Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22167

117 (2018) 118–141
June

Removal of fluoride from aquatic environment

Michał Bodzek[a,*], Krystyna Konieczny[b]

[a]*Institute of Environmental Engineering, Polish Academy of Sciences, M. Curie Sklodowskiej 34, 41-819 Zabrze, Poland, email: michal.bodzek@polsl.pl*
[b]*Silesian University of Technology, Faculty of Energy and Environmental Engineering, Institute of Water and Wastewater Engineering, Konarskiego 18, 44-100 Gliwice, Poland, email: krystyna.konieczny@polsl.pl*

Received 5 December 2017; Accepted 4 March 2018

ABSTRACT

High fluoride concentrations in aquatic environment, even above 30 mg/L, are often detected in many parts of the world. Due to fluoride effects on health, World Health Organization (WHO) as well as national health authorities have established its maximum permissible concentration in drinking water at the level of 1.5 mg/L. This review article aims to provide detail information on researchers' efforts in the field of fluorides removal during potable water production. The contaminant elimination methods have been broadly divided into three sections, that is, coagulation/precipitation, adsorption and membrane techniques. Both, precipitation with the use of calcium salts or coagulation with aluminum sulfate and ferric salts followed by sedimentation are used for fluoride removal. In electrocoagulation, a coagulant is generated in situ by means of oxidation of anode usually made of aluminum or iron. Adsorption is broadly utilized as it offers acceptable results and it is most appealing technique for the removal of fluorides regarding costs, simplicity of outline and operation. Alumina/aluminum-based materials, clays and soils, some minerals and carbon-based materials as well as layered double oxides, nanosorbents and biosorbents, they all have been tested as adsorbents for fluorides removal. Among membrane techniques reverse osmosis, nanofiltration, ultrafiltration in integrated systems, electrodialysis and Donnan dialysis have been discussed.

Keywords: Water treatment; Fluorides removal; Coagulation/precipitation; Adsorption; Membrane processes; Review

1. Introduction

Recent UNICEF and WHO reports have confirmed that ca. 748 million of people have no access to safe water of proper quality, while more than 1.8 billion of people use water contaminated with feces to potable purposes [1,2]. Even though groundwater resources correspond to 0.6% of global water resources, more than 50% of them are used to potable purposes, especially in developing countries. Moreover, the economic growth results in contamination of natural and anthropogenic water reservoirs due to urban and industrial activities, deep percolation from intensive agriculture, utilization of liquid and solid hazardous wastes, including industrial ones, wastewater deposition, soil degradation and unsustainable water use. This all leads to degradation of water quality and limits its accessibility per capita in many countries.

The presence of several natural and anthropogenic elements and compounds, such as fluorides, arsenic, nitrates, sulfates, iron, manganese, chlorides, selenium, heavy metals and radioactive substances may significantly affect water quality and cause harmful health effects. In many cases, available water resources have become too contaminated, not only for human's consumption, but also for industry and agriculture. According to WHO, the most dangerous inorganic substances appearing in groundwater, which reveal global effect to human health, are fluorides and arsenic [3].

The presence of F^- in natural water is connected with its appearance in natural minerals, local geological structure and industrial activities [4]. Fluorides are naturally released

---

[*] Corresponding author.

Presented at the 13th Conference on Microcontaminants in Human Environment, 4–6 December 2017, Czestochowa, Poland.

to water during dissolution of minerals and soils rich with these elements, and observed fluoride concentrations are directly proportional to the rate of extraction/dissolution of crystal alloys. The most prevalent fluorine containing minerals are: fluorite (CaF_2), cryolite (Na_3AlF_6), fluoroapatite ($Ca_5(PO_4)_3F$) and sellaite (MgF_2) [3]. The concentration of F^- in water is limited by minerals' solubility, especially in case of CaF_2, the lowest value of which measured in 18°C is equal to 15 mg/L. Moreover, the solubility itself depends on a material chemical composition, groundwater age and depth of the water layer [5]. Except for natural sources, the elevated concentrations of fluorides, as well as other environmental contaminations, in water are caused by industry, which deposits fluoride-containing wastewater to natural surface water. The most important industrial branches in this field are galvanic, glass, ceramic and fertilizers industries as well as the production of semiconductors, coal-based heat and power plants and iron and aluminum works [6–8]. Wastewater generated by those industries characterizes with fluorides concentrations much higher than naturally appearing levels, starting from several dozen up to several thousands of mg/L, for example, in case of phosphates production, concentration of fluorides in wastewater may reach up to 3,000 mg/L [6].

2. The impact of fluoride on human's health

Fluoride may reveal either advantageous or disadvantageous health effects, depending on their dose and exposure time [9]. While the concentration of fluorides in potable water ranging from 0.5 to 0.7 mg/L is desired in order to avoid dental caries among children [10], their higher amount is regarded as serious health problem. The regular consumption of water containing 1.5–4 mg F/L results in bone tissue problems [11] (fluorosis, arthritis and osteoporosis) as well as in neurological issues, and it may lead to lever damage, carcinogenic and gastrological effects.

Fluorine, as a highly electronegative element, possesses the affinity to attract positively charged calcium ions. Thus, it causes demineralization of bone and teeth tissues, which contain high amount of calcium, by formation of fluoroapatite. During the reaction, hydroxyl ions are replaced with fluorides, as fluoroapatite is more stable than hydroxyapatite. Hence, a high amount of fluorides is bonded in tissues, while its negligible amount is excreted with sweat, urine or feces. Dental fluorosis as well as bone fluorosis are primary and most harmful damages caused by fluorides in human body [9,10]. Teeth enamel is mostly composed of hydroxyapatite crystals. Normally, the progress of dental fluorosis depends mainly on the amount of fluorides dosed to 8–10 years old children, as then fluorides decolor growing teeth and bones below gums. In case of bone fluorosis, fluorides deposit mainly in neck, knees, pelvis and arm bones causing syndromes similar to spine or joints dysfunction by impeded movement, walking, etc. [12]. However, bone and dental fluorosis are not only effects the fluoride overdose, which may also lead to muscles fibrosis, lowering of hemoglobin level, erythrocyte deformation, inordinate thirst, headache, stress, neurological symptoms (Alzheimer disease), depression, stomachache, bowels issues, urinary system dysfunction, nausea, hands and feet tingling, immunity decrease and procreativity problems, etc. [12]. While consumed, initially fluoride irritates stomach mucosa, while lately formed hydrofluoric acid is highly irritating to stomach and bowel tissues [12]. Some studies also indicate that chromic overconsumption of fluorides may affect procreative functions, causes kidney stones and thyroid dysfunction and lowers children intelligence [12]. Various forms of fluorosis are shortly discussed in Table 1 [12,13]. Overdosed and chronic consumption of fluoride by animals results in analogical problems as in case of humans. Additionally, watering of plants with water of high fluoride content affects their growth.

Table 1
Exemplary health effects of chronic consumption of water of different fluoride content

Fluorides concentration (mg/L)	Health effect
<0.5	Teeth caries
0.5–1.5	Optimal dental effect
1.5–4.0	Dental fluorosis
4.0–10	Bones and teeth fluorosis
>10.0	Devastating fluorosis

Due to fluoride effects on health, World Health Organization (WHO) as well as national health authorities have established its maximum permissible concentration in potable water at the level of 1.5 mg/L, while the recommended range is from 0.5 to 1.0 mg F/L [14,15]. Such concentration of fluoride in water minimizes its harmful effects on human's health.

Considering toxicity and harmfulness of fluoride, there exists an urgent need to develop effective and reliable techniques of its removal from water dedicated to potable purposes, but also from wastewater.

3. Technologies for fluoride removal from water

Due to the high solubility of fluorides in water, its defluoridation is difficult and expensive process. Regarding raw water quality and available technical solutions, a range of methods dedicated to fluorides removal have been proposed, among which three main groups can be distinguished [2–4,13,16,17]:

- precipitation with calcium and magnesium salts combined with coagulation with aluminum, followed by sedimentation and filtration,
- adsorption and ion-exchange processes and
- membrane separation.

Each of those methods possesses a range of advantages and limitations and can be used with satisfactory efficiency if process parameters are properly selected to fluoride removal in desired concentration range. Ayoob et al. [2] have published a detail review on sustainable techniques dedicated to fluoride removal from water. A range of methods was critically evaluated by presenting their benefits and limitations. It has been found that precipitation methods are efficient for defluoridation, however, by their means the permissible concentration of fluorides in water cannot be obtained [2]. On the other hand, membrane techniques do not require the addition of external chemicals, but they are expensive and affected by fouling, scaling and membrane degradation [2]. Electrochemical methods are also economically ineffective, especially in case of investment and maintenance costs [2].

In Fig. 1, a typical fluoride concentration range and removal efficiencies established for particular treatment methods are presented [3].

3.1. Chemical methods

Among chemical methods used to fluoride removal from water one may find: precipitation–coagulation with the use of calcium salts, coagulation with aluminum sulfates followed by fluorite and aluminum hydroxide precipitation and sedimentation, precipitation and coagulation with ferric salts as well as calcium softening [3,18–21].

3.1.1. Precipitation–coagulation

Calcium and aluminum compounds are the most commonly used coagulants. During precipitation with calcium, fluorides are removed from water due to formation of hardly soluble CaF_2 and co-precipitation of $Mg(OH)_2$ according to Eqs. (1) and (2):

$$Ca(OH)_2 + 2F^- \rightarrow CaF_2 + 2OH^- \quad (1)$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad (2)$$

The efficiency of precipitation is limited by solubility of CaF_2, which at pH = 10 reaches up to 10 mg/L. However, the removal of fluorides from water during the process can be enhanced by co-precipitated $Mg(OH)_2$. On the other hand, in order to assure the desired effect, high doses of magnesium has to be used, for example, in order to decrease fluorides content from 5.0 to 1.5 mg/L up to 100 mg/L of magnesium has to be added, while pH has to be adjusted to ca. 11.3. If the amount of fluorides remaining in water is ca. 8 mg F/L or higher, the process is integrated with coagulation with $Al_2(SO_4)_3$, in order to assure the desired final concentration of fluorides [20]. At the first stage of the treatment, precipitation of CaF_2 takes place by dosing of calcium, while at the second stage alum is introduced to the system in order to induce coagulation process. First, alum hydrolyzes to form insoluble $Al(OH)_3$, and next non-hydrolyzed alum reacts with fluoride ions [20]. However, the required dose of the coagulant is very high (ca. 115 g $Al_2(SO_4)_3$ per 1 g of fluoride), while the optimum pH range is 5.5–7.0. Moreover, as in case of the previous technique, the method characterizes with generation of significant amounts of sediments [20].

The beginning of water defluoridation can be noted in 1930s of 20th century, when scientists started to sick for sustainable and economically effective methods assuring removal of fluoride from water. In Nagpur, India, the technology dedicated to fluorides removal from potable water, called Nalgonda has been developed, and it has quickly become a popular technique commonly used for this purpose in developing counties (e.g., India, Kenia, Senegal and Tanzania) [2,16]. The process relies on addition of a proper amount of alum, calcium and perchlorate to raw water, which is processed by intensive stirring, flocculation, sedimentation, filtration and disinfection. First, calcium reacts with fluoride containing compounds such as NaF, HF, etc., to form insoluble calcium fluoride (Eq. (3)).

$$Ca(OH)_2 + 2F^- \rightarrow CaF_2 + 2OH^- \quad (3)$$

At the second stage, aluminum sulfate or chloride is added separately or together to act as a coagulant forming insoluble $Al(OH)_3$ flocks, which precipitate and co-precipitate fluoride, while calcium perchlorate assures disinfection. Such defluoridation is dedicated to water plants supplying small communities with potable water (up to 200 citizens), it takes about 2–3 h and it can be repeated during the day [2]. The main advantages of Nalgonda process are low start-up costs and high efficiency. Its main disadvantage is a relatively high concentration of remaining aluminum (2–7 mg/L) in purified water, which, according to WHO standards, should not be higher than 0.2 mg/L [2,15,16]. Additionally, operational costs of Nalgonda process are relatively high, the taste of produced water is unacceptable, while generated

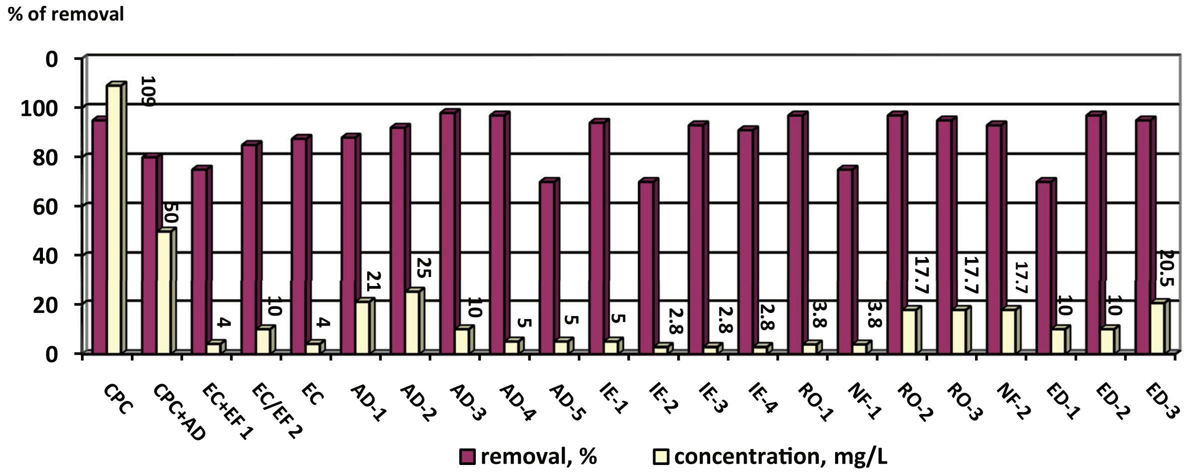

Fig. 1. Efficiency of fluoride removal by different technologies. CPC, precipitation/coagulation; EC, electrocoagulation; AD, adsorption; EF, electroflotation; IE, ion-exchange; RO, reverse osmosis; NF, nanofiltration and ED, electrodialysis.

sludge requires significant drying areas [21]. Moreover, a negative impact of natural organic matter (NOM) on fluoride removal, especially in case of low alum doses (0–100 mg/L) has been observed. The presence of already 5 mg/L of NOM increase two times the required dose of alum, affects water turbidity and increases aluminum concentration; the presence of NOM decreases the efficiency of fluoride removal if the same dose of alum is applied [22].

Co-precipitation and coagulation with aluminum salts possess a number of benefits as well as limitations [23]. The most important advantages are commonly used and simple operation in regard to other defluoridation methods. On the other hand, among disadvantages, one may find: high reagents doses required, problems with separation and utilization of sludge, inefficient operation at high initial fluoride concentrations and high final concentration of dissolved aluminum. Hence, considering the latter, a number of studies focused on replacement of chemicals and improvement of coagulation/precipitation with aluminum sulfates are carried out.

3.1.2. Electrocoagulation

A growing interest in application of electrocoagulation (EC) to a treatment of wastewater containing organic contaminants, heavy metals and fluoride has been recently observed [24–26]. EC is a favorable technique in regard to process conditions, as no additional, inert substances are introduced, while useable components present in water can be separated and reused.

EC is a technique, in which coagulant is generated in situ by means of oxidation of anode usually made of aluminum or iron. Typical EC reactor comprises of several electrolytic cells, each containing a cathode and an anode, which can be made of the same or different materials [26]. Due to the electrical current supply (electrons flow) aluminum or iron are transferred from an anode material to a solution in the form of Al^{3+} or Fe^{2+}. Simultaneously, evolution of hydrogen gas and release of hydroxide anions occur at a cathode [27]. Hydroxide anions move towards an anode and form ionic pairs with metals' cations. Those pairs form polymeric aluminum or iron hydroxides, that is, compounds responsible for coagulation [28]. In case of aluminum, anodic dissolution can be expressed according to Eqs. (4)–(7).

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^{-}(aq) \qquad (4)$$

At alkaline or acidic conditions following reactions take place [28]:

$$Al^{3+}(aq) + 3OH^{-} \rightarrow Al(OH)_3\downarrow(s) \qquad (5)$$

$$Al^{3+}(aq) + 3H_2O \rightarrow Al(OH)_3\downarrow(s) + 3H^{+}(aq) \qquad (6)$$

$$n\,Al(OH)_3\downarrow(s) \rightarrow Al_n(OH)_{3n}\downarrow(s) \qquad (7)$$

In case of iron anode, summary reaction can be expressed as follows [26]:

$$4Fe^{2+}(aq) + 10H_2O + O_2(g) \rightarrow 4Fe(OH)_3\downarrow(s) + 4H_2(g) \qquad (8)$$

In both cases, a reduction reaction (9) occurs at a cathode:

$$2H_2O + 2e \rightarrow H_2 + 2OH^{-} \qquad (9)$$

EC comprises of three step-by-step stages, that is, (i) an anode oxidation, (ii) a generation of gas bubbles and (iii) flotation and sedimentation of flocks [28]. EC process leads to destabilization of particles, suspensions and breakage of emulsions [3]. $Al(OH)_3$ or $Fe(OH)_3$ flocks act mainly as adsorbents of contaminants, which are present in water. Adsorbed contaminants either float on the surface due to the generation of gas bubbles at an anode (oxygen) and a cathode (hydrogen) or settle at the bottom of a tank. In order to remove coagulated particles, electroflotation, sedimentation and filtration can be applied.

A number of studies have shown that EC is an effective technique for removal of fluoride from either water dedicated to potable purposes or industrial wastewater [3,23,24,29] leading to decrease of its concentration to <1.5 mg/L at initial value of 10–20 mg/L or higher [25]. The mechanism of fluoride removal is connected with competitive adsorption of OH^{-} and F^{-} ions and precipitation of cryolite ($Al(OH)_{3-x}F_x$). Removal of fluoride can be improved by adjustment of pH, which should be in the range of 6–8 [26,30].

Another advantage of the process is the separation of precipitates by means of flotation, involving hydrogen bubbles generated at cathode, which force ($Al(OH)_{3-x}F_x$) to move towards a surface. Moreover, EC process results in generation of smaller amount of sludge in comparison with conventional coagulation and does not require the addition of external chemicals. However, the technique involves electric current supply, what affects operational costs. EC efficiency depends on a range of parameters, among which one may distinguish: initial fluoride concentration, water/wastewater pH, electric potential, reaction time, presence of co-ions and surface of electrodes [27,28].

The removal of fluoride by EC method with the use of four monopolar combined Al electrodes has been investigated by Behbahani et al. [31]. The efficiency of the process at predetermined optimal conditions has reached 94.5% at the initial concentration 25 mg F/L, pH = 7, current density 11.1 mA/cm^2 and reaction time 25 min. The authors have also elaborated a model, which explains the impact of main process parameters on fluoride removal and operational costs. The model has predicted 90% removal of fluoride at optimal conditions. Moreover, a part of the research on the impact of pH, which has been varied from 3 to 11, shows 5% difference in fluoride removal efficiency.

The treatment of synthetic solutions containing fluoride by means of EC method with the use of Al electrodes has also been investigated by Drouiche et al. [32]. They have determined the impact of voltage (10–30 V), electrolysis time and NaCl (0–100 mg/L) on EC efficiency. The results have shown that the increase of voltage and the elongation of the process lead to aluminum ions concentration increase and favor removal of fluoride. It has been found, using X-ray diffraction (XRD) and Fourier transform infrared spectroscopic (FTIR) analyses, that deposits found on Al electrodes comprise mainly of $Al(OH)_3$ and aluminum hydroxyoxides. The authors have also investigated the efficiency of fluoride removal from synthetic photovoltaic wastewater. They have found that for initial fluorides concentration equal to 25 mg/L the best results are obtained at 30 V, pH = 6 and reaction time 40 min.

Emamjomeh and Sivakumar [28] have observed the decrease of F^- concentration from initial 10 mg/L to final below 1.4 mg/L within 55 min of EC carried out with the use of five Al electrodes at a current intensity 1.5 A. Additionally, they have found that the increase of either an initial fluoride concentration or a distance between electrodes results in less effective removal of contaminant. They have also run a research on EC carried out in continuous system at various initial fluoride concentration (5–25 mg/L), flow rate (150–400 mL/min), current density (12.5–50 A/m^2) and initial pH (4–8). They have found that final pH should be within 6–8 as it results in the formation of sufficient amount of $Al(OH)_3$ available for fluoride complex formation.

Khatibikamal et al. [29] have studied the removal of fluoride from industrial steel plant wastewater by means of EC with the use of Al anode and cathode. They have investigated the impact of various operational conditions such as temperature, voltage, hydraulic retention time and number of electrodes on the efficiency of fluoride removal. They have obtained the decrease of contaminant concentration from 4.84 to 0.48 mg F/L with the removal rate above 90%.

Hu et al. [26] have studied the efficiency of fluoride removal in dependence of pH, alkalinity, initial concentration, type of coexisting anions and other wastewater properties. Experiments have been carried out in a bipolar reactor equipped with seven Al electrodes arranged in parallel, at current density ranging from 5.56 to 8.16 mA/cm^2. The initial concentration of fluoride has been established at 25 mg/L, while raw solutions have additionally contained chlorides and nitrates. The efficiency of fluoride removal has reached 100% for solutions contaminated only with it, while at the presence of co-ions, that is, chlorides or nitrates, it has decreased to 80%–90%. They have also found that optimal initial ratio of OH^- to Al^{3+} should be kept above 2.4, while the sum of molar ratios of OH^- to Al^{3+} and F^- to Al^{3+} should be above 3. The studies have enabled to propose the mechanism of fluoride removal by means of EC, which is most probably based on co-precipitation of fluorides and hydroxides with Al^{3+} in the form of $Al(OH)_{3-x}F_x$.

Zhu et al. [33] have investigated solutions containing trace amounts of F^- and explained that at higher pH the formation of soluble $Al(OH)_4^-$ ion occurs, while this ion is not able to flocculate and it cannot defluorize water. Additionally, they have compared EC with chemical coagulation to show that EC characterizes with a higher efficiency at lower Al^{3+} doses which refer to conventional system.

Ghosh et al. [34] have investigated the removal of fluoride from potable water containing 2–10 mg F/L by means of EC with the use of monopolar and bipolar electrodes. They have found that bipolar arrangement is more efficient than monopolar, as the former system assures larger effective surface of electrodes. Hence, the application of an identical current density results in higher efficiency of fluoride removal in bipolar system. The authors have obtained the decrease of fluoride concentration from 10 to 1 mg/L within 30 min at current density 62.5 mA/cm^2. Operational costs established for monopolar and bipolar systems are equal to 0.38 and 0.62 USD/m^{-3}, respectively.

It has already been mentioned that gas bubbles formed during EC process may cause the flotation of post-coagulation flocks. Hu et al. [35] have investigated bipolar continuous EC–flotation reactor to remove high amounts of fluoride in the presence of sodium dodecyl sulfate (SDS). They have found that in order to assure the effective removal of fluoride, SDS concentration should be kept above 30 mg/L for continuous system, but it should not exceed 50 mg/L. In case of batch system, 5 mg SDS/L has been found to be efficient enough to assure satisfactory fluoride removal rate. The authors have suggested that SDS causes not only foaming, but also acts as a collector of precipitated CaF_2 within the whole continuous reactor system.

Shen et al. [8] have investigated a hybrid system of EC and electroflotation for defluoridation of industrial water. With this method, the concentration of fluoride has been decreased from 15 mg/L, after precipitation with calcium, to 2 mg/L in the effluent (pH = 6). Even lower concentrations can be achieved when Fe^{3+} and Mg^{2+} ions concentration is 50 mg/L in the coagulation chamber.

Bennajah et al. [36] have investigated removal of fluoride from synthetic solutions by means of EC–electroflotation method in two EC chambers (i.e., stirred tank reactor and air lift reactor) of volume 20 L equipped with Al electrodes. Air lift type reactor is more favorable to perform fluoride removal due to the lower energy consumption. It enables to run flotation with the use of electrochemically generated gas bubble with no need for addition of either a surfactant or compressed air. Another advantage of the air lift reactor, in comparison with a stirred tank reactor, is the recovery of flocks without the use of additional unit operation (e.g., filtration or sedimentation). Generally, flotation replaces settling tanks.

Cui et al. [37] have investigated a carbon electrode modified with poly(aniline co-o-phenol) (PAOA) to fluoride removal by means of continuous EC process. The reactor could be operated at high pH range due to the cover with PAOA copolymer of ion-exchange properties. Electrodes made of porous carbon have characterized with high conductivity and faster mass transport from solution to electrode surface. The removal of fluoride has increased with the voltage increase from 0.8 to 1.2 V, while it has been affected by the initial fluoride concentration increase. Optimal fluoride removal has been reached for 1.2 V, pH = 7.2 and initial concentration 10 mg F/L.

To sum up, main EC advantages are [23] simple basic equipment, simple service and low costs, high quality of finally produced water (colorless, odorless and drinkable), formation of small amounts of precipitates, which easily dewater, as they comprise mainly of metal hydroxides and oxides and can be effectively separated by means of flotation and filtration. On the other hand, main limitations of the technique are dissolution of electrodes, which leads to their replacement/fulfillment requirement, high energy consumption, significant raw water/wastewater conductivity and formation of insoluble oxides on electrodes surface, which may lead to a decrease of the overall process efficiency.

3.2. Ion exchange

Ion exchange is a method, which can be applied to remove excess amounts of fluoride from water. Strongly basic anion-exchange resins containing quaternary ammonium functional groups are used. The removal mechanism can be described by means of Eq. (10) [16,23]:

$$\text{Matrix-NR}_3^+\text{Cl}^- + \text{F}^- \rightarrow \text{Matrix-NR}_3^+\text{F}^- + \text{Cl}^- \quad (10)$$

Fluorides replace chlorides, and the process runs until all active centers of the resin are occupied. The regeneration of a resin is made by washing with saturated NaCl solutions. During regeneration, chlorides replace fluorides and the process can be run again. The driving force of the process results of the higher electronegativity of fluorides in reference to chlorides. Defluoridation capacity (DC) and selectivity towards F^- depends mainly on a resin type. Ionic charge of metals strongly affects the removal of fluorine, due to differences in their electrostatic properties [3]. It is considered that mechanism of F removal using ionites does not only rely on the ion-exchange, but it also involves the adsorption [3]. The main reason of such a conclusion is the fact that the concentration of fluorides in purified water is much lower than concentration of other anions present in the stream.

Chikuma and Nishimura [38] have applied anion-exchange Amberlite resin IRA-400 operated by means of chlorides replacement. Solangi et al. [39] have modified anionic resin Amberlite XAD-4TM, by introducing anionic group to aromatic resin structure and they have efficiently applied it to fluorides removal. The modified resin has been found to be very effective, especially at pH = 9, and, moreover, it has acted perfectly at the presence of other co-ions such as Br^-, NO_2^-, NO_3^-, HCO_3^- and SO_4^{2-}. They have also modified Amberlite XAD-4TM resin by introduction of thiourea to aromatic rings bonds [39]. The modified resin has revealed a high efficiency towards removal of fluorides from useable water. Ku et al. [40] have run a research on the application of Duolite C-467 resin occupied with aluminum ions to remove fluorides from water. The process has been found to be efficient at relatively stable raw stream pH. Viswanathan and Meenakshi [41] have investigated defluoridation properties of chelating resins of Indion FR 10 (IND) and Ceralite IRA 400 (CER) type. The obtained results have revealed that chelating resins are more suitable to fluoride removal than conventional anion-exchange resins. They have also applied Indion FR 10 ionite chemically modified with Ce^{3+}, Fe^{3+}, La^{3+}, Zr^{4+} and Al^{3+} ions operated in hydrogen mode [41]. Maximum capacity of defluoridation of all modified resins has been established at ca. 0.5 mg/g. The authors have noted that in such a case defluoridation is the effect of both, electrostatic adsorption and complexation.

Chubar et al. [42] have investigated simultaneous removal of different ions, such as F^-, Cl^-, Br^- and bromates, from water using novel ionite containing coupled hydrated oxides ($Fe_2O_3{\cdot}Al_2O_3 \cdot xH_2O$) obtained by means of sol–gel method from widely available raw materials. It has been found that impact of pH in the range 3–10 on adsorption of F^- and Br^- depends on ions speciation. Adsorption of fluorides, equal to 88 mg/g, has been the highest among all investigated ions.

Sundaram and Meenakshi [43] have used organic–inorganic ion exchangers to remove fluoride. Within the research, polyacrylamide ion exchanger has been modified with $Ce(SO_4)_2{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $ZrOCl_2{\cdot}8H_2O$. The modified ionite has characterized with slightly higher DC (i.e., 2,290 mg F^-/kg) than other materials.

The main advantages of ion-exchange are high degree of fluorides removal from water (90–95%) and acceptable taste and color of purified water. Among limitations of the method, one may distinguish [13,23] the negative impact of other ions such as sulfates, carbonates, phosphates, formation of fluorides rich side streams during regeneration, which must be separately utilized, high costs, very low pH and high concentration of chlorides in the effluent as well as relatively long contact time required.

3.3. Adsorption

Among various methods available to fluorides removal, adsorption process is commonly used and it seems to be the most attractive method due to technical and economic features. In order to remove fluorides from water efficiently, a number of various adsorbents have been developed and tested in regard to adsorption capacity, process parameters and adsorption isotherms and kinetics models [12,22]. Among available adsorbents, one may find activated and impregnated aluminum oxide, metal oxides, adsorbents based on calcium and iron salts, activated clays and minerals, including zeolites, carbon materials, agricultural and industrial by-products, alum, aluminum sludge, chitosan and other biosorbents, and, recently, layered double hydroxides (LDHs) and nanosorbents [12,44]. During the last decade, metal oxyhydroxides in powder form and supported on different matrixes have been of great interest for fluoride removal [45].

Theoretically, the mechanism of fluoride adsorption on solid particles comprises of three main stages [46]:

- diffusion/transport of fluorides to external surface of adsorbent from a solution,
- adsorption of fluorides on particles' surface and
- ion-exchange or diffusion to a particle's interior.

In order to evaluate the possibility of application of an adsorbent in practice, one should consider adsorption capacity in diluted solutions, pH, contact time, adsorbent's stability, its regeneration, impact of other anions and cations as well as total costs [44].

3.3.1. Activated aluminum

One of the most important methods used to remove F^- from water is adsorption on aluminum oxide. So-called activated aluminum oxides are transient aluminum oxides, obtained during calcination of hydrated Al_2O_3 at 400°C–800°C, which appear as crystalline hydrates or amorphous Al_2O_3 and hydrates [47]. Usually, pyrolysis of gibbsite $Al(OH)_3$ and gibbsite containing materials, or slow or fast high-temperature calcination are carried out. Slow decomposition is usually obtained in a water vapor atmosphere, while fast degradation is carried out in a flue gas atmosphere. Fast activated Al_2O_3 characterizes with transient structure between gibbsite and Al_2O_3 and contains 0.2–1 mol of crystallized water per mol of Al_2O_3. The product is less crystalline than gibbsite of aluminum oxide prepared with the use of slow calcination and reveals fast and efficient adsorption of fluoride, due to the large specific surface area up to 200 m^2/g Al_2O_3. Activated aluminum oxide, as an amphoteric compound, is able to adsorb both anions and cations. At pH < 9.5 it adsorbs anions, while at alkaline environment it reveals the affinity towards cations [20]. The selectivity series of anions adsorption on activated Al_2O_3 at pH range 5.5–8.5 is established according to (11) [44]:

$$\begin{aligned}&OH^- > H_2AsO_4^- > Si(OH)_3O^- > HSeO_3^- > F^- > \\ &SO_4^{2-} > CrO_4^{2-} >> HCO_3^- > Cl^- > NO_3^- > Br^- > I^-\end{aligned} \tag{11}$$

The affinity to anions removal is used in order to eliminate fluorides from water. Complete process cycle covers swelling, regeneration, washing and neutralization of sorption bed and sorption of anions, which, for fluorides and activated Al_2O_3, can be expressed by means of Eq. (12):

$$=Al\text{-}OH + H^+ + F^- \leftrightarrow =AlF + H_2O \tag{12}$$

In case of activated Al_2O_3 regenerated with $Al_2(SO_4)_3$, sulfate ions are exchanged as shown in Eq. (13) [20]:

$$(Al_2O_3)_2{\cdot}SO_4 + 2F^- \rightarrow 2(Al_2O_3)F + SO_4^{2-} \tag{13}$$

The capacity of activated aluminum oxide depends on pH of a treated water, while the optimum parameter range is established between 5.0 and 6.0 (precisely 5.5). The optimum concentration of H^+ is very important, hence, sorption is usually preceded with the adjustment of raw water pH. Among available granulation of sorbents, grains of 0.3–0.6 mm size are usually used. In case of fluorides removal, multivalent ions, for example, SO_4^{2-}, are competing ones, and their concentration of 500 mg/L decreases the efficiency of activated aluminum oxide adsorption by ca. 33%. The pilot-scale research has confirmed the applicability of such sorbent to remove F^- from water, and the obtained sorption capacity has reached 6.7 g F^-/dm^3 of bed at pH = 5.5 and initial fluorides concentration 5 mg/dm^3 [20].

The regeneration of activated Al_2O_3 can be made with the use of NaOH of concentration 0.5%–2% proceeded by the ionite neutralization with H_2SO_4 or HCl [44,47]. The regeneration with NaOH runs according to Eq. (14):

$$=Al\text{-}F + OH^- \rightarrow =Al\text{-}OH + F^- \tag{14}$$

After regeneration, due to the required pH, the remaining NaOH has to be washed out of the bed, hence neutralization with acidic solution of pH = 2.0–2.5 is carried out until the desired pH of the effluent is obtained.

Ku and Chiou [48] have investigated the impact of selected operational parameters on fluoride removal from aqueous solutions using Al_2O_3. It has been found that the optimum pH, at which the maximum fluorides removal occurs (up to 16.3 mg/g), is in the range of 5–7. The adsorption of fluoride in more acidic solutions is less efficient due to electrostatic repulsion of F^- ions by negatively charged adsorbent surface and competitive character of excess OH^- ions. In acidic and neutral solutions, adsorption of fluoride ions on aluminum oxide is affected by the presence of sulfates. Models of Langmuir–Freundlich isotherms well describe the equilibrium of the adsorption process.

Valdivieso et al. [49] have checked the impact of temperature on zeta potential and fluorides adsorption at phase boundary of α-Al_2O_3/aqueous solution in order to determine the mechanism of F^- removal. They have found that isoelectric point (pzc) of α-Al_2O_3 at 20°C appears at pH 9.2. The potential of α-Al_2O_3 in the presence of fluoride changes the charge to more acidic pH in reference to pzc indicating on the specific adsorption of fluoride. The measurements of zeta potential have revealed that fluoride is adsorbed by α-Al_2O_3 due to exchange of OH^- ions with positively charged surface and by hydrogen bond formed at conditions close to or above pH_{pzc}. Protonic desorption from α-Al_2O_3 surface occurs when pH_{pzc} is shifted to lower values at temperature range from 10°C to 40°C. The adsorption of fluorides runs according to Langmuir adsorption isotherm and depends on the charge at the boundary phase of α-Al_2O_3/aqueous solution and surface density of hydroxyl groups. At temperatures 25°C and 40°C the maximum fluorides adsorption has been obtained at pH between 5 and 6 and it has decreased with the temperature increase.

Ghorai and Pant [50] have investigated fluorides removal by means of activated Al_2O_3 adsorption carried out in batch and continuous mode. They have obtained adsorption capacity reaching 1,450 mg/kg at pH = 7. The amount of removed fluoride has increased within pH 4–7 and then it has started to decrease. Silicate and OH^- ions have competed with F^- ions during the adsorption at pH > 7, while at pH < 7 soluble Al–F complexes have been formed.

3.3.2. Modified aluminum oxide

In order to improve the efficiency of activated aluminum oxide, a number of techniques of its surface modification have been developed.

One of the methods is the impregnation of activated Al_2O_3 with La(III) and Y(III) compounds [51]. The adsorption properties of impregnated and original Al_2O_3 have been compared according to fluoride and other anions removal at various process conditions. The selectivity has changed in a following series: fluoride > phosphate > arsenate > selenite. The adsorption capacity of original Al_2O_3 has reached 0.170–0.190 mM F^-/g, while for one impregnated with La(III) it has been 0.350 mM F^-/g. The use of the adsorbent has resulted in the decrease of F^- concentration from 7 to 0.003 mM at pH range 5.7–8.0.

Tripathy et al. [52] have modified Al_2O_3 surface by impregnation with alum. Fluoride adsorption has increased with pH increase and it has reached the maximum efficiency equal to 92.6% at pH = 6.5, while further pH increase has led to the efficiency decrease due to the competitive action of OH^- ions. At pH range < 6.5, the removal of fluoride has been lowered due to the appearance of non-dissociated HF or a common impact of both, chemical and electrochemical interactions between the oxide surface and F^- ions. The adsorption capacity, calculated using Langmuir model, has been established at 40.68 mg/g at pH 6.5. The energy dispersive X-ray spectroscopy analysis has proved that F^- ion has been bonded on the surface of Al_2O_3 impregnated with alum.

Maliyekkal et al. [53] have modified Al_2O_3 with MnO_2 (MOCA), which has further been used as an adsorbent in potable water defluoridation carried out in batch and continuous modes. The optimum pH of the process has been established within the range of 4–7, while maximum adsorption capacity, due to Langmuir model, has been 2.65 times greater than the one established for original Al_2O_3 (2.851 mg/g). MOCA has been efficiently regenerated with the use of 2.5% NaOH. The sorption capacity of investigate adsorbents (MOCA and Al_2O_3) towards fluoride at the moment of breakthrough has depended on the volume of bed. Teng et al. [54] have also prepared the adsorbent to defluoridation by coating Al_2O_3 surface with hydrated manganese oxide. The developed adsorbent has enabled to decrease fluoride concentration from 6.0 to 0.45 mg/L at pH = 5.2, while the efficiency obtained for activated Al_2O_3 has reached 45% at the same conditions. The mechanism of fluoride removal by modified adsorbent relies on the exchange between OH^- and F^- ions at acidic pH, while at pH > 6.0 fluorides are adsorbed due to van der Waals forces. The presence of HCO_3^-, SO_4^{2-} and PO_4^{3-} affects fluorides adsorption efficiency.

Bansiwal et al. [55] have modified Al_2O_3 by coating with copper oxide (COCA). The adsorbent has been prepared by impregnation of Al_2O_3 with $CuSO_4$ solution followed by calcination at 450°C in air. The adsorption capacity of modified COCA sorbent, due to Langmuir model, has reached 7.22 mg/g and it has been three times greater than the one established for non-modified Al_2O_3 (2.232 mg/g). The significant increase of adsorption capacity of COCA has been explained by the increase of zeta potential connected with the appearance of additional active centers. The impact of pH on the process efficiency has been negligible. Additionally, leachate of copper to treated solution has not been observed.

Maliyekkal et al. [56] have developed a novel adsorbent by modification of Al_2O_3 by means of MgO and they have tested it towards fluoride removal. 95% efficiency has been obtained within 3 h at neutral pH. The mechanism of F^- sorption has been explained by replacement of OH^- ions in crystalline brucite, but the crystal structure of the compound has not been damaged. The adsorption capacity of F^- ions has reached 10.12 mg/g at optimum pH range 5.0–7.5. The elevated concentrations of bicarbonate and sulfates have affected the efficiency of fluorides sorption.

Jain and Jayaram [57] have applied $Al(OH)_3$ impregnated with limestone (AlLS) to effective removal of fluoride from contaminated potable water. The efficiency of the process has significantly decreased at pH = 2, what has been connected with decomposition of $Al(OH)_3$ at acidic environment. The maximum adsorption capacities established for limestone and AlLS have reached 43.10 and 84.03 mg/g, respectively. The FTIR analysis has shown that the adsorption of fluoride on AlLS sorbent has been a physical phenomenon.

Liu et al. [58] have prepared a hybrid sorbent by means of co-precipitation by neutralizing solution containing 0.2 mol $AlCl_3$/L and 0.05 mol/L of cerium(III) nitrate. The produced precipitate has next been dried at 80°C and evaluated towards fluoride removal. The results obtained during scanning electron microscopy (SEM) and XRD analyses have shown that the hybrid adsorbent has possessed an amorphous structure and aggregated nanoparticles could be found within its structure. The maximum adsorption capacity established for the sorbent has been equal to 91.4 mg/g at 25°C and pH = 6. The mechanism of fluoride removal from an aqueous solution has relied on electrostatic interactions between fluorides and negatively charged sorbent surface (isoelectric point potential –9.6).

Karthikeyan and Elango [59] have investigated aluminum titanate (AT) and bismuth aluminate (BA) as potential adsorbents to fluoride removal. The adsorbed amounts of fluoride by AT and BA have been equal to 0.85 and 1.55 mg/g, respectively, at 40°C and initial fluoride concentration 4 mg/L. The results have revealed that adsorbents have characterized with relatively high DC at acidic conditions, what has been confirmed by pH_{pzc} (7.4 for AT and 7.1 for BA). Moreover, co-ions present in the solution have not affected the efficiency of defluoridation carried out at AT adsorbent. FTIR and XRD analyses performed before and after adsorption have indicated on chemisorption mechanisms of fluorides.

Patra et al. [60] experiments have conducted to remove fluoride from aqueous solution using alumina and HCl treated activated alumina in a continuous mode. A spiral rib was introduced in the cylindrical part of the conventional hydrocyclone to increase the performance. Experiments were carried out to analyze the performance of the ribbed hydrocyclone and compared the results with the conventional hydrocyclone of the same dimension. The efficiency of conventional and ribbed hydrocyclone at a slurry flow rate of 50 L/min for the solid concentration of 1.4 wt% were 80% and 93.5%, respectively. Fluoride removal efficiency using alumina and HCl-treated alumina was also investigated in a continuous mode by the ribbed hydrocyclone. Maximum fluoride removal efficiency was 49.5%, and 80% for alumina and HCl-treated alumina for the initial concentration of 10 mg/L at a slurry flow rate of 50 LPM.

The application of LDHS to water defluoridation has recently gained more attention, as LDHs are synthesized using cheap raw materials and can be easily regenerated. Lv et al. [61] have run a systematic study on the impact of calcination and adsorption conditions on removal of fluorides from water using layered double magnesium-aluminum hydroxides. The selected temperatures of calcination at Mg/Al ratio = 2.0 have been equal to 200°C, 400°C, 500°C, 600°C and 800°C. The maximum adsorption capacity has been noted after calcination at 500°C, while above this temperature the efficiency of fluorides removal has drastically decreased due to significant lowering of specific surface area. At Mg/Al ratios 3.0 and 4.0 the adsorption capacity has also been lower than in case of Mg/Al = 2, as the charge of metal hydroxide layer has decreased with the amount of Mg^{2+}. At optimum conditions, that is, pH = 6, Mg/Al ratio = 2, calcination temperature = 500°C and adsorbent dose 1.8–2.1 g/L, 80 mg of fluorides have been removed per 1 g of solid adsorbent from solution containing 100 mg F^-/L within 6 h of the process at 30°C. The impact of anions accompanying fluorides in the solution on the efficiency of its adsorption could be arranged in a following series: $PO_4^{3-} < Cl^- \approx SO_4^{2-} < Br^- \ll NO_3^-$. The results of Roentgen ray diffraction, FTIR and TG-MS have revealed that the adsorption has been accompanied with rehydration with simultaneous involvement of fluorides in recovery of the original layered structure. In order to eliminate energy consumption to zeolites calcination, Mandal and Mayadevi [62] have investigated LDH sorbents of various Zn:Al ratios and compared them with calcined products. Adsorbents such as pure $Zn(OH)_2$, Zn:Al = 3.47, 0.97, 0.34 and 0.17 as well as pure $Al(OH)_3$ have been tested without calcination. The determined adsorption capacities have been arranged in a following series: Zn/Al = 0.97 > 0.34 > 0.17 > 3.47 > $Al(OH)_3$ > $Zn(OH)_2$.

3.3.3. Iron-based sorbents

Due to relatively high affinity of iron to fluoride, a range of iron-containing materials have also been tested to remove fluoride by means of adsorption. It has been found that if $Al(OH)_3$ and $Fe(OH)_3$ are co-precipitated from chlorides mixture and in equal molar amounts using ammonia, the obtained mixed hydroxides, after maturing and drying, reveal better adsorption capacity towards fluoride than single component products [44]. Moreover, those compounds are chemically bonded and FTIR indicate an appearance of Fe–O–Al bonds. Additionally, SEM analysis shows practically irregular morphology of high porosity and large specific surface area.

Sujana et al. [63] and Sujana and Anand [64] have run water defluoridation studies using mixtures of amorphous aluminum and iron hydroxides of various molar ratios, that is, Fe/Al = 1:0, 3:1, 2:1, 1:1 and 0:1. The optimum pH for adsorbents of molar ratio 1:0, 3:1 and 2:1 has been established at 4–5, while for 1:1 and 0:1 it has been 4.0–7.5. All compositions have characterized with high adsorption capacity, which has reached its maximum, that is, 91.7 mg/g, for the adsorbent of molar ratio equal to 1. The XRD analysis has shown the formation of novel complexes of fluoride on an adsorbent surface [64]. The presence of accompanying anions, that is, PO_4^{3-}, SO_4^{2-} and arsenates has revealed a negative impact on the efficiency of fluoride removal. The regeneration rate using 0.5 M NaOH has reached 80.5%.

Due to both, the stability at low pH and magnetic properties, iron oxy-hydroxy sulfate $Fe_8O_8(OH)_{8-2x}(SO_4)_x$ ($1 \le x \le 1.75$) has been used to remove fluorides from wastewater generated during metals polishing [65]. The maximum fluoride adsorption efficiency has reached 50.2–55.3 mg/g at various temperatures and at pH 3.7 and it has decreased with pH increase. At pH < 3.7, the adsorption of fluorides has also been poor as the appearance of non-dissociated HF takes place, while at pH > 3.7 active sorption centers are deprotonated, what results in repulsion of negatively charged fluorides ions by post-deprotonation centers.

Streat et al. [66] have run adsorption studies in batch and cascade mode using granulated $Fe(OH)_3$ to remove various ions, including fluorides, and they have compared their results with commercial products. Adsorption of fluoride on $Fe(OH)_3$ has strongly depended on pH and it has decreased with the parameter increase. Granulated $Fe(OH)_3$ characterizes with structure similar to akaganeite, and it has also been used to defluoridation by Kumar et al. [67] at various operational parameters. The observed adsorption capacity has been equal to 7.0 mg/g at pH = 6.0–7.0, and it has also decreased with pH increase, especially above 8.

In order to improve the adsorption capacity of ferric hydroxide towards removal of fluoride from water, Biswas et al. [68] have introduced highly positively charged cation (Sn(IV)) to crystalline structure of ferric hydroxide and they have applied it to fluoride removal from aqueous solutions. The adsorption capacity of synthetic mixture of Fe(III)–Sn(IV) oxides has been found to be practically stable at pH range 5.0–7.5 and it has reached 10.50 mg/g. The research has also shown that the mechanism of fluorides removal relies mainly on the anion exchange. Biswas et al. [69] have also prepared a synthetic adsorbent based on mixture of ferric and chromium(III) oxides (HICMO) and they have tested it in removal of fluoride from water. The maximum efficiency has been observed at initial pH = 3, and it has been assigned to strong affinity of fluoride to positively charged adsorbent surface and surface exchange of OH^- and F^- ($pH_{zpc} = 6.5$). The adsorption capacity, according to Langmuir model, has been equal to 16.34 mg/g. The removal of fluoride has decreased within pH range 3–5, what has been explained by the decrease of either positive charge of surface or the ability of the ligand to exchange with HICMO. The same authors have also synthesized a three component oxide from a mixture of iron(III)–aluminum(III)–chromium(III) (HIACMO) and they have investigated its potential to remove fluoride [70]. Fluoride sorption has depended on pH, which optimum range has been established between 4.0 and 7.0. The adsorption capacity has been determined at the level of 31.889 mg/g.

Wu et al. [71] have developed triple metal oxide Fe–Al–Ce with relatively high pH_{zpc} (7.5) and they have tested it towards fluoride removal. The adsorbent has kept relatively stable efficiency for calcination temperatures below 600°C. The maximum adsorption capacity (178 mg/g) has been reached at adsorbent dose 150 mg/L and pH = 7. The material has also revealed high adsorption capacities within pH range 5.5–7.0, while at pH > 7.5 zeta potential has been found to be negative and it has decreased with pH increase, what has resulted in fluorides ions removal by electrostatic repulsion.

A novel layered Zr–Al–La tri-metal composite (AZL) adsorbent was fabricated via co-precipitation method for fluoride removal [72]. The results showed that the layered structure existed and the AZL exhibited the maximum adsorption capacity of 90.48 mg/g at 308 K and pH 3.0. The as-prepared AZL composite has excellent fluoride removal performance for the practical groundwater and satisfies the permissible limit of fluoride in drinking water recommended by standards. The adsorption kinetics was well fitted by the pseudo-second-order equation, and the adsorption isotherms were well described by the Langmuir equation. Adsorption thermodynamics result was indicated endothermic reaction in the process of adsorption of AZL to fluoride. The adsorption mechanism of fluoride on AZL was electrostatic interaction between the protonated surface of AZL and fluoride, as well as ion-exchange by hydroxyl group and fluoride.

Chen et al. [73] prepared a novel Fe–Mg–La tri-metal nanocomposite by co-precipitation without calcination for the removal of fluoride. Various influencing factors such as coexisting anions, pH and contacting time were studied in detail. Sorption isotherms showed that the sorption capacity of fluoride is 13.2 mg/g at the equilibrium fluoride concentration of 1 mg/L, and the maximum sorption capacity is 47.2 mg/g, indicating the high defluoridation performance of the adsorbent. Adsorption mechanism indicated that F ions were able to substitute for all three metal–OH groups, and strong interactions happened between fluoride and the metals in the adsorption.

3.3.4. Sorbents based on natural materials

Materials widely appearing in nature and often applied to industrial purposes have been used as sorbents for fluoride removal from water. The most popular materials are clays and soils, but also minerals such as bentonite, kaolinite, bauxite, laterite, zeolites and others [13,44,74]. The structure of a clay or a mineral plays a significant role in determination of an adsorbent's surface charge and exchange mechanism, which may occur between ions in a solution [44]. The adsorption capacity is strongly pH dependent, as the parameter modifies charge of minerals and clays, but also the initial concentration of fluorides is important. Sorbents' surface potentials are in general positive in acidic environment and negative at basic conditions, whereas the more positively charged surface, the better sorption of negatively charged anions such as fluorides.

A number of papers on the use of baked clays to fluorides removal has been published [44,75,76]. Hauge et al. [75] have investigated the impact of firing temperature on fluorides adsorption and they have found that rate and ability of fluorides adsorption has been diversified at different firing temperatures. The clay fired at ca. 600°C has been the most efficient. The firing in higher temperatures has resulted either in decrease of fluorides removal (>700°C) or sorption disability (900°C and above), while clays fired at temperature ca. 500°C and below have decomposed in water solutions. Moges et al. [76] have applied calcined clays to defluoridation of water obtaining maximum removal rate equal to 90% and 80% at pH = 3 and 9, respectively.

Chemical pretreatment with diluted Na_2CO_3 and HCl improves the adsorption capacity of many clays and soils, as well as materials coating during mixing with solution containing Al^{3+} or Fe^{3+} accompanied with pH adjustment to hydroxides precipitation levels [13,44]. The modification process first results in removal of naturally appearing fluoride by ion-exchange with OH^-, after which clays are washed with Na_2CO_3 followed by diluted HCl rinsing and final rinsing, drying and milling to grains <2 µm. Such prepared clays are coated with 1 M solution of aluminum or iron(III) salt and finally rinsed with deionized water [44].

The possibility of use of three Tunisian clays (H, MK and ZB) to fluoride removal from acidic waste solutions has been investigated by Hamdi and Srasra [77]. They have checked the efficiency of sorption in dependence of solids content in the solution (10%, 20% and 30%). The adsorption equilibrium has been obtained after 48 h, and the highest adsorption has been noted for the suspension containing 10% of MK clay. Samples of clays MK and H used as 10% suspensions have revealed satisfactory adsorption capacity towards fluorides (93.45 mg/g) and lowers the pH.

Fan et al. [78] have investigated the adsorption of F^- using a number of minerals such as fluorite, calcite, quartz and iron activated quartz and they have compared their efficiencies towards the contaminant removal. They have used very detail radioisotope analysis (^{18}F) to define form of fluoride adsorbed at calcite, hydroxyapatite, fluorite, quartz and iron activated quartz from diluted solutions (0.025–6.34 mg/L). They have found that among investigated minerals, calcite and other adsorbents are suitable for fluoride removal from diluted solutions except for unmodified quartz.

Turner et al. [79] have run investigations on the removal of fluorides by means of crushed limestone (99% of pure calcite) carried out at a batch mode using solutions of fluoride concentration from 3 to 2,100 mg/L. By means of atomic force microscopy and X-ray photoelectron microscopy (XPS), as well as by zeta potential measurements, the authors have found that fluoride is removed from solutions according to both, surface adsorption and precipitation, and the removal rate depends on calcite specific surface area.

Activated and typical calcium oxide have also been evaluated as potential adsorbents of fluoride [80]. The removal rate of the contaminant at optimum conditions has reached 80.6% for initial F^- concentration 50 mg/L. The maximum capacity of the activated calcium oxide has been calculated as 16.67 mg/g. SEM and XRD analyses have shown that the removal of fluoride is possible mainly due to chemisorption and precipitation. The presence of other anions in a solution affects fluorides adsorption process in a following series: $PO_4^{3-} > SO_4^{2-} > NO_3^-$.

Fluoride sorption by calcite in the presence of metal ions (Co, Mn, Cd and Ba) has been investigated [81]. Kinetic results were used to determine the thickness of a calcite permeable reactive barrier required to achieve up to 99.9% fluoride removal for a groundwater. Fluoride removal half-life ($t_{0.5}$) values were found to increase in the order Ba < Cd < Co < Mn.

In Table 2, results obtained after coating kaolin clays, loamy minerals and bentonite with aluminum and iron(III) hydroxides [44] are presented. The results are compared with the ones obtained for uncoated materials revealing the beneficial character of the coating and favorable aluminum behavior in reference to iron-coated materials.

The removal of fluorides by means of acid activated kaolinite clay has been evaluated by Gogoi and Baruah [82]. The activation has been made using concentrated H_2SO_4. The maximum adsorption has been established for clays of grain size ca. 50 µm as they have revealed the highest specific surface area. The optimum pH for fluoride removal has been determined at 4, while the maximum sorption of the acid activated clay has varied from 0.0450 to 0.0557 mg/g at various temperatures. Activated kaolinite clays have also been found to be relatively more efficient to defluoridation than raw kaolinite.

Ma et al. [83] and Kamble et al. [84] have modified bentonite clays with electropositive elements (zirconium, lanthanum, magnesium and manganese) in order to increase their affinity towards fluorides adsorption. Bentonite modified with zirconium has revealed adsorption capacity of

Table 2
Adsorption of fluoride at pH = 6 by aluminum and iron(III) coated and uncoated kaolin and bentonite

Material	Coating	Adsorbed fluoride (%)
Kaolin	None	45.1
	Al oxide	72.3
	Fe oxide	61.3
Bentonite	None	49.6
	Al oxide	95.3
	Fe oxide	80.4

755 mg/kg at pH = 6.97 and at initial fluoride concentration 6.43 mg/L. Bentonite containing 10% of La has characterized with higher adsorption of fluorides from water in reference to bentonites modified with Mg and Mn and to non-modified material. The maximum adsorption capacity established for 10% La bentonite has reached 1.4 mg/g at the dose of 1 g/L. The removal of fluoride in acidic environment (optimum pH = 5) has been higher than at alkaline conditions. The mechanism of F^- removal has relied on either replacement or exchange of OH^- from bentonite surface.

The removal of fluoride by means of montmorillonite clays has been investigated by Karthikeyan et al. [85]. The maximum adsorption has been reached at pH = 2 and it has decreased with pH increase. The maximum adsorption capacity has varied within 1.485–1.910 mg/g at various temperatures. The efficiency has been affected only by HCO_3^-. XRD analysis has confirmed the deposition of fluoride on the clay surface, while FTIR results have revealed that OH groups present in clay's structure have also been involved in the adsorption process. Similar studies on fluorides removal from aqueous solutions using montmorillonite have also been run by Tor [86] and the best effects have been obtained at pH = 6, while at pH below 5 the adsorption has been affected by the appearance of non-dissociated HF due to acidic environment. At higher pH, on the other hand, the sorption has been affected by negative charge of montmorillonite's surface ($pH_{pzc} = 6.5$).

The impact of various process parameters on the removal of fluoride using laterite, a mineral composed mainly of aluminum and iron oxides, has been investigated by Sarkar et al. [87]. The adsorption capacity has decreased from 0.2014 to 0.1586 mg/g with pH increase from 2.1 to 6.7 and it has continued to decrease at pH > 7.5. During the studies run at a column mode, the optimum flow rate has been established at 5 cm^3/min, while the column breakthrough has depended on solution pH according to a series: pH 7.5 > pH 5.0 > pH 10.0. The raw laterite has also been modified (TL) using 6.0 M HCl and it has been evaluated towards fluoride removal [88]. The maximum removal rate has been obtained at pH = 5, and it has been shown that the presence of HCO_3^- and PO_4^{3-} ions has significantly affected fluoride adsorption. Iriel et al. [89] conducted the experiments with lateritic soil from Argentina in batch mode at room temperature under controlled conditions of pH (4–8) and ionic strength (1^{-10} mM KNO_3). Fluoride adsorption data were successfully adjusted to Dubinin–Ataskhov model determining that the fluoride adsorption onto soil particles mainly followed a physical mechanism with a removal capacity of 0.48 mg/g. Finally, a natural groundwater was tested with laterite obtaining a reduction close to 30% from initial concentration and without changing significantly the physicochemical properties of the natural water.

Das et al. [90] have studied the adsorption of fluorides on thermally activated, titanium-rich bauxite. Thermal activation at moderate temperatures (300°C–450°C) has significantly improved the adsorption efficiency. Fluoride removal rate has increased with pH increase reaching the maximum at pH = 5.5–6.5, above which it has started to decrease. The presence of co-ions has not affected the process efficiency. Mohapatra et al. [91] have also investigated calcined (RGB) and raw (FB) bauxites as fluorides adsorbents. The experiments have shown that RGBs reveal higher affinity towards fluoride removal than FBs. It has been found that RGB adsorption capacity increases with pH increase up to 5.5 and it starts to decrease with further pH increase. RGB is a material, which comprises mainly of aluminum and iron oxides, hence in water solutions, it undergoes hydroxylation gaining negative surface charge. The adsorption is an exothermic operation, hence the efficiency decreases with process temperature increase. A novel sorbent, lanthanum-impregnated bauxite (LIB), was prepared to remove fluoride from water [92]. The results showed that LIB, at a dose of 2 g/L could remove 99% of fluoride from an initial concentration of 20 mg F/L. The sorption followed Langmuir isotherm model and the maximum sorption capacity of LIB for removal of fluoride was found to be 18.18 mg/g. Naturally occurring pH of water was found to be favorable for sorption. Salifu et al. [93] performed the study on the defluoridation efficiency of granular aluminum coated bauxite (GACB). GACB performed better than raw bauxite and was able to reduce fluoride concentration in groundwater from 5 to 1.5 mg/L. The fluoride adsorption capacity of GACB based on the Langmuir model was 12.29 mg/g. Kinetic and isotherm analysis, thermodynamic calculations, as well as FTIR and Raman analysis suggested the mechanism of fluoride adsorption onto GACB was complex and involved both physical adsorption and chemisorption processes.

Zeolites have also been applied to defluoridation of aqueous solutions. Onyango et al. [94] have investigated sorption of fluorides using F-9 zeolite modified by exchange of Na^+ ion, present in the material structure, with Al^{3+} or La^{3+}, that is, one which reveal good affinity towards fluoride. Zeolite prepared with Al^{3+} ions has shown better adsorption efficiency than zeolite with La^{3+} ions within the investigated concentration range. The mechanism of fluorides adsorption on Al^{3+} containing material has relied on either ion-exchange or chemisorption, while for material modified with La^{3+} ions it has been resulted in physical adsorption. The removal of fluorides has been depended on pH and HCO_3^- ions content in treated solution, and the latter has decreased the amount of available active centers in zeolite structure. The advantages of synthetic zeolites of low silica content are high internal surface area, hydrophilicity and ion-exchange ability to create active centers for fluorides adsorption. Onyango et al. [95] have additionally checked the efficiency of surface modified zeolites, that is, Al-F9 and Al-HUD to water defluoridation during column mode studies. The results suggest that beds containing high amount of adsorbent are more efficient in obtaining optimum adsorption conditions. The highest flow rate of solution through the column, the highest process effectiveness has been observed. Moreover, the presence of Al ions in the column effluent has not been reported, what indicates on strong bonding of the metal in the zeolite structure.

Zeolites of clinoptilolite type, after introduction of selected ions (Al^{3+}, La^{3+} and ZrO^{2+}) to natural mineral structure, have also been applied to remove fluoride from water [96]. Natural material samples (<45 μm) have been first conditioned with HNO_3 (ZEO-1), $NaNO_3$ solution (ZEO-2) and deionized water (ZEO-3) before introduction of metals to their structures. ZEO-1 type zeolite has revealed higher affinity towards fluorides than ZEO-2 and ZEO-3 as Na^+ ions present in ZEO-1 can be easily substituted with other cations

(Al, La and Zr). The maximum equilibrium sorption capacity observed during the research has varied between 2.04 and 4.13 mg/g in dependence of metal ion introduced to the zeolite structure. The removal of fluorides from solution containing 2.5 mg F/L has reached ca. 94% for zeolite ZEO-1 at the adsorbent dose 6.0g/L. The impact of metal ions (Cd^{2+}, Ba^{2+} and Mn^{2+}) on the kinetics of fluoride removal from solution by natural zeolite was investigated [97]. Results indicate that the presence of Mn (100 mg/L) and Cd (100 mg/L), respectively, increases the rate of fluoride sorption by a factor of ~28.3 and ~10.9, the maximum sorption capacity is increased by ~2.2 and ~1.7. The presence of Ba (100 mg/L) only initially inhibited fluoride removal.

3.3.5. Carbon-based sorbents

There are three well recognized allotropic forms of carbon, that is, diamond, graphite and fullerene. Diamond is not considered as a material suitable to be applied to fluorides removal, however, graphite and fullerenes can be regarded as good sorbents if they are properly modified [44].

The removal of fluorides from water has been performed using natural carbon adsorbents such as lignite (LN), fine coke (FC) and bituminous coal (BC) [98]. FC and BC have revealed higher fluoride removal in acidic pH, while for LN higher pH values ranging from 6 to 12 have been preferable. The efficiency of fluorides removal established for all investigated sorbents has varied within 77.0%–85% at initial F^- concentration 90 mg/L, and the established adsorption capacities have been from 7.44 to 6.9 mg/g.

Kaseva [99] has run an optimization of the adsorption using bone char to defluoridation of water in Tanzania. The obtained results have shown that the highest removal rate and the highest adsorption capacity have reached 70.64% and 0.75 mg/g, respectively. Bone char grains of size 0.5–1.0 mm have characterized with the highest efficiency of the contaminant removal.

The adsorption of fluorides using impregnated chars from coconut fibers or rice straw is said to be several time higher than the one obtained for typical activated carbons due to relatively high specific surface area [13]. Daifullah et al. [100] have investigated fluorides adsorption on activated rice straw, which is a product of high porosity. Rice straw-based activated carbon has been modified with strong oxidants such as HNO_3, H_2O_2 and $KMnO_4$. The obtained adsorption has been much better than the one observed for the non-modified material. The best results have been reached for the material modified with $KMnO_4$, next with HNO_3 and finally H_2O_2.

Gupta et al. [101] have applied suspension of waste char originated from heating oil to defluoridation of water to the level <1.5 mg F/L. The suspension has been activated by heating in air at 450°C and washing with NaOH and water and the final drying at 100°C. Both, fluorides adsorption and regeneration rate have been found to depend on pH, optimum level of which has been established at 7.6.

Granular activated carbon (GAC) covered with manganese oxides (GAC-MnO_2) has also been used to remove fluoride from water solutions [102]. The adsorption capability of GAC-MnO_2 sorbent obtained with the use of 0.3 M $MnCl_2$ has been three times greater than the one observed for non-modified GAC. Solution pH has also influenced on fluoride removal efficiency and its optimum level has been established at 3. Different types of graphite have also been tested towards removal of F^- from aqueous solutions [103]. The sorption capacity has been established at 3.13 mg/g for graphite of specific surface area 818 m^2/g. The tested adsorbents have revealed satisfactory fluoride sorption in wide pH range and the process has not been affected by the presence of other anions in the solution.

Vences-Alvarez [104] conducted research onto impregnation of the lanthanum oxyhydroxides on a commercial GAC to remove fluoride from water considering the effect of the solution pH, and the presence of co-existing anions and organic matter. The results showed that lanthanum ions prefer binding to carboxyl and phenolic groups on the activated carbon surface. The modified carbon (GAC–La) possesses positive charge at a pH lower than 9. The adsorption capacity of the modified GAC increased five times in contrast to an unmodified GAC adsorption capacity at an initial F^- concentration of 20 mg/L.

3.3.6. Nanosorbents

The growing interest in the application of nanoparticles as sorbents to water treatment has recently been observed. Nanoparticles characterize with high specific surface area in reference to conventional materials, what is a promising benefit regarding adsorption process. In case of fluoride, carbon nanotubes (CNTs) as well as other nanomaterials have been investigated.

CNTs are very popular due to their small size, large surface area, high mechanical stability and electric conductivity, what makes them potential adsorbents. The application of nanotubes to fluoride adsorption has been investigated by Li et al. [105–107]. The preparation of activated CNTs has been made by means of xylene decomposition. The authors have stated that such material may adsorb 4.5 mg F/g from solution of concentration 15 mg F/L at pH = 9, and the optimum fluoride removal has been reported within pH range 3–9. The comparison of adsorption rates determined at identical conditions for activated carbon, γ-Al_2O_3, typical soil and CNTs has been arranged in a following series: CNTs > soil > γ-Al_2O_3 > activated carbon. The sorption of fluoride from water by means of aluminum oxide impregnated with CNTs has also been tested [106,107]. Nanotubes have been prepared by means of catalytic pyrolysis of propylene/hydrogen mixture, the product of which has next been milled and mixed with proper amount of $Al(NO_3)_3$ solution. Further heating in nitrogen atmosphere at 450/500°C has led to the formation of porous Al_2O_3 layer on CNTs. The most efficient adsorption of fluoride on Al_2O_3/CNT has been obtained at pH range 5.0–9.0. The adsorption capacity of CNTs/Al_2O_3 has been 13.5 times higher than in case of AIC-300 carbon, four times higher than the one noted for γ-Al_2O_3 and also higher than the one observed for polymeric resin IRA4. It has also been found that fluoride sorption occurs due to ligand formation, surface of which is positively charged and due to ion-exchange mechanism, when its surface is neutral.

Wang et al. [108] have run defluoridation studies using aluminum oxide-hydroxide nanotubes as a sorbent. The maximum capacity of defluoridation of nano-Al-OOH has reached 3,259 mg/kg and it has significantly increased with pH increase. The best result has been obtained at pH = 6.8, at which the removal rate has reached 96.7, while further pH increase has led to the decrease in the efficiency. The mechanism of fluorides removal from low pH solutions ($pH < pH_{pzc}$) has relied on a two steps reaction of ion-exchange, while adsorption of fluoride at pH > 7.8 has been assigned to van der Waals forces.

Patel et al. [109] have checked the potential of CaO nanotubes, which have been synthesized by means of the sol–gel method, towards fluoride removal. The rate of fluorides removal has decreased from 98% to 89% with temperature increase from 298 to 353 K at initial F^- concentration 100 mg/L. The main reason of the phenomenon has the ability of fluoride to leave the CaO nanoparticles surface at higher temperature, what affects the adsorption rate. The sorption capacity has reached 163.3 mg/g and has practically been pH independent at parameter's range 2–8. At pH = 8 the stepwise decrease of adsorption efficiency has been observed due to electrostatic fluoride repulsion by negatively charged surface and competitive actions of excess OH^- ions. The mechanism of fluorides sorption on CaO nanotubes has been explained by conversion of CaO to $Ca(OH)_2$ in water and surface adsorption due to exchange of OH^- ions with F^- ions and formation of CaF_2.

Novel Monetite nanorods were successfully prepared for fluoride removal [110]. The results showed that the Monetite nanorods were transformed to fluoroapatite after adsorbing fluoride. The maximum adsorption capacity was 222.88 mg/g at pH 7 and temperature 328 K when the initial fluoride concentration was 300 mg/L and the adsorbent dose was 1 g/L. The thermodynamic analysis showed that the adsorption of fluoride onto Monetite nanorods was spontaneous and endothermic. The adsorption capacities decreased with the increase of adsorbent dosage and pH. Electrostatic attraction and ion-exchange were found to be the major mechanisms governing the adsorption of fluoride onto Monetite nanorods.

Considering benefits of magnetic separation process and defluoridation potential of activated aluminum oxide, Chang et al. [111] have synthesized two types of complex nanosorbents containing bayerite, SiO_2 and Fe_3O_4. The preparation has covered precipitation of Fe_3O_4, coating with SiO_2 by acidification and further embedment of bayerite ($Al(OH)_3$) layer on SiO_2/Fe_3O_4 composite using sol–gel method (MASG) or homogenous precipitation (MAHP). The comparison of potential of the developed nanosorbents with commercially available activated aluminum oxide has revealed the higher efficiency of former composites, especially MASG, the adsorption capacity of which has reached 38 g/kg. The removal of fluorides using MASG and MAHP has been assigned to functional groups and composites present on adsorbents' surface. Zhao et al. [112] have developed magnetic nanosorbents of large surface area, high affinity towards fluorides and good magnetic separation properties. They have embedded Fe_3O_4 nanoparticles on hydrated aluminum oxide ($Fe_3O_4@Al(OH)_3$). The obtained nanosorbent has revealed strong fluoride sorption at pH 5.0–7.0, which has been explained by electrostatic attraction between positively charged ($Fe_3O_4@Al(OH)_3$) surface and fluorides. The calculated capacity has been equal to 88.48 mg/g at pH = 6.5. The affection of the process efficiency at other co-ions presence in the solution has been arranged in a following series: $PO_4^{3-} < SO_4^{2-} < Br^- \approx NO_3^- \approx Cl^-$.

Maliyekkal et al. [113] have synthesized MgO nanoparticles by means of combustion of $Mg(NO_3)_2$ trapped in cellulose fibers in order to increase MgO capacity towards fluoride adsorption. Thanks to spectroscopic analysis it has been found that fluoride adsorption mechanism relies on substitution of OH^- groups by F^- in crystalline cells of brucite. The reaction has been possible as both, F^- and OH^- characterize with similar size and radius of ions. The maximum adsorption capacity of fluoride has equaled to 267.82 mg/g. Moreover, fluoride adsorption by nano-MgO is found to be insensitive to pH changes.

MgO nanoparticle loaded alumina has been synthesized and used as a cost-effective method for removal of fluoride from water [114]. Synthesized adsorbents possess high surface area with mesoporous structure. MgO nanoparticle loading on mesoporous Al_2O_3 enhances the F^- adsorption capacity of Al_2O_3 from 56% to 90% (initial F^- concentration = 10 mg/L).

The studies on preparation of nano-Al_2O_3 and its evaluation to fluoride removal from aqueous solutions have been run by Kumar et al. [115]. The maximum adsorption capacity of nano-Al_2O_3 has been established at 14.0 mg/g at 25°C and pH = 6.15. The sorption efficiency has depended on the presence of PO_4^{3-}, SO_4^{2-} and CO_3^{2-}.

3.3.7. Biosorbents

Biosorption is a novel and developing technique of water treatment, which involves the use of available biomaterials. A range of various biosorbents have been developed to fluoride removal, that is, chitins and chitosan derivatives due to their abundance and low price, as well as rich amino and hydroxyl groups [116]. However, there are some drawbacks hindering its practical use, such as low mechanical strength, low solubility in acidic mediums, low adsorption capacity and lack of selectivity. Therefore, a variety of modification methods, including physical and chemical modifications, have been investigated to improve the physicochemical properties of chitosan.

Kamble et al. [117] have applied chitins and chitosan (raw and modified with 20% admixture of lanthanum(III) (20% La-chitosan)) to remove excess fluoride from potable water. The latter compound has revealed the highest sorption capacity towards fluoride in reference to raw chitin and chitosan. The maximum adsorption rate has been observed at pH = 6.7, while in acidic or alkaline environment the process efficiency has decreased. The presence of other anions, especially carbonates and bicarbonates, has been found to affect the process significantly. The mechanism of ligand exchange between F^- and OH^- ions, coordinated by lanthanum(III) immobilized on chitosan has been responsible for fluoride adsorption at 20% La-chitosan sorbent.

Yao et al. [118] have evaluated chitosan modified with neodymium in removal of excess fluoride from water. The optimum pH has been established at 7.0 and the process efficiency has been found to increase with temperature increase. The presence of other anions such as Cl^-, SO_4^{2-} and NO_3^- has not affected the adsorption efficiency within the investigated concentration range. The maximum equilibrium sorption, according to Langmuir, has varied between 11.411

and 22.380 mg/g depending on the process temperature. The adsorption of fluoride has occurred according to the exchange mechanism between F^- and OH^- ions coordinated by Nd(III) immobilized on the adsorbent. Additionally, in order to investigate defluoridation of water solution, chitosan covered by silica (CCS) has been prepared [119]. The results of FTIR analysis have shown that hydroxyl and amino groups are responsible for sorption of fluoride using CCS. The removal rate of fluoride has increased with increase of pH up to 4 and above this value, it has started to decrease. The sorption capacity has been established at 44.4 mg/g.

Viswanathan and Meenakshi [120] have run chitosan carboxylation (CCB) followed by chelating of amine groups with La(III) in order to involve both groups to fluoride adsorption. CCB has revealed DC at a level of 1,385 mg F^-/kg, while for sorbent modified with La^{3+} DC has reached 4,711 mg F^-/kg, whereas raw chitosan (CB) has adsorbed only 52 mg F^-/kg. The maximum DC has been observed at neutral pH. The same authors have also modified chitosan by carboxylation and chelating with Fe^{3+} (Fe-CCB) [121,122]. The modified adsorbent has revealed adsorption capacity equal to 4,230 mg F^-/kg, which has been slightly affected by solution pH. Other researches connected with modification/impregnation of chitosan with titanium(IV), zirconium(IV), iron(II) and aluminum(III) salts have also been carried out [12].

Biosorbents other than chitosan, for example, biomass, algae and fungi such as *Spirogyra, Anabaena fertilissima* and *Chlorococcum humicola* can also be used to fluoride removal from water [123,124]. The rate of fluoride sorption by *Spirogyra* algae is found to decrease with pH increase from 2.0 to10.5. At acidic pH, due to protonation of amino, carboxylic or thiol functional groups, algae' surface becomes positively charged, what favors fluoride sorption, the capacity of which at pH = 7.0 reaches 1.272 mg/g. Algae biomass, modified with Ca^{2+} solution (50 mg Ca^{2+}/L), has adsorbed 2.8 mg/g of dry mass in case of *A. fertilissima* and 4.4 mg/g in case of *C. humicola* [124]. The research on defluoridation of water solutions using fungi waste biomass (*Pleurotus ostreatus* 1804) generated during laccase fermentation has also been run [125]. The maximum sorption capacity has reached 1.272 mg F^-/g and its significant decrease has been noted with pH increase from 2.0 to 10.0.

Shell of a Gastropod (GS) was calcined at different temperatures and the defluoridation efficiencies of the raw and calcined GS were evaluated [126]. The highest defluoridation efficiency was obtained with the GS calcined at 1,000°C (i.e., TGS1000). The determination of the effects of hydrochemistry on the defluoridation showed that variations in pH, organic load and ionic strength had no visible influence on the adsorbent efficiency. On the other hand, the residual F^- in the defluoridated water increased with initial F^- concentration. Experimental evidences revealed that the mechanisms of the defluoridation process were diverse, that is, ionic bond formation, electrostatic attraction, ion-exchange and occlusion into $Ca(OH)_2$ framework.

3.3.8. Agricultural and industrial wastes as water defluoridation sorbents

Waste materials from agriculture or industry, due to their economic and environmentally friendly properties such as unique chemical composition, accessibility, renewability and low price are an actual option for water and wastewater remediation.

Parmar et al. [127] have investigated sorption using powdered adsorbents, raw and modified with aluminum chloride (Al-ccp) or calcium chloride (Ca-ccp), produced from corn cobs. Non-modified powder has not been useful considering adsorption effect, while modified sorbents have revealed satisfactory adsorption capacity equal to 18.9 and 15.12 mg/g for Ca-ccp and Al-ccp, respectively, at initial fluoride concentration 12.60 mg/L. The efficient pH range for fluorides adsorption has varied between 5.0 and 6.5. Mohan et al. [128] have developed cheap adsorbents using various agricultural wastes such as coconut shells, coconut shell's fibers, rice hulls and palm grains and they have applied them to remove various contaminants, including fluoride, from industrial wastewater. The best efficiency has been observed for coconut shell's fibers char, next for coconut shells char and for rice hulls' char at temperature 40°C. The adsorption usability of zircon impregnated char derived of cashew nut shell to fluoride removal from water has also been investigated and compared with the efficiency of non-modified char (CNSC) [129]. ZICNSC has revealed 80.33% removal rate of fluoride, while for CNSC it has been 72.67%. Both adsorption processes have been run for 180 min at pH = 3. Paddy husk ash, commonly available biowaste rich in silica coated with aluminum hydroxyl, becomes a good adsorbent for the removal of fluoride from water [130]. This is due to the high affinity of Al^{3+} ions towards F^-. It was observed that the fluoride ion was immobilized in the cement matrix in a form that was difficult to leach out.

Salomón-Negrete [131] reports the synthesis of novel adsorbents for fluoride removal from water using avocado kernel seeds and pyrolysis with and without physical activation. Results showed that the adsorbent obtained via pyrolysis had the highest adsorption properties, while its counterpart obtained with CO_2 activation decreased its defluoridation performance where the carbonization temperature was the main synthesis variable. Physicochemical characterization suggested that fluoride adsorption with the avocado-based adsorbents could be governed by electrostatic interactions and a ligand exchange mechanism involving Si moieties. Avocado-based adsorbents showed better defluoridation properties than those reported for other activated carbons obtained from both inorganic and organic precursors.

Various industrial branches generate huge amounts of solid wastes. One of their most favorable use is the application as cheap sorbents to water and wastewater detoxification, including removal of fluoride. The possibility of removal of F^- from water and wastewater using fly ash (from power and heat and power plants) has been investigated by Chaturvedi et al. [17]. The satisfactory effect of fluorides removal has been reached at low initial concentration of F^-, high temperature and acidic pH. The maximum sorption capacity established for the investigated fly ash has varied from 20.0 to 20.3 mg/g. The removal of fluoride from water solutions using raw and activated with HCl red mud (a waste from aluminum production) has also been investigated [132]. The adsorption capacity of modified sorbent has been better than for the raw material. The maximum sorption efficiency has been reached at pH = 5.5 and the maximum sorption capacity of the modified mud has been established at 0.331 mmol/g.

A low-cost and highly efficient biosorbent was prepared by loading Al/Fe oxides onto tea waste and was tested for the ability to remove fluoride from drinking water [133]. It was found that the solution pH played an important role in the removal of fluoride. The biosorbent combinations Tea–Al or Tea–Al–Fe could reduce the fluoride concentration to below 1.5 mg/L in the drinking water, a level which meets the drinking water standard recommended by the World Health Organization (WHO).

The adsorption of fluoride using coal slurries (wastes from fertilizers production) has been studied by Gupta et al. [101]. The efficiency of fluoride adsorption has increased with pH increase up to 7.58, while with the further parameter increase it has decreased. The maximum sorption capacity (4.861 mg/g) has been noted for fluorides concentration 15 mg/L and adsorbent dose 1.0 g/L. The usability of coal mining wastes to fluoride removal has been investigated by Cinarli et al. [134]. The maximum sorption capacity has reached 15.67 mg/g. Moreover, the best efficiency of the process has been noted at acidic conditions, while the optimum pH for fluorides removal has been established at 3.5.

3.3.9. Summary

The removal of fluorides from water and wastewater can be performed with the use of many different types of adsorbents, which are either applied already at industrial scale or still tested in the laboratory or pilot scale. The adsorption on activated aluminum oxide is already a common technology of fluoride removal from water and wastewater, and it is also indicated as the one of the best available technique in this field [12]. However, the adsorbent price is relatively high, while its efficiency mostly depends on pH and co-ions presence. Recently, a lot of effort has been devoted to develop an effective method of aluminum oxide modification with the use of metals' oxides impregnation, which reveals significant defluoridation efficiency. Nevertheless, despite satisfactory effectiveness of those novel adsorbents, some of them have been too expensive to be used in industrial scale. The applicability of carbon-based sorbents is less efficient than aluminum compounds, hence a number of studies on modification of carbon-based materials towards defluoridation improvement are carried out. The special attention is dedicated to CNTs. Among many natural materials, which are usable to fluoride adsorption, many different types of clays and minerals have been tested. Biosorbents, especially modified chitosan, also offer promising results in fluoride removal process. Additionally, a group of waste materials (e.g., red mud, slag or sludge), which contain metal oxides, have also been examined to fluorides concentration decrease in contaminated aqueous streams, and those can be considered as alternative cheap sorbents. Synthetic LDHs, hydrocalcite-like compounds and nanosorbents have also gained a lot of attention as potential fluoride adsorbent, as they reveal high affinity toward the contaminant.

3.4. Membrane methods

In recent years, membrane processes have gained a lot of interest, due to their high capacity and reliability, in water and wastewater treatment, including fluoride removal. Membrane separation techniques applied to fluoride removal from aquatic environment are reverse osmosis (RO), nanofiltration, electrodialysis (ED) and Donnan dialysis (DD) [135–141], as well as integrated systems such as coagulation–ultrafiltration/microfiltration (MF) [142].

3.4.1. Reverse osmosis and nanofiltration

RO can be applied to fluorides removal in case of potable water production; however, one should consider removal of not only fluorides, but also partial demineralization of raw water, which is an unfavorable phenomenon [11]. Desalinating osmotic membranes are able to reject up to 99% of salts present in water, what, in practice, results in complete elimination of fluoride from the treated stream.

Diawara et al. [143] have applied low pressure driven RO to remove fluoride and salinity from brackish groundwater in one of Senegal village and they have obtained 97%–98.9% retention of fluoride. Gedam et al. [144] have received 95%–98% fluorides removal rate from groundwater of Chandrapur village in Moradgaon region using polyamide RO membrane. Schoeman [145] has applied RO to water defluoridation in selected regions of South Africa and he has found that fluoride can be rejected from water of initial concentration 10–17 mg F^-/L to ca. 0.2 mg/L in permeate. Briao et al. [146] have used RO to desalination of Guarani region groundwater in order to produce potable water in Southern Brazil. 100% retention of fluorides, 97% removal of total dissolved solids and 94% decrease of sulfates have been obtained using RO at 2.0 MPa pressure and linear velocity over the membrane surface equal to 1.61 m/s. 93% recovery of potable water have been reached by mixing of permeate with raw water.

Sehn [136] has operated large-scale RO installation in southern Finland to treat water for 3 years. The installation of capacity 6,000 m^3/d (Kuivalia) has been used since 2003 and it produces water of fluorides content below 0.03 mg/L (initial concentration 1.3–1.8 mg/L) [136]. The process involves the use of FilmTec XLE-440 membranes (99% rejection of NaCl), which are operated at constant pressure of ca. 0.8 MPa and temperature 8°C, what significantly improves the energy consumption and operational costs (0.09 €/m^3). The process is carried out with 80% water recovery rate with no need of scaling inhibitors addition, despite often exceeding of calcium fluoride solubility. It is assumed that NOM present in water acts as scaling inhibitor. The only parameter of the produced water, which does not correspond to standards, is the alkalinity [136].

Nanofiltration membranes characterize with poor retention of monovalent ions, but a significant rejection of bivalent and multivalent ions and organic substances of molecular weight 200–500 Da is obtained [147]. Hence, in this case, one may assume the removal of neutrally charged compounds of several nanometer in size, and the rejection of ions, mainly multivalent ones. The mechanism of retention of ionic substances by NF relies on interactions between uniformly charged membrane surface and ions (Donnan exclusion). A surface of an asymmetric nanofiltration (NF) membrane is usually negatively charged, what minimizes the adsorption of negatively charged substances present in natural water and increases the retention of dissolved salts [147]. NF is operated at lower pressure than RO and the obtained rate of water desalination is also lower. In treatment of fluoride-rich water, NF can partially remove fluorides, while their optimum content in permeate can be obtained with the use of proper operational conditions. NF is a suitable process for direct production of potable water from its resources containing excess amount of fluorides, as it does not require remineralization [11].

Despite the fact that NF is usually used to separate monovalent ions from bivalent ones, the separation of ions of the same valence is also possible due to the differences in their transport mechanisms. Model studies have shown that NF membranes selectively separate salts of different halogens: NaF, NaCl, NaI, LiF and LiCl [148]. The analysis of retention has shown that smaller ions (fluorides) are rejected in higher extent than others due to the difference in hydration energy of particular ions, whereas the higher the hydration energy is, the higher rejection of an ion is obtained (Table 3) [148]. Hence, the selective desalination of fluorides containing brackish water is possible and the direct production of potable water at costs lower than in case of RO is enabled.

Diawara et al. [137,148] have run a research on removal of fluorides from solutions containing various salts (NaF, NaCl, $NaNO_3$ and Na_2SO_4) by means of three commercially available polyamide nanofiltration membranes: NF-70 (Filmtec), Desal-5-DL (Osmonics) and MT-08 (PCI), at 0.8 MPa pressure and temperature 293 K. In order to identify the selectivity mechanism, various combinations of salts have been applied to simulate real composition of natural brackish water. Retention coefficients observed for membranes applied to treat solutions containing NaF have been higher (83%–91%) than for chlorides (62%–92%). The high retention of sulfates, fluorides and chlorides results of double negative charge of those ions (Donnan effect), higher hydration energy and ion radius [137]. The presence of chlorides has slightly influenced on F^- retention obtained for particular membranes, whereas the increase of SO_4^{2-} concentration from 50 to 200 mg/L has affected the retention coefficient of F^- in case of NF 70 and Desal membranes (83%–95%) [137]. It has resulted in the increase of solution ionic strength, which decreases F^- ion hydration, hence, consequently, it affects its retention [137]. Thus, the retention of fluorides in nanofiltration depends on composition of treated solution (mainly its ionic composition). The ionic strength of a solution also plays a significant role in membrane selectivity due to a surface charge of a membrane material and intensity of interactions between a membrane surface and a dissolved substance.

Tahaikt et al. [135] have compared the efficiency of fluorides removal from water using three commercial polyamide membranes: NF90 (Filmtec), NF270 (Filmtec) and TR60 (Toray) of molecular weight cut off 90, 270 and 400 Da, respectively (Table 4). Solutions of NaF of concentration equal to 3.32, 6.32 and 22.32 mg/L have been treated at 1.0 MPa. Membranes NF270 and TR60 have characterized with similar separation properties and those can be directly applied to remove fluorides from solutions of lower contaminant concentration, while NF90 membrane, which is similar to an osmotic membrane, can be used as a single stage barrier for separation of fluorides from solutions of higher concentration of the anion.

Choi et al. [149] have investigated the impact of accompanying ions on the removal of fluorides using two commercial NF membranes (NTR-7250 and NTR-7450 – Nitto Denko, Japan), which differ in surface potential (–5 and –10 mV, respectively) measured at pH = 7. Retention coefficients of nitrates and fluorides have in general been comparable (70.4%–85.7%), whereas sulfates have been rejected in much higher extent (98.5%–99.6%). NTR-7450 membrane, that is, one of the higher surface potential, has characterized with higher retention coefficient in case of all investigated ions. The experimental results have shown that fluorides have interacted with membranes' surface charge in lower extent than nitrates or sulfates.

Table 3
Radius and hydration energy of selected ions

Ion	Radius (nm)	Hydration energy (kJ/mol)
F^-	0.136	515
Cl^-	0.180	381
NO_3^-	0.189	329
SO_4^{2-}	0.240	561

Table 4
Fluorides concentration in feedwater and NF permeates after treatment with the use of different membrane types (mg/L)

Feedwater	2.32	3.32	6.32	22.32
NF270 permeate	0.4	0.53	0.75	3.87
TR60 permeate	0.6	0.7	0.9	4
NF90 permeate	0.05	0.05	0.09	0.2

Hu and Dickson [150] have investigated both, permeate flux and retention of sodium fluoride (NaF) for three commercial NF membranes (SR-1 by Koch and DS-5-DLandi DS-51-HL by Osmonics). In case of all tested membranes, permeate fluxes have increased with the pressure increase, whereas NaF retention has increased with capacity increase and feedwater fluorides concentration decrease. The tested membranes have revealed different retentions due to differences in both, pore size and surface electrostatic potential.

Malaisamy et al. [151] have modified commercially available NF membrane by introduction of thin layer of a polyelectrolyte in order to improve the membrane selectivity towards monovalent ions, especially F^- and Cl^-. Polystyrene sulfonate (PSS) has been applied as an anionic polyelectrolyte, whereas ammonium polydiallyldimethylchloride (PDADMAC) as a cationic one. Thin (0.5–8.5 μm) layers of double PDADMAC/PSS have been embedded on membrane surface. It has enabled to increase F^- retention from 40% (non-modified membrane) to 70% (modified membrane).

The combination of adsorption process and NF treatment was studied for the removal of fluoride [152]. Results of this study demonstrated that the nature diatomite was viable and effective to be used as the pretreatment adsorbent for NF system to defluoridation of water with high fluoride concentration.

Dolar et al. [7] have compared the possibility of fluorides removal using RO/NF membranes and they have found >96% retention for RO membranes, >90% for compact NF membranes and >50% rejection for open NF membranes. On the other hand, Lhassani et al. [153] and Pontie et al. [154] have stated that NF membranes are more beneficial than

RO membranes due to the fact that NF removes fluoride in a selective way in reference to other halogen ions. While comparing properties of NF and RO membranes, Pontie et al. [155] have stated that NF enables a partial salinity decrease and removes fluoride efficiently enough to fulfill standards established by WHO in case of fluorides concentration in feedwater up to 15 mg/L at lower energy demand than in case of RO. Richards et al. [156] have used four commercial NF/RO membranes to treat Australian groundwater. The performed research has indicated on the impact of Sun radiation on F, Mg, NO_3, K and Na retention. Ca. 85% of total dissolved solids has been removed at optimum Sun radiation level.

Bejaoui et al. [157] have applied nanofiltration (NF-90) and RO to decrease both, F^- concentration and total salinity in industrial wastewater generated in production of metallic packages. The retention of fluorides obtained for both membranes has been above 90%.

Shen and Schäfer [158] performed study onto feasibility of NF and RO in treating challenging natural tropical waters within northern Tanzania containing high fluoride and NOM. Bench-scale experiments with 22 representative waters (selected based on fluoride concentration, salinity, origin and in some instances organic matter) and six NF/RO membranes revealed that ionic strength and recovery affected fluoride retention and permeate flux. Different membranes had distinct fluoride removal capacities, showing different raw water concentration treatability limits regarding the WHO guideline compliance. BW30, BW30-LE and NF90 membranes had a feed concentration limit of 30–40 mg/L at 50% recovery. NOM retention was independent of water matrices but is governed predominantly by size exclusion. NOM was observed to have a positive impact on fluoride removal.

A pilot-scale autonomous membrane system powered directly by solar energy was used to treat the water with the high fluoride concentration and examine the impact of fluctuating energy on three different membranes (BW30, NF90 and NF270) [159]. The results demonstrated that the BW30 and NF90 membranes achieved the WHO guideline. Real water pH and ionic strength vary greatly, which influences the performance of membrane processes such as NF and RO. Systematic variation of pH (3–12) and ionic strength (2–10 g/L as total dissolved solids) was undertaken with a real Tanzanian water to investigate how water quality affects retention mechanisms of fluoride (F) and NOM.

An autonomous solar powered NF/RO system driven by a solar array simulator was supplied with constant power from a generator [160]. An open NF (NF270) and a brackish water RO (BW30) membrane were used. A surface water with a very high F (59.7 mg/L) and NOM (110 mg C/L) was used. Retention of F by NF270 was <20% at pH <6, increased to 40% at pH 6, and 60%–70% at pH 7–12, indicating a dominance of charge repulsion while being ineffective in meeting the guideline of 1.5 mg/L. Increase in ionic strength led to a significant decline in retention of F (from 70% to 50%) and electrical conductivity (from 60% to 10%) by NF270, presumably due to charge screening. In contrast, BW30 retained about 50% of F at pH 3, >80% at pH 4, and about 99% at pH > 5, due to the smaller pore size and hence a more dominant size exclusion. In consequence, only little impact of ionic strength increase was observed for BW30. The concentration of NOM in permeates of both NF270 and BW30 was typically <2 mg/L. This was not affected by pH or ionic strength due to the fact that the bulk of NOM was rejected by both membranes through size exclusion.

3.4.2. Microfiltration/ultrafiltration

Direct removal of low molecular weight compounds by means of conventional ultrafiltration/MF is practically impossible due to relatively large pore size of those membranes. Hence, in order to assure efficient removal of contaminants from water and wastewater integrated/hybrid processes, especially in combination with coagulation/precipitation, complexation with polymers/surfactants, oxidation or biological processes are used.

Zhang et al. [142] have applied integrated process of coagulation– MF, that is, membrane coagulation reactor to remove fluoride. $Al_2(SO_4)_3$ has been used as coagulant, while to membrane separation capillary polyvinylidene fluoride MF membranes of pore size 0.22 μm and internal diameter 0.5 mm have been applied. The mechanism of fluoride bonding has relied on hydrolysis of $Al_2(SO_4)_3$ (Eq. (15)), co-precipitation of aluminum and fluoride (Eq. (16)) and adsorption of fluorides on precipitated $Al(OH)_3$ (Eq. (17)). The solubility rate of aluminum hydroxide is very low (1.9×10^{-33}), hence the formed aluminum-fluoride complex, similarly as $Al(OH)_3$, is hardly soluble, so it can be easily separated from water by means of MF membranes.

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3\downarrow \tag{15}$$

$$Al^{3+} + (3\text{-}x)OH^- + xF^- \rightarrow Al(OH)_{3-x}F_x\downarrow \tag{16}$$

$$Al(OH)_3 + xF^- \rightarrow Al(OH)_{3-x}F_x\downarrow + xOH^- \tag{17}$$

The impact of coagulant dose and feedwater pH on fluoride removal rate has also been examined [142]. At selected pH, the concentration of fluoride after coagulation has decreased with $Al_2(SO_4)_3$ dose increase. Above the dose of 120 mg/L, the concentration of F^- has started to increase, what has been accompanied with significant pH decrease. At optimum dose and pH, the reduction of F^- concentration from 4.0 mg/L in feedwater to 1.0 mg/L and below in purified water has been reached, while the remaining amount of aluminum has not exceed 0.05 mg/L [142].

The study on the use of integrated process of aluminum sulfate coagulation and membrane filtration (Al-CMF) to remove fluoride from potable water has also been discussed by Kowalchuk [161]. In the laboratory research, it has been found that removal of fluoride during Al-CMF process has been independent of pH within the range of 5.5–9.5 and at Al dose from 0 to 50 mg/L. The reaction of Al–F complex precipitation is very fast, hence the removal of F^- depends on stirring intensity, which favors the homogeneous distribution of Al^{3+} ions in solution before precipitation. It has been shown that per every 10 mg/L of aluminum dose ca. 1 mg F^-/L is removed. Al-CMF process has next been tested in pilot-scale installation of capacity 1.2 L/min for several weeks. UF membranes by Koch have been used. The rate of fluoride removal has been established as a function of water recovery rate and aluminum dose. The dependence of fluoride removal on water recovery has not been observed, and the rejection rate has varied from 50% to above 98%. The pilot research has also shown that per every 10 mg/L of aluminum dose 0.8 mg F^-/L is removed, what is slightly less efficient than that in case of laboratory-scale observations.

It has been stated that *Moringa oleifera*, a well-known natural coagulant widely applied worldwide, can substitute aluminum sulfate. The removal of fluoride by means of coagulation method using *M. oleifera* seeds, followed by UF, has been investigated by dos Santos Bazanella et al. [162]. The feedwater of initial fluorides concentration 10 mg/L has been coagulated using aqueous extract of *M. oleifera* seeds as coagulant. After the process, ultrafiltration with the use of ceramic membranes by Tami (cut off 4 and 5 kDa) at various pressures (0.1, 0.2, 0.3 and 0.4 MPa) has been run. The coagulation process with the dose of 2.5 g/L of *M. oleifera* extract has resulted in 90.9% decrease of fluorides content in purified water, what has enabled the use of the purified stream as a potable water.

Lu and Liu [163] have investigated the effectiveness of integrated process of precipitation-MF to remove fluorides and phosphates from wastewater generated during production of thin film transistor liquid crystal displays. $CaCl_2$ has been used as precipitating agent due to higher solubility and formation of lower amount of sludge than in case of calcium hydroxide. In order to separate solids from aqueous phase the suspension has been undergone to MF operated in a cross-flow mode. The impact of chemical precipitation conditions, membrane type, MF pressure and linear velocity on both, process capacity and permeate quality, has been investigated. The results have shown that the excess of $CaCl_2$ may lead to efficient removal of fluoride (and phosphates) at pH 8.5 and 10.5. Hydroxyapatite ($Ca_5(PO_4)_3OH$), amorphous calcium phosphate (AKP), fluoroapatite ($Ca_5(PO_4)_3F$) and calcium fluoride (CaF_2) have been main precipitated salts. Precipitation conditions have influenced on MF process performance, that is, the more severe fouling has been found at pH 8.5 than at pH = 10.5. The analyses of permeate have shown the improved removal of fluoride (and phosphates) by integrated process accompanied with efficient turbidity decrease.

Micellar enhanced ultrafiltration (MEUF) with the use of complexation with surface active compounds leading to micelles formation is proposed to remove fluoride from water and wastewater. The diameter of micelles is usually larger than a membrane pore size and UF enables the rejection of micelles, which remain in retentate, whereas permeate contains non-solubilized particles of separated compounds and some amount of surfactant's monomers [164]. Klimonda et al. [165] and Grzegorzek and Majewska-Nowak [166] have investigated the possible use of MEUF to remove F^- ions water solutions. The experiments involving the use of cellulose (5 kDa) and polyethersulfone (4 kDa) membranes have been run. Solutions containing 10 and 100 mg F^-/L as well as cationic surfactants such as octadecyloamine octane and hexadecylopyridene chloride have been used. The concentration of surfactants has been varied from 320 to 960 mg/L, while UF process has been carried out at transmembrane pressure of 0.2 MPa. It has been determined that the increase of a surfactant concentration improves separation process, while it affects the permeate flux. The efficiency of the processes has depended on membrane and surfactant types. The permissible concentration of fluoride in the final product (below 1.5 mg F^-/L) has been reached for solution of initial contaminant concentration 10 mg F^-/L, polyethersulfone membrane use and hexadodecylo pyridene chloride doses 644 and 966 mg/L.

Akanyeti and Ferrari [167] have proposed hybrid system of sorption–ultrafiltration to remove fluoride from water. Laterite and bone char have been chosen as sorption agents due to their low price and availability in developing countries. The removal rate and membrane permeability at various initial F^- concentration, solution pH and sorbent dose have been investigated. For fluoride concentration 1.5 mg/L the sorption capacity of bone char (1.1 mg/g) has been higher than for laterite (0.4 mg/g), what has been explained by higher specific surface area of the former sorbent. In case of laterite–UF system, it has been observed that the increase of F^- concentration results in permeability decrease, whereas the parameter has no impact on bone char–UF system performance. The optimum solution pH has been established at 5–6 for laterite–UF system, and at pH = 7 for bone char–UF system, and for those values the highest sorption capacity as well as fouling prevention have been obtained.

A new adsorption membrane for rapid removal of fluoride from drinking water was prepared. Both zirconium metal-organic frameworks (Zr-MOFs) adsorbent and membrane with large specific surface area of 740.28 m^2/g were used for fluoride removal [168]. The maximum of adsorption capacity was 102.40 mg/g at pH 7.0 when the initial fluoride concentration was 200 mg/L. The FTIR and XPS analyses of Zr-MOFs revealed that both surface hydroxyl groups and Zr(IV) active sites played important roles in fluoride adsorption process. For membrane experiments, Zr-MOFs membrane supported on alumina substrate could remove fluoride efficiently through dynamic filtration. The fluoride removal capability of Zr-MOFs membrane depended on flow rate and initial concentration of fluoride.

3.4.3. Electrodialysis

ED relies on selective transport of ions through alternately arranged anion- and cation-exchange membranes operated in a constant electrical field. At such conditions, anions present in the solution freely permeate through positively charged anion-exchange membrane towards anode, while they become rejected in the neighbor hooding chamber by negatively charged cation-exchange membrane. On the other hand, cations flow towards cathode through cation-exchange membrane and are rejected by neighboring anion-exchange membrane. Hence, in every second chamber of an electrodialyser there is a solution deprived of ions, while in the remaining chambers ions concentration increases [169]. Such ED features adjust its application to treatment of water containing elevated amounts of fluoride, as the process is technically simple and eliminates problems appearing during chemical treatment (precipitates formation) [140]. Moreover, ED characterizes with low sensitivity to seasonal change in fluoride concentration, high selectivity and low external chemicals demand. Additionally, the removal of fluorides can be even higher than in case of RO. The rate of removal of fluorides and other dissolved substance increases with the increase of voltage, temperature and flow rate [140].

In order to minimize the possibility of bivalent anions salts precipitation (sulfates, bicarbonates) in concentrating chamber (scaling) it is proposed to run ED process in a two-stage mode [140,170], in which the first stage is dedicated to bivalent ions elimination by means of chemical methods or with the use of ED membranes selective to monovalent anions. The latter method is the preferable one due to its simplicity and addition of no chemicals. Kabay et al. [171] have investigated the efficiency of fluorides removal from aqueous solution by means of ED, during which they have changed the operational parameters such as voltage, flow rate, fluoride concentration and the presence of chlorides and sulfates. They have found that the separation effectiveness increase with the initial fluoride concentration increase and with the voltage elevation. On the other hand, feed flow rate has not affected the capacity of the process.

The research run by Amor et al. [140,170], focused on ED of brackish water containing fluorides, has shown that the process is effective, and fluorides content can be decreased from 3 to 0.63 mg/L in the option with pretreatment at ion-exchange membrane and to 0.81 mg/L in the second arrangement. Sahli et al. [172] have proposed the use of chitosan and ED to remove Cl^- and F^- from brackish groundwater in one of Moroccan cities, of initial fluorides concentration 3 mg/L. The combination of adsorption and ED seems to be economically attractive and better method of fluorides removal from brackish groundwater.

Zeni et al. [173] have tested two ion-exchange membranes, that is, selenic anion-exchange (AMP®) and photopolymeric (MZA-Asahi Glass Co.) membranes in ED process dedicated to removal of fluoride from artesian wells. AMP membrane, operated at current density 0.1 A/dm^2, has removed 69% of fluorides, while at 0.7 A/dm^2 has 97%. MZATM membrane has rejected only 40% of the contaminant at the same current density.

The research on the removal of fluorides by means of pilot-scale ED from groundwater has been run in Morocco [174], where the concentration of F^- ion depends on the season. The efficiency of two commercial membranes Neosepta ACS and AXE 01 (Tokuyama Co.) operated at optimum conditions has been compared. The best results have been obtained for ACS membrane due to the highest removal of F^- and relatively low rejection of SO_4^{2-}. At the applied conditions, the produced water has contained suitable amount of dissolved substances (1,127 mg/L in the influent and 656 mg/L in the effluent), nitrates and fluorides (1.8 mg/L in the influent and 0.5 mg/L in the effluent). 95% removal of fluorides has been obtained.

In Lahnid et al. [175], the costs of fluorides removal by means of ED on the basis of industrial exploitation data have been estimated. The investment costs have been established at 833.2 thousands of € for industrial scale installation of capacity 2,200 m^3/d of water, while operational costs at such conditions have been calculated at 0.154 €/m^3. Both types of costs, that is, investments and operational ones, in case of ED, strongly depend on quality of feed and purified water, total membrane surface area and membrane's price, installation capacity, investment localization and other factors.

The study on the use of ED to remove fluorides from water solutions has also been run by Majewska-Nowak et al. [176] and Grzegorzek and Majewska-Nowak [177]. The efficiency of F^- removal at the presence of organic substances has been evaluated. Solutions containing fluorides (5, 10, 100 and 200 mg F^-/L), mineral salt (0.5 g/L of NaCl) and organic substances (5, 10 and 15 mg/L of humic acids) have been treated. The removal rate of fluoride have varied from 78% to 80% for initial concentration 5 mg F^-/L and it has increased to 86%–89% for initial fluoride concentration 10 mg/L, what has been sufficient to fulfill potable water standards. In case of high fluoride concentrations, that is, 100 and 200 mg/L, the obtained retention has ranged within 80%–91% and 86%–92.5%, respectively. The impact of organic substances presence on the process performance and efficiency has depended on fluorides concentration in feed solution. The lowest energy consumption has been equal to 0.195 kWh/m^3 for feed of 5 mg F^-/L and at the presence of 5 and 15 mg/L of humic acids, whereas the highest has been noted for solution containing 200 mg F^-/L and 15 mg HA/L.

3.4.4. Donnan dialysis

DD is potentially attractive membrane separation process, which can be used to concentration of valuable substances in ionic form or to their removal from diluted solutions [11,138,139]. DD is operated with an anion-exchange membrane, the driving force for which is the concentration gradient. Hence, it can be considered as an effective and a simple method for the removal of fluorides from water [138,139,178,179]. Even though DD is slower than ED, it reveals some advantageous features such as lower costs and low energy demand as well as simple technological requirements.

DD relies on the exchange of ions of the same charge between two solutions separated by an ion-exchange membrane. In case of fluorides, an anion-exchange membrane separates two solutions which differ in composition and concentration, that is, feed solution (raw water) and receiving solution (NaCl or Na_2SO_4 solution of a salt concentration from 0.1 to 1.0 mol/L), while the concentration of F^- in feedwater is much lower – usually from 0.001 to 0.1 mol/L [138,139]. Due to the high concentration gradient, anions present in receiving solution diffuse to feed solution in order to balance the concentration. On the other hand, in order to keep the electroneutrality of both solutions, the equivalent flow of ions of the same charge is forced in the opposite direction – from feed to receiving stream. The exchange of ions runs until so-called Donnan equilibrium is established.

The removal of fluorides from a diluted solution using anion-exchange membrane Neosepta AHA in DD process has been investigated [178]. The impact of concentration, pH and accompanying anions in feedwater as well as composition of receiving solution has been determined. The results obtained for AHA membrane have been compared with Neosepta AFN and polysulfone membrane SB-6407. The efficiency of transmembrane transport has been arranged in a following series AFN > AHA > SB-6407.

In laboratory research on DD process, Boubakri et al. [179] have stated that the increase of fluorides concentration in feedwater and decrease of temperature have resulted in decrease of the removal efficiency. Fluorides separation rate obtained with the use of membrane AM3 (Tokyuma Soda), at their initial concentration 5–15 mg/L has varied from 34.14%

to 75.52%. In case of solution of the lowest fluorides concentration (5 mg F^-/L) and process temperature above 35°C, the concentration of contaminant in the final product has not exceeded 1.5 mg/L.

Recently, the removal of fluorides from water solution using plasma modified AFX anion-exchange membrane in DD [180,181] has been investigated as a function of concentration, pH and membrane structure. Both, the flux and the recovery obtained for plasma modified AFX membranes have been higher than for non-modified ones, what has been explained by the change in both, wettability and morphology of the former membranes.

In Garmes et al. [138], the effect of defluoridation by means of combined system of DD and adsorption has been presented. It has been found that the use of monoanion-selective membrane (Neosepta ACS) enables to decrease fluorides concentration below permissible level and it limits the leakage of electrolyte from receiver to purified water stream. The usability of aluminum oxide and zirconium dioxide as adsorbents present in receiving solution has also been confirmed. In such arrangement, the backward diffusions of fluorides is prevented, and the purified water contains lower amount of fluorides.

3.5. Final remarks

The most important benefits offered by membrane processes are very high removal efficiency (up to 98%), single stage treatment, simultaneous water disinfection and low requirement for additional chemicals. However, the removal of other anions present in treated water is a serious disadvantage of those techniques, as it results in the need of water remineralization to assure the proper quality of finally produced potable water. Additionally, membrane processes are quite expensive due to relatively high initial prices of membranes and their exploitation. Moreover, the utilization of retentate, that is, concentrated solution containing fluoride may become a significant problem.

References

[1] WHO/UNICEF, Progress on Drinking-Water and Sanitation – 2014 Update, World Health Organization, Vol. 1, 2014, p. 1.

[2] S. Ayoob, A.K. Gupta, V.T. Bhat, A conceptual overview on sustainable technologies for the defluoridation of drinking water, Crit. Rev. Environ. Sci. Technol., 38 (2008) 401–470.

[3] S.V. Jadhav, E. Bringas, G.D. Yadav, V.K. Rathod, I. Ortiz, K.V. Marathe, Arsenic and fluoride contaminated groundwaters: a review of current technologies for contaminants removal, J. Environ. Manage., 162 (2015) 306–325.

[4] J. Shen, A. Schafer, Removal of fluoride and uranium by nanofiltration and reverse osmosis: a review, Chemosphere, 117 (2014) 679–691.

[5] W. Kwasnik, Fluorine Compounds, G. Brauer, Ed., Handbook of Preparative Inorganic Chemistry, Vol. 1, Academic Press, New York, USA, 1963.

[6] P.I. Ndiaye, P. Moulin, L. Dominguez, J.C. Millet, F. Charbit, Removal of fluoride from electronic industrial effluent by RO membrane separation, Desalination, 173 (2005) 25–32.

[7] D. Dolar, K. Košutic, B. Vucic, RO/NF treatment of wastewater from fertilizer factory—removal of fluoride and phosphate, Desalination, 265 (2011) 237–241.

[8] F. Shen, X. Chen, P. Gao, G. Chen, Electrochemical removal of fluoride ions from industrial wastewater, Chem. Eng. Sci., 58 (2003) 987–993.

[9] J. Fawell, K. Bailey, J. Chilton, E. Dahi, L. Fewtrell, Y. Magara, Fluoride in Drinking Water, London World Health Organization, 2006.

[10] W.M. Edmunds, P. Smedley, Essentials of Medical Geology: Impacts of the Natural Environment on Public Health, O. Selinus, B. Alloway, J.A. Centeno, Eds., Fluoride in Natural Waters, Academic Press, USA, 2005.

[11] A.B. Kołtuniewicz, E. Drioli, Membranes in Clean Technologies, Wiley-VCH Verlag GmbH, Weinheim, 2008.

[12] D. Ozsvath, Fluoride and environmental health: a review, Rev. Environ. Sci. Biotechnol., 8 (2009) 59–79.

[13] A. Bhatnagar, E. Kumara, M. Sillanpaa, Fluoride removal from water by adsorption—a review, Chem. Eng. J., 171 (2011) 811–840.

[14] Regulation of the Ministry of Health of 13 November 2015 on the Quality of Water for Human Consumption (Dz.U. item 1989), 2015 (in Polish).

[15] WHO, Guidelines for Drinking-Water Quality, 3rd ed., World Health Organisation, Geneva, 2004.

[16] R.C. Meenakshi, R. Maheshwari, Fluoride in drinking water and its removal, J. Hazard. Mater., 137 (2006) 456–463.

[17] A.K. Chaturvedi, K.P. Yadava, K.C. Pathak, V.N. Singh, Defluoridation of water by adsorption on fly ash, Water Air Soil Pollut., 49 (1990) 51–61.

[18] E.J. Readon, Y. Wong, A limestone reactor for fluoride removal from wastewaters, Environ. Sci. Technol., 34 (2000) 3247–3253.

[19] C. Castel, M. Schweizer, M.O. Simonnot, M. Sardin, Selective removal of fluoride ions by a two-way ion-exchange cyclic process, Chem. Eng. Sci., 55 (2000) 3341–3352.

[20] A.L. Kowal, M. Świderska-Bróż, Water Treatment, Polish Scientific Publishers PWN, Warszawa-Wrocław, 1996 (in Polish).

[21] R. Liu, L. Zhu, W. Gonga, H. Lan, H. Liu, J. Qu, Effects of fluoride on coagulation performance of aluminum chloride towards Kaolin suspension, Colloids Surf., A, 421 (2013) 84–90.

[22] D.F. Lawler, L.E. Katz, K.A. Alfredo, M.L. Stehouwer, Fluoride Removal in Small Water Systems: A Coagulation Approach, US EPA Archive Document, 2007.

[23] S.S. Waghmare, T. Arfin, Fluoride removal from water by various techniques: review, Int. J. Innovative Sci. Eng. Technol., 2 (2015) 560–571.

[24] S. Pulkka, M. Martikainen, A. Bhatnagar, M. Sillanpää, Electrochemical methods for the removal of anionic contaminants from water – a review, Sep. Purif. Technol., 132 (2014) 252–271.

[25] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC) – science and applications, J. Hazard. Mater., 84 (2001) 29–41.

[26] C.Y. Hu, S.L. Lo, W.H. Kuan, Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes, Water Res., 37 (2003) 4513–4523.

[27] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol., 38 (2004) 11–41.

[28] M.M. Emamjomeh, M. Sivakumar, Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes, J. Environ. Manage., 90 (2009) 1663–1679.

[29] V. Khatibikamal, A. Torabian, F. Janpoor, G. Hoshyaripour, Fluoride removal from industrial wastewater using electrocoagulation and its adsorption kinetics, J. Hazard. Mater., 179 (2010) 276–280.

[30] M.M. Emamjomeh, M. Sivakumar, A.S. Varyani, Analysis and the understanding of fluoride removal mechanisms by an electrocoagulation/flotation (ECF) process, Desalination, 275 (2011) 102–106.

[31] M. Behbahani, M.R. Alavi Moghaddam, M. Arami, Techno-economical evaluation of fluoride removal by electrocoagulation process: optimization through response surface methodology, Desalination, 271 (2011) 209–218.

[32] N. Drouiche, S. Aoudj, H. Lounici, M. Drouiche, T. Ouslimane, N. Ghaffour, Fluoride removal from pretreated photovoltaic wastewater by electrocoagulation: an investigation of the effect of operational parameters, Procedia Eng., 33 (2012) 385–391.

[33] J. Zhu, H. Zhao, J. Ni, Fluoride distribution in electrocoagulation defluoridation process, Sep. Purif. Technol., 56 (2007) 184–191.

[34] D. Ghosh, C.R. Medhi, M.K. Purkait, Treatment of fluoride containing drinking water by electrocoagulation using monopolar and bipolar electrode connections, Chemosphere, 73 (2008) 1393–1400.

[35] C.Y. Hu, S.L. Lo, W.H. Kuan, Y.D. Lee, Treatment of high fluoride-content wastewater by continuous electrocoagulation–flotation system with bipolar aluminum electrodes, Sep. Purif. Technol., 60 (2008) 1–5.

[36] M. Bennajah, M. Maalmi, Y. Darmane, M.E. Touhami, Defluoridation of drinking water by electrocoagulation/electroflotation – kinetic study, J. Urban Environ. Eng., 4 (2010) 37–45.

[37] H. Cui, Y. Qian, H. An, C. Sun, J. Zhai, Q. Li, Electrochemical removal of fluoride from water by PAOA-modified carbon felt electrodes in a continuous flow reactor, Water Res., 46 (2012) 3943–3950.

[38] M. Chikuma, M. Nishimura, Selective sorption of fluoride ion by anion exchange resin modified with alizarin fluorine bluepraseodymium(III) complex, React. Polym., 13 (1990) 131–138.

[39] B. Solangi, S. Memon, M.I. Bhanger, An excellent fluoride sorption behavior of modified amberlite resin, J. Hazard. Mater., 176 (2010) 186–192.

[40] Y. Ku, H.M. Chiou, H.W. Chen, Removal of fluoride from aqueous solution by aluminium-loaded Duolite C-467 resin, J. Chin. Inst. Eng., 34 (2011) 801–807.

[41] N. Viswanathan, S. Meenakshi, Role of metal ion incorporation in ion exchange resin on the selectivity of fluoride, J. Hazard. Mater., 162 (2009) 920–930.

[42] N.I. Chubar, V.F. Samanidou, V.S. Kouts, G.G. Gallios, V.A. Strelko, I.Z. Zhuravlev, Adsorption of fluoride, chloride, bromide, and bromate ions on a novel ion exchanger, J. Colloid Interface Sci., 291 (2005) 67–74.

[43] C.S. Sundaram, S. Meenakshi, Fluoride sorption using organic-inorganic hybrid type ion exchangers, J. Colloid Interface Sci., 333 (2009) 58–62.

[44] M. Mohapatra, S. Anand, B.K. Mishra, D.E. Giles, P. Singh, Review of fluoride removal from drinking water, J. Environ. Manage., 91 (2009) 67–77.

[45] L.H. Velazquez-Jimenez, E. Vences-Alvarez, J.L. Flores-Arciniega, H. Flores-Zuniga, J.R. Rangel-Mendez, Water defluoridation with special emphasis on adsorbents-containing metal oxides and/or hydroxides: a review, Sep. Purif. Technol., 150 (2015) 292–307.

[46] T. Ben Amor, I. Bejaoui, M. Gritli, M. Ben Amor, Fluoride removal from natural water by modified cationic resin, Res. J. Chem. Environ., 21 (2017) 1–5.

[47] J. Nawrocki, Ed., Water Treatment Physical, Chemical and Biological Processes, Polish Scientific Publishers PWN, Warszawa-Poznań, 2010 (in Polish).

[48] Y. Ku, H.M. Chiou, The adsorption of fluoride ion from aqueous solution by activated alumina, Water Air Soil Pollut., 133 (2002) 349–361.

[49] A.L. Valdivieso, J.L. Reyes Bahena, S. Song, R. Herrera Urbina, Temperature effect on the zeta potential and fluoride adsorption at the α-Al_2O_3/aqueous solution interface, J. Colloid Interface Sci., 298 (2006) 1–5.

[50] S. Ghorai, K.K. Pant, Investigations on the column performance of fluoride adsorption by activated alumina in a fixed-bed, Chem. Eng. J., 98 (2004) 165–173.

[51] S.A. Wasay, S. Tokunaga, S.W. Park, Removal of hazardous anions from aqueous solutions by La(III)- and Y(III)-impregnated alumina, Sep. Sci. Technol., 31 (1996) 1501–1514.

[52] S.S. Tripathy, J.L. Bersillon, K. Gopal, Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina, Sep. Purif. Technol., 50 (2006) 310–317.

[53] S.M. Maliyekkal, A.K. Sharma, L. Philip, Manganese-oxide-coated alumina: a promising sorbent for defluoridation of water, Water Res., 40 (2006) 3497–3506.

[54] S.X. Teng, S.G. Wang, W.X. Gong, X.W. Liu, B.Y. Gao, Removal of fluoride by hydrous manganese oxide-coated alumina: performance and mechanism, J. Hazard. Mater., 168 (2009) 1004–1011.

[55] A. Bansiwal, P. Pillewan, R.B. Biniwale, S.S. Rayalu, Copper oxide incorporated mesoporous alumina for defluoridation of drinking water, Microporous Mesoporous Mater., 129 (2010) 54–61.

[56] S.M. Maliyekkal, S. Shukla, L. Philip, I.M. Nambi, Enhanced fluoride removal from drinking water by magnesia-amended activated alumina granules, Chem. Eng. J., 140 (2008) 183–192.

[57] S. Jain, R.V. Jayaram, Removal of fluoride from contaminated drinking water using unmodified and aluminium hydroxide impregnated blue lime stone waste, Sep. Sci. Technol., 44 (2009) 1436–1451.

[58] H. Liu, S. Deng, Z. Li, G. Yu, J. Huang, Preparation of Al-Ce hybrid adsorbent and its application for defluoridation of drinking water, J. Hazard. Mater., 179 (2010) 424–430.

[59] M. Karthikeyan, K.P. Elango, Removal of fluoride from water using aluminium containing compounds, J. Environ. Sci., 21 (2009) 1513–1518.

[60] G. Patra, P. Das, S. Chakraborty, B.C. Meikap, Removal of fluoride from wastewater using HCl-treated activated alumina in a ribbed hydrocyclone separator, J. Environ. Sci. Health, Part A, 53 (2018). https://doi.org/10.1080/10934529.2018.1429728

[61] L. Lv, J. He, M. Wei, D.G. Evans, X. Duan, Factors influencing the removal of fluoride from aqueous solution by calcined Mg–Al–CO_3 layered double hydroxides, J. Hazard. Mater., 133 (2006) 119–128.

[62] S. Mandal, S. Mayadevi, Adsorption of fluoride ions by Zn–Al layered double hydroxides, Appl. Clay Sci., 40 (2008) 54–62.

[63] M.G. Sujana, G. Soma, N. Vasumathi, S. Anand, Studies on fluoride adsorption capacities of amorphous Fe/Al mixed hydroxides from aqueous solutions, J. Fluorine Chem., 130 (2009) 749–754.

[64] M.G. Sujana, S. Anand, Iron and aluminium based mixed hydroxides: a novel sorbent for fluoride removal from aqueous solutions, Appl. Surf. Sci., 256 (2010) 6956–6962.

[65] A. Eskandarpour, M.S. Onyango, A. Ochieng, S. Asai, Removal of fluoride ions from aqueous solution at low pH using schwertmannite, J. Hazard. Mater., 152 (2008) 571–579.

[66] M. Streat, K. Hellgardt, N.L.R. Newton, Hydrous ferric oxide as an adsorbent in water treatment: part 3: batch and mini-column adsorption of arsenic, phosphorus, fluorine and cadmium ions, Process Saf. Environ. Prot., 86 (2008) 21–30.

[67] E. Kumar, A. Bhatnagar, M. Ji, W. Jung, S.H. Lee, S.J. Kim, G. Lee, H. Song, J.Y. Choi, J.S. Yang, B.H. Jeon, Defluoridation from aqueous solutions by granular ferric hydroxide (GFH), Water Res., 43 (2009) 490–498.

[68] K. Biswas, K. Gupta, U.C. Ghosh, Adsorption of fluoride by hydrous iron(III)-tin(IV) bimetal mixed oxide from the aqueous solutions, Chem. Eng. J., 149 (2009) 196–206.

[69] K. Biswas, S. Debnath, U.C. Ghosh, Physicochemical aspects on fluoride adsorption for removal from water by synthetic hydrous iron(III)-chromium(III) mixed oxide, Sep. Sci. Technol., 45 (2010) 472–485.

[70] K. Biswas, K. Gupta, A. Goswami, U.C. Ghosh, Fluoride removal efficiency from aqueous solution by synthetic iron(III)-aluminum(III)-chromium(III) ternary mixed oxide, Desalination, 255 (2010) 44–51.

[71] X. Wu, Y. Zhang, X. Dou, M. Yang, Fluoride removal performance of a novel Fe-Al-Ce trimetal oxide adsorbent, Chemosphere, 69 (2007) 1758–1764.

[72] J. Zhou, W. Zhu, J. Yu, H. Zhang, Y. Zhang, X. Lin, X. Luo, Highly selective and efficient removal of fluoride from ground water by layered Al-Zr-La Tri-metal hydroxide, Appl. Surf. Sci., 435 (2018) 920–927.

[73] P. Chen, T. Wang, Y. Xiao, E. Tian, W. Wang, Y. Zhao, L. Tian, H. Jiang, X. Luo, Efficient fluoride removal from aqueous solution by synthetic Fe-Mg-La tri-metal nanocomposite and the analysis of its adsorption mechanism, J. Alloys Compd., 738 (2018) 118–129.

[74] A. Vinati, B. Mahanty, S.K. Behera, Clay and clay minerals for fluoride removal from water: a state-of-the-art review, Appl. Clay Sci. 114 (2015) 340–348.

[75] S. Hauge, R. Osterberg, K. Bjorvatn, K.A. Selvig, Defluoridation of drinking water with pottery: effect of firing temperature, Scand. J. Dent. Res., 102 (1994) 329–333.

[76] G. Moges, F. Zewge, M. Socher, Preliminary investigations on the defluoridation of water using fired clay chips, J. Afr. Earth Sci., 21 (1996) 479–482.
[77] N. Hamdi, E. Srasra, Removal of fluoride from acidic wastewater by clay mineral: effect of solid-liquid ratios, Desalination, 206 (2007) 238–244.
[78] X. Fan, D.J. Parker, M.D. Smith, Adsorption kinetics of fluoride on low cost materials, Water Res., 37 (2003) 4929–4937.
[79] B.D. Turner, P. Binning, S.L.S. Stipp, Fluoride removal by calcite: evidence for fluorite precipitation and surface adsorption, Environ. Sci. Technol., 39 (2005) 9561–9568.
[80] M. Islam, R.K. Patel, Evaluation of removal efficiency of fluoride from aqueous solution using quick lime, J. Hazard. Mater., 143 (2007) 303–310.
[81] Q. Cai, B.D. Turner, D. Sheng, S. Sloan, Application of kinetic models to the design of a calcite permeable reactive barrier (PRB) for fluoride remediation, Water Res., 130 (2018) 300–311.
[82] P.K. Gogoi, R. Baruah, Fluoride removal from water by adsorption on acid activated kaolinite clay, Indian J. Chem. Technol., 15 (2008) 500–503.
[83] Y.X. Ma, F.M. Shi, X.L. Zheng, J. Ma, J.M. Yuan, Preparation of granular Zr-loaded bentonite and its defluoridation properties from aqueous solutions, J. Harbin Inst. Technol., 12 (2005) 236–240.
[84] S.P. Kamble, P. Dixit, S.S. Rayalu, N.K. Labhsetwar, Defluoridation of drinking water using chemically modified bentonite clay, Desalination, 249 (2009) 687–693.
[85] G. Karthikeyan, A. Pius, G. Alagumuthu, Fluoride adsorption studies of montmorillonite clay, Indian J. Chem. Technol., 12 (2005) 263–272.
[86] A. Tor, Removal of fluoride from an aqueous solution by using montmorillonite, Desalination, 201 (2006) 267–276.
[87] M. Sarkar, A. Banerjee, P.P. Pramanick, A.R. Sarkar, Use of laterite for the removal of fluoride from contaminated drinking water, J. Colloid Interface Sci., 302 (2006) 432–441.
[88] A. Maiti, J.K. Basu, S. De, Chemical treated laterite as promising fluoride adsorbent for aqueous system and kinetic modeling, Desalination, 265 (2011) 28–36.
[89] A. Iriel, S.P. Bruneel, N. Schenone, A.F. Cirelli, The removal of fluoride from aqueous solution by a lateritic soil adsorption: kinetic and equilibrium studies, Ecotoxicol. Environ. Saf., 149 (2018) 166–172.
[90] N. Das, P. Pattanaik, R. Das, Defluoridation of drinking water using activated titanium rich bauxite, J. Colloid Interface Sci., 292 (2005) 1–10.
[91] D. Mohapatra, D. Mishra, S.P. Mishra, G.R. Chaudhury, R.P. Das, Use of oxide minerals to abate fluoride from water, J. Colloid Interface Sci., 275 (2004) 355–359.
[92] C.M. Vivek Vardhan, M. Srimurali, Removal of fluoride from water using a novel sorbent lanthanum-impregnated bauxite, SpringerPlus, 5 (2016) 1426–1444.
[93] A. Salifu, B. Petrusevski, E.S. Mwampashi, I.A. Pazi, K. Ghebremichaelf, R. Buamah, C. Aubry, G.L. Amy, M.D. Kenedy, Defluoridation of groundwater using aluminum-coated bauxite: optimization of synthesis process conditions and equilibrium study, Chem. Eng. J., 191 (2016) 108–117.
[94] M.S. Onyango, Y.O. Kojima, O. Aoyi, E.C. Bernardo, H. Matsuda, Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9, J. Colloid Interface Sci., 279 (2004) 341–350.
[95] M.S. Onyango, T.Y. Leswifi, A. Ochieng, D. Kuchar, F.O. Otieno, H. Matsuda, Breakthrough analysis for water defluoridation using surface-tailored zeolite in a fixed bed column, Ind. Eng. Chem. Res., 48 (2009) 931–937.
[96] S. Samatya, U. Yuksel, M. Yuksel, N. Kabay, Removal of fluoride from water by metal ions (Al^{3+}, La^{3+} and ZrO^{2+}) loaded natural zeolite, Sep. Sci. Technol., 42 (2007) 2033–2047.
[97] Q. Cai, B.D. Turner, D. Sheng, S. Sloan, The kinetics of fluoride sorption by zeolite: effects of cadmium, barium and manganese, J. Contam. Hydrol., 177–178 (2015) 136–147.
[98] A. Sivasamy, K.P. Singh, D. Mohan, M. Maruthamuthu, Studies on defluoridation of water by coal-based sorbents, J. Chem. Technol. Biotechnol., 76 (2001) 717–722.
[99] M.E. Kaseva, Optimization of regenerated bone char for fluoride removal in drinking water: a case study in Tanzania, J. Water Health, 4 (2006) 139–147.
[100] A.A.M. Daifullah, S.M. Yakout, S.A. Elreefy, Adsorption of fluoride in aqueous solutions using $KMnO_4$-modified activated carbon derived from steam pyrolysis of rice straw, J. Hazard. Mater., 147 (2007) 633–643.
[101] V.K. Gupta, I. Ali, V.K. Saini, Defluoridation of wastewaters using waste carbon slurry, Water Res., 41 (2007) 3307–3316.
[102] Y. Ma, S.G. Wang, M. Fan, W.X. Gong, B.Y. Gao, Characteristics and defluoridation performance of granular activated carbons coated with manganese oxides, J. Hazard. Mater., 168 (2009) 1140–1146.
[103] M. Karthikeyan, K.P. Elango, Removal of fluoride from aqueous solution using graphite: a kinetic and thermodynamic study, Indian J. Chem. Technol., 15 (2008) 525–532.
[104] E. Vences-Alvarez, L.H. Velazquez-Jimenez, L.F. Chazaro-Ruiz, P.E. Diaz-Flores, J.R. Rangel-Mendez, Fluoride removal in water by a hybrid adsorbent lanthanum–carbon, J. Colloid Interface Sci., 455 (2015) 194–202.
[105] Y.H. Li, S.G. Wang, X.F. Zhang, J.Q. Wei, C.L. Xu, Z.K. Luan, D.H. Wu, Adsorption of fluoride from water by aligned carbon nanotubes, Mater. Res. Bull., 38 (2003) 469–476.
[106] Y.H. Li, S. Wang, A. Cao, D. Zhao, X. Zhang, C. Xu, Z. Luan, D. Ruan, J. Liang, D. Wu, B. Wei, Adsorption of fluoride from water by amorphous alumina supported on carbon nanotubes, Chem. Phys. Lett., 350 (2001) 412–416.
[107] Y.H. Li, S. Wang, X. Zhang, J. Wei, C. Xu, Z. Luan, D. Wu, B. Wei, Removal of fluoride from water by carbon nanotube supported alumina, Environ. Technol., 24 (2003) 391–398.
[108] S.G. Wang, Y. Ma, Y.J. Shi, W.X. Gong, Defluoridation performance and mechanism of nano-scale aluminum oxide hydroxide in aqueous solution, J. Chem. Technol. Biotechnol., 84 (2009) 1043–1050.
[109] G. Patel, U. Pal, S. Menon, Removal of fluoride from aqueous solution by CaO nanoparticles, Sep. Sci. Technol., 44 (2009) 2806–2826.
[110] J. Shen, M.F. Evangelista, G. Mkongo, H. Wen, R. Langford, G. Rosair, M.R.S. McCoustra, V. Arrighi, Efficient defluoridation of water by Monetite nanorods, Adsorption, 24 (2018) 135–145.
[111] C.F. Chang, P.H. Lin, W. Holl, Aluminum-type superparamagnetic adsorbents: synthesis and application on fluoride removal, Colloids Surf., A, 280 (2006) 194–202.
[112] X. Zhao, J. Wang, F. Wu, T. Wang, Y. Cai, Y. Shi, G. Jiang, Removal of fluoride from aqueous media by Fe_3O_4@$Al(OH)_3$ magnetic nanoparticles, J. Hazard. Mater., 173 (2010) 102–109.
[113] S.M. Maliyekkal, K.R. Anshup, T.A. Pradeep, High yield combustion synthesis of nanomagnesia and its application for fluoride removal, Sci. Total Environ., 408 (2010) 2273–2282.
[114] D. Dayanandaa, V.R. Sarvab, S.V. Prasadc, J. Arunachalamb, P. Parameswarand, N.N. Ghosh, Synthesis of MgO nanoparticle loaded mesoporous Al_2O_3 and its defluoridation study, Appl. Surf. Sci., 329 (2015) 1–10.
[115] E. Kumar, A. Bhatnagar, U. Kumar, M. Sillanpaa, Defluoridation from aqueous solutions by nano-alumina: characterization and sorption studies, J. Hazard. Mater., 186 (2011) 1042–1049.
[116] J. Wang, S. Zhuang, Removal of various pollutants from water and wastewater by modified chitosan adsorbents, Crit. Rev. Environ. Sci. Technol., 47 (2017) 2331–2386.
[117] S.P. Kamble, S. Jagtap, N.K. Labhsetwar, D. Thakare, S. Godfrey, S. Devotta, S.S. Rayalu, Defluoridation of drinking water using chitin, chitosan and lanthanum-modified chitosan, Chem. Eng. J., 129 (2007) 173–180.
[118] R. Yao, F. Meng, L. Zhang, D. Ma, M. Wang, Defluoridation of water using neodymium-modified chitosan, J. Hazard. Mater., 165 (2009) 454–460.
[119] Y. Vijaya, A. Krishnaiah, Sorptive response profile of chitosan coated silica in the defluoridation of aqueous solution, e-J. Chem., 6 (2009) 713–724.
[120] N. Viswanathan, S. Meenakshi, Enhanced fluoride sorption using La(III) incorporated carboxylated chitosan beads, J. Colloid Interface Sci., 322 (2008) 375–383.

[121] N. Viswanathan, S. Meenakshi, Selective sorption of fluoride using Fe(III) loaded carboxylated chitosan beads, J. Fluorine Chem., 129 (2008) 503–509.

[122] E. Christina, P. Viswanathan, Development of a novel nano-biosorbent for the removal of fluoride from water, Chin. J. Chem. Eng., 23 (2015) 924–933.

[123] S.V. Mohan, S.V. Ramanaiah, B. Rajkumar, P.N. Sarma, Removal of fluoride from aqueous phase by biosorption onto algal biosorbent *Spirogyra* sp.-IO$_2$: sorption mechanism elucidation, J. Hazard. Mater., 141 (2007) 465–474.

[124] M. Bhatnagar, A. Bhatnagar, S. Jha, Interactive biosorption by microalgal biomass as a tool for fluoride removal, Biotechnol. Lett., 24 (2002) 1079–1081.

[125] S.V. Ramanaiah, S.V. Mohan, P.N. Sarma, Adsorptive removal of fluoride from aqueous phase using waste fungus (*Pleurotus ostreatus* 1804) biosorbent: kinetics evaluation, Ecol. Eng., 31 (2007) 47–56.

[126] N.A. Oladoja, B. Helmreich, H.A. Bello, Towards the development of a reactive filter from green resource for groundwater defluoridation, Chem. Eng. J., 301 (2016) 166–177.

[127] H.S. Parmar, J.B. Patel, P. Sudhakar, V.J. Koshy, Removal of fluoride from water with powdered corn cobs, J. Environ. Sci. Eng., 48 (2006) 135–138.

[128] D. Mohan, K.P. Singh, V.K. Singh, Wastewater treatment using low cost activated carbons derived from agricultural byproducts—a case study, J. Hazard. Mater., 152 (2008) 1045–1053.

[129] G. Alagumuthu, M. Rajan, Equilibrium and kinetics of adsorption of fluoride onto zirconium impregnated cashew nut shell carbon, Chem. Eng. J., 158 (2010) 451–457.

[130] S. Sarmah, J. Saikia, D.K. Bordoloi, P.J. Kalita, J.J. Bora, R.L. Goswamee, Immobilization of fluoride in cement clinkers using hydroxyl-alumina modified paddy husk ash based adsorbent, J. Chem. Technol. Biotechnol., 93 (2018) 533–540.

[131] M.Á. Salomón-Negrete, H.E. Reynel-Ávila, D.I. Mendoza-Castillo, A. Bonilla-Petriciolet, C.J. Duran-Valle, Water defluoridation with avocado-based adsorbents: synthesis, physicochemical characterization and thermodynamic studies, J. Mol. Liq., 254 (2018) 188–197.

[132] Y. Cengeloglu, E. Kir, M. Ersoz, Removal of fluoride from aqueous solution by using red mud, Sep. Purif. Technol., 28 (2002) 81–86.

[133] H. Cai, G. Chen, C. Peng, Z. Zhang, Y. Dong, G. Shang, X. Zhu, H. Gao, X. Wan, Removal of fluoride from drinking water using tea waste loaded with Al/Fe oxides: a novel, safe and efficient biosorbent, Appl. Surf. Sci., 328 (2015) 34–44.

[134] A. Cinarli, O. Bicer, M. Mahramanlioglu, Removal of fluoride using the adsorbents produced from mining waste, Fresenius Environ. Bull., 14 (2005) 520–525.

[135] M. Tahaikt, R. El Habbani, A. Ait Haddou, I. Achary, Z. Amor, M. Taky, A. Alami, A. Boughriba, M. Hafsi, A. Elmidaoui, Fluoride removal from groundwater by nanofiltration, Desalination, 212 (2007) 46–53.

[136] P. Sehn, Fluoride removal with extra low energy reverse osmosis membranes: three years of large scale field experience in Finland, Desalination, 223 (2008) 73–84.

[137] C.K. Diawara, L. Paugam, M. Pontie, J.P. Schlumpf, P. Jaouen, F. Quemeneur, Influence of chloride, nitrate, and sulphate on the removal of fluoride ions by using nanofiltration membranes, Sep. Sci. Technol., 40 (2005) 3339–3347.

[138] H. Garmes, F. Persin, J. Sandeaux, G. Pourcelly, M. Mountadar, Defluoridation of groundwater by a hybrid process combining adsorption and Donnan dialysis, Desalination, 145 (2002) 287–291.

[139] A. Tor, Removal of fluoride from water using anion-exchange membrane under Donnan dialysis condition, J. Hazard. Mater., 141 (2007) 814–818.

[140] Z. Amor, B. Bariou, N. Mameri, M. Taky, S. Nicolas, A. Elmidaoui, Fluoride removal from brackish water by electrodialysis, Desalination, 133 (2001) 215–223.

[141] K. Majewska-Nowak, M. Grzegorzek, Skuteczność usuwania fluorków z roztworów wodnych metodami konwencjonalnymi i technikami membranowymi, Ochrona Środowiska, 38 (2016) 29–37 (in Polish).

[142] G. Zhang, Y. Gao, Y. Zhang, P. Gu, Removal of fluoride from drinking water by a membrane coagulation reactor (MCR), Desalination, 177 (2005) 143–155.

[143] C.K. Diawara, S.N. Diop, M.A. Diallo, M.A. Farcy, Determination performance of nanofiltration (NF) and low pressure reverse osmosis (LPRM) membranes in the removal of fluorine and salinity from brackish drinking water, J. Water Resour. Prot., 3 (2011) 912–917.

[144] V.V. Gedam, J.L. Patil, S. Kagne, R.S. Sirsam, P. Labhasetwar, Performance evaluation of polyamide reverse osmosis membrane for removal of contaminants in ground water collected from Chandrapur district, J. Membr. Sci. Technol., 2 (2012) 1–5.

[145] J.J. Schoeman, Water Defluoridation, Water Denitrification and Water Desalination in Rural Areas in South Africa, Proc. Third IASTED African Conference, Power and Energy System (AfricaPES 2010), Gaborone, Botswana, September 6–8, 2010, pp. 244–247.

[146] V.B. Briao, J. Magoga, M. Hemkemeier, E.B. Briao, L. Girardelli, L. Sbeghen, D.P.C. Favaretto, Reverse osmosis for desalination of water from the Guarani Aquifer System to produce drinking water in southern Brazil, Desalination, 344 (2014) 402–411.

[147] A.W. Mohammad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal, Nanofiltration membrane review: recent advances and future prospects, Desalination, 356 (2015) 226–254.

[148] C.K. Diawara, S.M. Lo, M. Rumeau, M. Pontie, O. Sarr, A phenomenological mass transfer approach in nanofiltration of halide ions for a selective defluorination of brackish drinking water, J. Membr. Sci., 219 (2003) 103–112.

[149] S. Choi, S. Yun, K. Hong, K. Ahn, The effect of coexisting ions and surface characteristics of nanomembranes on the removal of nitrate and fluoride, Desalination, 133 (2001) 53–64.

[150] K. Hu, J.M. Dickson, Nanofiltration membrane performance on fluoride removal from water, J. Membr. Sci., 279 (2006) 529–538.

[151] R. Malaisamy, A. Talla-Nwafo, K.L. Jones, Polyelectrolyte modification of nanofiltration membrane for selective removal of monovalent anions, Sep. Purif. Technol., 77 (2011) 367–374.

[152] L. Xub, X. Gao, Z. Li, C. Gao, Removal of fluoride by nature diatomite from high-fluorine water: an appropriate pretreatment for nanofiltration process, Desalination, 369 (2015) 97–104.

[153] A. Lhassani, M. Rumeau, D. Benjelloun, M. Pontie, Selective demineralization of water by nanofiltration. Application to the defluorination of brackish water, Water Res., 35 (2001) 3260–3264.

[154] M. Pontie, H. Buisson, C.K. Diawara, H. Essis-Tome, Studies of halide ions mass transfer in nanofiltration—application to selective defluorination of brackish drinking water, Desalination, 157 (2003) 127–134.

[155] M. Pontie, H. Dach, A. Lhassani, C.K. Diawara, Water defluoridation using nanofiltration vs. reverse osmosis: the first world unit, Thiadiaye (Senegal), Desal. Wat. Treat., 51 (2012) 164–168.

[156] L.A. Richards, B.S. Richards, A.I. Schafer, Renewable energy powered membrane technology: salt and inorganic contaminant removal by nanofiltration/reverse osmosis, J. Membr. Sci., 369 (2011) 188–195.

[157] I. Bejaoui, A. Mnif, B. Hamrouni, Performance of reverse osmosis and nanofiltration in the removal of fluoride from model water and metal packaging industrial effluent, Sep. Sci. Technol., 49 (2014) 1135–1145.

[158] J. Shen, A.I. Schäfer, Factors affecting fluoride and natural organic matter (NOM) removal from natural waters in Tanzania by nanofiltration/reverse osmosis, Sci. Total Environ., 527–528 (2015) 520–529.

[159] J. Shen, G. Mkongo, G. Abbt-Braun, S.L. Ceppi, B.S. Richards, A.I. Schafer, Renewable energy powered membrane technology: fluoride removal in a rural community in northern Tanzania, Sep. Purif. Technol., 149 (2015) 349–361.

[160] I. Owusu-Agyeman, J. Shen, A.I. Schäfer, Renewable energy powered membrane technology: impact of pH and ionic

strength on fluoride and natural organic matter removal, Sci. Total Environ., 621 (2018) 138–147.

[161] E. Kowalchuk, Selective Fluoride Removal by Aluminum Precipitation and Membrane Filtration, Master of Science Thesis in Civil Engineering, University of New Mexico Albuquerque, New Mexico, 2011.

[162] G.C. dos Santos Bazanella, G.F. da Silva, A.M.S. Vieira, V.R. Bergamasco, Fluoride removal from water using combined *Moringa oleifera*/ultrafiltration process, Water Air Soil Pollut., 223 (2012) 6083–6093.

[163] N.C. Lu, J.C. Liu, Removal of phosphate and fluoride from wastewater by a hybrid precipitation–microfiltration process, Sep. Purif. Technol., 74 (2010) 329–335.

[164] K. Prochaska, M. Bielska, K. Dopierała, Selected Physico-Chemical Aspects of Membrane Filtration, Membranes Theory and Practice, No. III, Monographic and Specialist Lectures, Toruń, 2009, pp. 80–108 (in Polish).

[165] A. Klimonda, M. Grzegorzek, K. Majewska-Nowak, Removal of fluoride ions by ultrafiltration in the presence of cationic surfactants, Environ. Prot. Eng., 44 (2017) 5–13.

[166] M. Grzegorzek, K. Majewska-Nowak, The use of micellar-enhanced ultrafiltration (MEUF) for fluoride removal from aqueous solutions, Sep. Purif. Technol., 195 (2018) 1–11.

[167] I. Akanyeti, M.C. Ferrari, Hybrid sorbent-ultrafiltration systems for fluoride removal from water, Sep. Sci. Technol., 51 (2016) 348–358.

[168] J. He, X. Cai, K. Chen, Y. Li, K. Zhang, Z. Jin, F. Meng, N. Liu, X. Wang, L. Kong, X. Huang, J. Liu, Performance of a novelly-defined zirconium metal-organic frameworks adsorption membrane in fluoride removal, J. Colloid Interface Sci., 484 (2016) 162–172.

[169] H. Strathmann, Ion-Exchange Membrane Separation Processes, Elsevier, Netherlands, 2004.

[170] Z. Amor, S. Malki, M. Taky, B. Bariou, N. Mameri, A. Lrnidaoui, Optimization of fluoride removal from brackish water by electrodialysis, Desalination, 120 (1998) 263–271.

[171] N. Kabay, O. Arar, S. Samatya, U. Yuksel, M. Yuksel, Separation of fluoride from aqueous solution by electrodialysis: effect of process parameters and other ionic species, J. Hazard. Mater., 153 (2008) 107–113.

[172] M.A. Sahli, A. Annouar, S. Tahaikt, M. Mountadar, A. Soufiane, A. Elmidaoui, Fluoride removal for underground brackish water by adsorption on the natural chitosan and by electrodialysis, Desalination, 212 (2007) 37–45.

[173] M. Zeni, R. Riveros, K. Melo, R. Primieri, S. Lorenzini, Study on fluoride reduction in artesian well—water electrodialysis process, Desalination, 185 (2005) 241–244.

[174] M. Tahaikt, I. Achary, M.A. Menkouchi-Sahli, Z. Amor, M. Taky, A. Alami, A. Boughriba, M. Hafsi, A. Elmidaoui, Defluoridation of Moroccan groundwater by electrodialysis: continuous operation, Desalination, 189 (2006) 215–220.

[175] S. Lahnid, M. Tahaikt, K. Elaroui, I. Idrissi, M. Hafsi, I. Laaziz, Z. Amor, F. Tiyal, A. Elmidaoui, Economic evaluation of fluoride removal by electrodialysis, Desalination, 230 (2008) 213–219.

[176] K. Majewska-Nowak, M. Grzegorzek, M. Kabsch-Korbutowicz, Removal of fluoride ions by batch electrodialysis, Environ. Prot. Eng., 41 (2015) 67–81.

[177] M. Grzegorzek, K. Majewska-Nowak, Use of the electrodialysis process for fluoride ion and salt removal from multi-constituent aqueous solutions, Archit. Civil Eng. Environ., 4 (2016) 107–113.

[178] F. Durmaz, H. Kara, Y. Cengeloglu, M. Ersoz, Fluoride removal by Donnan dialysis with anion-exchange membranes, Desalination, 177 (2005) 51–57.

[179] A. Boubakri, N. Helali, M. Tlili, M.B. Amor, Fluoride removal from diluted solutions by Donnan dialysis using full factorial design, Korean J. Chem. Eng., 31 (2014) 461–466.

[180] E. Kir, E. Alkan, Fluoride removal by Donnan dialysis with plasma-modified and unmodified anion-exchange membranes, Desalination, 197 (2006) 217–224.

[181] E. Alkan, E. Kir, L. Oksuz, Plasma modification of the anion-exchange membrane and its influence on fluoride removal from water, Sep. Purif. Technol., 61 (2008) 455–460.