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Bis-Catecholamide-Based Materials for Uranium Extraction

Guillaume Mossand⁺, Evan Lelong⁺, Chen Xing, Frantz Ndebulia Watchou, Antoine Leydier, Guilhem Arrachart,^{*} and Stéphane Pellet-Rostaing^{*[a]}

This work reports the synthesis of formo-phenolic resins containing four catecholamide (CAM) moieties with admixture of phenol, catechol or resorcinol. These chelating resins have been developed to selectively extract U(VI) from seawater. This media is a challenging environment due to a pH around 8.2 and a large excess of alkaline and earth-alkaline cations. From the various sorption experiments investigated, the results

indicate that the synthesized material exhibit good sorbent properties for U(VI) with uptake capacity about 50 mg/g for the more promising resins with a pronounced selectivity for uranium even under saline conditions. Thermodynamic and kinetic adsorption data were determined for the best resin (Langmuir adsorption model and pseudo-second order model).

Introduction

According to the IAEA (International Atomic Energy Agency), the global nuclear electrical generating capacity should increase by 82% from 392 GWe in 2019 with 443 operational nuclear power reactors to 715 GWe expected by 2050 (high case scenario). Therefore, the demand for natural uranium should increase up to 85% by 2040 (demand was 59,200 t in 2019).^[1,2] Thus, there is a real need to search for new exploitable uranium resources. Since 71% of the Earth's surface is covered by adjacent oceans and seas, this area represents a total volume of seawater of $1.37 \times 10^9 \text{ km}^3$. Among the main constituents of seawater, Cl, Na, sulphate, Mg, Ca, K, Sr and hydrogen carbonate at concentrations ranging from a hundred ppm to several g/L, uranium is present on average at 3.3 $\mu\text{g/L}$. Nevertheless, this very low value, especially in front of the macro-concentrations of alkalis and alkaline-earth metals, represents the largest uranium resource on Earth with approximately 4.5 billion tonnes – approximately 500 times more than the terrestrial uranium.^[3–5]

Regardless of the future increase in uranium demand, the costs and economic changes, exploitation of seawater as uranium source presents two main obstacles:

(1) Uranium is present in seawater at 92% in a strongly complexed anionic form – tricarbonatouranate (VI) ($\text{UO}_2(\text{CO}_3)_3^{4-}$) – and in extreme dilution with macro-concentrations of competing ions.^[6,7] In view of the high concentration of Ca^{2+}

ions in seawater, it has been shown that this species is mainly in the form of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$.^[8]

(2) The extraction of metals from large volumes of seawater is extremely complicated and its set up is very expensive. To be economically sustainable, the separation must be carried out by solid-liquid extraction using an extractant which is efficient and very selective at the pH and ionic strength of seawater. In addition, it must be insoluble in this medium and resist to corrosivity and biofouling.^[9]

The first studies dealing with the recovery of uranium from seawater date back to the early 1960s. Many countries took an interest in it such as Japan, United States, India, China and a few European countries. Adsorption by chelating materials appears to be the most promising method for recovering uranium from seawater in terms of easy operation, operating cost, environmental risk and adsorption capacity, compared to other separation methods such as coagulation, coprecipitation or membrane filtration.^[10–13] One of the most important aspects in the uranium recovery from seawater is the development of new materials with large adsorption coefficients and very high selectivity to avoid competing cations. The materials developed over the past few decades can be divided into four categories: i) polymers, ii) biopolymers, iii) inorganic and composite materials and iv) porous carbon polymers.

Among this materials, polymers received the most interest for uranium recovery from seawater.^[14] Different chemical functions known to selectively extract uranium can be easily grafted onto polymer matrices to increase the material's adsorption capacities. They have the advantage to be available in different forms (powders, blocks, fibers, foams, etc.). Among the most studied polymers, the resins containing amidoxime groups were probably the most promising, especially as poly (acrylamidoxime).^[15] Zhang *et al.* achieved absorption coefficients (Q_{ads}) of 44 mg/g at pH=8.^[16] Other functional groups studied shown good extracting properties, such as 5,7-dichloroquinoline-8-ol ($Q_{\text{ads}}=33 \text{ mg/g}$) or succinic acid ($Q_{\text{ads}}=27 \text{ mg/g}$).^[17] Otherwise, Shinkai *et al.* obtained adsorption coefficients of 123 mg/g thanks to resins based on calix[6]arene but under conditions different from seawater.^[18]

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More recently, many teams drew inspiration from results obtained with amidoxime-based polymers to improve adsorption capacities. Teams from the Oak Ridge National Laboratory (ORNL) focused on modifying the amidoxime function in order to increase the affinity of the extractant for uranium. Thus, under real conditions, a uranium adsorption coefficient of 4.5 mg/g was reached^[19,20] but the resin also extracts a large amount of Mg and Ca (around 40 mg/g). Despite this low selectivity, the study of a selective back-extraction of competing metals was initiated and shew good results for Mg and Ca.^[21] In Japan, an offshore platform made up of 52,000 adsorbent sheets (350 kg) spread over three stages enabled the recovery of approximately 1 kg of uranium U₃O₈, after 240 days of submersion.^[22] The most recent publications concerning the extraction of uranium from seawater tell us that certain materials exhibit a very strong affinity for uranium in a synthetic medium but a drastic decrease of this affinity in a real environment, with a very low selectivity with respect to the competing metals. Therefore, there is a real challenge in developing new materials with a very strong affinity for uranium and very high selectivity. For this purpose, metal-organic frameworks (MOF)^[23,24] as well as polydopamine materials^[25–27] have been proposed.

Based on the performance of uranium sequestration agents, the objective is to incorporate them into solid matrices to achieve adsorbent materials.

Since the pioneering work of K. Raymond and co-workers^[28,29] on uranyl-sequestering agents based on sulfocatecholamide (CAMS) moiety as efficient bio-compatible siderophores for in vivo chelation of U(VI), various sequestration agents have been proposed.^[30–32]

In this context, we described and studied the synthesis and the evaluation of several CAMS analogues^[33] incorporating various diamine skeletons (Figure 1). We also described several calixarene,^[34] binaphthyl,^[35] EDTA and DTPA^[36] based compounds functionalized with CAMS chelating units and their properties towards uranium chelation in aqueous media with pronounced affinity at pH varying from 5 to 9. The incorporation of CAMS in a polymeric matrix was described only as a Polymer-Supported CAMS (PS-5-LICAMS) devoted to divalent metal ion removal from aqueous solution without any evaluation toward uranyl

cation.^[37] Interestingly, to our knowledge, no evidence in the literature relates the development of phenolic resin incorporated bis-catecholamide derivatives for uranium U (VI) extraction. Since their discovery by Baekland,^[38] these resins were widely investigated as thermosetting materials used for liquid/solid extraction and ion exchange properties thanks to the –OH groups in their polymeric structure. So, phenolic resins have been used for extraction of transition and heavy metals,^[39–43] lanthanides,^[44–46] and radio-nuclides.^[47–50] Chelating scaffolds can be incorporated in order to modify the affinity and/or selectivity of ions,^[51] especially cesium,^[52] metalloids such as germanium^[53] as well as lanthanides.^[54]

Here we describe different combination of bis-catecholamide derivatives (CYCAM, 5-LICAM, *m*-BENZCAM, IPACAM, (Figure 1) and phenolic group such as Phenol (P), Catechol (C) or Resorcinol (R) resulting to formo-phenolic resins devoted to improve the existing sorbents system developed for uranium extraction.

The series of obtained bis-catecholamides-resol type resins have been implemented in solid-liquid extraction of uranium U (VI) and competing elements Mg, Sr, Ca, Na, K. The evaluation was carried out at pH 8.25, varying the nature and the concentrations of materials.

Results and Discussion

Synthesis of CAM phenolic precursors. CYCAM, *m*-BENZCAM and 5-LICAM were synthesized as already described in two steps starting from 2,3-dimethoxybenzoic acid with respectively 1,3-cyclohexane-bis-methylamine, *m*-xylylenediamine or 1,5-diaminopentane.^[33] IPACAM was synthesized in five steps (Scheme 1), on one hand 2-methoxyisophthalic acid (1) was obtained by oxidation of 2,6-dimethylanisole and on the other hand *N*-(2-aminoethyl)-2,3-dimethoxybenzamide (2) was prepared from the reaction of the acid chloride analogue of 2,3-dimethoxybenzoic acid with *N*-Boc-ethylenediamine followed by a deprotection step to recover the expected amine intermediate 3. Peptide coupling of 1 and 3 with HOBT/DCC afforded the pentamethoxy derivative 4 with 97% yield then a final deprotection step was achieved using BBr₃ in dichloromethane to give IPACAM in 95% yield.

From the preliminary synthesized bis-catecholamide derivatives, 17 formo-phenolic type of resins were prepared by polycondensation in basic medium (Scheme 2) by varying:

The nature and the ratio of the CAM compounds; the nature and the ratio of the co-monomer Phenol (P), Catechol (C) or Resorcinol (R); the ratio of formaldehyde H₂CO; the ratio of NaOH. The molar ratio of CAM monomer and phenolic monomer were reported in the Table 1. The molar ratio of NaOH/H₂O/HCHO used depends of the resin type: 1.5/100/2.5 for the resins with only phenol, catechol or resorcinol, 3/100/3.75, for the resin with IPACAM and 3/100/2.5 in all other cases. All the resins can be obtained as insoluble powder under protonated form (OH) or deprotonated form (O⁻Na⁺) depending on washing solution (acid or alkaline).

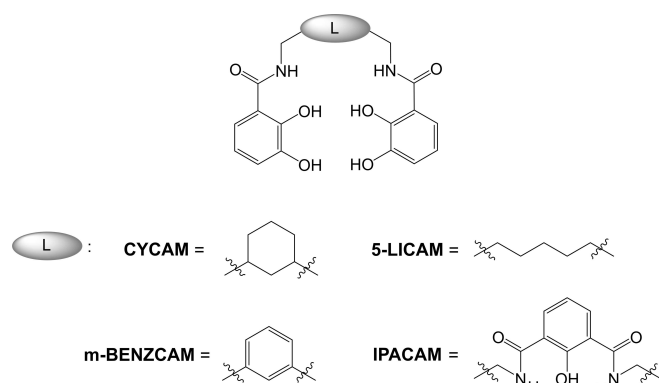
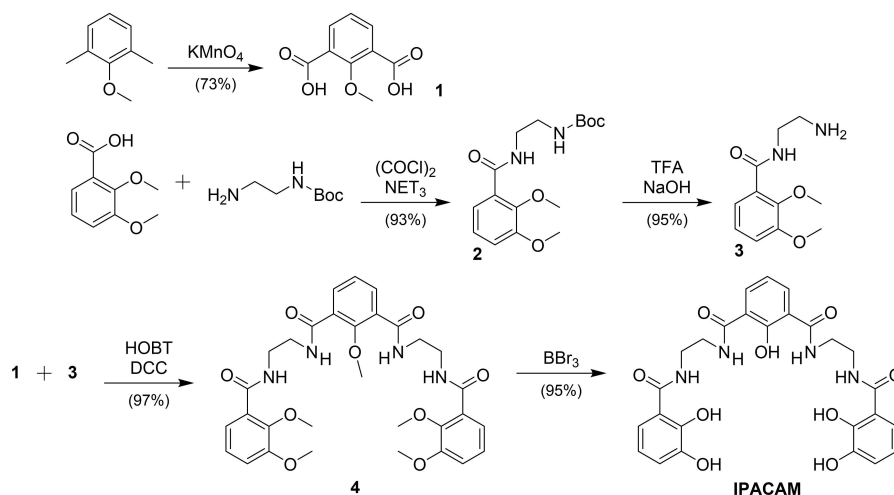
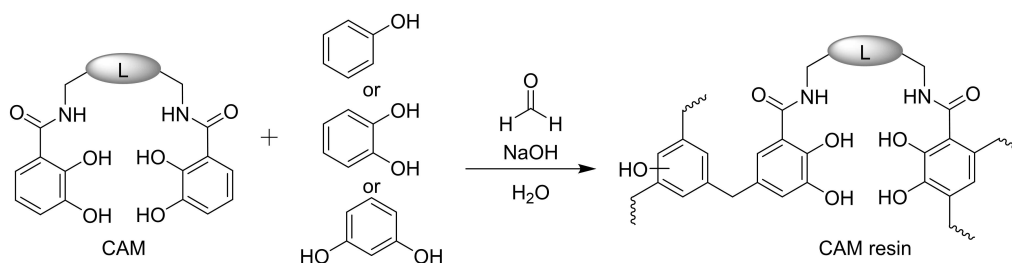


Figure 1. General structure of biscatecholamide precursors (CYCAM, *m*-BENZCAM, 5-LICAM and IPACAM).



Scheme 1. Synthesis pathway of IPACAM monomer (Characterizations of IPACAM and intermediate are provided in ESI see Figure S1 to S10).



Scheme 2. General synthesis of CAM resins.

Table 1. Molar ratio of CAM/phenolic co-monomer of the synthesized resins.

Resin	CAM monomer	ratio	co-monomer	ratio
CYCAM100	CYCAM	1	–	–
5-LICAM100	5-LICAM	1	–	–
<i>m</i> -BENZCAM100	<i>m</i> -BENZCAM	1	–	–
IPACAM100	IPACAM	1	–	–
CYCAM50-P50	CYCAM	0.5	Phenol	0.5
CYCAM34-P66	CYCAM	0.34	Phenol	0.66
IPACAM50-P50	IPACAM	0.5	Phenol	0.5
IPACAM34-P66	IPACAM	0.34	Phenol	0.66
IPACAM50-C50	IPACAM	0.5	Catechol	0.5
IPACAM34-C66	IPACAM	0.34	Catechol	0.66
5-LICAM50-R50	5-LICAM	0.5	Resorcinol	0.5
5-LICAM34-R66	5-LICAM	0.34	Resorcinol	0.66
<i>m</i> -BENZCAM50-R50	<i>m</i> -BENZCAM	0.5	Resorcinol	0.5
<i>m</i> -BENZCAM34-R66	<i>m</i> -BENZCAM	0.34	Resorcinol	0.66
P100	–	–	Phenol	1
C100	–	–	Catechol	1
R100	–	–	Resorcinol	1

Thus, the ion exchange type resins (Table 1) were functionalized by chelating groups derived from the synthetic chelating monomers covalently incorporated in the polymer matrix since they were obtained by polycondensation. The incorporation of the complexing groups has been verified by IR and solid-state NMR. By way of example, the IR and ^{13}C NMR spectra for resin *m*-BENZCAM34-R66 are provided in the Figure S11. FT-IR analysis highlighted the presence of the amide bands corre-

sponding to the CAM are observed at 1620 and at 1530 cm^{-1} in the polymer matrix. Evidence of the presence of the amide group was also provided through the ^{13}C solid state NMR with the peak at 169 ppm characteristic of the carbonyl C=O unit of the CAM.

Similar observations have been noticed for the polymers prepared starting from CYCAM, LICAM and IPACAM.

Extraction experiments

Even if the uranium concentrations are very low in the targeted solutions such as seawater, extraction experiments were carried out with uranium concentration between 50 and 200 mg/L in order to highlight the extraction performance and for a better reliability of the analytical results.

For these concentrations and at a pH of around 8.25, the quantity of carbonate was adjusted to avoid any precipitation of uranium. Speciation diagrams of uranium in the different solution studied are provided in ESI (Figure S12–S14), showing that it is in its U(VI) form.

Adsorption capacity of the resins was first studied as a function of the crushing time. As reported in Figure S15, an increase in the adsorption capacity from 130 mg/g to 300 mg/g is observed parallel to the crushing time of the resin *m*-BENZCAM34-R66-H from 5 to 25 minutes. The increase in the duration of the grinding leads to smaller grain sizes and better

size homogeneity (size centred at 10–20 μm , see Figure S16), and therefore increase in sorption capacities related to a greater availability of contacted surface. These dense materials do not present singular porosity and specific surface from Brunauer–Emmett–Teller (BET) method. The active surface during the contact between liquid and solid phases mostly depends on the grain size, therefore grinding step is essential. Thus, before each sorption experiments, the resins were crushed during 15 minutes.

Extraction capacities were then evaluated (Table 2), formo-phenolic resins exhibited a good affinity for U(VI) which increases with the nature of the CAM monomer when it was directly polymerized without phenolic co-monomers P, C and R (BENZCAM > IPACAM > LICAM > CYCAM – entries 1, 4, 10, 13).

Excepted for *m*-BENZCAM100-H, the other CAM100-H materials were less efficient than the formo-phenolic resins P100H, C100H and R100H (entries 16, 17, 18) with an uranium (VI) extraction over 90% in solution 1. Copolymerization of CAM derivatives with phenol, catechol and/or resorcinol increased the adsorption capacity of each material. The reduction of CAM monomer ratio also increased capacities, no changes were observed for *m*-BENZCAM resins, whatever its ratio, extraction was complete in Solution 1 (entries 14, 15).

This trend was confirmed when resins were used in the uranium extraction of Solution 2 with a substantial increase in the Q_{ads} of *m*-BENZCAM34-R66-H and 5-LICAM34-R66-H close to 200 mg/g (entries 11, 12, 14, 15) while Q_{ads} of IPACAM34-C66-H only increased from 30 to 36 mg/g (entry 8). It can also be noticed that uranium extraction with C100-H increased from 50.3 (E = 99%) to 128.5 mg/g (E = 68%). The deprotonated resin (ONa) also shew an increase of adsorption capacity.

This character is due to the saturation of the chelating sites with Na that are exchanged with U(VI) instead of standard complexation step.

Table 2. Values of E(%) and Q_{ads} obtained for U(VI) extraction with the synthesized resins and solutions 1 ($[\text{U}^{\text{VI}}] = 50 \text{ ppm}$, $[\text{CO}_3^{2-}] = 60 \text{ ppm}$, pH = 8.25) and 2 ($[\text{U}^{\text{VI}}] = 200 \text{ ppm}$, $[\text{CO}_3^{2-}] = 226 \text{ ppm}$, pH = 8.25) for V/m = 1. H and Na represent protonated (OH) and deprotonated (Na) forms.

Entry	Resins	Solution 1		Solution 2	
		E [%]	Q_{ads} [mg/g]	E [%]	Q_{ads} [mg/g]
1	CYCAM100-H	38	19	–	–
2	CYCAM50-P50-H	60	30	–	–
3	CYCAM34-P66-H	84	43	–	–
4	IPACAM100-H	46	24	–	–
5	IPACAM100-Na	–	–	46	88
6	IPACAM50-C50-H	52	26	9	17
7	IPACAM50-C50-Na	–	–	41	78
8	IPACAM34-C66-H	59	30	19	37
9	IPACAM34-C66-Na	–	–	44	84
10	5-LICAM100-H	44	23	3	6
11	5-LICAM50-R50-H	99	50	99	200
12	5-LICAM34-R66-H	99	50	99	200
13	<i>m</i> -BENZCAM100-H	99	50	99	200
14	<i>m</i> -BENZCAM50-R50-H	99	50	99	200
15	<i>m</i> -BENZCAM34-R66-H	99	50	99	200
16	P100-H	89	45.1	–	–
17	C100-H	99	50	68	129
18	R100-H	92	46.9	–	–

Some experiments have been performed using a ratio volume over resin mass, V/m = 4, to appreciate the influence of diluted media on the extraction capacity (Table 3).

In the absence of competing metals, *m*-BENZCAM34-R66-H resin was able to extract almost half of its mass in uranium ($Q_{\text{ads}} = 446 \text{ mg/g}$) corresponding to an adsorption efficiency of 55% and suggesting that maximal adsorption capacity have been reached.

From these experiments, it appears that the affinity of resin for uranium was greater when they contain a CAM chelating monomer (*m*-BENZCAM > LICAM > IPACAM > CYCAM with a ratio of 34% \approx 50% > 100%) was copolymerized with phenolic derivatives (R > C > P) and even greater when they were in the deprotonated –ONa form.

This behaviour was already observed in the literature for formo-phenolic resins and was explained according to a higher polymerisation rate when chelating polymers are copolymerized and a possible competition between the H^+ and the cations extracted.^[54]

Characterization of kinetic and adsorption model. Adsorption mechanism studies were investigated for *m*-BENZCAM34-R66-H which is one of the most efficient system for the extraction of uranium. Kinetics experiments highlighted that equilibrium was achieved in 4 h, indicating all extraction experiments done represent true equilibrium conditions.

In order to investigate the adsorption kinetic mechanism, the experiment data for *m*-BENZCAM34-R66-H were subjected to the pseudo-second-order and pseudo-first-order models according to the equations 1 and 2 (Figure 2 and S17). The values t/q_t exhibit a perfect linear relationship with the contact time (t), with correlation coefficient (R^2) over 0.99 (Figure 2b). The calculated q_e values are 111 mg/g for samples with initial uranium concentrations of 200 ppm and 10.8 equivalent of carbonates

The correlation coefficient of the linear fitting plot $\log(q_e - q_t)$ in function of contact time (t) is 0.5 (Figure S17) and the calculated value of adsorption capacity is lower than the value of experimental adsorption capacity at 24 h.

Therefore, the adsorption of uranium on *m*-BENZCAM34-R66-H follows pseudo second-order better than pseudo-first-order model, indicating that the chemical adsorption was the rate-limiting step.^[55]

Consequently, the result suggested chemical sorption or chemisorption, which occur by the polar functional group of phenolic resins.^[56,57]

Table 3. Values of E(%) and Q_{ads} obtained for uranium extraction with the synthesized resins and Solution 2 ($[\text{U}^{\text{VI}}] = 200 \text{ ppm}$, $[\text{CO}_3^{2-}] = 226 \text{ ppm}$, pH = 8.25) for V/m = 4.

Resins	Q_{ads} [mg/g]	E [%]
5-LICAM50-R50-H	353	44
5-LICAM34-R66-H	409	50
<i>m</i> -BENZCAM100-H	354	44
<i>m</i> -BENZCAM50-R50-H	418	52
<i>m</i> -BENZCAM34-R66-H	446	55
C100-H	143	19

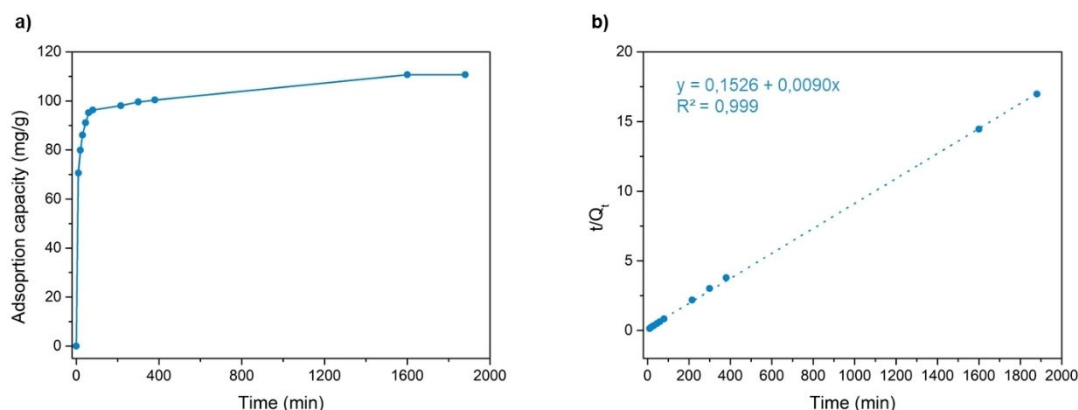


Figure 2. a) Kinetic of U(VI) extraction for *m*-BENZCAM34-R66-H ($[U^{VI}] = 200$ ppm and $[CO_3]/[U] = 10.8$). b) Points and linear modelling of the value t/Q_t as function of the time.

The isotherm for uranium adsorption onto the *m*-BENZCAM34-R66-H resin at 25 °C was performed from aqueous solutions at pH = 8.25 and the initial concentration ($[U]_0$) varying from 1 to 500 ppm, while other parameters were kept constant (Figure 3). At low concentrations, a rapid increase was observed with a linear correlation between capacity (Q_{ads}) and the initial concentration of the metal ($[U]_0$) (Figure 3a).

This proportionality is no longer observed at the highest concentrations, and a plateau is reached above 200 ppm.

The adsorption behaviours of U(VI) and the surface properties of the resins were investigated using Langmuir's isothermal adsorption model (Figure 3b) provided by the equation 3. All the point have been plotted, however for $[U]_0 < 200$ ppm since the extraction efficiency is over 99% then $Q_{ads} \approx [U]_0$ meaning that $[U]_{eq}$ is close to 0.

The isotherm is well fitted with the Langmuir model of adsorption indicating an isothermal chemisorption mechanism. From the slopes and intercepts of the plots, the Langmuir parameters (Langmuir constant L and maximal sorption capacity Q_{max}) were calculated.^[58]

Thus it could be established that the Q_{max} calculated from the curves was 222 mg/g for *m*-BENZCAM34-R66-H with a Langmuir coefficient of about 0.4 L/mg. Therefore, it can be assumed that the surface of the adsorbent is homogeneous in terms of adsorption energy; assuming that all the sites where uranium is adsorbed are similar in energy

Evaluation of selectivity, desorption and reusability. The resins were then studied in presence of competing metal (Na, Mg, K, Ca, Sr) with concentration from 5 to 48 time higher than uranium U(VI). In the presence of competing metals, most resins kept a good affinity for uranium with an extraction over 95% for the best ones but also an excellent selectivity towards all of the competing metals investigated (Table 4, full results are available in Table S1). The selectivity toward sodium was not calculated because the concentration in solution is often higher than initial concentration due to a possible sodium release from the resin.

In the presence of competing metals, *m*-BENZCAM and LICAM based resins seemed to stand out from the others with extraction over 95% and separation factors from 48 to 37041.

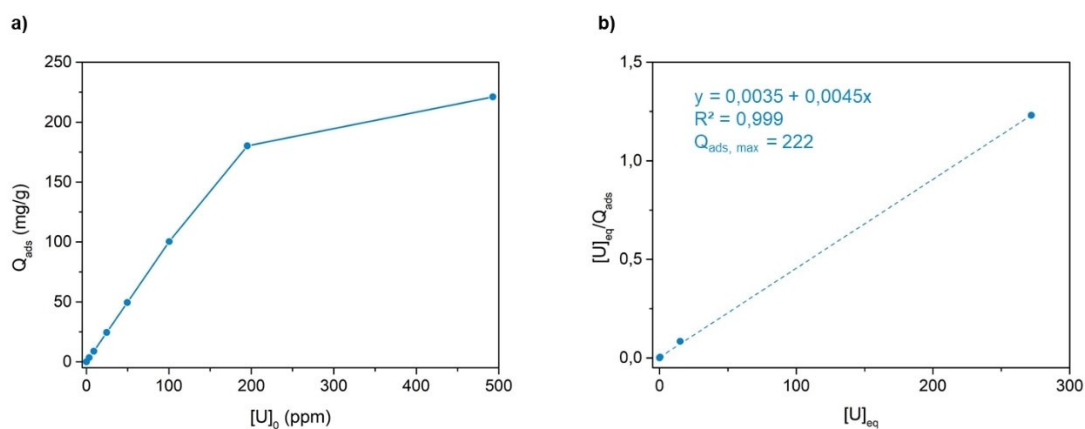


Figure 3. a) Adsorption capacity of U(VI) of *m*-BENZCAM34-R66-H in function of $[U]_0$ ($[CO_3]/[U] = 5.1$). b) Points and linear modelling of the value $[U]_{eq}/Q_t$ as function of $[U]_{eq}$.

Table 4. Values of Q_{ads} and $FS_{\text{U/M}}$ obtained for uranium extraction with the synthesized resins and Solution 3 ($[U^{VI}] = 50$ ppm; $[Sr^{2+}] = 100$ ppm; $[K^+]$, $[Na^+]$, $[Ca^{2+}]$ and $[Mg^{2+}] = 200$ ppm, $[CO_3^{2-}] = 60$ ppm, pH = 8.25) for $V/m = 1$.

resins	Solution 3				
	$Q_{\text{ads}} \text{ U [mg/g]}$	$FS_{\text{U/Sr}}$	$FS_{\text{U/Ca}}$	$FS_{\text{U/Mg}}$	$FS_{\text{U/K}}$
IPACAM100-H	16	19	10	19	20
IPACAM100-Na	49	825	355	754	7212
5-LICAM34-R66-H	51	392	259	810	2038
5-LICAM34-R66-Na	49	2422	1556	5204	30491
<i>m</i> -BENZCAM34-R66-H	51	323	209	914	3167
<i>m</i> -BENZCAM34-R66-Na	49	1530	1026	3690	22135
R100-H	30	34	20	58	41
R100-Na	19	7	5	15	30
Lewatit TP 107	48	5790	4305	4170	5200

As previously demonstrated for adsorption capacity, the selectivity of deprotonated forms (ONa) are systematically higher than protonated one – except for non-CAM materials. These resins were a striking example of the importance of the addition of a chelating phenolic monomer within the resin in order to increase the selectivity, since the R100-Na resin which contain only resorcinol, had separation factors only between 5 and 35. Whatever the considered resin, selectivity increases according to the sequence $Ca < Sr < Mg < K$ – the selectivity is higher for monovalent cations (K and probably Na) than for divalent (Ca, Sr, Mg). Also, in comparison to commercial Lewatit TP 107 resin, similar trends can be observed regarding the sorption capacities with a more pronounced selectivity for monovalent cations than for divalent ones for the bis-catecholamide-based materials.

Resins containing *m*-BENZCAM monomer offering the best properties overall, they were used for selectivity toward vanadate which has the greatest interference with uranyl. Resins offer selectivity $SF_{\text{U/V}}$ of 15–18 for protonated forms and twice more (28–32) for the deprotonated ones (Table 5).

Finally, the sorption in synthetic seawater and desorption behaviour was investigating for *m*-BENZCAM34-R66-H, one of the most efficient resin. Extraction was performed in water at 36.88 g/L of alkali/alkaline-earth salt doped with 100 ppm of U(VI). After 72 h at 25 °C, the resin exhibits an interesting adsorption capacity of 50 mg/g. Uranium recovery was performed contacting the resin with HCl 1 M solution for 12 hours, this process allows to extract 95 % of adsorbed U(VI). This resin – used for adsorption and desorption – was then washed with H₂O and use again for extraction experiment keeping around 85 % of its initial capacity.

Table 5. Values of E_{U} , $Q_{\text{ads, U}}$, E_{V} and $SF_{\text{U/V}}$ obtained for uranium extraction with the synthesized resins and solution 4 ($[U^{VI}] = 49$ ppm, $[V^{VI}] = 38$ ppm and $[CO_3^{2-}] = 364$ ppm, pH = 8.25) for $V/m = 1$.

Resins	E_{U} [%]	$Q_{\text{ads, U}}$ [mg/g]	E_{V} [%]	$SF_{\text{U/V}}$
<i>m</i> -BENZCAM34-R66-H	73	37	14	15
<i>m</i> -BENZCAM50-R50-H	82	41	19	18
<i>m</i> -BENZCAM34-R66-Na	78	39	10	28
<i>m</i> -BENZCAM50-R50-Na	86	43	15	32

Conclusion

Extraction of uranium from seawater constitute a good alternative to mining but needs to develop solid material with large adsorption capacity and high selectivity for uranium in presence of competitive cations. The synthesis of CAM formo-phenolic resins and their copolymerization with phenolic derivatives – mainly with Resorcinol – and formaldehyde have been developed and afford suitable material for cations extraction. Among all the resins prepared, *m*-BENZCAM34-R66 and LICAM34-R66 exhibit U(VI) adsorption capacity up to 400 mg/g and are able to extract over 95 % of U(VI) in a solution doped at 50 and containing various competing cations in a large excess (Sr, Ca, Mg, K and Na). The use of deprotonated form (ONa) while protonated (OH) leads to an increase of capacity and selectivity. Studies of the adsorption kinetic showed that *m*-BENZCAM34-R66 reaches its maximal capacity within 400 minutes and follows pseudo second-order – rate-limiting step is chemical adsorption. The adsorption respects Langmuir model – formation of uranium monolayer and all coordination sites are equivalent. In addition, the extraction in highly salty water lead to a good adsorption capacity of 50 mg/g, the back extraction of U(VI) at 95 % can be performed easily using HCl solution and the resin can be re-used maintaining an excellent 85 % of its adsorption capacity.

Experimental Section

All chemicals were analytically pure (Sigma–Aldrich or Alfa Aesar) and used without further purification, anhydrous solvent (AcroSeal) were obtained from Acros. Thin layer chromatography (TLC) were performed on silica plate 60F254 adsorbed onto alumina sheet (Merck TLC Silica Gel 60 F254). NMR and mass analysis were performed for the characterization of the different compounds. ¹H and ¹³C NMR spectra were recorded on a Bruker Advance 400 MHz instrument. Displacements are reported in ppm using deuterated solvents as an internal reference.

¹³C NMR MAS spectra were recorded at rotation speed of 12 KHz (4 mm outer diameter rotors). Attenuated total reflection FTIR (ATR) was recorded on a Perkin Elmer 100 spectrometer equipped with ATR crystal (working range: 4000–615 cm⁻¹; resolution 4 cm⁻¹).

Cation concentration in solution (before and after batch experiments) was quantified using an ICP/OES SPECTRO ARCOS and an ICP/MS iCAP RQ spectrometer from Thermo Scientific. The wavelengths were chosen to avoid any spectral interference between the elements.

Synthesis of phenolic CAM precursors. The phenolic precursors CYCAM, LICAM and *m*-BENZCAM were synthesized according to the procedure already described in the literature.^[33] Synthesis pathway of IPACAM is described below and all details are available in the supporting information.

General synthesis of P-, C- and R- CAM polymers. Respective ratio of CAM monomer (CYCAM, 5-LICAM, *m*-BENZCAM, IPACAM) and phenolic monomer (Phenol, Catechol or Resorcinol) was dissolved in a solution of NaOH under stirring. 100 equivalents (relative to CAM + phenolic derivative) of water was then added and the resulting solution was stirred before formaldehyde solution at 37 % was added. The reaction mixture was stirred 24 h, then transferred to a crystallizer glass and heated in a ventilated oven at 100 °C for

96 h. The solid and tough resin formed was recovered, ground using a ball mill, and then washed with NaOH/HCl/H₂O or NaOH/H₂O depending on the desired resin form (protonated OH or deprotonated O⁻Na⁺ phenol moieties).

Finally, washed resins were dried in a ventilated oven at 80 °C for 24 h, dispersed by ball milling, dried again at 80 °C for 24 h, then stored for extraction experiments.

Batch contact with cation solutions. The ability of thermosetting resins to selectively extract U(VI) from seawater was assessed by extraction tests which were carried out in batch experiments, using, as aqueous solution, four different solutions, referred as Solutions 1, 2, 3 and 4 respectively, and consisting of:

- **Solution 1:** a solution simulating seawater doped at 50 ppm of U(VI) (1.9 10⁻⁴ M in uranyl) and 60 ppm in carbonates (1.010⁻³ M, [CO₃]/[U]=5.3) at pH=8.25 ± 0.1.
- **Solution 2:** a solution simulating seawater doped at 200 ppm of U(VI) (7.4 10⁻⁴ M in uranyl) and 226 ppm in carbonates (3.8 10⁻³ M, [CO₃]/[U]=5.1) at pH=8.25 ± 0.1.
- **Solution 3:** a solution simulating sea water doped at 50 ppm of U(VI) (1.9 10⁻⁴ M in uranyl), 100 ppm of strontium (1.2 10⁻³ M, [Sr]/[U]=6.3), 200 ppm of sodium (8.7 10⁻³ M, [Na]/[U]=47.8), 200 ppm of potassium (5.2 10⁻³ M, [K]/[U]=27.4), 200 ppm of calcium (5.1 10⁻³ M, [Ca]/[U]=26.8), 200 ppm of magnesium (8.4 10⁻³ M, [Mg]/[U]=44.2) and 60 ppm carbonates (1.0 10⁻³ M, [CO₃]/[U]=5.1) at pH=8.25 ± 0.1.
- **Solution 4:** A solution simulating seawater doped at 49 ppm of U(VI) (1.9 10⁻⁴ M in uranyl), 38 ppm of V(V) (7.5 10⁻⁴ M in vanadyl, [V⁵⁺]/[U⁶⁺]=3.9) and 364 ppm in carbonates (6.1 10⁻³ M, [CO₃]/[U+V]=6.5) at pH=8.25 ± 0.1.

In these experiments, a known amount of resin was brought into contact with a volume of Solution 1, 2, 3 or 4 and stirred at 22 °C for 15 h. the mixture was then centrifugated, the supernatant was removed and filtered on a 0.22 μm cellulose acetate membrane. The concentration of the various cations present in the filtrate was analysed by atomic emission spectrometry with inductively coupled plasma (ICP-OES) or by mass spectrometry with coupled plasma by induction (ICP-MS) when the uranium concentrations were very low.

The cation uptake capacity Q_{ads} (mg/g) was calculated using the equation:

$$Q_{ads} = (C_i - C_f) \cdot \frac{V}{m}$$

with C_i the initial concentration of the metal ion in solution, C_f the residual metal ion concentration, and V/m the ratio of solution volume by resin-mass.

The adsorption efficiency E (%) was calculated according to the equation:

$$E = \frac{C_i - C_f}{C_i} \cdot 100$$

The distribution coefficient, noted K_D and expressed in mL/g, represents the ratio between the quantity of cation uptake by the resin and the quantity of cation remaining in solution after extraction, and was determined by the formula:

$$K_D = \frac{C_i - C_f}{C_f} \cdot \frac{V}{m} \cdot 1000$$

The separation factor $FS_{U/M}$, with M the metal competitor, represents the ratio between the K_D of uranium and the K_D of the other metal. $FS_{U/M}$ allows to quantify the selectivity of a resin to extract uranium rather than other metal and was calculated by formula:

$$FS_{U/M} = \frac{K_{D_U}}{K_{D_M}}$$

The back-extraction or stripping efficiency S (%) is defined by the equation:

$$S = \frac{Q_e - Q_f}{Q_e} \cdot 100$$

with Q_e the concentration of the metal ion loaded into the polymer and Q_f the residual metal ion concentration in the polymer after the release.

Kinetics experiments were run similarly as batch contacts, excepted that aliquots were removed at specified time intervals, filtered through a 0.22 μm filter, and subjected to ICP analysis.

Kinetics data were fitted using pseudo-first-order and pseudo-second-order kinetic models.^[59,60] The pseudo-first-order model suggested by Lagergren based on solid sorption capacity describes the adsorption phenomenon as a diffusion-controlled process suggesting, in the concentration range studied, a formation of monolayer coverage of the adsorbate on the surface of adsorbent.^[61,62] This model was used to describe the sorption kinetics.^[63,64] The pseudo-first-order rate is given as:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303} \cdot t \quad (1)$$

where Q_e is the equilibrium metal ion concentration in solid-phase (mg/g), Q_t is the equilibrium metal ion concentration in solid-phase at time t (mg/g), K_1 is the pseudo-first-order equilibrium rate constant (min⁻¹) and t is the time (min).

The pseudo-second-order model is also based on solid-phase sorption capacity.^[65,66] The pseudo-second-order rate is given as:

$$\frac{t}{Q_t} = \frac{1}{Q_e} \cdot t + \frac{1}{K_2 Q_e^2} \quad (2)$$

where Q_e is the equilibrium metal ion concentration in solid-phase (mg/g), Q_t is the equilibrium metal ion concentration in solid-phase at time t (mg/g), K_2 is the pseudo-first-order equilibrium rate constant (min⁻¹) and t is the time (min).

Langmuir isotherm parameters^[66] were estimated by the equation:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{max}} + \frac{1}{Q_{max}} \cdot C_e \quad (3)$$

with C_e the concentration of the metal ion in solution at equilibrium, Q_e the amount of metal ion adsorbed at equilibrium, Q_{max} is the maximum amount of metal ion adsorbed at equilibrium and K_L is the Langmuir constant. The maximum sorption capacity was estimated from this isotherm when a plateau is obtained.^[67]

A 24 h shaking-time at 25 °C was used in all the experiments to ensure thermodynamic equilibrium.

Uranium speciation. According to simulation by PhreeqC using NEA TDB database updated in December 2020, we obtained the speciation distribution of U species in Solution 1, 2 and 3 (Figure S12 to S14). In all these solution systems, concentration of carbonates was five times higher than those of uranium and no precipitation occurred. In absence of divalent cation (Solution 1 and 2), U is mainly present as $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ complexes. When divalent cations are added (Solution 3), U constitutes for 95% two very stable complexes, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: catecholamides · chelation · resins · sorbent polymers · uranium extraction

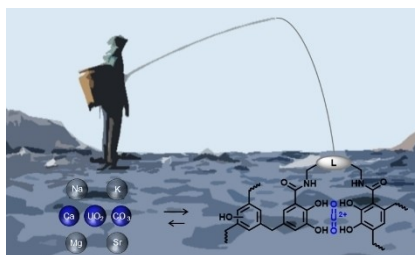
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RESEARCH ARTICLE

Extraction of uranium from seawater constitutes a good alternative to mining but needs to develop solid materials with large adsorption capacity and high selectivity for uranium in presence of competitive cations. The synthesis of CAM from phenolic resins and their copolymerization with phenolic derivatives – mainly with Resorcinol – and formaldehyde have been developed and afford suitable material for cation extraction. This work highlights the development of bis-catecholamide polymer materials as efficient adsorbents for uranium from seawater.



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Bis-Catecholamide-Based Materials for Uranium Extraction

