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Selectivity of bicarbonate-form anion exchange for drinking water contaminants: Influence of resin properties

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ABSTRACT

Bicarbonate was investigated as a new counterion for six strong-base anion exchange resins considering the selective removal of six drinking water contaminants: nitrate, bromide, perchlorate, sulfate, chromate, and Suwannee River natural organic matter (SRNOM). The most selective bicarbonate-form resin for each contaminant was evaluated based on qualitative binary ion exchange plots and quantitative separation factor calculation. The influence of resin properties and ion characteristics was evaluated on resin selectivity for each contaminant. The type of functional group and polymer composition of the resin were shown to influence selectivity for inorganic contaminants, and the pore structure and polymer composition of resin were shown to influence selectivity for SRNOM. Bicarbonate-form resin with wide spacing of functional groups (i.e., triethylamine) and polystyrene composition was favorable for monovalent, hydrophobic contaminants, including nitrate, bromide, and perchlorate, whereas resin with close spacing of functional groups (i.e., trimethylamine) and polystyrene composition was favorable for relatively hydrophobic chromate and resin with same functional group and polyacrylic composition was favorable for relatively hydrophilic sulfate ion. For organic contaminant, bicarbonate-form resin with macroporous structure and polyacrylic composition was most selective for SRNOM. In addition, the resin selectivity sequence for each contaminant based on separation factor calculations was compared with adsorption isotherm parameters, and the similarities and differences are discussed. The separation factor method is based on ion exchange stoichiometry, whereas adsorption method is robust in terms of simplifying calculation.

1. Introduction

Ion exchange is a water treatment process in which the mobile counterion on the resin phase is stoichiometrically exchanged with contaminant ions in the aqueous phase. In drinking water treatment, anion exchange is used to remove regulated and problematic contaminants, such as nitrate, perchlorate, and natural organic matter (NOM) [1–3]. Other advantages of ion exchange include low capital cost and high efficiency at producing high quality water [4]. However, concentrated sodium chloride solution is required for regeneration of strong-base anion exchange resin, and thus the management of waste brine is a major challenge to implementing ion exchange, especially for areas that lack disposal options. The direct discharge of brine to land or surface water can lead to harmful impacts on plant growth and wildlife [5,6]. The discharge of brine to wastewater treatment plants requires a large dilution and can be adverse to biological treatment [7]. In order to improve the management of waste brine, an alternative salt for resin regeneration has been proposed to broaden the acceptable disposal options. Previous work has demonstrated the potential of using sodium bicarbonate for resin regeneration, and using bicarbonate-form resin for contaminant removal. The similar performance of using sodium bicarbonate and sodium chloride in terms of regeneration and contaminant removal was observed [8]. Moreover, the use of sodium bicarbonate for resin regeneration and bicarbonate-form resin for contaminant removal is beneficial both for waste disposal and treated water. Bicarbonate contributes alkalinity to natural water and it is also a benefit to biological wastewater treatment. For example, lack of alkalinity will prevent nitrification [9]. In addition, increasing alkalinity of treated water is beneficial to drinking water distribution systems by reducing certain types of corrosion [10,11].

Only a few studies have reported using sodium bicarbonate for resin regeneration and using bicarbonate-form resin for contaminant removal [8,12,13]. Bicarbonate-form magnetic ion exchange (MIEX) resin was previously compared with chloride-form MIEX resin with regard to its affinity, regeneration, and stoichiometry

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for sulfate, nitrate, and NOM (measured by dissolved organic carbon (DOC) and UV absorbance at 254 nm (UVA254)) [8]. The similar performance was demonstrated for both bicarbonate-form and chloride-form resins with respect to selectivity and regeneration. Moreover, the long-term DOC and bromide removal and regeneration was also investigated by using bicarbonate-form MIEX resin [12]. The chloride-form MIEX resin was used as a baseline for comparison. Both bicarbonate-form MIEX resin and chloride-form MIEX resin demonstrated similar trends for long-term regeneration. The maximum contaminant removal efficiency was achieved with virgin resin and contaminant removal decreased with increasing number of regeneration cycles. The contaminant removal sequence was the same for both bicarbonate-form and chloride-form MIEX resin. In another research, the regeneration efficiency of several different strong-base anion exchange resins was studied using different bicarbonate salts, namely sodium bicarbonate and potassium bicarbonate, and compared with chloride-form resin [13]. The regeneration efficiency of bicarbonate was higher than chloride for polyacrylic type resin, whereas it was lower for polystyrene type resin. Furthermore, the use of resin in bicarbonate form, hydroxide form, and chloride form, to exchange with chloride, nitrate, and sulfate was investigated with several selected adsorption isotherm models and thermodynamic models [14,15], and showed the Dubinin–Astakhov had the best data fitting among adsorption models and nonideal thermodynamic model had the best fitting than other models.

The previous studies have demonstrated the effectiveness of using sodium bicarbonate for resin regeneration and the potential of a few different bicarbonate-form resins, mostly MIEX resin, in terms of contaminant removal. Therefore, there remains a major gap in the literature pertaining to the treatment efficiency of bicarbonate-form resin across a range of resin types and contaminants. In this work, six strong-base anion exchange resins were selected to represent a wide range of resin properties. The interactions between these resins and six regulated and/or problematic drinking water contaminants were studied. The contaminants included nitrate, bromide, perchlorate, sulfate, chromate, and Suwannee River natural organic matter (NOM). Nitrate, perchlorate, and chromate (i.e., hexavalent chromium) were selected because of adverse effects on human health [16–18]. Bromide and Suwannee River NOM were selected because of their contribution to disinfection byproduct formation [19]. Lastly, sulfate was included in this study because it is a known competitor for ion exchange sites [20].

The goal of this research was to generate new data on anion exchange selectivity using bicarbonate as the mobile counterion for anion exchange removal of important drinking water contaminants. The specific objectives were to: (1) evaluate the effect of resin properties on selectivity of each contaminant; (2) determine the resin selectivity sequence for each bicarbonate-form resin based on separation factors and isotherm parameters; and (3) quantify contaminant removal as a function of resin type and resin dose. All data were generated using batch equilibrium experiments in which bicarbonate-form resin was mixed with synthetic water containing a single contaminant. The purpose of using synthetic contaminant solutions was to enable an isolated investigation of each contaminant's interactions with the selected resins and varying resin properties.

2. Materials and methods

2.1. Anion exchange resins

The resin properties of the six selected resins are listed in Table 1. All resins were obtained from the manufacturer in the chloride form. Resin density was calculated in triplicate by measuring 1 mL of wet settled resin in a graduated cylinder. Resin was dried in a desiccator at room temperature. Finally, dry mass was measured. Density was used for determination of the dry resin dose. All resins were converted from the chloride form to the bicarbonate form by mixing the resins in highly concentrated sodium bicarbonate solution. The concentration of sodium bicarbonate (CAS# 144558) was 25 times greater than the equivalent amount of anion exchange resin capacity. pH was measured to confirm that the bicarbonate ion was the dominant ion in solution. A jar test apparatus was used for conditioning the resin by mixing at 100 rpm for 24 h. After mixing, the resin was carefully rinsed with deionized (DI) water until the conductivity was ~1 μS/cm. The conditioned resins were stored in a desiccator to dry until used.

2.2. Chemical contaminants

The chemical contaminants used in this work were sodium nitrate (CAS# 7631994 ACS grade, Fisher Scientific), sodium bromide (CAS# 7647156, ACS grade, Fisher Scientific), sodium chromate (CAS# 7775113, ACS grade, Sigma Aldrich), sodium sulfate (CAS# 7757826, ACS grade, Fisher Scientific), sodium perchlorate (CAS# 7601890, ACS grade, Sigma Aldrich), and Suwannee River NOM (SRNOM, 1R101N, International Humic Substances Society). The synthetic contaminant solutions were prepared by dissolving 5 meq/L of each inorganic contaminant ion (0.24 meq/L Suwannee River NOM) in DI water. The concentration of 0.24 meq/L NOM was chosen to make the concentration of dissolved organic carbon (DOC) equal to 30 mg/L as C.

2.3. Batch equilibrium experiments

Batch equilibrium tests were conducted with various resin doses and each synthetic contaminant solution in 125 mL amber glass bottles. Resin doses were selected for all inorganic contaminants to theoretically achieve 5%, 25%, 50%, 100%, 150%, and 300% removal of the equivalent initial contaminant concentration. The calculation of percent resin dose was resin dose (meq/L) divided by initial contaminant concentration (meq/L), expressed as percent. For each resin dose, control samples included contaminant solution without resin (measured in duplicate) and all other samples were measured in triplicate. All samples were put on shaker table for 24 h at room temperature (approx. 22 °C). The shaker table was operated horizontally at 250 rpm. The pH of each sample was measured before and after the batch equilibrium test. After equilibrium, all samples were filtered through 0.45 μm membrane filters.

2.4. Analytical methods

Ion chromatography (IC) (Dionex 3000 equipped with AS22 guard column and analytical column) was used for analysis of nitrate, sulfate, bromide, perchlorate, and chloride. The IC method followed U.S. EPA method 300.1 [21]. Eluent was prepared as 4.5 mM Na_2CO_3/1.4 mM $NaHCO_3$ and filtered through 0.45 μm membrane filter before use. A chloride selective electrode (Thermo Orion) was used for analysis of chloride concentration in NOM batch test. Total organic carbon (TOC) analyzer (Shimadzu TOC-VCH) was used for analyzing dissolved inorganic carbon (DIC) and DOC. Bicarbonate concentration was calculated based on pH and DIC [22]. Inductively coupled plasma (ICP) (Thermo ICAP 6200) was used to analyze hexavalent chromium following U.S. EPA method 6010C [23]. Chemical standards were purchased and analyzed to assess the accuracy of the results, i.e., seven anion standard (Dionex) for IC, inorganic carbon and organic carbon standards (Ricca) for TOC analyzer, and hexavalent chromium standard