Removal of co-existing fluoride, calcium, magnesium, and carbonates, by non-chemical induced electrolysis system for drinking and industrial purposes

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Abstract

An electrolysis (ELC) system was proposed to remove co-existing F\(^-\), Ca\(^{2+}\), Mg\(^{2+}\), CO\(_3\)\(^{2-}\), and HCO\(_3\)\(^-\) from groundwater without the addition of any chemicals. The proposed system utilized an ELC cell composed of non-corrosive platinum and stainless steel electrodes. Ion removal mechanisms, performance against different ion concentrations, and charge loading were studied and compared with drinking and industrial water quality guidelines. System performance with real groundwater was also examined. Results revealed that ELC effectively removes (CO\(_3\)\(^{2-}\) + HCO\(_3\)\(^-\)) in the anode as CO\(_2\), and (CO\(_3\)\(^{2-}\) + HCO\(_3\)\(^-\)), Ca\(^{2+}\), and Mg\(^{2+}\) in cathode as MgCO\(_3\), CaCO\(_3\), and Mg(OH)\(_2\). F\(^-\) was removed by co-precipitation with Mg(OH)\(_2\) and Coulomb transfer. Maximum removal of 58%-F\(^-\), 42%-Ca\(^{2+}\), and 95%-Mg\(^{2+}\) were observed at a charge loading of 1500 C/L. With increasing Ca\(^{2+}\) and Mg\(^{2+}\), removal increments of cathode F\(^-\), Ca\(^{2+}\), Mg\(^{2+}\), and (CO\(_3\)\(^{2-}\) + HCO\(_3\)\(^-\)) were noticed. To meet drinking water guidelines value of 1.5 mg/L of F\(^-\), initial ion concentration ranges should be within F\(^-\), 4.29–6 mg/L, Mg\(^{2+}\), 75–125 mg/L, Ca\(^{2+}\), 50 mg/L, and (CO\(_3\)\(^{2-}\) + HCO\(_3\)\(^-\)) < 10–0 mmol/L for 1500 C/L. The anode delivered the quality water which meets industrial boiler water alkalinity guideline for the initial (CO\(_3\)\(^{2-}\) + HCO\(_3\)\(^-\)) < 12.5 meq/L. The community-scale treatment system established in Sri Lanka confirmed smooth operation with a higher removal of F\(^-\) and Ca\(^{2+}\) in the cathode and (CO\(_3\)\(^{2-}\) + HCO\(_3\)\(^-\)) in the anode which can be slightly approximated with laboratory results.

Key words: calcium, carbonates, electrolysis removal, fluoride, groundwater, magnesium

INTRODUCTION

The usability of groundwater for domestic and industrial purposes depends upon the water quality. However, the quality of natural groundwater deteriorates day by day, mainly due to the change of natural conditions as well as human and industrial activities. Over the last two decades, fluoride (F\(^-\)) occurred by natural pathways was identified as a foremost groundwater contaminant and was reported in more than 20 countries worldwide (Meenakshi & Maheshwari 2006). As per estimates, 200–260 million people from various nations are at dire risk of fluorosis due to the consumption of groundwater abundant in F\(^-\) (Ayoob & Gupta 2006; Amini et al. 2008). The mineralogical nature of the aquifer material mainly controls the occurrence of F\(^-\) in groundwater. According to many studies, either Ca\(^{2+}\), Mg\(^{2+}\), HCO\(_3\), CO\(_3\)\(^{2-}\) (hardness- and alkalinity-causing
agents) ions, or a mixture of those ions have co-existed with F$^-$ ion (Kim & Jeong 2005; Rafique et al. 2009; Ketata et al. 2011; Rango et al. 2012; Salifu et al. 2012; Su et al. 2013; Singaraja et al. 2014; Wickramarathna et al. 2017; Karimi et al. 2018; Luo et al. 2018; Thapa et al. 2018). Even though co-existing Ca$^{2+}$, Mg$^{2+}$, CO$_3^{2-}$, and HCO$_3^-$ in drinking groundwater show a non-negative influence on human health, it impacts water palatability and causes scaling problems in both household and industrial equipment (Zhi & Zhang 2016). Therefore, not only F$^-$ but also co-existing Ca$^{2+}$, Mg$^{2+}$, CO$_3^{2-}$, and HCO$_3^-$ removal are essential to meet the standards for drinking and industrial water quality.

The most common technologies for removing coexisting F$^-$, Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$, and CO$_3^{2-}$ in industrial and drinking purposes are reverse osmosis (RO), nanofiltration (NF), ion exchange (IE), chemical treatment (CT), as well as two electrochemical methods, electrochemical precipitation (ECP) and electrodialysis (ELD) (Gascó & Méndez 2005; Gabrielli et al. 2006; Kuokkanen et al. 2013; Shen & Schafer 2014; Zhi & Zhang 2016; Janson et al. 2018). However, except for RO, NF, and ELD, the main disadvantage of IE, CT, and ECP methods are that they need to introduce extra chemicals or they release extra ions into the water during the treatment process. Besides, RO, ELD, and NF are complicated in technology, cost-ineffective, and quantity of water rejections are high. Therefore, RO, ELD, and NF are not suitable for water scarce regions and developing nations expecting lower unit costs for groundwater purification.

However, ECP technology, electrocoagulation (EC) overcomes the above problems. It attracts much attention as a process for removing coexisting Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$, CO$_3^{2-}$ as well as F$^-$ since EC operation can be performed with minimal cost and minimal chemicals introduction to the source water (Zeppenfeld 1998, 2011; Gabrielli et al. 2006; Zhi & Zhang 2016). However, the introduction of chemicals is the major drawback of EC since it affects the final water quality and operational costs. So far, none of the ECP or EC studies were found to avoid any chemical addition in F$^-$ or coexisting Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$, or CO$_3^{2-}$ removal. Therefore, developing an ECP or EC system without any chemical addition that removes coexisting F$^-$, Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$, and CO$_3^{2-}$ will be attractive to the scientific community. Moreover, it can be beneficial to developing nations seeking low-cost and effective technology to meet both industrial and drinking water quality guidelines.

Usually, ECP’s EC is performed in a communal cell reactor and using a high pH environment around the cathode to facilitate the removal of ions by coagulation. Dissociation of anode material provides a coagulation agent to the solution for Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$, CO$_3^{2-}$ as well as F$^-$ removal. Therefore, by using a communal cell EC reactor, as well as a corrosive anode, the chemical introduction cannot be controlled or terminate appropriately. However, by separating the anode and the cathode electrodes using a diaphragm (with simple electrolysis (ELC) cell configuration) and utilizing non-corrosive anode (platinum (Pt)) introduction of the chemical can be stopped. Also, ELC cell configuration allows the maintenance of adequate pH, prevent mixing the anode and the cathode solutes as well as the transference of positive and negative ion through a diaphragm similarly to ELD without any specific ion selectivity. Moreover, ELC ion-removal technologies were reported only a few times in our previous studies, and only for F$^-$ removal (Kawakami et al. 2018; Amarasooriya & Kawakami 2019).

Therefore, the main objective of this study was to explore the removal of co-existing F$^-$, Ca$^{2+}$, Mg$^{2+}$, CO$_3^{2-}$, and HCO$_3^-$ from groundwater by ELC. The system’s performance against charge loading and various initial concentrations of F$^-$, Ca$^{2+}$, Mg$^{2+}$, CO$_3^{2-}$, and HCO$_3^-$ were studied on a laboratory scale. The proposed system performance and stability were studied on a community scale as well in the northern part of Sri Lanka where the groundwater was highly contaminated with F$^-$, Mg$^{2+}$, and Ca$^{2+}$, and with HCO$_3^- +$ CO$_3^{2-}$ for drinking purposes.
MATERIAL AND METHODS

Experimental and field-scale ELC cell configuration

The ELC reactor design was adopted from our previous studies (Amarasooriya & Kawakami 2019). Accordingly, as an ELC reactor for the laboratory experiments, a tank made of transparent acrylic resin material was used (length 20 cm × height 10.2 cm × width 5 cm). The tank was divided into two equal volumes (effective volume 490 mL) cells with a 2 mm thick (effective area: 20 cm × 10.2 cm) commercial ceramic diaphragm F-C1 (Nikkato corp., Japan). This diaphragm helped to separate the anode solution from the cathode solution, facilitated the transference of ions between cells without any selectivity, and prevented the mixing of sludge formed in the cathode (Figure 1). To increase the length of the water flow, individual cells were further divided into two equal slots with an acrylic plate, keeping open 10 mm from the bottom. U-shaped stainless steel (SS) (Effective length = 30 cm, ϕ = 1.00 mm) and platinum (Pt) (effective length = 30 cm, ϕ = 0.40 mm) wires were used as electrodes for the cathode and the anode, respectively. The distance between electrodes was kept as 3.3 cm. The assembly was connected to a constant current power supply for all experiments, and inflow rates were kept at 10 mL/min for both the anode and the cathode in all experiments. The ELC system employed for the laboratory and field experiments is shown in Figure 2.

Figure 1 | Electrolysis cell configuration.

Figure 2 | Electrolysis System.
For the community-scale treatment system, series-connected two reactors made out of the same material similar to that of the laboratory experimental ELC reactor were utilized. The effective total volume of the anode and the cathode was 12 L (28 cm × 40 cm × 5.357 cm × 2) and equivalent with the laboratory scale system’s resident time (0.77 hr). U shaped Pt wires (30 cm × 2) and SS mesh (2 cm × 2 cm) with a size of 24 cm × 36 cm × 2 were used as anode and cathode electrodes, respectively.

Operational conditions, sample collection, and storage

For the experiments, a series of $\text{F}^-$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, and $(\text{HCO}_3^- + \text{CO}_3^{2-})$ spiked tap water (hereafter initial concentrations will be denoted as $\text{F}_0$, $\text{Mg}_0^{2+}$, $\text{Ca}_0^{2+}$, and $(\text{HCO}_3^- + \text{CO}_3^{2-})_0$) was used as synthetic groundwater. The initial ion concentrations were selected so that it exceeds the Sri Lankan and WHO recommended drinking water guideline values. By applying a constant current to the immersed SS and Pt electrodes, synthetic groundwater was pumped continuously to the ELC reactor anode and cathode. Electrolysis time (Current applied for unit flow rate ampere per (liter per second) = (A/(L/s))) or charge loading (coulomb per liter = C/L) are the key parameters that affected ion removal efficiencies. Accordingly, by changing the applied current, different charge loadings were applied to the system. The initial ion concentrations, flow rates and the applied charge loading for the various experiments were summarized in Table 1.

A groundwater source located in Sri Lanka’s Medawachchiya area (8°32’02.8″N 80°29’57.6″E) of the Anuradhapura District was selected for the field study. Samples were collected after three hours of system stabilizing time form ELC reactor anode and cathode outlets. The Anode and the Cathode pH stability was considered for the system stabilization point determination. Both water samples from the field and the laboratory were filtered with 0.45 μm pores membrane filter to eradicate bacteriological activities affecting the water quality and to remove non-dissolved particles. Collected samples from the field and laboratory were stored into 50 mL polyethylene bottles on location and analyzed within the 45 days of their collection in Japan. For the isotherm experiments, precipitates in the cathode of the ELC was filtered and dried at 70 °C for 4 hours. Dried samples were weighed and transferred to the 50 mL polyethylene tubes containing 10 mg/L F$^-$ solution. Samples were then shaken in an electrical shaker for 0.77 hours (similar to the resident time of the cathode). After 0.77 hours, samples were filtered with a membrane filter with 0.45 μm pores to the 50 mL polyethylene bottles until the analysis was performed.

Chemicals and instruments

Chemicals purchased from Wako Chemicals from Japan were used for preparing artificial groundwater. The platinum electrode for anode was bought from the Nilaco Corporation, Japan, and a stainless steel electrode for cathode was purchased from the local market in Japan. Anions were analyzed using an ion chromatograph (Thermo ICS-2000; Thermo Scientific, USA) with separation column (IonPac AS18; Thermo Scientific, USA) and eluent: KOH 25–40 mmol/L gradient was used. Cations were analyzed using an ion chromatograph (Thermo ICS-1500; Thermo Scientific, USA) with separation column (Ion Pac CS12 Thermo Scientific, USA) and eluent (MSA 30 mmol/L isocratic; Thermo Scientific, USA) was used. The calibration standard solution after every 20 samples was analyzed for the observation of the stability of the ion chromatographic detector. If the overall concentration variability of the examined calibration standard solution was not below 5%, a re-analysis of the samples and standards were performed. X-ray diffraction (XRD) analysis of the precipitates was performed with a RIGAKU MiniFlex (Japan) machine equipped with CuK-Alpha radiation (configuration: 2 theta/min 30 KV, 15 mA (450 W)).
| Laboratory conditions | Initial Concentrations | Inflow rate (mL/min) | Outflow rate (mL/min) |
|-----------------------|------------------------|----------------------|----------------------|
| **Versus ion Removal/Experiment** | **Charge loading (C/L)** | **Current (A)** | **F⁻ (mg/L)** | **Mg²⁺ (mg/L)** | **Ca²⁺ (mg/L)** | **HCO₃⁻ + CO₃²⁻ (mmol/L)** | **Anode** | **Cathode** | **Anode** | **Cathode** |
| Charge loading         | 0–1500                 | 0–0.25               | 10                  | 100                | 100                | 10                  | 10      | 10      | 10      | 10      |
| Anode flow rate        | 1500                   | 0.25                 | 10                  | 100                | 100                | 10                  | 10      | 10      | 10      | 10      |
| Mg²⁺                  | 1500                   | 0.25                 | 5–20                | 100                | 100                | 10                  | 10      | 10      | 10      | 10      |
| Ca²⁺                  | 1500                   | 0.25                 | 10                  | 0–125              | 100                | 10                  | 10      | 10      | 4–10    | 14–10   |
| (HCO₃⁻ + CO₃²⁻)₀      | 1500                   | 0.25                 | 10                  | 100                | 0–125              | 10                  | 10      | 10      | 8–10    | 12–10   |
| **Field conditions**   |                        |                      |                     |                    |                    |                     |         |         |         |         |
| Average               | 1324                   | 5.74                 | 2.71                | 130.8              | 54.7               | 13.8                | 260     | 260     | 260     | 260     |
pH measurements were conducted with the glass electrode method (Orion Star A324; Thermo Scientific, USA). Voltage logging for calculating applied current and charge loading in a community-scale treatment system was performed with a data logger (ONSET, HOBO). As a power source, a constant voltage power supply (max 10 A) was used.

RESULTS AND DISCUSSION

Process description and ion removal mechanisms

As electrolysis proceeded, $\text{H}^+$ ions produced in the anode cell create a low pH environment (Equation (1)) while $\text{OH}^-$ ions produced in the cathode cell and caused a high pH environment (Equation (4)). In the anode, $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ should be removed as carbon dioxide by reacting with $\text{H}^+$ (Equations (2) and (3)). The majority of ions could be removed in the cathode by reacting either with $\text{CO}_3^{2-}$ or $\text{OH}^-$ (Equations (5)–(9)).

The anode reactions:

$$
\text{H}_2\text{O}(l) \rightarrow \frac{1}{2} \text{O}_2(g) + 2\text{H}^+(aq) + 2e^- \tag{1}
$$

$$
\text{HCO}_3^-(aq) + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3(aq) \rightarrow \text{CO}_2(g) \uparrow + \text{H}_2\text{O}(l) \tag{2}
$$

$$
\text{CO}_3^{2-}(aq) + 2\text{H}^+ \rightarrow \text{CO}_2(g) \uparrow + \text{H}_2\text{O}(l) \tag{3}
$$

The cathode reactions:

$$
2\text{H}_2\text{O}(l) + 2e^- \rightarrow 2\text{OH}^-(aq) + \text{H}_2(g) \tag{4}
$$

$$
\text{HCO}_3^-(aq) + \text{OH}^- \rightleftharpoons \text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \tag{5}
$$

$$
\text{CO}_3^{2-}(aq) + \text{Ca}^{2+}(aq) \rightleftharpoons \text{CaCO}_3(s) \downarrow \tag{6}
$$

$$
\text{CO}_3^{2-}(aq) + \text{Mg}^{2+}(aq) \rightleftharpoons \text{MgCO}_3(s) \downarrow \tag{7}
$$

$$
\text{Mg}^{2+}(aq) + 2\text{OH}^-(aq) \rightleftharpoons \text{Mg(OH)}_2(s) \downarrow \tag{8}
$$

$$
\text{Ca}^{2+}(aq) + 2\text{OH}^-(aq) \rightleftharpoons \text{Ca(OH)}_2(s) \downarrow \tag{9}
$$

To verify the described removal mechanisms in the cathode, XRD analysis was performed for the precipitates collected from the cathode for charge loading of 1500, 1250, and 1000 C/L. The XRD pattern showed only the presence of $\text{CaCO}_3$, $\text{MgCO}_3$, and $\text{Mg(OH)}_2$ (Figure 3). According to the peak intensities; the predominant mineral phase of $\text{CaCO}_3$ was calcite; nevertheless, the aragonite mineral phase was found significantly. In comparison, the peak intensities of $\text{CaCO}_3$ and $\text{MgCO}_3$ decreased with decreasing charge loading; thus, crystallinity seems to be reduced due to the formation of $\text{Mg(OH)}_2$.

Due to the higher pH environment in the cathode, $\text{Mg}^{2+}$, $\text{F}^-$, $\text{Ca}^{2+}$, and ($\text{HCO}_3^- + \text{CO}_3^{2-}$) ions start precipitating, which could be involved in removing $\text{F}^-$ (Equations (10)–(13)). Moreover, the applied current-generated Coulomb’s force could be an advantage for ion transfer between the cathode and the anode. Accordingly, plausible $\text{F}^-$ removal mechanisms can be presented as
Equations (11)–(13)

\[ x\text{Mg}^{2+}(aq) + (2z - y)\text{OH}^- (aq) + y\text{F}^- (aq) \rightarrow \text{Mg}_x\text{F}_y(\text{OH})_{2z-y}(s) \] (co precipitation) \hspace{1cm} (10)

\[ \text{Mg}^{2+}(aq) + 2\text{F}^- (aq) \xrightarrow{k_{sp} = 5.16 \times 10^{-11}} \text{Mg}(\text{F})_2(s) \] \hspace{1cm} (11)

\[ \text{Ca}^{2+}(aq) + 2\text{F}^- (aq) \xrightarrow{k_{sp} = 3.45 \times 10^{-11}} \text{Ca}(\text{F})_2(s) \] \hspace{1cm} (12)

\[ (\text{Ca.Mg})(\text{CO}_3)_2(s) + x\text{F}^- (aq) \xrightarrow{\text{adsorption}} (\text{Ca.Mg})(\text{CO}_3)_2+x\text{F}_x + x\text{CO}_2 \] \hspace{1cm} (adsorption) \hspace{1cm} (13)

The absence of MgF$_2$ and CaF$_2$ peaks in XRD (Figure 3) revealed that fluoride could be removed by either adsorption or co-precipitation, with predominantly formed CaCO$_3$, MgCO$_3$, and Mg(OH)$_2$. Turner (2005) reported that CaCO$_3$ has a high affinity for removing F$^-$ ion by surface adsorption dependent on the CaCO$_3$ surface area. Furthermore, Masindi (2015) investigation suggested that cryptocrystalline MgCO$_3$ could effectively remove F$^-$ by adsorption (Turner et al. 2005; Masindi et al. 2015). However, ELC experiments cathodes maintained high pH values than that of those studies; therefore, the possibility of adsorptive F$^-$ removal was verified with adsorptive experiment.

Precipitates generated in the absence of F$^-$ under the experiment conditions (listed in Table 1) were collected, and adsorption isotherm was performed with F$^-$ water (Figure 4). The Freundlich isotherm was found to be the best fit for the results. In Figure 4, C is F$^-$ concentration in the solution expressed in a unit of mg/L. Q is the adsorption capacity (mg/g) at a specific concentration of F$^-$ ion. According to the Freundlich isotherm, the F$^-$ adsorption capacity was 0.60 mg/g at the F$^-$ concentration of 3.52 mg/L. By assuming total Ca$^{2+}$ and Mg$^{2+}$ (107.2 and 65.62 mg/L; Section ‘Effect of charge loading on ion-removal efficiencies’ Figure 5(a), removal at 1500 C/L) were removed either as CaCO$_3 +$ MgCO$_3$ or CaCO$_3 +$ Mg(OH)$_2$, as well as F$^-$ was removed only by adsorption (4.88 mg/L; Figure 5(a), removal at 1500 C/L), F$^-$ adsorption capacity by (CaCO$_3 +$ MgCO$_3$) and (CaCO$_3 +$ Mg(OH)$_2$) can be calculated as 8.15 and 9.42 mg/g respectively. These calculated adsorptive values were much higher than the Freundlich isotherm, given the F$^-$ adsorption capacity of 0.60 mg/g. Therefore, it can be concluded that the fraction of F$^-$ adsorbed by a mixture of CaCO$_3$, MgCO$_3$, and Mg(OH)$_2$ was not
**Figure 4** | Freundlich isotherm for the precipitate collected from ELC without F⁻.

**Figure 5** | Influence of the charge loading in the electrolytes on the ion removal and pH. (a) Cathode, (b) Anode, (c) pH variation; F₀ = 10 mg/L, Ca²⁺₀ = 100 mg/L, Mg²⁺₀ = 100 mg/L, and (HCO₃⁻ + CO₃²⁻)₀ = 10 mmol/L.
significant. Therefore, another precipitative F⁻ removal mechanism should be incorporated to remove the F⁻.

Kawakami (2018) proposed that F⁻ co-precipitation occurred by Mg(OH)₂ (Kawakami et al. 2018). Besides, previous studies of the de-fluoridation of water using nano-magnesium oxide suggested that F⁻/C₀ exchange between Mg(OH)₂'s OH⁻ and F⁻ could take place due to the isoelectric nature and the similar radius of F⁻ and OH⁻ ions (Devi et al. 2012; Oladoja et al. 2016), and the co-precipitation mechanism for F⁻ removal by Mg(OH)₂ was proposed by Devi et al. (2012). Accordingly, F⁻ removal mainly took place by co-precipitation with Mg(OH)₂ other than the adsorption to the CaCO₃ + MgCO₃, and by Coulomb force transfer to the anode.

**Effect of charge loading on ion-removal efficiencies**

After three hours of ELC stabilizing time, flow through the diaphragm was found to be negligible, and ion removal percentages were calculated without further corrections. Due to the diprotic nature of carbonic acid (H₂CO₃) in the solution, both CO₃²⁻ and HCO₃⁻ exist, and their concentrations change with the solution’s pH. Therefore, the sum of the carbonate (HCO₃⁻ and CO₃²⁻) concentrations (hereafter (HCO₃⁻ + CO₃²⁻)) as mmol/L accounts for the alkalinity. The charge of water samples' (HCO₃⁻ + CO₃²⁻) was calculated by accounting for the system's ion charge balances. Trace ion concentrations were neglected, and the calculation focused on major ions in Equation (14). For calculating HCO₃⁻ and CO₃²⁻ concentrations as mmol/L, as described in Equations (19) and (18), the carbonates' charge balance equation (Equation (15)) and HCO₃⁻ ↔ CO₃²⁻ equilibria (Equations (16) and (17)) were employed. The K₂ = 4.69 × 10⁻¹¹ (mol/L) (value was taken from the findings of Plummer & Busenberg (1982) study's).

\[ T_C = \text{Total charge of CO}_3^{2-} \text{ and HCO}_3^- = (\text{the sum of cation charge} - \text{the sum of anion charge except for CO}_3^{2-} \text{ and HCO}_3^-) \]

\[ (\text{eq/L}) \]

\[ (\text{eq/L}) \]

\[ (\text{eq/L}) \]

\[ \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} \text{ equilibria:} \]

\[ \text{HCO}_3(aq) \rightleftharpoons \text{CO}_3^{2-} \text{ (aq)} + \text{H}^+(aq) \] (16)

\[ K_2 = \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \] (17)

By rearranging Equation (17),

\[ \text{CO}_3^{2-} = \frac{K_2 \times [\text{HCO}_3^-] 	imes 10^3}{[\text{H}^+]} \text{ (mol/L)} \] (18)
By substituting CO$_3^{2-}$ in Equation (15) for Equation (18),

$$\text{HCO}_3^- = \frac{T_C \times 10^3}{1 + \left( \frac{2K_2}{[H^+]} \right)} \text{ (mol/L)} \quad (19)$$

Figure 5 shows the effect of charge loading (0–1500 C/L) on ion removal and related pH under the initial conditions described in Table 1. According to that plot, the highest F$^-$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, and (HCO$_3^-$ + CO$_3^{2-}$) removal efficiencies 65, 96, 44, 36, and 45%, respectively were achieved at 1500 C/L charge loading in the cathode. Hence, for further experiments, 1500 C/L was selected. According to the cathode ion removal, higher charge loading resulted in removing F$^-$, Mg$^{2+}$, Ca$^{2+}$, and Cl$^-$ positively and Na$^+$ negatively from the cathode. The ELC reactor generates an electric field between its electrodes; thus, charged particles experience a force (hereafter Coulomb force) according to Coulomb's law, which results in the movement of ions. Therefore, Na$^+$ was transferred by Coulomb forces to the cathode from anode which caused negative removal in the anode. Na$^+$ removal in the anode showed positive removal since it transferred to the cathode. The positive removal of the Cl$^-$ ions in the cathode was obviously due to transfer by Coulomb force to the anode, which can be seen in Figure 5(b) as a negative removal in the anode. However, the difference between Cl$^-$ removal in the cathode and the anode was non-negligible and increased from 1–7% for 250 to 1500 C/L, respectively. With ion chromatographic analysis, the presence of the OCl$^-$ ion was confirmed. Usually, Cl$_2$(g) react with water molecules and form the Hypochlorous acid (HOCl) which was added advantages to the ELC system since it can disinfect the water. Accordingly, Cl$^{-}$ should be removed as Cl$_2$(g) in the anode, which caused a 1–7% difference between Cl$^-$ removal in the cathode and the anode.

Due to the electron acquisition for Cl$_2$(g) generation, H$^+$ and OH$^-$ production was evidently reduced in the ELC reactor. Calculated OH$^-$ and H$^+$ based on the introduced charge loading (Equation (20)) and based on the Mg(OH)$_2$ precipitated, and the CO$_3^{2-}$ and CO$_2$ formed are shown in Table 2. According to the results, OH$^-$ and H$^+$ concentrations calculated in both ways were very similar except for the 1500 C/L charge loading. The Coulomb force transfer of H$^+$ and OH$^-$ between anode and cathode resulted in neutralization and caused this deviation. Moreover, H$^+$ and OH$^-$ concentrations calculated based on Mg(OH)$_2$ precipitated and CO$_3^{2-}$ and CO$_2$ formed were very similar in anode and cathode, exhibiting a slight increment for the charge loading of 1250–1500 C/L. The increase of Coulomb forces contributes to high H$^+$, and OH$^-$ neutralization could be the reason. On the other hand, an increase in the charge loading >1250 C/L slightly affects

| Charge Loading (C/L) | Calculated with Equation (20) (mol/L) | Calculated with experimental results (mol/L) |
|----------------------|--------------------------------------|--------------------------------------------|
| Cl$^-$ removed       | H$^+$                                | OH$^-$                                    |
| 250                  | 0.00070                              | 0.0019                                    |
| 500                  | 0.00088                              | 0.0043                                    |
| 750                  | 0.00107                              | 0.0067                                    |
| 1000                 | 0.00104                              | 0.0093                                    |
| 1250                 | 0.00116                              | 0.0118                                    |
| 1500                 | 0.00092                              | 0.0146                                    |

H$^+$ and OH$^-$ calculated with Equation 20 and experimental results
the removal of Mg\(^{2+}\) and F\(^{-}\) ions.

\[
\frac{\text{Charge Loading (}\frac{C}{L}\text{)}}{\text{Faraday constant (96485.33)}(C/\text{mol})} = \frac{\text{Total Cl removed from both anode and cathode (}\frac{\text{mol}}{L}\text{)}}{\text{OH}^-/H^+ \text{ introduced (}\frac{\text{mol}}{L}\text{)}}
\]  

According to Figure 5(a), removal of (HCO\(_3\)\(^{-}\) + CO\(_3\)\(^{2-}\)) increased marginally over the increasing charge loading, likely transferred to the anode by Coulomb force. The increase in the removal of Mg\(^{2+}\), Ca\(^{2+}\) and (HCO\(_3\)\(^{-}\) + CO\(_3\)\(^{2-}\)) with increasing charge loading in the cathode occurred due to the increased in OH\(^{-}\) production. Mainly, groundwater was used as boiler water in industrial requirements. American Boiler Manufacturers Association (ABMA) and the Japan International Cooperation Agency’s alkalinity guideline for boiler water was 50–400 mg/L and 1–8 meq/L as CaCO\(_3\) (Electric Power Development Co. et al. 2013). Safe levels of F\(^{-}\), Mg\(^{2+}\), Ca\(^{2+}\), and HCO\(_3\)\(^{-}\) + CO\(_3\)\(^{2-}\) recommended by the World Health Organization (WHO)’s guidelines for drinking water were 1.5, 50, 75 mg/L, and 6.1 mmol/L, respectively. According to the results, maximum removal (at a charge loading of 1500 C/L) was only good enough to remove Ca\(^{2+}\) and HCO\(_3\)\(^{-}\) + CO\(_3\)\(^{2-}\) from the cathode to meet the guideline value for drinking water. However, HCO\(_3\)\(^{-}\) + CO\(_3\)\(^{2-}\) reduced in the anode was able to meet both industrial and drinking water quality guidelines. However, depending on the initial water quality and the expected guideline values, either anode water or cathode water should be discarded. To minimize the discarding water quantity, flow rate vs. ion removal was examined in detail, as discussed in section ‘Effect of the anode flow rate on ion removal’.

**Effect of the anode flow rate on ion removal**

To minimize the rejected water quantity and to find the best ion removals, the anode outflow rate variation with a constant cathode outflow rate was studied under Table 1 conditions. Figure 6 illustrates the removal of ions in the cathode (Figure 6(a)), those in the anode (Figure 6(b)), and pH variations in the anode and the cathode (Figure 6(c)). According to Figure 6(a), the removal of Ca\(^{2+}\), Mg\(^{2+}\), and HCO\(_3\)\(^{-}\) + CO\(_3\)\(^{2-}\) reached its maximum in 10, 15, and 15 mL/min of the anode flow rates, respectively. Fluoride removal reached its maximum at the anode flow rate of 20 mL/min. However, with increasing anode flow rate 5–20 mL/min, F\(^{-}\) removal increased marginally due to the slight removal increment of Mg\(^{2+}\). With increasing anode flow rate, the charge loading and H\(^{+}\) generation in the anode decreases, resulting in CO\(_2\) generation decrease as well as decrees of OH\(^{-}\) neutralizing in the cathode. That causes the HCO\(_3\)\(^{-}\) + CO\(_3\)\(^{2-}\) removal decrees in the anode as well as the slight removal increment of Mg\(^{2+}\) in the cathode. Accordingly, the anode flow rate around 10 mL/min was found better for maximizing the F\(^{-}\), Mg\(^{2+}\), and Ca\(^{2+}\) removal in the cathode, and (HCO\(_3\)\(^{-}\) + CO\(_3\)\(^{2-}\)) removal in the anode by minimizing the rejected water quantity. Therefore, the anode flow rate of 10 mL/min was selected for further experiments.

**Effect of initial F\(^{-}\) concentration on ion removal**

Removal of the F\(^{-}\) is crucial for the drinking water treatment, and this section describes the effect of initial F\(^{-}\) (F\(_0\)) concentration on F\(^{-}\) and other ion removals. After three hours of ELC time, flow through the diaphragm was found negligible, and ion removal percentages were calculated without concentration correction. As shown in Figure 7(a), removal of F\(^{-}\) decreased slightly from 66% to 58% as F\(^{-}\) increased presumably, due to the F\(^{-}\) co-precipitation increment.
The higher concentration of $F_0$ ion, which replaces $OH^-$ ion in the precipitate due to increased competition between $OH^-$ and $F^-$ due to the similar radius, causes an increment of $F^-$ ion co-precipitation. The same observation was described in Kawakami et al. (2018) study. Furthermore, the coulomb transfer of $F^-$ to the anode was noticed and found constant over the increasing $F_0$ due to no change of the charge loading (Figure 7(b)). Also, no significant change in the removal rates of, $Ca^{2+}$, $Mg^{2+}$, $(HCO_3^- + CO_3^{2-})$, $Na^+$ and $Cl^-$, and no pH changes were observed in both the anode and the cathode with increasing $F_0$ obviously, due to no change in applied charge loading. According to the $F^-$ removal trend in the cathode, $F^-$ removal for $F_0 < 5$ mg/L will not be reduced by less than 66%. By accounting 66% removal of $F^-$, maximum $F_0$ which can be treated to meet the drinking water quality guideline, can be calculated. Accordingly, a maximum of 4.29 mg/L $F_0$ can be treated to meet the WHO guideline of 1.5 mg/L. However, the calculated value was valid only for the initial
The Mg\(^{2+}\) (Mg\(_0^{2+}\)) concentration of 100 mg/L used in this experiment. For lower Mg\(_0^{2+}\), the same removal percentage may be possible. Therefore, the effect of Mg\(_0^{2+}\) on F\(^{-}\) removal is studied in detail in section 'Effect of the initial Mg\(^{2+}\) concentration on ion removal'.

**Effect of the initial Mg\(^{2+}\) concentration on ion removal**

This section describes the effect of the initial Mg\(^{2+}\)(Mg\(_0^{2+}\)) concentration (0–125 mg/L) on ELC ion removal under the experimental conditions described in Table 1. After three hours of system stabilization, flow through the diaphragm was observed as 4.20, 3.66, 3.16, 1.99, 0, and 0 mL/min from the anode to the cathode, respectively, for Mg\(_0^{2+}\) concentrations of 0, 25, 50, 75, 100, and 125 mg/L. Accordingly, the removal percentage was calculated by accounting the inflow weight and outflow weight of the elements.

According to Figure 8(a) and 8(b), it is clear that even in the absence of Mg\(^{2+}\), F\(^{-}\) was removed from the cathode by both precipitation(6.9%) (adsorbed to the CaCO\(_3\)) and Coulomb's transfer to the anode (19.4%). For Mg\(_0^{2+}\) > 50 mg/L, the removal of F\(^{-}\) increased sharply and became mostly
steady (58–67%) in the range of Mg\(^{2+}\) 75–125 mg/L. Since OH\(^-\) was limited in the reactor, the increase of Mg\(^{2+}\) removal (Mg\(^{2+}\) – Mg\(^{2+}\)) varies slightly according to the solubility product calculation \((\text{Mg}^{2+}) = \frac{\text{KSp}}{(\text{OH}^-)^2}\). However, even in the highest Mg\(^{2+}\) concentration, the system was unable to remove sufficient F\(^-\) to meet the WHO guideline. Therefore, both Mg\(^{2+}\) and F\(^-\) concentrations in groundwater, as well as applied charge loading, should be balanced to meet guideline values. However, with the above limitations and results, minimal Mg\(^{2+}\) required to treat F\(^-\) solution to meet the WHO guideline.

With increasing Mg\(^{2+}\) in the cathode, the removal of (HCO\(_3\)\(^-\) + CO\(_3\)\(^{2-}\)) was increased gradually and reached a maximum of 45% while (HCO\(_3\)\(^-\) + CO\(_3\)\(^{2-}\)) removal in the anode was increased marginally (Figure 8(a) and 8(b)). This is clear evidence that the amount of MgCO\(_3\) formed in the cathode increased with increasing charge loading. However, lower removal of (HCO\(_3\)\(^-\) + CO\(_3\)\(^{2-}\)) in the cathode for lower Mg\(^{2+}\) restricted the system’s usability for (HCO\(_3\)\(^-\) + CO\(_3\)\(^{2-}\)) removal for drinking purpose. The higher removal efficiency of (HCO\(_3\)\(^-\) + CO\(_3\)\(^{2-}\)) in the anode even at lower Mg\(^{2+}\) concentration,
proves that anode treated water the anode even at lower $\text{Ca}_2^{2+}$ concentration, proves that anode treated water meets both industrial and drinking water quality guidelines.

**Effect of initial $\text{Ca}^{2+}$ concentration on ion removal and related pH**

This section describes the effect of the $\text{Ca}^{2+}$ concentration on the ion removal under the conditions described in Table 1. After three hours of stabilizing time, the anode and the cathode water out-flow rates were measured. It was found that 2.40, 1.99, 0.51, 0.24, 0, and 0 mL/min flowed through the diaphragm from the anode to the cathode for the initial $\text{Ca}^{2+}$ concentrations of 0, 25, 50, 75, 100, and 125 mg/L, respectively. Accordingly, the removal percentage was calculated by accounting for the inflow weight and the outflow weight of the elements for a better comparison. The calculated removal rates against increasing initial $\text{Ca}^{2+}$ concentrations are illustrated in Figure 9(a) and 9(b) for the cathode and the anode, respectively. Figure 9(c) shows the pH levels in the anode and the cathode for different $\text{Ca}_2^{2+}$ concentrations. No significant

![Figure 9](https://iwaponline.com/h2open/article-pdf/doi/10.2166/h2oj.2020.022/653766/h2oj2020022.pdf)
fluctuation of pH was observed with increasing Ca\textsubscript{2+} in both the anode and the cathode (Figure 9(c)) ensuring the no effect of the Ca\textsubscript{2+} for OH\textsuperscript{-} and H\textsuperscript{+} consuming reactions were negligible.

According to Figure 9(a), the removal of F\textsuperscript{-} and Mg\textsuperscript{2+} increased marginally for Ca\textsubscript{2+} < 50 mg/L and maximized after Ca\textsubscript{2+} > 50 mg/L. Accordingly, the addition of Ca\textsubscript{2+} (0–50 mg/L) contributed to the increment of F\textsuperscript{-} removal up to 24% (39–63%). On the other hand, with increasing Ca\textsubscript{2+} (0–50 mg/L), removal of F\textsuperscript{-} increased negatively by 11% (–12% to –23%) in the anode by transferring via the Coulomb force. Hence, the contribution of the Ca\textsubscript{2+} increment from 0 to 50 mg/L for F\textsuperscript{-} removal was approximately 13%. By accounting for the findings discussed in section ‘Effect of initial F\textsuperscript{-} concentration on ion removal’ and this section, for Ca\textsubscript{2+} >50 mg/L and F\textsuperscript{-0} < 4.29 mg/L, the WHO guideline level of F\textsuperscript{-} for drinking purposes was attainable in the cathode. According to Figure 9(b), a slight increase in (HCO\textsubscript{3} + CO\textsubscript{3})\textsuperscript{2-} removal in the cathode was observed above the increase in Ca\textsubscript{2+}. Obviously, this has resulted in an increase in the formation of CaCO\textsubscript{3} above the increase in Ca\textsubscript{2+} (Lin & Singer 2009). Moreover, the removal of (HCO\textsubscript{3} + CO\textsubscript{3})\textsuperscript{2-} in the cathode increased from 2.4 to 46% (Figure 9(b)). Higher removal efficiency (more than 90%) of (HCO\textsubscript{3} + CO\textsubscript{3})\textsuperscript{2-} in the anode even at lower Ca\textsubscript{2+} concentration, proves that anode treated water meets both industrial and drinking water quality guidelines.

**Effect of the initial HCO\textsubscript{3} + CO\textsubscript{3}\textsuperscript{2-} concentration on ion removal and related pH**

From the previous section ‘Effect of charge loading on ion-removal efficiencies, Effect of the anode flow rate on ion removal, Effect of initial F\textsuperscript{-} concentration on ion removal, Effect of the initial Mg\textsuperscript{2+} concentration on ion removal and Effect of initial Ca\textsuperscript{2+} concentration on ion removal and related pH’ data, the presence of HCO\textsubscript{3} + CO\textsubscript{3}\textsuperscript{2-} significantly alters the removal of Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, and F\textsuperscript{-}. HCO\textsubscript{3} + CO\textsubscript{3}\textsuperscript{2-} directly involved for the OH\textsuperscript{-} and H\textsuperscript{+} acquisition reactions (Equations (3) and (4)). Therefore, for detail investigation, ion removal at different initial concentrations of (HCO\textsubscript{3} + CO\textsubscript{3})\textsuperscript{2-} was studied at 1500 C/L by following the experimental conditions listed in Table 1. The water flow through the diaphragm from the anode to the cathode was found negligible. The calculated removal percentages of ions in the cathode, the anode, and pH values are shown in Figure 10(a)–10(c), respectively. In the absence of HCO\textsubscript{3} + CO\textsubscript{3}\textsuperscript{2-}, the removal of F\textsuperscript{-} and Mg\textsuperscript{2+} increased to 70% in the cathode. The removal of 70% can be observed. Generated OH\textsuperscript{-} was used only for the formation of Mg(OH)\textsubscript{2}. Equal positive and negative removal percentages of Ca\textsuperscript{2+} ions in the anode and the cathode further confirmed that there was no possibility of removing Ca\textsuperscript{2+} as a precipitate, even in the form of Ca(OH)\textsubscript{2} or CaF\textsubscript{2} in the absence of (HCO\textsubscript{3} + CO\textsubscript{3}\textsuperscript{2-}). Therefore, the only mechanism that could remove F\textsuperscript{-} was co-precipitation with Mg(OH)\textsubscript{2}. Only 1% of F\textsuperscript{-} was transferred from the cathode to the anode by the Coulomb force, and 69% was removed by co-precipitation in the cathode (Figure 10(a)). Moreover, with increasing (HCO\textsubscript{3} + CO\textsubscript{3}\textsuperscript{2-})\textsubscript{0}, F\textsuperscript{-} transferred to the anode was increased. The ion concentration gradient between the anode and the cathode created by F\textsuperscript{-} co-precipitation in the cathode seems stronger than the Coulomb force. Therefore, F\textsuperscript{-} transfer to the anode by the Coulomb force was reduced as (HCO\textsubscript{3} + CO\textsubscript{3}\textsuperscript{2-})\textsubscript{0} was reduced. Furthermore, 19% of Mg\textsuperscript{2+} was transferred from the anode to the cathode due to the Coulomb force.

Following the removal percentages of F\textsuperscript{-} in the cathode, maximum treatable F\textsubscript{0} concentrations can be calculated as 5–6 mg/L (assuming same 74% removal observed for 10 mg/L F\textsubscript{0}) to meet WHO guideline for drinking water when (HCO\textsubscript{3} + CO\textsubscript{3}\textsuperscript{2-})\textsubscript{0} concentration was lower than 5 mmol/L. The higher removal rate of (HCO\textsubscript{3} + CO\textsubscript{3}\textsuperscript{2-}) in the anode more than 90% for (HCO\textsubscript{3} + CO\textsubscript{3}\textsuperscript{2-})\textsubscript{0} = 0–12.5 mmol/L showed that the proposed ELC system would be applicable to removal from both industrial and drinking water (HCO\textsubscript{3} + CO\textsubscript{3}\textsuperscript{2-}).
Model treatment system and its performance in real conditions

The ELC system was implemented in Sri Lanka as a model treatment system for 5–6 families where there was an urgent need for qualified groundwater for drinking purposes. Accordingly, a groundwater source located in the Medawachchiya area of the Anuradhapura District (location: 8°32′02.8″N 80°29′57.6″E) of Sri Lanka was selected. The treatment system was established with a production capacity of 374 L/day, having the same retention time of laboratory experiments. The anode water was rejected since the system was utilized for drinking purposes. During the operation, negligible flow through the diaphragm was observed.

The water quality of well water (WW), ion removals in the anode and the cathode are shown in Table 3. According to Table 3, there was a high concentration of F⁻ in the well water, exceeding the Sri Lankan guideline of 1 mg/L, as well as the WHO guideline of 1.5 mg/L (SLSI 2013; WHO 2017). The concentrations of other ions were also found to be extremely high and did not fluctuate significantly during the operating period except HCO₃⁻ + CO₃²⁻. Figure 11 shows the charge loading...
| Date               | mg/L       | mmol/L     |
|-------------------|------------|------------|
|                   | F          | Cl         | SO₄²⁻ | Na⁺       | Mg²⁺       | Ca²⁺       | HCO₃⁻ + CO₃⁻ | pH        |
| Avg.              | 2.71 ± 0.02| 2532.71 ± 5.17| 602.71 ± 0.96| 2052.71 ± 3.32| 1312.71 ± 1.85| 542.71 ± 1.08| 13.82 ± 0.21| 7.9V1 ± 0.11|
| Avg. Anode        | 3.45 ± 0.13| 360.00 ± 16.29| 87.63 ± 4.28| 125.37 ± 10.45| 81.71 ± 4.81| 33.49 ± 1.65| 1.9 ± 0.78| 6.45 ± 0.40|
| Avg. cathode      | 1.25 ± 0.12| 173 ± 12.76| 44 ± 2.55| 243 ± 7.36| 95 ± 11.16| 0.1 ± 0.03| 11.3 ± 0.59| 9.36 ± 0.15|
| WHO guideline Limit | 1.50       | 250        | 500   | 200       | 50        | 75       | 6.1       | 8.5       |
| Sri Lankan Guideline | 1.0        | 1200       | 400   | –         | 30        | 240      | 8.0       | 9.0       |

Table 3 | Well water (WW) quality

WHO guideline Limit 1

Sri Lankan Guideline 1

Limit

250 500 200 50 75 6.1 8.5

– 30 240 8.0 9.0
applied at the sampling time during 30 days of continuous operation. The charge loading was found to be fluctuated 1152–1474 C/L. The ion removal efficiencies for the cathode, the anode, and related pH are shown in Figure 12(a)–12(c), respectively. According to Figure 12(a), after treatment by the ELC

![Figure 11](https://iwaponline.com/h2open/article-pdf/doi/10.2166/h2oj.2020.022/653766/h2oj2020022.pdf)

**Figure 11** | Charge loading changes in the pilot-scale treatment plant.

![Figure 12](https://iwaponline.com/h2open/article-pdf/doi/10.2166/h2oj.2020.022/653766/h2oj2020022.pdf)

**Figure 12** | Ion removal percentage and pH variation of the pilot-scale treatment plant (a) Cathode, (b) Anode, (c) pH variation.
system, the F\(^-\) concentration in the cathode was reduced dramatically and was found stable during the operation. The average concentration of F\(^-\) in the treated water was 1.25 mg/L, which was less than the WHO guideline. However, F\(^-\) and Mg\(^{2+}\) removal in the cathode decreased with time which could be caused by the increment of HCO\(_3^-\) + CO\(_3^{2-}\) concentration over time in the W/W.

The average concentration of Mg\(^{2+}\) in the cathode was observed as 81.7 mg/L (27.9\% of average removal), which did not meet the WHO guideline of 50 mg/L. This lower removal could be as a result of the high HCO\(_3^-\) + CO\(_3^{2-}\) concentration in the WW, as described in section ‘Effect of the initial HCO\(_3^-\) + CO\(_3^{2-}\) concentration on ion removal and related pH’. The removal of Ca\(^{2+}\) in the cathode was significantly high (>99\%), but the removal of HCO\(_3^-\) + CO\(_3^{2-}\) did not meet the WHO guideline of 6.1 mol/L (Table 5). In the cathode, only F\(^-\), and Ca\(^{2+}\) was removed sufficiently to meet the WHO and Sri Lankan drinking water quality Guidelines. HCO\(_3^-\) + CO\(_3^{2-}\) removal in the anode was high enough to

![Figure 13](https://iwaponline.com/h2open/article-pdf/doi/10.2166/h2oj.2020.022/653766/h2oj2020022.pdf)
meet the drinking water quality standard of both WHO and Sri Lanka as well as an industrial guideline of 4 mmol/L (Figure 12(b) and Table 3).

Figure 13 compares the average water quality data of the community-level water treatment plant (CWTP) with the experimental data obtained in previous sections ‘Effect of initial F\(^-\) concentration on ion removal, Effect of the initial Mg\(^{2+}\) concentration on ion removal, Effect of initial Ca\(^{2+}\) concentration on ion removal and related pH and Effect of the initial HCO\(_3^-\) + CO\(_3^{2-}\) concentration on ion removal and related pH’. It was observed that the average ion removal of Ca\(^{2+}\) in the cathode of CWTP was mostly similar to the laboratory-scale treatment system (Figure 13(a)). However, the removal of F\(^-\), Mg\(^{2+}\), and CO\(_3^{2-}\) + HCO\(_3^-\) in both anode and cathode was different due to changes in the initial concentrations. Therefore, a rough estimation of the quality of water output based on the initial ion concentration can be performed with laboratory experimental data.

**CONCLUSION**

A novel method of ELC to remove coexisting F\(^-\), Ca\(^{2+}\), Mg\(^{2+}\), CO\(_3^{2-}\), and HCO\(_3^-\) from drinking and industrial groundwater was used without introducing any chemicals. Results were used to set the operational guidelines, to propose the mechanisms of ion removal, and to study the system’s operation under real groundwater conditions. The ELC system was found to remove ions satisfactorily. The removal of F\(^-\), Ca\(^{2+}\), and Mg\(^{2+}\) in the cathode was found to be significant; thus, cathode outlet water was most suitable for drinking purposes. (CO\(_3^{2-}\) + HCO\(_3^-\)) removal in the anode as CO\(_2\) was found to be the best and most suitable for industrial purposes. F\(^-\) was removed from the cathode mainly by co-precipitation with Mg(OH)\(_2\) and by Coulomb force transfer to the anode. The minor adsorptive removal of F\(^-\) by CaCO\(_3\) + MgCO\(_3\) was also observed. To meet the WHO drinking water guideline levels for F\(^-\), a range of initial ion concentrations was recognized as F\(^-\)\(_0\) = 4.29–6 mg/L, Mg\(^{2+}\)\(_0\) = 75–125 mg/L, Ca\(^{2+}\)\(_0\) > 50 mg/L, and (HCO\(_3^-\) + CO\(_3^{2-}\))\(_0\) < 10 mmol/L in place of 1500 C/L.

**ACKNOWLEDGEMENTS**

This research was partly supported by JSPS KAKENHI Grant Numbers 23404003 and 15H05120. Furthermore, the authors gratefully acknowledge Prof. Masamoto Tafu, Dept. Appl. Chem. & Chem. Eng., National Institute of Technology, Toyama College, Japan, for providing the XRD analytical facility.

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