Removal of strontium from aqueous solutions and synthetic seawater using resorcinol formaldehyde polycondensate resin

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ABSTRACT

Strontium (Sr) is a valuable metal found in abundance in seawater. However, its recovery from seawater has received little attention despite its many industrial applications. Batch and column adsorption experiments were conducted on the removal of Sr by resorcinol formaldehyde (RF) resin in the presence of co-existing cations at pH 7.5–8.5, where maximum adsorption was found. Batch adsorption capacities of cations followed the decreasing order of Sr > Ca > Mg > K, the order being the same as that of reduction of negative zeta potential. The adsorption data for Sr, Ca and Mg satisfactorily fitted to the Langmuir adsorption model with maximum adsorption capacities of 2.28, 1.25 and 1.15 meq/g, respectively. Selectivity coefficients for Sr with respect to other metals showed that Sr was selectively adsorbed on RF. Column adsorption data for Sr only solution fitted well to the Thomas model. Sr adsorption capacity in the presence of seawater concentrations of Ca, Mg, K and Na was reduced in both batch and column experiments with highest effect from Ca and Mg. However, if Ca and Mg are removed prior to RF adsorption process by precipitation, the negative effect of these ions on Sr removal can be significantly reduced.

1. Introduction

Seawater is becoming an important source of several valuable mineral resources because of the depletion of high-grade mineral ores on land and recent problems associated with land-based industries resulting from sustainable water and energy demand and environmental issues [1]. Due to its large reserve, seawater is an attractive resource for valuable minerals such as lithium, uranium, rubidium, and strontium (Sr) despite their very low concentrations. Among these valuable minerals, Sr is one of the most abundant minerals in seawater with an average concentration of 6–7 mg/L [2]. Strontium, which is an alkaline earth metal, has many industrial applications, such as in ceramic ferrite magnets, ceramics, glass and pyrotechnics industries, fluorescent lights and fire-works, and also for drilling mud in the oil and gas industries [1,3]. To date, however, the recovery of Sr from seawater has received little attention despite its many industrial applications.

Moreover, the removal of Sr from radioactive waste water is a very critical issue as it is considered one of the most dangerous radionuclides to human health due to its high solubility, transferability, and easy assimilation [4,5]. Strontium has four major naturally occurring stable isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr in addition to 31 unstable isotopes and the longest-lived unstable isotope is ^{90}Sr with a half-life of 28.9 years. The ^{90}Sr isotope is a beta-emitter that genetically affects seawater organisms and ultimately causes harm to humans [6]. Removing radioactive Sr from seawater is also important particularly since the Fukushima nuclear plant accident in 2011, which led to serious seawater contamination by radioactive strontium ^{90}Sr [7,8].

Strontium genetically impacts on seawater organisms and eventually causes serious damage to humans. In countries like the USA, Jordan and Japan, Sr contamination in groundwater and other water sources has been reported and the United States Environmental Protection Agency (U.S. EPA) has recommended a permissible limit of 4.0 mg/L of Sr in drinking water [9]. High Sr concentrations in drinking water sources may potentially lead to many diseases increasing, including neurological disorders ranging from learning disabilities to severe mental retardation [10]. It is therefore important to develop appropriate removal techniques for the removal of Sr from water both to decontaminate waters and to recover Sr for beneficial uses.

Of the various methods for removing Sr such as solvent extraction [11], adsorption [12,13], ion exchange [14], electrocoagulation [15], and membrane filtration [16], adsorption/ion exchange is a promising method for removing Sr from seawater and radioactive wastewaters because of its potential to separate Sr from seawater despite the low concentration levels of this metal, low cost, and a simple process to implement with less chemical waste production. As ion exchange is one type of adsorption process which leads to adsorption of ions [17], in

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this paper it is discussed under the general process of adsorption. Different studies have been conducted to investigate Sr adsorption using various adsorbents such as hydrous ferric oxide [18], dolomite [19], strontium-ion imprinted hybrid gel [20], alginate-based biosorbent [21] and titanosilicate [22]. Not all adsorbents, however, were found to have high adsorption capacities. Moreover, most of these Sr adsorption studies were conducted in batch experiments and not in column experiments which are more appropriate for practical application.
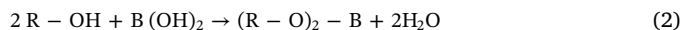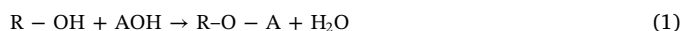
Resorcinol formaldehyde (RF) resin is an effective phenolic resin which is formed by the polycondensation of resorcinol and formaldehyde in alkaline solution [23]. Commercial phenol formaldehyde resins – similar to RF resin – were utilised to treat low and high level alkaline radioactive wastes [24], as well as laboratory synthesised phenol formaldehyde resins for the removal of both Cs and Sr from radioactive wastewaters [25]. Previous research reported that the phenol formaldehyde resins that are similar to RF resin were generally conditioned with alkaline solutions. This is because the main functional weakly acidic phenolic –OH groups of the resin responsible for ion exchange were expected to fully realise their ion-exchange properties only if the –OH groups were ionised to the highest extent which occurs in alkaline solutions [23]. It was reported that RF resin could be used to simultaneously adsorb Sr along with Cs from radioactive waste solutions [25], but Banerjee et al. [26] found that the RF resin used in their study was highly selective for the removal of Cs compared to Sr from simulated radioactive waste solution. However, no detailed study has been done on Sr removal and recovery from seawater using RF resin, especially in the presence of co-ions using both batch and column methods. The concentration of Cs ($4-50 \times 10^{-5}$ M) is much higher than that of Sr ($3-15 \times 10^{-7}$ M) in radioactive wastewater [27]. Therefore, Cs was preferentially adsorbed on RF. However, in seawater, the opposite is expected to occur because Sr concentration (1×10^{-4} M) is much higher than that of Cs (6×10^{-9} M) [1].

The objectives of this study were to: (i) synthesise and evaluate the performance of RF resin for Sr adsorption in batch and column adsorption methods; (ii) evaluate the pH effect on Sr adsorption and study the adsorption mechanism using zeta potential measurements; (iii) investigate the effect of co-ions in seawater on Sr adsorption using synthetic seawater in batch and column adsorption methods; and (iv) evaluate the Sr desorption characteristics of the RF resin to obtain useful information on Sr recovery.

2. Materials and method

2.1. Adsorbents

The main adsorbent used in this study was RF resin but four other commercially available adsorbents namely CsTreat, ammonium molybdophosphate (AMP), Zeolite, and Amberlite FPC 3500 were also used to compare their Sr adsorption capacities [28,29]. RF resin was prepared by following the procedure described by Samanta et al. [23] where a mixture of solutions with resorcinol: formaldehyde: NaOH: H$_2$O mole ratio of 1:2.5:1.5:50 was used. The dark-red coloured mixed solution was then oven dried at 100 °C for 24 h and the dried reddish brown RF resin was ground and sieved to 0.25–0.45 mm particle size. The sieved RF resin was then washed with 1 M HCl to convert RF resin to an acid form (H$^+$). After that, the resin was washed thoroughly with MQ water to convert it to a neutral form and dried at room temperature (24 ± 1 °C) for 24 h. To increase the ion exchange capacity, the H$^+$ form of the resin was conditioned separately with alkaline solutions of 1 M NaOH, KOH and Ca(OH)$_2$ by shaking 5 g of the resin in 500 mL solution of each of the metal hydroxides separately at 150 rpm for 24 h. Following that, the resin was thoroughly washed with MQ water to remove excess NaOH, KOH and Ca(OH)$_2$ and then dried at room temperature (24 ± 1 °C) for 24 h and kept stored in air tight containers. The reactions involved in the conditioning of RF resin with the different metal hydroxides are given in Eqs. (1), (2).

$$R - OH + AOH \rightarrow R\text{–}O - A + H_2O \tag{1}$$

$$2\,R - OH + B\,(OH)_2 \rightarrow (R - O)_2 - B + 2H_2O \tag{2}$$

where R is the resorcinol formaldehyde polymer and A is Na$^+$ or K$^+$ and B is Ca^{++}.

Based on earlier research on the adsorption of Cs by RF resin, it can be said that the phenolic OH group of the resin is ionised to phenolate ion under alkaline conditions [23,26,30] and then it participates in ion exchange reaction of Sr. The uptake of Sr ions by the resin conditioned with Na$^+$, K$^+$, Ca^{++} is shown by similar ion exchange reactions in Eqs. (3), (4).

$$2\,R\text{–}O - A + Sr^{++} \rightarrow (R - O)_2 - Sr + 2A^+ \tag{3}$$

$$(R - O)_2 - B + Sr^{++} \rightarrow (R - O)_2 - Sr + B^{++} \tag{4}$$
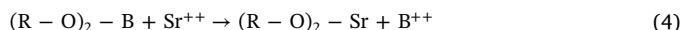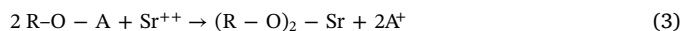
The virgin and the three RF resins conditioned with NaOH, KOH and Ca(OH)$_2$ were used in the adsorption experiments.

2.2. RF resin characterisation

Zeta potential is an important parameter for understanding the mechanism of adsorption as it is the electrical potential close to a particle surface where adsorption of ions from solution phase occurs and it is positively related to the surface charge. The zeta potential values were measured on 0.5 g/L of RF resin suspensions in the presence of 10^{-3} M of NaCl, KCl, CaCl$_2$, MgCl$_2$, or SrCl$_2$ 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 being < 5%) and the average value was used for data analyses.

RF resin was also characterised using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The FTIR pattern was obtained using a Miracle-10 Shimadzu FTIR spectrometer. The spectra were obtained at 4 cm^{-1} resolution by measuring the absorbance from 400 to 4000 cm^{-1} using a combined 40 scans. XRD was carried out using a PANalytical Empyrean instrument operated at 60-kV with Cu-Ka1 radiation on powdered samples of RF resin.

Ion exchange capacity of the RF resin was measured using two methods [23,28]. In both methods, the RF was equilibrated with known concentrations of NaOH and NaCl and the amounts of NaOH consumed in the ion exchange reaction were determined by titrating the remaining NaOH with 0.1 M HCl using phenolphthalein indicator. The measurements were made in triplicate and the average values were recorded.

2.3. Feed solutions and chemical analysis

Feed solutions were prepared using analar grade chemicals - KCl, NaCl, CaCl$_2$, MgCl$_2$ and SrCl$_2$ (Sigma-Aldrich) - at pH 7.5–8.5. Sr, K, Na, Ca, and Mg concentrations were determined using Microwave Plasma - Atomic Emission Spectroscopy (MP-AES) (Agilent 4100).

2.4. Batch adsorption experiments

2.4.1. Sr adsorption by different RF resins
The first batch experiment was conducted with virgin RF resin and RF resin conditioned separately with NaOH, KOH, and Ca(OH)$_2$ at adsorbent doses of 0.1–1.0 g/L and fixed Sr concentration of 10 mg/L to select the adsorbent having the highest Sr adsorption capacity. The amount of Sr adsorbed at equilibrium, q$_e$ (mg/g), was calculated using Eq. (5).

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{5}$$

where C$_0$ = initial concentration of Sr (mg/L); C$_e$ = equilibrium concentration of Sr (mg/L); V = volume of the solution (L); and M = mass