

1 **Rubidium extraction using an organic polymer encapsulated potassium copper** 2 **hexacyanoferrate sorbent**

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10 11 **Abstract**

12 Sea water reverse osmosis (SWRO) brine contains significant quantity of Rb. As an economically
13 valuable metal, extracting Rb using a suitable and selective extraction method would be beneficial. An
14 inorganic sorbent, copper based potassium hexacyanoferrate (KCuFC), exhibited high selectivity to
15 extract Rb compared to potassium hexacyanoferrate consisting of other transition metal combinations
16 such as Ni, Co and Fe. An organic polymer (polyacrylonitrile, PAN) encapsulated KCuFC (KCuFC-
17 PAN) achieved a Langmuir maximum Rb sorption capacity of 1.23 mmol/g at pH 7.0 ± 0.5. KCuFC-
18 PAN showed Rb selectivity over a wide concentration range of co-existing ions and salinity of SWRO
19 brine. High salinity (0.5-2.5 M NaCl) resulted in 12-30% sorption capacity reduction. At a molar ratio
20 of Li:Rb (21:1), Cs:Rb (0.001:1) and Ca:Rb (14,700:1) commonly found in SWRO brine, sorption
21 reduction of only 18% occurred. Nevertheless, at a very high K:Rb molar ratio (7700:1), KCuFC-PAN
22 sorption capacity of Rb reduced significantly by 65-70%. KCuFC-PAN was well suited for column
23 operation. In a fixed-bed KCuFC-PAN column (influent concentration 0.06 mmol Rb/L, flow velocity

24 2 m/h), two sorption/desorption cycles were successfully achieved with a maximum Rb sorption
25 capacity of 1.01 (closely similar to the batch study) and 0.85 mmol/g in the first and second cycles,
26 respectively. Around 95% of Rb was desorbed from the column with 0.2 M KCl. Resorcinol
27 formaldehyde (RF) resin showed promising results of separating Rb from K/Rb mixed solution in
28 effluents from a fixed-bed column, and a subsequent sequential acid desorption, producing 68%
29 purified Rb.

30

31 **Keywords** *potassium copper hexacyanoferrate, purification, reverse osmosis brine, rubidium,*
32 *seawater, sorption.*

33

34 1. Introduction

35 Sea water reverse osmosis (SWRO) brine contains trace alkali metals that are economically
36 valuable. Presently, much attention has been focused on rubidium (Rb) recovery in view of its high
37 economic potential at 7857 Euros/kg in comparison to other metals such as cesium (Cs), lithium (Li),
38 germanium and indium [1]. Rb is used in specific fields such as fibre optic telecommunication and
39 laser technology [2]. In SWRO brine, Rb is present at low concentrations (0.19 to 0.21 mg/L) with
40 other dominant ions such as sodium (Na), potassium (K), calcium (Ca), magnesium (Mg) and Li in
41 highly saline condition [1,3].

42 Inorganic ion-exchange sorbents are widely used in the extraction of metals found in low
43 concentration due to its high selective sorption capacity in mixed metals solutions [4]. In this context,
44 potassium metal hexacyanoferrate (K(M)FC (M refers to transition metals such as cobalt (Co), copper
45 (Cu), iron (Fe), zinc (Zn) and nickel (Ni)), is known for its versatile applications for trace alkali metal
46 extraction under high saline conditions [1,5]. Considerable effort has been made on the development

47 of K(M)FC especially for radioactive Cs removal from nuclear waste solutions [6]. A variety of metal
48 combinations are used to make K(M)FC sorbent including Co, Ni, Fe (Prussian Blue), Zn and Cu
49 [7,8]. Potassium cobalt hexacyanoferrate (KCoFC) is commercially available due to its high selectivity
50 for radioactive Cs removal [6,9]. K(M)FC with other metal based combinations such as Cu (KCuFC),
51 Zn (KZnFC), Fe (KFeFC) and Ni (KNiFC) have also shown satisfactory results in Cs extraction from
52 nuclear waste [7-9]. K(M)FC with different metal combinations to increase selective sorption of Rb
53 has not been compared in a single study so far. This information would be useful in identifying a
54 specific K(M)FC with high affinity for Rb.

55 The practical use of K(M)FC sorbent in fixed-bed sorption systems is challenged due to the
56 occurrence of fine-grained powder of microcrystalline natured K(M)FC sorbent resulting in clogging
57 of bed and decrease in filtration rates. One of the approaches to overcome this limitation is to
58 functionalise/immobilise K(M)FC sorbents on appropriate materials, such as carbon fibrous materials,
59 biosorbent polymers and biopolymers [8,10-12].

60 Furthermore, desorption of the sorbed Rb is important in determining the degree of recovery
61 of Rb from an encapsulated sorbent. It is worth highlighting that most of the available studies on
62 K(M)FC were focused on retaining radioactive Cs on the sorbent for solid disposal. Thus, desorption
63 was not an essential factor in those studies. Some studies have highlighted Cs and Rb desorption using
64 0.5 M (up to 3.0 M) KCl, NH₄Cl and HNO₃ [5,11,13]. Upon desorption, Rb would be found mixed
65 with other desorbed ions from K(M)FC and ions derived from the desorbing agent. Thus, subsequent
66 purification process from these unwanted ions is essential to obtain a high quality Rb.

67 The objectives of this study were to (i) identify a suitable K(M)FC metal combination (Co, Cu,
68 Fe and Ni) for Rb sorption, (ii) characterise and evaluate the performance of encapsulated K(M)FC-
69 PAN beads for Rb sorption under high salinity and in the presence of competing metal ions, (iii) test
70 the practical Rb sorption and desorption performances of K(M)FC-PAN in a fixed-bed column and the
71 sorbent's regeneration capacity for its reuse, and (iv) purify Rb from the desorbed solution.

72

73 **2 Material and methods**

74 **2.1 Materials**

75 **2.1.1 Solutions**

76 Solutions used for making the sorbents include potassium ferrocyanide trihydrate
77 ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), nickel nitrate hexahydrate
78 ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and ferric chloride hexahydrate
79 ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). Stock solutions of Rb, Cs, Li, K, Na and Ca were prepared by dissolving RbCl, CsCl,
80 LiCl, KCl, NaCl and CaCl_2 , respectively, in deionised (DI) water. The binder materials used for sorbent
81 encapsulation were polyacrylonitrile (PAN, MW = 150,000 g/mol), dimethyl sulfoxide (DMSO,
82 $(\text{CH}_3)_2\text{SO}$, 99.9%) and Tween80. All reagents were of analytical grade (Sigma Aldrich) and were used
83 without further purification.

84

85 **2.1.2. Sorbent preparation**

86 **2.1.2.1 Potassium metal hexacyanoferrate, K(M)FC**

87 K(M)FC sorbents were prepared by adding one volume of 0.5 M $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ to 1.5
88 volumes of excess transition metal (0.5 M Fe, Co, Cu, and Ni). This resulted in a metal/Fe molar ratio
89 of 1.5. Similar metal hexacyanoferrate combinations with metal/Fe molar ratios from 1.4 to 1.8 were
90 reported in previous studies [6-9]. Nitrate salts of metals were used for all the metal sorbent mixtures
91 except for Fe (as per the Prussian blue procedure, ferric chloride was used). The solutions were stirred,
92 followed by centrifuging, washing the residue with DI water based on the different metal combinations
93 of Fe [14]; Co [9], Cu [15]; and Ni [16].

94

95 **2.1.2.2. Particle form K(M)FC**

96 Each K(M)FC mixture was dried for 24 h based on the previous studies (Co-115 °C, Fe-90 °C,
97 Ni-70 °C, and Cu-55 °C) [9, 14-16]. The dried granules were ground to a particle size of 0.25 - 0.45
98 mm. This is referred to as particle form K(M)FC.

99

100 **2.1.2.3. Bead form K(M)FC (K(M)FC–PAN)**

101 K(M)FC-PAN was prepared with 70 wt% of sorbent loaded on PAN according to the procedure
102 of Moon et al. [17]. 20 g powdered K(M)FC and 0.8 g Tween80 were mixed with 100 mL DMSO.
103 After stirring the solution at 50 °C for 1 h, 8 g PAN was added to the mixed solution and stirred for
104 another 5 h to obtain a homogeneous solution. The mixture was made into spherical 2 mm diameter
105 beads by dropping it into a beaker of MQ water, using a syringe pump with needle. The K(M)FC–
106 PAN beads were washed three times with DI water and oven dried at 60 °C for 24 h. The steps involved
107 in the preparation of the K(M)FC–PAN beads are illustrated in **Fig. 1**.

108 **2.1.2.4 Resorcinol formaldehyde polycondensate resin (RF resin)**

109 RF resin was prepared by polycondensation of formaldehyde with resorcinol. A resorcinol:
110 formaldehyde:NaOH:H₂O mole ratio of 1:2.5:1.5:50 was used as per the procedure described by
111 Samanta et al. [18]. The mixture was oven dried at 100 °C for 24 h. The dried RF resin was ground
112 and sieved to 0.25 - 0.45 mm particle size. It was then converted to an acid form (H form) by using
113 HCl, followed by filtration and air drying of the residue.

114 2.2 Sorbent characterisation

115 2.2.1 Mineralisation analysis

116 Samples (0.05 g) of particle form K(M)FC as well as original and column regenerated
117 K(M)FC-PAN were decomposed in 1 mL of concentrated H₂SO₄ (98%) as per the procedure of Naidu
118 et al. [5]. Concentrations of K, Fe and transition metals in the aqueous samples were measured using
119 Agilent technologies 7700 inductively coupled plasma mass spectrometry (ICP–MS). The procedure
120 was repeated in triplicate. The average results are reported in this study. The deviation between the
121 replicated values was lower than 10%.

122

123 2.2.2 pH and zeta potential

124 The effect of pH on sorption at equilibrium condition was investigated by suspending 0.005 g
125 sorbent in a beaker containing 100 mL of 0.06 mmol Rb/L solution with initial solution pH set in the
126 range of pH 3 to 9. The beakers were agitated for 12 h in a flat shaker. The final pH at equilibrium was
127 recorded, which was reported as pH_{eq}.

128 To investigate the zeta potential of the particle form K(M)FC at equilibrium condition,
129 suspensions of 1 g/L particle form K(M)FC in 100 mL DI water (with initial solution pH set in the
130 range of pH 3 to 9), were agitated for 12 h in a flat shaker. The final pH_{eq} was recorded. The zeta
131 potential was measured by a Zetasizer nano instrument (Nano ZS Zen3600, Malvern, UK) using laser
132 doppler micro-electrophoresis technology that detected the dispersion of K(M)FC particles in solution
133 which was placed in a capillary cell with electrodes. Measurements were done in triplicate (with
134 differences between replicates being less than 5%). Results of the average value were reported.

135

136 **2.2.3 Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX)**
137 **analysis**

138 The surface and cross sectioned sorbent morphology and element contents before and after Rb
139 sorption were evaluated with scanning electron microscopy (SEM) coupled with energy dispersive X-
140 ray spectroscopy (EDX) operated at 15 kV (Zeiss Supra 55VP Field Emission) as in the procedure of
141 Naidu et al. [5].

142

143 **2.2.4 X-ray diffraction (XRD) analysis**

144 XRD patterns were recorded using a Siemens D5000 diffractometer operated with CuK α
145 radiation and a rotating sample stage. The samples (particle form K(M)FC, K(M)FC-PAN and column
146 regenerated K(M)FC-PAN) in powder form were scanned at room temperature in 2 Θ angular range of
147 10°–80°.

148

149 **2.3 Sorption experiments**

150 **2.3.1 Sorption isotherms**

151 Equilibrium sorption experiments were conducted in a set of glass flasks containing 100 mL
152 solutions of 0.06 mmol Rb/L and different doses of particle form K(M)FC sorbents as well as K(M)FC-
153 PAN ranging from 0.03 to 0.50 g/L. The pH value of the solutions was maintained at 7.0 \pm 0.5. The
154 suspensions were agitated for 24 h to reach the sorption equilibrium. The supernatant solution was
155 analysed for Rb and K using contrAA[®] 300 Analytikjena atomic absorbance spectrometry (AAS). The
156 experiments were duplicated (\pm 2% difference) and the average values were taken for data analysis.
157 The Rb sorption amount at equilibrium, q_e (mmol/g), was calculated using Eq. (1):

158

$$q_e = \frac{(C_0 - C_e) \cdot V}{M} \quad (1)$$

159 where, C_0 and C_e are the initial and equilibrium concentration of Rb in the bulk solution (mmol/L), V
160 is volume of solution (L) and M is mass of sorbent (g).

161 The sorption data were modelled according to Langmuir and Freundlich isotherms based on
162 the model equations presented in another study [5].

163

164 **2.3.2 Sorption kinetics**

165 Batch sorption kinetic test was conducted in a set of glass flasks containing 100 mL RbCl (0.06
166 mmol Rb/L) and sorbent dose 0.05 g/L. The pH value of the solutions was maintained at 7.0 ± 0.5 .
167 The suspensions were agitated in a flat shaker and samples were collected at different time intervals
168 up to 48 h and the Rb concentration was measured. The sorption data were analysed using pseudo-first
169 order (PFO) and pseudo-second order (PSO) kinetic models based on the equations presented in
170 another study [5].

171

172 **2.3.3 Influence of salinity and co-existing SWRO brine ions on Rb sorption**

173 The influence of salinity on K(M)FC-PAN selectivity towards Rb sorption was studied by
174 varying the salinity from 0.2 M to 3.0 M representing saline SWRO brine. Further, the influence of
175 dominant inorganic ions present in SWRO brine (K, Ca, Li and Cs) on K(M)FC-PAN selectivity
176 towards Rb sorption was evaluated individually and in a mixed solution representing simulated SWRO
177 brine. All experiments were conducted with an initial Rb concentration of 0.06 mmol/L and sorbent
178 dose of 0.2 g/L while the competitor ion concentrations were set at a range of concentration ratio
179 emulating SWRO brine [1,3] as listed in **Table 1**. The pH value of the solutions was maintained at 7.0
180 ± 0.5 .

181

182 2.3.4 Column experiments

183 2.3.4.1 K(M)FC-PAN

184 Dynamic sorption tests were performed in a fixed-bed column (1.1 cm internal diameter (ID)
185 and 50 cm length) packed with 5 g of K(M)FC-PAN. A feed solution containing 0.06 mmol Rb/L was
186 fed upwards into the column with a peristaltic pump at a flow rate of 157 mL/h (superficial velocity
187 of 2 m/h). The effluent at the column outlet was collected at regular time intervals and the
188 concentrations of Rb, K, Fe and other metals were measured using AAS analyser. The breakthrough
189 curve is usually expressed in terms of inlet Rb concentration (C_o), outlet Rb concentration (C_t) or
190 normalized concentration defined as the ratio of Rb outlet concentration to Rb inlet concentration
191 (C_t/C_o) as a function of time or **bed volume, BV** ($BV =$ flow velocity (m/h) x time (h) / bed height
192 (m)). The maximum column capacity, q_{total} (mmol Rb), for a given feed concentration and filtration
193 velocity Q (mL/min) is equal to the area under the plot of the sorbed Rb concentration, ($C_o - C_t$)
194 (mmol/L) versus effluent time (t , min) (Eq. (2)). It was calculated manually from the breakthrough
195 curves using Microsoft Excel spreadsheet.

196

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=total} (C_o - C_t) dt \quad (2)$$

197

198 Equilibrium uptake, q_e (mmol Rb/g), is defined by Eq. (3) as the total amount of adsorbed Rb (q_{total})
199 per g of sorbent (M) at the end of the experiment:

200

$$q_e = \frac{q_{total}}{M} \quad (3)$$

201

202 **2.4 Rb desorption and K(M)FC-PAN regeneration**

203 **2.4.1 Batch experiment**

204 Potassium chloride (KCl) was used to desorb Rb from K(M)FC-PAN, based on the positive
205 results obtained in our previous study [5]. To determine the suitable KCl concentration for the
206 regeneration of K(M)FC-PAN, desorption was carried out using different molar concentrations of KCl
207 from 0.1 M to 0.5 M after saturating Rb on K(M)FC-PAN by equilibrating 0.06 mmol Rb/L with 0.1
208 g/L of K(M)FC-PAN. The procedure of desorption was similar to that described previously [5].

209

210 **2.4.2 Column experiment**

211 In the column study, upon the complete breakthrough, K(M)FC-PAN was washed with DI
212 water followed by KCl (suitable concentration determined from the batch study) at an upward velocity
213 of 6 m/h. The Rb concentrations in the desorbed solution were measured periodically. Two cycles of
214 K(M)FC-PAN sorption followed by desorption were carried out to establish the sorbent's regeneration
215 capacity.

216

217 **2.5 Purification of Rb from desorbed KCl solution**

218 Resorcinol formaldehyde polycondensate resin (RF resin) was used for the purification of Rb
219 from desorbed K(M)FC-PAN column solution containing up to 0.2 M KCl [18,19]. For this purpose,
220 3 g RF in H⁺ form was loaded in a glass column (ID: 1.1 cm). The bed was conditioned by passing 50
221 mL of 1.0 M KOH solution to convert all the phenolic group (–OH⁺) to potassium phenoxide group
222 (O–K⁺). The desorbed solution containing Rb and KCl was passed upward through the RF column at
223 a low filtration velocity of 2 m/h. The progress of Rb loading was monitored by periodic measurement
224 of Rb in the effluent samples. Finally, purified Rb was eluted from the resin with 115 ml of 0.1 M HCl
225 followed by 230 ml of 1.0 M HCl at a flow rate of 5 m/h. Lower concentration of HCl was used in the

226 first elution to desorb mainly K and subsequently a higher concentration was used to desorb the
227 strongly sorbed Rb.

228

229 **3. Results and discussion**

230 **3.1 Evaluation of Rb sorption by particle form K(M)FC**

231 The performance of K(M)FC sorbent for selective Rb sorption capacity was evaluated. The
232 sorption study was carried out with an initial 0.06 mmol Rb/L for a viable analysis detection limit.
233 Correspondingly, higher molar ratios of competition ions (Ca, K, and Na) were used, emulating the
234 conditions of SWRO brines.

235

236 **3.1.1 Chemical composition**

237 The chemical stoichiometric composition of K(M)FC was deduced on the basis of one mole of
238 Fe complexed to six moles of cyanide ion (CN). The moles of metal, M per mole of K(M)FC was
239 calculated by normalising the amount of metal to the amount of Fe [20]. The number of moles of K
240 per K(M)FC mole was calculated by balancing the charges of cations and CN anion in K(M)FC
241 (electrical neutrality) (**Table 2**). Similarly, Loos-Neskovic et al. [21] represented K(M)FC with a
242 model structure of $K_{2x}M_{2-x}[Fe(CN)_6]$. A slight excess of K amount detected in the measured contents
243 compared to the calculated stoichiometric composition was related to the water soluble K in the
244 pores/channels of K(M)FC as observed in a previous paper [5].

245 The chemical compositions of the different K(M)FC combinations were relatively similar, with
246 Ni combination having the highest K content (**Table 2**). A number of K(M)FC studies on Cs sorption
247 relate the major part of the K content of the sorbent to its sorption capacity due to the exchange
248 between K and Cs [22]. This potentially suggests that Rb sorption capacity of the sorbent would be in
249 the order of $KNiFC > KCuFC > KCoFC > KFeFC$ if all the K in the structure are exchanged with Rb.

250 3.1.2 Surface potential

251 Surface potential of sorbent is an important contributing factor that correlates to the sorbent
252 uptake affinity for ions. An increased negative potential on the sorbent is expected to increase the
253 sorption capacity of positively charged ions such as Rb by electrostatic adsorption (outer sphere
254 complexation). The surface potential of K(M)FC was investigated with zeta potential analysis in the
255 pH range from 3 to 9 (Fig. 2). KCuFC displayed the highest negative surface potential (-30 to -32 mV)
256 at all equilibrium pH (pH_{eq}) values. Meanwhile for KCoFC and KNiFC, the highest range of negative
257 surface potential trend was observed around pH_{eq} 7 (KCoFC = -20 to -25 mV and KNiFC = -10 to -14
258 mV). The negative surface potential trends suggest that KCuFC with the highest negative surface
259 potential has the highest potential to electrostatically adsorb the positively charged Rb and KNiFC
260 with the lowest negative surface potential has the lowest potential to adsorb Rb. Unlike the other
261 sorbents, KFeFC showed positive surface potential suggesting that the electrostatic sorption of Rb
262 would be minimal on KFeFC. The positive surface potential of KFeFC could be due the presence of
263 higher positively charged Fe^{3+} in KFeFC structure which resulted from the use of $FeCl_3$ to produce
264 this sorbent.

266 3.1.3 XRD analysis

267 It is a well-established fact that sorption capacity and mechanisms depend on the crystal
268 structure of the sorbent. For this purpose, the X-ray diffraction peaks of the different K(M)FC were
269 analysed as shown in Fig. S1. The different metal K(M)FC's showed a similar general crystal
270 characteristic pattern with three major peaks at 2θ positions: 17-18, 24-25, and 35-36. These peak
271 patterns were consistent with other studies on potassium metal hexacyanoferrate that described the
272 crystal structure to be face-centred cubic [11, 14, 21].

273

274 3.1.4 Rb sorption isotherm

275 Rb sorption isotherm was carried out at pH_{eq} of 7.0 ± 0.5 with the different K(M)FC
276 combinations. The different K(M)FC isotherm data fitted well to both Langmuir and Freundlich
277 models ($R^2 = 0.89$ to 0.98) (**Fig. 3** and **Table 3**). Rb sorption capacity of the sorbents were in the order
278 of $\text{KCuFC} > \text{KNiFC} > \text{KCoFC} > \text{KFeFC}$. In line with the Rb sorption (mmol/g), a closely similar
279 amount of K was released (mmol/g), indicating a stoichiometric electrochemical balance in the
280 exchange process between Rb and K. The majority of K release occurred when Rb exchanged with K
281 inside the K(M)FC lattice according to $\text{K}_2[\text{MFe}(\text{CN})_6] + 2 \text{Rb}^+ \rightarrow \text{Rb}_2[\text{MFe}(\text{CN})_6] + 2 \text{K}^+$ [5].
282 Naturally, KCuFC with the highest K release, showed the highest Rb sorption. The results indicated
283 that the accessibility and availability of functional site and surface charge are essential factors in
284 determining K(M)FC capacity [8]. Hence the exchangeable structural K content as well as the high
285 negative surface charge inferred from the high negative surface potential (**Fig. 2**) could be the reason
286 for the higher Rb sorptivity of KCuFC (**Table 3**) compared to the predicted higher sorptivity of KNiFC
287 based on its higher total structural K content (**Table 2**). Naturally KFeFC with the lowest exchangeable
288 structural K content and having positive surface potential resulted in the lowest Rb sorptive capacity.
289 Although the results of this study exhibit that the different metals do play a role in influencing Rb
290 sorption capacity of K(M)FC, more in-depth evaluation need to be carried out to explicitly describe
291 the role of metals here. In line with the high sorptivity of KCuFC towards Rb, a few studies have
292 highlighted high Cs sorption capacity with KCuFC compared to other transition metals [8,23]. Based
293 on these results, further studies were conducted with K(M)FC containing Cu transition metal, KCuFC.

294 **3.2 Evaluation of Rb sorption with bead form KCuFC (KCuFC-PAN)**

295 To overcome the limitation of micro crystalline sorbent application in filter columns, KCuFC
296 was encapsulated with PAN polymer (**Fig. 1**), to obtain bead form KCuFC-PAN. In this section, the
297 characterisation and performance of bead form KCuFC-PAN for Rb extraction is presented.

298

299 **3.2.1 Surface characteristics of KCuFC-PAN (SEM-EDX)**

300 The surface and cross sectional SEM images showed the porous and rough morphology
301 appearance of KCuFC-PAN (**Fig. 4a**). After Rb sorption, no significant morphological changes were
302 observed (**Fig. 4b**). The EDX revealed the predominant presence of K, Fe, and Cu peaks, well
303 representing the elemental constituents of KCuFC (**Fig. 4c**) and the EDX element mapping (**Fig. 4a**
304 **& 4b**) established the homogenous distribution of the elements across the bead structure. Upon Rb
305 sorption, a peak of Rb was observed in the EDX spectra with a reduction of K peak intensity,
306 suggesting the sorption of Rb with the exchange of K (**Fig. 4c**). Consistent with this, the K/Fe atomic
307 ratio (0.9) of original KCuFC-PAN reduced to 0.5 with Rb sorption. Meanwhile, minimal difference
308 was observed for the Cu/Fe atomic ratio between the original and the Rb sorbed KCuFC-PAN,
309 suggesting that the Cu metal was not involved in the Rb sorption and exchange mechanism.

310

311 **3.2.2 XRD analysis of KCuFC-PAN**

312 The encapsulated KCuFC-PAN showed similar XRD peak pattern to particle form KCuFC,
313 indicating that both KCuFC-PAN and particle form KCuFC had the same crystal structure (**Fig. 5**)
314 This established that the encapsulation did not change the crystal structure. Similarly, Nilchi et al. [24]
315 observed matching XRD patterns for KCoFC in particle and encapsulated forms and concluded that
316 they had the same crystal structure. Du et al. [10] reported on the XRD pattern of KNiFC-PAN, which
317 showed similar peak patterns to KNiFC particle in **Fig. S1**, validating that the organic polymer
318 encapsulation did not change the crystal structure of the sorbent.

319 3.2.3 Influence of pH on KCuFC-PAN

320 Maximum Rb sorption capacity was achieved at the range of pH_{eq} 6 to 8 with KCuFC-PAN
321 (**Fig. 6**). One reason for the increase in sorption at this pH range compared to that at lower pH values
322 could be related to the increase in electrostatic sorption (outer sphere complexation) resulting from the
323 increased negative zeta potential (**Fig. 2**) as explained by Naidu et al. [5]. The other reason is that there
324 was competition for Rb sorption from the high concentration of protons (H^+) at low pH. The high
325 sorption capacity around pH 6-8 is an advantage in using KCuFC-PAN as a sorbent in removing Rb
326 from SWRO brine which generally is in this pH range. All further experiments were carried out at
327 $\text{pH}_{\text{eq}} 7.0 \pm 0.5$.

328

329 3.2.4 Equilibrium isotherm and kinetics of KCuFC-PAN

330 The Rb sorption with KCuFC-PAN fitted very well to Langmuir and Freundlich models ($R^2 =$
331 0.98 and 0.89, respectively) (**Fig. 7a**). KCuFC-PAN achieved a slightly lower Rb sorption (Langmuir
332 $Q_{\text{max}} = 1.23 \text{ mmol/g}$), compared to KCuFC particles (Langmuir $Q_{\text{max}} = 1.68 \text{ mmol/g}$) (**Table 3**) when
333 sorption is expressed per unit weight of the sorbent. The lower Rb sorption with KCuFC-PAN was
334 related to the 30% additional mass of the inert polymer encapsulation. Upon deduction of the polymer
335 mass, similar sorption capacity was obtained between the KCuFC particles and KCuFC-PAN.
336 Similarly, Moon et al. [17] attributed the lower Cs sorption capacity of PAN nickel potassium
337 hexacyanoferrate (1.945 mmol Cs/g) compared to powder form (2.36 mmol Cs/g) to the inert polymer
338 mass content.

339 Rb sorption capacity of KCuFC-PAN increased with time, achieving a maximum sorption within
340 15 h (900 min) (**Fig. 7b**). The data fitted well to the PFO model ($R^2 = 0.93$), however the model derived
341 $q_e = 1.38 \text{ mmol/g}$ differed from the experimental $q_e = 0.85 \text{ mmol/g}$. Meanwhile, the PSO model
342 achieved a data fitting with $R^2 = 0.97$ and $q_e = 0.86 \text{ mmol/g}$, matching very well to the experimental
343 value (**Fig. 7b**). Therefore the PSO is a better model for use in describing the kinetics of Rb sorption

344 by KCuFC-PAN. In correspondence with Rb sorption, K release was detected throughout the entire
345 duration of sorption confirming the Rb sorption mechanism of ion exchange of Rb with structural K.
346 In contrast, Cu and Fe releases were not detected, indicating the mechanical stability of bead form
347 KCuFC-PAN. Rb (1.48 Å) diffused into the pore/cavities of the beads containing KCuFC particles and
348 easily displaced K (1.33 Å) from the lattice due to their similar sizes (Table 4) as reported in previous
349 studies [5, 14, 25]. In addition to this mechanism of ion exchange inside the crystal structure, Rb would
350 have also sorbed on the negatively charged surface of KCuFC.

351

352 3.2.5 KCuFC-PAN performance in the presence of SWRO brine ions

353 KCuFC-PAN performed well as a sorbent for Rb in the presence of salinity (0.5 to 2.5 M NaCl)
354 with only a 12-30% reduction of Rb sorption (Fig. 8a). The percentage reduction increased with NaCl
355 concentration. Other studies have also shown similar trends [11,26]. The presence of Na did not
356 significantly affect the Rb sorption in spite of the relatively much higher Na concentration (10,000
357 times and more) than that of Rb. This was associated with the higher hydrated ionic radius of Na
358 making it less attractive to the sorbent surface [5] and the inability of Na to exchange with structural
359 K inside the KCuFC lattice as Rb does, which contributes to the selectivity of the sorbent for Rb (Table
360 4). Most importantly, these results demonstrated the suitability of KCuFC-PAN application for
361 selective Rb sorption in highly saline conditions such as SWRO brine.

362 The presence of other alkali metals, namely Li and Cs spiked at molar concentration
363 representing SWRO brine, minimally affected Rb sorption capacity of KCuFC-PAN (Fig. 8b). Only
364 2-3% reduction of Rb sorption (0.06 mmol/L) was observed in the presence of Li (molar Rb:Li = 1:
365 21). The minimal influence of Li could be related to its inability to exchange with structural K and
366 higher hydrated radius (Li = 3.40-4.70 Å) that makes the Li difficult to compete with Rb. Potentially,
367 a significant competition could occur between Rb and Cs due to its similar hydrated radius for surface
368 sorption and similar unhydrated radius for exchangeability with structural K [5] (Table 4). However,

369 at a significantly low concentration in the Rb:Cs molar ratio = 1:0.001 (as present in SWRO brine), Cs
370 would not affect the sorption of Rb in KCuFC-PAN.

371 Meanwhile, at a Rb:K molar ratio = 1:7700, a significant Rb sorption reduction of 65-70% was
372 observed (**Fig. 8b**). Similarly, other studies on Cs sorption have observed stronger competition of K
373 with Cs compared to Na. This was explained to be due to the similar hydrated radius which determines
374 surface sorption and similar unhydrated radius which controls the exchange within the crystal lattice
375 of K and Cs compared to Na and Cs [26].

376 Generally, Rb sorption was not significantly affected by the presence of Ca ions, despite Ca
377 ions having higher charge (divalent) than Rb (monovalent), due to the larger size of the hydrated Ca
378 (**Table 4**) as observed in a number of studies [12,27] and the inability of Ca to exchange with structural
379 K [5]. However at high Ca concentration, representing the Rb:Ca = 1:14,700 molarity in SWRO brine,
380 a 15-18% Rb sorption reduction was observed. This could be related to non-specific surface sorption
381 where the concentrations of ions determine the competition of ions for sorption [28].

382 In a simulated SWRO brine solution (containing dominant ions of SWRO brine), a 80-85% Rb
383 sorption capacity reduction was observed. Based on the individual solution competition results, the
384 significant sorption capacity reduction in the simulated SWRO brine could be attributed predominantly
385 to the presence of K and minimally to the other ions. These results reflect that the presence of K in
386 SWRO brine must be removed to ensure an efficient performance of KCuFC for Rb sorption.
387 Alternatively, further sorbent enhancement to increase the capacity of KCuFC-PAN could be carried
388 out. For instance, Lin et al. [29] showed substantially high Cs removal capacity in seawater containing
389 K using modified KCuFC with mesoporus silica.

390

391 **3.3 KCuFC-PAN fixed-bed column**

392 **3.3.1 Sorption capacity**

393 **Fig. 9** shows the breakthrough obtained using 5 g of KCuFC-PAN for the treatment of 0.06
394 mmol/L of Rb in a column at a flow rate of 2 m/h. The KCuFC-PAN breakthrough curve is
395 characterised by (a) a first step where Rb was completely sorbed, (b) a breakthrough upon approaching
396 4000 BVs (200 h), (c) a gradual increase of the outlet concentration in an S-shaped curve pattern, and
397 (d) a saturation plateau at about 13,400 BVs (636 h). A sorption capacity of 1.01 mmol/g was achieved
398 in the column at 100% breakthrough. A high BV (13,400 BVs) to achieve the column breakthrough
399 established the efficiency of KCuFC-PAN for Rb sorption.

400 The calculated sorption capacity in the column (1.01 mmol/g) was mostly similar to the batch
401 Langmuir sorption capacity ($Q_{\max} = 1.23$ mmol/g) establishing the suitability of KCuFC-PAN for
402 column operation. The sorption capacity could be further enhanced by reducing the flow rate as shown
403 by Du et al. [10] as well as by increasing the bed size [30].

404

405 **3.3.2 Rb desorption and regeneration of KCuFC-PAN**

406 **3.3.2.1 KCuFC-PAN batch desorption**

407 Different concentrations of KCl ranging from 0.1 M to 1.0 M were used to desorb Rb from
408 KCuFC-PAN (**Fig. 10**). A 70% desorption was achieved with 0.1 M KCl. From 0.2 M KCl onwards,
409 it was possible to achieve more than 90% desorption. Based on these results, 0.2 M KCl was selected
410 to desorb Rb from KCuFC-PAN in the column.

411

412 **3.3.2.2 KCuFC-PAN column desorption and regeneration**

413 Rb was eluted from the Rb-saturated KCuFC-PAN sorbent in the column using 0.2 M KCl at
414 a velocity of 6 m/h with 480 BV achieving a 95% recovery (**Table 5**). It is important to highlight that
415 KCuFC-PAN retained most of the sorbent material, as such the desorbed solution predominantly
416 contained Rb (1.20 mmol/L) and 0.2 M KCl with traces of Fe and Cu. These evidently highlights that

417 the encapsulation of KCuFC with PAN mitigated the issue of sorbent material losses. Comparatively,
418 our recent study using particle form KCoFC detected around 0.04 mmol/L of Fe and Co from the
419 column effluent with poor regenerative capacity [31]. On the other hand, KCuFC-PAN showed good
420 regeneration capacity. In the second cycle, a sorption capacity of 0.85 mmol/g was achieved with a
421 92% desorption (**Fig. 9** and **Table 5**). Though the sorption capacity decreased to 0.85 mmol/g in the
422 second cycle it was still much higher than that of many other sorbents such as several ion exchange
423 resins, zirconium phosphate and ammonium molybdophosphate [1,13].

424 The XRD analysis showed no structural changes to the regenerated KCuFC-PAN compared to
425 the original KCuFC-PAN (**Fig. 5**). At the same time, the chemical stoichiometry showed that the
426 regenerated KCuFC-PAN contained similar metal contents to the original KCuFC-PAN (**Table 6**)
427 supporting the detection of only traces of metal ions in the desorbed solution (**Table 5**). However,
428 evident reduction of K contents by 25% was observed in the regenerated KCuFC-PAN, indicating that
429 the reduction of K in the regenerated KCuFC-PAN contributed to the reduced Rb sorption capacity in
430 the second column cycle.

431 The column results are based on complete sorption/desorption up to $C_t/C_0 = 1$. In this context,
432 it is worth highlighting that the majority of sorption/desorption in the column occurred within $C_t/C_0 =$
433 0.4 to 0.5. As such, on a practical plant operation, the column could be terminated by $C_t/C_0 = 0.4$ to
434 0.5. Most importantly, the desorbed solution had approximately 20 times concentrated Rb compared
435 to the influent concentration.

436 Overall, the two cycles established the good performance capacity of KCuFC-PAN in a column
437 operation and indicated its fairly satisfactory regenerative capacity. Batch studies were conducted with
438 0.06 mmol Rb/L and KCuFC dose of 0.2 g/L for 5 cycles of sorption and desorption (0.2 M KCl), and
439 the sorption capacity was observed to decrease by up to 30% (**Table S1**). In view of the lower sorption
440 capacity in multiple cycles, a further KCuFC-PAN column study with multiple sorption/desorption

441 cycles must be carried out to establish the economic efficiency of KCuFC-PAN's regenerative capacity
442 for its reuse.

443

444 3.4 Rb purification using RF resin

445 The H⁺ form RF resin consists of phenolic hydroxide (OH) group as the functional group. The
446 phenol OH in the RF resin was converted to the ionised potassium phenoxide group (O—K⁺) under
447 alkaline condition using 1 M KOH. Rb uptake by RF resin in the presence of K is governed by
448 replacing K in the resin (R is the resorcinol formaldehyde polymer) as shown below [32]:

449



450

451 The batch study showed that the RF resin was able to achieve a Langmuir maximum Rb sorption
452 capacity of 0.23 mmol/g (**Fig. S2**).

453 The treatment of the desorbed solution (1.20 mmol/L Rb and 0.2 M KCl) was carried out using
454 the RF resin column. The RF resin reached saturation with Rb and achieved a Rb sorption capacity of
455 0.17 mmol/g at 83 BV (90 mins) (**Fig. 11a**). A sequential desorption was carried out at a flow rate of
456 5 m/h using 0.1 M HCl (115 ml) on the Rb saturated RF to firstly desorb the K from the resin followed
457 by further desorption with 1.0 M HCl (230 ml), to desorb Rb, the order of desorption being in
458 accordance with the higher sorption affinity of Rb than K [18,32]. A 97% Rb desorption was achieved
459 with a 68% recovery of the desorbed Rb in purified form from 60 to 100 BV (**Fig. 11b**).

460

461 4. Conclusions

462 The following conclusions were obtained from the study:

- 463 • KCuFC showed the highest Rb sorption (Langmuir maximum sorption, $Q_{\max} = 1.68$ mmol/g)
464 compared to other metal combinations (KNiFC, $Q_{\max} = 1.43$ mmol/g; KCoFC, $Q_{\max} = 1.19$

465 mmol/g; and KFeFC, $Q_{\max} = 0.61$ mmol/g), emerging as the most suitable sorbent among the
466 ones tested to extract Rb. Along with the Rb sorption, an equal number of mmoles of K were
467 released, indicating the stoichiometric exchange of Rb with lattice K in K(M)FC. The higher
468 affinity of KCuFC towards Rb sorption was attributed to the higher amounts of K exchanged
469 from the sorbent crystal lattice and its higher negative surface potential causing greater surface
470 sorption of Rb.

- 471 • KCuFC was successfully encapsulated with an organic polymer (PAN), producing KCuFC-
472 PAN beads (Langmuir Q_{\max} for Rb of 1.23 mmol/g KCuFC). Rb sorption capacity by KCuFC-
473 PAN reduced by only 12-30% under high salinity (0.5-2.5 M NaCl), establishing its suitability
474 for Rb extraction from saline conditions such as SWRO brine. However, the presence of K in
475 SWRO brine resulted in 65-70% reduction of Rb sorption, reflecting the need to further address
476 the challenge of efficiently extracting Rb from complex matrices such as SWRO brine
- 477 • In a fixed-bed column condition, KCuFC-PAN achieved a Rb sorption capacity of 1.01
478 mmol/g, (closely similar to the batch study) and 95% desorption of sorbed Rb with 0.2 M KCl.
479 The sorption capacity reduced only by 16% in the second cycle of Rb sorption/desorption,
480 establishing the suitability of KCuFC-PAN for column operation and its regenerative capacity
481 of KCuFC-PAN.
- 482 • Rb was selectively separated from K in the desorbed solution, using RF resin in a fixed-bed
483 column and a sequential HCl desorption, producing 68% of purified Rb.
- 484 • The approach of Rb sorption with KCuFC-PAN and purification with RF resin demonstrated
485 in this study provides useful information for its potential application in extracting Rb from
486 SWRO brine. Nevertheless, a number of factors must be still evaluated for a full practical
487 implementation of Rb sorption from SWRO brine. In light of this, technology integration such
488 as membrane distillation to increase the Rb concentration in SWRO brine prior to sorption

489 would be beneficial to increase the efficiency of Rb extraction by KCuFC-PAN in SWRO
490 brine.

491

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