Affinity of potassium-form cation exchange resin for alkaline earth and transition metals

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ARTICLE INFO

ABSTRACT

This research conducted bench-scale batch equilibrium tests to generate new selectivity data for the alkaline earth metals Ca^{2+}, Sr^{2+}, and Ba^{2+} and the transition metals Cd^{2+} and Co^{2+} for binary cation exchange involving sulfonic acid, polystyrene, gel and macroporous resins using the potassium (K^+) mobile counterion. Calculations for separation factor, and Langmuir and Freundlich isotherm models were used to investigate the sorption behavior of metals onto the cation exchangers. The separation factor and Langmuir isotherm were used to determine the selectivity sequence of cations for the resins. It was determined that the K-form cation exchangers were more selective for alkaline earth metals than the corresponding sodium (Na^+) form resin, and the gel resin was more selective than the macroporous resin for all metals. Using the separation factor to determine the selectivity sequence for K-form cation exchange resin showed similar order as published selectivity sequences for Li- and Na-form resins. The hydrated radius and ionic radius of the metals had a strong influence on the selectivity sequence for both types of cation exchange resins. Smaller hydrated radius resulted in an increase in the affinity of the resin for contaminants. Overall, K-form cation exchange resin has the potential to replace Na-form resin, as indicated by higher selectivity and comparable selectivity sequence for common metal contaminants.

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1. Introduction

Metals represent an important category of drinking water contaminants due to adverse impacts to human health. For example, barium (Ba^{2+}) and cadmium (Cd^{2+}) are regulated as drinking water contaminants in the U.S. and by the World Health Organization [1,2]. Other metals such as cobalt (Co^{2+}), which is on the U.S. EPA Contaminant Candidate List 3 [3], and strontium (Sr^{2+}) have been considered for regulation [4], with Sr^{2+} likely to become regulated in the U.S. as a primary drinking water contaminant. In addition to health effects, metals can be a concern for economic and aesthetic reasons. For instance, high levels of calcium (Ca^{2+}) in water can lead to scaling of boilers and water heaters and decrease the effectiveness of detergents and soaps, all of which can have an adverse economic impact. In order to lessen the impact of these metals in drinking water sources and provide potable drinking water physical-chemical processes may be used. Physical-chemical processes that can be used to remove metal cations from water include precipitation, membrane separation, and ion exchange [5]. Cation exchange, as a specific mechanism of ion exchange, was investigated in this research.

Cation exchange is considered a viable technology for removing inorganic cations such as Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, and Cd^{2+} from different water sources. Since ion exchange reactions occur at fast time scale (on the order of minutes), the removal of metals can be achieved quickly using strong-acid polymer resins, which perform independent of the pH of the source water. However, when cation exchange resins become exhausted, the capacity of the cation exchanger can be replenished through regeneration. During the regeneration step, a concentrated salt solution is introduced to the system to displace the adsorbed contaminant. Sodium chloride (NaCl) regeneration solution is commonly used to elute contaminants from exhausted resins at drinking water treatment plants. The main drawback of regeneration and using a concentrated solution such as NaCl is that it requires subsequent disposal and there is no alternative use for the waste regeneration solution. The disposal of concentrated NaCl solution pose several impacts, such as the inhibition of microbiological activity during wastewater treatment if disposed to sewer and deterioration of soil structure and fertility if land applied [6–8]. Accordingly, potassium (K)-form cation exchange resin and potassium chloride (KCl) regeneration

are proposed as an alternative to Na-form cation exchange resin and NaCl regeneration, which has benefits in terms of waste regeneration solution disposal and composition of the treated water. Potassium is an important macronutrients for plants [9], which makes K$^+$ waste regeneration solution an attractive option for land disposal and reuse in agriculture for fertilizer or soil conditioner. The reuse of KCl waste regeneration solution is dependent on the types of contaminants in solution. Furthermore, K$^+$ can be important in wastewater treatment during enhanced biological phosphorus removal [10,11]. Using K$^+$ instead of Na$^+$ will generate a KCl waste regeneration solution that has the potential for more favorable disposal options, and will increase K$^+$ and reduce Na$^+$ in the treated water. This would be especially helpful in offsetting deficiency of K$^+$, as individuals globally get insufficient amount in their diet and it is an important nutrient for normal body functions [12–14]. Furthermore, using K$^+$ instead of Na$^+$ can be beneficial in places that regulate Na$^+$ concentration in finished drinking water [15].

Only a few previous researchers have investigated the use of K$^+$ salts as a regeneration solution for cation exchange. Maul et al. [16] investigated the regeneration efficiency of KCl and KHCO$_3$ and showed that polystyrene gel and macroporous cation exchange resins were more efficiently regenerated with K$^+$ than Na$^+$; however as the regeneration solution concentration increased both ions performed similar at regeneration. Clifford and Zhang [17] studied the removal of uranium and radium from groundwater and found that KCl was a superior regenerant over NaCl. Wist et al. [18] investigated the use of KCl as a regeneration solution for residential water softening units and found that K-form cation exchange resin had similar treatment capacity as Na-form cation exchange resin with K$^+$ having a higher regeneration efficiency over Na$^+$. The higher regeneration efficiency of K$^+$ over Na$^+$ was attributed to K$^+$ having a higher affinity over Na$^+$ for cation exchange resins [18]. K$^+$ is more selective than Na$^+$, because both are alkali metals and metals in the same family affinity increases as atomic number increases [19]. Other researchers investigated reuse of waste regeneration solution for irrigation. Irrigation with KCl-based wastewater was shown to sustain soil fertility and the exchangeable form of K$^+$ was more readily available for plant uptake compared to solid fertilizers [20]. It was also shown that the maximum concentration of K$^+$ that catalyzes enzymes for starch was in the range of 50–100 mM and higher concentrations can inhibit plant development [21]. Wu et al. [22] found that Ca^{2+} and K$^+$ were not significantly taken up or increased in plant tissues by using KCl waste regeneration solution for irrigation of landscape plant species. While K$^+$ was important for plant development, it was found that irrigation sources with high chloride (Cl$^-$) can be detrimental to plants and that water that contains Ca^{2+} helps to protect plants from this damage [21]. Overall, the disposal of KCl waste regeneration solution by land application was not harmful to soil structure or plant growth under proper management [20].

The previous paragraphs document the efficiency of KCl regeneration and the beneficial disposal options for KCl waste regeneration solution. The next consideration is the selectivity of K-form cation exchange resin for contaminants. The selectivity sequence in previous work were mostly determined by mass action law, separation factor, and isotherm models [5,23–25]. The general developed selectivity sequence, based on equilibrium constants, for lithium (Li) form cation exchanger is summarized as Ba^{2+} > Sr^{2+} > Ca^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > K$^+$ > Na$^+$ [24,26,27]. The separation factor for strong-acid Na-form resin was used to determine similar selectivity sequence for alkaline earth metals, however the separation factor for Cd^{2+} and Co^{2+} was not reported [5]. Oancea et al. [25] used the Langmuir isotherm to classify the selectivity of gel and macroporous resins. Using gel resins it was found that

the ionic radius was strongly related to the amount of ions removed from solution and the Langmuir and Dubinin-Radushkevich isotherm models were more appropriate than the Freundlich isotherm model to describe the data [28]. Metals, such as Cd^{2+}, were preferred by gel resins and the preference of cation contaminants on exchangers were less selective when the hydrated radius increased [19]. Even though these studies demonstrated the usefulness of cation exchange resins and gave mechanisms that govern selectivity, none of these papers evaluated the K-form cation exchangers for selectivity preference for a variety of metal contaminants in drinking water. It is important to evaluate the K-form selectivity sequence because the use of K-form cation exchange resins is proposed in place of Na-form cation exchange resins. This will help to determine the preference of K-form cation exchange resins for contaminants and will therefore be especially helpful when designing ion exchange systems to remove multiple contaminants.

Hence, the goal of this research was to generate new selectivity data for K-form cation exchange resins for relevant metal cations. Two strong-acid polystyrene cation exchange resins of gel (C100) and macroporous (C150) structures were chosen to represent the most frequently used cation exchange resin properties, and the results of this work are expected to be directly transferable to similar cation exchange resins by different manufacturers. The specific objectives of this research were (1) to determine the separation factors for Ca^{2+}/K$^+$, Sr^{2+}/K$^+$, Ba^{2+}/K$^+$, Co^{2+}/K$^+$, and Cd^{2+}/K$^+$; (2) to evaluate the selectivity sequence, resin capacity, and adsorption behaviors that exist between resin and contaminants using isotherm models; and (3) compare available Na-form cation exchangers selectivity sequence and separation factors to K-form resins.

2. Materials and methods

2.1. Cation exchange resin

The properties of Purolite C150 and C100 resins are listed in Table 1. The two most prominent uses of these resins are for softening and demineralization. The resins were provided by the manufacturer in Na-form and were pre-conditioned using concentrated KCl solution at 25 times the equivalent capacity of each resin. A volume of 15 mL of resin was pre-conditioned on a Phipps and Bird PB-700 jar tester by mixing at 100 rpm for 24 h. The resins were rinsed with deionized (DI) water until conductivity was approximately 1 μS/cm, dewatered, and stored in a desiccator until use. The average density for each type of resin was determined by the triplicate measurements of desiccated dry mass per 2 mL of wet settled resin.

2.2. Chemical contaminants

The chemical contaminants used in this work were calcium chloride dihydrate (CAS# 10035-04-8, ACS grade, Fisher Scientific), barium chloride dihydrate (CAS# 10326-27-9, ACS grade, Acros Organics), strontium chloride hexahydrate (CAS# 10025-70-4, ACS grade, Acros Organics), cadmium chloride (CAS# 10108-64-2, ACS grade, Acros Organics), and cobalt chloride hexahydrate (CAS# 7791-13-1, ACS grade, Acros Organics). Synthetic solutions of 5 meq/L of Ca^{2+}, Ba^{2+}, Sr^{2+}, Cd^{2+}, and Co^{2+} were each prepared in 18.2 MΩ cm ultrapure water for individual batch experiments.

2.3. Batch equilibrium experiments

Batch experiments were done in triplicate using 125 mL of 5 meq/L synthetic solution at six resin doses of 5%, 25%, 50%, 100%, 150%, and 300%. The volume of resin that would be