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Selective sorption of rubidium by potassium cobalt hexacyanoferrate



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ABSTRACT

Recovering economically valuable rubidium (Rb) from natural resources is challenged due to its low concentration and limited selectivity of extracting agents. Equilibrium and kinetic studies were conducted on the sorptive removal of Rb at low concentration (5 mg/L) using a commercial and a laboratory prepared potassium cobalt hexacyanoferrate (KCoFC). These laboratory and commercial KCoFCs exhibited similar characteristics in terms of chemical composition, surface morphology (scanning electron microscopy) and crystal structure (X-ray diffraction peaks). KCoFC exhibited a higher sorption capacity for Rb (Langmuir maximum sorption 96.2 mg/g) and cesium (Cs) (Langmuir maximum sorption 60.6 mg/g) compared to other metals such as lithium (Li), sodium (Na) and calcium (Ca) (sorption capacity < 2 mg/g). KCoFC sorption capacity for Rb was affected only when Cs was present at twice the concentration of Rb, while the influence of other metals (Li, Na, and Ca) was minimal even at high concentrations. High Rb sorption capacity was due to the exchange of Rb for K inside the crystal lattice and strong sorption on the sorbent surface. These were evident from the data on K release during Rb sorption and reduced negative zeta potential at the sorbent surface in the presence of Rb, respectively. Kinetic sorption of Rb was satisfactorily described by the pseudo-second order model with intraparticle diffusion and exchange of Rb with structural K acting as major rate limiting steps. Up to 74% desorption of Rb was achieved with 0.1 M KCl. Overall, the results established the superior selectivity of KCoFC for Rb sorption.

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1. Introduction

In the last few decades attention has been focused on extracting rubidium (Rb) due to its application in many fields of science and technology. Rb is used in fibre optic telecommunication systems, semiconductor technology and night-vision equipment [1,2]. In recent years, new and more efficient techniques have been established in optical and laser application with the usage of warm Rb vapour [3,4]. Although considerable Rb mineral resources are available, it is much more difficult to extract Rb than other alkali metals [2]. The application potential coupled with the mineral extraction challenge has increased the economic value of Rb. The price of Rb is much higher (€7856.64/kg) in comparison to lithium (Li) (€1.22/kg) and potassium (K) (€0.11/kg) [5].

This has led to the development of new methods for the extraction of Rb from resources such as oilfield water, mining industry, ores with low Rb content, seawater and salt lakes [2,6–8]. Potential methods of alkali metal extraction from natural resources include evaporation, precipitation, use of emulsion membranes and liquid–liquid extraction techniques [9,10]. Nevertheless, the effec-

tiveness of recovering trace metals with these methods are challenged in natural resources by the low concentration of the target metals, the limited selectivity of the extracting agents, and the presence of other constituents. In this regard, inorganic ion-exchange sorbents offer a practical approach in that they have the capacity to selectively extract low concentration metals from mixed solutions [7].

A number of diverse inorganic sorbents have been used for selective alkali metal sorption including Prussian blue [11], potassium metal hexacyanoferrate [12], zeolite [13], titanium dioxide [14] and ammonium molybdophosphate [15]. Most of these studies have focused on the removal of radioactive cesium (Cs) in nuclear waste brine. Cs and Rb have similar physico-chemical properties and on this basis, a few studies have examined the prospect of Rb extraction by sorbents [5,16]. These studies have highlighted the high Rb sorption capacity of potassium metal hexacyanoferrate. However, we still lack a detailed understanding of: firstly, the mechanism and kinetics of Rb sorption by potassium metal hexacyanoferrate; and secondly, the effect of the presence of other alkali metals on Rb sorption. Moreover, these studies were conducted using high concentrations of the target alkali metal in the 20 to >500 mg/L range. The concentration of the target metal is an important factor in establishing the effective performance

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of a sorbent. As Rb is present in a relatively low concentration (<1.0 mg/L) in natural resources such as seawater, experiments at high concentration levels may not reflect the performance of the sorbent in a practical scenario. Further, apart from the sorption performance, desorption capacity is an important factor in establishing the viability of a sorbent if the target metal has to be recovered in concentrated form in solutions. This aspect has not been discussed thus far for Rb sorption with potassium metal hexacyanoferrate.

Hence, the objective of this study was to establish the selective affinity of potassium cobalt hexacyanoferrate (KCoFC) for Rb sorption. The specific objectives were to: (1) synthesise KCoFC in the laboratory (KCoFC(L)) and compare its properties and characteristics with a commercial KCoFC sorbent (KCoFC(C)) in terms of chemical composition, crystal structure, surface area and pore size distribution, surface charge characteristics, and efficiency of Rb sorption; (2) determine the effect of pH and co-existing alkali metal ions on Rb sorption; (3) model the equilibrium and kinetics of Rb sorption; (4) determine the mechanism of Rb sorption; and (5) investigate the desorption of Rb using different acid, alkaline, and salt solutions.

2. Material and methods

2.1. Materials

2.1.1. Commercial sorbent (KCoFC(C))

KCoFC(C) also known as CsTreat was supplied by Fortum Engineering Ltd, (Finland). This sorbent consisted of dark brown-black granules ranging in size from 0.25 to 0.85 mm [17]. The granules were ground to particle sizes of 0.25–0.45 mm for this study.

2.1.2. Laboratory sorbent (KCoFC(L))

KCoFC(L) was prepared in the laboratory by adding 1 volume of 0.5 M potassium ferrocyanide trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$) to 2.4 volumes of 0.3 M cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) as described by Prout et al. [18]. The mixture was stirred for 1 h at room temperature, followed by centrifuging and washing with deionised water. The concentrated mixture was dried at 115 °C for 24 h. The dried granules were ground to a particle size of 0.25–0.45 mm, washed again with deionised water and then dried.

2.1.3. Solutions

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 water. All reagents were of analytical grade (Sigma-Aldrich) and were used without further purification.

2.2. Sorbent characterisation

2.2.1. Chemical analysis

Samples of KCoFC (0.05 g) were decomposed in 1 mL of concentrated H_2SO_4 by heating at 200 °C for 5 h. 10 mL of 0.1 M H_2SO_4 was added to the residue, and diluted to 50 mL with deionised water as per the procedure of Nilchi et al. [19]. Concentrations of K, iron (Fe) and cobalt (Co) in the aqueous samples were measured after filtration through a 1.2 μm syringe membrane filter using Microwave Plasma-Atomic Emission Spectroscopy (MP-AES) (Agilent 4100). The procedure was carried out in triplicate and the average results are reported in this study. The deviation between the replicated values was <10%.

2.2.2. SEM–EDX analysis

The morphology and detection of elements on the KCoFC before and after Rb sorption was carried out with scanning electron

microscopy (SEM) coupled with Energy Dispersive X-ray spectrometry (EDX) operated at 15 kV (Zeiss Supra 55VP Field Emission).

2.2.3. Powder X-ray diffraction analysis (XRD)

XRD data (on powders) were collected on a Siemens D5000 diffractometer operating with Cu K α radiation and a rotating sample stage. The samples were scanned at room temperature in the 2θ angular range of 20–110°.

2.2.4. Surface area and pore volume

Nitrogen adsorption–desorption on KCoFC(C) and KCoFC(L) was determined at 77 K using the nano POROSITY (Mirae SI, Korea) adsorption analyser. Approximately 0.1 g of freeze-dried sample was used for the analysis following an overnight degassing at 80 °C under vacuum. The specific surface area was calculated using the standard Brunauer–Emmett–Teller (BET) method. The total pore volume (V_{tot}) was determined from the nitrogen adsorption at a relative pressure of about $p/p_0 \approx 0.99$. Average pore diameter was calculated using the equation, $4V_{tot}/S_{BET}$.

2.2.5. pH and zeta potential

To investigate the effect of pH and zeta potential on sorption, suspensions of 1 g/L KCoFC sorbents in different solutions (100 mL) were agitated for 12 h in a flat shaker at a shaking speed of 120 rpm at room temperature (24 ± 1 °C). The pH values of the feed solution were set in the 3–10 range by adjusting the initial pH using 0.1 M HCl and 0.1 M NaOH. The initial and final pHs at the end of the sorption period were measured using a HQ40d portable pH Meter. To maintain a constant pH, pH was adjusted to its initial value after 4 and 8 h for all sorption experiments. The zeta potential was measured using a Zetasizer nano instrument (Nano ZS Zen3600, Malvern, UK) on the suspensions. Measurements were done in triplicate to minimise undesirable biases (with differences between replicates always being less than 5%).

2.3. Sorption experiments

In view of the low concentrations of Rb and Cs in natural resources, and in order to reliably measure the metals concentrations utilising analytical instruments, sorption experiments were carried out at a maximum initial concentration of 5 mg/L for Rb and Cs. However, higher concentrations of Li, Na, and Ca were used as these metals had very low sorption capacity at low concentrations. All experiments were performed in a set of glass flasks containing 100 mL of metal solutions and different doses of sorbents agitated in a flat shaker at a shaking speed of 120 rpm at room temperature (24 ± 1 °C). The experiments were duplicated and the average values were recorded for data analysis. The difference between duplicate values was within $\pm 2\%$. The concentrations of Rb, Li, Na and Ca in the supernatants were measured using MP-AES. The Cs concentration was measured using ICS-MS (PerkinElmer® NexION® 300).

2.3.1. Sorption isotherms

Equilibrium sorption experiments were conducted with different doses of sorbent (KCoFC) ranging from 0.02 to 0.20 g/L at pH 7.0 ± 0.5 . The suspensions were agitated for 24 h to reach the sorption equilibrium. The supernatant solution was examined using MP-AES analysis after filtration through a 1.2 μm syringe membrane filter. The sorption amount at equilibrium, q_e (mg/g), was calculated using Eq. (1):

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

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

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