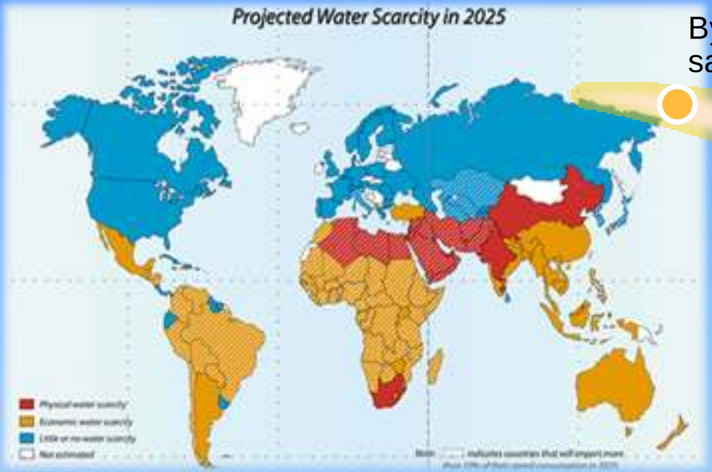
Sustainable Rubidium Recovery from Reverse Osmosis Concentrate Using Membrane Distillation - Ion Exchange process

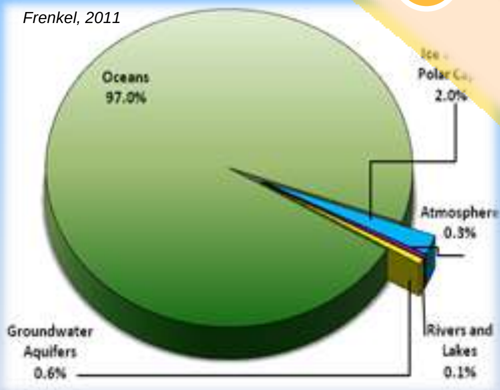
Gayathri Naidu, Sanghyun Jeong,
Saravanamuthu Vigneswaran , Jaya Kandasamy,
Tony Fane, Rong Wang

MANAGING WATER SCARCITY



By 2020 => 50% population lack safe drinking water

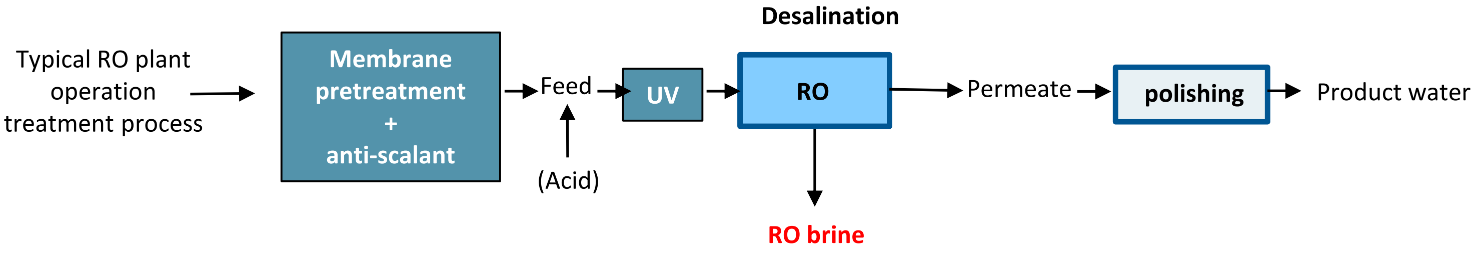
97% of world water source is ocean



Sustainable water production to meet fresh water demands

SEAWATER REVERSE OSMOSIS BRINE DISPOSAL

Desalination plants using reverse osmosis desalination process are being successfully operated in many parts of the world

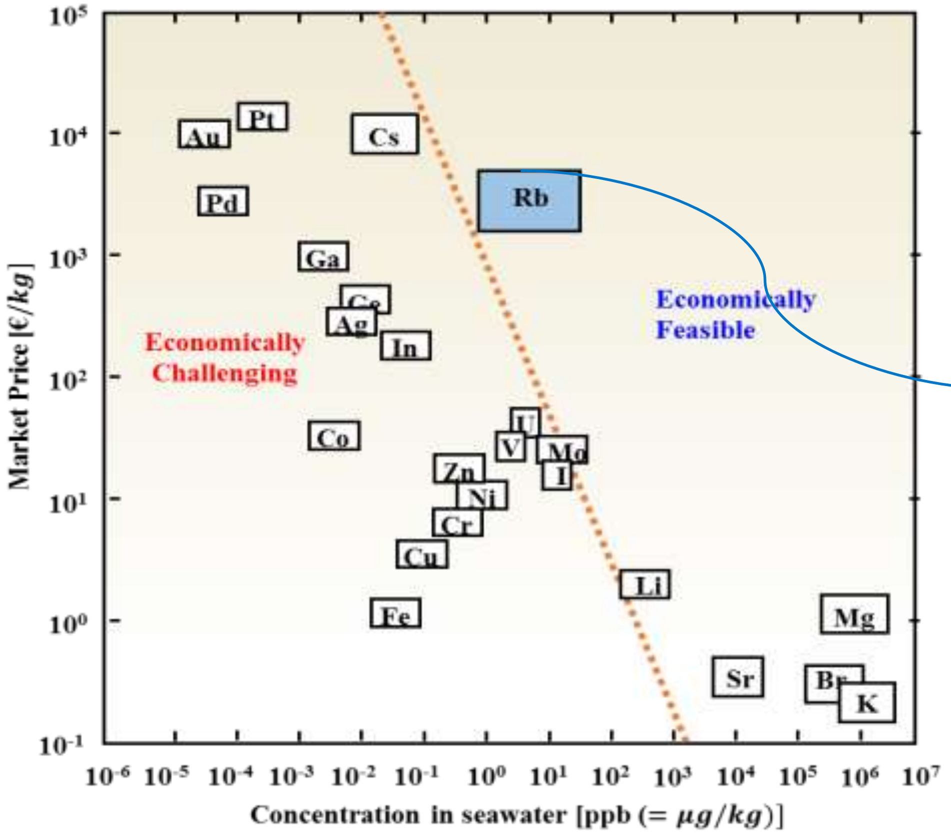


A **major problem of the SWRO** process is the need to dispose concentrated brine waste, incurring addition cost and environmental issues

Brine disposal cost for seawater desalination	Source
Direct sea discharge - US$0.04/$m^{-3}$ Evaporation pond - US$0.56/$m^{-3}$	*Malaeb & Ayoub [2011]*

Resourcefully using the SWRO brine, rather than simply disposing it, would **reduce the brine disposal cost and adverse environmental effect while gaining economic benefit.**

VALUABLE METAL RECOVERY FROM SWRO BRINE- RUBIDIUM (Rb)



Element	Content in SW RO brine, (mg/L)	Price, (euro/kg)	Potential Benefit, (Million Euro/yr)
Na	27,520	0.09	188
Mg	2450	1.97	367
B	4.45	299	101
Li	0.27	1.22	0.12
Rb	0.194	7856	116
Cs	0.0008T	10780	0.66
U	0.0039	70.27	0.02

Rb application:

The **market price of Rb is very high (AUD$10,000/kg)** compared to Na, Mg, K, and Li (AUD$0.1-3/kg). This price is expected to increase as Rb resources are rare in the world, and is in demand from industries - fiber optics, inorganic chemicals, lamps, night vision devices

METHODS FOR Rb RECOVERY FROM SWRO

Ion exchange materials such as hexacyanoferrate, ammonium molybdophosphate, zirconium phosphate, zeolite and phenol formaldehydes have **high adsorption capacities for Rb** and Cs

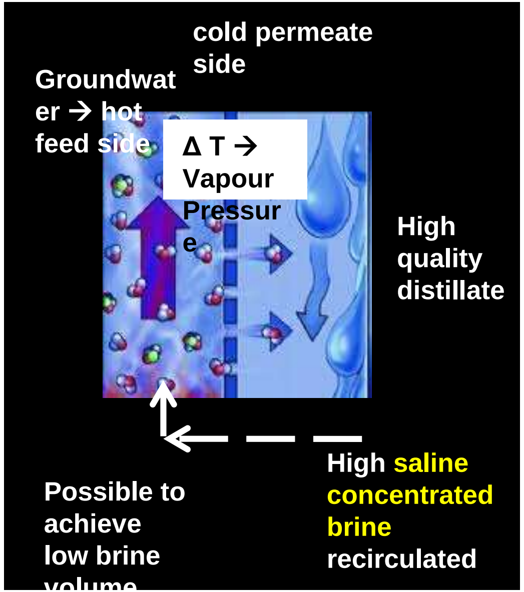
Hexacyanoferrate-based material has high adsorption capacity for both Cs (32.36mg/g) and Rb (46.73 mg/g) was observed compared to the other adsorbents (0.36-3.32 mg/g).

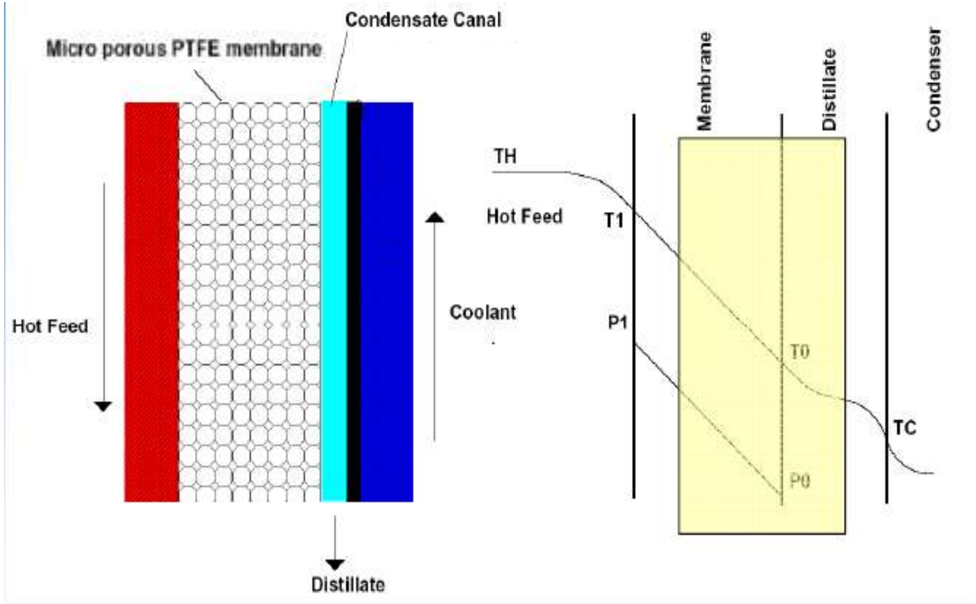
Rb concentration in SWRO brine is 0.19 mg/L. SWRO brine can be further concentrated using **membrane distillation (MD).**

Potassium hexacyanoferrate ion exchange resin ($K_2CoFe(CN)_6$) for Rb recovery

Membrane distillation (MD) performance with SWRO concentrate

MEMBRANE DISTILLATION (MD) FUNDAMENTALS





MD ENERGY REQUIREMENT

MD

Thermal Energy
175–350 kWh/m^3
Electrical energy
0.75–1.0 kWh/m3

RO

Thermal Energy
0 kWh/m^3
Electrical energy
4.0 – 4.5kWh/m^3

Application of alternative energy (solar) for MD around the world

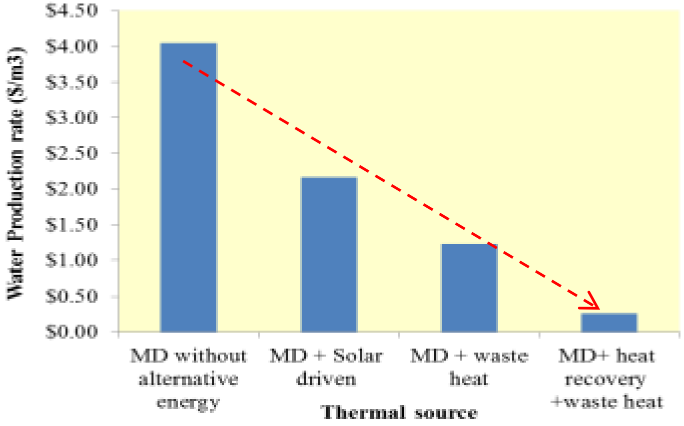
Pozo Izquierdo Gran Cacaria

Alexandria, Egypt

Irbid, Jordan

Fraunhofer ISE

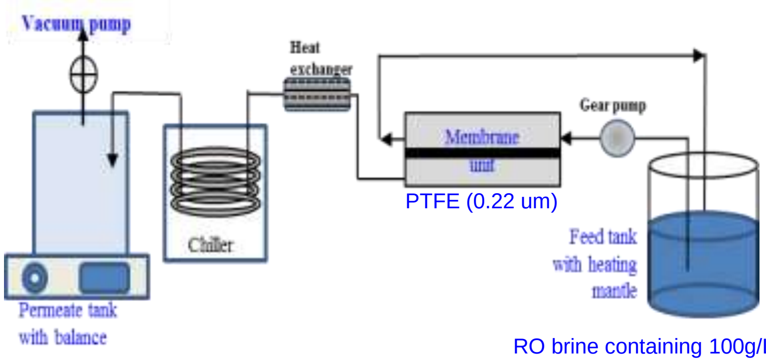
MD ECONOMICS WITH ALTERNATIVE ENERGY



Year	System description	WPC ($ m^{-3})	Ref
2007	- MD only - MD with low grade heat energy source	1.17 0.64	Obaidani, 2003
2007	- MD with industrial waste heat	0.26	Hanemaaijer, 2006
2007	- NF + RO with ERD and MD with heat energy -NF + RO without ERD and MD with heat energy -NF + RO with ERD and MD without heat energy *(ERD -energy recovery device)*	0.56 0.80 0.73	Macedonio, 2007
2004	- RO + MD - MD only	1.25 1.32	Alklaibi, 2005

VACUUM MD PERFORMANCE WITH **SWRO CONCENTRATE**

Experiment with saline RO brine



PTFE (0.22 um)

RO brine containing 100g/L of NaCl with main inorganic elements (0.8 g/LCa^{2+} , 3 g/L Mg^{2+} , 1g/L K^{+})

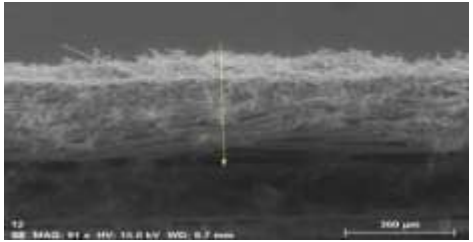
(Operation :

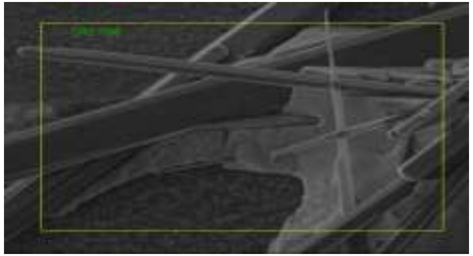
70°C feed temperature,
25° C cooling temperature,
1.0 L/min flow rate,
100 mbar vacuum pressure)

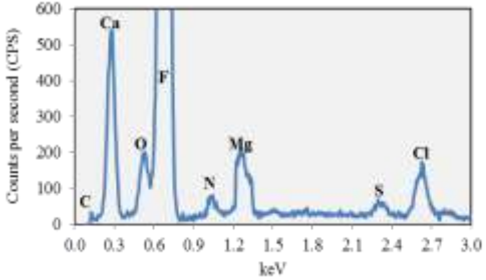
Flux declined by 70%

Permeate TDS increased to 3g/L at the end of the experiment

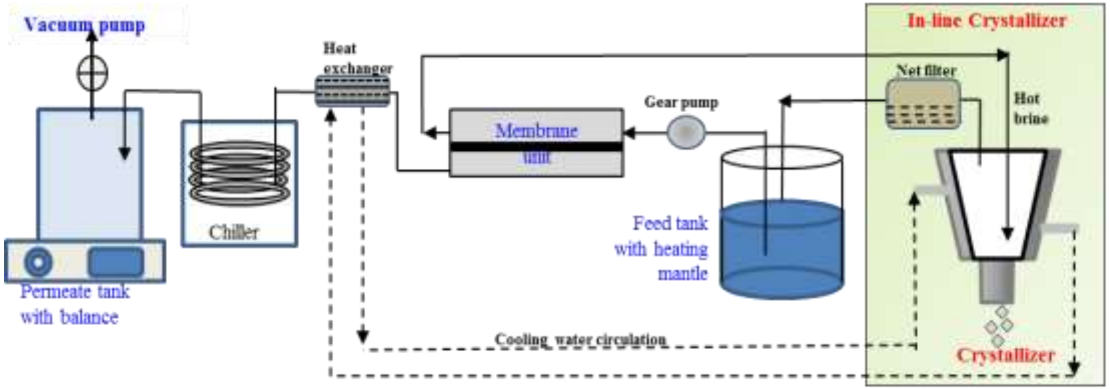
Inorganic element deposition on the membrane (mainly Ca and salt)





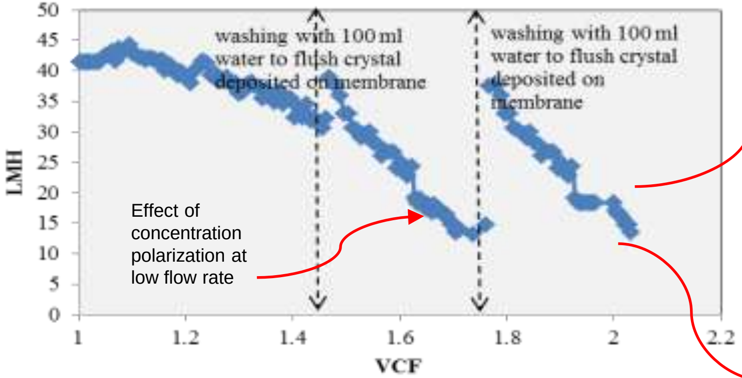


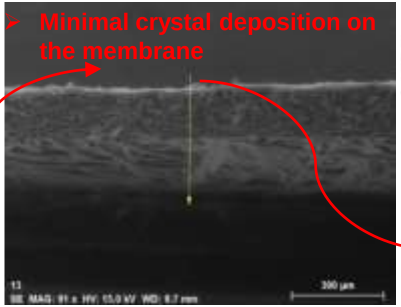
VMD **IN-LINE CYSTALLIZATION** PERFORMANCE WITH **HYPERSALINE RO CONCENTRATE**

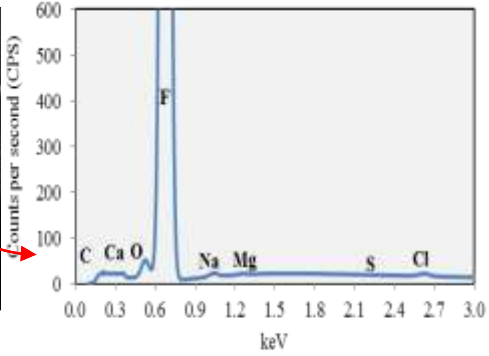


- Duration = 12 hours with **periodic water flushing (every 4 hours)**
- **Low feed flow** (**0.5 l/min**) = to increase contact time in crystallizer

(Operation : 70°C feed temperature, 25°C cooling temperature, 0.5 L/min feed flow, 100 mbar vacuum)

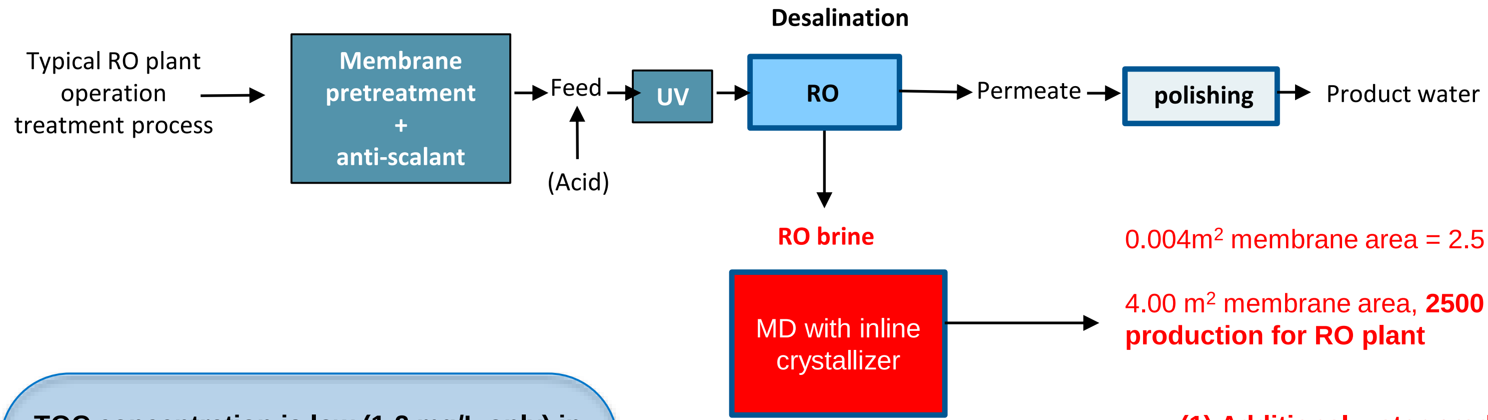






- Permeate TDS remained low ~3 mg/L

RO BRINE MANAGEMENT WITH MD



0.004m^2 membrane area = 2.5 L/d of water production

4.00 m^2 membrane area, **2500 L/d additional water production for RO plant**

(1) Additional water production

(2) Scaling mitigation

(3) Minimize RO brine management

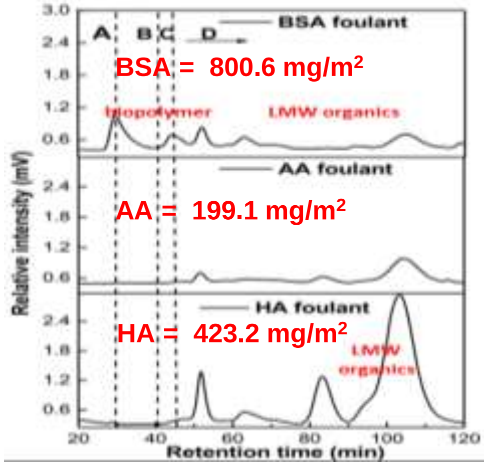
Effect of organics in concentrated RO solution?

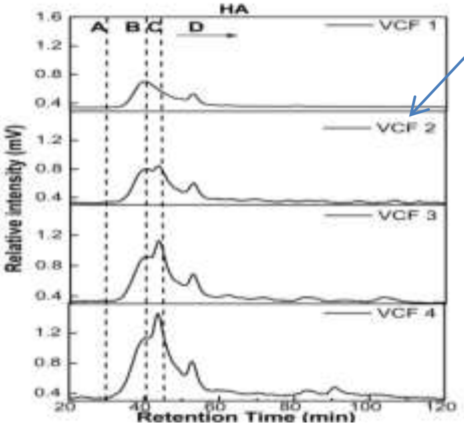
TOC concentration is low (1-2 mg/L only) in RO concentrate - *enough to cause organic and biofouling*

when further concentrated in an MD system, the organic concentration is increased by 4-5 times.

Further, previous studies: Ji et al. (2007) and Wang et al. (2008) - MD crystal size inhibition in the presence of organics observed

Organic Fouling Analysis



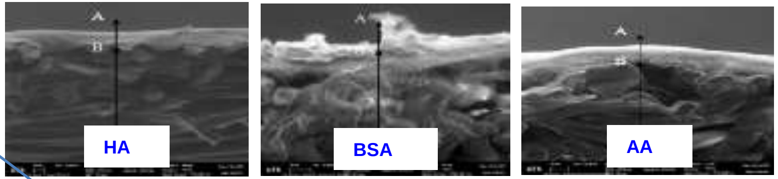


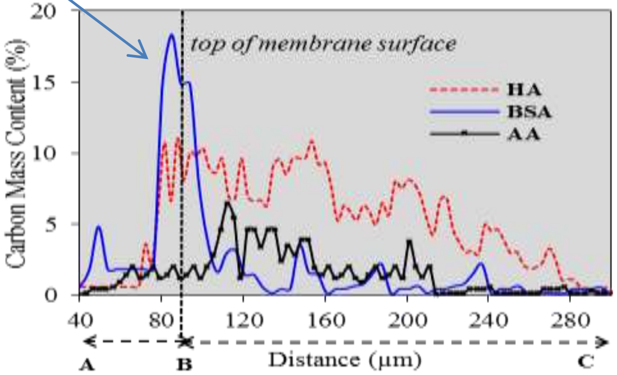
AA- hydrophilic repulsion with MD membrane- low fouling

BSA- hydrophobic in nature, highest membrane deposition

HA -thermally disaggregated to LMW –organics penetrated through the membrane (SEM cross section, high LMW-HA membrane deposition

Feed Organics Characteristics (mg/L)	BSA		AA	
	Initial	Final	Initial	Final
Total DOC	9.6	13.1	10.8	33.3
Hydrophobic	**7.1**	5.1	1.0	8.6
Hydrophilic	2.5	8.0	**9.8**	24.7





SEM cross section, high LMW-HA membrane deposition

G.Naidu, S. Jeong, S. Kim, I.S. Kim, S. Vigneswaran. Organic fouling behaviour in direct contact membrane distillation, Desalination. 347 (2014) 230-239.

Organic Fouling Analysis

Membrane hydrophobicity (contact angle analysis)

Virgin = 139.9 ± 1.2°

AA = 130.6 ± 4.7

BSA = 84.2 ± 4.7°

HA = 93.5 ± 6.2°

Membrane cleaning – flushing DI water through the feed channel (restored hydrophobicity)

AA = 130.6 ± 4.7

BSA = 104.3 ±3.8°

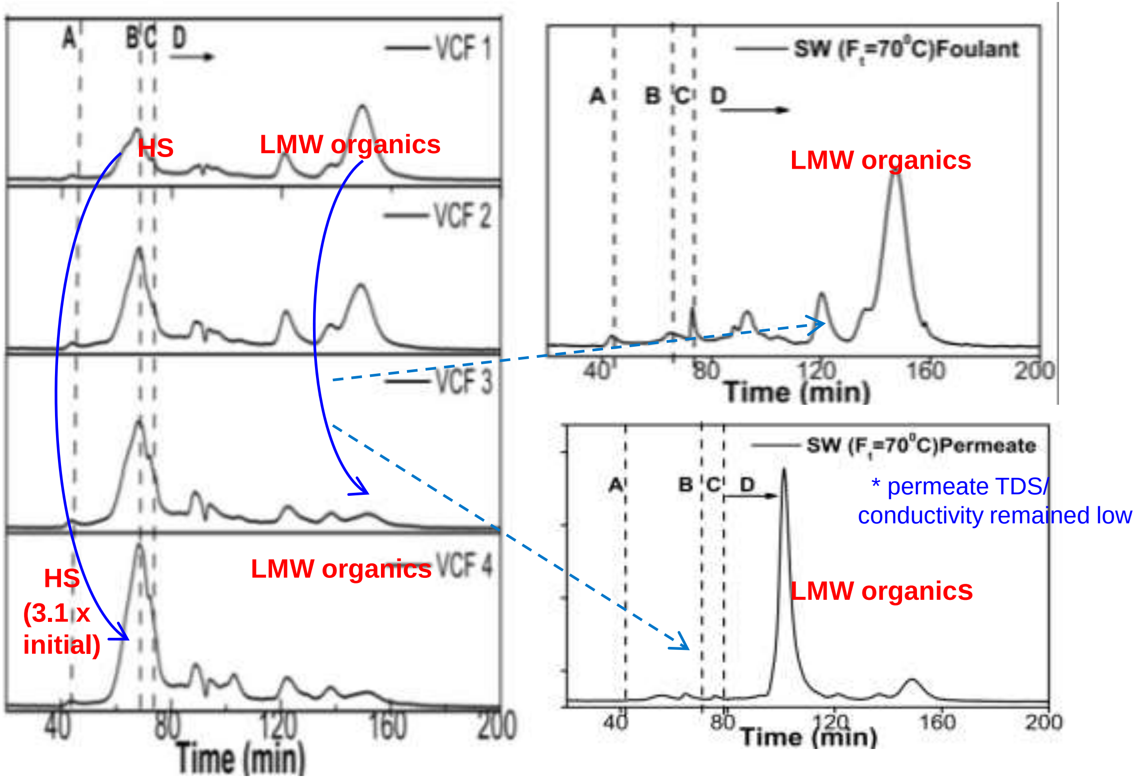
HA = 98.3 ± 4.1°

Flux recovery (97–98%) restoration period

BSA = 20 min

HA = 34 min

Seawater Organic Fouling Analysis



LC-OCD analysis

- Initial DOC (1.85 mg L^{-1}) **HS (0.49 mg L^{-1})** & **LMW organics (1.31 mg L^{-1})** + biopolymers (0.04 mg L^{-1}) & BB (0.005 mg L^{-1}).
- At VCF 4:
  - **HS** = (**3.1 x initial**) = thermal disaggregation
  - **LMW organics** = from VCF 3.0 = **deposited to foulant** => permeate, **flux decline at VCF 2.6**
  - **-LMW high increase** (not proportional to **VCF 2.0**) ➔ **Thermal disaggregation** of HS to LMW-HS did occur

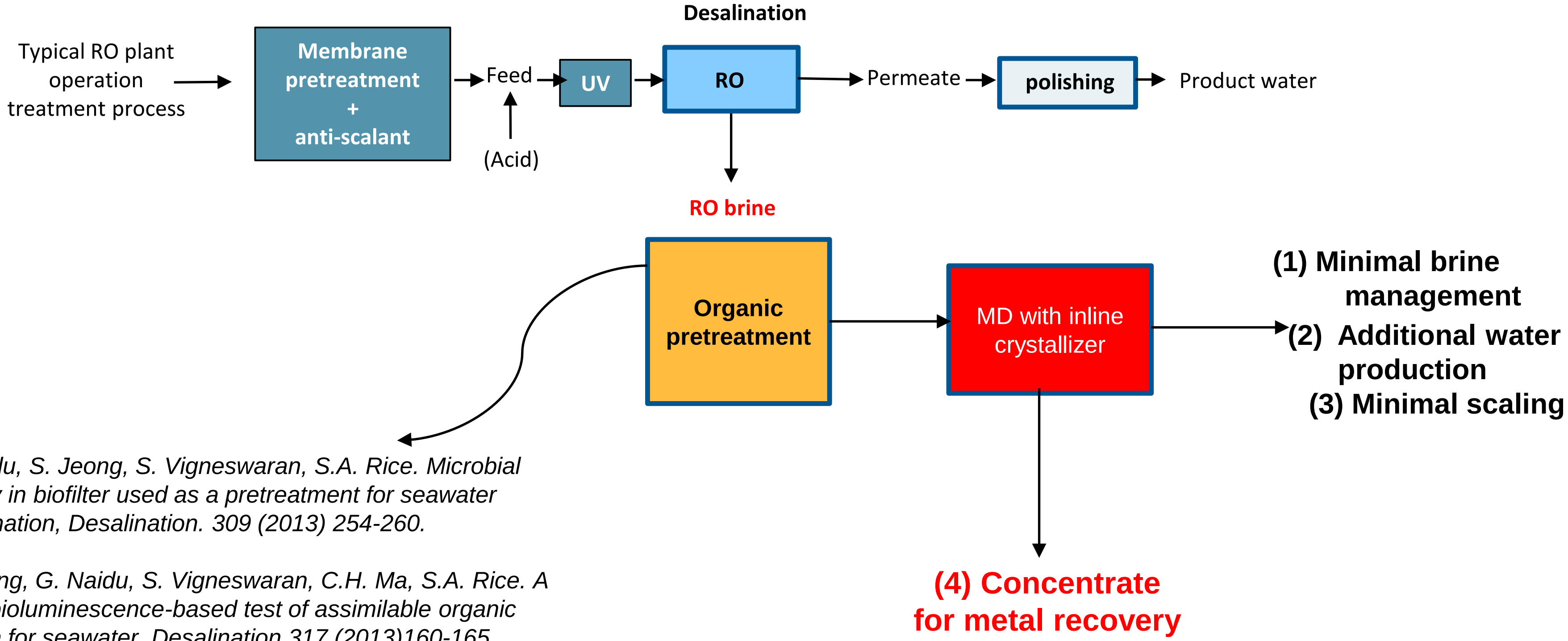
G.Naidu, S. Jeong, S. Vigneswaran. Interaction of humic substances on fouling in membrane distillation for seawater desalination, Chemical Engineering Journal.262 (2015) 946-957

Both feed LMW and LMW-HS contributed to =>LMW in membrane foulant & permeate

- HS Thermal **disaggregation not as prevalent** as HA synthetic => presence of **$CaSO_4$ binding agent and salt**

RO BRINE MANAGEMENT with MD and Rb RECOVERY

RO BRINE MANAGEMENT WITH MD



G.Naidu, S. Jeong, S. Vigneswaran, S.A. Rice. Microbial activity in biofilter used as a pretreatment for seawater desalination, Desalination. 309 (2013) 254-260.

S. Jeong, G. Naidu, S. Vigneswaran, C.H. Ma, S.A. Rice. A rapid bioluminescence-based test of assimilable organic carbon for seawater, Desalination 317 (2013)160-165

SWRO BRINE METAL RECOVERY WITH MD AND ION EXCHANGE

- **Rb** in SWRO brine is around 0.19 to 0.25 mg/L -> concentrated in **MD by 5x to 1.0 to 1.3 mg/L**
  The increase in Rb concentration by MD would enhance the efficiency of $K_2CoFe(CN)_6$ ion exchange

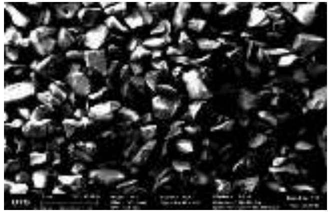
	RO brine (mg/L)	MD concentrated RO brine (mg/L)
Rubidium	0.19 - 0.25	0.95 - 1.25
Lithium	0.3 - 0.5	1.5 - 2.5
Potassium	1,300 - 1,500	6,500 - 7,500
Cesium	~0.0003	~0.0015

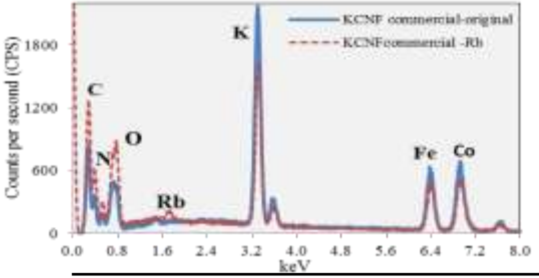
Divalent Ions in MD concentrated RO brine (g/L)

Calcium	0.8 - 1.0
Magnesium	6.4 - 10.1
Strontium	0.04 - 0.06

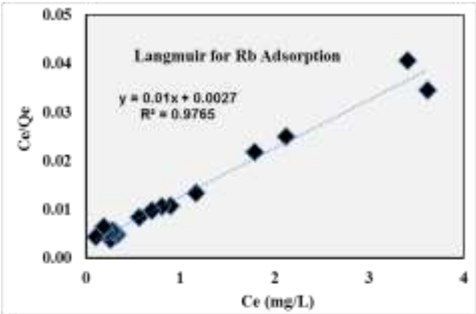
RO BRINE MANAGEMENT WITH MD AND Rb RECOVERY

➢ **Commercial Potassium Cobalt Hexacyanoferrate ion exchange resin** ($K_2CoFe(CN)_6$: performance with Rb^+





C normal (wt.%)	Commercial $K_2CoFe(CN)_6$ (original)	Commercial $K_2CoFe(CN)_6$ (Rb)
K	15.25	10.80
Fe	20.78	15.96
Co	31.52	23.69
Rb	0	0.54

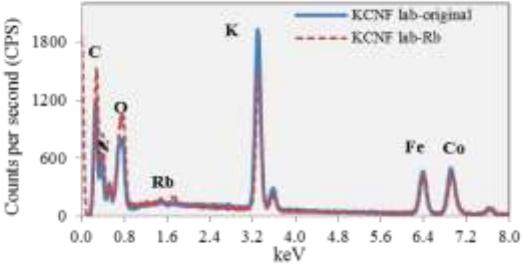


Commercial **KCnF**
Langmuir = $\mathbf{Q_{max}}$= **100.1 mg/g**

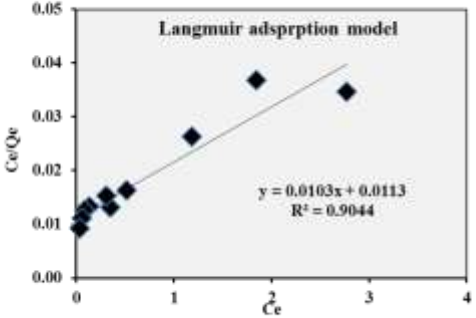
Chemical composition of lab and commercial **KCnF**

Enable to be made/produced in lab easily

➢ **Lab prepared Potassium Cobalt Hexacyanoferrate ion exchange resin** ($K_2CoFe(CN)_6$): performance with Rb^+



C normal (wt.%)	Lab $K_2CoFe(CN)_6$ (original)	Lab $K_2CoFe(CN)_6$ (Rb)
K	13.06	9.25
Fe	15.33	13.19
Co	22.09	19.40
Rb	0	0.52

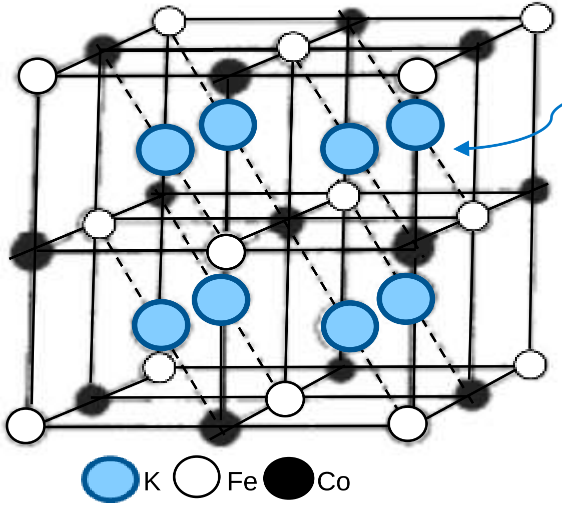


Lab **KCnF**
Langmuir =$\mathbf{Q_{max}}$= **97.4 mg/g**

RO BRINE MANAGEMENT WITH MD AND Rb RECOVERY

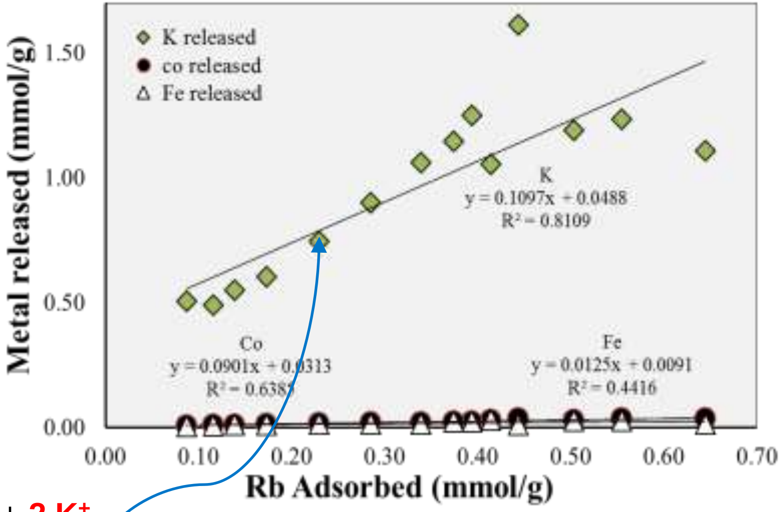
$K_2CoFe(CN)_6$ adsorption mechanism

Cubic crystal structure of $K_2CoFe(CN)_6$



Fe and Co at cube corners
K in the cube body

Therefore mostly surface and inter-ion exchange with K^+ would occur with Rb^+ with some release of Co and Fe



$K_2[CoFe(CN)_6] + 2\mathbf{Rb} \rightarrow \mathbf{Rb_2}[CoFe(CN)_8] + \mathbf{2\ K^+}$

Experimental results showed the increase of K (mmol/g) as Rb adsorption (mmol/g) increased

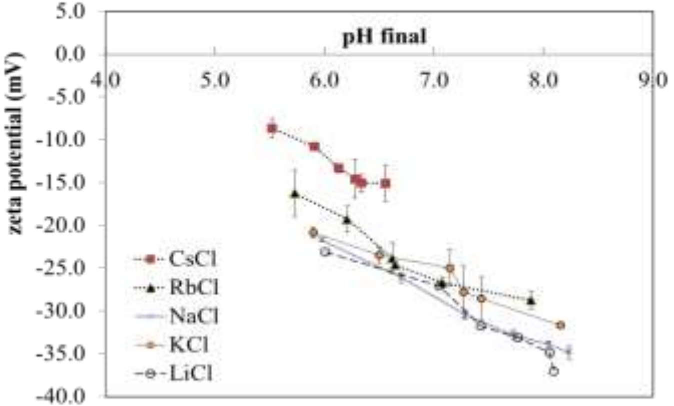
RO BRINE MANAGEMENT WITH MD AND Rb RECOVERY

$K_2CoFe(CN)_6$ adsorption mechanism

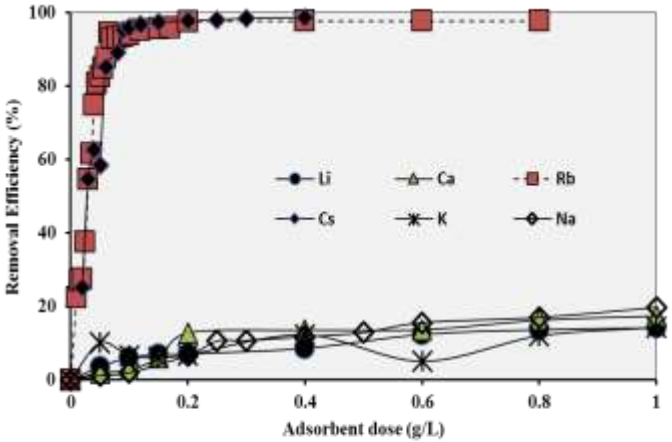
Based on **hydration ion size** the strength ions are held to the KCFCN surface in the order **Cs+> Rb+> K+ > Na+> Li+.**

Mono valent metal	Ionic radius (pm)	Hydrated Radius (pm)
Cs^+	167	226-228
Rb^+	152	228
K^+	138	232-331
Na^+	102	276-360
Li^+	76	340-470

Less hydrated monovalent cations (Rb+, Cs+) bind more strongly to **KCFCN surface, lowering the negativity of the surface zeta potentials**.



Cs+ and Rb+ have small hydrated ionic radii, could enter the **KCFCN** easily giving high removal %



RO BRINE MANAGEMENT WITH MD AND Rb RECOVERY

$K_2CoFe(CN)_6$ performance with **competition/ coexisting ions in RO brine**

Presence of monovalent alkali metal

5 mg/L element concentration (*Dose 0.03 g/l*)	Uptake (mg/g)
Rb	**96.7**
Rb **with Cs**	88.7
Rb **with Li**	95.2
Rb **with K**	94.8

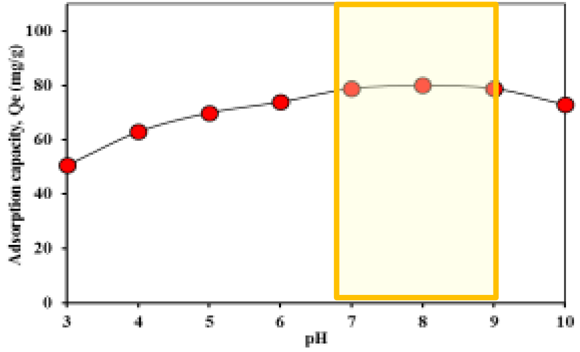
Based on hydration ion size the strength with which ions are held to the surface of KCFCN in the order Cs+> Rb+> K+ > Na+> Li+.

Presence of other elements

Element concentration (*Dose 0.03 g/l*)	**Uptake (mg/g)**		
	5 mg/L	**100 mg/L**	**500 mg/L**
Rb	**96.7**		
Rb **with Ca**	95.9	92.3	91.9
Rb **with Mg**	96.1	94.4	93.6
Rb **with Na**	95.1	92.7	90.8
Rb with K	94.8	85.1	57.1

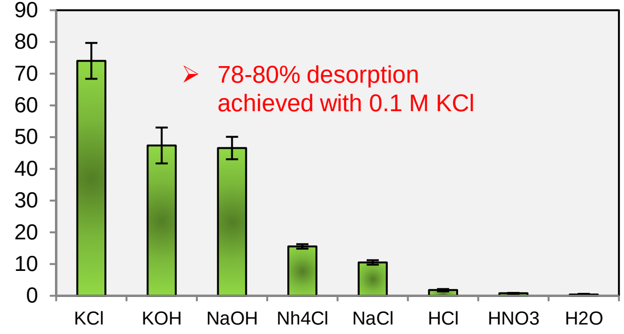
- At equal low concentrations, Rb^+ uptake by $K_2CoFe(CN)_6$ is **affected by Cs>K>Li**
- Significant **competitor is cesium** (but Cs^+ in RO brine is **< 0.002 mg/L**)
- Rb^+ uptake by $K_2CoFe(CN)_6$ is **minimally** affected by **NaCl & divalent ions**
- Rb^+ uptake by $K_2CoFe(CN)_6$ is **affected** by the presence of **potassium at high concentrations >100 g/L and above**

- **$K_2CoFe(CN)_6$) performance at different pH**



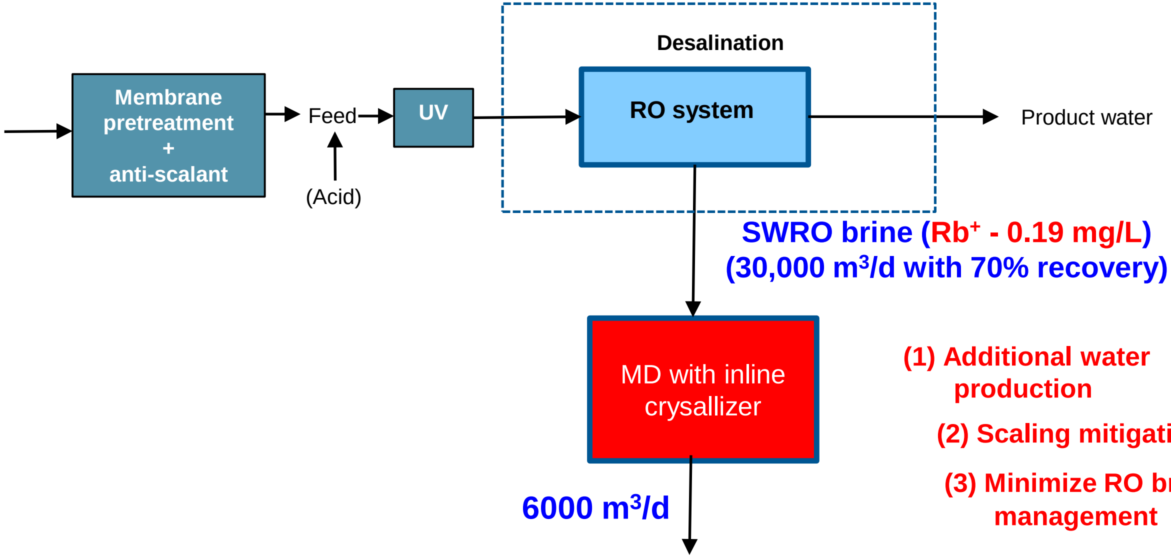
- Suitable pH range : 6.5 -9
- Changing pH /acidification of SWRO brine would affect the performance of KCFCN for metal recovery

- **($K_2CoFe(CN)_6$) desorption**



SWRO BRINE MANAGEMENT AND Rb RECOVERY WITH MD –ION EXCHANGE

SWRO plant (100,000 m^3/d Rb$^+$ - 0.10 mg/L)



SWRO brine (Rb$^+$ - 0.19 mg/L)
(30,000 m^3/d with 70% recovery)

(1) Additional water production

(2) Scaling mitigation

(3) Minimize RO brine management

MD concentrate (Rb$^+$ - 1.0 to 1.3 mg/L) [*19.4 kg Rb$^+$*]

(4) MD Concentrate for Rb metal recovery
56-60% Rb recovery with ion exchange resin (*90k euro/day*)

Element	Content in brine, (mg/L)	Price, (euro/kg)
Na	27,520	0.09
Mg	2450	1.97
B	4.45	299
Li	0.27	1.22
Rb	0.194	7856
Cs	0.0008	10780
U	0.0039	70.27

Synthesis of new adsorbents

Hexacyanoferrate adsorbents
$K_2Fe(CN)$ with different **metal composition**

- **Cu**
- **Ni**
- **Zn**

Preliminary analysis showed that **Ni hexacyanoferrate metal** achieved better performance compared to Co hexacyanoferrate composition for **Rb^+ removal**

- K_2**Co**$Fe(CN)_6$ **langmuir - 100.1 mg/g**
- K_2**Ni**$Fe(CN)_6$ **langmuir - 123.2 mg**

Encapsulated with support material for stablliiy – *zeolites, meso-porous silica and polyurethane sponges.*

- ***Zeolite*** **:** *Analyse* **various zeolites and select the one having** high adsorption capacity as well as selectivity of adsorption for Rb^+ to encapsulate the new adsorbents.
- ***Mesoporous silica*** :Use synthesised **mesoporous silica with appropriate pore size to selectively accommodate** Rb^+ into the pores.
- ***Polyurethane sponge*** **:** a non-toxic material with high internal porosity and surface area. Our research group has successfully used a polyurethane sponge to mechanically support ferric hydroxide for the adsorptive removal of arsenic from water (*Nguyen et al. 2010*).

THANK YOU

FUNDED BY AUSTRALIAN RESEARCH COUNCIL