



# Fluoride and nitrate removal from brackish groundwaters by batch-mode capacitive deionization



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## ABSTRACT

Capacitive deionization (CDI) is an emerging water desalination technology in which pairs of porous electrodes are electrically charged to remove ionic species from water. In this work, the feasibility of fluoride and nitrate removal from brackish groundwaters by batch-mode CDI was investigated. Initially, the effects of flow rate, initial fluoride concentration, and initial coexisting NaCl concentration on fluoride removal were studied. The steady-state fluoride concentration declined as the initial fluoride concentration decreased while initial NaCl concentration remained constant. Due to the competitive electrosorption between fluoride and chloride for limited pore surface sites, a higher initial chloride concentration resulted in a higher equilibrium dissolved fluoride concentration. A simplified one-dimensional transport model for dual anions was developed and found to reliably describe the dynamic process of removal of both fluoride and chloride ions in CDI cells over a range of well-defined operating conditions. Based on the ability of the model to describe fluoride removal, it was extended to description of nitrate removal from brackish groundwaters and also found to perform well. Thus, the approach to description of ion removal, at least in batch studies, appears robust and should assist in optimization of design and operating conditions such that optimal removal of trace ionic species is achieved even when high background concentrations of salt are present.

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## 1. Introduction

While all waters contain anions, particularly chloride and sulfate, these species are not very troublesome provided the levels of salt present (i.e. the total concentrations of both anions and cations) are not excessive. Some anions, however, including fluoride and nitrate, can cause health problems. Fluoride ( $F^-$ ) pollution of groundwaters is particularly troubling with many subsurface waters, especially in South Asia, Africa and the Middle East, exhibiting excessive concentrations of this anion (Bhatnagar et al., 2011; Amini et al., 2008). The presence of  $F^-$  in drinking water is recognized to have either beneficial or harmful effects depending on the concentration and total amount ingested. An  $F^-$  level of 0.5–1.0 mg  $L^{-1}$  has beneficial effects on human teeth and bones, especially for young children, while excessive  $F^-$  levels ( $>1.5$  mg  $L^{-1}$ ) cause permanent bone and joint deformations, and dental or skeletal fluorosis (Liao and Shi, 2005; Fan et al., 2003). The presence of excessive concentrations of nitrate ( $NO_3^-$ ) in

groundwaters is also problematic as consumption of nitrate-contaminated groundwater might lead to methemoglobinemia in infants and alimentary canal cancers with the maximum  $NO_3^-$  concentration in drinking water stipulated to be 50 mg  $L^{-1}$  by the World Health Organization (Hirayama and Kamiya, 2014). Although several methods for removal of  $F^-$  or  $NO_3^-$  from water are available including adsorption, ion exchange, reverse osmosis and electro-dialysis (Jagtap et al., 2012; Bhatnagar and Sillanpää, 2011; Xu et al., 2012), these methods all suffer limitations of low efficiency and high operational cost, restricting their practical application.

Capacitive deionization (CDI) has been receiving increasing attention in recent years as a cost effective, energy efficient and environmental friendly electrochemical desalination technology with charged species removed from the aqueous phase on passing the source water through spacer channels located between positive and negative electrodes made from porous carbonaceous materials (Porada et al., 2013b). Although recent literature reports suggest that CDI, in addition to removing the major ions responsible for the brackish nature of the waters, is also effective in removing other ions present at low concentrations (Oren, 2008; Macias et al., 2014; Avraham et al., 2011b; Farmer et al., 1997; Huang et al., 2014; Li

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et al., 2010a; Lado et al., 2014), limited quantitative information is available in regard with the effectiveness of CDI in removing trace levels of specific ions (such as  $F^-$  and  $NO_3^-$ ) in the presence of higher concentrations of “major” ions.

The movement of ions from bulk solution to charged electrodes is termed ion electrosorption with several basic models developed to describe the dynamic electrosorption process in CDI cells. Jande and Kim (2013a, 2013b, 2014) proposed models both for CDI batch-mode and single-pass operation at constant charging voltage or constant charging current by using NaCl and compared the different responses obtained to the operating parameters. However, the models assumed unity charge efficiency and neglected electrical double layer (EDL) effects, which is a convenient simplification at the expense of reduced accuracy and the ability to model multiple ionic species. A simplified dynamic CDI transport model for batch-mode operation (Porada et al., 2013b) and a modified Donnan-based porous electrode theory for single-pass operation (Porada et al., 2013a) have been developed enabling reasonably accurate prediction of NaCl ( $Cl^-$ ) concentration as a function of time. In reality, however, typical solutions contain multiple anions rather than a single anion (such as  $Cl^-$ ). A Gouy–Chapman–Stern (GCS)-based porous electrode model (Biesheuvel et al., 2011) has been used to describe the uptake of ions from NaCl solution and subsequently extended to a scenario of mixtures of two cations and one common anion (Zhao et al., 2012; Biesheuvel et al., 2012). This model, however, was used to describe the concentration variation of ions within the electrodes rather than that in the effluent.

In this work, we develop a model for the electrosorption of  $F^-$  or  $NO_3^-$  in the presence of relatively high concentrations of NaCl with our approach based on the simplified transport model developed by Porada et al. (2013b) for dynamic electrosorption of a single anion ( $Cl^-$ ) in batch-mode CDI. This new model should assist in gaining fundamental understanding of the electrosorption process of co-existing anions, and enable prediction of the ion removal kinetics and equilibrium ion removal capacity when CDI is applied to brackish groundwater treatment. As such, the work described here should contribute to the optimization of parameter settings and improvement in performance of CDI when applied to source waters containing multiple contaminants exhibiting different concentration ranges.

## 2. Experimental section

### 2.1. CDI system

The CDI system used in this study (AQUA EWP, USA) and the schematic diagram of the inner structure of the CDI module are displayed in Figs. S1 and S2 in Supporting Information (SI), respectively. The CDI system consists of three CDI modules, which are connected electrically in series and in parallel with regard to fluid flow. Each CDI module contains 100 pairs of graphite sheets as current collectors, and 100 cell pairs consisting of activated carbon electrodes with total micropore (<2 nm) volume of approximately 160  $cm^3$  and projected surface area for one pair of 0.02  $m^2$ . The charging voltage between two carbon electrodes is set to  $V_{charge} = 1.6$  V. During discharge, simple short-circuit is used, i.e.,  $V_{discharge} = 0$  V. Each carbon electrode pair is separated by a non-conductive, porous polymeric material to prevent short circuit and to act as a spacer channel with thickness of 250  $\mu m$ . There are no ion exchange membranes in the system.

### 2.2. Experimental methods

The schematic diagram of the batch-mode CDI test procedure is shown in Fig. S3. The whole system consisted of a CDI system, a

recycling tank, a centrifugal pump (DAB Pumps S.p.A., Italy) with frequency controlled by a variable speed drive (Delta Electronics, Inc., Taiwan), a flowmeter (SCINTEX, Australia) and a digital electrical conductivity (EC) meter (F-54, HORIBA, Japan). The feed solution containing electrolytes was pumped from the recycling tank, passed through the CDI system where ion electrosorption took place, and then flowed back to the recycling tank. The total water volume in the system, excluding the recycling tank, was 7.7 L (see Section S2, SI). Prior to each experiment, the whole system was flushed to a baseline salinity of less than 30  $\mu S/cm$  using Milli-Q water with short circuit mode applied. The valve was then closed and the water in the recycling tank was drained and replenished with a certain volume of Milli-Q water. The initial feed solution with different ion concentrations was prepared by adding the appropriate amount of relevant chemicals and, subsequently, by thorough mixing at a charging voltage of zero volt as indicated by the steady readings of the EC meter. Analytical grade sodium chloride (NaCl), sodium fluoride (NaF) and sodium nitrate ( $NaNO_3$ ) were used for the preparation of CDI feed solutions. Next, the electrosorption experiments began with the power supply of the CDI system and pump turned on simultaneously, and ended when adsorption equilibrium was reached. Only the first adsorption step was studied, not a complete cycle involving both adsorption and desorption steps. The system was used for several months of discontinuous operation. Duplicate runs were carried out for each set of experimental conditions and the average value was plotted. The total dissolved solids (TDS) concentration was monitored using the EC meter in the recycling tank.

Experiments were conducted to investigate the effect of flow rate (4.6  $L\ min^{-1}$ , 7.5  $L\ min^{-1}$ , 10.5  $L\ min^{-1}$ ) on ion electrosorption, including  $Cl^-$  electrosorption with NaCl as the sole solute and  $F^-$  electrosorption (initial  $F^-$  concentration 20  $mg\ L^{-1}$ ) in the presence of an initial 2  $g\ L^{-1}$  NaCl. The total water volume in these studies was maintained at 11.7 L. For sole NaCl electrosorption, the variation of  $Cl^-$  concentration was determined from the conductivity reading. For the electrosorption of  $F^-$  and  $Cl^-$ , water samples were collected from the recycling tank at appropriate intervals, and  $F^-$  and  $Cl^-$  concentrations were measured using fluoride and chloride ion selective electrodes (Thermo Scientific, USA), respectively.

Electrosorption kinetics of  $F^-$  at different initial  $F^-$  concentrations (5.6  $mg\ L^{-1}$ , 10.4  $mg\ L^{-1}$ , 20.9  $mg\ L^{-1}$ , 27  $mg\ L^{-1}$ ) in the presence of an initial NaCl concentration of 2  $g\ L^{-1}$ , and at different initial NaCl concentrations (0.5  $g\ L^{-1}$ , 1.0  $g\ L^{-1}$ , 1.5  $g\ L^{-1}$ , 2.0  $g\ L^{-1}$ , 3.0  $g\ L^{-1}$ ) in the presence of an almost constant initial  $F^-$  concentration (approximately 20  $mg\ L^{-1}$ ) were studied at a liquid flow velocity of 4.6  $L\ min^{-1}$  with total water volume of 11.7 L.

For investigation of the electrosorption kinetics of  $NO_3^-$ , experiments were conducted at different initial  $NO_3^-$  concentrations (100  $mg\ L^{-1}$ , 300  $mg\ L^{-1}$ , 500  $mg\ L^{-1}$ ) in the presence of an initial NaCl concentration of 2  $g\ L^{-1}$ , and at different initial NaCl concentrations (1.5  $g\ L^{-1}$ , 2.0  $g\ L^{-1}$ , 3.0  $g\ L^{-1}$ ) in the presence of constant initial  $NO_3^-$  concentration (300  $mg\ L^{-1}$ ) at 4.6  $L\ min^{-1}$  with total water volume 11.7 L. Water samples were collected from the recycling tank at appropriate intervals, and  $NO_3^-$  concentration was determined using an ICS-3000 ion chromatograph (Dionex, USA).

## 3. Model derivation

In this section, the simplified one-dimensional (1D) dynamic CDI selective transport model for batch-mode (i.e., closed system) dual anion removal is developed according to the porous electrode approach used by Porada et al. (2013b). The ions are primarily adsorbed in electric double layers (EDLs) at the interface between the solid and the solution in the CDI electrodes. The porous CDI

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