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Removing rubidium using potassium cobalt hexacyanoferrate in the membrane adsorption hybrid system

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ABSTRACT

Highly-priced rubidium (Rb) can be effectively extracted from seawater using potassium cobalt hexacyanoferrate (KCoFC) and ammonium molybdophosphate (AMP) adsorbents in the membrane adsorption hybrid system (MAHS). KCoFC (< 0.075 mm), KCoFC (0.075–0.15 mm), and AMP (< 0.075 mm) had Langmuir adsorption capacities of 145, 113, and 77 mg/g at pH 6.5–7.5, respectively. When KCoFC (< 0.075 mm) at a dose of 0.2 g/L was initially added to 4 L of a solution containing 5 mg Rb/L in the MAHS and 25% of the initial dose was repeatedly added every hour, the amount of Rb removed remained steady at 90–96% for the experiment's 26 h duration. The removal of Rb by AMP under similar conditions was 80–82%. The cumulative Rb removed by KCoFC (< 0.075 mm) in MAHS was only 33% reduced in the presence of high concentrations of other cations in synthetic seawater compared to that in solution containing only Rb. Approximately 30% of the adsorbed Rb was desorbed using 1 M KCl. When the desorbed solution was passed through a column containing resorcinol formaldehyde (RF), 35% of the Rb in the desorbed solution was adsorbed on RF. Furthermore 50% of the Rb adsorbed on RF was recovered by 1 M HCl leaching of the column. This sequence of concentration and separation of Rb in the presence of other cations in synthetic seawater is an efficient method for recovering pure Rb from real seawater and seawater reverse osmosis brine.

1. Introduction

Rubidium (Rb) is one of the world's most highly priced alkali metals and it has a range of uses, such as glass types for electrical conductivity, fibre optic and telecommunication systems and night-vision equipment [1,2]. It also has applications in soporifics, sedatives and the treatment of epilepsy and optical application with the usage of warm Rb vapour [3,4]. Because of its high price and numerous uses, Rb extraction from solutions can be very cost-effective [5]. Sea water and sea water rejected brine are good sources of Rb, but its recovery from these sources is challenging due to: firstly, its low concentration; and secondly, limited selectivity of chemicals utilised for its extraction in the presence of high concentrations of other ions in sea water and the brines [6]. The methods currently employed for extracting Rb consist of ion exchange/adsorption, evaporation, precipitation, use of emulsion membranes and liquid–liquid extraction techniques [7,8]. Of these, the ion exchange/adsorption process is the most suitable and widely utilised, since it is able to selectively extract low concentrations of Rb from mixed solutions [9–11].

A wide range of adsorbents such as clay materials [12], prussian blue[13], potassium metal hexacyanoferrate [6,14], zeolite [15], titanosilicate [16] and ammonium molybdophosphate [17] have been used to selectively remove alkali metals. Most of these studies were conducted in batch experiments, and only a few had been reported in fixed-bed column system studies [18]. Of the various adsorbents, potassium cobalt hexacyanoferrate (KCoFC) and ammonium molybdophosphate (AMP) have indicated high adsorption capacity and selectivity for Rb and cesium (Cs) extraction in both batch and column studies [10,11,17]. Since AMP and KCoFC are of small size (0.075–0.45 mm), they can cause practical problems in column operations due to high-pressure development and the pores becoming clogged. These problems can be overcome by either encapsulating the material in a coarser material or physically mixing it with a coarser material such as granular activated carbon [11,19].

The MAHS is a combination of adsorption and membrane filtration of the adsorbent that can be easily regenerated and reused in the process. Interest in this hybrid process of removing organic and inorganic materials has recently increased because of the continuous removal process with new addition or replacement of adsorbent when the initially added adsorbent is exhausted, which leads to the process costing less [20,21]. Moreover, it has various advantages such as the process is dynamic with treatment employing a large quantity of water,

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controllable membrane fouling, low capital and operational costs, and considerably less energy requirements [20,21].

The main advantage of the MAHS in comparison to the traditional fixed-bed column adsorption in real water/wastewater treatment plant is that very small sized adsorbent particles can be employed in MAHS. This cannot be done in column experiments because the small particles reduce the flow rate and more energy is needed to pump the feed water [22]. Smaller sized particles can increase the interface area and result in higher adsorption capacity. In MAHS the particles are kept in suspension by pumping air into the system, and this reduces membrane fouling via the scouring effect of adsorbents on the membranes [23,24]. Studies using MAHS have reported the removal of organic micropollutants [25], boron [26], phosphate [27], nitrate [28], colour and reactive dyes [29]. However, no analysis has yet reported the removal of alkali metals such as Rb using MAHS.

The objectives of this research were to: (i) evaluate the performance of KCoFC and AMP for Rb adsorption in batch and MAHS methods; (ii) investigate the effect of adsorbent dose and particle size and water flux on Rb adsorption in the MAHS system; (iii) evaluate the effect of co-existing ions in seawater on Rb adsorption by KCoFC in the MAHS method; and (iv) investigate the efficiency of recovery of Rb by desorption of Rb previously adsorbed on KCoFC in the MAHS experiment followed by its purification using resorcinol formaldehyde (RF) ion exchange resin.

2. Material and methods

2.1. Adsorbent

2.1.1. Potassium hexacyanoferrate (KCoFC)

A commercially available adsorbent, KCoFC (also known as CsTreat) acquired from Fortum Engineering Ltd., Finland was used as the primary adsorbent in this study. This granular adsorbent was dark brown-black in colour and size ranged from 0.25 to 0.85 mm [30]. It has a surface area of 72.1 m^2/g, total pore volume of 0.37 cm^3/g and pore diameter of 20.5 nm which indicate the adsorbent consists mainly of mesopores (2–50 nm). These and other characteristics of the adsorbent are reported in our previous research [10]. In our previous studies, KCoFC with a 0.15–0.25 mm particle size range was used. In order to increase the adsorption capacity a smaller particle size range of < 0.075 mm–0.15 mm was utilised in this study.

2.1.2. Ammonium molybdophosphate (AMP)

AMP, which consists of the inorganic salt of phosphomolybdic acid with the chemical formula of $(NH_4)_3PMo_{12}O_{40}$ was also used as an adsorbent in the study. It was obtained in powder form (< 0.075 mm) from Sigma-Aldrich (Australia). It is a phosphomolybdate ion complex previously used for Cs removal [17].

2.2. Zeta potential analysis

Zeta potential is the electrical potential close to a particle surface where adsorption of ions from the solution phase occurs, and it is positively related to the surface charge. It is an important parameter used for understanding the mechanism of adsorption. The zeta potential values were measured separately on 0.05 g/L of KCoFC and AMP suspensions in solutions of DI water and 10^{-3} M RbCl in the pH range of 2.5–10.0 using a Zetasizer Nano instrument (Nano ZS Zen3600, Malvern, UK). Triplicate measurements were made to minimise undesirable biases (with differences between replicates always been less than 5%), and the average value was used for data analyses.

2.3. Feed solutions and chemical analysis

Feed solutions of different concentrations were prepared using analar grade chemicals – RbCl, KCl, NaCl, $CaCl_2$ and $MgCl_2$ (Sigma-Aldrich). Rb, K, Na, Ca, and Mg concentrations were determined using Microwave Plasma - Atomic Emission Spectroscopy (MP-AES) (Agilent 4100).

2.4. Batch adsorption experiment

2.4.1. Effect of pH on Rb adsorption

The influence of pH on Rb adsorption was studied by adding 0.05 g of KCoFC or AMP to 100 mL solutions containing 5 mg Rb/L, and the suspensions were agitated in a flat shaker at a shaking speed of 120 rpm at room temperature (24 ± 1 °C) for 24 h. The solutions' pH levels were initially set at different values within a range of 2.5–10.0 using 0.1 M HCl and 0.1 M NaOH. Because the pHs changed during the adsorption process, they were adjusted back to their initial values after 4 h and the shaking of the suspensions continued. The final pHs at the end of the shaking period were measured. A HQ40d portable pH Meter was used for all pH measurements.

2.4.2. Adsorption equilibrium

Equilibrium adsorption experiments were conducted with KCoFC and AMP at adsorbent doses of 0.03–1.0 g/L in a set of glass flasks with 100 mL solutions spiked with Rb at a concentration of 5 mg/L and pH 6.5–8.0. This concentration of Rb was selected to achieve a close match with the low concentrations of Rb in seawater and to consistently measure the metal concentration using standard analytical instruments. The suspensions were shaken in a flat shaker with a shaking speed of 120 rpm at room temperature (24 ± 1 °C) for 24 h. The amount of Rb adsorbed at equilibrium, qe (mg/g), was calculated using Eq. (1).

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

where C_0 = initial concentration of Rb (mg/L); C_e = equilibrium concentration of Rb (mg/L); V = volume of the solution (L); and M = mass of adsorbent (g). The adsorption data were fitted to the Langmuir adsorption model described elsewhere [10].

2.4.3. Adsorption kinetics

Batch adsorption kinetic experiments were conducted with a fixed dose of 0.2 g/L of KCoFC and AMP with the Rb feed solution concentration of 5 mg/L. The flasks were agitated in a flat shaker at a shaking speed of 120 rpm at room temperature (24 ± 1 °C) and samples were taken at different time intervals. The concentrations of Rb in the samples were measured and the amount of Rb adsorption at time t, q_t (mg/g) was calculated using Eq. (2).

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{2}$$

where C_0 = initial concentration of Rb (mg/L); C_t = concentration of Rb at time t (mg/L); V = volume of the solution (L) and M = mass of dry adsorbent used (g).

2.5. Membrane adsorption hybrid system (MAHS)

A schematic diagram of MAHS is shown in Fig. 1 where a hollow fibre microfilter membrane was submerged in a reactor tank of 6 L capacity which was filled with 4 L feed water. The hollow fibre membrane had the specifications of 0.1 µm nominal pore size and 0.1 m^2 surface area. It consisted of hydrophilic modified ploy acrylic nitrile (PAN) with 1.1 mm inner and 2.1 mm outer diameters and was obtained from Mann + Hummel, Singapore. The membrane module was positioned in the centre of the reactor tank. Air bubbles were continuously passed at a fixed rate of 1.8 m^3/m^2 membrane area from the bottom of the tank which was predetermined and could sufficiently keep the adsorbent particles in suspension. A peristaltic pump served to withdraw the effluent and to feed new synthetic water at a controlled flux. Two flux rates (10 and 20 L/m^2h) were utilised in these