Separation of Uranium(VI) from Aqueous Solution by Textile Bound Calix[6]Arenes

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The separation of uranium(VI) from aqueous solution by textile bound uranophile calix[6]arenes was studied as a function of pH value and uranium concentration in the absence and presence of competing ions by means of batch experiments. Furthermore, the kinetics of the uranium binding was studied as well as the possibility for remobilization of the bound uranium by solutions of various pH values.

The results showed that calixarene modified textiles are suitable for the separation of uranium from aqueous solution at pH values ≥ 4. The applicability in the acidic pH range is limited. Maximal 7.6×10^{-7} mol uranium per 1 g of the calixarene modified textile is bound at pH 5. The influence of competing ions (sodium, potassium, calcium, magnesium, carbonate and sulfate) on the uranium separation at pH 5 is very small. At pH 7 in carbonate rich waters, calcium ions have a competing effect due to the formation of the $Ca_2UO_2(CO_3)_3$ (aq) complex.

Under environmentally relevant pH conditions (near-neutral pH range) the uranium is strongly bound to the calixarene modified textile and cannot be mobilized. On the other hand, under acidic conditions an almost complete regeneration of the calixarene modified textile is feasible. The regenerated textile filter material can be utilized for further uranium separation cycles.

1   Introduction

The remediation of former uranium mining and milling sites like those in Saxony and Thuringia (Germany) requires, amongst others, the purification of seepage and mine waters from radioactive and non-radioactive contaminants. For this, cost-effective water treatment strategies have to be selected considering the quantity of the contaminated water as well as the concentration of the contaminants. Besides conventional water treatment methods (e.g., application of ion exchangers, direct precipitation, flocculation, microbiological methods) further methods have been described in the literature. For instance, solvent extraction applying calix[6]arenes, functionalized with carboxylic or hydroxamic groups at the lower rim, has been shown to be effective in separating uranium(VI) from aqueous solution (e.g., SHINKAI et al. 1987; NAGASAKI & SHINKAI 1991; SCHMEIDE et al. 2001).

However, to facilitate the separation of uranium from uranium contaminated waters in practice the calixarenes should be immobilized on certain substrates. For instance, the immobilization of calixarenes on silica gel (YAN et al. 2000) or on polymer resins (e.g., SHINKAI et al. 1988; AIHARA et al. 1992; GRAVETT et al. 1996) has been described in the literature.

Our objective is the development of a new procedure for purification of uranium contaminated waters by means of calixarenes immobilized on textile material. This procedure should enable the separation of uranium from diluted uranium solutions. Moreover, an easy handling of the calixarene material in the field is required (SCHMEIDE et al. 2004).

For this, a uranophile calix[6]arene (p-tert-butylcalix[6]arene hexacarboxylic acid) is statistically functionalized by spacer groups that allow its permanent fixation onto textile substrates. That means, ideally one tert-butyl group is substituted by one n-nonyl group per calixarene molecule leading to mono-p-nonyl-penta-p-tert-butylcalix[6]arene hexacarboxylic acid. For fixation, the diffusion of the n-nonyl group of the calixarene molecule into the textile material above its

glass transition temperature is used (JANSEN et al. 2002).

In this paper, we determined the binding properties of the calixarene modified textile towards uranium(VI) as a function of pH value and of initial uranium concentration in the absence and presence of competing ions by means of batch experiments. Furthermore, we studied the kinetics of the uranium binding as well as the possibility for remobilization of the bound uranium.

2 Experimental

2.1 Synthesis of calix[6]arene and its fixation onto textile material

In Figure 1 the formula of mono-p-nonyl-penta-p-tert-butyl-calix[6]arene hexacarboxylic acid is shown. Its synthesis and characterization is described in detail in JANSEN et al. (2002).

For fixation of Non^{t}But[6]CH$_2$COOH onto the textile material (polyester fabric) different experimental conditions were applied (cf. table 1). Four batches of the calixarene modified textile (A to D) were obtained by varying the amount of calixarene, the temperature and the finishing time, respectively.
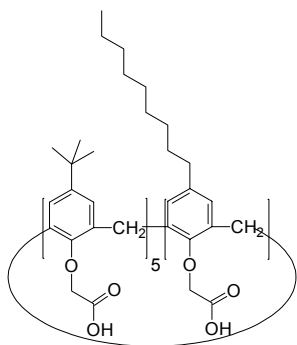

Figure 1: Calixarene used in this work (Non^{t}But[6]CH$_2$COOH).

2.2 Uranium separation and remobilization experiments

In separation experiments, 0.5 g calixarene modified textile was shaken with 20 mL uranium solution in 50 mL vials for 24 hours at room temperature. The initial uranium concentration was 1×10^{-6} M and 5.2×10^{-8} M to 2.2×10^{-4} M in experiments studying the uranium separation as a function of pH value, of competing ions and of uranium concentration, respectively. The pH value of the solution was initially adjusted, readjusted in the course of the experiments and measured after reaching equilibrium. The solution was filtered (450 nm, Minisart N) and subsequently, the initial and the equilibrium cation and anion content in aqueous solution was determined by inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS) and ion chromatography, respectively. From these data the amount of uranium bound by the material was calculated (results were corrected for uranium sorption onto vial walls).

For kinetic experiments, 2 g calixarene modified textile and 80 mL aqueous uranium solution (1×10^{-6} M) were applied. Samples were taken after different time intervals between 2.5 min and about 1600 min after addition of the components. The pH value of the aqueous solution was not readjusted in the course of the experiments. At each sampling time, a 3 mL aliquot of the continuously stirred solution was taken and filtered. The uranium content of each sample was determined by ICP-MS. The results were not corrected for uranium sorption onto bottle walls because of experimental reasons.

In remobilization experiments, 0.2 g uranium loaded calixarene modified textile from the separation experiments were washed 3 times with 7 mL Milli-Q water, subsequently 3 times with 7 mL 0.01 M HCl and finally 3 times with 7 mL 0.1 M HCl for 2 hours each time. The uranium content was determined in each washing solution by ICP-MS.

Table 1:   Experimental conditions of preparation of the calixarene modified textile.

Batch	Amount of calixarene	Temperature	Finishing time
A	0.8 g	100 °C	1 h
B	0.8 g	100 °C	2 h
C	1.6 g	100 °C	1 h
D	0.8 g	130 °C	1.5 h

3   Results and discussion

3.1   Uranium separation in the absence of competing ions

The results of the separation experiments in dependence on pH value are shown in Figure 2. As shown for batch A and C at pH 3, the uranium separation is with 23.4 % and 30.2 %, respectively, low in the acidic pH range. This indicates that the applicability of the calixarene modified textile in the acidic pH range is limited. However, already at pH 4, 85.4 % to 89.3 % of the uranium present in the initial uranium solution (1×10^{-6} M) is separated by the batches A to D of the calixarene modified textile. At pH 5 and pH 7 even 94.9 % to 97.8 % and 91.9 % to 96.7 %, respectively, of the initial uranium is separated.

For the various batches of the calixarene modified textile, prepared under different experimental conditions, a slight increase of the uranium separation from aqueous solution is observed from batch A to batch D. That means, compared to the experimental conditions applied to preparation of batch A, a doubling of the finishing time (batch B), a doubling of the amount of calixarene (batch C), as well as an increase of the temperature and of the finishing time (batch D) have an increasingly favourable effect on the separation capability of the calixarene modified textile. This information is necessary to optimize the amount of calixarene bound onto the textile material.

A uranium loading test performed at pH 5 for the calixarene modified textile applying an increasing uranium concentration in aqueous solution (5.2×10^{-8} M to 2.2×10^{-4} M) shows that up to an
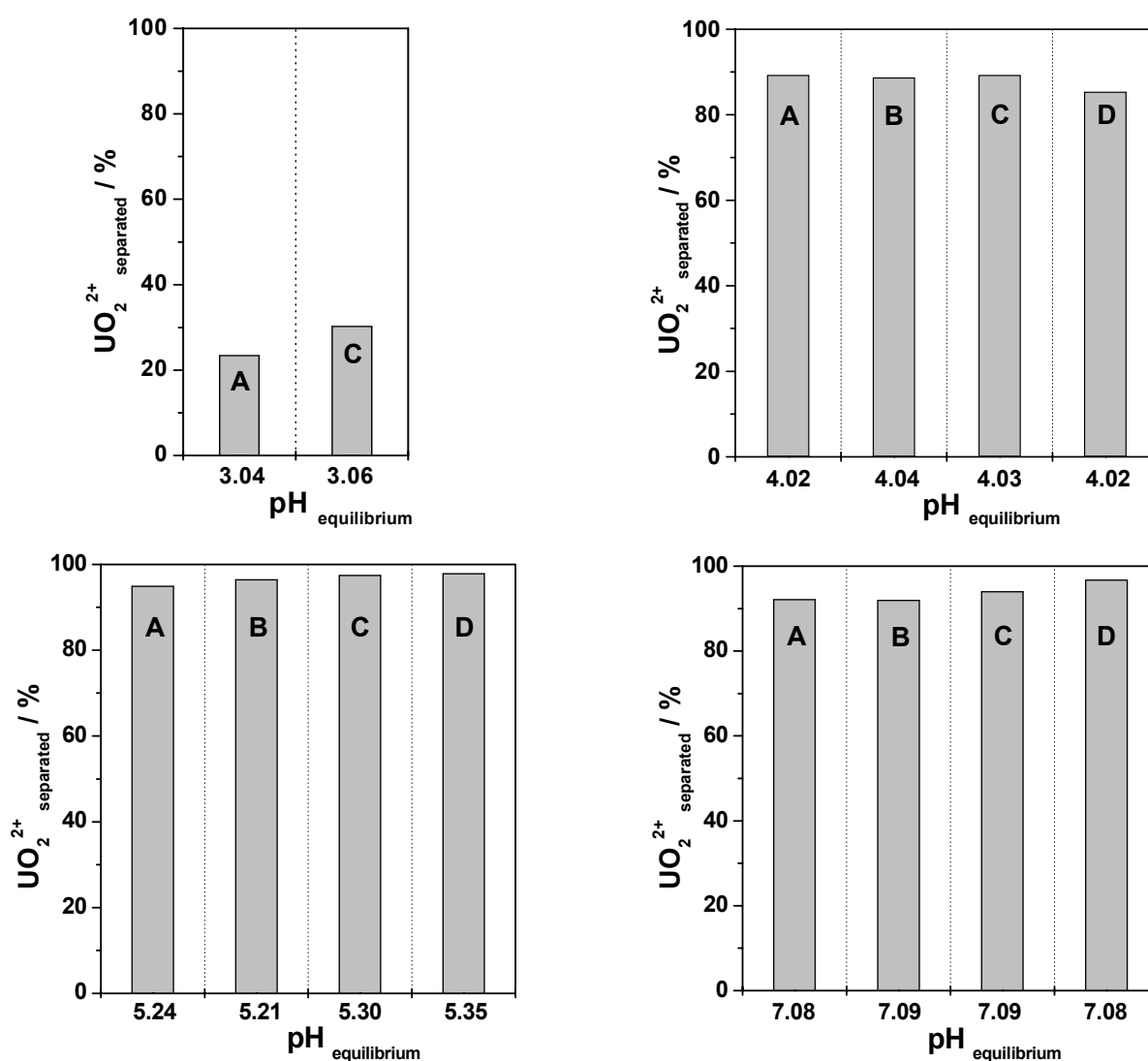

Figure 2: Separation of uranium from aqueous solution by calixarene modified textile (batches A to D) as a function of pH value ([UO22+] initial = 1×10^{-6} M).

initial uranium concentration of 9.8×10^{-6} M 92 % to 99 % of the uranium is separated by the calixarene modified textile. At higher initial uranium concentrations the uranium is only partly separated from the aqueous solution. Maximal 7.6×10^{-7} mol uranium is bound per 1 g of the calixarene modified textile.

The kinetics of the uranium separation from aqueous solution by calixarene modified textile was studied at pH initial 7. The results obtained for batch A and batch C (Figure 3) show that the uranium binding reaches equilibrium within about 165 min and 150 min, respectively. In contrast, using a previous batch of calixarene modified textile (batch PB) equilibrium was attained already within 30 min. This difference in the kinetics of the uranium separation can clearly be attributed to hydrophobicity differences of the samples. The lowest hydrophobicity was found for batch PB. That means to improve the kinetics of the uranium separation further the hydrophobicity of the textile material has to be lowered.

The remobilization of the bound uranium from the uranium loaded calixarene modified textile was studied to evaluate the binding strength as well as the possibility for regeneration of the calixarene modified textile. The results (Figure 4) show that merely 1 % to 5 % of the bound uranium is remobilized from the calixarene modified textile by rinsing the material with water. However, the uranium can be remobilized by washing this material successively with 0.01 M HCl (78 % to 90 %) and 0.1 M HCl (5 % to 22 %). These results indicate that the uranium is strongly bound by the calixarene fixed onto the polyester fabric in the near-neutral pH range and that under acidic conditions the textile filter material can be regenerated almost completely. The comparison of the various batches of calixarene modified textile shows that a part of the uranium is apparently more strongly bound by batch D since 22 % of the uranium can only be remobilized under very strong acidic conditions (0.1 M HCl). This again would mean that an increase of the temperature and the finishing time during the modification process, as applied to batch D, has a favourable effect on the uranium separation by calixarene modified textiles.

The suitability of the regenerated calixarene modified textiles for further uranium separation cycles was tested for batch B. The results show that by repeated use of the regenerated calixarene modified textile in a second and third uranium separation step again 91.9 % and 88.7 %, respec-
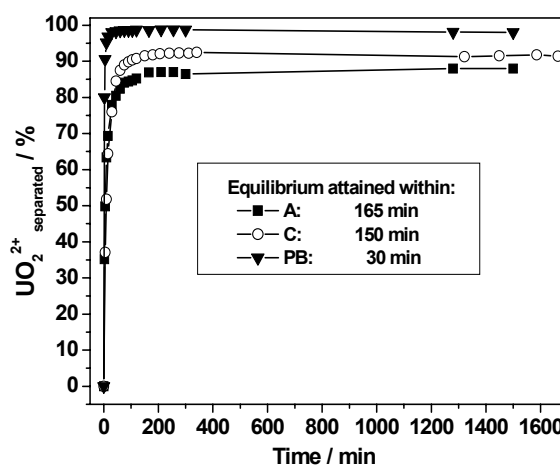

Figure 3: Separation of uranium from aqueous solution by calixarene modified textile (batches A, C, PB) as a function of time ($[UO_2^{2+}]_{initial} = 1 \times 10^{-6}$ M, $pH_{equil.} = 7.38 \pm 0.03$).
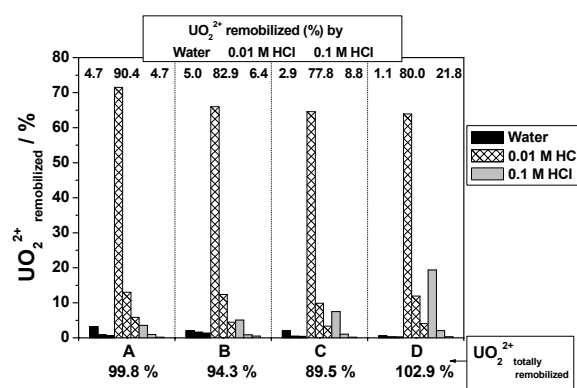

Figure 4: Remobilization of uranium from calixarene modified textile (batches A to D) by water, 0.01 M HCl and 0.1 M HCl.
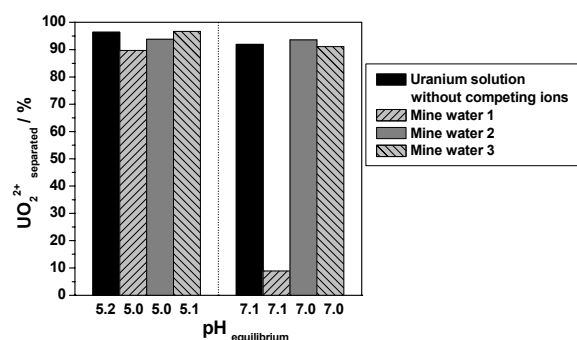

Figure 5: Uranium separation from a uranium solution without competing ions and from synthetic mine waters 1, 2 and 3 by calixarene modified textile (batch B) as a function of pH value ($[UO_2^{2+}]_{initial} = 1 \times 10^{-6}$ M).

tively, of the uranium present in the solution can be separated. That means, the textile filter material can be used for several uranium separation/remobilization cycles.

3.2 Uranium separation in the presence of competing ions

In order to test the separation capability of the calixarene modified textiles under real environmental conditions, the uranium separation from synthetic uranium mine waters was studied as a function of pH value and compared with that from uranium solutions without competing ions.

In table 2 and table 3, the composition and the uranium speciation, respectively, of the synthetic waters, used in this study, is given for pH 5 and pH 7. The uranium speciation was calculated with the geochemical computer code EQ3/6

(WOLERY 1992), based on the NEA TDDB (GRENTHE et al. 1992) with addition of the complexes $Ca_2UO_2(CO_3)_3$ (aq) and $CaUO_2(CO_3)_3^{2-}$ (BERNHARD et al. 2001) and $MgUO_2(CO_3)_3^{2-}$ (AMAYRI 2002).

The mine water 1 contains in addition to uranium the competing ions sodium, potassium, calcium, magnesium, carbonate and sulphate. With regard to its chemical composition the mine water 1 resembles uranium contaminated seepage waters in the former uranium mining regions of East Germany. Figure 5 shows that at pH 5 the uranium separation from aqueous solution without competing ions is reduced by only 6 % due to the presence of competing ions in the mine water 1. That means, that the change of the uranium speciation from mainly UO_2^{2+} (68 %) in the absence of competing ions to mainly UO_2SO_4 (aq) (62 %) in the presence of competing ions (cf. table 3) has only a very small effect on the ura-

Table 2:   Composition of synthetic mine waters at pH 5 and pH 7.

Component	Mine water 1	Mine water 2 Concentration / mmol/L	Mine water 3
Na^+	20	20	20
K^+	1.1	1.1	1
Mg^{2+}	11	12.4	11
Ca^{2+}	1.4	-	1.4
UO_2^{2+}	0.001	0.001	0.001
HCO_3^-/CO_3^{2-}	0.3 at pH 5; 6 at pH 7	0.5 at pH 5; 5 at pH 7	[*]; 0.07 at pH 7
SO_4^{2-}	19	19	21
Cl^-	-	-	2.8
Ionic strength / mol/L	0.05	0.05	0.06

[*] not detectable at pH 5

Table 3:   Uranium speciation in a uranium solution without competing ions and in synthetic mine waters at pH 5 and pH 7 ([UO22+]initial = 1×10⁻⁶ M).

Species	Without competing ions [a]		Mine water 1 [b]		Mine water 2 [c]		Mine water 3 [a,d]	
	pH 5	pH 7	pH 5	pH 7	pH 5	pH 7	pH 5	pH 7
UO_2^{2+}	68.2 %		18.1 %		18.0 %		18.0 %	
UO_2OH^+	19.3 %	1.3 %	5.0 %		5.0 %		4.9 %	1.0 %
$UO_2(OH)_2$ (aq)	11.5 %	75.7 %	3.9 %		3.9 %		3.7 %	77.8 %
$(UO_2)_2(OH)_2^{2+}$	0.7 %							
$UO_2(OH)_3^-$		1.2 %						1.2 %
UO_2SO_4 (aq)			62.0 %		61.2 %		63.0 %	
$UO_2(SO_4)_2^{2-}$			9.1 %		8.8 %		10.3 %	
$(UO_2)_2CO_3(OH)_3^-$		18.2 %						18.2 %
UO_2CO_3 (aq)		1.7 %	1.8 %		3.0 %	0.8 %		
$UO_2(CO_3)_2^{2-}$		1.8 %	10.2 %			50.4 %	1.5 %	
$UO_2(CO_3)_3^{4-}$			11.7 %			47.2 %		
$Ca_2UO_2(CO_3)_3$ (aq)			75.0 %					
$CaUO_2(CO_3)_3^{2-}$			2.7 %					
$MgUO_2(CO_3)_3^{2-}$						1.0 %		

[a] p_{CO2}: $10^{-3.5}$ atm   [b] with calcium, high carbonate content
[c] without calcium, high carbonate content   [d] with calcium, low carbonate content

nium separation. However, at pH 7 the uranium separation is strongly reduced from 92 % to 9 % due to the presence of competing ions. This is attributed to the $Ca_2UO_2(CO_3)_3$ (aq) complex which is formed with 75 % in mine water 1 at pH 7. To verify the influence of calcium and carbonate ions on the uranium separation in mine water 1, the uranium separation from mine water 2 and 3 was studied.

In mine water 2 the calcium ions were replaced by magnesium ions, however, the carbonate content is comparable to that of mine water 1. At pH 7, the uranium separation from mine water 2 is comparable to that from the uranium solution without competing ions.

The same result was found for the mine water 3, which again contains calcium ions, however, has a very low carbonate content (it is comparable with the carbonate content in the uranium solution without competing ions and follows from the CO_2 content of the air (p_{CO2}: $10^{-3.5}$ atm)). For the experimental conditions applied in this study ($[Ca^{2+}]/[UO_2^{2+}]$ = 1400), the results show that calcium ions have only a competing effect in carbonate rich waters. At pH 5 the effect of calcium ions on the uranium separation is negligible. That means, the application of the calixarene modified textiles is possible even in calcium and carbonate rich waters in case the pH value is adjusted to pH 5 prior to the application of the textile material. Sodium, potassium, magnesium and sulphate ions influence the uranium separation by calixarene modified textiles neither at pH 5 nor at pH 7.

The remobilization of the uranium from the filter material which was previously loaded at pH 7 in the presence of competing ions (mine water 2) was again found to be quantitative with 98.9 %.

4   Conclusions

These first results have shown that calix[6]arene modified textiles are useful for remediation of uranium contaminated water. In our future studies we intend to optimize the amount of calixarene bound onto the textile material in order to increase the total amount of uranium that can be separated from aqueous solution.

In dependence on the specific requirements on-site the textile filter material can be used in batch or column operation. Especially for smaller remediation objects and for objects with lower contamination levels ($[UO_2^{2+}] \leq 1\cdot10^{-6}$ M) this method provides a lower cost alternative to con-

ventional water treatment methods. The applicability of this separation principle to further actinides is expected.

For a further improvement of the selectivity of the calixarene modified textile towards uranyl ions in real waters, calixarene derivatives with an enhanced selectivity towards uranyl ions should be fixed onto the textile material. Results of solvent extraction experiments showed that the selectivity towards uranyl ions in the presence of carbonate ions and competing metal ions (e.g., Mg^{2+}, Ni^{2+}, Zn^{2+}) is higher for the hexacarboxylate derivative of calix[6]arene-p-hexasulfonate (SHINKAI et al. 1986, 1987) as well as for calix[6]arenes bearing three carboxylate groups arranged in C_3 symmetry (ARAKI et al. 1993) or six hydroxamic groups (NAGASAKI & SHINKAI 1991) at the lower rim.

5   Acknowledgment

6   References

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