

1 Article

# 2 Optimisation of the Hydrophilic Conditioning of 3 Amidoximated Polymers and Evaluation of their 4 Uranium Adsorption Capability

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## 13 Abstract:

14 We report a study on the optimization of hydrophilic conditioning of polyacrylonitrile (Poly-AN)  
15 for application in economically competitive uranium extraction from seawater. Poly-AN is typically  
16 modified in a two-step conditioning method: 1) initial introduction of amidoxime chelation sites for  
17 selective uranium adsorption and 2) further conversion of said sites to carboxylic acids to reduce  
18 the hydrophobicity of the polymer using a strong base. Here, using design of experiments (DOE)  
19 statistical computer models to predict trends from a limited set of physical experiments, the primary  
20 factors in the second step conditioning of amidoximated polymers that may influence uranium  
21 adsorption have been determined. It is found that conditioning temperature and concentration of  
22 the base used are the only statistically significant factors that may affect total uranium uptake in  
23 these materials. Furthermore, analysis of the DOE modelled data for both factors suggests that  
24 conditioning temperatures in excess of 50°C and NaOH concentrations >0.5 M are optimum in  
25 producing bi-functionalised Poly-AN materials with the highest possible uranium adsorption  
26 capacity.

27 In addition to the process optimization study, bi-functionalized Poly-AN uptake of uranium from  
28 real seawater has also been compared with laboratory prepared simulants and deionized water. No  
29 statistically significant differences in this data set were found between the three water types,  
30 suggesting that despite the abundant cations found in real seawater and seawater simulants there  
31 is no significant reduction in uranium uptake ability for bi-functionalised Poly-AN.

32 **Keywords:** Amidoximation, Desorption, Sorption, Polyacrylonitrile, Uranyl ions, Design of  
33 Experiments  
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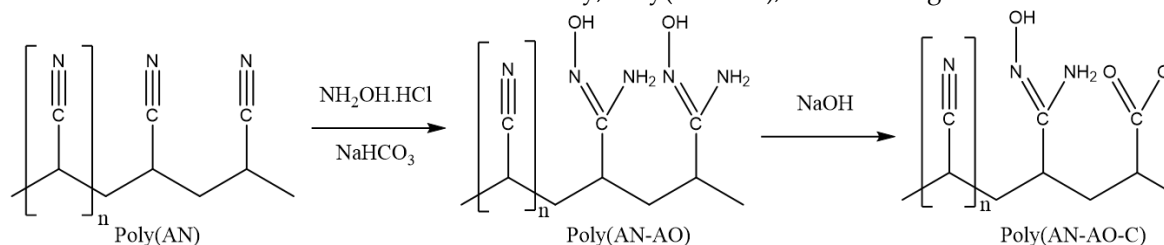
## 35 1. Introduction

36 Availability and cost of uranium for nuclear fuel is a critical factor in the future viability of the  
37 nuclear power industry. Currently, uranium is extracted from solid ore deposits of the mineral  
38 uraninite. However, such deposits are relatively finite and the mining of uranium from underground  
39 deposits in particular can have many negative health effects for workers. Interestingly, while found  
40 at considerably higher concentrations in solid ore deposits, dissolved uranium is also present in  
41 seawater at lower concentrations (3 ppb). Accounting for the total volume of the oceans yields an  
42 estimated oceanic aqueous uranium mass of  $4 \times 10^{12}$  kg, which is equivalent to 1000 times the mass

43 of uranium traditionally mined to date. Thus, the ocean represents a vast untapped reservoir of  
 44 uranium.

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

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



59 **Figure 1.** Functionalization of polyacrylonitrile (Poly(AN)) with hydroxylamine, and subsequent  
 60 conversion with sodium hydroxide.

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

66 Within the last five years there have been reports in the literature that controllably increasing  
 67 the degree of hydrophilicity of an amidoximated polymer adsorbent increases metal ion uptake  
 68 above that of amidoximation alone (5, 6). This must be carried out in a second base exposure step to  
 69 enable careful control of the amount of carboxylic groups introduced so as not to deteriorate overall  
 70 uranium adsorption performance through removal of too many amidoxime sites (*vide supra*). While  
 71 various methods to increase the hydrophilicity have been outlined in the literature, one of the most  
 72 promising and simplistic is the use of potassium hydroxide or sodium hydroxide to convert  
 73 amidoxime moieties into carboxylic moieties, as shown in step 2 of Figure 1.

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

81 The primary aim of the work reported here is to address this by using design of experiments  
 82 (DOE) software to optimise experimental design across three key physical factors: (i) NaOH  
 83 concentration, (ii) conditioning time and (iii) conditioning temperature. Methods from the DOE field  
 84 have been applied to quality control problems in many engineering disciplines for several decades.  
 85 DOE software seeks to maximize the amount of information gained in an experiment by optimizing  
 86 the combinations of independent variables. Often referred to as combinatorial testing methods, such  
 87 models provide an efficient means of providing an excellent coverage of the experimental or physical  
 88 factors with a small number of tests.

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

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

112 Thus, using the DOE method outlined above, the secondary aim of the work reported here has  
113 been to examine the adsorption of uranium from real seawater by functionalised Poly(AN) materials  
114 and compare uptake with both a seawater simulant containing sodium chloride and magnesium  
115 chloride, as well as an ultrapure deionized water uranium solution.

## 116 2. Materials and Methods

### 117 2.1. Materials

118 Polyacrylonitrile (Poly-AN) was purchased from MP Biomedical, LLC (product code  
119 0521753805). The seawater (2L) was collected off the coast of the Wirral in the North West of England  
120 in March 2018 and was used in the experiments without any pre-treatment. The Water Purification  
121 System used was a Millipore Elix 3 (resistivity specification  $>5 \text{ M}\Omega\cdot\text{cm}$  at  $25 \text{ }^\circ\text{C}$ ).

### 122 2.2. Polyacrylonitrile functionalisation

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

### 130 2.3. Conditioning of Amidoximated Polyacrylonitrile

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

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**Table 1.** Suggested experimental conditioning parameters determined using MODDE DOE software.

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

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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 of Table 1, followed by the addition of deionised 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

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#### 2.4 Adsorption of Metal Ions

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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.

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**Table 2.** Initial solution composition for adsorption experiments

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

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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 then placed on a shaker table at 120 min<sup>-1</sup> 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.

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#### 2.5 Elution/desorption of Uranium Ions

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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<sup>-1</sup> for 24 hrs. The vial contents were vacuum filtered, and the filtered eluate set aside for ICP-MS analysis.

## 158 2.6. Inductively Couple Plasma – Mass Spectroscopy (ICP-MS)

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

$$162 \text{ Adsorption Capacity } \left( \frac{\text{g of metal}}{\text{kg of adsorbent}} \right)$$

$$163 = [\text{metal}] \text{ in acid wash } \left( \frac{\text{g}}{\text{L}} \right) \times \text{acid wash to adsorbent ratio } \left( \frac{\text{L}}{\text{kg}} \right)$$

## 165 3. Results

166 As described in section 2.3. the influence of three factors for converting amidoxime  
 167 functionality into carboxylic acid groups was methodically investigated using a design of experiment  
 168 matrix (L9 orthogonal array) within MODDE. The limits of the factors, shown in Table 3, were chosen  
 169 to allow the entire parameter space to be mapped efficiently and to show factor-factor interactions.

170 171 **Table 3.** Conditioning parameter constraints used.

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

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

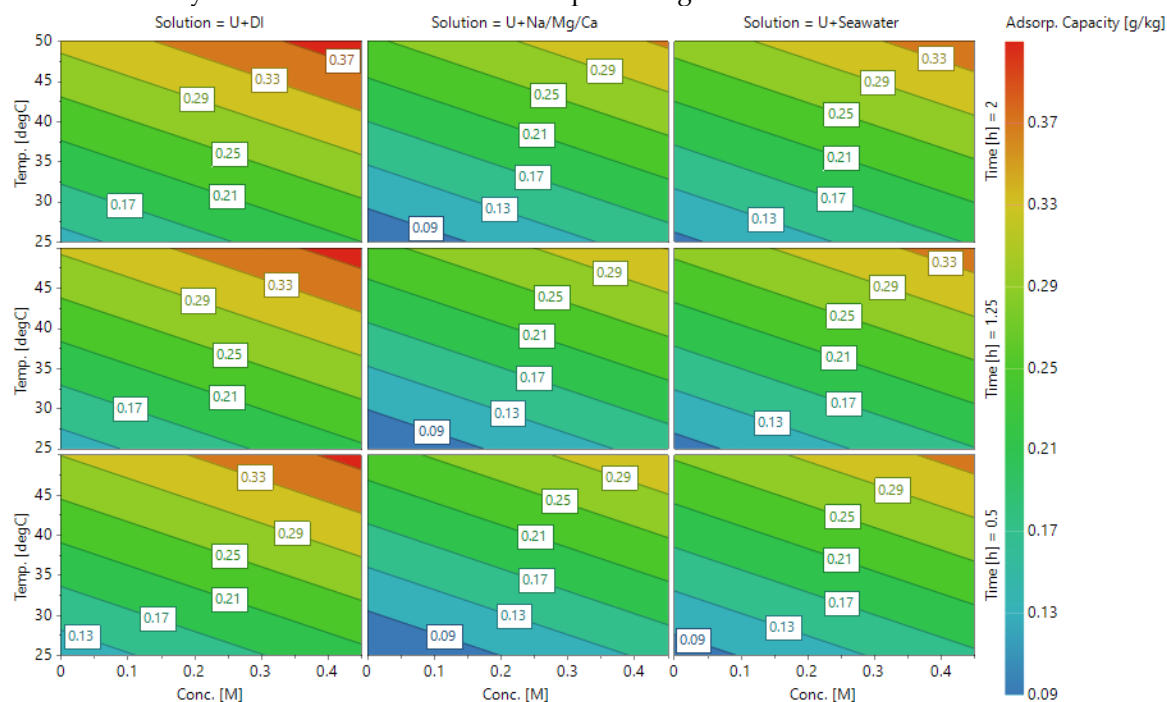
175 176 177 178 **Table 4.** Uranium adsorption for unmodified, amidoxime modified and bi-functionalised polyacrylonitrile adsorbents prepared under a range of conditioning parameters

Entry	Product Name	Conditioning			Uranium adsorbed (g.kg <sup>-1</sup> )		
		[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	0.13	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	0.21
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)	0.3	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

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

183 Using the dataset of Table 4, the design of experiment software MODDE was used to produce a  
 184 Multiple Linear Regression model in order to predict the behaviour of each parameter with regards  
 185 to uranium adsorption (concentration of NaOH, conditioning temperature, conditioning time and  
 186 water composition). The coefficient of determination ( $R^2$ , also reported as R-squared) is a statistical  
 187 metric that reports the variation of outcome by the variation in the independent variables. The  $R^2$   
 188 determined for this data set is 62% of the variance in the observed activities for the training set.  $Q^2$ ,  
 189 also reported as Q-squared, is a measure of how well the model and the data collected can interpolate  
 190 new data points accurately. It is derived from the Predicted Residual Sum of Squares which is  
 191 converted to the same scale as  $R^2$ . A  $Q^2$  value should match  $R^2$  in a good model, and should be greater  
 192 than 50%. For this data set the value obtained is close to 50% being 46%, but is similar to the  $R^2$  of  
 193 61%, validating the use of the model in this context.

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



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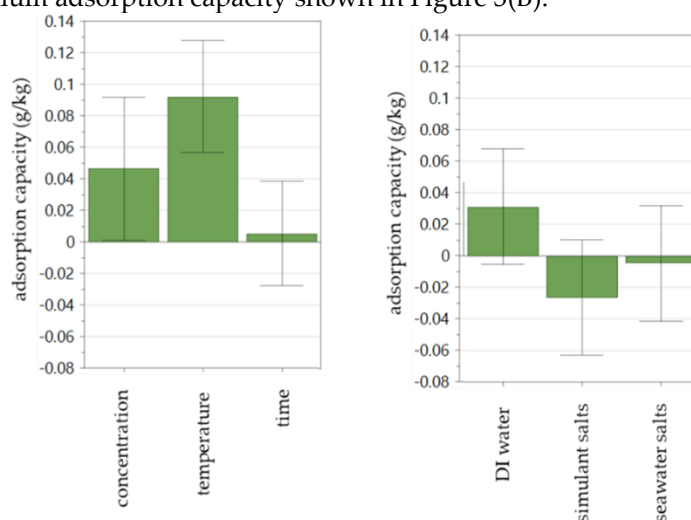
202 The four dimensional contour plot consists of a 3x3 array of single x,y plots. In order to  
 203 understand the significance of figure 2, let us first consider a single x,y plot in the bottom left of Figure  
 204 2. This area has sodium hydroxide concentration on the x-axis and conditioning temperature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

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

213 increase in uranium adsorption capacity of Poly(AN-AO-C), albeit the degree of increase less than  
214 that caused by an increase in temperature.

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

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



232 **Figure 3.** Coefficients plots for sorption response, with confidence level of 95%.  
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235 Considering initially the general form of the plots of Figure 3, it can be seen that the relative  
236 uncertainty between categories is quite high as a result of the low  $R^2$  and  $Q^2$  values, suggesting future  
237 applications of DOE software to this problem would benefit from the use of a larger number of  
238 physical experiments. Indeed, if the uncertainty overlaps with  $y = 0$ , then that parameter can be  
239 deemed to be statistically non-significant within this collected dataset.

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

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

262 Finally, conditioning temperature has the largest and most significant effect on the uranium  
263 adsorption capacity of Poly(AN-AO-C). Such an observation suggests that the reaction of sodium  
264 hydroxide with Poly(AN-AO) to form Poly(AN-AO-C) is very much temperature dependent. Again,  
265 the contour plot of Figure 2, assuming the predicted trend continues, suggests that temperatures  
266 greater than 50°C could further improve the uranium adsorption capacity of Poly(AN-AO-C) and  
267 such investigations as well as the determination of a kinetic rate constant for the carboxylation  
268 process will form the focus of future investigations.

269 Considering finally the effect of seawater type shown in Figure 3(B), both the seawater simulant  
270 and real seawater have negative averages for uranium adsorption capacity compared to the positive  
271 average of absorption experiments performed in deionized water. Like Figure 2 this would initially  
272 suggest that significantly fewer interfering ions present in the deionised water vs. either the  
273 simulated or real seawater has a detrimental effect on the selective uranium adsorption capacity of  
274 Poly(AN-AO-C). The magnitude of reduction in adsorption capacity shows that laboratory prepared  
275 seawater simulants may not be realistic comparison for actual seawater samples as the scaled  
276 coefficient shows a greater negative effect. This is likely due to the organic components from marine  
277 life. However, despite the calculated averages the degree of uncertainty between the three water  
278 types overlaps the x-axis, and any observed trends are therefore not significant. While we accept this  
279 analysis for the dataset of Table 4, based on the extrapolation of the contour plot of Figure 2 and  
280 comparisons across the existing literature (2, 7-9) we suspect that a further study with a greater  
281 number of initial input experiments (in order to improve  $R^2$  and  $Q^2$ ) may result in the positive effect  
282 of deionised water on the uranium adsorption capacity of Poly(AN-AO-C) becoming statistically  
283 significant. Nevertheless, returning to the current dataset analysis of Figure 3(B) from the lack of any  
284 significant difference in uranium adsorption capacity between the three water types we may draw  
285 the tentative conclusion that despite the abundant cations found in real seawater and seawater  
286 simulants there is no significant reduction in uranium uptake ability for Poly(AN-AO-C). Such an  
287 observation thus highlights the specificity of such materials for the extraction of uranium in complex  
288 aqueous ionic media.  
289

## 290 Conclusions

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

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

301 Using the same coefficients analysis, both conditioning temperature and NaOH concentration  
302 are found to have a significant effect on the uranium adsorption capacity of Poly(AN-AO-C). In the



303 case of the former, increasing the conditioning temperature from 25 to 50°C almost doubles the  
304 uranium adsorption capacity of Poly(AN-AO-C) and interpolated contour plots suggest that further  
305 improvements in the uranium adsorption capacity of Poly(AN-AO-C) could be produced if the  
306 reaction were to be performed at even higher temperatures. In the case of the latter, a smaller but  
307 again significant increase in the uranium adsorption capacity of Poly(AN-AO-C) is observed over the  
308 NaOH concentration range of 0 to 0.5 M. As with conditioning temperature, interpolated contour  
309 plots suggest that further improvements in the uranium adsorption capacity of Poly(AN-AO-C)  
310 could be produced if the reaction were to be performed at even higher NaOH concentrations.

311 Finally, in addition to the process optimization study, bi-functionalized Poly-AN uptake of  
312 uranium from real seawater has also been compared with laboratory prepared simulates and  
313 deionized water. Despite a calculated positive average for uranium extraction of Poly(AN-AO-C) in  
314 the deionized water condition, no statistically significant differences were found between the three  
315 water types in this data set. This suggests that despite the abundant cations found in real seawater  
316 and seawater simulants there is no significant reduction in uranium uptake ability for Poly(AN-AO-  
317 C). Such an observation highlights the specificity of such materials for the extraction of uranium in  
318 complex aqueous ionic media.  
319

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