as R-squared) is a statistical metric that reports the variation of the outcome by the variation in the independent variables. The R² determined for this data set is 62% of the variance in the observed activities for the training set. Q², also reported as Q-squared, is a measure of how well the model and the data collected can interpolate new data points accurately. It is derived from the Predicted Residual Sum of Squares which is converted to the same scale as R². A Q² value should match R² in a good model and should be greater than 50%. For this data set,

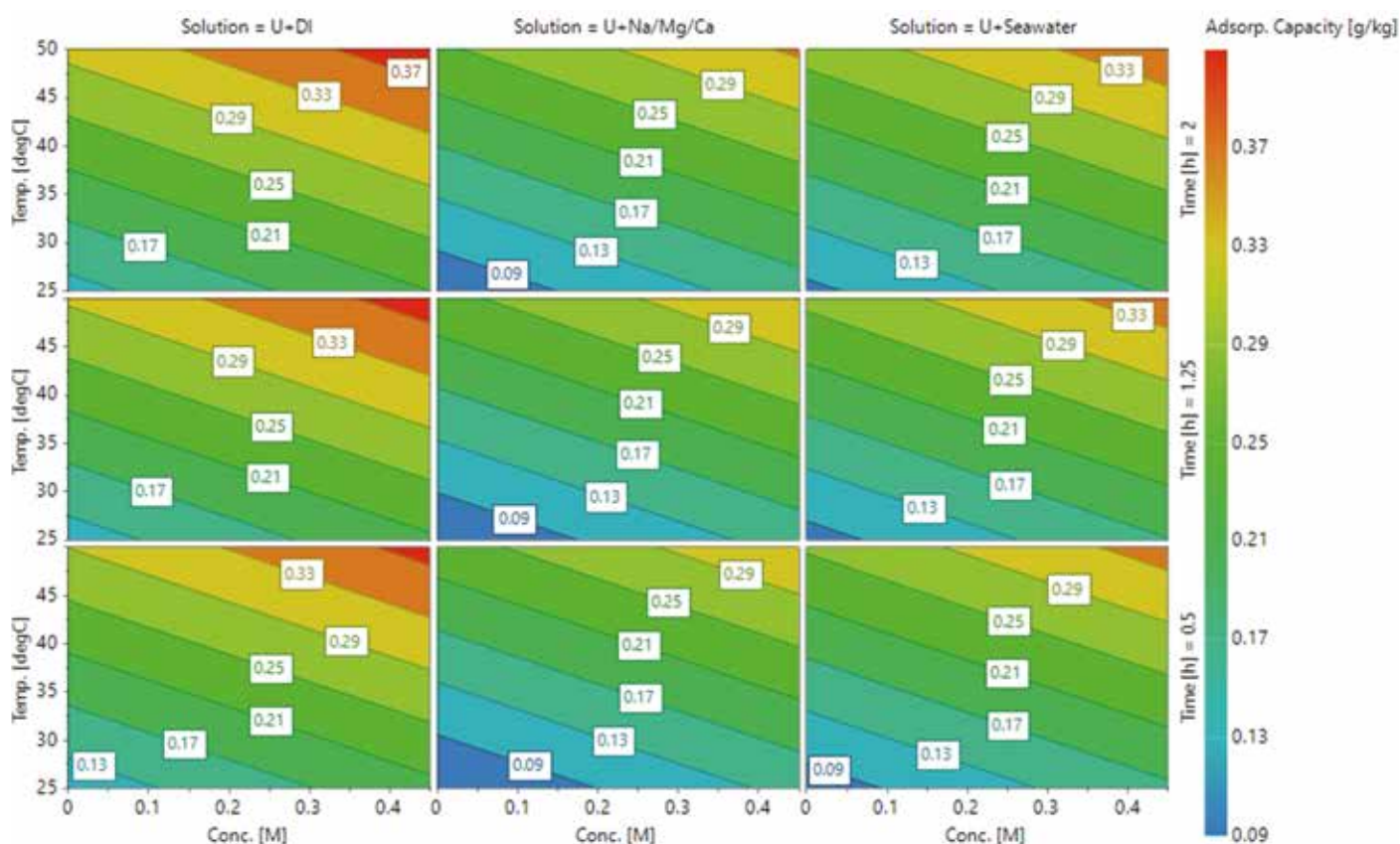


FIGURE 2: Four-dimensional plot of the entire parameter space performed in MODDE.

the value obtained is close to 50% being 46%, but is similar to the R2 of 61%, validating the use of the model in this context.

In order to rapidly identify trends in conditioning parameters and solution composition, the results derived from the MLR analysis were interpolated to provide a map of the entire landscape of the parameter space. Such a map provides an insight into the factor interactions that could not be rapidly achieved using a traditional large experimental series, e.g. by altering one variable at a time and is shown visually as a four-dimensional contour plot in Figure 2.

The four-dimensional contour plot consists of a 3x3 array of single x and y plots. In order to understand the significance of figure 2, let us first consider a single x,y plot in the bottom left of Figure 2. This area has sodium hydroxide concentration on the x-axis and conditioning temperature on the y-axis. Expanding our selection to the data columns now, each column (1x3 vertical) is associated with a different water composition, visually showing the effect from left to right of more complex salt solutions. Finally, expanding the selection further to each row (1x3 horizontal) shows the effect of conditioning time, moving from 0.5 to 2 hours conditioning time moving up each column.

From Figure 2 several trends can be observed. First, and regardless of water type conditioning time or NaOH concentration, it appears that increasing the conditioning temperature results in large improvements in the uranium adsorption capacity of Poly(AN-AO-C). Secondly, an increase in sodium hydroxide concentration regardless of temperature, conditioning time, or water type also shows an increase in uranium adsorption capacity of Poly(AN-AO-C), albeit the degree of increase less than that caused by an increase in temperature.

Turning now to the row and column categories of conditioning time and water type, in the former visually there appears to be no discernible trend between the examined times. As there is little improvement with increased reaction time, this indicates that the chemical reaction reaches steady state within the first 30 minutes, showing that longer reaction times are not significant in improving uranium adsorption. Across the columns small differences in uranium adsorption capacity exist between the simulated seawater and real seawater at the higher temperature limit, generally, there appears to be very little difference in uranium adsorption capacity of Poly(AN-AO-C) across the two ion heavy water types. However, further comparison with the deionised water, only plots of the first column reveal that uranium adsorption capacity of Poly(AN-AO-C) is much greater across the entire temperature range in this water type vs. the two ion heavy water types. Such a result is not unsurprising, as significantly fewer interfering ions will be present in this water type vs. either the simulated seawater or real seawater samples.

In order to determine if these observed effects are statistically significant, each parameter as a scaled coefficient was plotted with error bars added. These plots are shown in Figure 3, with the effect of the physical parameters of NaOH concentration, conditioning time, and conditioning temperature on uranium adsorption capacity of Poly(AN-AO-C) shown in Figure 3(A) and the effect of differing water types on uranium adsorption capacity shown in Figure 3(B).

First considering the general form of the plots of Figure 3, it can be seen that the relative uncertainty between categories is quite

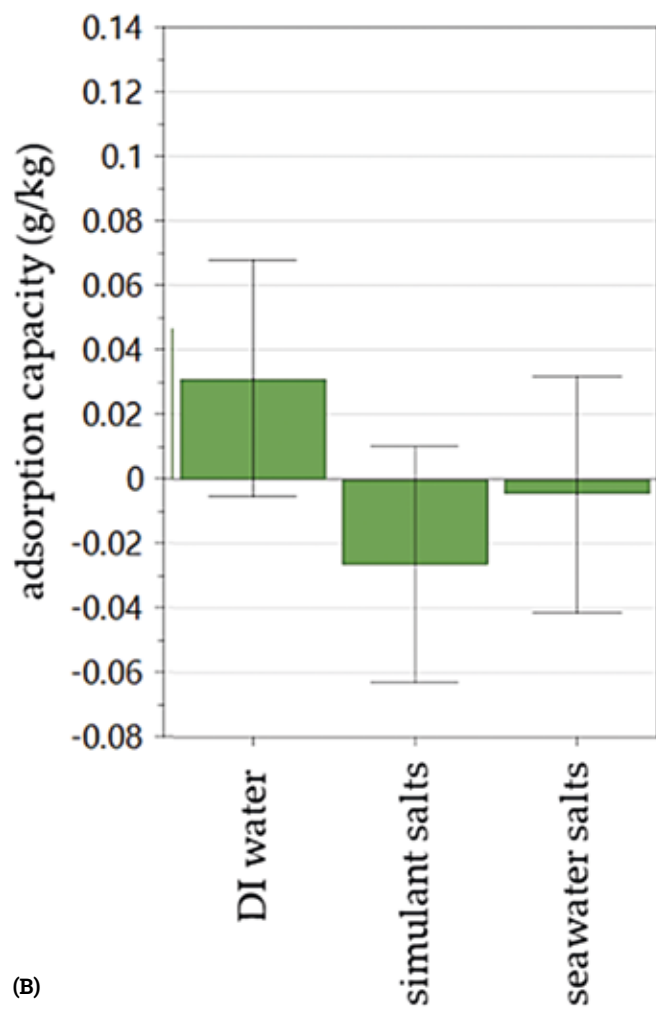
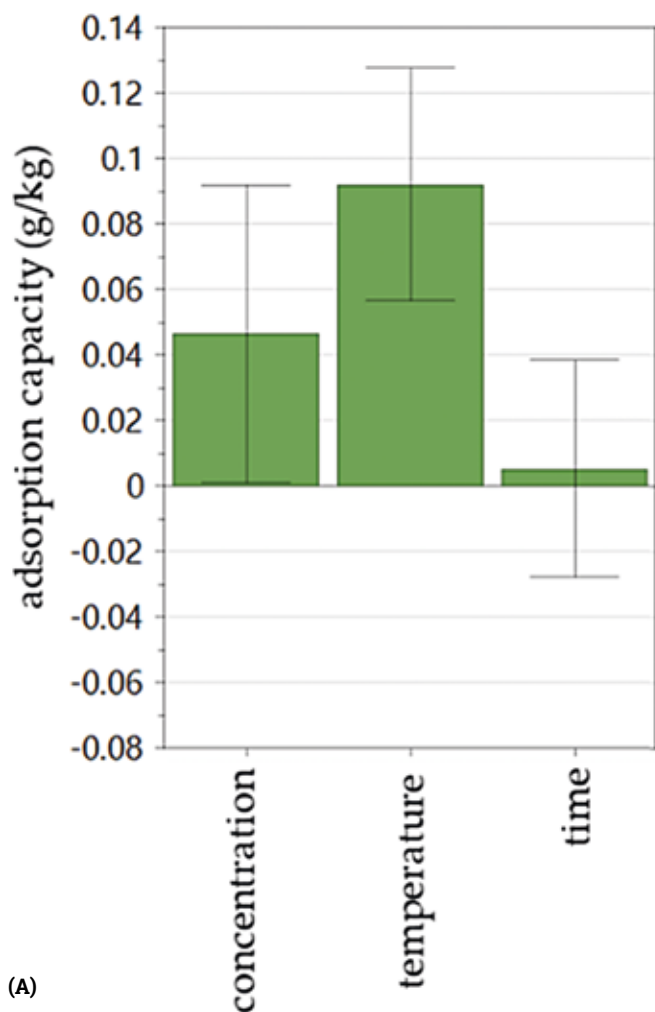


FIGURE 3: Coefficients plots for sorption response, with a confidence level of 95%.

high as a result of the low R2 and Q2 values, suggesting future applications of DOE software to this problem would benefit from the use of a larger number of physical experiments. Indeed, if the uncertainty overlaps with $y = 0$, then that parameter can be deemed to be statistically non-significant within this collected dataset.

Considering Figure 3(A) first and specifically focusing on the effect of conditioning time, despite a positive average uranium adsorption capacity with increasing conditioning time, the degree of uncertainty strongly suggests that no correlation exists between the two. This is surprising as it would be expected that a greater conditioning time would increase the number of carboxylic acid groups created at a set concentration of NaOH. One possible explanation for this is that a maximum number of attached carboxylic groups required to make the molecule suitably hydrophilic are created quicker than 0.5 hours. As a maxima of sites exist at 0.5 hours, no further improvement in the uranium adsorption capacity of Poly(AN-AO-C) occurs at conditioning times > 0.5 hours. If correct, such an observation has interesting implications for the industrial scale-up of the manufacture of such materials, i.e. synthesis times and associated costs can be significantly decreased while still maintaining the maximum

uranium adsorption capacity of the polymer. Thus, future work will look to study conditioning times shorter than 0.5 hours.

Turning now to the effect of NaOH concentration, as suggested by the contour plots of Figure 2, the calculated statistical error of Figure 3(A) shows that increasing concentrations of NaOH during conditioning do indeed significantly increase the uranium adsorption capacity of Poly(AN-AO-C). Returning to Figure 2 and comparing across the tested concentration range at a set temperature it appears that despite the relatively high concentration of NaOH used (0.5 M) further improvements in uranium adsorption capacity of Poly(AN-AO-C) could still be possible at NaOH conditioning concentrations greater than 0.5 M, assuming the software predicted trend continues. Again, finding the upper limit of conditioning concentration above which further improvement in uranium adsorption capacity of Poly(AN-AO-C) does not occur due to excessive removal of the actively chelating amidoxime sites will form the subject of future studies.

Finally, conditioning temperature has the largest and most significant effect on the uranium adsorption capacity of Poly(AN-AO-C). Such an observation suggests that the reaction of sodium hydroxide with Poly(AN-AO) to form Poly(AN-AO-C) is

very much temperature-dependent. Again, the contour plot of Figure 2, assuming the predicted trend continues, suggests that temperatures greater than 50°C could further improve the uranium adsorption capacity of Poly(AN-AO-C) and such investigations, as well as the determination of a kinetic rate constant for the carboxylation process, will form the focus of future investigations.

Considering finally the effect of seawater type shown in Figure 3(B), both the seawater simulant and real seawater have negative averages for uranium adsorption capacity compared to the positive average of absorption experiments performed in deionized water. Like Figure 2 this would initially suggest that significantly fewer interfering ions present in the deionised water vs. either the simulated or real seawater has a detrimental effect on the selective uranium adsorption capacity of Poly(AN-AO-C). The magnitude of reduction in adsorption capacity shows that laboratory prepared seawater simulants may not be a realistic comparison for actual seawater samples as the scaled coefficient shows a greater negative effect. This is likely due to the organic components from marine life. However, despite the calculated averages, the degree of uncertainty between the three water types overlaps the x-axis, and any observed trends are therefore not significant. While we accept this analysis for the dataset of Table 4, based on the extrapolation of the contour plot of Figure 2 and comparisons across the existing literature (2, 7-9) we suspect that a further study with a greater number of initial input experiments (in order to improve R2 and Q2) may result in the positive effect of deionised water on the uranium adsorption capacity of Poly(AN-AO-C) becoming statistically significant. Nevertheless, returning to the current dataset analysis of Figure 3(B) from the lack of any significant difference in uranium adsorption capacity between the three water types we may draw the tentative conclusion that despite the abundant cations found in real seawater and seawater simulants there is no significant reduction in uranium uptake ability for Poly(AN-AO-C). Such an observation thus highlights the specificity of such materials for the extraction of uranium in complex aqueous ionic media.

4. CONCLUSIONS

Using Design of Experiments (DOE) software the primary factors that determine uranium adsorption capacity in the carboxylic functionalisation (conditioning) of amidoximated polyacrylonitrile, reported as Poly(AN-AO-C), materials have been elucidated. Three key factors in the synthesis of such materials have been tested in total, conditioning temperature, conditioning time, and base concentration (NaOH).

Analysis of the scaled coefficient of conditioning time suggests that no correlation exists between the conditioning time and uranium adsorption capacity. Such an observation has been hypothesised to be due to a maxima of carboxylic sites forming at times < 0.5 hours, suggesting synthesis times and associated costs can be decreased while still maintaining maximum uranium adsorption capacity of the polymer.

Using the same coefficients analysis, both conditioning temperature and NaOH concentration are found to have a significant effect on the uranium adsorption capacity of Poly(AN-AO-C). In the case of the former, increasing the conditioning temperature from 25 to 50°C almost doubles the uranium adsorption capacity of Poly(AN-AO-C) and interpolated contour plots suggest that further improvements in the uranium adsorption capacity of Poly(AN-AO-C)

could be produced if the reaction were to be performed at even higher temperatures. In the case of the latter, a smaller but again significant increase in the uranium adsorption capacity of Poly(AN-AO-C) is observed over the NaOH concentration range of 0 to 0.5 M. As with conditioning temperature, interpolated contour plots suggest that further improvements in the uranium adsorption capacity of Poly(AN-AO-C) could be produced if the reaction were to be performed at even higher NaOH concentrations.

Finally, in addition to the process optimization study, bi-functionalized Poly-AN uptake of uranium from real seawater has also been compared with laboratory-prepared simulants and deionized water. Despite a calculated positive average for uranium extraction of Poly(AN-AO-C) in the deionized water condition, no statistically significant differences were found between the three water types in this data set. This suggests that despite the abundant cations found in real seawater and seawater simulants there is no significant reduction in uranium uptake ability for Poly(AN-AO-C). Such an observation highlights the specificity of such materials for the extraction of uranium in complex aqueous ionic media.

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**BRUCE HANSON**

Bruce Hanson holds a Leadership Chair in Nuclear Process Engineering at the University of Leeds and is an Honorary Professor of Nuclear Engineering at University College London. He is a named investigator on 10 grants, leading EPSRC's ATLANTIC programme, and a Co-Director of the GREEN CDT. Before his appointment at Leeds, he spent 25+ years in the nuclear and chemical industries, across a range of functions, specialising in actinide separations and treatment of irradiated nuclear fuel. Most recently, he was the Technical Authority for Spent Fuel and Nuclear Materials at the National Nuclear Laboratory, where he is a Visiting Senior Fellow.

**ALASTAIR BAKER, MChem PH. D., MRSC FHEA**

Alastair Baker gained an MChem Chemistry (2011) at Cardiff University/ Prifysgol Caerdydd where he also received his PhD (2016). Then undertook postdoctoral studies in catalyst development in self-optimising reactors between the Institute of Process Research and Development and the University of Nottingham. He has since commissioned the Leeds Nuclear Lab (2018) and undertaking process intensification studies from lab scale to pilot plant to deliver a viable next-generation aqueous recycling cycle for the UK.

