

Review and analysis of defluoridation of drinking water by electrocoagulation

Kruttika R. Apshankar and Sudha Goel

ABSTRACT

Excess fluoride in water and food is associated with dental and skeletal fluorosis and affects several parts of the world. Electrocoagulation is a potential method for removal of fluoride from drinking water. The aim of this paper was to review and analyse electrocoagulation-based defluoridation studies. Several factors are known to impact defluoridation efficiency and are discussed in detail in this paper. Major factors include: types of reactors and their operating parameters such as current or voltage; contact time; electrodes materials, configuration, spacing and shape; feed water composition; solution chemistry including pH, conductivity and competing ions. In general, highest removal efficiencies were observed in batch reactors while continuous-flow reactors showed greater variability in performance. Aluminium (Al) electrodes have been studied to a far greater extent than iron electrodes and comparative studies show better performance with aluminium. Highest removal efficiencies were observed with distilled or deionized water and lowest with synthetic water. This is mainly due to competition from other ions present in synthetic solutions which lowers removal efficiency for the contaminant of concern. Sludge and electrode analyses and various types of statistical and kinetic modelling are also reviewed. In conclusion, electrocoagulation can be successfully and economically applied for defluoridation of drinking water.

Key words | defluoridation, drinking water treatment, electrodes, feed water, interfering ions, modelling

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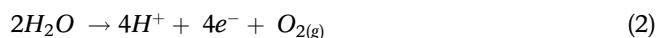
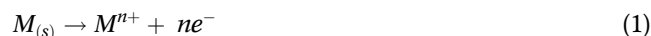
INTRODUCTION

Fluoride is found in all waters, especially groundwater, in several parts of the world including Africa, Asia, southern parts of Europe, USA and the former USSR (Fawell *et al.* 2006; Brindha & Elango 2011). The WHO guideline for maximum fluoride concentration in drinking water is 1.5 mg/L. At least 25 countries in the world are estimated to be affected by health problems related to excess fluoride in drinking water (Andezhath & Ghosh 2000; Brindha & Elango 2011). Reliance on groundwater is increasing and it is likely that the problems associated with excess fluoride in groundwater will increase in the future. Intake of fluoride via foodstuffs and agricultural produce is also becoming a matter of concern (Mumtaz *et al.* 2014).

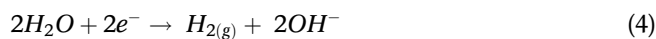
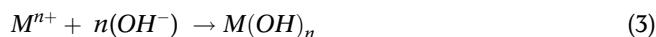
Treatment technologies used for the removal of fluoride include coagulation-precipitation, adsorption, reverse osmosis, ion exchange, nanofiltration, membrane separation, chemical treatment and electrocoagulation (Gwala *et al.* 2011). Singh *et al.* (2013) have compared these methods in detail. Electrocoagulation (EC) is a process in which the anode metal dissolves, leading to the formation of metal-hydroxide complexes. These complexes act as coagulants and are responsible for the removal of dissolved contaminants along with turbidity from water. Colloidal particles which contribute to turbidity are removed by charge neutralization and electrostatic attraction, while dissolved contaminants are removed by adsorption on coagulant floc

and metal-ligand formation (Amirtharajah & O'Melia 1990; Daneshvar *et al.* 2006). Aluminium and iron are the most commonly used anode materials. Reactions at the anode and cathode that are widely accepted are noted below (Mollah *et al.* 2004; Gomes *et al.* 2007).

Anode: Dissolution of metal



Cathode: Formation of metal-hydroxide complexes



Hydrogen gas is formed at the cathode whereas oxygen is produced at the anode in the form of gas bubbles. A thin oxide layer is formed at the cathode which leads to reduced electrocoagulation efficiency due to increased electrical resistance over the long-term and is termed passivation. Polarity reversal has been used by most researchers to overcome this problem. When the contaminant is oxidized in an electrolytic cell, the process is termed electro-oxidation (EO) and can be combined with EC. If bubbles generated at the cathode are used to enhance flocculation, then scum will float to the top of the reactor and can be removed from there. This process is termed electroflotation (EF). The remaining floc settles as sludge and has to be removed from the bottom of the reactor. Thus, EC often includes electro-oxidation and electroflotation (Emamjomeh *et al.* 2004; Apshankar & Goel 2017).

Electrocoagulation has several advantages over conventional coagulation (CC) (Zhu *et al.* 2005; Dolo *et al.* 2010). No external salts or polymers need to be added in EC; instead, the coagulant is generated *in situ*. The hydrogen gas evolution at the cathode raises the pH and provides a buffering effect due to which post-treatment neutralization is generally not required. In the case of CC, addition of coagulants like alum or ferric chloride results in the formation of acidic compounds which lower the pH and may need to be neutralized. A few researchers have reported

better defluoridation efficiencies with EC as compared to CC (Zhu *et al.* 2007). However, optimization of operating parameters is required to make EC economically viable.

EC has been used successfully for treating wastewater since 1887 and for drinking water since 1889, but with limited success (Vik *et al.* 1984). The objective of this paper was to review electrocoagulation studies for defluoridation of water and examine the factors influencing fluoride removal in drinking water. At the time of writing, 56 peer-reviewed publications were accessed and their results are discussed in this paper. The 56 publications accessed for this review included a total of 83 experimental studies since many publications have reported multiple studies with various operating factors.

FACTORS AFFECTING ELECTROCOAGULATION

Electrocoagulation efficiency depends on several factors which are discussed below.

- **Reactor design:** Type of reactor, configuration, duration of experiment and hydraulic retention time.
- **Electrodes:** Materials, configuration and number, spacing, shape and combinations of metals/materials.
- **Feed water:** Solutions of distilled or deionized water, tap water, groundwater and synthetic water.
- **Solution chemistry:** pH, conductivity, interfering or competing ions and temperature.

REACTOR DESIGN

Different reactor types and configurations have been used by various research groups. Contaminants are removed using electrocoagulation through four basic processes: electrolysis, flotation, settling and filtration. Most researchers have combined these processes in either one or two stages in their reactors.

Types of reactors

Electrocoagulation can be conducted in batch or continuous-flow reactors. Batch studies can be useful for

decentralized treatment, e.g., in rural areas where small quantities of water are required and can be generated as and when required in small community systems. Continuous-flow treatment can be developed as an alternative to CC in large-scale water treatment plants that are common in cities and towns.

Batch reactors

A summary of the batch studies reviewed for this paper is provided in Table 1. Of the 83 studies reviewed for this paper, 67 studies were in batch mode (44 publications) with maximum removal efficiencies (RE) ranging from 43% to 100%.

Of the 44 publications listed in Table 1, 32 publications did not report settling. Filtration was provided by all researchers for analytical purposes. Many research groups analysed their samples immediately after electrolysis and membrane filtration (asterisks in Table 1). Ün *et al.* (2010) and Ün *et al.* (2013) analysed their samples after electrolysis and centrifugation.

Continuous-flow studies

Only 12 publications were found for continuous-mode EC and are summarized in Table 2. Maximum removal efficiency of 95% was achieved under optimum conditions with seven electrodes (Guzmán *et al.* 2016). The duration of these studies ranged from 1 to 36 hours.

Reactor configuration

Reactor configuration plays an important role especially in continuous-flow studies. The basic geometry of the reactor, placement of the electrodes, flow direction, presence of baffles, inlet and outlet positions and various other factors can influence defluoridation efficiency. It is also important to design the reactors so that the dynamic voltage (IR) drop is minimized, the accumulation of bubbles between the electrodes is avoided and mass transfer is not hindered in any way (Paul 1996).

Many researchers have used a combination of EC with EF for fluoride removal (Emamjomeh *et al.* 2004; Aps Shankar & Goel 2017). Zuo *et al.* (2008) used a combined EC chamber, a flocculation-enhanced chamber

and an EF chamber for defluoridation. Two different sets of electrodes were connected to the same DC power supply in different configurations – bipolar in the EC cell and monopolar in the EF cell. The main objective of the EF cell was to separate the flocs formed in the EC cell. Emamjomeh & Sivakumar (2005, 2009) used a conventional reactor which included separate sedimentation and flotation tanks.

Reactor geometry and baffles

Most batch reactors were cylindrical beakers (or buckets) into which electrodes were inserted in monopolar or bipolar mode, connected to a power supply and mixed with magnetic stirrers. However, some studies were conducted with rectangular batch reactors (Mameri *et al.* 1998; Emamjomeh *et al.* 2004; Emamjomeh & Sivakumar 2005; Ghosh *et al.* 2008, 2011; Behbahani *et al.* 2011a, 2011b; Orescanin *et al.* 2011a, 2011b; Naim *et al.* 2012, 2015; Takdastan *et al.* 2014; Thakur & Mondal 2016). Baffles were used by several researchers in continuous-flow reactors to increase mixing and, therefore, removal efficiency (Zuo *et al.* 2008; Sandoval *et al.* 2014; Guzmán *et al.* 2016; Aps Shankar & Goel 2017). An exception in these designs was the flow column electrocoagulation reactor (FCER) used by Hashim *et al.* (2017), in which perforated stacked aluminium plates were used, of which six were submerged and the rest were above water (unsubmerged). An electric current was applied to the submerged electrodes while the unsubmerged electrodes acted as water diffusers and assisted in the aeration and mixing process. Aps Shankar & Goel (2017) found that increasing the depth-width ratio from 0.96 to 2.14 increased the removal efficiency from 36% to 46%. The laminar flow conditions in their reactor created a floc layer at the surface which enhanced defluoridation efficiency.

Flow direction

Reactors can also be classified as tank-type or horizontal-flow reactors and up-flow or vertical flow reactors. Tank-type reactors are most commonly used because of their ease of operation and simplicity.

Table 1 | Summary of defluoridation batch studies reviewed for this paper

S. no.	References	Year of publication	Type of water	Electrolysis time (h)	Settling time (h)	Electrodes	Initial conc. (mg/L)	No. of electrode pairs, inter-electrode distance [mm]	Current, current density, charge loading or applied voltage	Maximum removal efficiency (RE %)	Remarks	No. of studies
1	Andey	2013	GW	1–1.5	2.00	Al Al	2 to 5	3	16–20 A	81.7	Monopolar; pilot-scale	1
2 ^a	Babu & Goel	2013	DW	3.00	0.00	Fe Fe	10	1 [30]	10–25 V	84.9	Monopolar	2
			GW	3.00	0.00	Fe Fe	10	1 [30]	10–25 V	79.4		
3 ^a	Bazrafshan <i>et al.</i>	2012	DI	1.00	0.00	Al Al	1 to 10	2 [15]	10–40 V	97	Bipolar	1
			DI			Fe Fe				94		
4 ^a	Behbahani <i>et al.</i>	2011a	DW	0.042–0.33	0.00	Fe Fe	20 to 200	2,4,6 [30]	1–3 A	67.68	Monopolar parallel	5
			DW			Al Al				98.53		
			DW			Al Al				99		
			DW			Al Al				99		
5 ^a	Behbahani <i>et al.</i>	2011b	DW	0.42	0.00	Al Al	25 to 125	2 [30]	0.0083–0.033	94.5	RSM study; monopolar	1
			DW			Al Al						
6	Bennajah <i>et al.</i>	2010b	TW	0.50	NM	Al Al	10 to 20	1 [20]	0.5–3 A	93 (max)	Monopolar	1
7 ^a	Emamjomeh <i>et al.</i>	2004	SynW	1.00	0.00	Al Al	10	5 electrodes [5]	0.5–2.5 A	92.7	Monopolar	1
8 ^a	Emamjomeh & Sivakumar	2006	DI	1.00	0.00	Al Al	10 to 25	5 electrodes [5 to 15]	1–2.5 A	91.1 (max)	Monopolar	1
9 ^a	Emamjomeh <i>et al.</i>	2011	SynW	1.00	0.00	Al Al	10, 25	5 electrodes [5]	0.5–2.5 A	92	Monopolar	1
10 ^a	Essadki <i>et al.</i>	2009	DrW	0–0.67	0	Al Al	5 to 20	1 [20]	2.8–17 mA/cm ²	95	Monopolar	1
11 ^a	Essadki <i>et al.</i>	2011	DrW	0–0.58	0	Al Al	10 to 20	1 [20]	2.8–17 mA/cm ²	100	Monopolar	1
12 ^a	Ghanizadeh <i>et al.</i>	2016	DW	0.33, 0.67, 1	0	Al Al	8	2 [10]	15, 25, 40 V	98.3	Monopolar	4
			DW			Fe Fe				95.4		
			DW			– –				95.4		
			DW			– –				98.3		
13 ^a	Ghosh <i>et al.</i>	2008	TW	0.75	0.00	Al Al	10	Monopolar (1) [5]	250 A/m ²	78	Monopolar	2
			TW			Bipolar (2) [5]			85	Bipolar		
14	Ghosh <i>et al.</i>	2011	DrW	0.75	3–5	Al Al	4 to 10	1 [5 to 15]	250–625 A/m ²	90	Monopolar	1
15	Govindan <i>et al.</i>	2015	DI	0.75	2.00	Al Al	0.53 mM	1 [20]	0–1,620 C/L	60	Monopolar	4
			DI			Fe Fe				18		
			DI			Fe assisted by Al ³⁺				90		
			DI			Al assisted by Mg ²⁺				99		

(continued)

Table 1 | continued

S. no.	References	Year of publication	Type of water	Electrolysis time (h)	Settling time (h)	Electrodes		Initial conc. (mg/L)	No. of electrode pairs, inter-electrode distance [mm]	Current, current density, charge loading or applied voltage	Maximum removal efficiency (RE %)	Remarks	No. of studies
16 ^a	Gwala <i>et al.</i>	2011	TW	3.00	0.00	Al	Al	2 to 20	1 [5]	1, 1.5, 2 A	98	Monopolar: one cathode, two anodes	1
17 ^a	Hu <i>et al.</i>	2003	DI	0.15	0.00	Al	Al	20	7/2 [10]	5.56–8.16 mA/cm ²	100	Bipolar	1
18 ^a	Hu <i>et al.</i>	2007	DI	0.15	0.00	Al	Al	15 to 25	7/2 [10]	0.25–4 A	90	Bipolar	1
19 ^a	Kodikara <i>et al.</i>	2015	GW	2.00	0.00	C	Pt	0.91–10	1	31.7–91.6 V	97 (max.)	Monopolar	1
20 ^a	Mameri <i>et al.</i>	1998	SynW GW	0.67 0.033–0.55	0.00 0.00	Al	Al	3 to 10 2.5	>2 [5 to 30] 1 [20]	3.3–40 A/m ² 28.9–289 A/m ²	90 80	Bipolar Monopolar	2
21	Ming <i>et al.</i>	1987	GW	0–0.27	NM	Al	Al	0.5–5	1 [3]	14 A/m ²	83	Monopolar	1
22	Montero-Ocampo & Villafane	2010	GW SynW	0.025–0.067	NM	Al	Al	5.12 5	2	1.5–3 mA/cm ²	72 90	Monopolar	2
23 ^a	Naim <i>et al.</i>	2012	DW TW	0.083–0.583	0.00	Al	Al	4.93–30.4	4, 7 [10.5]	10.5 V	100	Monopolar and bipolar	2
24 ^a	Naim <i>et al.</i>	2015	DW	0.083–0.25	0.00	Al	Al	6.44–57.9	9 electrodes [10.5]	10.5 V	100	Bipolar	1
25	Narasimham & Silaimani	1992	TW	2–2.67	0.25	Al	Al	2–99	1 [10]	0.1–1 A/dm ²	99	Monopolar	1
26	Orescanin <i>et al.</i>	2011a	GW	0.17 [Fe] +0.17 [Al]	0.5	Fe pair followed by Al pair in 2-step treatment		0.37	3 [10]	15 V	51.4	Monopolar	1
27	Orescanin <i>et al.</i>	2011b	GW	0.093 [SS] +0.083 [Al]	0.5	SS pair followed by Al pair		0.945	2	6 A	82.65	Monopolar	1
28 ^a	Sinha <i>et al.</i>	2014	TW	0.78	0	Al	Al	6 (opt.)	[20]	0.27 A (opt.)	87.2	Monopolar	1
29	Sinha <i>et al.</i>	2015	TW	10, 30, 50	0.5	Al	Al	2, 5 & 8	1	0.31, 0.53, 0.75 A	99.5	Monopolar	1
30	Sinha & Mathur	2016	TW	10, 30, 50	0.5	Al	Al	2, 5 & 8	1	0.31, 0.53, 0.75 A	99.5	Monopolar	1
31 ^a	Takdastan <i>et al.</i>	2014	DI DI	0.167–0.67	0	Al Fe	Al Fe	5	4 [20]	20 V	97.86 43.09	Bipolar	1 1
32 ^a	Thakur & Mondal	2016	DW	0.167–2	0	Al	Al	6.3, 12	2 [10]	10–60 A/m ²	87.5, 96.7	Monopolar	1
33 ^a	Thakur & Mondal	2017	DW	0–2	0	Al	Al	12	2 [5 to 20]	10–60 A/m ²	83.33	Monopolar	1

(continued)

Table 1 | continued

S. no.	References	Year of publication	Type of water	Electrolysis time (h)	Settling time (h)	Electrodes		Initial conc. (mg/L)	No. of electrode pairs, inter-electrode distance [mm]	Current, current density, charge loading or applied voltage	Maximum removal efficiency (RE %)	Remarks	No. of studies
34 ^a	Ün <i>et al.</i>	2010	DI	0.5	0	Fe	Fe	5	1 [int. dia. = 10 cm]	0.5–3 mA/cm ²	85.9	Monopolar	1
35 ^a	Ün <i>et al.</i>	2013	DI DI	0.5	0	Al Fe	Al Fe	0.12–5	Cylindrical anode; rotating impeller cathode	1 mA/cm ²	94.2 83.6	Monopolar	2
36	Vasudevan <i>et al.</i>	2009	TW	0.5	NM	Mg-Al-Zn	SS	5	3 electrodes [5]	0.5 A/dm ²	96	Monopolar	1
37 ^a	Vasudevan <i>et al.</i>	2011	DI DI	1.5	0	Al alloy	Al alloy	5	5 electrodes [5]	AC (0.25–1.5 A/dm ²) DC (0.25–1.5 A/dm ²)	95.5 95	Monopolar Monopolar	1 1
38 ^a	Waikar & Dhole	2015	TW	3	0	Fe	Fe	20	2 [30]	5–25 V	91	Monopolar	1
39 ^a	Wang <i>et al.</i>	2017	Geothermal water	0–0.3	0	Al	Al	7.5	4 [5 to 25]	5–25 A/m ²	90	Monopolar	1
40 ^a	Zhang <i>et al.</i>	2014	Geothermal water	0.33	0.00	Al	Al	7.4–9.5	3 [5 to 20]	6.5, 10, 15, 20 A/m ²	95	Monopolar	1
41 ^a	Zhao <i>et al.</i>	2009	GW	0.17	0.00	Al	Cu	9–10	1 [10]		>90	Monopolar	1
42 ^a	Zhao <i>et al.</i>	2010	DI	0.17	0.00	Al	Cu	10	1 [10]	0.15 A	98	Monopolar	1
43 ^a	Zhao <i>et al.</i>	2011	DI DI DI DI DI	0.67	0.00	3 Fe + Al 3 Al + Fe 4 Al 4 Fe 3 Al + Fe		4.5	2 DSA + 4 Al/Fe [2]	4 mA/cm ²	87 81 89 8.1 92.5	Bipolar	5
44 ^a	Zhu <i>et al.</i>	2007	DI	0.17	0.00	Al	Al	5 to 19	1 [10]	4.63 to 92.59 A/m ²	95	Monopolar	1

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Note: Publications marked with ^aare studies where settling was not provided. Removal efficiencies are based on values provided in the publications or estimates based on graphs in publications. MS, mild steel; NM, not mentioned; DI, deionized water; DW, distilled water; DD, double distilled water; GW, groundwater; TW, tap water; SynW, synthetic water.

Table 2 | Summary of defluoridation continuous-flow studies reviewed for this paper

S. no.	References	Year of publication	Type of water	Electrodes	Initial conc. (mg/L)	No. of electrode pairs, interelectrode distance (mm)	Current, current density, charge loading or applied voltage	Maximum RE (%)	Remarks	No. of studies
1	Apshankar & Goel	2017	GW	Fe Fe	10	1 [10–20]	20, 25, 30 V	46.7	Monopolar	1
2	Babu & Goel	2013	DW GW	Fe Fe Fe Fe	10 10	1 [30] 1 [30]	10–25 V 25 V	79.6 28.7	Monopolar	2
3	Emamjomeh & Sivakumar	2005	SynW	Al Al	5 to 15	1 [5]	2–8 A	86	Monopolar; pilot-scale	1
4	Emamjomeh & Sivakumar	2009	TW	Al Al	5 to 15	1 [5]	12.5–50 A/m ²	95	Monopolar	1
5	Guzmán <i>et al.</i>	2016	GW	Al Al	2.5	7 electrodes [6]	4, 5, 6 mA/cm ²	94.8	Monopolar; 3 anodes, 4 cathodes	1
6	Hashim <i>et al.</i>	2017	DI	Al Al	10, 15, 20	6 Al plates [5,8,11]	1, 2, 3 mA/cm ²	98	–	1
7	Kim <i>et al.</i>	2016	DI	Al Al	190	3 electrodes [5 to 15]	3, 6, 12 mA/cm ²	84.5	Monopolar	1
8	Mameri <i>et al.</i>	2001	DW DW GW	Al Al Al Al Al Al	2.5 2.5 3	4 4 4	53 A/m ² 6.1–19.1 A/m ² 25 A	68 70 73.33	Monopolar Bipolar Bipolar	1 1 1
9	Mumtaz <i>et al.</i>	2014	TW	Al Al	5, 6, 8, 10	3 electrodes [5]	2–3 A	90	Monopolar	1
10	Sandoval <i>et al.</i>	2014	SynW	Al Al	10	3 [6]	4–8 mA/cm ²	89.20		1
11	Sinha <i>et al.</i>	2012	DW GW	Al Al	6 6.2	1 [10]	12.5–37.5 A/m ²	79 68	Monopolar; double stage treatment applied – improved removal efficiency by 52%; until pseudo steady state was achieved	2
12	Zuo <i>et al.</i>	2008	DI	Al Al	4 to 6	3 electrodes [4]	0–3.5 F/m ³	78.25	Bipolar	1

Note: Removal efficiencies are based on values provided in the publications or estimates based on graphs in publications.

MS, mild steel; NM, not mentioned; DI, deionized water; DW, distilled water; DD, double distilled water; GW, groundwater; TW, tap water; SynW, synthetic water.

Non-conventional reactors

Some researchers used packed-bed reactors to ensure proper contact between the contaminant and the electrodes. Others used continuous filter-press reactors when operating in continuous mode (Sandoval *et al.* 2014; Guzmán *et al.* 2016). Perforated plate reactors, solid-tube reactors and perforated-tube reactors were reported in a review paper by Mollah *et al.* (2004).

Andey *et al.* (2013) designed pilot-scale hopper bottom reactors which recirculate water in the EC tank to keep floc in suspension. External-loop airlift reactors (ELAR) were used by Bennajah *et al.* (2010a, 2010b), where electrolytic gases produced *in situ* assisted in the circulation of the reactor solution. ELARs were also used by Essadki *et al.* (2009, 2011). Iron cylindrical reactors served as anodes in Ün *et al.*'s (2010) study while a mechanical stirrer consisting of two iron blades served as cathodes. A similar model was used in their next study, where iron was replaced by aluminium in both the anode and the rotating impeller cathode with four blades (Ün *et al.* 2013). Vasudevan *et al.* (2009, 2011) used a water jacket outside their electrolytic cell to control the temperature. Other innovative designs include an all-in-one EC chamber, a flocculation enhanced chamber and an EF chamber (Zuo *et al.* 2008). They also inserted perforated plates in the flocculation chamber with holes of diameters varying from 1 mm at the bottom to 2 mm at the top.

Guzmán *et al.* (2016) used a pre-pilot-scale filter press cell in which coagulant was produced. The resulting solution was then passed through a serpentine array of perforated baffles to induce better mixing and fluid turbulence. A similar apparatus with 5 mm diameter holes was used to retain bigger floc inside the reactor (Sandoval *et al.* 2014). The flocculator had a serpentine arrangement to enhance the flocculation process. An unglazed clay diaphragm was used to separate the anode and cathode baths by Kodikara *et al.* (2015) with different volumes while maintaining the same water level.

Very few researchers have tried mathematical modelling of the hydrodynamic conditions of their reactors for any given flow. Such modelling can be useful for reactor design where different reactor geometries can be evaluated and the best possible option chosen for implementation.

This can help in saving time and money involved in conducting experimental studies for different reactor geometries.

Duration of experiment or study

Removal of contaminants by electrocoagulation is generally dependent on two processes within the reactor: electrolysis time (also called reaction time) and settling time. Electrolysis time is the period during which coagulant is generated *in situ* due to the passage of current. In some studies, settling time is provided simultaneously along with electrolysis, while in other studies, settling time is separated from electrolysis time by switching off the power supply. Settling time was not provided in several studies.

Electrolysis time

The rate of dissolution of coagulant from the electrodes is given by Faraday's law, as noted below (Vik *et al.* 1984):

$$w = \frac{itM}{nF}$$

where w = quantity of electrode material dissolved, g of metal/cm²; i = current density, Amp/cm²; t = time, s; M = molecular weight of electrode metal, g/mol; n = number of electrons in redox reactions (n is 3 for Al and Fe); and F = Faraday's constant = 96,485 Coulomb/mol = 96,485 Amp-s/mol.

Electrolysis time determines the amount of aluminium or iron ions dissolved in solution, and hence, greatly affects removal efficiency (Sivakumar & Emamjomeh 2006). Figure 1 shows the impact of electrolysis time on fluoride removal efficiency using distilled water solutions of NaF in batch reactors (Babu & Goel 2013). No settling time was provided in this study.

Settling time

Settling time in batch reactors is necessarily separate from electrolysis time. The same may or may not be true in continuous-flow reactors. Results for different contaminants like turbidity, total organic carbon (TOC), nitrate and

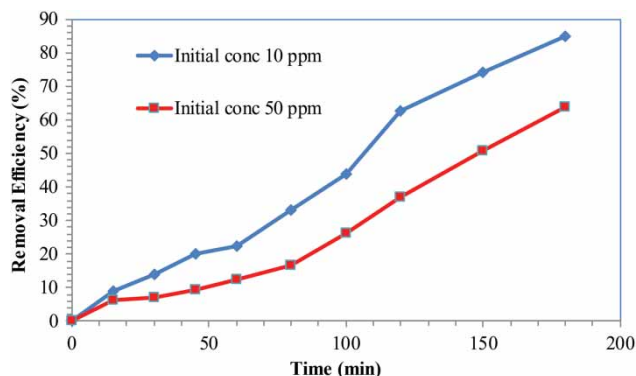


Figure 1 | Defluoridation removal efficiency increases with increase in electrolysis time.

fluoride in batch studies indicate that settling is important for the removal of suspended solids, i.e., turbidity, but not for dissolved compounds like TOC, nitrate and fluoride (Adapureddy & Goel 2012; Apshankar & Goel 2017).

Hydraulic retention time

Hydraulic retention time (HRT) is a function of flow rate, and flow rate influences the rate of dissolution of coagulant ions into the solution, which in turn affects fluoride removal (Sivakumar & Emamjomeh 2006). Low flow rates mean that a higher coagulant dosage is available for the same concentration of pollutants, which in turn results in higher removal efficiency. When flow rates were increased, defluoridation efficiency decreased for the same voltage or current density in each of these studies (Emamjomeh & Sivakumar 2005, 2009; Sinha *et al.* 2012; Mumtaz *et al.* 2014; Sandoval *et al.* 2014; Guzmán *et al.* 2016; Kim *et al.* 2016; Apshankar & Goel 2017). However, Zuo *et al.* (2008) found in their study that HRT has a small or negligible effect on defluoridation. The minimum time tested was 20 min and 30 min was found to be optimum. After 30 min, the effect of HRT on fluoride removal was insignificant.

ELECTRODES

Material

The removal of contaminants depends upon the type of hydroxide formed, which in turn depends on the electrode material used. Aluminium and iron or steel are the most common materials for electrodes and the number of papers along with the electrode material and highest removal efficiencies are summarized in Table 3. The choice of electrodes is based on the contaminant to be removed, cost, inertness of the electrodes, final water quality and oxidation potential. Comparatively, more electrocoagulation studies were done using aluminium electrodes than iron electrodes. As a result, mechanisms and complexes formed with aluminium have been thoroughly studied while the same with iron electrodes remain to be fully explored. Mechanisms for removal with iron electrodes have been proposed by several researchers and were reviewed by Mollah *et al.* (2001).

Vasudevan *et al.* (2009) have noted that the usage of a contaminant-free ion source allowed maximum adsorptive removal of various metals. On experimenting with magnesium, magnesium alloy, aluminium and mild steel, they obtained the highest F removal efficiency (96%) with magnesium alloy, followed closely by aluminium, and the lowest RE was for magnesium (53%). Better defluoridation removal efficiencies have been obtained with aluminium electrodes due to the formation of cationic, hydroxyl-aluminium complexes (Holt *et al.* 2002; Ghosh *et al.* 2008; Emamjomeh & Sivakumar 2009; Essadki *et al.* 2009; Behbahani *et al.* 2011a; Govindan *et al.* 2015). However, these complexes exist only below pH 6 (Hao & Huang 1986). Two mechanisms, namely, surface complexation or electrostatic attraction, are responsible for contaminant removal (Singh *et al.* 1998). Many researchers have obtained equally good removals with iron electrodes (Bazrafshan *et al.* 2007;

Table 3 | Number of studies with different electrode materials and the best defluoridation efficiencies obtained

Electrode material	Al	Fe	Mg	Al + Fe	SS + Al	Mg-Al-Zn + SS	Al + Cu	Al + Gr
No. of papers	40	12	1	3	1	1	2	1
Highest removal efficiency, %	>99	95.4	56	94.5	67.23	96	95	70.79

Configuration, number, shape and surface area.
SS, stainless steel; Gr, graphite.

Babu & Goel 2013). A few have found that both metals give similar removal efficiencies (Bazrafshan *et al.* 2012). Combining aluminium and iron electrodes was also found to give good results (Phalakornkule *et al.* 2010; Orescanin *et al.* 2011a; Zhao *et al.* 2011).

Configuration, number, shape and surface area

The potential drop through an electrolytic cell is determined by the shape and thickness of the electrodes. Paul (1996) states that the 'maximum potential drop is directly proportional to the square of the height of the electrode and inversely proportional to its thickness'. The potential drop can be estimated by the following equation (Vik *et al.* 1984):

$$\eta_{IR} = \frac{I * d}{A * \kappa}$$

where η_{IR} = potential due to solution resistance, V, also called IR-drop; I = current, Amp; d = distance between electrodes, m; A = anode surface area, m²; κ = specific conductivity of the solution, Siemens/m or Amp/V-m.

When current density is constant, increasing the surface area of the electrodes increases removal efficiency (Zhang *et al.* 2014).

Electrodes can be arranged in monopolar or bipolar mode. In monopolar mode, each electrode is connected to the power supply, i.e., the ones connected to the positive terminal are anodes and the ones connected to the negative terminal are cathodes. This is the most popular arrangement of electrodes. In bipolar mode, only electrodes at the ends are connected to the power supply; one to the positive terminal and the other to the negative terminal. The electrodes in between develop a charge due to induced polarization when voltage is applied to the electrodes at the end. This configuration has been found by many researchers to increase contaminant removal efficiency (Hu *et al.* 2003, 2007; Ghosh *et al.* 2008; Zuo *et al.* 2008; Behbahani *et al.* 2011a; Zhao *et al.* 2011; Bazrafshan *et al.* 2012; Naim *et al.* 2012, 2015; Takdastan *et al.* 2014). However, bipolar mode also leads to greater energy consumption and greater dissolution of the sacrificial anode.

Another important parameter that determines removal efficiency by EC is electrode surface area/reactor volume

(S/V or A/V) ratio. Zhang *et al.* (2014) experimented with the number of plates keeping current density constant. They found that an increase in the number of plates led to an increase in defluoridation, and an increase in energy consumption. Takdastan *et al.* (2014) kept the voltage constant, and observed the same. Therefore, an optimum number of plates was selected to minimize energy consumption and save electrode material. The increase in area was related to current density, coagulant dose or the electrode S/V or A/V ratio. According to Mameri *et al.* (1998), the rate of formation of fluoro-aluminium complexes was directly related to current density up to an optimum value, which in turn, depended upon the S/V ratio. Hu *et al.* (2003) used a value of 40.9 m⁻¹, higher than the value recommended by Mameri *et al.* (1998). Thus, it was concluded that high S/V ratios were needed, whereas it was recently proved that low S/V ratios give better defluoridation efficiency (Essadki *et al.* 2009). Mass ratio or the ratio of electrode metal ions to fluoride ions has been considered as a criterion by some researchers (Emamjomeh *et al.* 2004). Others have varied the current concentration, i.e., the current-to-volume ratio (Emamjomeh & Sivakumar 2006).

Spacing

In general, an optimum inter-electrode spacing was found in most studies where removal efficiency was maximum (Escobar *et al.* 2006; Sivakumar & Emamjomeh 2006; Ghosh *et al.* 2008, 2011; Adapureddy & Goel 2012; Takdastan *et al.* 2014; Zhang *et al.* 2014). Behbahani *et al.* (2011a) found in their study that inter-electrode distance affected cell resistance and as a result, cell voltage. Narrow gaps enhance mass transfer characteristics and decrease ohmic losses. However, a decrease in the gap also led to increased electrolyte resistance, especially when gaseous products are present (Paul 1996). Hence, the optimum distance was reported to be around 20 mm.

CHARGE LOADING, VOLTAGE, CURRENT AND CURRENT DENSITY

Several terms have been used in the literature to express the amount of charge applied. Current density is the amount of

current passed per unit of effective surface area submerged in the solution (amperes/unit area), whereas charge loading is the charge passed per unit area (faraday/unit area). The current passing through an EC reactor determines the coagulant dosage, which in turn, influences removal efficiency, bubble production rate and the size and growth rate of the flocs formed (Holt *et al.* 2002; Bazrafshan *et al.* 2012). As applied voltage or current increases, removal efficiency also increases. However, the increase in current density will also increase passivation of electrodes, and hence, an optimal current density has been suggested (Zhu *et al.* 2007; Zhang *et al.* 2014). Operational costs are also directly linked to the passage of current and reaction time. Alternating current (AC) has been used to avoid passivation, but Ghanizadeh *et al.* (2016) found that direct current (DC) was more effective than AC while Vasudevan *et al.* (2011) found AC to be more effective than DC.

MODELLING OF FLUORIDE REMOVAL BY ELECTROCOAGULATION

Fluoride removal followed first-order kinetics with respect to initial fluoride concentration (Mameri *et al.* 1998; Sivakumar & Emamjomeh 2006). Reaction rate changed with initial concentration and it has been suggested that defluoridation follows a pseudo-first order model (Bennajah *et al.* 2010a; Mounir *et al.* 2010).

The use of response surface methodology (RSM) as a tool in the design of experiments, model making, finding the optimum values and significance of factors is being explored by many researchers. Behbahani *et al.* (201b) and Thakur & Mondal (2016) applied RSM to evaluate the effect of initial pH, reaction time, current density and initial fluoride concentration, and obtained high R^2 values. Behbahani *et al.* (201b) found that all parameters except initial pH made a significant difference, while Thakur & Mondal (2016) found that the initial pH, run time and interaction of current density and run time were highly significant factors. However, both these studies observed current density, run time and their interaction to influence operating costs significantly.

Zhu *et al.* (2007) fit Freundlich and Langmuir isotherms to their data and found that the Langmuir isotherm was a better fit. Hu *et al.* (2007) developed a variable-order-kinetic

(VOK) model using Langmuir adsorption isotherm while Bennajah *et al.* (2010a) showed that a VOK approach coupled with a Langmuir–Freundlich adsorption model was suitable. In another study, the model was applied successfully to an airlift reactor accounting for the degree of mixing and coagulation beyond monolayer deposition which takes place in large reactors (Mounir *et al.* 2010). Multi-objective optimization (Sinha *et al.* 2014), multivariate studies (Naim *et al.* 2015) and Taguchi experiments (Sinha *et al.* 2015; Ghanizadeh *et al.* 2016; Sinha & Mathur 2016) have also been used by researchers. A notable fact is that all these modelling studies were conducted with aluminium electrodes only.

FEED WATER AND SOLUTION CHEMISTRY

An important factor that is known to influence removal efficiency is the type of feed water. The number of studies conducted with each type of feed water and their corresponding maximum removal efficiencies are shown in Table 4. Several studies were done with either tap water (TW) or drinking water (DrW), i.e., 16 out of the 83 studies reviewed in this paper (19.3%). Most studies were done with deionized (DI) water (26 out of 83 or 31.3%) or groundwater (GW) (16 out of 83, 19.3%). The remaining studies were done with either double distilled water (DD) or distilled water (DW) (19 out of 83 or 22.9%) or synthetic water (6 out of 83 or 7.2%). In all these studies, maximum removal efficiency reported was 97% for GW, 92.7% for synthetic water, 99.5% for tap water and >99% for DW or DI.

Table 4 | Distribution of EC defluoridation studies based on types of feed water and maximum removal efficiencies (in %) reported

	Feed water				
	DI	DD or DW	GW	TW or DrW	Synthetic
Batch (67 studies)	23	15	11	14	4
Max. removal efficiency, %	>99	>99	97	>99.5	92.7
Continuous (16 studies)	3	4	5	2	2
Max. removal efficiency, %	98	79.6	94.8	95	89.2

The greater purity of distilled water or deionized feed water and lack of competition from other ions in solution accounts for the higher removal efficiencies observed in these feed waters.

pH

Since pH determines the speciation of aluminium or iron ions, it plays a crucial role in all coagulation processes including EC (Stumm & Morgan 1981; Amirtharajah & O'Melia 1990). There are two major issues with respect to pH during EC:

- i. *Change in pH during the EC process*: The pH of the solution increases as electrocoagulation progresses due to hydrogen evolution at the cathodes, and liberation of hydroxide ions from metal hydroxides. The final pH is mostly basic and is a major advantage over CC where the final acidic pH often needs to be neutralized to meet the desired range of 6.5 to 8.5. However, if the final pH is more than 8.5, neutralization will again be required.
- ii. *Effect of initial pH*: Initial pH of the solution has been found to affect removal efficiency. The optimum initial pH was observed to be around 6 to 7 (Chen *et al.* 2000; Adhoum *et al.* 2004; Zuo *et al.* 2008; Vasudevan *et al.* 2009, 2011; Ün *et al.* 2010; Behbahani *et al.* 2011a; Gwala *et al.* 2011; Babu & Goel 2013; Ün *et al.* 2013). Some researchers have observed a buffering effect where the pH of the solution increases if the initial pH was acidic and decreases if the initial pH was basic (Chen *et al.* 2000; Adapureddy & Goel 2012; Sharma *et al.* 2014). However, others have found that the initial pH does not influence removal efficiency significantly (Zhao *et al.* 2011; Behbahani *et al.* 2011b; Bazrafshan *et al.* 2012). Under acidic conditions, below pH 4.5, Hao & Huang (1986) found that hydrogen ions react with fluoride forming HF, while at alkaline pH, they are more likely to react with HCO_3^- and OH^- ions.

Conductivity

Solution conductivity can be increased by adding salts or salt solution to the water thereby improving removal

efficiency (Lin & Wu 1996; Ün *et al.* 2010; Behbahani *et al.* 2011b; Bazrafshan *et al.* 2012; Thakur & Mondal 2016). However, increasing conductivity from 100 $\mu\text{mhos/cm}$ to 10,000 $\mu\text{mhos/cm}$ helped reduce contact times for the same experimental conditions only marginally (Emamjomeh *et al.* 2004). Ün *et al.* (2010) reported lesser energy consumption with increase in conductivity of their solution because of decreased resistance.

Interfering ions

The effects of competing or interfering ions on fluoride removal efficiency were studied using synthetic solutions under controlled conditions and are summarized in Table 5. In general, most anions (sulphate, phosphate, nitrate and chloride) had a negative effect on defluoridation due to competition with F^- especially when aluminium electrodes were used.

The anion with the most negative impact on fluoride removal efficiency was sulphate, followed by nitrate (Hu *et al.* 2007). Zuo *et al.* (2008) suggested that ion exchange competition between SO_4^{2-} and F^- ions may be the reason as they found traces of S during sludge analyses. In another study, phosphate was also found to have a negative impact on fluoride removal efficiency (Ün *et al.* 2013). Govindan *et al.* (2015) used salts of Ca, Mg and Al to evaluate the impact of different cations and anions on F removal. Al cations were effective as coagulants while Ca and Mg were not significantly effective. Using EC along with these salts improved fluoride removal. Comparison of Al salts showed that maximum F removal was obtained with chloride followed by nitrate and sulphate. Calcium was found to have a positive impact on fluoride removal efficiency by Zuo *et al.* (2008) but not by Montero-Ocampo & Villafañe (2010). Mg^{2+} and Ca^{2+} assist in electrocoagulation probably due to the formation of nano-crystalline MgF_2 and CaF_2 (Shen *et al.* 2003; Zuo *et al.* 2008; Montero-Ocampo & Villafañe 2010; Govindan *et al.* 2015). Silicate, carbonate and arsenate were also reported to affect defluoridation negatively (Vasudevan *et al.* 2011). Further insight into the influence of ions affecting defluoridation efficiency positively or negatively can help in improving fluoride removal from waters like ground and river water where a mixture of ions are present.

Table 5 | Effect of co-existing anions and cations on fluoride removal efficiency

Researcher and year	Type of water	Electrode/ Coagulant material	Ion	Conc.	Units	Initial F conc.	Final F conc.	Units	Removal efficiency (%)	Effect on defluorination efficiency
Hu <i>et al.</i> (2003)	Deionized water	Al	None	–	–	25	–	mg/L	100	–
			SO ₄ ²⁻	5	mM	25	–	mg/L	21.1–67.3	Negative
			Cl ⁻	1, 5 and 10	mM	25	–	mg/L	86.5–88.7	Negative
			NO ₃ ⁻	1, 5 and 10	mM	25	–	mg/L	80.1–86.8	Negative
			SO ₄ ²⁻ + Cl ⁻	10 + 1, 10	mM	25	–	mg/L	46–65	Negative
			SO ₄ ²⁻ + NO ₃ ⁻	10 + 1, 10	mM	25	–	mg/L	33–40	Negative
Zuo <i>et al.</i> (2008)	Deionized water	Al	None	–	–	4	0.55	mg/L	86.25	pH = 3.4
			None	–	–	4	0.87	mg/L	78.25	pH = 7
			SO ₄ ²⁻	250	mg/L	4	1.85	mg/L	53.75	Negative
			Cl ⁻	290	mg/L	4	0.87	mg/L	78.25	Neutral
			Ca ²⁺	250	mg/L	4	0.23	mg/L	94.25	Positive
Montero-Ocampo & Villafañe (2010)	Model or deionized water and groundwater (GW)	Al	None	–	–	5.12	0.50	mg/L	90.23	–
			None, GW	–	–	5	1.45	mg/L	71.00	–
			SO ₄ ²⁻	320	mg/L	5	2.00	mg/L	60.00	Negative
			Cl ⁻	1,000	mg/L	5	0.81	mg/L	83.80	Negative
			Ca ²⁺	120	mg/L	5	1.56	mg/L	68.80	Negative
			Fe ³⁺	240	mg/L	5	0.89	mg/L	82.28	Negative
Vasudevan <i>et al.</i> (2009)	Deionized water	Al alloy	CO ₃ ²⁻	0–250	mg/L	5–20	–	mg/L	93–16	Negative
			PO ₄ ³⁻	0–50	mg/L	–	–	mg/L	93–49	Negative
			SiO ₃ ²⁻	0–15	mg/L	–	–	mg/L	93–21	Negative
			AsO ₄ ³⁻	0–5	mg/L	–	–	mg/L	93–35	Negative
Zhao <i>et al.</i> (2010)	Deionized water	Al	Ca ²⁺	0–10	mM	10	–	mg/L	62–96	Positive
			Mg ²⁺	0–1.872	mM	10	–	mg/L	70–92	Positive, optimal exists
Behbahani <i>et al.</i> (2011a)	Distilled water	Fe	None	–	–	25	–	mg/L	67.68	–
		Al	None	–	–	25	–	mg/L	98.53	–
		SO ₄ ²⁻	–	–	25–200	–	mg/L	59.2	Negative	
		NO ₃ ⁻	–	–	–	–	mg/L	90.56	Positive	
Ün <i>et al.</i> (2013)	Deionized water	Al	Cl ⁻	–	–	–	–	mg/L	98.53	Positive
			SO ₄ ²⁻	0.96–2.98	g/L	–	–	mg/L	94.2–91.4	electrolyte in all experiments
			PO ₄ ³⁻	5	mg/L	5	1.41	mg/L	71.8	Negative
			Mg ²⁺	50	mg/L	5	0.21	mg/L	95.8	Positive
			Ca ²⁺	200	mg/L	5	0.12	mg/L	97.6	Positive
			Al ³⁺ , without EC	0–0.9	mM	1.06	0.95	mM	–1,257.14	–

(continued)

Table 5 | continued

Researcher and year	Type of water	Electrode/ Coagulant material	Ion	Conc.	Units	Initial F conc.	Final F conc.	Units	Removal efficiency (%)	Effect on defluoridation efficiency	
Govindan <i>et al.</i> (2015)	Deionized water	Al	None	-	-	0.53	0.25	mM	-206.67	-	
			Cl ⁻	0-0.75	mM		0.05	0.05	mM	33.33	Positive
			NO ₃ ⁻	0-0.48	mM		0.07	0.07	mM	6.67	Positive
			SO ₄ ²⁻	0-0.28	mM		0.08	0.08	mM	0.00	Positive
			Al ³⁺	0-0.25	mM		0.11	0.11	mM	-46.67	Positive
			Mg ²⁺ , without EC	0.59	mM		0.38	0.38	mM	-406.67	-
			Mg ²⁺	0.59	mM		0.06	0.06	mM	20.00	Positive
			Ca ²⁺ , without EC	0.816	mM		0.39	0.39	mM	-420.00	-
			Ca ²⁺	0.816	mM		0.06	0.06	mM	20.00	Positive
			None	-	-		0.43	0.43	mM	-473.33	-
			Cl ⁻	0-0.75	mM		0.06	0.06	mM	20.00	Positive
			NO ₃ ⁻	0-0.48	mM		0.15	0.15	mM	-100.00	Positive
			SO ₄ ²⁻	0-0.28	mM		0.10	0.10	mM	v33.33	Positive
			Al ³⁺	0-0.25	mM		0.06	0.06	mM	20.00	Positive
Mg ²⁺	0.59	mM		0.33	0.33	mM	-340.00	Positive			
Ca ²⁺	0.816	mM		0.34	0.34	mM	-353.33	Positive			

Initial concentration

Initial contaminant concentration also influences its removal efficiency. Most papers indicate that an increase in initial concentration reduces F⁻ removal efficiency (Zhu *et al.* 2007; Zuo *et al.* 2008; Emamjomeh & Sivakumar 2009; Behbahani *et al.* 2011a, 2011b; Babu & Goel 2013; Takdastan *et al.* 2014). Figure 2 shows a decrease in removal efficiency from 84.9% at an initial fluoride concentration of 10 mg/L to 63.6% at an initial fluoride concentration of 50 mg/L (Babu & Goel 2013). These results were obtained after passing current through a batch reactor containing a distilled water solution for 180 min and filtering the sample for fluoride analysis through a 0.45 micron cellulose nitrate filter.

However, Vasudevan *et al.* (2011) found that fluoride adsorption increased on increasing initial concentration and remained constant after 90 min using AC and after 120 min using DC. Increasing fluoride concentration may have increased the ratio of aqueous fluoride to available complexation sites, thereby decreasing fluoride removal. An increase in initial concentration has also been found to increase the amount of sludge produced (Ghosh *et al.* 2008) and the cost of treatment (Ghosh *et al.* 2011).

Temperature and conductivity

Zhang *et al.* (2014) found that increasing temperature from 18 to 38 °C increases fluoride removal efficiency. In experiments with geothermal water, it was observed that

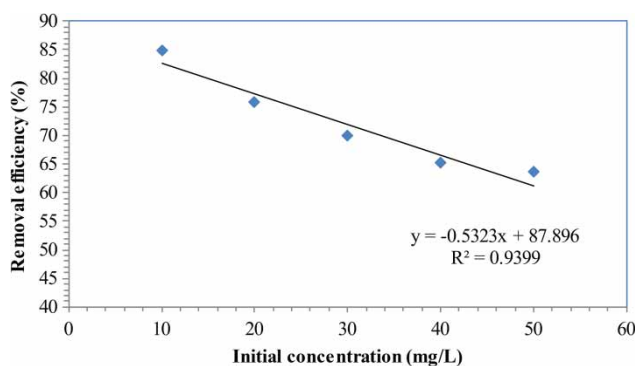


Figure 2 | Decrease in removal efficiency with increase in initial fluoride concentration in batch studies with distilled water solutions. Applied DC voltage was 25 V in all cases.

removal efficiency increased and energy consumption decreased when the temperature was increased from 18 to 45 °C, resolubilization of fluoride occurred when the temperature of water increased from 45 to 55 °C (Wang *et al.* 2017). However, Narasimham & Silaimani (1992) found that a temperature of 313 °K (39.85 °C) gave the best removal efficiencies in the range of 303–323 °K. Thus, it can be concluded that increase in temperature up to a certain point aids in removing fluoride, after which it will inhibit it. In both batch and continuous-flow experiments conducted by the first author (unpublished data), the temperature of the solution in the electrocoagulation reactor was found to increase over a period of time due to heat generated at the electrodes. In one continuous-flow experiment, temperature increased from 27.9 °C to 30.37 °C from the start of the experiment to its end (Figure 3). Temperature rise can be seen even more clearly in the batch experiment, where the temperature increased from 24.6 °C to 27.48 °C during electrolysis and decreased after that (Figure 4). Conductivity decreased after 3 hours in the batch reactor due to coagulation and settling of sludge. Temperature studies conducted by Vasudevan *et al.* (2011) showed that adsorption was spontaneous and exothermic in nature in the temperature range they studied (313–343 °K).

CHARACTERIZATION OF THE SLUDGE

Identification of elements or compounds present in sludge and electrode material can help to identify reactions taking place during electrolysis. Many researchers have

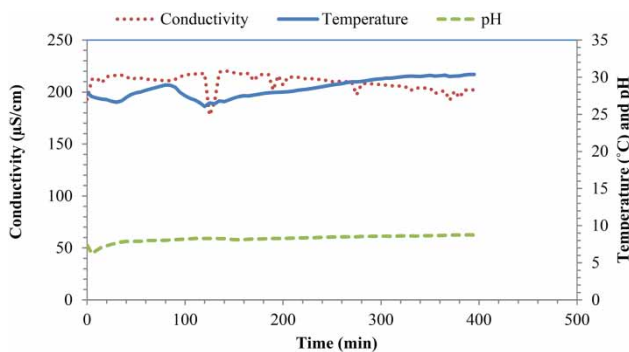


Figure 3 | Change in pH, temperature and conductivity in continuous-flow defluoridation experiments using EC.

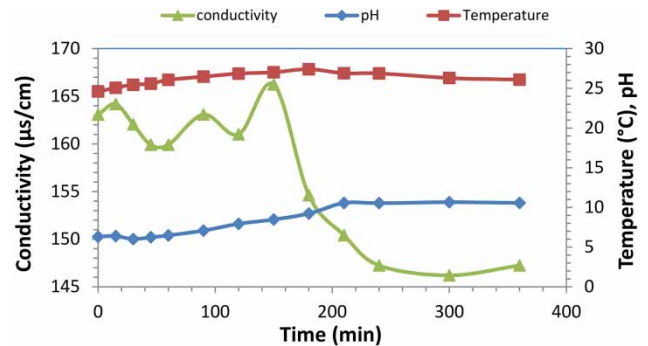


Figure 4 | Change in pH, temperature and conductivity in batch defluoridation experiments using EC.

analyzed sludge and electrode surfaces using SEM, EDS, TEM, FTIR and XRD.

Scanning electron microscopy (SEM)

SEM analyses of EC sludges show the presence of crystal structures (Figure 5(a) and 5(b)). Govindan *et al.* (2015) showed that the sludge particles or floc formed by iron electrodes were much smaller in size as compared to those formed by aluminium electrodes. Guzmán *et al.* (2016) reported irregular aluminium flocs of around 500 µm size. Hu *et al.* (2003) and Vasudevan *et al.* (2009) have shown SEM images with fine coagulant particles on the surfaces of their anode. The whitish by-products of sludge found by Ghosh *et al.* (2008, 2011) contained mostly aluminium hydroxides since the amount of dissolved electrode material was much higher than the quantity of fluoride. Essadki *et al.* (2009) found that the sludge generated at pH 4 was slightly more porous than the sludge generated at pH 7. A large number of indentations on the surface of the anode were observed by Vasudevan *et al.* (2011). Less disordered pores were formed by AC as compared to DC, which indicated uniform dissolution of aluminium electrodes as opposed to consumption of the electrodes at active sites due to oxygen generation at the surface.

Energy dispersive atomic spectroscopy (EDAX/EDS)

The formation of alumina-fluoro complexes has been verified by EDAX analysis wherein Al, F and O were detected by Ghosh *et al.* (2008, 2011) and Vasudevan *et al.* (2011).

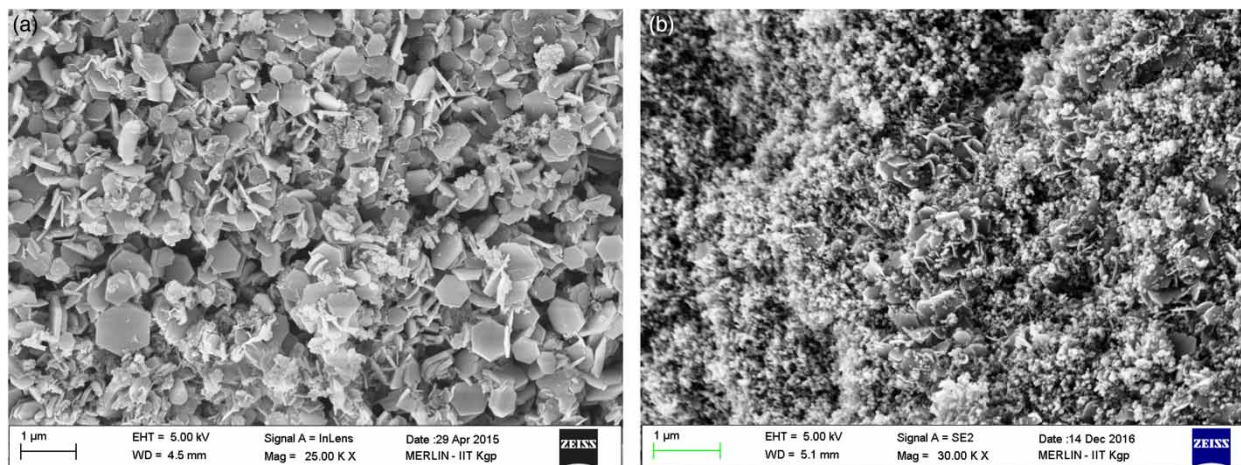


Figure 5 | SEM images of sludge obtained in defluoridation experiments using a batch EC reactor: (a) 25,000 magnification and (b) 30,000 magnification.

Oxygen and aluminium were always present in the flocs analyzed by Guzmán *et al.* (2016). The occasional presence of silica indicated the formation of aluminium hydro-silicates and small quantities of arsenic and fluoride were also found. Arsenic, fluoride and aluminium were present in EC sludges of Thakur & Mondal (2016). Sinha *et al.* (2015) confirmed entrapment of fluoride within aluminium-hydroxide complexes in EDAX analysis. The elements detected in sludges depend on the type of feed water used. C, O, Si and Fe were found in sludge and deposits on electrodes (Babu & Goel 2013). However, fluoride was found only in the sludge; no traces of fluoride were detected on the electrodes. Essadki *et al.* (2009) obtained greater fluoride content in their sludge at pH 4, whereas the amounts of oxygen and aluminium increased as the pH increased, a fact partly confirmed by XRF-WDS analysis.

Fourier transform infrared spectroscopy (FTIR)

Stretching bonds of H-O-H, Al-O, Al-F-Al and Al-O-H were detected by FTIR analysis (Ghosh *et al.* 2008, 2011; Vasudevan *et al.* 2011; Govindan *et al.* 2015; Sinha *et al.* 2015). O-H, Na-F, Al-O-Si, Si-O and As-O bonds were reported by Guzmán *et al.* (2016), who found mainly aluminium silicates in aluminium sludge. Si-O-Al bonds were also reported in the study by Sinha *et al.* (2015) since they used bentonite for the removal of alumina-fluoro complexes. Thakur & Mondal (2016) found O-H, Al-H and Al-O

stretching bands. Wave numbers in all studies ranged from 400 to 4,000 cm^{-1} . Mg-O and Mg-F were found in sludge by Vasudevan *et al.* (2009).

X-ray power diffraction (XRD)

When aluminium electrodes dissolve, they form several different aluminium-fluoride-hydroxide complexes ($\text{Al}(\text{OH})_{3-x}\text{F}_x$) depending on the solution pH (Sivakumar & Emamjomeh 2006; Zuo *et al.* 2008). These complexes have been identified by several researchers using XRD along with FTIR in their sludge analysis. XRD analysis of aluminium sludge showed that the phase was amorphous or poorly crystalline in nature (Ghosh *et al.* 2008, 2011; Vasudevan *et al.* 2011; Guzmán *et al.* 2016). Aluminium hydroxide flocs of $\beta\text{-Al}(\text{OH})_3$ were confirmed by Govindan *et al.* (2015). Other probable compounds were $\text{AlF}(\text{OH})_2$. Emamjomeh & Sivakumar (2005, 2009) have reported aluminium fluoride hydroxide and aluminium hydroxide (bayerite) in their sludge. Their XRD results indicated competition between OH^- and F^- . $\text{Na}_3(\text{AlF}_6)$, $\text{AlF}_3(\text{H}_2\text{O})_3$ and $\text{AlO}(\text{OH})$ were reported by Sinha *et al.* (2015), which indicates aluminium-fluoride-hydroxide complex formation. Zhao *et al.* (2010) added calcium and magnesium in their feed water to analyze their effects on defluoridation and found that four wide diffraction peaks were observed in the system when magnesium was added as compared to calcium. They inferred that Mg-Al

layered double hydroxides were being generated in the Mg^{2+} containing solution.

Iron oxide hydroxide crystals ($Fe_{21}HO_{32}$) have been reported by Govindan *et al.* (2015) and Apshankar & Goel (2017). However, no compound with fluoride was observed in XRD analysis with iron sludges. Govindan *et al.* (2015) attributed this to the similar ionic radii of fluoride and the replaced oxygen atom. This may also be due to the low concentration of fluoride relative to Fe.

CONCLUSIONS

Use of electrocoagulation for wastewater treatment has been studied to a far greater extent than for drinking water treatment. A limited number of studies were found in the literature regarding the use of electrocoagulation for fluoride removal in drinking water treatment. Several factors were found to influence defluoridation efficiency and the most important factors are reactor configuration, applied voltage, electrolysis time, initial contaminant concentration, pH and the presence of competing ions. All studies reviewed here are bench-scale or pilot-scale studies and no reports of full-scale drinking water treatment using EC for defluoridation were found. Most studies have been done with aluminium, and fluoride removal mechanisms with aluminium are understood to some extent. The mechanisms and chemistry of defluoridation with iron electrodes are still not clear.

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