

Rubidium recovery using potassium cobalt hexacyanoferrate sorbent

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Abstract

Rubidium is a highly valued and economically important metal present in large quantities in many natural and waste waters. However, its recovery is hampered by its low concentration and extracting agents' limited selectivity. A batch sorption study showed that a potassium cobalt hexacyanoferrate (KCoFC) sorbent had much higher sorption capacities for Rb and Cs than for Li, Na, and Ca. Equilibrium sorption data at pH 7 and $24 \pm 1^\circ\text{C}$ for Rb and Cs satisfactorily fitted to the Langmuir model with sorption maxima of 96 and 61 mg/g, respectively. A fixed-bed column (12 cm height) containing a mixture of 2.2 g KCoFC and 19.8 g granular activated carbon (GAC) had a breakthrough sorption capacity of 61 mg/g when a solution containing 5 mg Rb/L was passed through the column at a velocity of 2.5 m/h (0.7 L/h). When 1 and 5 mg Cs/L were added to the Rb solution, Rb sorption capacity dropped to 46 and 41 mg/g, respectively. During Rb sorption, K from the KCoFC lattice was released. Leaching the column containing sorbed Rb with 0.1 M KCl for 60 min at a velocity of 10 m/h, desorbed 99% of sorbed Rb. A process for recovering Rb from sea water reverse osmosis brine is presented.

1. Introduction

Rubidium (Rb) has been widely utilised in many industries such as the manufacture of solid-state lasers, phosphors, photoelectric cells, and components of electrolytes for fuel cells [1-3]. It is also used as an additive in the form of rubidium carbonate to produce some special glasses utilised in fibre optics, telecommunication systems and night-vision devices [4]. Moreover, it has important applications in pharmacy and medicine, especially soporifics and sedatives and the treatment of epilepsy [3,5-6]. Because of the numerous applications of Rb in science, technology, and medicine and its low extractability from natural systems and wastes, the demand for and price of Rb in recent decades have increased in the international market [7-10]. For example the price for 100 g of Rb rose from US\$998 in 2001 to US\$1283 in 2010 [2,9].

Generally, apart from existing in ore minerals, Rb is also found in salt lakes, sea water, geothermal water, and rejected brines from desalination plants and oil fields. It usually coexists with other metals such as cesium (Cs), lithium (Li), calcium (Ca), sodium (Na), magnesium (Mg) and potassium (K) in widely distributed liquid resources. Extraction of Rb is much more difficult than other alkali metals due to its low concentration, although Rb is more abundant than Cs (Table 1). Despite the concentration of Rb being small compared to other metals, it still has an economic value higher than that of other metals. Of the metals found in the sea water reverse osmosis concentrate (SWROC), only the price of Cs is higher than that of Rb (Table 1). However, the concentration of Cs is 250 times smaller than that of Rb, which makes the potential benefit of extracting Rb 177 times greater than that of Cs.

Table 1

List of valuable elements economically extractable from sea water reverse osmosis concentrate

(brine) (adapted from Petersková et al. [11]).

	Na	Mg	Li	Rb	Cs	U
Concentration in brine (mg/L)	27,520	2450	0.27	0.19	0.0008	0.0039
Price (\$/kg)	0.10	2.21	1.37	8802	12078	78.73

Due to the low concentration, limited selectivity of extracting agents and complexity of brines, it is difficult to extract Rb from solutions. The methods currently available for extracting Rb include sorption, evaporation, precipitation, use of emulsion membranes and liquid–liquid extraction techniques [12,13]. Of these applications, ion exchange and sorption are the most widely used [14,15]. One of the main problems encountered in most studies on the sorption of Rb is that they mostly focused on its sorption from solutions containing only Rb. They did not consider solutions containing a mixture of metals where there may be competition between metals for sorption [14,15]. To remove alkali metals from solution, different types of sorbents such as clay materials [16], Prussian blue [17], potassium metal hexacyanoferrate [11,18], zeolite [19], titanium dioxide [20], and ammonium molybdophosphate [21] had been used. All of these sorbents revealed a high capacity to remove Cs from nuclear waste brine with varying degrees of success. Very few studies have been reported on these sorbents for the extraction of Rb [11,15,22]. Previous studies have shown that potassium metal hexacyanoferrate had high sorption capacity for Rb compared to other sorbents. Most of these studies were conducted using high concentrations of Rb (20 to > 500 mg/L) in batch experiments and only a few had been reported in fixed-bed systems [22]. Consequently the results of these studies with high concentrations would not be relevant for extracting Rb when present in relatively low concentration in natural resources such as SWROC (e.g. 0.19 mg/L, Table 1).

Generally, batch experiments conducted on Rb sorption do not provide information about the hydrodynamic parameters of fixed-bed columns such as the dispersion coefficient [23].

Another drawback is their discontinuity and the need to perform complicated phase separation operations. Fixed-bed column experiments, on the other hand, do not have the above drawbacks, and the results of such experiments can be directly applied to: firstly, obtaining reliable solutions to design optimisation; and secondly, predicting the breakthrough curves of fixed bed columns in real-life scenarios. Desorption of the sorbed Rb and recovering it as Rb salts is easier when sorption experiments are conducted in column mode. Despite the numerous advantages of column mode sorption experiments, a major problem encountered is that using finely divided materials such as potassium metal hexacyanoferrate can cause the columns to clog. This can lead to pressure head loss. However, this problem can be overcome by either encapsulating the material on a coarser material [24,25] or physically mixing it with a coarser material such as granular activated carbon (GAC) [26].

The long-term broad objective of this research was to recover the valuable Rb from SWROC. Before doing this, however, the focus was on recovering Rb from synthetic water having an elevated concentration of Rb. The specific objectives of this study were to: (i) synthesise potassium cobalt hexacyanoferrate (KCoFC) in the laboratory and characterise it; (ii) study the sorption of Rb in batch and fixed-bed column systems; (iii) determine the effect of co-existing alkali metals ions on Rb sorption; and (iv) assess the desorption of the sorbed Rb for its recovery.

2. Material and methods

2.1. Preparation of KCoFC

KCoFC was produced in the laboratory by mixing one volume of 0.5 M potassium ferrocyanide trihydrate ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) and 2.4 volumes of 0.3 M cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) [27]. After mixing the suspension for 1 h at room temperature, it was centrifuged and the precipitate was washed with deionised water. The precipitate was then dried at 115°C for 24 h and the dried material was ground to a particle size of 0.25 - 0.45 mm, then washed again with deionised water and dried.

2.2. Feed solutions and chemical analysis

The feed solution consisted of distilled water spiked with metals to produce solutions of predetermined concentrations. Rb, Cs, Li, Ca and Na were added in the form of Analar grade (Sigma-Alrich) RbCl, CsCl, LiCl, CaCl_2 and NaCl, respectively. Rb, Cs, K, Li, Na, Ca, iron (Fe) and cobalt (Co) concentrations were determined using Microwave Plasma - Atomic Emission Spectroscopy (MP-AES) (Agilent 4100).

2.3. Sorbent characterisation

The chemical composition of KCoFC was determined by heating 0.05 g of the material in 1 mL of 98% H_2SO_4 at 200°C for 5 h according to the procedure used by Nilchi et al. [28]. This was followed by adding 10 mL of 0.1 M H_2SO_4 to the residue and diluting the suspension to 50 mL with deionised water. The concentrations of K, Fe and Co in the solution were measured after filtration through a 1.2 μm syringe membrane filter. The X-ray diffraction (XRD) data of KCoFC powder was obtained on a Siemens D5000 X-ray diffractometer operated with CuK α radiation and a rotating sample stage; scanning was done at room temperature in the 2θ angular range of 20 - 110°. The BET surface area and porosity were measured using a nano-porosity (Mirae SI, South Korea) adsorption analyzer at 77°K.

The pH of 100 mL suspensions containing 1 g/L KCoFC sorbent was adjusted to different values (3.0 – 10.0) using 0.1 M HCl and 0.1 M NaOH. pH measurements were made using a HQ40d portable pH meter. The suspensions were then agitated for 24 h in a flat shaker at a shaking speed of 120 rpm at room temperature ($24 \pm 1^\circ\text{C}$) to investigate the effect of pH on zeta potential. Zeta potential was measured on a portion of the suspensions using a Zetasizer nano instrument (Nano ZS Zen3600, Malvern, UK) after measuring the pH. Measurements were done in duplicate to minimise undesirable biases (with differences between duplicates always being less than 5%).

2.4. Batch sorption **experiments**

The effect of pH on Rb sorption was determined by shaking 100 mL solutions containing Rb at 5 mg/L and 0.5 g/L sorbent at different pHs at room temperature ($24 \pm 1^\circ\text{C}$) similar to the experiment conducted for measuring zeta potential. The amount of metal sorbed at equilibrium, q_e (mg/g), was calculated using Eq. (1):

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

where C_0 = initial concentration of metal (mg/L); C_e = equilibrium concentration of metal (mg/L); V = volume of the solution (L); and M = mass of KCoFC (g).

Equilibrium metals sorption experiments were conducted in a set of glass flasks containing 100 mL solutions spiked with Rb, Cs, Na, Li and Ca (5 mg/L) and KCoFC doses of 0.03 – 1.0 g/L at room temperature ($24 \pm 1^\circ\text{C}$) and pH 7.0. The suspensions were agitated in a flat shaker at a speed of 120 rpm for 6 h, pH adjusted back to 7.0 and agitation continued for 24 h to ensure that the sorption equilibrium was reached. The percentage of metal sorbed was calculated by dividing the difference between initial and final metal concentrations by the initial metal concentration and multiplying it by 100. **In this study the sorption of all metals was**

investigated using the same initial metal concentration so that their relative sorption capacities could be compared. Our future studies will test the metals' sorption capacities individually and when present in combinations at the concentrations present in SWROC (Table 1)

The experimental results were treated with the Langmuir isotherm model using Eq. (2):

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (2)$$

All the experiments were duplicated and average values were recorded. The difference between duplicate values was within $\pm 2\%$.

2.5. Column sorption experiments

The fixed-bed column used for the experiments consisted of a Pyrex glass tube where a stainless steel sieve was attached to the bottom followed by a layer of glass beads in order to provide a uniform flow of the solution through the column. A known quantity of GAC (19.8 g) + KCoFC (2.2 g) was packed in the column to yield the desired bed height, i.e. 12 cm (KCoFC content in the column was 10% of the total column mass). GAC was employed to provide physical stability and good hydraulic conductivity to the columns. Since the batch experiment showed that, of the metals tested, KCoFC had high sorption capacity only for Rb and Cs, the column experiments were conducted to determine the competitive effect of only Cs on removing Rb. Therefore, the influent solutions had Rb only at 5 mg/L, Rb at 5 mg/L + Cs at 1 mg/L, and Rb at 5 mg/L + Cs at 5 mg/L. Initial trials showed that GAC alone as a medium had negligible Rb adsorption capacity (data reported in Results and Discussion section). Therefore the column's adsorption capacity was assumed to be due to only KCoFC. The metals solutions were pumped through the column at a desired flow velocity (2.5 m/h) which was controlled by a peristaltic pump. Effluents at the column's outlet were collected at regular time intervals and

the Rb concentration was measured. The breakthrough curves exhibited the loading behaviour of Rb to be removed from the solution in a fixed-bed column. These curves are usually expressed in terms of adsorbed Rb concentration (C_{ad}), inlet Rb concentration (C_o), outlet Rb concentration (C_t) or normalised concentration defined as the ratio of outlet Rb concentration to inlet Rb concentration (C_t/C_o) as a function of number of bed volumes (**one bed volume = flow velocity (m/h) * time (h) / bed height (m)**). The maximum column capacity, q_{total} (mg Rb), for a given feed concentration and filtration velocity is equal to the area under the plot of the adsorbed Rb concentration, C_{ad} ($C_{ad} = C_o - C_t$) (mg/L) versus bed volume. Furthermore it was calculated manually from the breakthrough curves using a Microsoft Excel spreadsheet according to Eq. (3) where Q is the flow rate of the solution (L/min):

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=total} C_{ad} dt \quad (3)$$

2.6. Desorption of Rb

A previous batch desorption study showed that of the following reagents - 0.1 M of HNO_3 , KOH, KCl, NaCl, HCl, and NaOH - 0.1 M KCl was the most efficient in desorbing Rb [15]. Therefore this reagent was used in the column desorption study. Initially, Rb was saturated on the KCoFC column containing 10% KCoFC (2.2 g) and 90% GAC (19.8 g) by passing a Rb solution of 5 mg/L through the column at a velocity of 2.5 m/h until complete breakthrough of Rb occurred. Then the column was washed with 1600 mL distilled water at a flow velocity of 2.5 m/h to remove Rb in the column pores followed by leaching with 0.1 M KCl at a velocity 10 m/h for 60 min. The desorbed solutions collected at 13 - 83 bed volumes (10 – 60 min) were analysed for Rb to determine the amount of Rb desorbed.

3. Results and discussion

3.1. KCoFC characterisation

3.1.1 Chemical decomposition analysis

Chemical analysis of the acid decomposed KCoFC showed that the K, Fe and Co contents of KCoFC were 8.4%, 7.1% and 10.13%, respectively. These values are equivalent to 2.14, 1.27, and 1.72 mmol/g of K, Fe, and Co, respectively. The empirical chemical composition of KCoFC was calculated by taking the amount of Fe as one and normalising the amount of Co to this value (mmol Co/mmol Fe). Furthermore the amount of K was calculated by balancing the total number of positive charges in Fe, Co, and K to the six negative charges in the CN group as described by Mimura et al. [29]. The calculation resulted in an empirical chemical composition of $K_{1.30}Co_{1.35}Fe(CN)_6$ which is similar to that of: firstly, the composition $K_{1.34}Co_{1.33}Fe(CN)_6$ reported for a KCoFC by Kameník and Šebesta [30]; and secondly, a KNiFC ($K_{1.45}Ni_{1.27}Fe(CN)_6$) documented by Mimura et al. [29]. The surface area of KCoFC was $55.4 \text{ m}^2/\text{g}$ with a total pore volume of $0.26 \text{ cm}^3/\text{g}$ while the average pore diameter was 18.8 nm. The average pore diameter of 18.8 nm for the KCoFC indicates that the material is mesoporous (2 – 50 nm).

3.1.2. Powder X-ray diffraction (XRD) analysis

The XRD pattern of KCoFC confirmed its crystal structure and the main peaks appeared at the same 2θ angle, which confirms findings in previous studies for this sorbent synthesised by others and a standard KCoFC (Fig. 1) [18,31]. The sharp peaks detected in the XRD analysis of KCoFC were at $2\theta = 17.7, 25.2, 36.1, 40.6, 43.9, \text{ and } 51.2$.

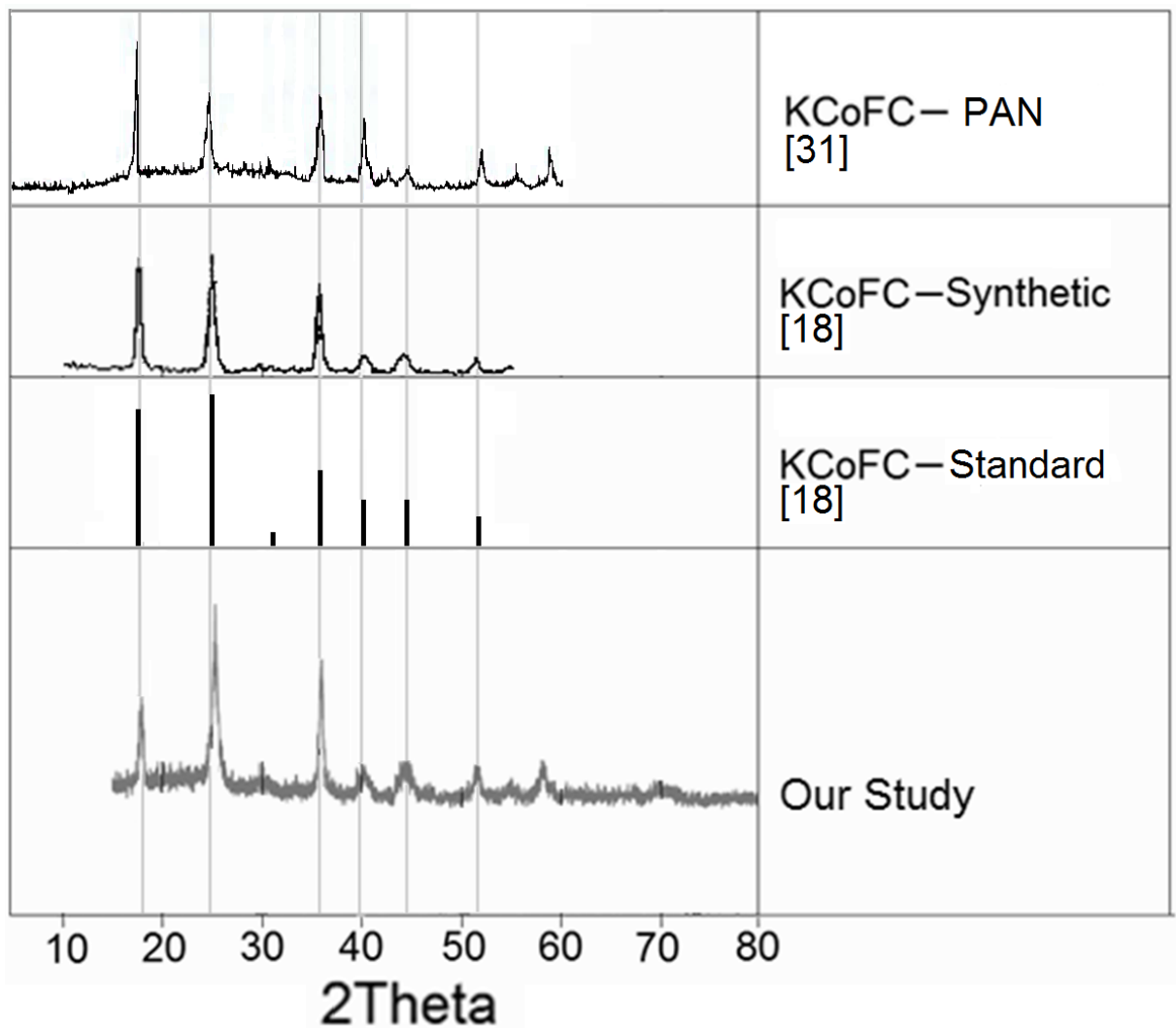


Fig. 1. XRD pattern of KCoFC compared with that of others

3.2. Batch sorption experiments

3.2.1. Effect of pH on zeta potential and Rb sorption

Zeta potential of KCoFC decreased from -1 to -15 mV as the pH increased from 3 to 10 (Fig. 2). This indicates that the number of negative charges on the surface of the sorbent increased with pH. Consistent with the increase in negative charges, Rb sorption also increased (Fig. 2) as a result of electrostatic adsorption of positively charged Rb on the negatively charged surface sites. However, at pH 3 when the zeta potential was very low (≈ -1.7 mV), Rb sorption

did not decrease in proportion to the fall in negative zeta potential. This may be due to Rb sorption arising from exchange with structural K in the KCoFC lattice [15].

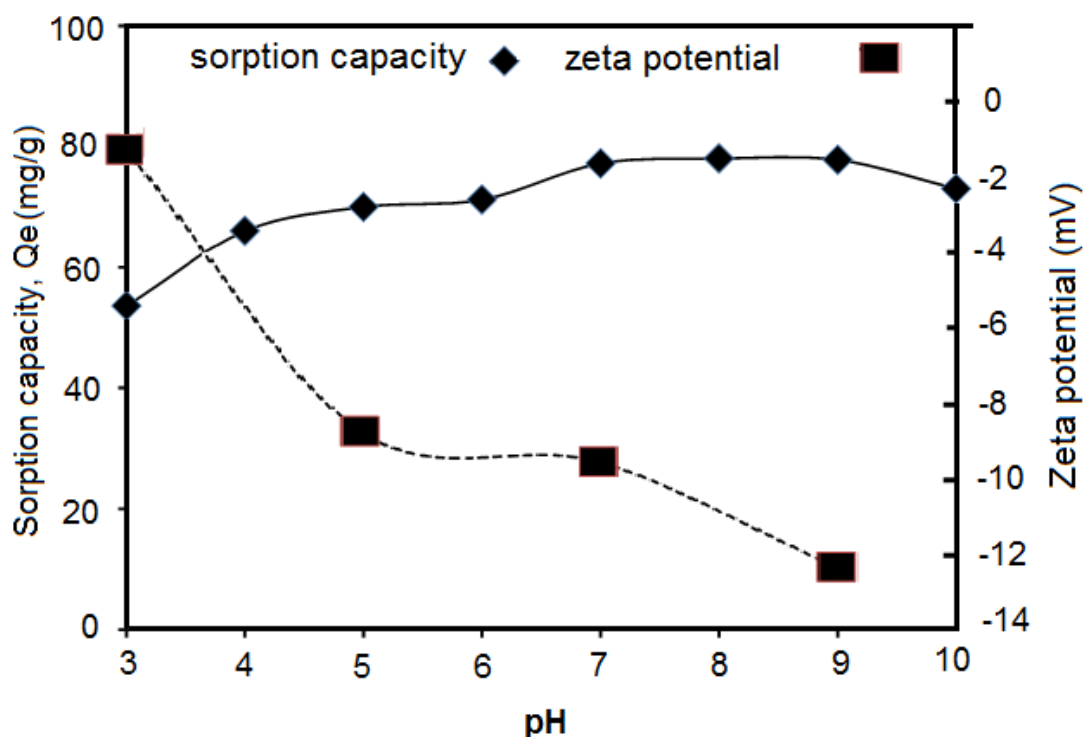


Fig. 2. Effect of pH on Rb sorption and zeta potential of KCoFC (KCoFC dose 1 g/L and initial Rb concentration 5 mg/L)

3.2.2. Sorptive removal efficiencies for Rb, Cs, Li, Na, and Ca

The KCoFC sorbent demonstrated greater efficiency in removing Rb and Cs than Li, Na and Ca at different dosages which ranged from 0.1 – 1.0 g/L for an initial concentration of all metals of 5 mg/L from a solution volume of 100 mL (Fig. 3). The maximum removal efficiency was 98-99% for Rb and Cs at the sorbent dose of 1 g/L, whereas for the other metals it was 2-19% with Na^+ having higher sorption capacity than Li^+ and Ca^{2+} in accordance with their hydrated ionic radius (Na^+ 2.76-3.60 Å, Li^+ and Ca^{2+} 3.40-6.00 Å) [15]. The explanation for Rb and Cs having higher sorption capacities than Li, Na, and Ca is that Rb and Cs could penetrate

the KCoFC crystal lattice and exchange with structural K in the body centre of the lattice due to their similar unhydrated ionic radii (Rb 1.48 Å, Cs 1.61 Å) as the cavities within the lattice (1.47 Å) [15]. Conversely, Na, Li, and Ca with much lower unhydrated radii (0.60-0.99 Å) were not able to exchange with the structural K in the lattice. The sorption data for Rb and Cs fitted satisfactorily to the Langmuir model ($R^2 = 0.94$ to 0.97) with the sorption capacity of 96 and 61 mg/g, respectively (Fig. 4). This matched the results reported by Petersková et al. [11] for Rb and Cs sorption on potassium hexacyanoferrate sorbent.

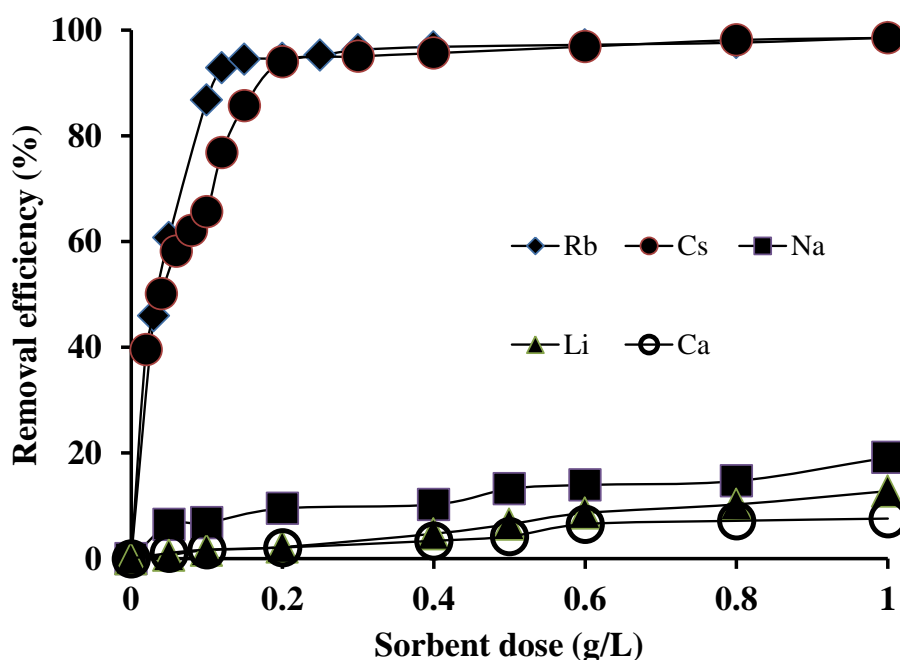


Fig. 3. Effect of KCoFC dose on the removal of Rb, Cs, Li, Na, and Ca (initial concentration for all metals was 5 mg/L).

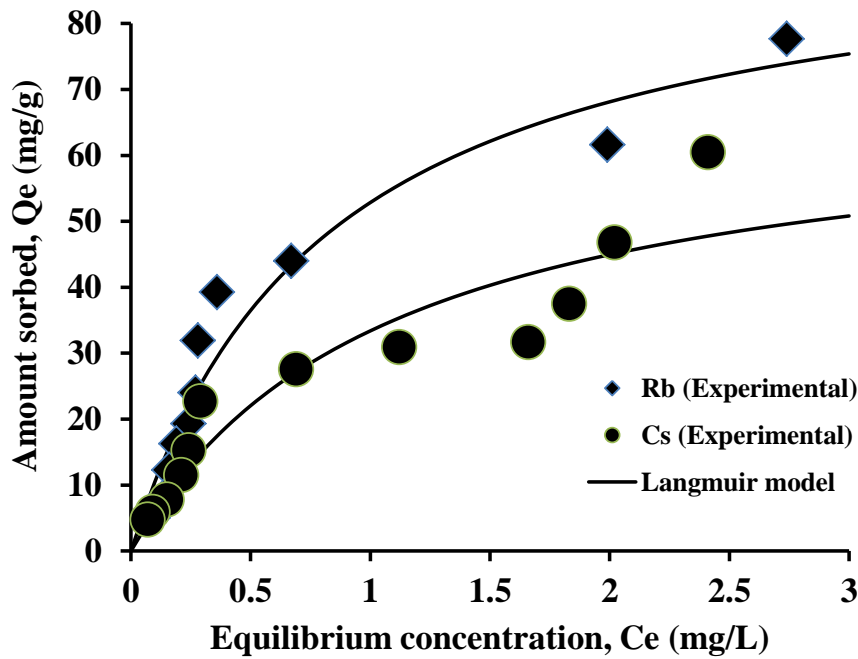


Fig. 4. Langmuir isotherm model (Equation 2) fit to sorption of Rb and Cs on KCoFC. The Langmuir parameters values obtained for the Rb and Cs plots were: $K_L = 1.23$ and 1.00 ; $q_{max} = 96$ and 61 mg/g; Coefficient of determination $R^2 = 0.97$ and 0.94 , respectively.

3.3. Fixed-bed column experiments

3.3.1. Breakthrough curves

Since the batch study showed that KCoFC had the highest sorption capacity for Rb and Cs, these two metals were chosen for the study using fixed-bed columns. Our hypothesis that GAC has very little sorption capacity for Rb is confirmed in the fixed-bed column experiment. A complete breakthrough of Rb did occur when the experiment began in the GAC only column (Fig. 5). Removal of Rb from aqueous solutions containing 5 mg Rb/L by KCoFC + GAC column at three initial C_s concentrations (0, 1 and 5 mg/L) was studied. In the case of Rb alone in the influent solution the breakthrough curves indicated that there was very little breakthrough of Rb during the first 50 bed volumes and then the concentration of Rb in the effluent increased progressively to reach the concentration of the influent (Fig. 5). The rapid breakthrough of Rb

was probably due to: firstly, the small amount of KCoFC in the column (only 2.2 g, 10% of total sorbent mass); and secondly, the low rate of diffusion of Rb into the KCoFC lattice for exchange with lattice K. When Cs was added to Rb in the influent solution the breakthrough of Rb was even faster due to Cs competing with Rb for sorption.

The results showed that the number of bed volumes required to reach the plateau of C_t/C_0 (equal to 0.98) was significantly higher (1875) when the solution contained only Rb than when Cs was present. Furthermore the curve was less steep in the absence of Cs. The sorption capacity of KCoFC from the breakthrough curve of Rb alone was 61 mg/g, which was among the highest values reported for most adsorbents in the literature for Rb [11,22,32]. However, the adsorption capacity fell to 47 and 42 mg/g in the presence of Cs at 1 and 5 mg/L, respectively. These results indicate that Cs had a competitive effect on Rb sorption. Nonetheless in many situations such as in SWROC, the Cs concentration (0.0008 mg/L) is much smaller than that of Rb concentration (0.19 mg/L) (Table 1) and therefore Cs is not expected to affect KCoFC's sorption of Rb.

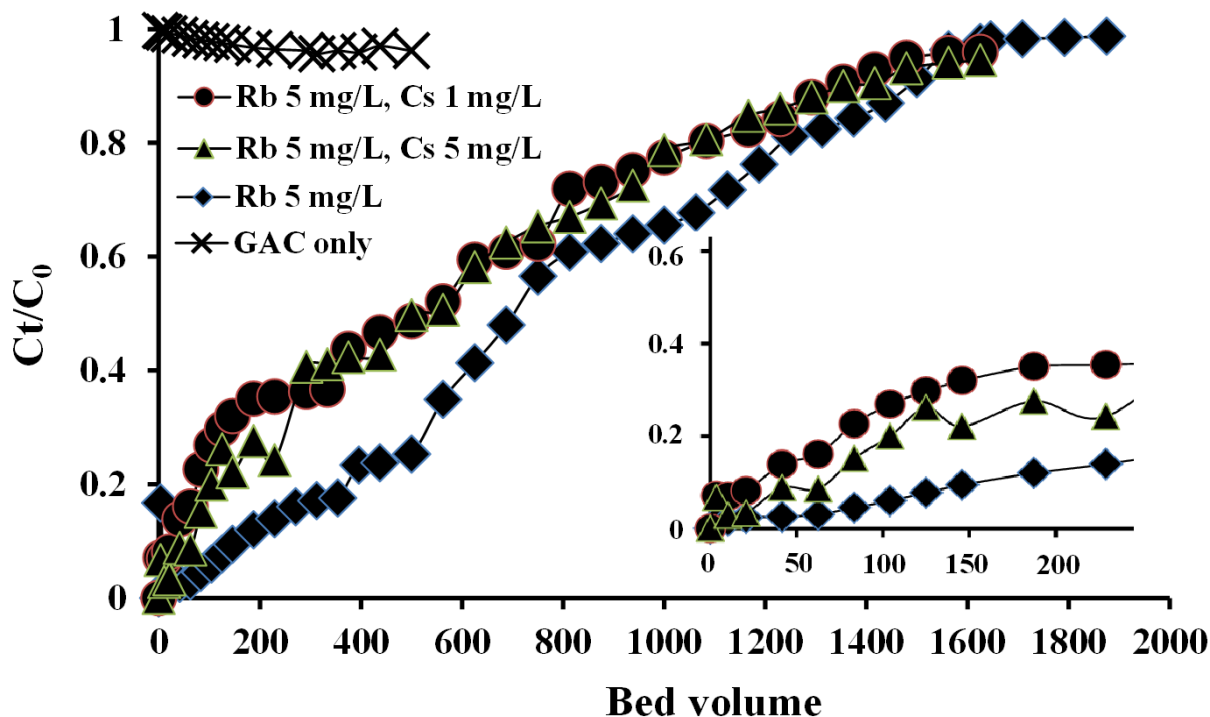


Fig. 5. Breakthrough curves for Rb sorption (filtration velocity 2.5 m/h, bed height 12 cm). The small graph within the large graph is an expanded version of the breakthrough curves up to 250 bed volumes.

Corresponding with the sorption of Rb, K release was detected over the sorption's entire duration (Fig. 6) due to Rb replacing K from inside the lattice of KCoFC as described in Equation (4). Naidu et al. [15] reported a ratio of 1:1 of moles of Rb sorbed to K release in a batch sorption experiment in accordance with Equation (4):



In the current column study, however, the number of moles of K released at any time was equivalent to almost the same number of moles of Rb sorbed at the first half of the breakthrough curve but less than the number of moles of K released/mole Rb sorbed for the rest of the curve.

The lower ratio of K release to Rb sorption in the latter part of the curve is probably due to the exhaustion of all the readily exchangeable K in the KCoFC structure at easily accessible larger pores of the KCoFC lattice. This allowed Rb to sorb mainly on the negatively charged surface sites of the sorbent. The more tightly held structural K was not able to be released unlike in the case of batch mode of sorption [15] because of less turbulent interaction between sorbent particles and solution in the columns. The inability of Rb exchanging with the tightly held lattice K in column study led to the lower Rb sorption capacity in the column study (61 mg/g) compared to the batch study (96 mg/g) where the turbulent action as well as the residence time of sorbed Rb were higher. Consistent with these results the cumulative Rb sorption was 0.71 mmol/g compared to cumulative K release of 0.52 mmol/g (Fig. 6b).

In contrast to K, very little Co and Fe were released during Rb sorption which indicated that Rb was not exchanging much with Co and Fe in the crystal lattice (Fig. 6). The reason for this is that Co and Fe were transitional metal cations bridged through cyano (CN) groups in the lattice structure which could not be easily exchanged with the alkali metal Rb [33].

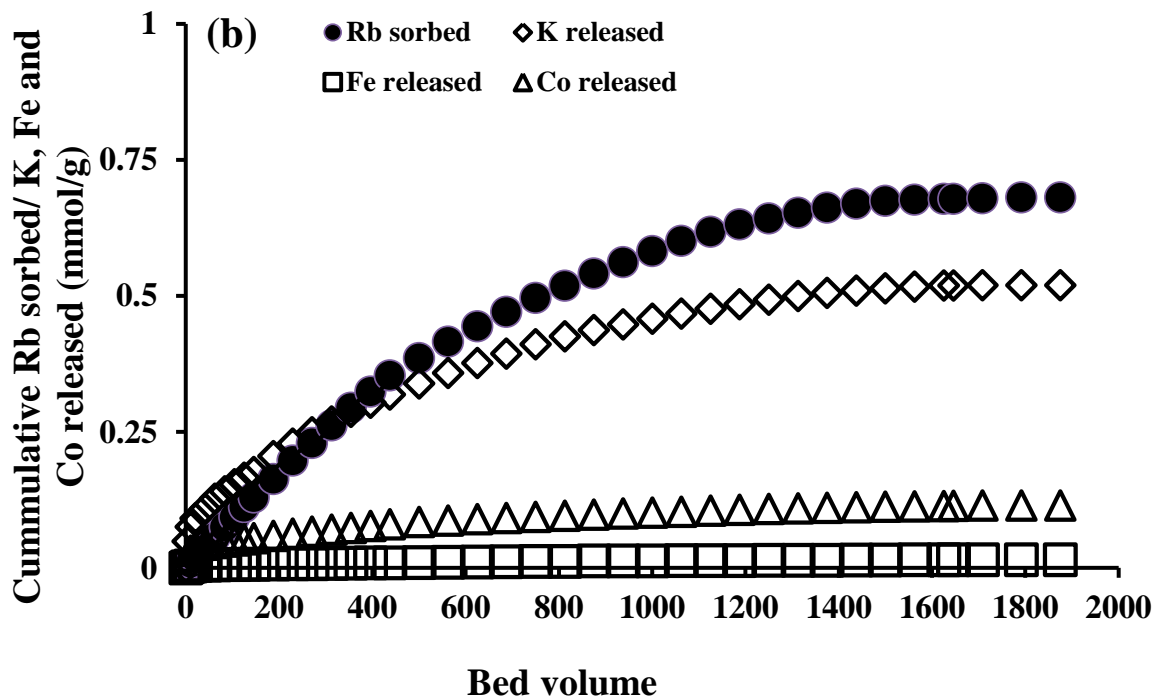
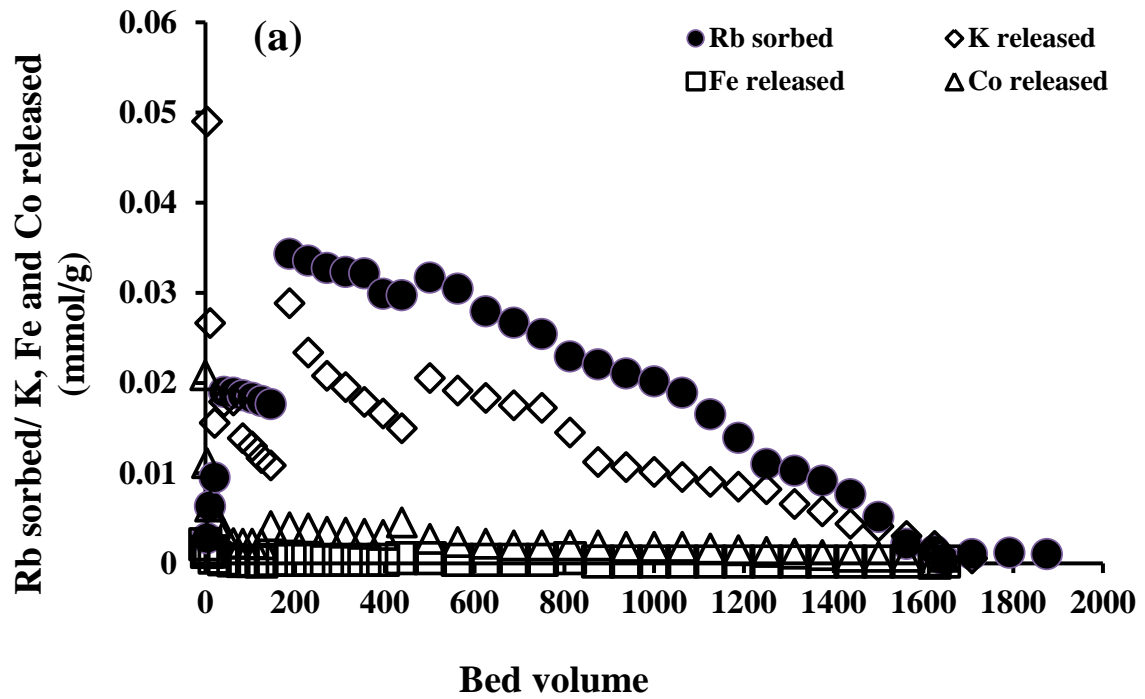


Fig. 6. (a) Individual and (b) cumulative Rb sorbed and K, Fe, Co released as a function of time in the column experiment (feed Rb concentration 5 mg/L, filtration velocity 2.5 m/h and bed height 12 cm).

3.3.2. Rb desorption capacity

Desorption of Rb by 0.1 M KCl indicated that approximately 70% of Rb was desorbed within 28 bed volumes (20 min) and by 83 bed volumes (60 min), 99% was desorbed (Fig. 7). Desorption was more efficient in the column study than in the batch study where only 74% of the sorbed Rb was desorbed when KCoFC was agitated with 50 mL of 0.1 M KCl for 30 min. The higher desorption efficiency in the column mode experiment was due to the continuous removal of desorbed Rb from the column, unlike in the batch mode experiment where the desorbed Rb remained in contact with the sorbent throughout the process [23].

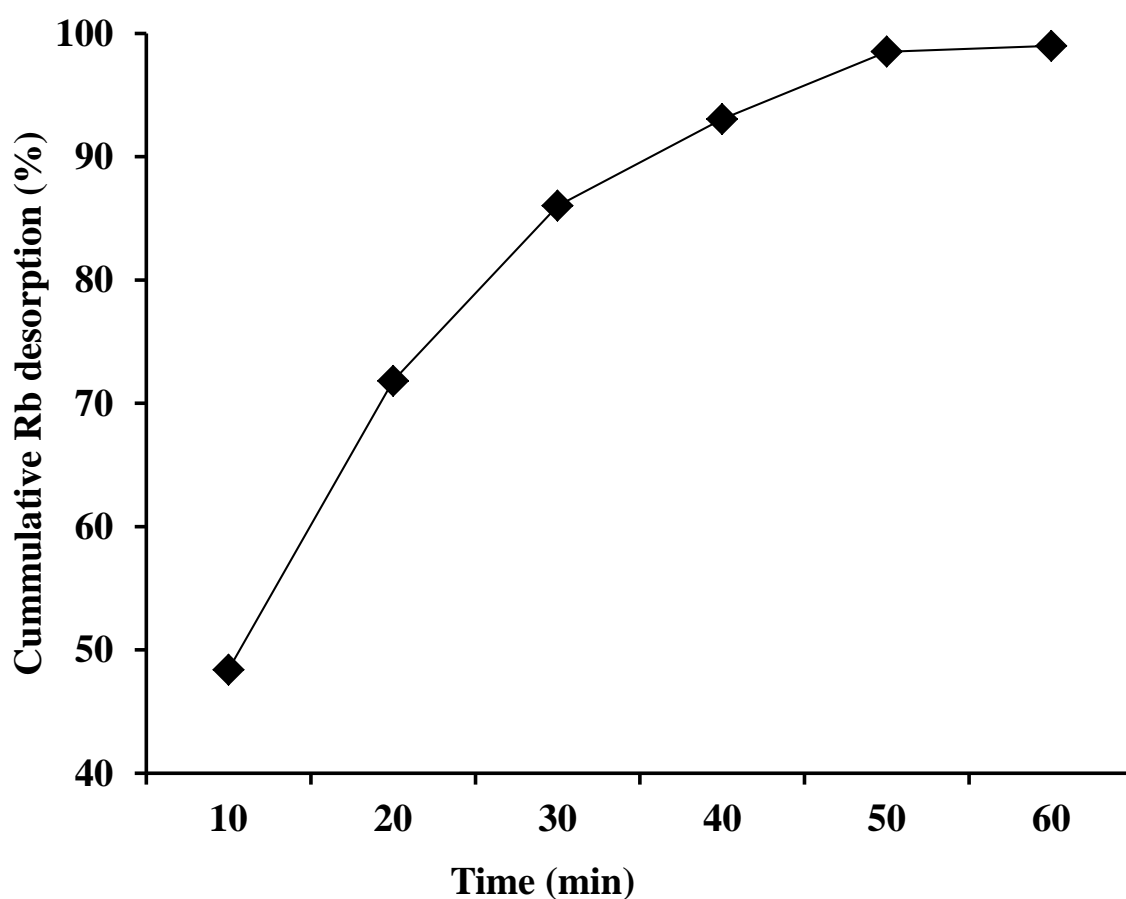


Fig. 7. Cumulative Rb desorption by 0.1 M KCl leaching with bed volumes.

3.3.3. Practical application of the study

A further increase of Rb concentration in SWROC will improve the efficiency in removing Rb. The concentration of metals in SWROC can be increased by employing membrane distillation [34]. Our preliminary experiments have shown that the concentration of Rb in SWROC from Perth, Western Australia increased from 0.19 mg/L to 0.79 mg/L by membrane distillation. Fig. 8 presents a possible procedure for the sustainable recovery of Rb from SWROC. As an example, a desalination plant of 100,000 m³/d capacity can potentially produce 5.9 kg of recoverable Rb/day. The recovery of Rb offset the energy cost of reverse osmosis (RO) and membrane distillation while producing additional clean water and contributing to a brine management solution.

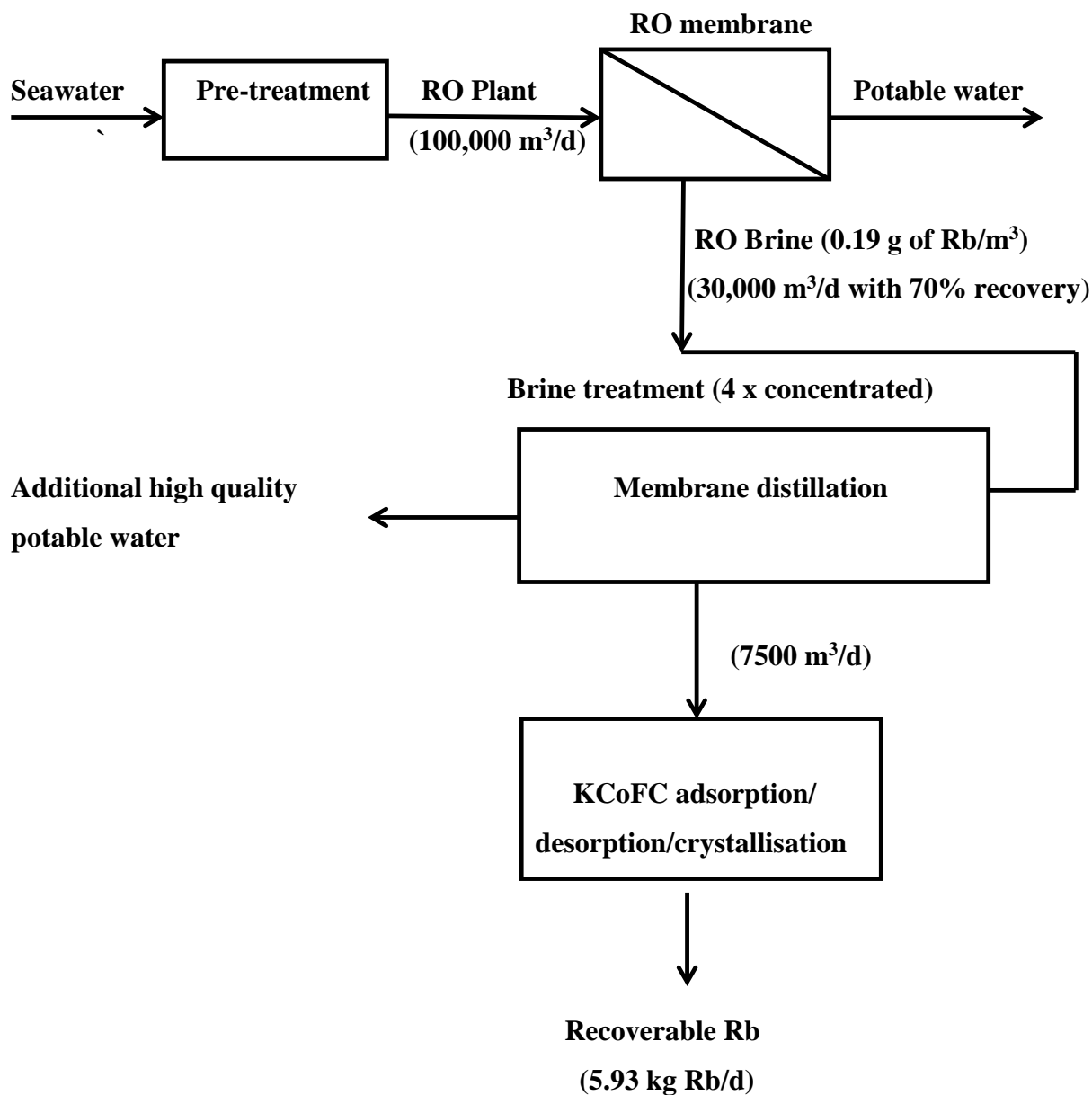


Fig. 8. Possible procedure for Rb recovery from SWROC

4. Conclusions

Batch experimental results at room temperature and pH 7 demonstrated that a laboratory prepared KCoFC had much higher sorption capacity for Rb and Cs than for Li, Na, and Ca. Langmuir sorption capacities for Rb and Cs were 96 and 61 mg/g, respectively, which are higher than those reported for many other sorbents. Fixed-bed column studies revealed that Cs

at concentrations 1 and 5 mg/L in the feed solution containing 5 mg/L of Rb reduced the sorption capacity of Rb. However, Cs concentration in most natural and waste waters such as SWROC is many times smaller than that of Rb and therefore it is not expected to affect Rb sorption. Sorbed Rb was successfully desorbed using 0.1 M KCl. The mechanism of Rb sorption is one of electrostatic adsorption on the negatively charged surface sites as well as exchange of K from inside the KCoFC's lattice. A potentially effective procedure for the recovery of Rb from the SWROC in a typical desalination plant is presented here. It includes a process of membrane distillation of the SWROC to further increase the Rb concentration. Suggestions are also made concerning the amounts of Rb that can be recovered. Recovered Rb and additional clean water production not only contribute to offsetting the desalination cost, but also help to improve brine management.

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