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Capacitive deionization: a promising technology for water defluoridation: a review

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ABSTRACT

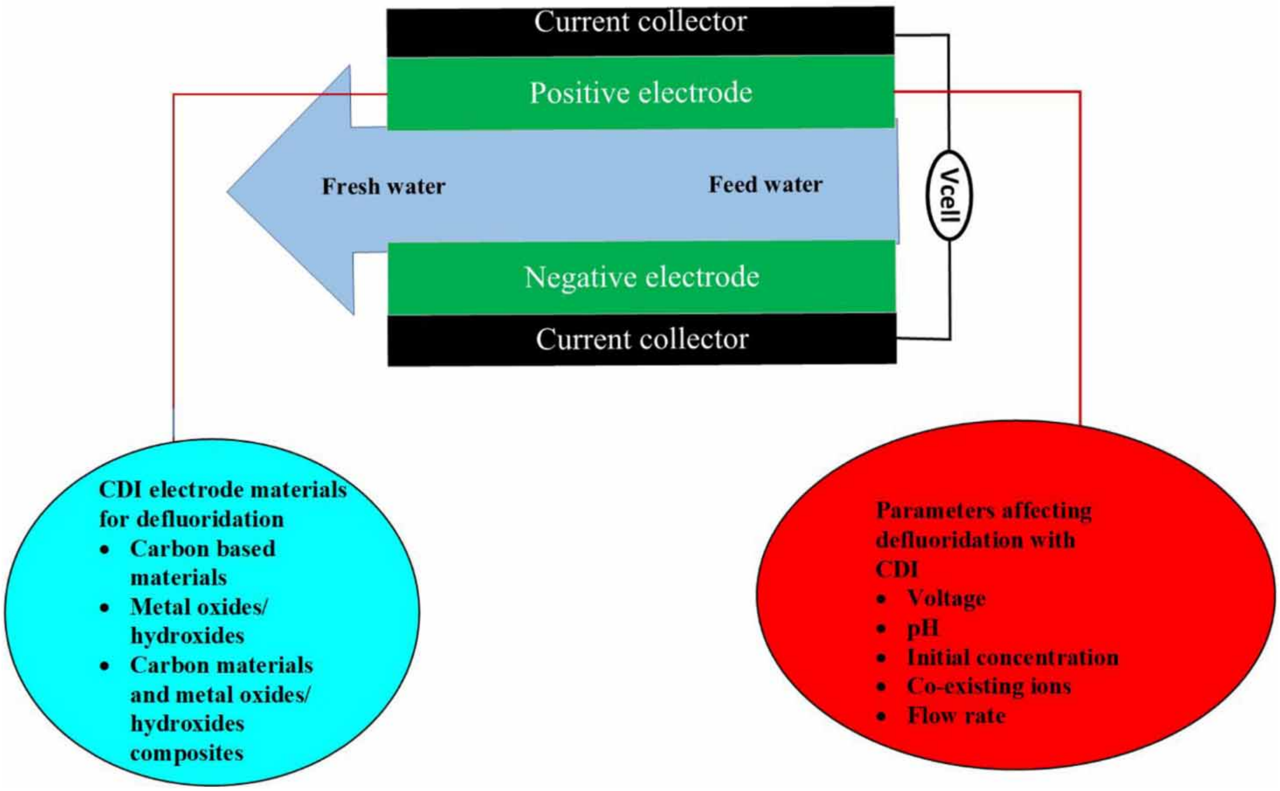
Capacitive deionization (CDI) is among the promising technologies employed for water purification. CDI has been studied for the removal of various ionic species from water including fluoride ion (F^-) with promising results. However, there is no comprehensive literature that summarizes the use of CDI for water defluoridation applications. Therefore, this review paper critically analyzes different electrode materials that have been studied for water defluoridation, their electrosorption capacities and F^- removal efficiencies. It further discussed the parameters that influence CDI efficiency during defluoridation and point out the issues of F^- selectivity when co-existing with other ions in the solution. We can conclude that different electrode materials have shown different abilities in electrosorption of F^-. The carbon-based materials possess high surface area and good electrical conductivity which is paramount for ion adsorption but gives lack selectivity for F^- removal. Metal oxides and hydroxides have been reported with improved electrosorption capacity and high selectivity to F^- due to the ion exchange between the F^- and the hydroxyls surface of the metal oxides/hydroxides. Apart from the good performance of these materials for defluoridation, the discovery of actual practical use of the electrode materials for defluoridation for commercial scale is still a need.

Key words: capacitive deionization, defluoridation, electrode materials, electrosorption

HIGHLIGHTS

- Water defluoridation by capacitive deionization (CDI) have been reviewed.
- The defluoridation efficiency of various CDI electrode materials has been reviewed.
- Metal oxides/hydroxides, as well as carbon materials and metal oxides/hydroxides composites, have shown good fluoride uptake in pilot-scale experiments.
- Parameters affecting the defluoridation process with CDI have been reviewed.

GRAPHICAL ABSTRACT



1. INTRODUCTION

About 70% of the total Earth's surface is covered by water; however only 0.002% of the available water is suitable for human consumption (Alrumman *et al.* 2016). This calls for sustainable methods to preserve the available freshwater. Preservation of water resources is still a global challenge because of its limited availability, industrialization and increase in the population (Hegde *et al.* 2020). Several factors including anthropogenic and geological factors (Yadav *et al.* 2018), uncontrolled industrialization, urbanization and unskilled utilization of water contribute to the contamination of groundwater and degradation of water quality, getting them below the World Health Organization (WHO) standards for safe drinking water (Hegde *et al.* 2020).

Groundwater is considered to be the major source of drinking water at the community and households' level in most parts of the world including Tanzania; however, in some areas, drinking water has been reported to contain an excess concentration of F^- above the WHO recommended limit, 1.5 ppm (Malago *et al.* 2017). The presence of high F^- concentrations in groundwater is attributed to anthropogenic or natural sources or a combination of the two (Brindha & Elango 2011; Khandare & Mukherjee 2019). Fluoride is characterized by having strong ligand action, a small radius and a tendency to form a large number of different inorganic and organic compounds in plants, soil, air and rocks. Normally fluoride exists on the ground and surface water because some of these compounds have high solubility in water, as they completely dissociated to F^- (Podgorski *et al.* 2018).

Fluoride is essential to human health when consumed at low concentrations. For instance, consumption of 0.5–1.0 mg/L is essential for dental health as it is important for teeth development (Lennon *et al.* 2004; Tiwari *et al.* 2017; Lizneva *et al.* 2018; Shi *et al.* 2018). Excessive F^- consumption above 1.5 mg/L (WHO standard) may lead to irreversible demineralization for the tooth and bone tissues, fluorosis and also may result in kidney, thyroid, brain and liver damage (Wambu *et al.* 2013; Vinati *et al.* 2015; Tiwari *et al.* 2017). Excess F^- concentration in water sources including groundwater (above 8 mg/L) has been observed in several regions globally including Tanzania, Cameroon, Kenya, China, Norway, Mexico, India and Japan (Yadav *et al.* 2018). Therefore, to make potable water safe and acceptable for human consumption, defluoridation is essential, particularly for water sources that have F^- concentrations over the WHO recommended limit 1.5 mg/L. These elevated F^- levels evidenced in ground and surface water almost all over the world, calls for the development of technologies for removing F^- from drinking water to make it safe for human consumption. Adsorption (Dąbrowski 2001; Ali & Gupta 2006), reverse osmosis (Mohapatra *et al.* 2009), electrodialysis (Mohapatra *et al.* 2009), Nalgonda technique (Kumar *et al.* 2019), coagulation (Turner *et al.* 2005; Khatibikamal *et al.* 2010; Gong *et al.* 2012) and membrane filtration (Ayoob *et al.* 2008) are some of the developed and practiced methods for F^- removal from drinking water. The above-mentioned technologies have shown marked results in removing F^- from drinking water. For instance reverse osmosis and membrane techniques are capable of removing and recovering F^- from wastewater, whereby more than 90% of the dissolved fluoride can be removed regardless of its initial concentration (Ndiaye *et al.* 2005), while adsorption can be applied in the large-scale advanced treatment of dispersed water sources (Sieliechi & Thue 2014; Aziz *et al.* 2020; Kumari *et al.* 2021) and achieve high adsorption capacity (Zhao *et al.* 2010; Thakur *et al.* 2014). Although these technologies possess unique advantages, complex regeneration, high energy consumption, cost factor (installation and maintenance), the requirement of experienced operators, membrane fouling, interference of other ions and poor water recoveries usually hinder their practical applications (Ayoob *et al.* 2008; Mohapatra *et al.* 2009). Therefore, capacitive deionization (CDI) technology, which is an efficient, sustainable and economical technology for defluoridation which may overcome the above-mentioned challenges, has been proposed.

Capacitive deionization is an emerging water treatment method that has received much attention recently in various applications. For instance, it has been used for water softening (Leonard *et al.* 2009), removal of ionic pollutants like fluoride, (Pan *et al.* 2018; Bai *et al.* 2019; Elisadiki *et al.* 2019), heavy metals such as lead (Alfredy *et al.* 2019) and cadmium (Peng *et al.* 2016), organic pollutants such as humic acid (Huang *et al.* 2016) and dyes (Senoussi & Bouhidel 2018), as well as salt removal (Li *et al.* 2009; Anderson *et al.* 2010; Li *et al.* 2010; Porada *et al.* 2012). The benefits of CDI are simple in the regeneration of the exhausted electrodes by applying zero voltage or changing the cell polarity, they are energy-saving and have high water recoveries as well as low fouling (Welgemoed & Schutte 2005; Saleem & Kim 2018).

The CDI system performance normally depends on electrode materials including carbon-based materials such as activated carbon (AC), graphene and carbon nanotubes (CNT), ion intercalation materials, such as metal carbides for example Ti_3C_2 and metal oxides like MnO_2 (Gabelich *et al.* 2002; Ryoo *et al.* 2003; Yang *et al.* 2011; Porada *et al.* 2013; Gao *et al.* 2015; Laxman *et al.* 2015; Omosebi *et al.* 2015; Agartan *et al.* 2019). Moreover, operating parameters including concentration, flow rate, salt type and applied potential (Gabelich *et al.* 2002; Mossad & Zou 2012; Han *et al.* 2014; Aldalbahi *et al.* 2018) and cell architectures like hybrid CDI, membrane CDI, inverted CDI and flow electrode CDI (Biesheuvel & van der Wal 2010; Jeon *et al.* 2013; Gao *et al.* 2015; Ikeshoji 2019) also affect the performance of CDI. Despite the noticeable improvement in CDI performance shown by the above-mentioned factors, commercialization of the CDI system has been unnoted especially for defluoridation. Therefore, this review specifically summarizes the performance of the existing CDI electrode materials that have been used for defluoridation and highlights the important parameters affecting CDI performance on the F^- removal from drinking water.

2. PERFORMANCE OF VARIOUS CDI ELECTRODE MATERIALS FOR DEFLUORIDATION

2.1. Carbon-based materials

Carbon-based electrode materials have been studied extensively for F^- removal as shown in Table 1 because carbon has a high affinity for F^- (Karthikeyan & Elango 2008). Carbon-based materials derived from biomass have been studied and show good defluoridation ability. For instance, Dong *et al.* (2021), successfully synthesized biochar from lignocellulosic waste for defluoridation with the highest removal efficiency of 91.98% and electrosorption capacity of 1.28 mg/g at 1.2 V. The improved CDI performance for F^- removal was ascribed by the electrostatic force generated when potential was applied as well as the effect of the electric double layer (EDL) formed. Also, the developed biochar was revealed to have the negative zeta potential which implies that the synthesized materials do not favor the electrosorption of negative ions including F^- because the electrode surface of the developed biochar was negatively polarized. Thus, it is important to understand the nature of the electrode materials surface by determining the potential of zero charge and zeta potential for the better improvement of CDI performance.

Gaikwad & Balomajumder (2017b), investigated the feasibility of AC derived from tea waste biomass (TWBAC) for defluoridation and hexavalent chromium removal simultaneously via CDI. The obtained highest electrosorption capacity of the

Table 1 | Carbon-based electrode materials for defluoridation with their maximum removal efficiency and electrosorption capacity

Electrode material	Water source	IFC (mg/L)	Voltage (V)	Flow rate (mL/min)	Removal (%)	EC (mg/g)	References
Biochar	Synthetic water	20	1.2	15	91.98	1.28	Dong *et al.* (2021)
Commercial AC	Synthetic water	10	1.2	16	94.20	0.82	Gaikwad & Balomajumder (2017a)
TWBAC	Synthetic water	10	1.2	–	85.20	0.74	Gaikwad & Balomajumder (2017b)
PANI-CNT	Synthetic water	38	1.6	5	–	9.88	(2021)
Commercial AC	Synthetic water	–	1.5	–	98.49	–	Kushwaha *et al.* (2020)
Micropore-dominant AC	Synthetic water	50	1.6	10	–	16.8	Li *et al.* (2017)
JFAC	Natural water	3.11	2.0	5	63	0.13	Elisadiki *et al.* (2019)
rGO/HA	Synthetic water	42	1.2	8	–	3.79	Park *et al.* (2021)

AC, Activated carbon; EC, Electrosorption capacity; IFC, Initial F^- concentration.

prepared TWBAC towards F^- was 0.74 mg/g (85.20%) and 2.49 (28.52%) at 10 and 100 mg/L F^- initial concentration respectively at a cell potential of 1.2 V. The results showed that the prepared TWBAC is more favorable for chromium (Cr^-) adsorption over F^- in the mixed feed solution (Figure 1) due to the difference in hydrated radius and valence as the hydrated radius of F^- is smaller than that of Cr(VI), also the electrosorption selectivity of multivalent anions is higher than that of monovalent (Li *et al.* 2016).

Also, similar behavior was observed when commercial AC was used as CDI electrode material for the simultaneous removal of F^- and Cr^- (Gaikwad & Balomajumder 2017a). The maximum F^- and Cr^- removal efficiency of AC was 94.20 and 97.1%, respectively, for the initial F^- concentration of 10 mg/L, pump flow rate 16 mL/min and applied potential of 1.2 V. Their results demonstrated the effect of Cr^- in the mixed solution towards electrosorption selectivity of F^-.

Elisadiki *et al.* (2019), studied the AC derived from jackfruit peel for the removal of F^- from natural water. Their results showed that the developed materials successful brought down the F^- concentration from 3.11 to 1.18 mg/L from natural water in the presence of natural organic substances and other ions. The highest electrosorption capacity achieved at the charging potential of 2.0 V and flow rate of 5 mL/min was 0.13 mg/g. Likewise, we studied the performance of commercial AC for F^- removal from simulated water and tap water. The maximum removal efficiency of 98 and 95% for simulated and tap water respectively at 1.5 V and pH 8.0 was reported. The slight decrease in the removal efficiency observed was due to the influence of other ions present in the tap water.

Park *et al.* (2021), studied the potential of reduced graphene oxide/hydroxyapatite composite (rGO/HA) prepared by the hydrothermal method for the selectivity of F^- from aqueous solution via the CDI. Park *et al.* (2021), compared the performance of the pristine AC and rGO/HA and found that the defluoridation performance of the rGO/HA electrode was superior

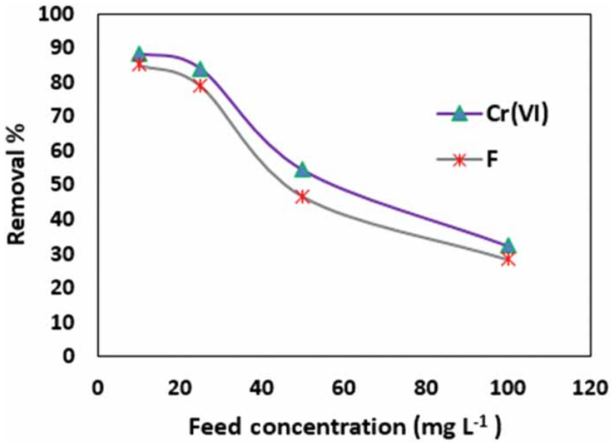


Figure 1 | Comparison of the electrosorption capacity of F^- and Cr (VI). Reprinted from (Gaikwad & Balomajumder 2017b), copyright (2017), with permission from Elsevier.

compared to that of the pristine AC electrode. The highest F^- removal capacity of rGO/HA and AC was found to be 0.2 and 0.041 mmol/g, respectively in the mixed feed solution of F^-, chloride (Cl^-), and nitrate (NO_3^-). They found that the F^- removal capacity of rGO/HA was not affected by the existence of Cl^- and NO_3^- in the feed solution. Also, the rGO/HA exhibited good cycle stability and reusability, as even after 50 cycles no significant loss of electrode capacity was observed. The good performance of rGO/HA towards F^- removal was explained by the high affinity of HA in the rGO/HA electrode to the selectivity of F^-.

Moreover, Wu *et al.* (2021) synthesized a Polyaniline-CNT (PANI-CNT) composite electrode for defluoridation with CDI. The highest removal capacity of PAN-CNT was reported to be 0.52 mmol/g at pH 7 and voltage of 1.6 V which was approximately 1.5 times more than that of CNTs. Wu *et al.* (2021) emphasized that the improved electrosorption capacity was because of the incorporation of PANI into CNTs.

From all these studies as summarized in Table 1, it has been observed that the selectivity of the carbon-based materials for defluoridation is still low. Thus, there is a need to focus more on the development of new CDI electrode materials with high selectivity which are environmentally friendly, cheap and efficient to improve the F^- electrosorption selectivity. Since the selectivity of the electrode materials for F^- is an important feature, as some of the electrode materials evidenced good efficiency in bench test but failed under real conditions at water treatment plants due to the reduction of the electrosorption capacity caused by electrodes' active sites occupation by other co-ions present in treated water. Moreover, from Table 1 one can see that most studies were conducted with simulated water, thus there is a need for conducting both simulated and natural water defluoridation studies to evaluate the effect of natural matters that present in water affecting the performance of CDI electrodes and come up with a clear solution on how to deal with that effect.

2.2. Metal oxides and their composite

Single, two or more metal oxides as summarized in Table 2 especially those prepared in nanoscale have been reported to have great potential for removing F^- from drinking water and showed marked adsorption capacities. This is due to their unique features including the large specific surface area of the metal oxides nanoparticles which is favorable for F^- adsorption (Maliyekkal *et al.* 2006; Kumar *et al.* 2011; Raul *et al.* 2012; Li *et al.* 2014; Prasad *et al.* 2014), fast adsorption kinetics rate, the presence of functional groups at the metal oxides nanomaterials surfaces (Khandare & Mukherjee 2019), good desorption potential, limited solubility in water, and non-toxicity in nature (Loganathan *et al.* 2013; Tomar *et al.* 2013).

Bai *et al.* (2019) studied the potential of NiAl-layered metal oxide (NiAl-LMO) as CDI electrode materials for selectivity of F^- from drinking water. The obtained maximum electrosorption capacity of NiAl-LMO towards F^- was 49.28 mg/g that was higher than the electrosorption capacity and selectivity of other anions present in solution (Cl^- and SO_4^-).

Likewise, Wang *et al.* (2021) successful synthesized and characterized nickel, iron, manganese layered metal oxide (NiFeMn-LMO) electrodes for defluoridation applications. The maximum defluoridation capacity of the developed electrode material reported was 16.7 mg/g at 500 mg/L initial F^- feed concentration. Wang *et al.* (2021) emphasized that the good defluoridation performance of NiFeMn-LMO electrodes for F^- selectivity depicted was due to the synergistic effect of the ternary metals.

Li *et al.* (2019) studied the electrosorptive performance of nickel, cobalt and aluminium (NiCoAl)-layered metal oxide (NiCoAl-LMO) nanosheets and reduced graphene oxide (rGO) composites (NiCoAl-LMO/rGO) which were prepared by a one-step urea precipitation method. The prepared electrodes achieved the electrosorption capacity of 24.5 mg/g, with the initial NaF concentration of 500 mg/L at 1.4 V applied voltage and maximum cycle stability of 40.

From these studies, the findings demonstrated that metal oxides nanomaterials and their composites have good potential for the selectivity of fluoride removal from water. The improved F^- electrosorption selectivity depicted was attributed to the

Table 2 | Comparison of the F^- maximum removal efficiency and electrosorption capacity of different metal oxides and their composites

Electrode material	Water source	IFC (mg/L)	Voltage (V)	Flow rate (mL/min)	Removal (%)	EC (mg/g)	References
NiAl-LMO	Simulated water	5	1.0	–	73.5	49.28	Bai *et al.* (2019)
NiFeMn-LMO	Simulated water	500	1.4	–	–	16.7	Wang *et al.* (2021)
NiCoAl-LMO/rGO	Simulated water	500	1.4	–	–	24.5	Li *et al.* (2019)

AC, Activated carbon; EC, Electrosorption capacity; IFC, Initial F^- concentration.

electrostatic interaction between charging surface and fluoride synergistic when potential is applied and the exchange of surface hydroxyl groups with F^- (Habuda-Stanic *et al.* 2014; Mukherjee *et al.* 2019). However, the cost analysis and environmental negative effect of these metal oxides need to be calculated so that the produced defluoridator is cheap and efficient to use at household, small community and industrial levels.

2.3. Carbon materials and metal oxides/hydroxides composites

The carbon materials were combined with metal oxides or hydroxides to form a composite to improve their properties especially for the selectivity of the targeted pollutants present in water including F^- as summarized in Table 3.

For instance, Li *et al.* (2018), studied titanium hydroxide ($Ti(OH)_4$) loaded AC (Ti-AC) for removal of F^- from the solution of different kinds of anions. The maximum adsorption capacity of the electrode made from $Ti(OH)_4$-loaded AC was 115.2 mg/g at 1.2 V applied voltage with the F^- initial concentration of 50 mg/L. For the investigation of the adsorption selectivity of the electrode on F^-, a mixed solution containing Cl^-, NO_3^- and SO_4^{2-} was prepared. The experimental results revealed that the competitive anions present in the feed solution did not affect the adsorption selectivity of F^-.

Min *et al.* (2020), also investigated the electrosorption performance of bismuth/reduced graphene oxide nanocomposite (Bi/rGO) for the selective removal of F^- and Cl^-. The findings revealed that the material exhibited a good selectivity toward the ions and better regeneration, as after 10 cycles there was no significant change in removal capacity for both Cl^- and F^-. The obtained maximum electrosorption capacity of F^- of 0.48 mmol/g was approximately four times lower than that of Cl^- which implies that Bi/rGO favours the selectivity of Cl^- rather than F^-.

Also, Wu *et al.* (2016) synthesized titanium oxide (TiO_2)-loaded AC (Ti-AC) and employed it as potential material for the electrosorption of F^- from water. The synthesized Ti-AC electrodes achieved a maximum F^- removal capacity of 157.8 μmol/g at an applied potential of 1.5 V. The improved removal capacity observed was attributed to the external electric field applied to the cell and chemical bonding between F^- and TiO_2.

From these studies, the results evidenced that the composite of carbon materials with metal oxide and hydroxide possesses high electrosorption capacity and excellent selectivity for F^- removal from water that was attributed to both electrostatic driving force induced by the potential applied on the electrode surfaces and the exchange of surface hydroxyl groups with F^- (Habuda-Stanic *et al.* 2014; Mukherjee *et al.* 2019). However, the available literature, focused on the efficiency of carbon materials loaded with single metal oxides for CDI defluoridation. Thus, more studies are needed to investigate the synergistic effect of bimetallic and trimetallic oxides loaded with carbon materials as electrode materials for defluoridation to enhance the performance of the CDI system.

2.4. MXenes

MXenes is the emerging materials that gained much attention from research groups for various applications such as water purification (Ying *et al.* 2015; Srimuk *et al.* 2016; Huang *et al.* 2019a, 2019b; Liu *et al.* 2020), energy storage (Anasori *et al.* 2017; Zhang & Nicolosi 2019), environmental remediation (Zou *et al.* 2016), and sensors (Zhu *et al.* 2017; Szuplewska *et al.* 2020). The application of MXenes as CDI electrode material for the removal of various pollutants present in water including F^- have been studied. MXenes evidenced significant sorption selectivity and efficient reduction capability for various targeted pollutants present in water due to its fascinating characteristics such as excellent selectivity towards specific pollutants, high surface area and the presence of different functional groups (-O and -OH), as well as reduction capabilities towards numerous pollutants (Zou *et al.* 2016; Huang *et al.* 2019b; Ihsanullah 2020; Szuplewska *et al.* 2020).

For instance, 2D Ni/MAX (Ti_3AlC_2) nanocomposite was employed as CDI electrode materials for defluoridation and removal of Pb and As (III) ions (Bharath *et al.* 2021). Ni/MAX (Ti_3AlC_2) nanocomposite demonstrated good selectivity of

Table 3 | Comparison of the F^- maximum removal efficiency and electrosorption capacity of different composites of carbon materials and metal oxides and hydroxides

Electrode material	Water source	IFC (mg/L)	Voltage (V)	Flow rate (mL/min)	Removal (%)	EC (mg/g)	References
$Ti(OH)_4$-AC	Simulated water	50	1.2	–	–	115.2	Li *et al.* (2018)
TiO_2-loaded AC	Simulated water	10	1.5	25	–	2.99	Wu *et al.* (2016)
Bi/rGO	Simulated water	420	1.2	–	–	9.12	(2020)

AC, Activated carbon; EC, Electrosorption capacity; IFC, Initial F^- concentration.

F$^-$ from water with the maximum removal capacity of 68 mg/g at the applied potential of 1.4 V, initial F$^-$ concentration of 100 mg/L, the flow rate of 5 mL/min and charging time of 150 min. The good electrosorption capacity obtained was attributed to the electrostatic force of attraction induced by the voltage applied and the presence of functional groups on the Ni/MAX (Ti_3AlC_2) surface. As per our review, limited studies have investigated the potential of MXenes for defluoridation with CDI. Many studies focused on the application of MXenes for the removal of heavy metals and organic contaminants such as dyes from water through adsorption and membrane processes. This is a call for the research community to study the practicality of MXenes for the removal of F$^-$ from water with CDI due to their hydrophilicity, high electrical conductivity, selective surface chemistry and tunable surface that are the required properties for CDI electrode materials (Oren 2008; Ihsanullah 2020) and therefore, can be promising materials in future water purification.

3. PARAMETERS AFFECTING DEFLUORIDATION PROCESS WITH CDI

This section summarizes some of the key parameters that contribute to the effectiveness of developed CDI electrode materials for defluoridation. The effective electrosorption selectivity of electrode materials for different ions including F$^-$ depends on several factors such as the surface area of the electrode materials, flow rate, initial concentration, charging time, applied voltage, cycle stability of the electrodes, pore size distribution, and type of electrolyte (Gabelich *et al.* 2002; Mossad & Zou 2012; Han *et al.* 2014; Aldalbahi *et al.* 2018).

3.1. Applied voltage

The applied voltage is among the significant parameters to consider in the electrosorption technique since it influences the electrosorption process due to the induced electrostatic attraction. It is well known that the adsorption of the ions in the CDI system normally depends on the voltage applied that will thicken the EDL which is paramount for ion adsorption (Huang *et al.* 2013). For instance, Park *et al.* (2021), investigated the impact of electric voltage on F$^-$ removal using the rGO/HA as CDI electrode material. The maximum F$^-$ removal capacity of rGO/HA achieved was 0.19 mg/g at 1.2 V that was 2.4 times higher than that operated at 0 V. Park *et al.* (2021), reported that the increase in charging potential enhances the electrosorption capacity when the electric potential increases from 0.5 to 1.2 V. However, at 1.5 V the F$^-$ removal capacity significantly decreased probably because of water electrolysis.

Bharath *et al.* (2021), also studied the effect of electric potential (0.8–1.8 V) on F$^-$ removal capacity. The results showed the increment in electrosorption capacity as potential was increased from 0.8 to 1.4 V, however above 1.4 V the electrosorption capacity decreased (Figure 2(a)). The negative trend observed when more than 1.4 V was applied was attributed to water electrolysis which normally results in high energy consumption.

Li *et al.* (2019) also investigated the effect of varying applied voltage from 0.6 to 1.4 V on defluoridation and found that increasing charging potential increases F$^-$ removal capacity from 9.1 to 24.5 mg/g (Figure 2(b)). Li *et al.* (2019) emphasized that the improved removal capacity exhibited was due to the stronger Coulomb force between the surface of the electrode and NaF as well as the increase in EDL capacity.

Moreover, Li *et al.* (2017) also investigated the effect of applied voltage for the voltage range of 0.4–1.6 V towards F$^-$ electrosorption in the CDI system. The maximum electrosorption capacity obtained was 16.8 mg/g at 1.6 V, at the flow rate of 10 mL/min and the initial concentration of 50 mg/L. Their result demonstrated the increase in electrosorption capacity as the voltage applied was increased due to the increase in coulombic force as voltage rises. Dong *et al.* (2021) also studied the influence of different applied voltages on the electrosorption performance of CDI towards F$^-$ removal and demonstrated the decrease in the F$^-$ concentration in the solution as the voltage applied was increased from 0.4 to 1.2 V (Figure 2(c)) which resulted in the improved electrosorption capacity.

The effect of applied voltage on F$^-$ removal using the PANI-CNT composite electrode was also investigated in the range 0 V–2.4 V by Wu *et al.* (2021). The maximum electrosorption capacity was observed at 1.6 V which was attributed to the strong electrostatic force of attraction that existed between the oppositely charged electrodes as agreed by other studies above. However, at more than 1.6 V a decreasing trend in the removal capacity was observed due to the oxidation reaction that occurred to the PANI-CNT electrode. Moreover, Gaikwad & Balomajumder (2017a), studied the defluoridation performance of CDI at different voltage ranges from 0.4 to 1.2 V and found that the best removal performance occurred at 1.2 V (Figure 2(d)).

Both of these experiments showed that as the applied potential increased, F$^-$ removal capacity increased. However, the maximum F$^-$ electrosorption capacity takes place at the voltages of 1.2 and 1.4 V, then we can conclude that the optimum voltage range for defluoridation with CDI should be between 1.2 and 1.4 V. Increasing voltage to values larger than 1.4 V

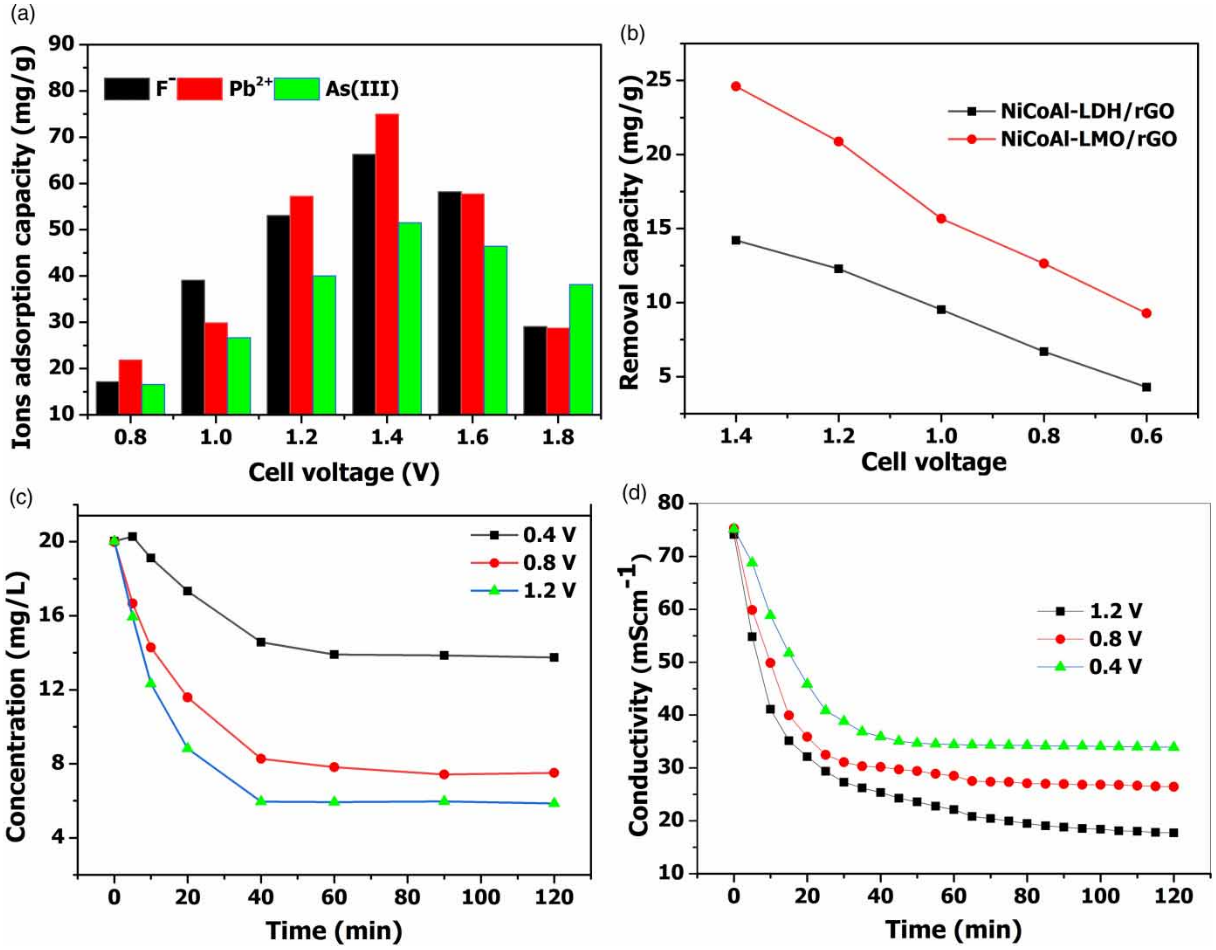


Figure 2 | (a) The effect of the applied voltage on the adsorption capacity. Reprinted from (Bharath *et al.* 2021), copyright (2020), with permission from Elsevier. (b) Fluoride removal capacities of NiCoAl-LDH/rGO and NiCoAl-LMO/rGO in NaF solution at the initial concentration of 500 mg/L. Reprinted (adapted) with permission from (Li *et al.* 2019), Copyright (2019), American Chemical Society. (c) Time versus concentration at the applied voltage of 0.4, 0.8 and 1.2 V. Reprinted from (Dong *et al.* 2021), copyright (2020), with permission from Elsevier. (d) Conductivity versus time at different applied voltages. Reprinted from (Gaikwad & Balomajumder 2017a), copyright (2017), with permission from Elsevier.

might result in water electrolysis and other side reactions on the electrode that might lead to high energy consumption (Jiang *et al.* 2018; Zhang *et al.* 2020).

3.2. pH of the solution

The pH is another significant factor affecting defluoridation and water quality in water treatment systems (Pan *et al.* 2018). Several research works have reported the influence of solutions pH on F^- removal in CDI systems. For instance, Bharath *et al.* (2021), investigated the effect of pH on the electrode performance for the removal of F^- at the pH range from 2 to 10. The results evidenced the increase in electrosorption capacity as the pH of the solution was increased from 2 to 6.5 and decreased as the pH solution was increased from 8 to 10 (Figure 3(a)). The highest electrosorption capacity obtained was 74 mg/g at the pH of 6.5, then it was reduced to 39 mg/g when pH was increased to 10. Bharath *et al.* (2021) emphasized that the negative trend observed above the pH of 6.5 was attributed to the increase in hydroxyl ions in the alkaline solution which competed with F^- on the adsorption sites to the electrode surface.

Kushwaha *et al.* (2020), also studied the effect of pH towards F^- removal through the CDI process. The pH range varied from 2.5 to 10 while other CDI operating parameters were kept constant. At a pH of 8, the maximum removal efficiency of 98.49% was achieved. Wu *et al.* (2016) investigated the effect of solution pH on the removal of F^- for the pH range of 3.2–11.32, initial concentration of 10 ppm, and applied potential of 1.5 V. Their findings revealed an increase in electrosorption capacity with increasing pH values, with a peak at pH 9.05, however above pH 9.05 the electrosorption capacity decreased (Figure 3(b)).

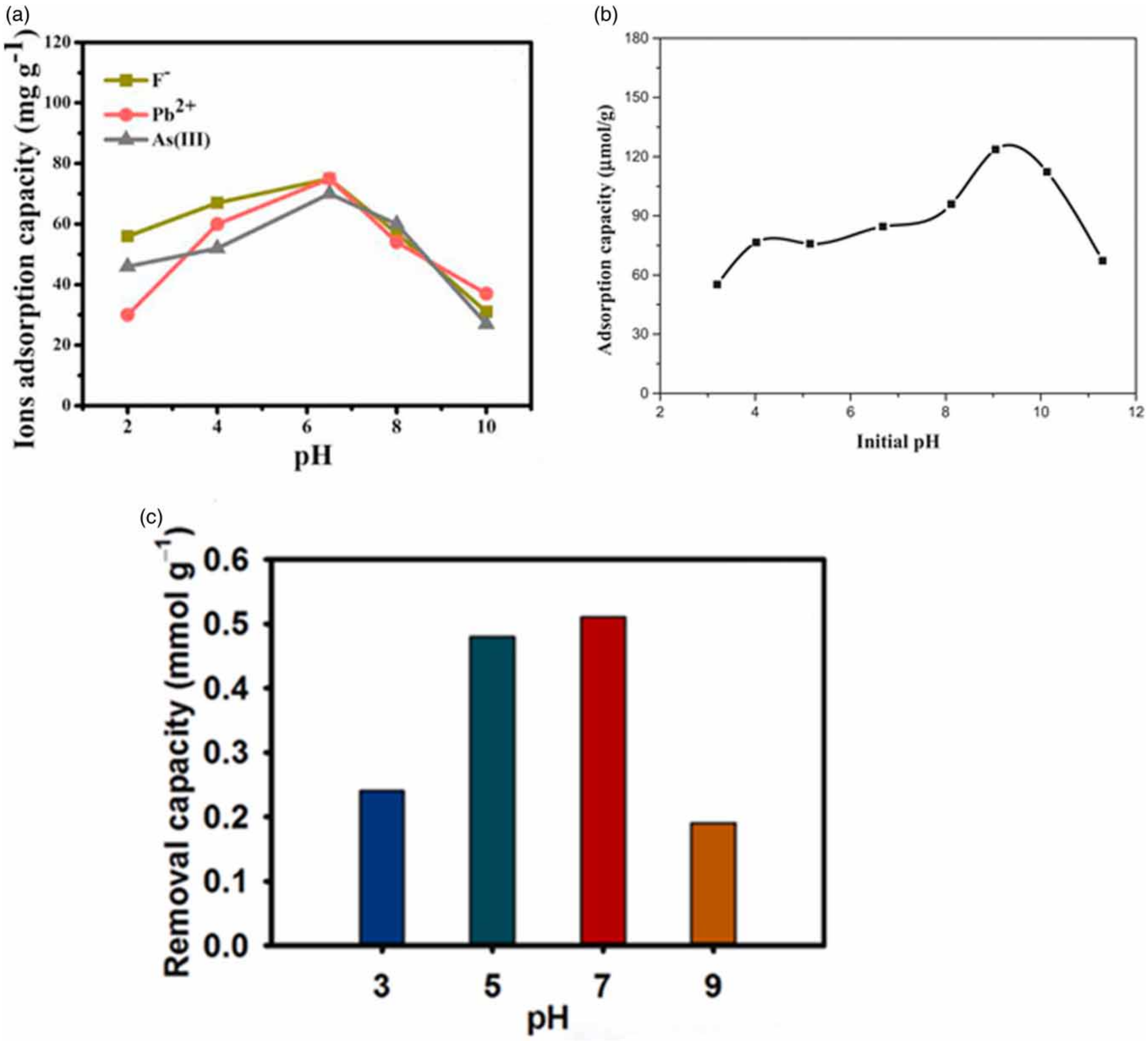


Figure 3 | (a) Operational pH versus ions adsorption capacity of Ni/MAX//pRGO asymmetric electrodes at 1.4 V. Reprinted from (Bharath *et al.* 2021), copyright (2020), with permission from Elsevier. (b) Fluoride electrosorption by Ti-AC at various initial pH values with a starting concentration of 10 ppm. Reprinted from (Wu *et al.* 2016), copyright (2016), with permission from Elsevier. (c) pH change with the electrochemical removal of F$^-$ of the PANI-CNT electrode at different pH values (3, 5, 7 and 9). Reprinted from (Wu *et al.* 2021), copyright (2020), with permission from Elsevier.

Kushwaha *et al.* (2020), highlighted that the lower electrosorption capacity observed in acidic medium and alkaline solution was due to the presence of different types of fluoride ions (F$^-$ and HF^{2-}) and hydroxyl ions respectively.

The effect of solution pH on the removal capacity of electrode materials for defluoridation was also studied by Wu *et al.* (2021), with different pH values ranging from 3 to 9 (Figure 3(c)). The electrosorption capacity was observed to increase with pH up to pH of 7. However, at pH 9 the removal capacity sharply decreases which was explained by deprotonation of the nitrogen atoms in PANI in alkaline medium and hydroxide ions that normally compete with the F$^-$ to the electrode active sites. From all these studies it is concluded that defluoridation with CDI works well with solutions with neutral pH. Therefore, the electrode materials that give the optimal results at neutral pH could be regarded as suitable defluoridation electrode materials for natural water systems.

3.3. Initial fluoride concentration

The initial concentration of the solution is another important parameter that greatly affects the CDI defluoridation process. The effect of different concentrations (10, 25, 50, and 100 mg/L) on the electrosorption potential of AC derived from tea waste biomass for defluoridation and Cr^- removal was investigated by Gaikwad & Balomajumder (2017b), (Figure 4(a)). The maximum F^- removal capacity observed at 100 mg/L was 2.49 mg/L which was 3.4 times higher than the electrosorption capacity achieved for 10 mg/L. The experimental results evidenced the increase in electrosorption capacity as concentration increases which can be attributed to the decrease in solution resistance as ionic concentration increased in the solution (Rasines *et al.* 2012).

Similarly, Li *et al.* (2019) studied the influence of initial F^- concentration from 100 to 700 mg/L to the F^- removal capacity by using NiCoAl-LMO/rGO as CDI electrode materials. Their results presented the increasing trend of electrosorption capacity as NaF increases from 100 to 500 mg/L (Figure 4(b)) by keeping the voltage at 1.4 V. However, at 700 mg/L the increase of electrosorption capacity ceased because of saturation limit; which means that fewer active sites were available for adsorption at higher concentrations. Therefore, the electrosorption capacity is strongly affected by the initial concentration of the feed solution as agreed by other studies (Wang *et al.* 2013).

3.4. The co-existing ions

Water with F^- normally is associated with other co-anions such as bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{2-}), nitrate (NO_3^-) and phosphate (PO_4^{3-}) which can compete with F^- during the electrosorption process. For example, Tang *et al.* (2016b) reported that the presence of Cl^- in the feed concentration affected negatively the defluoridation process. The F^- removal capacity was reported to be 1.71, 0.492, and 0.114 mg/g when a feed solution of 2 mM NaF was mixed with 0, 5 and 20 mM of Cl^-, respectively; at a flow rate of 56 mL/min and charging voltage of 1.2 V (Figure 5). This explained that the negative trend of F^- removal capacity observed as initial Cl^- concentration increased due to the competition of Cl^- with F^- for electrosorption sites on the electrode surfaces.

Also, Dong *et al.* (2021) investigated the effect of Cl^-, SO_4^{2-}, NO_3^- and HCO_3^- towards defluoridation. The findings revealed that the presence of other ions in the mixed feed solution, in addition to F^-, affected the defluoridation removal rate in the following order: $Cl^- > SO_4^{2-} > NO_3^-$. This order was explained in terms of their differences in ion valence and hydrated radius which were also described in other literature (Zhao *et al.* 2012; Hou & Huang 2013).

3.5. Flow rate

Pump flow rate also has been reported as a significant parameter affecting the CDI performance. For instance, Li *et al.* (2019) evidenced the dependence of CDI defluoridation performance on the flow rate. The study varied different flow rate range of 6, 9 and 12 mL/min (Figure 6(a)) at 500 mg/L NaF initial concentration through the CDI batch mode approach. Their findings demonstrated good electrosorption capacity at the flow rate of 9 mL/min due to high electrosorption of ions. However, at a flow rate of 12 mL/min, a decrease in electrosorption capacity was seen. Gaikwad & Balomajumder (2017a), also observed a

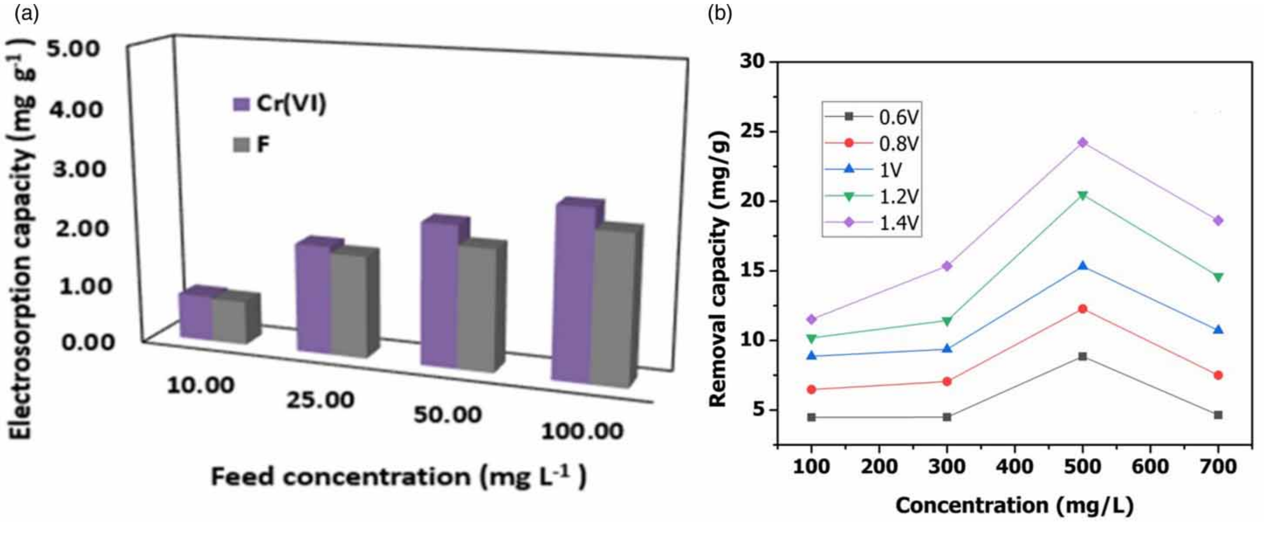


Figure 4 | (a) A plot of feed concentration versus electrosorption capacity. Reprinted from (Gaikwad & Balomajumder 2017b), copyright (2017), with permission from Elsevier. (b) Electrosorption capacities of NiCoAl-LMO/rGO with different concentrations of NaF solution. Reprinted (adapted) with permission from (Li *et al.* 2019). Copyright (2019), American Chemical Society.

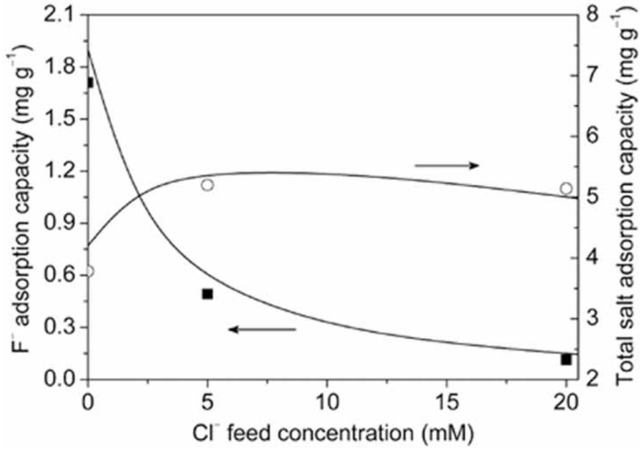


Figure 5 | The effect of Cl ion initial concentration on the F adsorption capacity. Reprinted from (Tang *et al.* 2016b), copyright (2016), with permission from Elsevier.

similar trend by batch mode CDI operation in their study. The effect of different flow rate (4, 8, 12, 16 and 20 mL/min) for the removal of Cr(VI) and F^- was investigated. The results showed an increase in electrosorption efficiency as the flow rate was increased up to 16 mL/min. The decrease in electrosorption capacity was observed beyond the flow rate of 16 mL/min. A similar trend was also observed by other groups (Jande & Kim 2014; Tang *et al.* 2015; Agartan *et al.* 2019) for the CDI batch mode system. They reported that ion removal performance improved with increasing flow rate and remained constant at a certain value of flow rate. This is because during batch mode operation mixing happens in the recycling tank, and a high flow rate (short residence time) is beneficial to the CDI system's performance when operating using the batch mode approach. This implies that, when the flow rate is low, the treated water circulation rate is also low, preventing continuous ion removal in the CDI cells. Therefore, more research may be needed to investigate further the above-observed trend for the batch mode operated CDI.

Tang *et al.* (2016b), also studied the effect of flow rate by using single-pass CDI operation whereby the lower minimum F^- effluent concentration was observed at a lower flow rate (Figure 6(b)) because in single-pass CDI operation mode sufficient contact time (greater residence time) is required for better ion electrosorption in the CDI cell (Seo *et al.* 2010; Jande & Kim 2013; Tang *et al.* 2016a). This means that for a given volume of the solution moving from the inlet to the outlet, more ions will

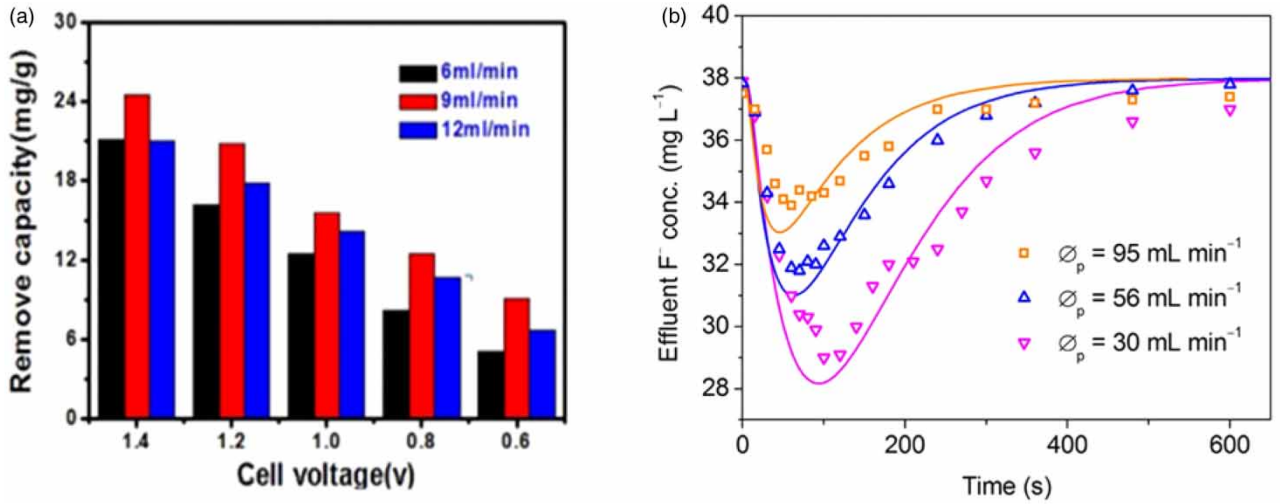


Figure 6 | (a) Fluoride removal capacity of NiCoAl-LMO/rGO in NaF solution at different flow rates with an initial concentration of 500 mg/L. Reprinted (adapted) with permission from (Li *et al.* 2019). Copyright (2019), American Chemical Society. (b) Effect of flow rate on effluent fluoride concentration in the presence of NaCl. Reprinted from (Tang *et al.* 2016b), copyright (2016), with permission from Elsevier.

be adsorbed, resulting in a lower effluent F^- concentration. However, if the flow rate is too low, dead zones in the spacer region are generated, resulting in reduced performance (Seo *et al.* 2010).

Likewise, in the study conducted by Dong *et al.* (2021), the influence of the pump flow rate on the defluoridation process was also studied. Fluoride removal rates decrease as the pump rate increased from 2.7 to 10 mL/min in single-pass operated CDI system. The maximum removal rates of F^- were achieved at 2.7 mL/min.

Therefore, the effect of flow rate in CDI performance differs for the two CDI modes of operation; batch mode and single pass. A low flow rate is preferable for the single-pass operating system and a relatively high flow rate is preferable for the batch mode system.

3.6. Other parameters

Several other parameters might affect the performance of CDI that need also to be considered during the CDI defluoridation process. These parameters include charging time, the number of electrode pairs and plate spacing. It has been reported that the solution concentration decreases with charging time (Jia & Zou 2012), and the best removal capacity can generally be associated with the more number of the electrode pairs, and plate spacing of electrodes as the stronger ion adsorption is attributed by the smaller gap between the electrodes as gap affects the electrosorption cell's volume performance (Huang *et al.* 2013).

4. CONCLUSION AND OUTLOOK

The capacitive deionization (CDI) process could be a potential technology for defluoridation because of its simple operation, usage of multiple electrodes, ecofriendly regeneration of electrodes and low energy consumption. Electrode materials are the key parameter for any CDI system. As per the literature, different electrode materials including carbon-based electrodes, metal oxides/hydroxides and their composites were investigated as CDI electrode materials for defluoridation. Carbon-based materials demonstrated low electrosorption capacity towards F^- removal while metal oxides and hydroxides and their composites evidenced the promising performance at the pilot scale; although among them none have been tested in the field. The challenges of most electrode materials reported in the literature are lack of selectivity in the presence of the co-existing ions which negatively affects the removal capacity of the targeted ions. Therefore, the key issues are to further develop new, effective, cheap and safe CDI electrode materials for defluoridation with high F^- selectivity that can make the commercialization process possible. Moreover, factors such as applied potential, flow rate, and pH of the solution should be considered for better performance.

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CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Tusekile Alfredy: Conceptualization, Methodology, Writing – original draft, Visualization. **Joyce Elisadiki**: Conceptualization, Methodology, Supervision, Writing – review & editing, Visualization. **Yusufu A.C. Jande**: Conceptualization, Methodology, Supervision, Writing – review and editing.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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