National Centre for Research and Development

Critical review of polymer membranes with crown ethers for lithium extraction

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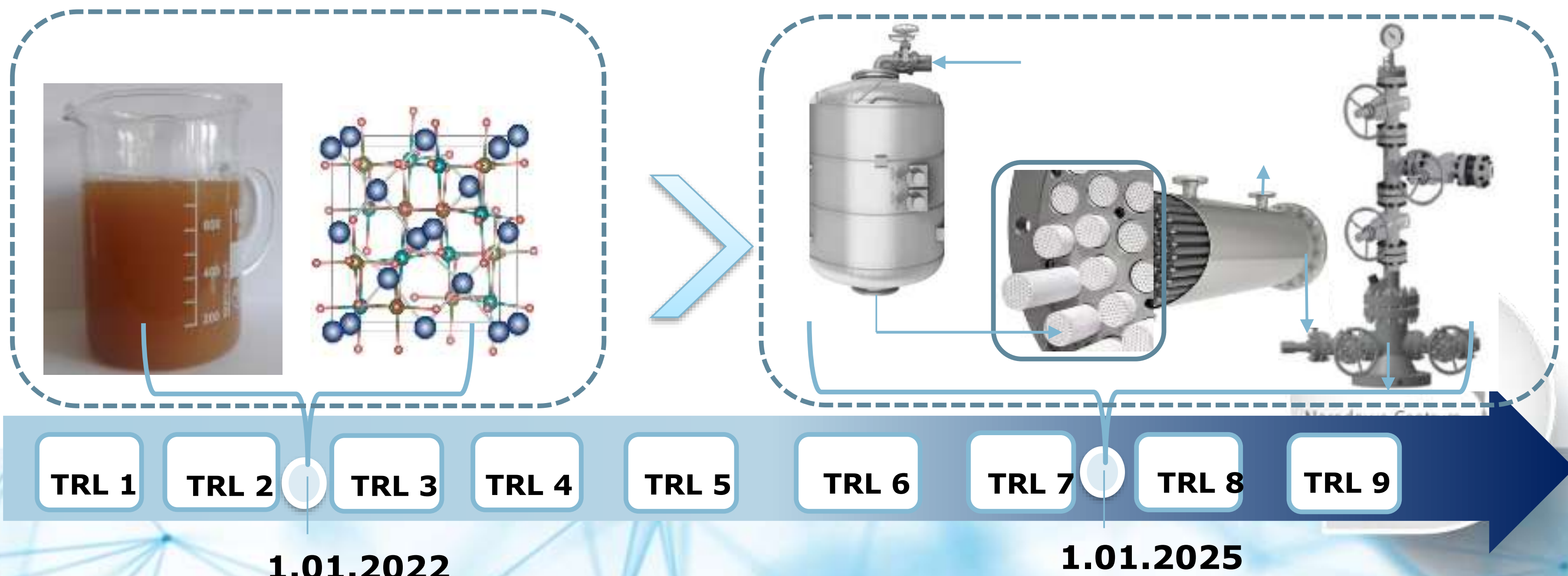
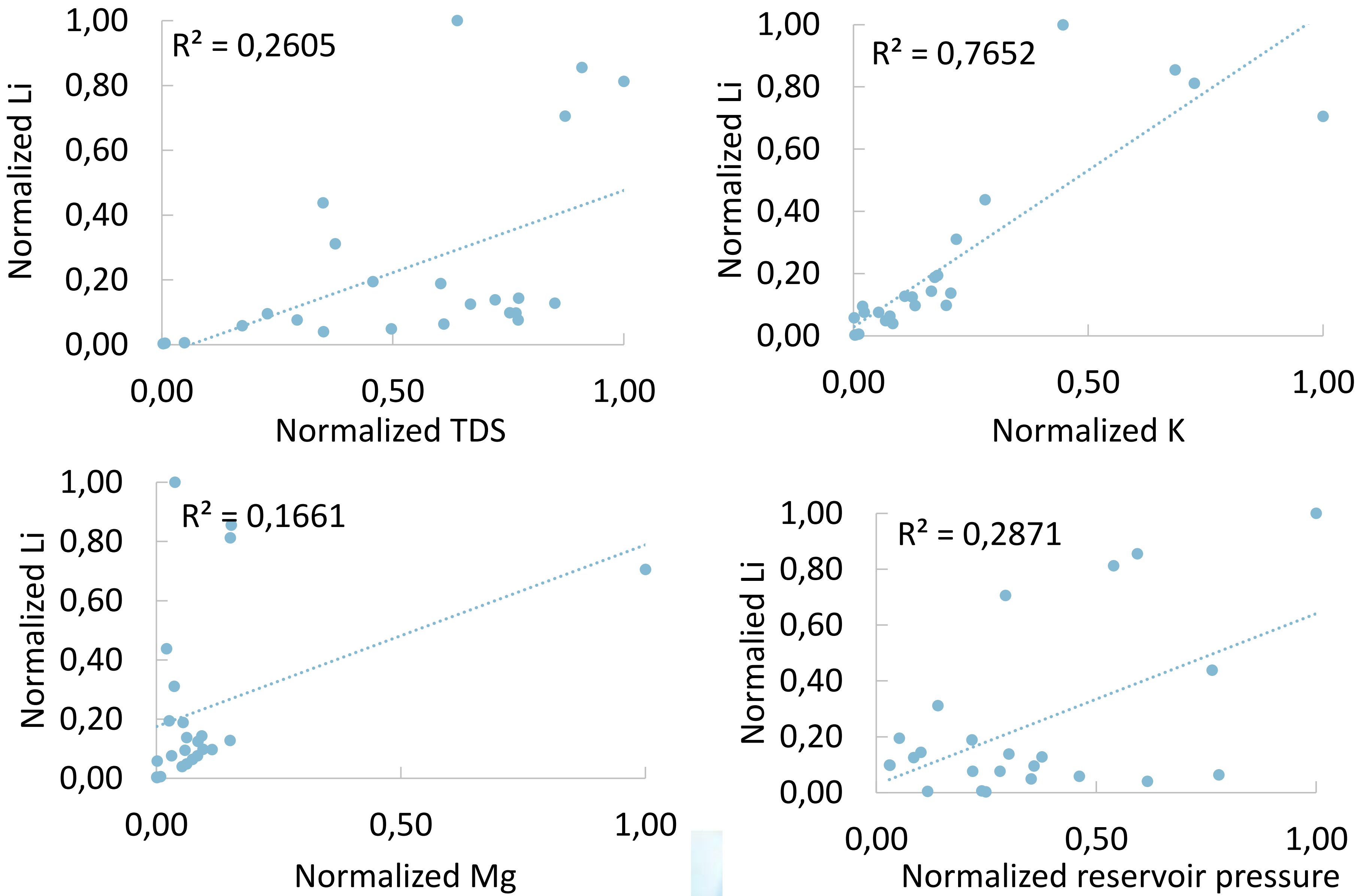
The CompLithium project - Complex technology for lithium and potable water recovery from produced waters

The aim of the project is to develop a technology for the recovery of lithium and potable water from waste reservoir brines based on combined sorption-membrane techniques. The proposed solution is a process innovation on a national and global scale. The elements of the novelty are:

- high-porosity sorbents made with the 3D printing technique for lithium recovery with improved selectivity and sorption capacity;
- nanofiltration membranes modified with crown ethers for the simultaneous production of desalinated water and sorption of residual lithium from brines.



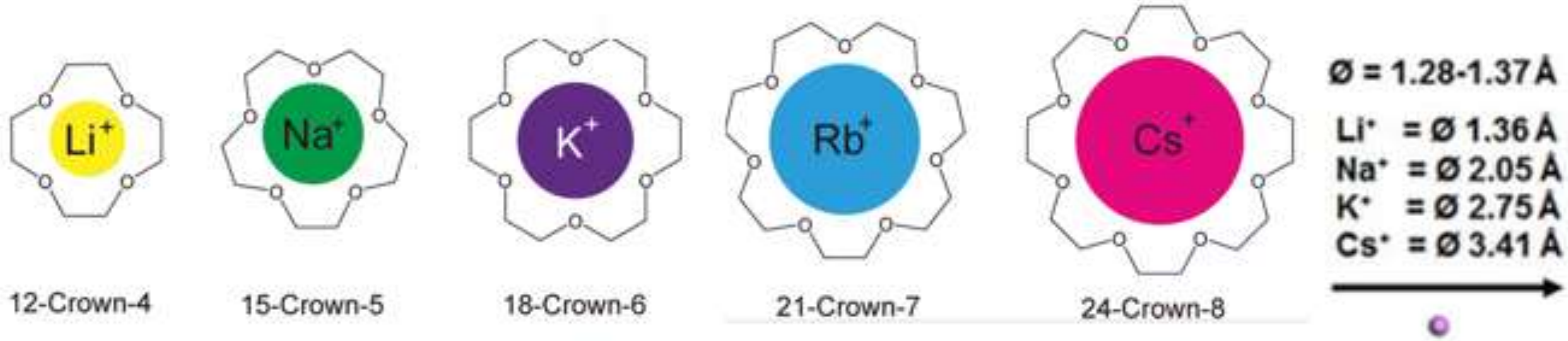
Lithium concentration in produced waters as a function of total dissolved solids, potassium concentration, magnesium concentration and reservoir pressure



Correlation matrix between selected parameters

	K	Na	Mg	Ca	Li	pH	TSS	TDS	OC	WP	RP	GP	WPW
K	1.00												
Na	0.20	1.00											
Mg	0.74	-0.01	1.00										
Ca	0.39	0.46	0.15	1.00									
Li	0.87	0.21	0.41	0.37	1.00								
pH	-0.07	-0.32	-0.13	-0.35	0.10	1.00							
TSS	0.39	0.15	0.01	0.33	0.43	-0.07	1.00						
TDS	0.62	0.79	0.44	0.79	0.51	-0.40	0.30	1.00					
OC	0.32	-0.20	0.28	0.19	0.22	-0.18	0.29	0.09	1.00				
WP	-0.05	-0.26	-0.08	-0.28	0.00	0.42	0.01	-0.28	-0.19	1.00			
RP	0.29	0.00	-0.05	0.16	0.54	0.02	0.21	0.07	0.04	-0.11	1.00		
GP	-0.39	-0.50	-0.28	-0.46	-0.31	0.34	-0.12	-0.60	-0.02	0.44	-0.12	1.00	
WPW	0.12	-0.03	-0.08	-0.12	0.22	0.35	0.05	-0.10	-0.18	0.22	0.42	0.29	1.00

OC – oilfield chemistry, WP – water production, RP – reservoir pressure,
GP – gas production, WPW – number of wells producing water



Crown ether is a sort of macrocyclic ligand possessing excellent complexing affinity to metal ions, which is able to form complexes through ion-dipole interaction of the negatively charged oxygen atoms with metal ions (in particular alkali metal and alkali earth metal ions) positioned in the center of the crown ether ring. **Li^+ has an ionic diameter of 1.36 Å, which matches best the cavity size of 14-crown-4.**

The interactions between dibenzo-14-crown-4 ether functionalized with an alkyl C16 chain and Li^+

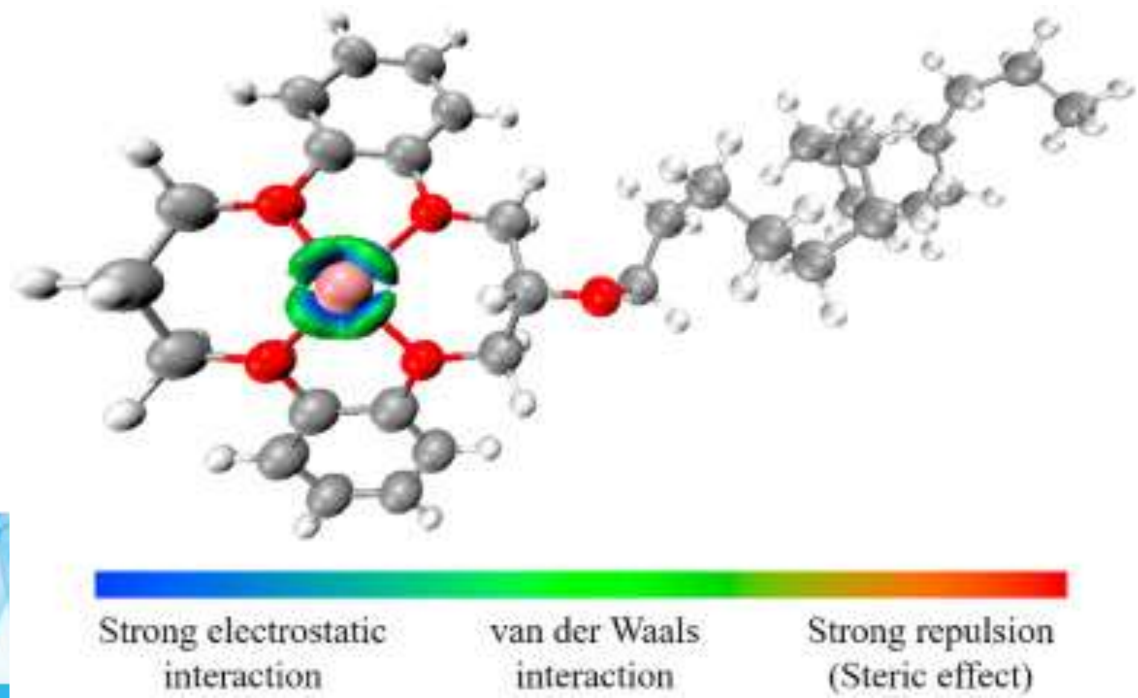


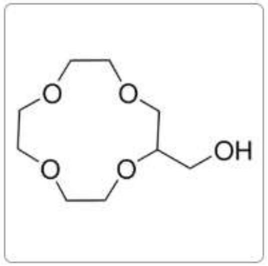
Table 1. Calculated geometric parameters of the complexes formed between DB14C4-C16 and Li^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}.

Bond (M-O)	Li^+-O	Mg^{2+}-O	Na^+-O	Ca^{2+}-O	K^+-O
Length (Å)	1.94-1.95	2.02-2.04	2.25-2.26	2.49-2.54	2.64-2.67

Table 2. Thermodynamic analysis results of the complexes formed by Li^+, Na^+, and Mg^{2+} with DB14C4-C16 and H_2O.

Complex	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔE (kJ/mol)	ΔS (kJ/mol/K)
DB14C4-C16-Li^+	-162.548	-125.813	-160.08	-0.12301
DB14C4-C16-Na^+	-90.2907	-55.7309	-87.8222	-0.1159
DB14C4-C16-Mg^{2+}	-241.04	-196.02	-238.572	-0.15104
H_2O-Li^+	-65.6051	-40.6078	-63.1294	-0.08368
H_2O-Na^+	-49.4214	-25.3559	-46.9428	-0.08075
H_2O-Mg^{2+}	-98.557	-71.4908	-96.0789	-0.09079

MERCK | Products | dibenzo-14-crown-4 ether | HR | EN



All Photos (1)

2-Hydroxymethyl-12-crown-4

Synonym(s): (12-Crown-4)-2-methanol, 1,4,7,10-Tetraoxacyclododecan-2-methanol

Empirical Formula (Hill Notation): $C_9H_{18}O_5$

CAS No.:	75507-26-5	**Molecular Weight:**	206.24
EC No.:	278-224-5	**Beilstein No.:**	4661968

Compare	Product No.	Description	SDS	Pricing
	382655	95%		Hide

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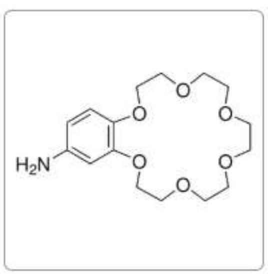
382655-1G	1 g	1 Available to ship on December 04, 2024 **Details...**	€149.00



4′-Aminobenzo-18-crown-6

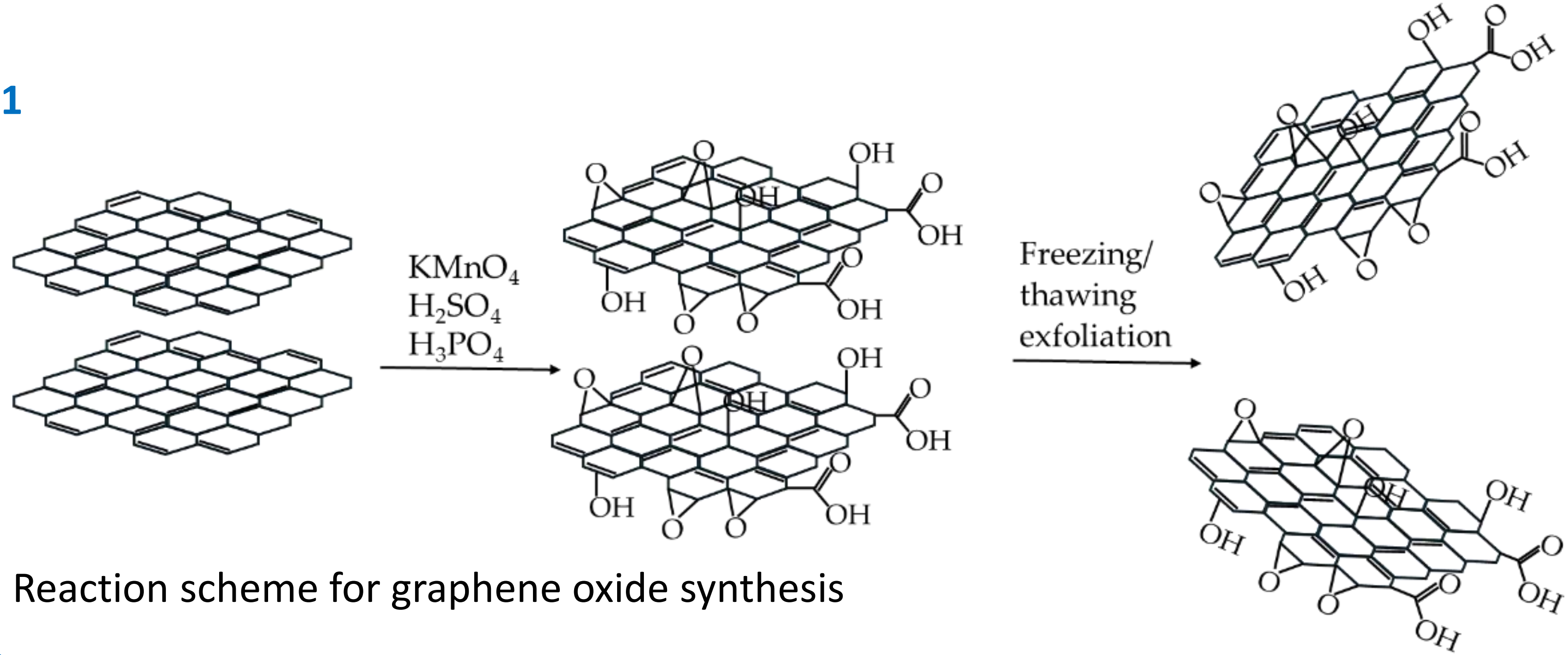
Synonym(s): (Benzo-18-crown-6)-4′-ylamine

Empirical Formula (Hill Notation): $C_{16}H_{25}NO_6$

CAS No.:	68941-06-0	**Molecular Weight:**	327.37
Beilstein No.:	5296463		

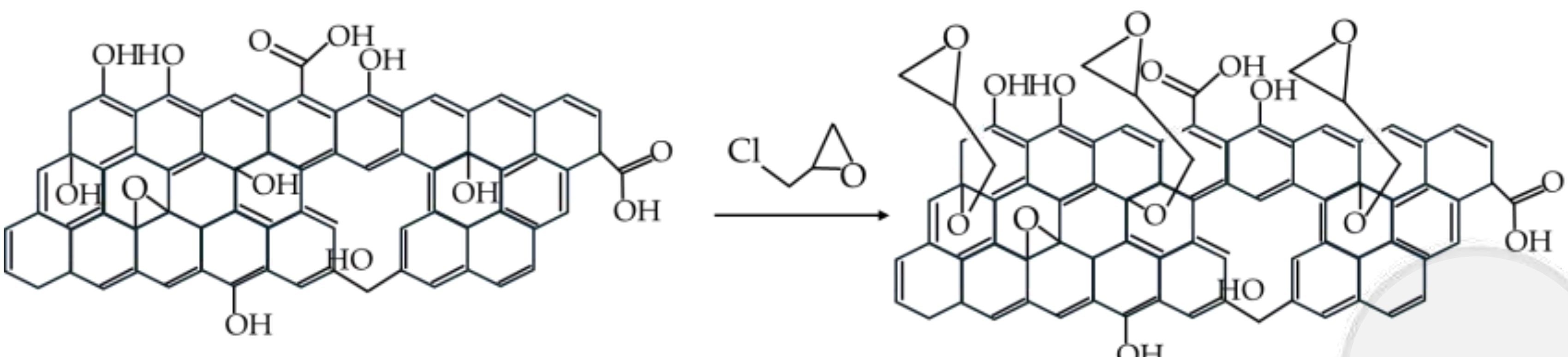
Compare	Product No.	Description	SDS	Pricing
06913-500MG	500 mg	1 Available to ship on December 04, 2024 **Details...**	€304.00	

Stage 1



Reaction scheme for graphene oxide synthesis

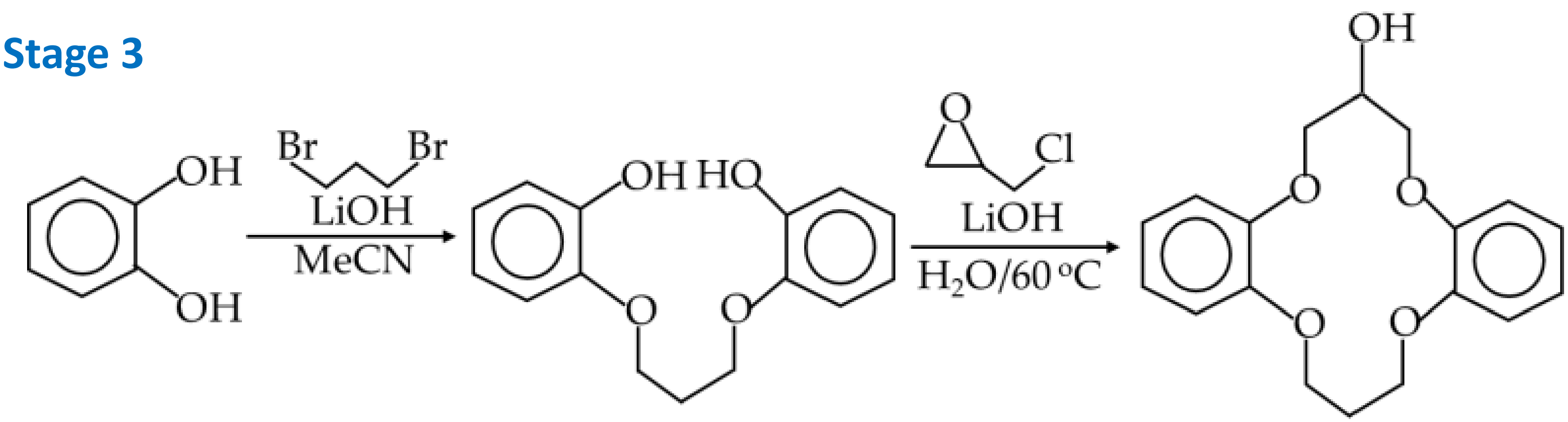
Stage 2



Scheme of graphene oxide modification with epichlorohydrin

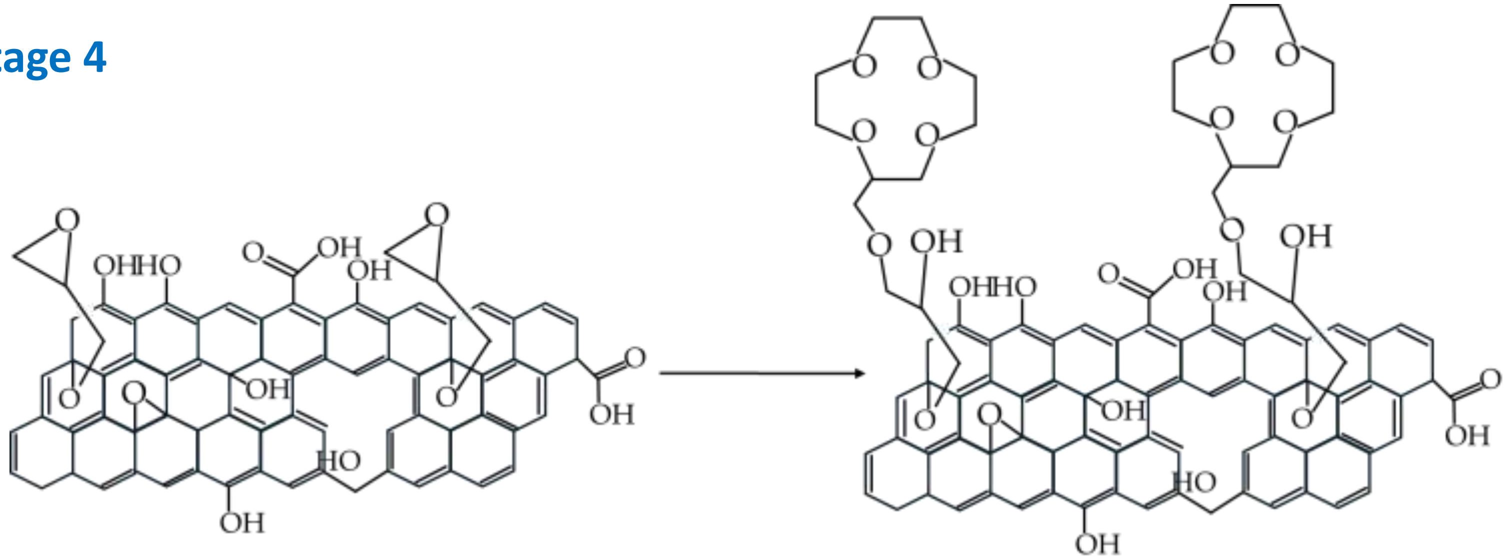
2-Hydroxymethyl-12-crown-4, which is commercially available, was used as a reference crown ether in the modification of graphene oxide. However, from the study on lithium capture selectivity of various crown ethers, it is known that the 12-crown-4 ring is less selective in comparison to the 14-crown-4 ethers. The selectivity coefficient of Li^+/Na^+ separation in model system is equal to 1.7 for the 12-crown-4 and 20 for the 14-crown-4.

Stage 3

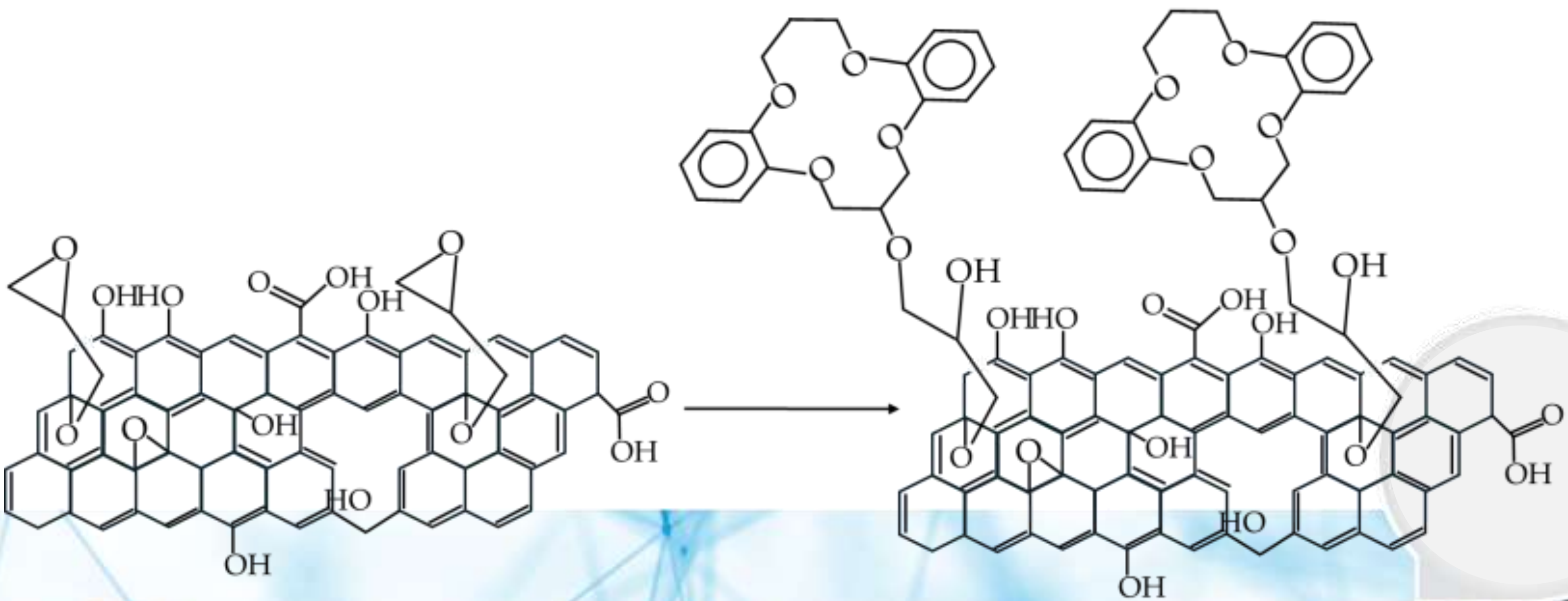


Reaction scheme for hydroxy-DB14C4 synthesis

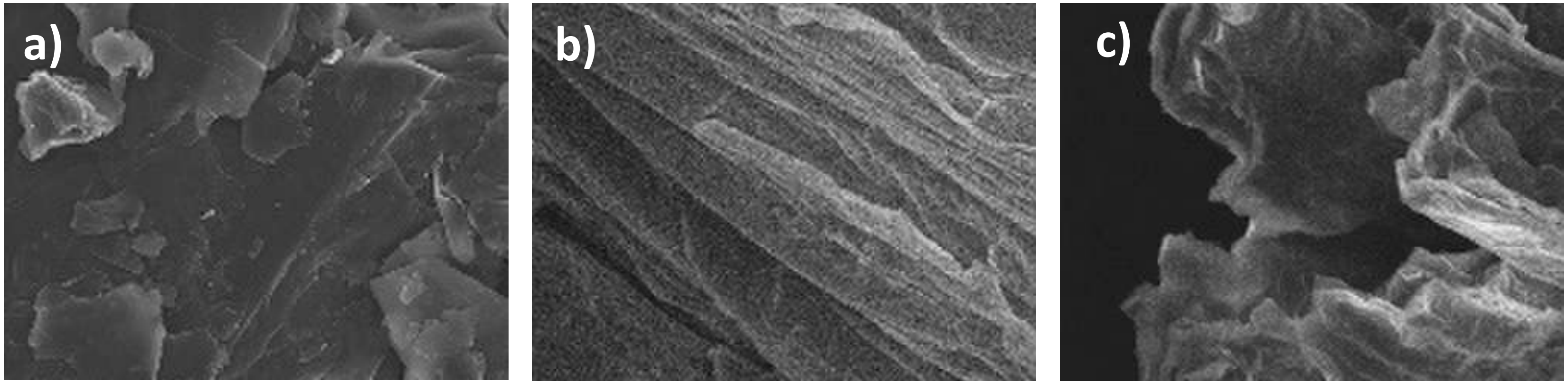
Stage 4

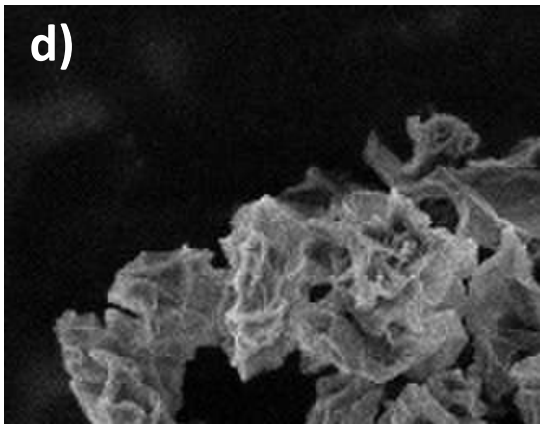


Reaction scheme for introduction of 12-crown-4 onto the modified GO

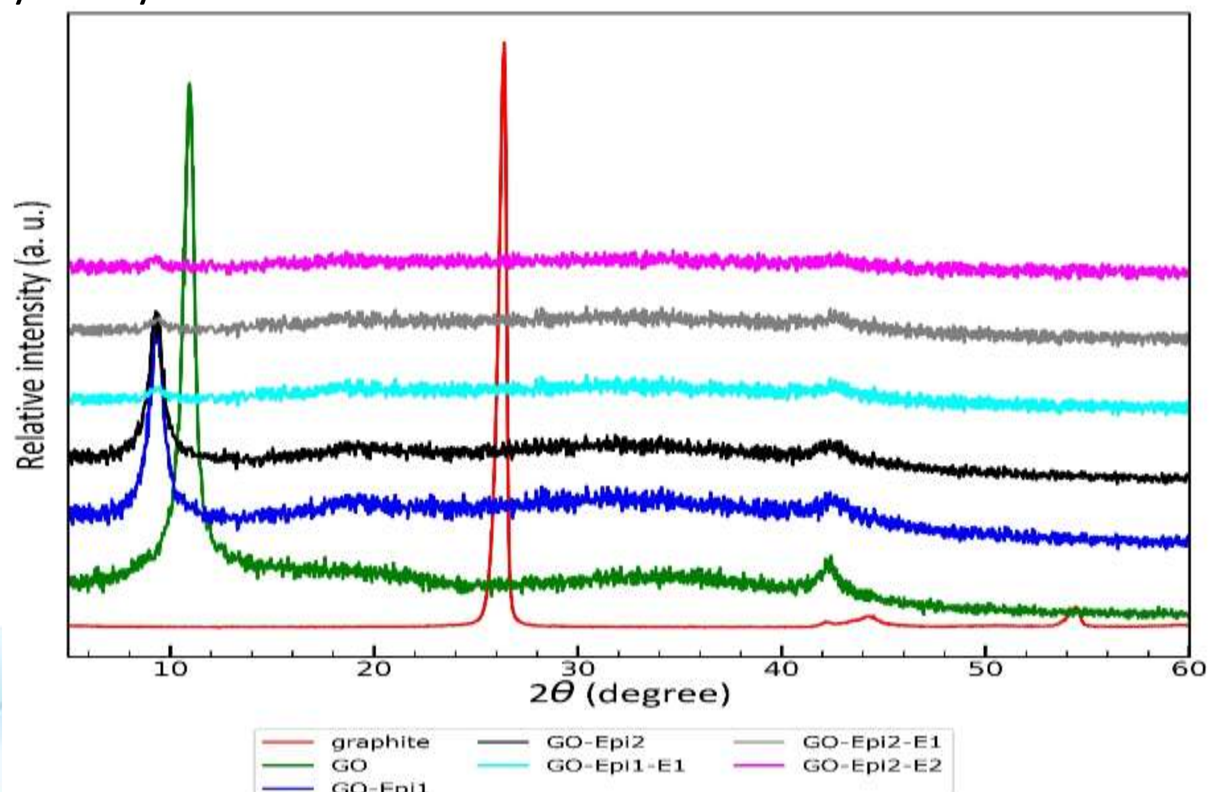


Reaction scheme for introduction of dibenzo-14-crown-4 onto the modified GO





SEM images of (a) raw graphite, (b) graphene oxide, (c) GO modified with epichlorohydrin, (d) GO modified with epichlorohydrin and 2-hydroxymethyl-12-crown-4.



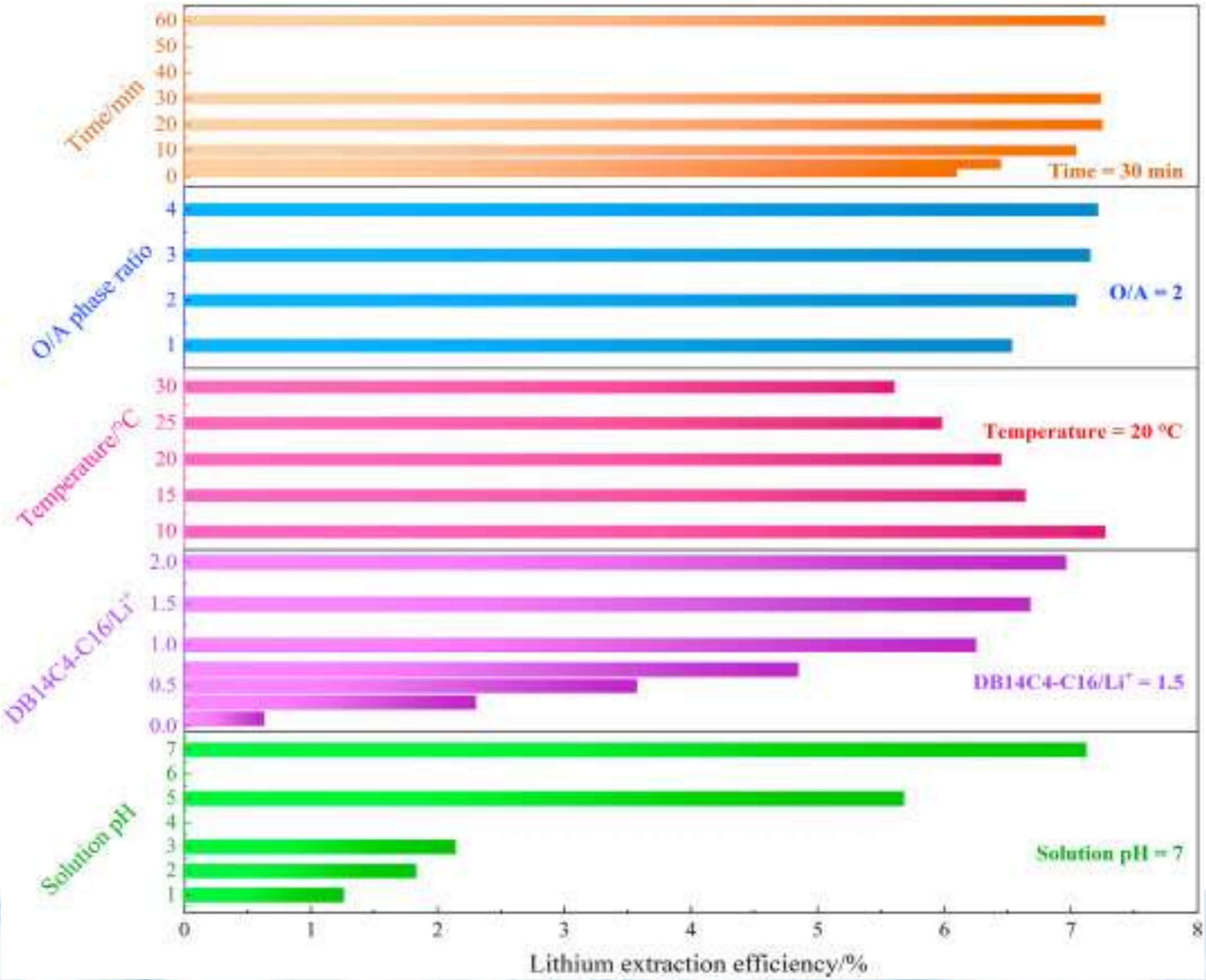
XRD patterns of raw graphite, graphene oxide and GO after epichlorohydrin and crown ethers immobilization.

Two series of experiments were performed, the first using pure lithium chloride solution with a lithium concentration of 200 mg/L and the second with real brine containing approx. 200 mg/L of lithium ions. The results presented in Table below include the recovery and operating capacity measured at pH 5 and pH 8 for various materials contacted with the brines at a solution to material mass ratio equal to 10/1.

Sample name	R Li* (R Li pH 8)	R Brine** (R Brine pH 8)	q Li* (q Li pH 8)	q Brine** (q Brine pH 8)
GO	28% (45%)	2% (4%)	0.89 (1.47)	0.05 (0.08)
GO-Epi2	75% (62%)	6% (2%)	1.96 (1.67)	0.17 (0.05)
E1 (2-Hydroxymethyl-12-crown-4)	3% (7%)	11% (8%)	0.16 (0.41)	0.32 (0.24)
E2 (dibenzo-14-crown-4 ether)	5% (6%)	8% (9%)	0.20 (0.24)	0.40 (0.42)
GO-Epi2-E1	68% (63%)	16% (18%)	1.11 (1.02)	0.22 (0.25)
GO-Epi2-E2	78% (76%)	17% (21%)	2.64 (2.62)	0.23 (0.32)
Chit-PVA	4% (4%)	6% (6%)	0.13 (0.16)	0.25 (0.23)
GO-Epi2-E1/Chit-PVA	22% (23%)	16% (16%)	0.40 (0.44)	0.35 (0.37)
GO-Epi1-E2/Chit-PVA	35% (37%)	16% (16%)	0.95 (0.98)	0.43 (0.45)

Effects of various parameters on Li^+ extraction process

Certain amount of the synthesized DB14C4–C16 was dissolved in CH_2Cl_2 to serve as the organic phase in the solvent extraction experiments. The solution contains pure Li^+ (200 mg/L).



source: https://doi.org/10.1016/j.jenvman.2022.114705

Comparative Study on Lithium Recovery with Ion-Selective Adsorbents and Extractants: Results of Multi-Stage Screening Test with the Use of Brine Simulated Solutions with Increasing Complexity

by Ewa Knapik [1], Grzegorz Rotko [1], Marta Marszałek [2,*] and Marcin Piotrowski [1,2]

Stage Number	Li^+ [mg/kg]	Na^+ [wt%]	Ca^{2+} [wt%]	Mg^{2+} [mg/kg]
1	300	0	0	0
2	300	0.10	0	0
3	297	1.00	0	0
4	240	7.86	0	0
5	240	7.86	0.1	0
6	220	7.21	3.0	0
7	220	7.21	3.0	300
8	220	7.21	3.0	1000

Sample Name	$R_{Li}1$ ($R_{Li}2$ pH 9)	$R_{Li}2$ ($R_{Li}2$ pH 9)	$R_{Li}3$ ($R_{Li}3$ pH 9)	$R_{Li}4$ ($R_{Li}4$ pH 9)	$R_{Li}5$ ($R_{Li}5$ pH 9)	$R_{Li}6$ ($R_{Li}6$ pH 9)	$R_{Li}7$ ($R_{Li}7$ pH 9)	$R_{Li}8$ ($R_{Li}8$ pH 9)
Other commercially available adsorbents								
CellPhos	47.4%	33.3%	16.7% (16.7%)	X	X	X	X	X
SiO_2-Et/Bu-$PO(OH)_2$	52.4%	60.0%	23.1% (33.3%)	9.1% (16.7%)	X	X	X	X
Manganese oxide-based adsorbents (prepared)								
LIS10	37.5%	16.7% (>99.7%)	9.1% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)
LIS11	33.3%	16.7% (>99.7%)	9.1% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (93.2%)
LIS12	33.3%	16.7% (>99.7%)	33.3%	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (96.8%)

Thank you for attention

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