

Fluoride-containing water: A global perspective and a pursuit to sustainable water defluoridation management -An overview

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ABSTRACT

High levels of fluoride, though, naturally occurring (which can reach as high as 2,800 mg F⁻/L) in the environment can be toxic to various living organisms. Moreover, it can be transported by water and by its confluences and exacerbated by anthropogenic activities making it an environmental and public health concern. World Health Organization has set the standard for drinking water at 1.5 mg F⁻/L while the average national effluent standard is 15 mg F⁻/L. Hence, different defluoridation techniques of aqueous solutions were developed in the past years. This study provides an overview of the popular methods in defluoridation (i.e. adsorption, ion-exchangers, precipitation, membrane, electrocoagulation, and electro-dialysis). The mechanisms, critical operational conditions, and research progress are presented. The results further reveal that adsorption, regarded as the primary technique for defluoridation, still needs further development and mostly on its bench-scale and is only proven effective at low initial concentrations. In this study, sorption techniques are also estimated to be 10 to 20 times more expensive in operational costs relative to the other treatments. Furthermore, the majority of the examined literature demonstrated defluoridation at limited initial concentration <100 mg F⁻/L. In contrast, industrial effluents may reach 250–1,000 mg F⁻/L (up to ~10,000 mg F⁻/L at extreme cases). Inadequate removal of fluoride in water by single treatment also compels researchers to explore hybrid treatments. In addition, due to the lack of wastewater treatment facilities requiring high capital cost, bioremediation, a commonly overlooked alternative, is presented for temporarily alleviating fluoride levels. Finally, challenges such as limited literature for disposal of secondary pollution and cost evaluation along with other potential research perspectives are further discussed.

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1. Introduction

Water is a very essential resource to sustain life and its contamination is a critical concern for health and the environment. Approximately, about 783 million people have no access to safe drinking water (Singh et al., 2017). In Tanzania, the World Bank projected that it would confront severe water stress with resources below 1.5 million liters per capita-day by 2025 (Shen and Schäfer, 2015). To counteract this looming concern, providing safe, clean, and affordable water is set as the 6th United Nations Sustainable Development Goals (UNSDG) benefiting 2.8 billion people in 2030.

Fluoride, incessant distress (which is a non-biodegradable, hazardous, and persistent pollutant) naturally occurs groundwater (GW), a predominantly major water source. High fluoride environmental levels can occur because of volcanic eruptions, natural transport conveyed by air and water, and weathering. In addition, fluoride enters the GW through the dissolution of fluoride-rich rocks and minerals (e.g. fluoroapatite, fluor spar, sellaite, and villiumite).

Due to the uncontrolled development in the past decades, this naturally occurring phenomenon can be severely aggravated by anthropogenic activities, especially by industrial processes (such as fertilizer, aluminum, semiconductor, steel, brick-manufacturing, and pesticide industries). Along these lines, Paudyal et al. inferred that fluoride pollution in water is extremely inevitable (Paudyal, 2017). Industrial effluents contain a high level of fluoride commonly varying from 250 to 1,500 mg/L (Liu and Liu, 2016) and may even reach about 10,000 mg/L in extreme cases (Bagastyo et al., 2017). Moreover, these fluoride effluences can also be accreted to the soil, water, and organic tissues of plants, animals, and humans increasing exposure, detrimental to health (Kusrini et al., 2015). Thus, it is becoming both an environmental and public health concern, requiring conscientious management.

World Health Organization (WHO) has set 1.5 mg F⁻/L as the maximum acceptable limit for drinking water (WHO, 2011). However, fluoride levels in several water sources around the globe exceed this standard limit. Various places worldwide are cited as substantially affected by high fluoride levels (i.e. Argentina, China, India, Italy, Middle East, Mexico, Mongolia, Netherlands, Norway, Pakistan, Poland, Spain, Thailand, West Indies, UK, various regions of the African continent and some regions from both North and

South America) (Chaudhary and Prasad, 2013; Mohan et al., 2011). Thus, it can be considered that the problem in fluoride is already a global pandemic.

Unwanted fluoride levels can further affect the metabolism of calcium, potassium, and phosphorus in the human body causing various illnesses (Fakhri and Adami, 2013). Fluoride is also an anabolic agent stimulating cell proliferation and can attach to the enzyme's active center commonly causing inhibition of its activity, at micromolar and at millimolar levels, respectively (Barbier et al., 2010). Dental and skeletal fluorosis (correlated to other bone defects including arthritis, osteoporosis, bone breakage, etc.) are the most evident fluoride-related and water-borne diseases. Initial symptoms are muscle weakening, chronic fatigue, and joint stiffness. In addition, it may also adversely affect (mainly lesions) the heart, arteries, liver, kidney, thyroid, endocrine glands, brain, and reproductive organs.

Due to the threat of fluoride effects, its removal has also long been a challenge in engineering and water resource management devoting various efforts for effective removal technologies. In addition, fluoride's ionic size and high reactivity augment the challenges associated with conventional techniques. Prevalent techniques for the removal of fluoride in water are adsorption, precipitation, membrane processes (viz. reverse osmosis (RO) and nanofiltration (NF)), electrodialysis (ED), and electrocoagulation (EC). However, these methods have inherent drawbacks such as complexity, enormous chemical usage, high operational cost, and voluminous generation of secondary pollution including sludge (Naghizadeh and Gholami, 2017). Hence, this review evaluates and compares the existing studies and how these techniques in fluoride removal and recovery advance in the global context and various standard limits.

2. Global standards and incidence of fluoride

In the developing countries, the immediate environment together its natural waters are the places of recreation and water source. Moreover, the raw or tap water which might not undergo adequate treatment is used for direct consumption. Although there are some household methodologies available in local markets such as using filters, it is not enough to remove fluoride. Notably, Xia et al. recently developed a simple defluoridation only by boiling

eggshell with the addition of acetic acid and sodium phosphate intended for household application (Xia et al., 2019). However, although this technique successfully lowered fluoride concentration to <1.5 mg/L, it is only proven for 10 mg F⁻/L initial concentration.

The uncontrolled concentration of fluoride can subsequently cause fluorosis, a common fluoride- and water-borne disease. Likewise, fluorosis can be endemic not only in developing but also in developed countries approximately over twenty countries worldwide (Chen et al., 2012). An adequate amount of fluoride in the environment may not only affect humans but also some aquatic animals. As early as the 1980's, low fluoride levels (0.3–0.5 mg/L) in water were reported to be harmfully affecting the migration of adult Salmon in John Dam in the Columbia River (Damkaer and Dey, 2011). Hence, a careful discernment of the appropriate water standards is very critical.

2.1. Fluoride in natural waters world-wide

The hydrologic cycle, geophysical and chemical processes, and anthropogenic activities are the major factors of the fate and transport of fluoride in natural waters. Singh et al. classified three major belts composed of group of countries distinguished for its fluoride contamination vulnerability (i.e. African, Middle-East-to-South-East Asian, and American belts) (Singh et al., 2018), an indication of transnational movement most probably via GW. Moreover, the situation can be aggravated by the presence of other contaminants in water. In Nepal, fluoride together with other contaminants (e.g. arsenic, lead, molybdenum, boron, and zinc) were identified in GW of Kailali district but extensive surveys are still very limited (Joshi et al., 2013).

The highest level of fluoride recorded in natural waters is about 2,800 mg/L (WHO, 2011). Chiefly, high fluoride levels can occur in the environment but industrial and agricultural activities exacerbate fluoride contamination as confirmed by Luo et al. in the case of the Yun Cheng Basin (Luo et al., 2018). Presented in Table 1 is a summary of the fluoride level studies in natural waters worldwide in the past 10 years. Many of the reported natural waters containing high levels of fluoride are GW to be employed as a water source. Similarly, Edmunds and Smedley reported a comprehensive data

collection titled “Fluoride in natural waters”, presented fluoride levels in various countries (Edmunds and Smedley, 2013). However, most of the available data are from literature published in the last 20–50 years.

2.2. Statistics of fluoride-related disease

Among the countries worldwide, India is the most affected by the high fluoride levels in the environment (Sharma et al., 2018). About 14 million of 85 million tons of fluoride on earth's crust are deposited in India which considered holding the largest deposits of carbonate-related fluorite, globally (Hayes et al., 2017). These natural deposits can further be dissolved by natural weathering and geochemical processes contaminating GW. Correspondingly, around 1.3 billion people in India depend heavily on GW, annually extracting about 75,000,000 m³, equivalent to one-third of the total extracted GW worldwide (Morton, 2019). A large portion of the population (consist of 17 states comprising 200 different territories) suffers from various fluoride-causing diseases such as dental/skeletal fluorosis, crippling, etc. (Khandare et al., 2017). Furthermore, Podgorski et al. recently estimated that about 120 million people are in the high-risk area for fluoride exposure (Podgorski et al., 2018). In total, around 411.4 million people (Mohapatra et al., 2012) including approximately 26 million children (Grzegorzec and Majewska-Nowak, 2018) are affected making it not only a geo-environmental but also toxicological issue. Hence, Morton further pointed out that to sustain this growing population, geochemical investigations are essential to discover and to further prohibit potential anthropogenic sources from worsening the contamination (Morton, 2019).

In Latin American countries (such as Argentina, Bolivia, Chile, El Salvador Mexico, Nicaragua, and Peru), people suffered from chronic and endemic hydroarsenicism also frequently linked with fluoride (Ingallinella et al., 2011). In Mexico, it was estimated that the majority (75%) of the population were dependent on fluoride contaminated aquifer (Rosales et al., 2018) above the Mexican standard for drinking water (Sandoval et al., 2019). Almost half (about 44%) of the main water source of Aguascalientes (a region in Mexico) has fluoride levels of 1.5 mg/L which may reach >10 mg/L in some extreme cases (Delgadillo-Velasco et al., 2017). Previous

Table 1
Fluoride levels in the global natural waters.

Location, Water Body	F ⁻ Levels (mg/L)	Reference
Argentina (Buenos Aires), GW	1.9–7.0	Ingallinella et al. (2011)
Brazil, Aquifer	5–20	Bhadja et al. (2016)
China (Yuncheng basin), GW and SW	0.1–15.36	Luo et al., 2018
East Africa (Rift Valley Lakes), SW	264.0	Alabdulaaly et al. (2013)
Estonia, Pagasi River	88.0	Shen and Schäfer (2014)
Ethiopia (Main Ethiopian Rift), Well water	10.0–68.0	Rango et al. (2012)
Kenya, Lake Nakuru	2,800	Malago et al. (2017)
India (Chhattisgarh), Aquifer	>10.0	Thakur et al. (2019)
India (Ansola and West Bengal), Pond and Well	0.6–19.2	Mukherjee et al. (2015)
India, Aquifer	38.5	Emamjomeh et al. (2011)
Indonesia (Asembagus, East Java), GW and river	4.2–14.2	Arahman et al. (2016)
India (Gujarat and Rajasthan), aquifer	3–15	Bhadja et al. (2016)
Iran, drinking water source	>1.5	Asgari et al. (2012)
Mexico (Central and NW regions) aquifer	1–9.5	Sandoval et al. (2014)
Mexico (Independence basin), Deep well (500 m)	5.5	Sandoval et al. (2019)
Mexico (North East Guanajuato), Deep Well (310 m)	4.4	Rosales et al. (2018)
Mexico (Bajio Guanajuato), Deep Well (320 m)	2.5	Guzmán et al. (2016)
Morocco, GW	1.8–18.0	Bhadja et al. (2016)
Poland (Busko, Ladek and Jedlina) SW (recreational)	3.5–12.0	Drobnik et al. (2011)
Spain (Tenerife Island), Lake	>7.0	Mena et al. (2019)
Saudi Arabia, GW	0.01–5.4	Alabdulaaly et al. (2013)
Tanzania, Arusha aquifer	330.0	Grzegorzec and Majewska-Nowak (2018)
Turkey (Isparta, Dogubeyazit and Tendurek), GW and SW	1.5–15.2	Tezcan Un et al. (2013)

studies in Mexico indicated that endemic fluorosis caused water-borne fluoride is correlated to neurodegeneration manifested in IQ score reduction (Rocha-Amador et al., 2007) and attention deficit disorder (Bashash et al., 2018).

In China, around 30 million people are exposed to highly concentrated fluoride in drinking water from which 2.7 million suffered from fluoride-induced crippling (as reported by WHO) (Chen et al., 2010a) and 1.3 million people from skeletal fluorosis (Silva et al., 2018). In Italy, likewise, over 100 districts (including Lazio and Tuscany which are critical domestic and economic regions) reportedly have exceeded fluoride levels in water sources (Lavecchia et al., 2012). Nonetheless, we have not found severe cases of endemic fluoride diseases in these Italian regions.

On the other hand, artificial municipal water fluoridation has been believed to be safe and practiced for supposed dental-cavity prevention for several decades reaching around 40 countries with 400 million people worldwide (Till and Green, 2020). Balancing this beneficial effect and the adverse effects at high concentration intuitively suggest an optimum level of fluoride. In the US, Federal Water Fluoridation Panel recommended an F^- level of 0.7 mg/L as optimum concentration (Centers for Disease Control and Prevention, 2015). However, Walker et al. revealed recently that US water systems have not been conforming with 0.7 mg F^- /L which are either over-fluoridating or under-fluoridating with concentration range (0–1.855 mg F^- /L) (Walker et al., 2020). Till and Green further reiterated the adverse prenatal effects of fluoride conforming with recent findings which apparently and constantly neglected in the previous years (Till and Green, 2020).

2.3. Water standards of fluoride in different countries

Various countries have developed different standards for water management prescribing quality of drinking water, effluent, and natural waters. From the numerous water quality parameters, some countries provided fluoride limits in water classifications to provide quality health, environment, and economic benefits. Presented in Table 2 are the summary of the fluoride standards worldwide.

Most of the countries also show following the 1.5 mg F^- /L concentration prescribed by the WHO. However, Addison et al. recently raised that Southern Malawi (in the lower East African Rift system) still follows the 6.0 mg F^- /L concentration, a former WHO fluoride limit (Addison et al., 2020). Correspondingly, a concentration ranges of 0.7–1.2 mg F^- /L is recommended to some regions to factor in consideration for semi-arid to arid places and effects of seasonal change (Centers for Disease Control and Prevention, 2015). Evidently, developing countries particularly in the South East Asian region (i.e. Philippines, Indonesia, and Vietnam) have stricter rules (specifically setting effluent limits dependent on the water use) than their developed counterparts. The Philippines does not allow levels of fluoride and its further disposal to natural pristine waters (for both non-coastal and coastal waters). Conversely, it is quite alarming that Indonesia does not provide fluoride levels for irrigational waters unlike Pakistan providing 1 mg/L limit equivalent to most drinking water standards. Narratives from previous years revealed that plants could bio-accumulate fluoride through soils and waters (Zuo et al., 2018). So, although fluoride might not be swallowed directly through water consumption, high fluoride might be ingested through fluoride-contained agricultural products.

On the other hand, most recurring effluent standards are at 10.0 and 15.0 mg/L ranging from 6.0 to 25.0 mg/L. However, the reported fluoride levels in the natural environment presented in Table 1 are too high which might not even pass as concentration for industrial effluents set by different countries. Natural waters do not conform to the ideal level of fluoride in waters. Hence, further development

of fluoride removing technologies is regarded as essential providing safe drinking water and environmental protection.

3. Literature analysis

Upon the review of literature, certain technologies for fluoride removal are frequently mentioned (such as adsorption, ion-exchange, NF, RO, precipitation, ED, and EC). Typical terms such as “adsorption”, “electro-chemical”, “precipitation”, and “membrane” are employed. These terms are added to the word “fluoride removal” to generate the number of publications from 2001 to 2018 gathered in Semantic Scholar. Fig. 1 shows that the number of publications in the previous years is increasing, inferring the growing interest of researchers on water defluoridation. In line with this, numerous reviews written on the development of water defluoridation techniques are summarized and discussed in Section 3.1.

3.1. Fluoride removal in water: previous reviews

In previous years, Waghmare and Arfin have given especial attention to the defluoridation technologies providing several reviews. Among these, the most comprehensive review examined wide-range of defluoridation techniques drawn upon 200 recently published papers (Waghmare and Arfin, 2015). These primarily consist of coagulation-precipitation techniques, membrane processes, and adsorption for both water treatment (WT) and wastewater treatment (WWT). Although the paper provided qualitative descriptions of benefits and drawbacks, there were limited quantitative data and point-to-point discussion for benchmarking different techniques. Similarly, Singh et al. discussed different defluoridation techniques but mainly focus on membranes and adsorption with few adsorbent materials (Singh et al., 2016).

Adsorption is apparently the most attractive among defluoridation technology due to its perceived simplicity, adequate efficiency, economic viability, and sustainability. Numerous investigations have been reported using adsorption which also manifested in several reviews. Correspondingly, Waghmare and Arfin were also motivated by the development of adsorbents particularly calcium- (Waghmare and Arfin, 2015), aluminum- (Waghmare and Arfin, 2015), biomass- and waste-product-based (from the industrial and agricultural sector) (Waghmare and Arfin, 2015). Remarkably, Bhattacharya emphasized the utilization of the nanostructured material due to the reported high surface-to-volume ratio (Bhattacharya, 2017). Meanwhile, Gandhi et al. specifically focused on the low-cost adsorbents including concrete, chalk powder, seed and peel powders, etc. (Gandhi et al., 2012). Among the evaluated review papers, Bhatnagar et al. comprehensively considered adsorbent materials including all adsorbents discussed above along with modified alumina, iron, natural materials, bio-sorbents, and mixtures of metals (complexing oxides, hydroxides, and oxyhydroxides) (Bhatnagar et al., 2011). In summary, most of the adsorption studies are typically at its preliminary stage (or still at lab-scale) focusing on material development and properties.

The membrane processes, however, were more established compared to other technologies due to its continuous development in the past decades. Reviews with membrane processes on defluoridation highlighted more its applications for drinking water (Mohapatra et al., 2009) and its simultaneous removal of other contaminants (e.g. iron (Thakuria and Buddharatna, 2016) and natural organic material (Shen and Schäfer, 2015)). In the same way, another review specifically discussed NF and RO for defluoridation and simultaneous removal of uranium together with the removal mechanisms and effect of operational conditions (Shen and Schäfer, 2014).

Table 2

Fluoride limit for drinking water, effluent, and natural water in the standard of different countries.

Country	Description	F ⁻ (mg/L)	Reference
Algeria	Industrial effluent	15.0	Drouiche et al. (2012)
Australia	Drinking-Water	1.5	Natural Resource Management Ministerial Council et al. (2006)
	Greywater	0.49–1.6	
	Long-term trigger value	1.0	
	Short-term trigger value	2.0	
	Sewer Waters	20.0	
China	Drinking-Water	1.0	Cai et al. (2015) (B. Y. Wang et al., 2013)
	Effluent (Chinese AQSIQ, 1996)	10.0	
	Effluent	2.0	
India	Water Source (SW)	0.5	Biswas et al. (2018)
Indonesia	Aquaculture and recreational use (SW)	1.5	Ministry of the Environment Republic of Indonesia (2014)
	Effluent at the water source	2.0	
	Effluent at non-water source	3.0	
	Agricultural irrigation	Not required	
Italy	Drinking-Water	1.5	Lavecchia et al. (2012)
Japan	Non-coastal Waters	8.0	(Ministry of Environment (Government of Japan), n.d.; Paudyal et al., 2018)
	Coastal Waters	15.0	
Malawi	Drinking-Water	6.0	Addison et al. (2020)
Mexico	Drinking-Water	<1.5	Guzmán et al. (2016)
Mongolia	Drinking-Water (MNS 0900: 2005)	0.7–1.5	Ministry of Roads Transport and Development and Asian Development Bank (2019)
	Surface Water Quality (MNS 4585: 2007)	1.2	
Morocco	Drinking-Water	0.7	El Jaoudi et al. (2012)
Nepal	Drinking-Water	0.5–1.5	DFTQC (2018)
Pakistan	Drinking-Water	≤1.5	Khawaja and Aslam (2018)
	Water for Irrigation	1.0	
	Water for supply, recreation, and aquaculture	1.5	
Philippines	For water source and Pristine Marine Waters	Not allowed	(Environmental Management Bureau DENR, 2016)
	Freshwater	1.0, 2.0*	
	Marine waters (for aquaculture and recreation)	1.5, 3.0*	
	Navigable fresh water	2.0, 4.0*	
	Navigable marine waters	3.0, 6.0*	
	*Effluent	2.0–6.0	
Poland	Drinking-Water	<1.5	Borysewicz-Lewicka and Opydo-Szymaczek (2016)
	Effluent	25.0	
Romania	Effluent	5.0	Majewska-Nowak et al. (2015)
Singapore	Drinking-Water	1.0	Stoica et al. (2012)
Taiwan	Effluent	15.0	Khawaja and Aslam (2018)
Tanzania	Effluent	8.0	Aoudj et al. (2015)
Thailand	Industrial Effluent	5.0	Tanzania Bureau of Standards (2005)
Vietnam	Drinking-Water, Domestic Effluent, Marine Waters (for aquaculture, recreation, etc.)	1.5	Industrial Estate Authority of Thailand (1998) (Vietnam Environment Administration, 2015; 2009)
	Industrial Effluent for residential reuse	5.0	
	Industrial Effluent for non-residential reuse	10.0	

3.2. Objective and methods

Hence, this study aims to present a comprehensive review of different defluoridation methodologies for both WT and WWT for pertinent for benchmarking. The review has principally classified these techniques with the processes shown in Fig. 2. Databases such as Google Scholar, Science Direct, and Web of Science are employed to retrieve various articles on the topic. Keywords such as “defluoridation”, “fluoride removal”, “water treatment”, and “wastewater treatment” are added to the techniques above-mentioned retrieving suitable articles. After a thorough search and eliminating articles with no direct connection to water defluoridation, a total of 125 original articles are primarily included in the content of the review. This excludes several review papers providing an understanding of different mechanisms of each treatment.

In our review, we prioritize the original articles published in recent years from 2010–2019 (about 98.4% of original articles) as a starting point of exploration of the development of various treatment methodologies. Moreover, it was further extended to

literature from the past decades published from 2000–2009 (the remaining 1.6%) for technologies with fewer published literature discussed as follows:

1. The presentation of the literature of popular methodologies in recent years as well as; (a) its basic concept and mechanism to remove fluoride in water and; (b) how it was developed in filling the research gaps of the prior investigations.
2. Hybrid treatments and bioremediation which have been rarely examined in the previous reviews are also added as a supplementary section.
3. The efficiency of treatments (inferred from various works of literature) will be discussed and presented in the context of the standards (specified in Section 3.2) to develop point to point discussion. Conceptual estimates of operational expenditure (OpEx) are also provided. (The detailed approach is discussed in Section 5.2).
4. Furthermore, the review also specified some perspectives which can be valuable in future research.

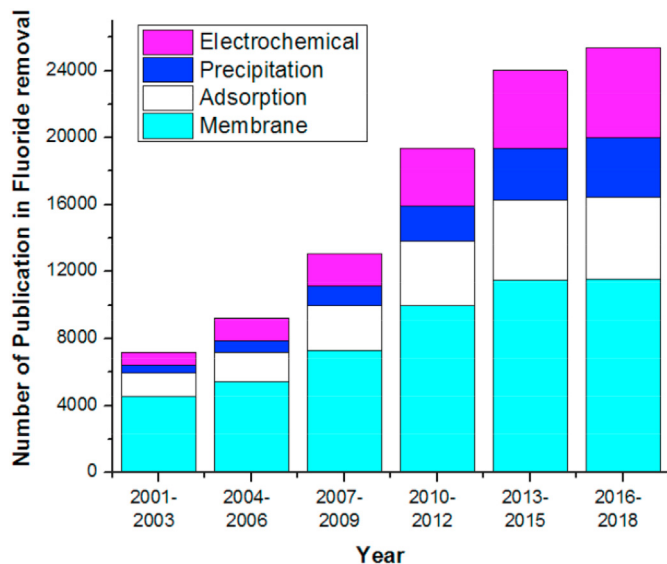


Fig. 1. Number of publications from 2001 to 2018 for defluoridation of the aqueous solution.

4. Fluoride treatments

4.1. Sorption

Adsorption and ion exchange including absorption (discussed in Section 4.4.2) can be generalized as sorption process. Sorption generally refers to an attachment of a substance to another substance by either physical or chemical processes. The mechanism of these processes is employed for the selective separation of various impurities in an aqueous solution. Moreover, desorption (the process reversal of sorption) is commonly included in various sorption

studies for the potential recovery of the sorbed substance and/or for sorbent regeneration.

Adsorption is basically the attraction between the sorbate and the surface of the sorbent which occurs in the environment. The two classifications of adsorption are the physisorption governed by van der Waals force forming a weaker bond and chemisorption causing the stronger chemical bond between sorbate and sorbent. In addition, Artioli indicated that industries have taken advantage of this natural phenomenon in applications such as air fractionation and depuration, and liquid discharge (Artioli, 2008). Utilization of the adsorption process in water treatment is a reliable separation process for inorganic and organic compounds, heavy metals, and other compounds causing foul odor and taste in water. In the context of defluoridation methodologies, adsorption is labeled as an “evolving front line of defense” (Mohan et al., 2011). Fig. 3-a presents the general mechanism of adsorption of fluoride in aqueous solution. Since fluoride is a negative ion, pH (that will induce a positive charge in the adsorbent) is a crucial factor to obtain the desired removal. Moreover, other operational condition such as adsorbent dose, contact time, and temperature are some other factor affecting adsorption. Contrariwise, adsorption technique also has some drawbacks. Guan and Zhao pointed out that adsorbents are difficult to regenerate and has subsequent complex desorption process (Guan and Zhao, 2016).

Similarly, the mechanism of the ion-exchange resin (IER) is somewhat similar to adsorbent but dealing in more mobile ions. Unlike the adsorbent, ions are initially attached to the IER and further release by replacing it with target ion to be removed (which is fluoride as shown in Fig. 3-b). Moreover, desorption in the IER (by manipulating the ionic strength) is relatively easier than adsorbent desorption.

Sorption process generally adopts the fixed- (or packed-) bed reactors (PBR) as general configuration offering ease to design and operation high degree of stability and reliability, and flexibility (Tovar-Gómez et al., 2013). Some pieces of literature also discussed

Treatment technologies for fluoride management

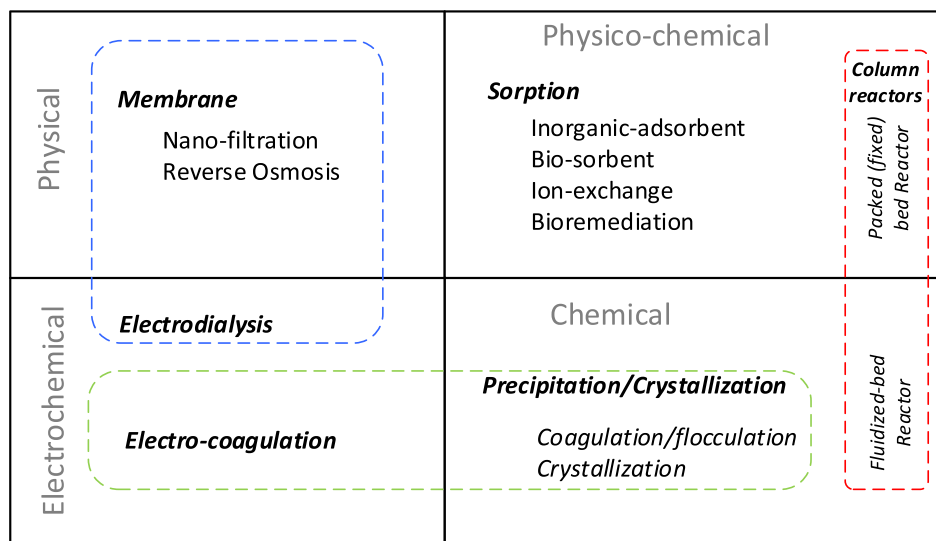


Fig. 2. Treatment technologies for fluoride management. Process in blue are membrane-based technologies, the green-colored are precipitation-based while the one in red corresponds to common column reactors for the corresponding treatments. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

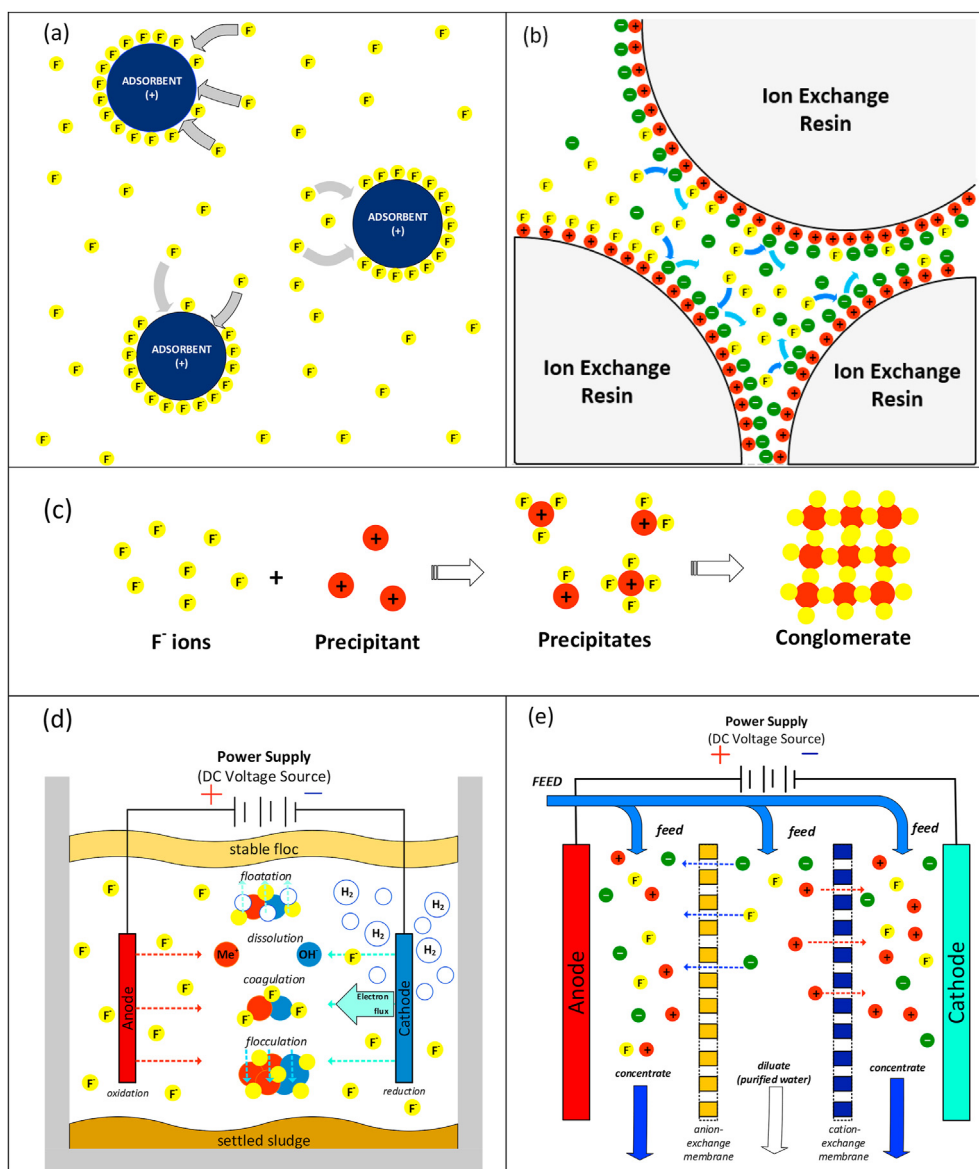


Fig. 3. Mechanisms of defluoridation processes: (a) adsorption, (b) ion exchange, (c) precipitation-coagulation, (d) electrocoagulation, and (e) electrodialysis.

packed-bed configuration used for defluoridation. Moreover, the desorption process though regenerates sorbent materials (i.e. adsorbent and IER) would free fluorides again in aqueous solution. Whereas, the disposal of the desorbed fluoride and exhausted adsorbents were not discussed.

4.1.1. Inorganic adsorbent

The synthesized and engineered adsorbent for defluoridation has still been of interest in recent years. In particular, zirconium-compound is employed as adsorbents such as ZrO_2 (Dou et al., 2012) and activated carbon impregnated by Zr(IV) (Velazquez-Jimenez et al., 2014). Another notable synthesis is the aluminum fumarate employing a metal-organic bond (Karmakar et al., 2016). Impregnation of metal such as calcium in activated carbon has also been applied in a batch reactor (BR) and PBR (Roy et al., 2017). Interestingly, Roy et al. further optimized the removal using a two-level-three-factored central composite design.

Moreover, the amalgamation of different metals forms multi-metal adsorbents providing synergistic effects for fluoride

removal. Bimetallics such as Ca-Al (Sun et al., 2017) and Fe-Ce (Tang and Zhang, 2016) in BR were reported while Mg-Al layered with hydroxides and NO_3^- in PBR (Kameda et al., 2015). He et al. also recently modified alumina by incorporating rare-earth elements (La and Ce) (He et al., 2019). Remarkably, tri-metal Fe-Al-Ce produced through the extrusion method is introduced in both BR and PBR (Zhao et al., 2012). A recent study also impregnates Mg-Mn-Zr in activated carbon using ultrasound described as environmental-friendly material synthesis (Mullick and Neogi, 2019).

On the other hand, the naturally available minerals are commonly associated with cheaper production gained interest among researchers such as dolomite (Chaudhary and Prasad, 2013), hydroxyapatite (Mourabet et al., 2015), lateritic soil (Iriel et al., 2018), lime (Guan and Zhao, 2016), pumice (Malakootian et al., 2011), and zeolite (Cai et al., 2015). Moreover, Kanuma mud (also investigated with BR) (Chen et al., 2011), as well as acid-treated limestone (Ghimire, 2012), were studied in PBR. Usually, these investigations are prompted by the lack of availability of a highly-

engineered adsorbent especially in the rural areas of developing countries which have locally-rich mineral deposits.

However, natural-mineral adsorbent alone is typically not adequate for contaminant removal particularly fluoride in water. As a result, the adsorption capacity (AC) is enhanced by metal doping or impregnation. Natural pumice has been reported modified with Mg and H_2O_2 (Sepehr et al., 2013), and Na (Asgari et al., 2012) while bauxite by Al compounds (Lavecchia et al., 2012). Recently, Akafu et al. have also modified properties of dolomite with $\text{Al}(\text{OH})_3$ (Akafu et al., 2019). Likewise, carboxylated aerobic granules (X. Wang et al., 2013) and pullulans (Ye et al., 2018) were integrated to Ce (III) and Mg, respectively, and further applied to PBR.

In the collected works, metal utilization as adsorbents as well as modifications is mainly dominated by Fe metals. For instance, Chen and co-workers concentrated their efforts on the development of Fe-modified ceramic from Kanuma mud as fluoride adsorbent (Chen et al., 2011b, 2010b; 2010a). Similarly, hydrous ferric oxide (Nur et al., 2014) and commercially available granular Fe^0 (Heimann et al., 2018) were also operated in PBR. In addition, the investigations on Fe-nanoparticles were conducted with zero-valent iron (Fakhri and Adami, 2013) and a mixture of goethite, hematite, and ferrihydrite (Mohapatra et al., 2011). Furthermore, bi-metal synthesis with nano-iron to form a new type of adsorbent was also accomplished with the amalgamation of Ti (Chen et al., 2012) and Mg (Mohapatra et al., 2012).

Since the adsorption efficiency highly depends on the materials' available sorbing surface, nano-material, as an adsorbent having a high surface to volume ratio, has a growing advantage. In other words, nanoparticles provide a lesser amount of material but more available surface to adsorb. Other nanoparticle and nanocomposite for defluoridation besides Fe-based adsorbents are cellulose-hydroxyapatite (Yu et al., 2013), cupric oxide (Bazrafshan et al., 2016), bentonite, and montmorillonite, (Naghizadeh and Gholami, 2017). Agglomerated Ce (IV) and Zr (IV) oxide nanoparticles were also employed in PBR (Ghosh et al., 2015).

It is also noteworthy the re-utilization of waste-product from other industries. Fly-ash cenosphere (usually a by-product of thermal power plants) loaded with Mg was reported to apply in PBR (Xu et al., 2012). Waste-sludge generated by other water treatment processes has also been investigated as adsorbents. However, this waste-sludge requires the pre-treatment process before its re-utilization as adsorbent material. Yilmaz et al. reported calcination of sludge (from EC process) (Yilmaz et al., 2015) while Li et al. pre-treated sludge with hydrochloric acid (Li et al., 2018). Though the recovery of these sludge can be initially perceived as waste reduction aiming for sustainability and economic benefit, long-term effects are not yet established.

4.1.2. Bio-adsorbent

Bio-adsorption in this review depends entirely on passive dead biomass and its affinity to sorbate. Plant remains are the usual preliminary point of investigations. In the recent years, feasible bio-adsorbents were discussed such as guava seeds (Sanchez-Sanchez et al., 2013), peepal leaf (*Ficus religiosa*) powder (Dwivedi et al., 2014), pineapple and orange peel (Gandhi et al., 2016), palm kernel shell (Bakar et al., 2016) and various parts of reed plant (Song et al., 2018) and Java plum (*Syzygium Cumini*) seeds (operated in PBR) (Singh et al., 2017). However, these raw biomass residues often constituted minimal ACs. To overcome this drawback, Sivasankar et al. proposed to fuse the biomass with metal by coating MnO_2 to Tamarind (*Tamarindus Indica*) shells (Sivasankar et al., 2010). Alternatively, chitosan composite is also impregnated with bi-metal $\text{Fe}(\text{OH})_3$ and nano- CaO (Sengupta et al., 2020).

Another alternative is biomass carbonization which mimics the characteristics of granular activated carbon (GAC). GAC is a well-

known highly efficient adsorbent with high surface area, micro-porous structure, and a high degree of surface reactivity but also relatively expensive. Majority of the bio-sorbents studies employed carbonization applied to different organic residues such as Bermuda grass (Alagumuthu et al., 2011), coffee grounds (Ogata et al., 2011), pinewood and bark (Mohan et al., 2011), and date palm (Ravanipour et al., 2017). Teff (*Eragrostis tef*, a native African species of lovegrass) straws were also recently utilized to develop biochar with relatively high surface area ($627.7 \text{ m}^2/\text{g}$) and loading capacity ($212 \text{ mg F}^-/\text{g}$) (Yihunu et al., 2020).

Similarly, another common source of biochar is the bovine bones (Gourouza et al., 2014; Medellin-Castillo et al., 2014). In a developing community (such as Aguascalientes), biochar adsorbent is regarded as a very useful and cost-effective alternative compared to conventional techniques. However, bone-char is also inherently biocompatible or an attractive site for bacterial activities (Mcevoy et al., 2013). Ramirez-Montoya further noted that bone-char was partly regulated for drinking water use due to some incidents of unsatisfactory physical quality of treated water (e.g. yellowish color with an unpleasant odor and taste) (Ramírez-Montoya et al., 2014). Hence, to make bio-char viable fluoride removal for drinking water, a suitable packing material is necessary (Delgadillo-Velasco et al., 2017). The mechanism (Kariuki et al., 2015) and modeling through hybrid neural networks (Tovar-Gómez et al., 2013) bone chars in PBR have also been explored.

Moreover, like the inorganic adsorbents, AC of the bio-char can be further utilized with metal impregnation such as Zr, Al, La, and Al-Fe bimetal applied to Lapsi seeds (Joshi et al., 2013), coconut fiber (Mondal et al., 2015), waste wood (Habibi et al., 2017) and cow dung (Rajkumar et al., 2015), respectively. In PBR applications, carbonized plum kernel and carbon were impregnated with calcium acetate (Ramírez-Montoya et al., 2014) while commercially available bone-char was modified with silver (Delgadillo-Velasco et al., 2017).

4.1.3. IER

IER can satisfactorily remove unwanted levels of dissolved solids. However, U.S. EPA limits the treatment using IER to $<500 \text{ mg/L}$ dissolved solids and $<120 \text{ mg/L}$ sulfate concentrations (U.S. EPA, 2001). Recently, the group of Paudyal worked on the development of both bio-sorbents (i.e. orange waste and seaweed alginate) (Paudyal, 2017) and IER (Paudyal et al., 2018). Although the developed bio-sorbents were low-cost and ecologically benign, it could naturally degrade, producing a foul smell and making it commercially unattractive. Thus, the utilization of spent IER recovered from an electronic industry was developed. In the context of defluoridation, IER has very little development and few works of literature in the previous years compared to its counterparts. Moreover, these few studies just investigated basic operational parameters employing commercially available IER (Bhattacharya, 2017; Li et al., 2016; Meenakshi and Viswanathan, 2007). Furthermore, IER using aluminum chelating resin (Millar et al., 2017) and non-conventional hybrid anion exchanger modified with ZrO_2 (Padungthorn et al., 2014) in PBR have also been reported. Recently, Zhang et al. pointed out the extremely slow kinetics of metal-based adsorbents (which have been the focus of contemporary research due to its high-capacity) (Zhang et al., 2019). To overcome this disadvantage, the authors further proposed an anion-exchange Zr-graphene hybrid adsorbent (mimicking the IER mechanism) resulting in rapid kinetics with high-capacity F^- removal.

4.2. Precipitation/crystallization

Precipitation and crystallization are both solute-solvent

separating technique by solidifying the solutes primarily called as a precipitate. The precipitate, then, settles at the bottom or remain as suspended solids. Shown in Fig. 3-c is the general precipitation and agglomeration of fluoride precipitate. However, most of the precipitates have high water content (93–99% raw sludge and ~35% after dewatering) not suitable for material recovery or at least not economically feasible to recover. This generated sludge becomes secondary pollutant and is generally hazardous requiring post-treatment before disposal.

On the other hand, crystallization can precipitate the solute to a pure solid crystalline phase without (or with very low) water content. This can simultaneously provide sanitary water and economically valuable salts without supplementary materials (e.g. reducing agent, membrane, etc.). Recently, Lu et al. enumerated these crystallization techniques (i.e. evaporation and cooling crystallization, reaction crystallization, and drowning-out crystallization) (Lu et al., 2017). Furthermore, the authors identified that evaporation (among crystallization techniques) is the most established with the most acceptable energy consumption. Among these crystallization techniques, we found that the reaction crystallization is the only technique employed for defluoridation, particularly the use of fluidized-bed reactor (FBR). However, it is generally regarded to have fundamental drawbacks such as partial precipitation, significant pH dependence, and still considerable sludge production.

Alternatively, EC has also been gaining popularity and utilization in the field of WWT, primarily employed for the removal of contaminants such as suspended solids, emulsified, oils, petroleum, hydrocarbons, etc. The technique also lessens the total dissolved solids. Besides, Guo et al. mentioned that EC is more cost-effective than conventional coagulation by avoiding the additives that produce soluble anions (Guo et al., 2014).

4.2.1. Coagulation-flocculation (CF)

Precipitation of fluoride forming CaF_2 (eq. (1)) has been cited in many reports. The use of calcium is considered as the most economical and feasible being a naturally occurring mineral.



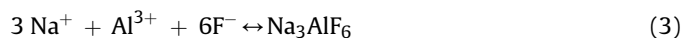
Nalgonda technique (primarily developed for Nalgonda, India due to endemic fluorosis) becomes a well-known precipitation technique for defluoridation (Rao et al., 2008). Now, these techniques are not only used for low-income communities in India but also in African households (Vithanage and Bhattacharya, 2015). In a recent study, Wang et al. also proposed the use of calcium-containing ores to induce precipitation in fluoride removal (Wang et al., 2019). The authors demonstrated the dissolution of calcite by acidic pH (predominant in actual F^- -containing WW). Although lime is the primary source of calcium used in the process, other cheap coagulants are also used including other alum, magnesium oxides, and other calcium salts (Ayooob et al., 2008).

In recent years, literature shows that CF is mainly developed for high fluoride effluents of industrial processes such as pesticide and semiconductor-electronic industry. Huang et al. also recently proposed the use of magnesium salts for both fluoride removal (eq. (2)) and other contaminants of a semi-conductor company (such as nitrogen and phosphates) (Huang et al., 2017).



Moreover, aluminum salts were used for the precipitation of fluoride for the unintentional recovery of perovskite-like minerals (Lee et al., 2015). The authors further discussed that cryolite (which precipitation and dissolution are shown in eq. (3)) and of elpasolite

were primarily the recovered materials due to the use of NaOH and KOH, respectively, for pH adjustment.



Remarkably, the seed addition is regarded as a recent innovation in CF batch-reactor. In some way, it mimics the mechanism of the fluidized-bed heterogeneous crystallization adding seed where precipitates can attach to seeds minimizing sludge and providing potential recovery. Similarly, Deng et al. precipitated fluoroapatite in calcite and fluoroapatite seeds (Deng et al., 2016). The latter results to recovery of a purer fluoroapatite precipitates. Additionally, Kumar et al. also employed sodium carbonate producing sodium fluorosilicate and cryolite treating more complex fluorine compounds (H_2SiF_6 and H_3AlF_6) (Kumar et al., 2010).

Despite the advantages of precipitation-coagulation methods removing a significant amount of fluoride ions in industrial WW, trace amounts tend to persist in treated water (Chen et al., 2011). Aoudj et al. ascertained that final fluoride concentrations could only range from 25 to 60 mg/L not satisfying 15 mg F^-/L effluent standard (Aoudj et al., 2015). On the contrary, Paudyal et al. claimed that the use of Ca (the most common fluoride precipitant) can provide a much lower level of fluoride adequate for the standard's requirement (Paudyal, 2017). The authors further explained that theoretically, precipitating insoluble CaF_2 can lower fluoride levels to 5 mg/L while actual concentration may vary from 10 to 20 mg/L.

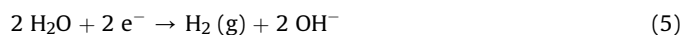
4.2.2. Electro-coagulation and floatation (ECF)

ECF is an innovation from the conventional chemical precipitation reducing significantly sludge generation by combining oxidation, floatation, and flocculation shown (in Fig. 3-d). Metals (Me) such as Al and Fe are recently reported to be utilized as an electrode for fluoride removal in the ECF process. Outlined below are the general electrode reactions.

At the Anode (eq. (4)):

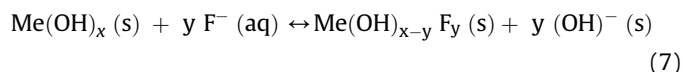
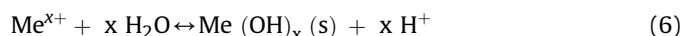


In Fig. 3-d and eq. (5), hydrogen bubbles (further float in the ECF reactor) are generated by redox reaction at the cathode:



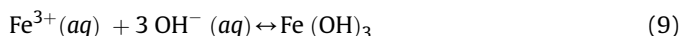
Moreover, the redox reaction produces hydroxides (which replaces the addition of compound-producing soluble anions in the conventional coagulation process further reducing the cost).

Then, metal ions can react with water creating metal hydroxides (by hydrolysis eq. (6)) which further forms flocs adhering with contaminants (e.g. fluoride in eq. (7)):

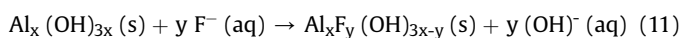
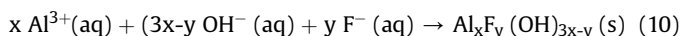


At a high concentration of metal ion commonly exceeding product solubility (particularly metal hydroxide), "sweep coagulation" occurs forming "sweep flocs". Theoretically, amorphous Al(OH)_3 (eq. (8)) and ferric hydroxide (eq. (9)) can form using aluminum (Emamjomeh et al., 2011) and iron electrode (Takdastan et al., 2015), respectively. Sweep flocs could then facilitate to rapidly adsorb soluble compound and to enmesh colloids while settling at the bottom.





Furthermore, two other main mechanisms for fluoride removal are co-precipitation (eq. (10)) and adsorption (eq. (11)). However, we only found literature discussing these mechanisms using Al-electrodes (Aoudj et al., 2015; Emamjomeh et al., 2011).



Al-electrode (found superior compared to its Fe-counterpart) forms $\text{Al}_x\text{F}_y(\text{OH})_{3x-y}$ which can promote higher fluoride removal than $\text{Fe}(\text{OH})_3$ (Govindan et al., 2015). Notably, both the recent (Rosales et al., 2018) and the earlier (Emamjomeh et al., 2011) literature commonly reported that the mechanism of the ECF fluoride removal is the competitive adsorption of OH^{-} and F^{-} from aluminum flocs.

Moreover, Govindan et al. also investigated both cations and anions in EC systems revealing that both cations and anions can enhance fluoride removal (Govindan et al., 2015). The presence of Ca^{2+} and Mg^{2+} (forming nano-crystalline fluoride compound) with Al-electrode demonstrated a 10% removal compared with Al^{3+} . Likewise, anions (SO_4^{2-} with most evident influence compared to NO_3^{-} and Cl^{-}) can also improve fluoride removal by pitting corrosion promoting to metal hydroxide formation.

In Mexico, Nava and research companions were ostensibly pioneering the development of EC for defluoridation primarily for the GW sources (Guzmán et al., 2016; Rosales et al., 2018; Sandoval et al., 2019). Moreover, like the conventional CF methods, ECF also highly depends on the solution pH also reflected in the previous investigations. Although ECF displayed high removal efficiency, like any other electric-current dependent technique, power cost is its major drawback. Among the reviewed literature in ECF for fluoride treatment, only Thakur et al. discussed a post-treatment management for the sludge generated proposing it as a brick material (Thakur et al., 2019).

4.2.3. Fluidized-bed crystallization (FBC)

In fluidized bed, the fluid generally permeates to a static solid-particle bed with a superficial velocity adequate to suspend particle resembling it to a fluid. Initially, fluidized bed is utilized in chemical, catalyst manufacturing, coating application, etc. and later utilized in WWT. Despite the massive WWT application, it remains an empirical science largely relying on heuristics (Bello et al., 2017). Moreover, the actual mechanism of the dewatering process under FBC is still indefinite to the researchers.

Like ECF discussed in Section 4.2.2, a fluidized bed is applied in improving CF through sludge reduction. CF produced CaF_2 with high water content making the precipitate abhorrent for fluoride reuse due to economic constraints (Van den Broeck et al., 2003). Conversely, due to the decreasing dumping area, the cost of dumping is also increasing especially for hazardous fluoride sludge. On that matter, FBC does not only reduce sludge generation but allows the recovery of precipitates (or crystals) with appealing economic value.

In the past decade, Aldaco and co-workers developed FBC techniques for both removal and recovery of fluoride in aqueous solution. In 2007, they emphasized that the superficial velocity, particle size, and supersaturation are the critical parameters in the fluidized-bed reactor for CaF_2 crystallization (Aldaco et al., 2007a). In the series of investigations, they established that the fluoride crystallization is only limited at 150 mg F^{-}/L due to supersaturation limitations (Aldaco et al., 2005). Primary nucleation (or the

nucleated precipitation), dominated process, lowers the efficiency by producing more fines. Hence, the authors further suggested that water recycling is essential to decrease fluoride concentration stimulating the secondary nucleation promoting crystal growth (Aldaco et al., 2006). Moreover, they also anticipated that employing heterogeneous crystallization (using seed) would decrease the purity of CaF_2 . To overcome this drawback, they utilized CaF_2 (virgin material, as seed) to increase the purity of crystallized CaF_2 to 99% (Aldaco et al., 2007b). After these investigations by Aldaco and co-workers, we have not found much development in fluoride removal using FBC. Though, recently, Zeng et al. explore the effects of varying seed characteristics such as material, size, and amount but still imploring CaF_2 precipitation with the use of FBC (Zeng et al., 2019).

We also obtained the study of Deng et al. claiming that the produced fluoroapatite can be further utilized as a raw material in the fertilizer industry (Deng et al., 2019). This also successfully removed fluoride in aqueous solution, but the proposed approach had an intrinsic issue. Although fluoroapatite is truly a raw material for the fertilizer industry, the fertilizer industry extracts phosphate as fertilizer by separating fluoride (an unwanted by-product) (Ramteke et al., 2018). We have also traced the fate and transport of fluoride in our recent work published elsewhere showing the fertilizer industry as a possible point-source of the various pathway of fluoride pollution (Lacson et al., 2020).

Apparently, the temperature which can be a factor for successful crystallization is not, nonetheless, explored. Moreover, our research group has also been attempting a homogenous crystallization of fluoride (without an initial use of seed) using calcium for around 20 years. However, multiple attempts failed to obtain crystallized CaF_2 using fluidized-bed.

4.3. Membrane

Membrane and ED are regarded as innovative methodologies (Iriel et al., 2018). Unlike the techniques discussed above, the membrane is a one-step technique with relatively very low chemical usage. Furthermore, Damtie et al. alluded sorption and precipitation methods as conventional techniques with inherent drawbacks reducing the easement of operation (Damtie et al., 2019). The authors further enumerated these drawbacks such as low fluoride removal efficiency, considerable sludge production, and intensive labor and massive space requirement.

4.3.1. Operational condition and removal mechanisms

The most evident membrane mechanism for contaminant rejection is the steric effects which various parameters should still be taken into consideration. Chakraborty et al. by comparing different nano-filters for defluoridation, determined the optimum operating conditions (viz. pH: 10.01, cross-flowrate: 750 L/h, flux: 158 $\text{L}/(\text{m}^2/\text{h})$, and pressure: 14 kgf/cm^2) (Chakraborty et al., 2013).

Generally, membrane efficiency is not pH-dependent (making it effective to a wide pH range) but nonetheless, pH adjustment is indispensable to avoid scaling. Moreover, pH may also influence the prevailing system conditions (viz. viscosity, hydration, zeta potential, and membrane pore size) further affecting the removal. Hence, although pH does not significantly affect the removal of the other contaminants, pH is a very important parameter for fluoride removal. At $\text{pH} < 3.0$, minimal fluoride rejection was observed due to the diffusion of fluoride to the membrane in HF form (Simons, 1993). Alternatively, an increase in alkalinity (at $\text{pKa} = 3.16$) stimulates the deprotonation dissociation of HF (Shen and Schäfer, 2014) as indicated in eq. (12).



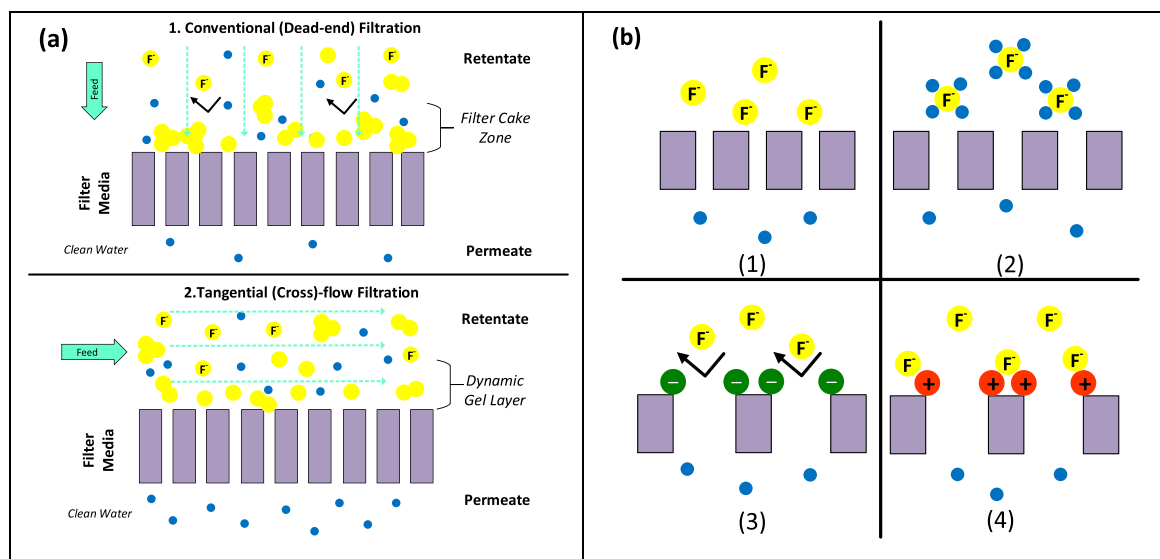


Fig. 4. Defluoridation mechanism of membrane processes: a) effect of flow regimes (i.e. (1) conventional flow and membrane fouling influence and (2) tangential flow) and b) retention mechanisms (i.e. size exclusion of (1) bare ion, and of (2) hydrated or precipitated fluoride) and charge interaction by (3) repulsion and (4) adsorption).

Meanwhile, the flow directions utilized in membrane technology is presented in Fig. 4. Traditionally, the flow direction is perpendicular to the membrane (shown in Fig. 4-a.1). This conventional approach has a high probability of developing dead-end filtration or excessive fouling. This will also generate cake accumulation leading to flow resistance and difficulty in cleaning, and ultimately resulting in higher operational cost. Conversely, preferential fouling could increase pollutant rejection by pore size reduction effect due to partial blockage of pores.

Alternatively, cross-flow (in Fig. 4-a.2) is just a modification of flow direction, tangential to the membrane which provides a more sustainable flow. This produces a “sweeping action” plummeting the filter cake formation. In addition, it maintains low flows and minimizes frequent backwashing which further lowers the operational cost.

Diffusion, electro-migration, and convection are the main transport mechanisms of fluoride within the membrane. Consequently, pressure, temperature, flow rate, operation time, and initial fluoride concentration (IFC) affect these mechanisms and further influence fluoride removal in the membrane (Damtie et al., 2019). Membrane defluoridation is, furthermore, governed by physio-chemical interactions which may follow various mechanisms (i.e. steric and charge effects). These mechanisms can be classified to size exclusion, solute-solvent interactions, and charge interferences as presented in Fig. 4. Size exclusion (by sieving effect) is the primary mechanism of membrane for the rejection of the pollutant shown in Fig. 4-b.1. Similarly, the attraction of fluoride with water (hydrated ion) and with another solute (precipitation) creates larger retentates, not requiring finer pores shown in Fig. 4-b.2. Finally, Fig. 4-b.3–4 demonstrated a charge-based fluoride

exclusion through the attraction (an adsorbent mechanism) and repulsion occasionally attributed to Donnan effects.

However, not all membranes are suitable for fluoride removal, generally, NF and RO are the most established membrane technologies for defluoridation as shown in Table 3. Although membranes with a larger pore size (e.g. ultrafiltration and microfiltration) can be employed, pre-treatments are required (which are classified as hybrid treatments in Section 4.4.1).

4.3.2. RO and NF

As envisaged, membrane technologies in the previous years are dominated by RO and NF membranes. Moreover, although RO demonstrates a very high-efficiency fluoride rejection, NF is more viable for the treatment of drinking water. RO requires extremely high pressure with consequential high power and high operation cost requisite. In addition, the RO process also removes essential nutrients needed in drinking water requiring further remineralization as post-treatment. In contrast, NF with bigger pores and with lower pressure requirements overcomes these limitations. In Argentina, small to mid-sized towns frequently refused RO plant installation having a poor reputation of being unaffordable and operationally cost-ineffective (Ingallinella et al., 2011).

In recent years, the majority of the literature investigating the fluoride removal using the membrane, heavily rely on commercial membranes such as NF90, NF270, and BW30 (for RO). In literature, only Bejaoui et al. demonstrated further membrane development consisting of two-layer thin-film composite (Bejaoui et al., 2011) while Malaisamy et al. have only made layer modification on commercially available NF270 (Malaisamy et al., 2011). These show that there has been a diminutive novel investigation in the

Table 3
Contaminant retentates for different membranes.

Membrane	Pore size (μm)	Retentate				
		SS/Bacteria/Precipitated Metals	Grease/Oil	Surfactant/Virus	Polyvalent	Univalent
Microfiltration	1×10^{-1}	✓	partially			
Ultrafiltration	1×10^{-2}	✓	✓	partially		
Nanofiltration	1×10^{-3}	✓	✓	✓	✓	
RO	1×10^{-4}	✓	✓	✓	✓	✓

development of the membrane technologies, but just variations and optimization of the well-established parameters. Moreover, it can also be inferred that as the constituents of the aqueous solution become complex, the operation time also increases requiring more energy and adding to operational cost. These can be collectively observed in different NF90 investigations: (i) without co-ions, 30 min (Bejaoui et al., 2014), (ii) with P_2O_5 , 5 h (Dolar et al., 2011), (iii) and with phosphate and nitrite, 48 h (Yousefi et al., 2016). Accordingly, Shen et al. remarkably integrated the innovation of renewable energy as a power source of NF and RO to potentially provide a cheaper power cost (Shen et al., 2016).

4.3.3. ED

ED is basically an electrically-assisted membrane technique applied primarily in desalination and salt production. Remarkably, ED has also been employed to remove fluoride in the infused instant brick tea which may contain extreme fluoride levels (Peng et al., 2019) ranging from 3.0 to 898.0 ppm (United States Department of Agriculture, 2005). ED was also used for water and wastewater defluoridation. Like NF/RO membranes, recent investigations only rely on commercially available membranes and just optimizing parameters appropriate for different applications. ED compared to RO/NF, is a simple and excellent defluoridation method, and more cost-effective with also relatively cheap pre- and post-treatment requirements (Damtie et al., 2019).

ED primarily operates with electrolysis assisted by the Donnan effects, as the driving force, instead of the hydraulic pressure used in RO/NF techniques. Hence, besides vital parameters in other membrane technologies (e.g. RO and NF), the current density is also a vital parameter to ED (Arahman et al., 2016; Belkada et al., 2018). The purification mechanism of ED is the one-way transport of the solute towards the concentrate regions and further purifying the diluate region. Then, both solute's passage and retention are attributed to the selective mechanism of the ion-exchange membranes. Thus, fluoride removal in the ED is defined by the passage of fluoride ions as shown in Fig. 3-e. Moreover, Amor et al. highlighted that reducing the boundary layer improves the passage of fluoride ions to the concentrate regions and further promotes the highest viable flow rate (Amor et al., 1998). In contrast, the main drawback of ED is its inefficiency to an aqueous solution with low salinity (<0.5 mS/cm) involving non-charged and light-molecule constituents but requiring high removal efficiency (Damtie et al., 2019). Subsequently, this can also be the reason why, from the reviewed fluoride removal techniques, ED comprises high IFCs. In summary, central tendencies of these IFCs range from 160 to 1,300 mg/L which is relatively very high compared to other techniques.

From the overall reviewed techniques, Bagastyo et al. remarkably demonstrated the treatment of the highest IFC at 9,720 mg/L (Bagastyo et al., 2017). Even though ED in this work, removes a substantial amount of 260 mg F^- /L, it only corresponds to 2–3% removal indicating very low efficiency. Contrariwise, some investigations successfully exhibited high-efficiency removal even at low IFCs (mg/L) 5.0–10 and 12.2–14.4 intended for drinking water (Bhadja et al., 2016; Majewska-Nowak et al., 2015). Additionally, Bhadja et al. compared commercial membranes (i.e. Interpolymer, Fujifilm type 1, and Ionsep) with a final concentration under the WHO standards. The authors further reported a defluoridation using ED with low IFC ranging from 12 to 15 mg F^- /L but with a high removal efficiency rate (87–91%). Lower IFCs (5 and 10 mg/L) were also reported successfully removing fluoride with a final concentration lower than 1.5 mg/L limit (Majewska-Nowak et al., 2015). Moreover, Majewska-Nowak et al. also investigated high IFCs 100 and 200 mg/L; however, only about 90% removal was carried out corresponding to 10–20 mg/L. Since the technique can significantly remove at low IFC, an extension of operation time or water

reprocessing can be done to attain the desired final concentration.

4.4. Hybrid treatments and bioremediation

In this section, we discuss hybrid treatments and bioremediation. Hybrid treatments are more applicable in the actual GW and WW containing a wide range of IFCs with other complex ions and constituents. Moreover, the treatments discussed from the previous sections, are not always available resulted in the lack of provisions of sanitary facilities usually caused by high capital cost. Henceforth, the development of bioremediation treatments can be an essential, a low capital cost, and a countryside-fitting alternative. Both defluoridation methodologies are also recently discussed in the literature.

4.4.1. Hybrid treatments

Researchers doing hybrid treatments from the previous years have also high regard with the adsorption and precipitation techniques. All the examined reports would discuss adsorption and/or precipitation as part of the hybrid defluoridation techniques while two out of seven treatments are precipitation-adsorption combinations. Precipitation coupled with larger pore membranes (i.e. MF and UF) was also reported. Remarkably, Khue et al. integrated three techniques primarily using current density to influence the movement of ions by EC and micro-electrolysis and further utilizing fluidized-bed (Khue et al., 2014).

In Argentina, precipitation-adsorption by Al (with only 50–55% removal efficiency) and Fe coagulants can satisfactorily compete with RO due to perceived simple and cost-effective operation (Ingallinella et al., 2011). In addition, fluoride is satisfactorily removed to pass for the drinking water standard. However, traced residuals of Al and Fe in treated water can also be contaminants causing foul taste, turbidity, disinfection-efficiency reduction in water, and precipitates in the distribution pipes. Similarly, Chaudhary and Prasad emphasized that although aluminum-based treatments have successfully shown high fluoride removal efficiencies, its residuals can be neurotoxic and carcinogenic (Chaudhary and Prasad, 2013). Moreover, the main drawback of aluminum precipitates is also the sludge production requiring expensive post-treatment.

Another precipitation-adsorption investigation is done by Melidis (2015). The prior studies by Ingallinella et al. described precipitation-adsorption as a simultaneous mechanism for removing fluoride (Ingallinella et al., 2011). Conversely, Melidis illustrated a binary treatment process having precipitation as pre-treatment prior to adsorption. The author further explained that this binary system can significantly remove 94.5% of fluoride (at IFC 74.5 ± 4.6 mg/L) from the WW of the aluminum industry (Melidis, 2015).

Alternatively, other researchers utilized the adsorption technique as the pre-treatment coupled with either flotation or NF. Although the utilization of the ferric oxyhydroxide could significantly reduce IFC, flotation was still necessary to obtain a final concentration below 5 mg F^- /L (Stoica et al., 2012). In the same way, the direct use of NF with IFC >4.5 mg/L would exceed the limit prescribed by the standards; thus, Xu et al. suggested the necessity of utilization of natural diatomite as adsorbent (Xu et al., 2015). Accordingly, both studies agreed that the stand-alone treatment can not sufficiently remove the fluoride to correspond to the drinking standards.

Another binary-system is precipitation and membrane processes utilized as pre-treatment and post-treatment, respectively. Table 3 shows that fluoride due to its fineness can only be removed by RO and NF membranes. Nonetheless, the free fluoride in water becomes larger through precipitation and can be further removed

by larger pores of MF and UF also shown in Fig. 4-b.2. These hybrid techniques are done with raw WW of thin-film-transistor-liquid-crystal-display (Lu and Liu, 2010) and semiconductor (Liu and Liu, 2016) companies. Majority of the hybrid treatments already investigated actual waters for treatment (i.e. GW and WW) diminishing the gap for its target applications.

4.4.2. Bioremediation (an absorption process)

Constructed wetlands are the main alternatives to sanitation and WWT facilities which are insufficiently provided causing further environmental and public health problems. Wetlands highly depend on the capability of organisms to bioremediate through the absorption of contaminants which is the main removal mechanism. Unlike adsorption, absorption assimilates through the bulk volume of the sorbent and not only through its surface. The sorbate (the permeating substance) is diffused through the sorbent during the absorption process. Moreover, unlike biosorption (discussed in Section 4.1.2), bioremediation highly depends on the biological process of living biomass to absorb contaminants.

Almuktar et al. mainly linked the efficiency of wetland to the macrophyte-composition (Almuktar et al., 2018). A local growing macrophyte (*Azolla pinnata* var. *imbricata*) in Vadodara, India was proposed to absorb fluoride including heavy metals from WW of oil and petroleum company (Parikh and Mazumder, 2015). The investigation of various aquatic macrophytes including *Pistia stratiotes*, *Eichhornia crassipes*, and *Spirodela polyrrhiza* was also recently reported (karmakar et al., 2016). Additionally, Gao et al. accounted that an increase of fluoride accumulation enhanced the growth of *Hydrilla verticillata*, but at a certain level (40 mg/L), fluoride will induce oxidative stress and metabolic imbalance degrading the plant physiology (Gao et al., 2018).

Various terrestrial plants have also been explored for the phytoremediation in removing and preventing fluoride to avoid further GW contamination. These plants must not only be fluoride resistant but also fluoride accumulators. Hybrid willow (*Salix willow*), sycamore (*Platanus* sp.), and black willow (*Salix nigra*) were also reported to have relatively high resistance to chlorosis and necrosis by fluoride and cyanide (Kang et al., 2008). The plants were not only used for contaminant removal but also for abatement of leachate volume. Subsequently, in comparison to eight tree-species from the semi-arid region, Baunthiyal and Sharma cited *Prosopis juliflora* as the utmost fluoride hyperaccumulator (Baunthiyal and Sharma, 2012). Under the same fluoride stress (10–50 mg F⁻/L) with Baunthiyal and Sharma, *Nerium oleander* is also recently reported as superior among three studied garden ornamental plants (Khandare et al., 2017).

Meanwhile, microorganism such as bacteria is also water contaminant which may cause severe infections. Bacteria have various mechanisms for adaptation and survivability even in a hostile environment (viz. production of biofilm, extracellular precipitation, mineralization, etc.) making it persistent in the water systems. In the past years, researchers also took advantage of these characteristics and gained interest in the evaluation of various bacteria for potential applications for fluoride treatment. These studies focused on bacterial isolation, identification, and characterization.

Chouhan et al. identified five bacterial strains (i.e. *Micrococcus luteus*, *Aeromonas hydrophilla*, *Micrococcus varians*, *Pseudomonas aeruginosa*, and *Escherichia coli*) which are fluoride resistant (Chouhan et al., 2012). Mukherjee et al. similarly reported *Acinetobacter* sp. RH5 growing at a high-level fluoride environment (100–250 mg F⁻/L) (Mukherjee et al., 2015). In similar work, it was observed that the bacterial colony can reduce the initial fluoride level (15 mg/L) by 25.7%.

Unlike earlier studies, Biswas et al. directly isolated

cyanobacteria (*Starrria zimbabwensis*) from wastewater effluents of coke-oven treatment plant (Biswas et al., 2018). The author further claimed that this bacterial strain constituted a higher removal efficiency (66.6% from 10 mg/L IFC) compared to earlier studies. Remarkably, Sharma et al. have isolated autochthonous bacteria (identified as *Aeromonas* sp., *Brevibacterium* sp. and *Paenibacillus* sp.) with very high resistant to fluoride (5,200 to 9,200 mg/L) with 76.7% removal out of ~1,000 mg F⁻/L after 8 days (Sharma et al., 2019). In summary, although bioremediation is regarded as a green technology, the main drawbacks are relatively low efficiency and longer operation time relative to chemical-based treatments.

5. Comparison of different treatments

5.1. Treatment efficiencies

Recent investigations for defluoridation by adsorption are still in bench-scale and still in pursuit of developing the most suitable and sustainable adsorbent being both cheap and effective. Although adsorption is credited as an inexpensive, simple, and vastly viable methodology for defluoridation, most of the sorbent is not proven at higher fluoride concentrations. This makes adsorption more suitable for drinking water sources defluoridation but not for industrial WWT.

Generally, the IFC treated using adsorption is only around 20 mg/L (or lower), a concentration more analogous to contaminated GW than industrial effluent. Similarly, Lee et al. affirm that adsorption may not be suitable for high concentrated fluoride wastewater (Lee et al., 2015). Even though high removal efficiencies were described, only 45% of the evaluated papers would satisfy the WHO drinking water standard. In addition, even if there are exceptional literature discussed high initial fluoride levels in industrial WW, the described high removal efficiency is not enough to comply with effluent standards. For instance, Guan and Zhao investigated 100–1,000 mg F⁻/L with 80% removal which will not constitute a final effluent lower than 15 mg/L (Guan and Zhao, 2016). Moreover, the authors further reported the recovery of CaF₂ making mechanism aided by co-precipitation.

The disposal of the secondary pollution from defluoridation by sorption methodologies was not discussed in the current narratives. Harikishore Kumar Reddy et al. enumerated some valorization of post-sorbent (Harikishore Kumar Reddy et al., 2017). Nonetheless, post-sorbents from the defluoridation process might only be applied as bioactive compounds limited to Cu, Zn, and Mn. Additionally, it is apparently not applicable as fertilizer and feed additives (due to toxicity issues) and/or as catalysts (with reported metals limited to Ni, Ru, and Pd).

In precipitation techniques, the Nalgonda method has been a very popular defluoridation of drinking water from the past decades. Ostensibly, precipitation techniques are not aggressively developed in recent years as compared to adsorption. Moreover, there was also a very slow development of crystallization methodology using fluidized-bed. Nevertheless, unlike adsorption, chemical precipitation is also believed to be also suitable for industrial WWT with an average initial fluoride level of 800 mg/L. In the reviewed papers, more than half would generally both satisfy 15 mg/L effluent limit and WHO drinking water drinking standard. Remarkably, 8 out of 10 of EC studies (also mainly developed for defluoridation of drinking water) constitutes final fluoride concentration lower than 1.5 mg/L.

Investigations, intended for defluoridation of WW discharges, have satisfying final concentrations range from 1.0 to 5.0 mg F⁻/L (Aoudj et al., 2015; Jadhao et al., 2019). However, sludge generation and its further disposal are still a looming concern. The ECF and FBC utilization is considered as a solution to reduce sludge generation

and to further recover materials with economic value. However, fluoride contained industrial WW may contain 1,000–9,000 mg F⁻/L while the optimum condition for FBR was reportedly limited at 150 mg F⁻/L. Ultimately, there are still very few studies and noticeable gradual development of precipitation techniques in defluoridation of industrial WW.

Lastly, membrane utilization is the most established treatment in the previous decades providing high removal efficiency for most of the unwanted water components. Similarly, membrane studies satisfactorily comply with the standards relative to the intended fluoride-containing water to be treated, suitable for WT and WWT. However, recent studies only focused on the investigation of commercially available membranes which do not give a novel development in the field of membrane technologies. Membrane techniques also fundamentally require high pressure and high-power consumption during the operation resulting in high cost. Hence, it is not an attractive economic option especially for defluoridation treatment of poor communities also considering power availability and high-power cost. Remineralization of the removed essential minerals will also constitute additional cost. Like precipitation/crystallization, IFC in membrane studies normally ranges around 200–1,000 mg/L.

Moreover, electrically-assisted defluoridation treatments (i.e. ED and EC) are recent developments regarded as innovative technology to improve efficiency. Nonetheless, power requirements can be its major drawbacks with high power costs and lack of access to electricity, especially in poor communities.

The relative performance of the defluoridation technologies (Fig. 5) shows that the majority of the defluoridation investigation is limited to an influent concentration of less than 100 mg/L. Otherwise, the influent with higher concentration could hardly be treated to obtain effluent-standard concentration, implying the necessity of defluoridation treating at higher-concentration influent. In addition, Table 4 summarizes and compares the examined papers from the previous years. These include the developmental phase, requirements (such as operation time (τ) and condition, and labor-skill requirement (LSR)), efficiency, sensitivity to interfering ions (II), relative cost with capital expenditure (CapEx), and environmental considerations.

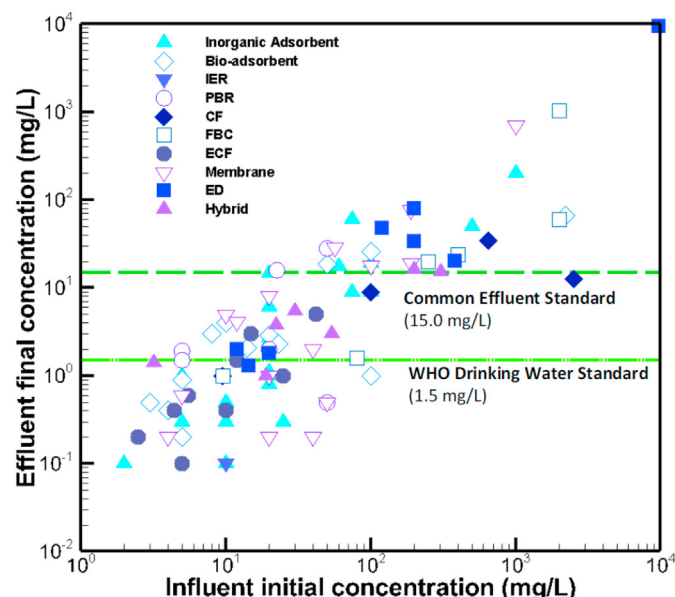


Fig. 5. Relative performance of the defluoridation techniques.

5.2. Operational cost comparison

The cost of both WT and WWT can have several considerations that require experience in the field to provide a decent and detailed estimate comparing various treatments. Material consideration, chemical usage, power consumption, and life cycles are some of the parameters to be considered including each corresponding cost. To provide a conceptual cost estimate, the following studies providing an itemized estimate of operational treatment cost have been reviewed:

- Estimation of OpEx of water defluoridation using ED and EC (Lahnid et al., 2008; Mena et al., 2019).
- Local construction cost and volume of water in the logarithmic variant of Williams Law cost function applying to popular defluoridation techniques (i.e. GAC, CF, membrane, etc.) (Guo et al., 2014)
- Comparison of cost between the traditional CF and EC (0.06 kg Al/m³ is adopted in our computation) (Cañizares et al., 2009)
- Evaluation of energy footprints and OpEx of several GAC and IER (Hardwick and Hardwick, 2017)

To extrapolate unreported OpEx of defluoridation techniques, ratio and proportion are used to parallel data of reviewed literature. In addition, to consider differences in years, an annual global inflation rate (4%) is factored in and then projected to 2019 as the present year. Hence, the conceptual estimate for OpEx per cubic meter of water input (€/m³) for different treatment for defluoridation is presented in Table 5.

From this rough estimate, the traditional CF process shows the cheapest with 0.184 €/m³ while the use of IER costs the highest at 4.675 €/m³, in terms of OpEx. Unexpectedly, adsorption using GAC (most established adsorbent material) follows IER with high treatment cost (3.74 €/m³). The extrapolated high operational cost of the sorption treatment can be attributed to the regular changing of the costly sorbent media and its disposal compared to cheaper chemical usage for CF. RO membrane is expected to have the highest cost because of the identified high-pressure requirement leading to high power and treatment cost but shows to be still relatively cheaper (0.316 €/m³) than sorption techniques. The OpEx of electro-based techniques have no significant difference and also provide relatively low-cost alternatives especially if power cost is also cheap.

6. Perspective and future research direction

We offer our perspective in the discussed defluoridation and suggest insights for water management and future research direction:

- In the course of data gathering for fluoride levels in the environment, evidently, there is still limited literature discussing fluoride environmental levels and its monitoring while the available literature was nonetheless not recent.
- Most of the treatment technologies (primarily intended for purification of drinking water) are still on the laboratory-scale stage using NaF-based synthetic solution. However, industrial WW containing high fluoride levels (HF as the usual source also decreasing solution pH) is more crucial to the environment and human health. This is further aggravated by the inherent inter-connection of water-related ecosystems conveying toxic fluorides towards water resources used for consumption, food production, and recreation.
- Accordingly, further development of affordable and highly efficient technologies is deemed essential to provide more

Table 4
Summary and comparison of different fluoride removal techniques.

Fluoride removal techniques	Component	No. of reviewed papers	Scale or Phase	Requirements	Qualitative efficiency	Relative Economic Cost	Secondary Pollution production	Material recovery
Sorption	Adsorption	52	bench-scale to basic process design, highly available	highly dependent on pH and temperature LSR: low-medium τ : 3 min.–7 days	High but at low concentration II: medium to highly sensitive	CapEx: Medium OpEx: Low-High	Low sludge production and disposal of used adsorbent	Desorbed fluoride and adsorbent re-utilization
	IER	4	validation of commercially available IER to plant-scale	highly dependent on pH LSR: low-medium τ : 30 min.–3 days	High but at low concentration II: highly sensitive	CapEx: Medium OpEx: Very High	Disposed eluate used for the regeneration of IER	No reported fluoride recovery from IER
	PBR	20	Basic Process Design	highly dependent on pH LSR: medium-high τ : 30 min.–3 days	adsorbent and IER dependent II: medium to highly sensitive	CapEx: Medium to High OpEx: Low-Very High	Low sludge production and disposal of used sorbent	adsorbent and IER dependent
Precipitation-Crystallization	CF	7	Widely use and available	highly dependent on pH LSR: low to high τ : 15–60 min (rapid)	High even at higher concentration II: low sensitivity	CapEx: Low-Medium OpEx: Low-Medium	High Sludge production precipitant can also be toxic	Sludge utilization
	FBC	8	Basic Process Design	highly dependent on pH LSR: medium-high τ : 1 h to 4.5 days	Effective at lower supersaturation	CapEx: Medium-High OpEx: Low-Medium	Low sludge production	Crystal recovery
	EC	11	Pilot-scale	highly dependent on pH LSR: Medium τ : 30–280 min	Highly effective at a relatively lower concentration	CapEx: Medium-High OpEx: Medium-High	Low sludge production	Sludge utilization
Membrane	NF	13	validation of commercially available NF	pH effects not significant τ : 0.5–2 days.	High II: not sensitive	CapEx: Very High OpEx: High Power: High	Very Low sludge production	No recovery
	RO	2	Basic Process Design to Actual Plant-scale	pH effects not significant LSR: very high Remineralization	Very High at all concentration II: not sensitive	CapEx: Very High OpEx: Very High Power: Very High	Very Low sludge production	No recovery
	ED	8	Pilot-scale	pH effects not significant LSR: very high	High Low capacity	CapEx: Very High OpEx: Medium-High Power: Medium	Concentrate Disposal	No recovery

Table 5
Conceptual estimates of operational cost of different defluoridation techniques.

Treatment	Estimated OpEx (€/m ³)
Adsorption (GAC)	3.740
IER	4.675
CF	0.184
EC	0.230
Membrane (RO)	0.316
ED	0.237

sanitation and treatment facilities. Further progress in developing discussed popular techniques has a high potential impact on the 6th UNSDG.

- Most of the reported hybrid treatment for fluoride removal is applied for the treatment of drinking water with a reduced significant amount of fluoride. However, there are still very limited reports discussing treatment using hybrid or multiple-phase treatment for the total removal of fluoride in water. This mix and match of various fluoride treatment technologies can further be explored in the future since a stand-alone treatment has limited ranges in removing fluorides.
- We also initially intend to compare the disposal methodologies in each treatment (e.g. used adsorbent, sludge, washed fluoride from IER, fluoride saturated plants, etc.) and the possible economic and environmental impact. However, there are still insufficient and incomparable data for each treatment. Thus, the

full life cycle assessment of different methodologies (comprising useful life and appraisal of maintenance and overhauls) can also be beneficial. After the life cycle assessment, cost evaluation of secondary pollution can also be regarded including possible recovery and assessment of potential economic value.

- Based on the examined literature, most of it do not provide enough quantitative data which can be employed to interpolate or extrapolate comparable information of various technologies. In addition, collected literature mostly discussed the removal of fluoride using adsorption technology. Nonetheless, there is a limited quantitative discussion on the cost-effectiveness of adsorbents.
- Bioremediation can be considered for indirect application in fluoride-containing effluent in the WWT facilities because of organism viability requirements and limited fluoride resistance. However, bioremediation can still be integrated with water management through trapping free fluorides in surface waters (by macrophytes) and by preventing the leaching fluoride in soil (by terrestrial plants) which can further transport to aquifers and other natural waters. Similar to other defluoridation techniques, recent studies do not discuss the feasible or sustainable material recovery of defluoridation through phytoremediation.
- In this study, we have provided a quantitative conceptual cost evaluation of OpEx and a relative cost description of popular treatments. However, an itemized estimate can be more beneficial especially for emerging bio-sorbents claiming cheaper cost.

7. Conclusion

The fluoride-contaminated water is still a looming concern affecting human health and further compelling for more intensive environmental protection and more rigorous water management.

To aid UNSDG for clean water, additional efforts to provide an efficient, cost-effective, and viable technique for the development of fluoride removal technologies are necessary. Although popular methods offer different individual advantages, it also restrained by its fundamental drawbacks. Moreover, the lack of enough and quantifiable data makes it hard to have precise and substantial benchmarks. On the other hand, some researchers do not focus on seeking the further development of specific methodology, rather combine different technologies creating a synergistic technique for fluoride removal. This contributes to the growth of water engineering using available methods with minimum efforts for practical applications. In addition, narratives from the evaluated literature are limited on the removal of fluoride from the aqueous solution and do not transcend to the further investigation of potential recovery, re-used, and/or disposal of the generated secondary pollution. Hence, we suggest to future researchers to have a more conscientious and holistic approach in future investigation.

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.

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