Rubidium extraction using an organic polymer encapsulated potassium copper hexacyanoferrate sorbent

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HIGHLIGHTS

- Potassium copper hexacyanoferrate (KCuFC) had higher Rb sorption than other forms.
- KCuFC encapsulated with polymer (KCuFC-PAN) was well suited for dynamic column.
- KCuFC-PAN in fixed-bed column regenerated well in Rb sorption/ desorption cycles.
- KCuFC-PAN showed Rb selectivity over a wide concentration of saline brine ions.
- Rb was purified from K/Rb mixed solution using an ion exchange resin.

GRAPHICAL ABSTRACT
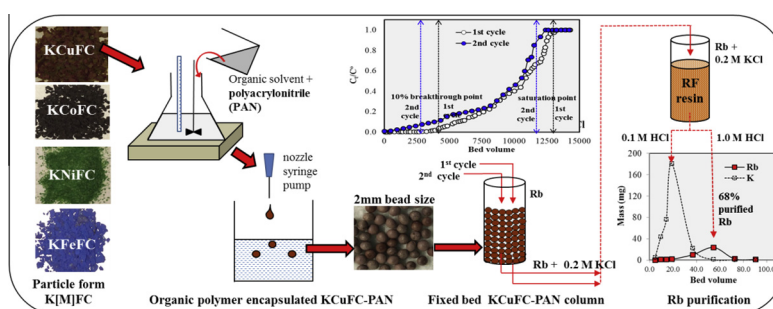
ABSTRACT

Sea water reverse osmosis (SWRO) brine contains significant quantity of Rb. As an economically valuable metal, extracting Rb using a suitable and selective extraction method would be beneficial. An inorganic sorbent, copper based potassium hexacyanoferrate (KCuFC), exhibited high selectivity to extract Rb compared to potassium hexacyanoferrate consisting of other transition metal combinations such as Ni, Co and Fe. An organic polymer (polyacrylonitrile, PAN) encapsulated KCuFC (KCuFC-PAN) achieved a Langmuir maximum Rb sorption capacity of 1.23 mmol/g at pH 7.0 ± 0.5. KCuFC-PAN showed Rb selectivity over a wide concentration range of co-existing ions and salinity of SWRO brine. High salinity (0.5–2.5 M NaCl) resulted in 12–30% sorption capacity reduction. At a molar ratio of Li:Rb (21:1), Cs:Rb (0.001:1) and Ca:Rb (14,700:1) commonly found in SWRO brine, sorption reduction of only 18% occurred. Nevertheless, at a very high K:Rb molar ratio (7700:1), KCuFC-PAN sorption capacity of Rb reduced significantly by 65–70%. KCuFC-PAN was well suited for column operation. In a fixed-bed KCuFC-PAN column (influent concentration 0.06 mmol Rb/L, flow velocity 2 m/h), two sorption/desorption cycles were successfully achieved with a maximum Rb sorption capacity of 1.01 (closely similar to the batch study) and 0.85 mmol/g in the first and second cycles, respectively. Around 95% of Rb was desorbed from the column with 0.2 M KCl. Resorcinol formaldehyde (RF) resin showed promising results of separating Rb from K/Rb mixed solution in effluents from a fixed-bed column, and a subsequent sequential acid desorption, producing 68% purified Rb.

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1. Introduction

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

Inorganic ion-exchange sorbents are widely used in the extraction of metals found in low concentration due to its high selective sorption capacity in mixed metals solutions [4]. In this context, potassium metal hexacyanoferrate (K(M)FC (M refers to transition metals such as cobalt (Co), copper (Cu), iron (Fe), zinc (Zn) and nickel (Ni)), is known for its versatile applications for trace alkali metal extraction under high saline conditions [1,5]. Considerable effort has been made on the development of K(M)FC especially for radioactive Cs removal from nuclear waste solutions [6]. A variety of metal combinations are used to make K(M)FC sorbent including Co, Ni, Fe (Prussian Blue), Zn and Cu [7,8]. Potassium cobalt hexacyanoferrate (KCoFC) is commercially available due to its high selectivity for radioactive Cs removal [6,9]. K(M)FC with other metal based combinations such as Cu (KCuFC), Zn (KZnFC), Fe (KFeFC) and Ni (KNiFC) have also shown satisfactory results in Cs extraction from nuclear waste [7–9]. K(M)FC with different metal combinations to increase selective sorption of Rb has not been compared in a single study so far. This information would be useful in identifying a specific K(M)FC with high affinity for Rb.

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

Furthermore, desorption of the sorbed Rb is important in determining the degree of recovery of Rb from an encapsulated sorbent. It is worth highlighting that most of the available studies on K(M)FC were focused on retaining radioactive Cs on the sorbent for solid disposal. Thus, desorption was not an essential factor in those studies. Some studies have highlighted Cs and Rb desorption using 0.5 M (up to 3.0 M) KCl, NH$_4$Cl and HNO$_3$ [5,11,13]. Upon desorption, Rb would be found mixed with other desorbed ions from K(M)FC and ions derived from the desorbing agent. Thus, subsequent purification process from these unwanted ions is essential to obtain a high quality Rb.

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

2. Material and methods

2.1. Materials

2.1.1. Solutions

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

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

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

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

2.1.2.4. Resorcinol formaldehyde polycondensate resin (RF resin).
RF resin was prepared by polycondensation of formaldehyde with resorcinol. A resorcinol: formaldehyde:NaOH:H$_2$O mole ratio of 1:2.5:1.5:50 was used as per the procedure described by Samanta et al. [18]. The mixture was oven dried at 100 °C for 24 h. The dried RF resin was ground and sieved to 0.25–0.45 mm particle size. It was then converted to an acid form (H form) by using HCl, followed by filtration and air drying of the residue.

2.2. Sorbent characterisation

2.2.1. Mineralisation analysis

Samples (0.05 g) of particle form K(M)FC as well as original and column regenerated K(M)FC-PAN were decomposed in 1 mL of concentrated H$_2$SO$_4$ (98%) as per the procedure of Naidu et al. [5]. Concentrations of K, Fe and transition metals in the aqueous samples were measured using Agilent technologies 7700 inductively coupled plasma mass spectrometry (ICP–MS). The procedure was repeated in triplicate. The average results are reported in this study. The deviation between the replicated values was lower than 10%.

2.2.2. pH and zeta potential

The effect of pH on sorption at equilibrium condition was investigated by suspending 0.005 g sorbent in a beaker containing 100 mL of 0.06 mmol Rb/L solution with initial solution pH set in the range of pH 3–9. The beakers were agitated for 12 h in a flat