Express Polymer Letters Vol.17, No.9 (2023) 913–931
Available online at www.expresspolymlett.com
https://doi.org/10.3144/expresspolymlett.2023.68

Review article

Polymers are paving their way into defluoridation of water

Vipin Chandra Joshi[1,3], *Saroj Sharma*[2,3], *Amit Bhattacharya*[2,3*]

[1]Process Design and Engineering Cell, Council of Scientific & Industrial Research-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Bhavnagar 364002 Gujarat, India.
[2]Membrane Science and Separation Technology Division, Council of Scientific & Industrial Research-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Bhavnagar 364002 Gujarat, India.
[3]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India

Received 3 February 2023; accepted in revised form 17 May 2023

Abstract. There are unequivocal shreds of evidence that polymers touched every sphere of life. They are very versatile and used in many applications depending on the specific intrinsic properties of the materials. Over the last few decades, there has been growing evidence that applying polymer materials in water-purifying has been adopted worldwide. Water fluorine toxicity is challenging us to develop water-purifying polymeric materials. We are presenting the polymeric adsorbent and membrane materials advancement in terms of defluoridation of water.

Keywords: *polymer membranes, adsorbent, water, defluoridation*

1. Introduction

The path of polymers began 100 years back. The concept of macromolecule (first coined term) originated from the idea of Herman Staudinger in 1922. Since it began, polymer researchers all over the world have now acquired a larger space. Interestingly, researchers of all disciplines may have taken a step toward polymers. Polymer science is one of the fastest-growing areas and connects many other scientific disciplines. Innovation and ease of productivity are the two most important drivers to shift in the direction of polymers.

Polymers permeate every facet of our day-to-day life and form the very basis of our civilization. Polymers now cover a broader spectrum of efforts and effects. Polymers have marked impressions from nano to macro-size applications. Polymers are at the forefront of new technology in separation science. Separation science addresses separating a part of a mixture/solution and the subsequent removal of impurities for purification purposes. Better understanding among separation science researchers and easy availability of modern separation science and technology are the key drivers towards including polymers. Separation science and technology are witnessing the shift from conventional to polymer materials. Polymers contribute to material science by providing unique model systems as easily manipulated substances to achieve unique morphologies and properties.

Polymeric materials are widely used as adsorbents, ion exchange, and membranes in separation and purification processes. The applications of polymers show great promise in the areas of water purification. This review deals with natural and synthetic polymers used in adsorption, ion exchange, and membranes to separate fluoride ions. The polymers used in each method are described in terms of their properties, structures, and functions. The design of novel polymers with triggered functions presents new opportunities for development in this arena.

Fluoride ions come into the water because of the interaction of water and the solid aquifer. Groundwater

*Corresponding author, e-mail: bhattacharyaamit1@rediffmail.com

is the primary source of drinking water in many countries [1, 2]. Groundwater is essential compared to other water because it can be drunk directly without treatment, provided it is not contaminated. The groundwater composition depends on the geology of the solid aquifer. Literature reports the fluoride-contaminated hotspots worldwide and the population at risk of its exposure [3–6]. Fluoride ions are in their mineral form on the earth's crust, *viz.* fluorite, biotite, and topaz [7, 8]. The other water fluoride source is industrial waste (*viz.* semiconductor, electroplating, aluminium smelter ceramic, steel, cement, fertilizers, glass etching) [9]. It is considered a vital contaminant in drinking water. Drinking fluoride in water increases the risk of dental and skeletal fluorosis [10–13]. Polymer materials are used in various methods for defluoridation from water. Adsorption, ion exchange, and membrane filtration (pressure and electric potential driven) are efficient methods in this arena.

Owing to the following unique characteristics of polymers, interest among chemists and researchers has increased toward separation science. Some of the features are mentioned below:

- **Unbelievably network:** It provides opportunities for tailoring chemical functionalities. The catenation property of carbon makes the polymers of having a long chain. Because of carbon, atoms are free to rotate in respect of one another, and close coiling or folding takes place. The cohesion forces between the molecules and those of the electronic forces (van der Waals forces, H-bond) join the atoms into chains or other structures. The design of specific surface topologies relates to precise functions.
- **Porosity generation:** Polymer structures can change the porosity generation depending on the variation of solvents/nonsolvents. Thus, it can tune the design as it demands. The property can be engineered into the polymeric system.
- **Charge generation:** There may be an inbuilt or tailored surface charge. The surface functionalization feasibility is there to form charged surface enabling adhered ions/solutes.
- **Feasibility of combining with other polymers/inorganics/organics:** Polymeric materials with synergetic or complementary behaviour between the polymer and the inorganics interacting at the molecular scale. The synergistic combination of multiferous functions by different (polymeric) materials and self-assembly are also feasible. Polymeric materials with its component and added components ensure structural integrity.
- **Choices of polymers:** There are legions of polymers in the market, and the options are easy as it demands.

2. Adsorbent materials

Adsorbent materials can take in another substance. It can also be stated as the condition where ions/compounds can attach. They are related to surface phenomena. The adsorbents are widely used in water purification, *viz.*, removal of contaminants in terms of ions/ molecules. There has been a growth in the use of polymers as adsorbents. Some of the features are mentioned below:

- **Availability of large sorbent:** The sorbent polymer materials are abundant. It may be natural or synthetic.
- **Easy tuning of sorbents:** Polymeric sorbent materials modification is easy as per requirement.
- **Insensitive to toxic substances:** Polymeric material is generally insensitive to toxic ions/substances.
- **Fit into simple operational design:** The polymeric sorbent materials can be fit in any functional arrangement. The use of polymeric materials makes the system economical. Thus, the system with polymer materials is commercially viable. The treatment of pollutants at a high concentration is also feasible.

The polymer adsorbent materials are of different categories: biopolymers, synthetic polymers, conducting polymers, and ion exchange resin.

3.1. Biopolymers

The origin of polymers from bio-resources are termed 'biopolymers'. Plenty of examples (*viz.* chitosan, alginate, carboxy methyl cellulose) of biopolymers acting as adsorbents to the fluoride. Chitosan, the natural biopolymer, has an affinity for negatively charged surfaces. The biodegradable, abundant in nature, the good chelating agent makes it one of the options to prepare low cost and efficiency in defluoridation [14–16]. The homogeneously charged nanoparticles can be incorporated into chitosan. Metal with chitosan *viz.* Fe-chitosan (15.38 mg/g) [17], Al- chitosan (1.7 mg/g) [18], carboxylated chitosan modified ferromagnetic nanoparticles, La^{+3} impregnated chitosan/β-cyclodextrin [19] are fluoride scavenging materials. Hydrous mixed metal

oxyhydroxide composites (Fe–Al–Mn@chitosan) make F^- ions easily accessible to active sites of the porous outer surface. The diffusion of F^- ions inside the composite matrix made it a better adsorber than fixed Fe–Al–Mn oxyhydroxides [20]. The composite exhibited a maximum adsorption capacity of 40±0.5 mg/g. Al doping chitosan–Fe(III) hydrogel (Al–CS–Fe) showed a high adsorption capacity of 31.16 mg/g [21]. They reported the multiple mechanisms of F^- adsorption.

I. Ion exchange between primary amine salt of chitosan and fluoride.

$$–NH_3^+Cl^- + F^- \leftrightarrow –NH_3^+F^- + Cl^-$$

II. In the presence of acid or near the neutralization, the fact of –OH and $–NH_2$ groups in the metal complex made it positively charged. The electrostatic interaction is as follows:

$$–NH_2– + –H^+ + F^- \leftrightarrow –NH_3^+ \ldots\ldots F^-$$

$$–OH + H^+ + F^- \leftrightarrow –OH^+ \ldots\ldots F^-$$

III. Ligand or ion exchange between metal and fluoride:

$$M–OH_2 + F^- \leftrightarrow M–F + H_2O$$

$$M–OH + F^- \leftrightarrow M–F + OH^-$$

Lanthanum has higher affinities for fluoride ions. The combination of gelatin [22], chitosan beads [14, 23] made the composite effective for defluoridation. In this direction, the combination of La(III) with carboxymethyl cellulose (CMC) showed excellent capabilities in defluoridation [24]. The active functionalities formed complexes with metal ions and crosslinking agents [25]. The maximum removal efficiencies of CMC-La and linked-CMC-La (by glutaraldehyde) were 98.85 and 99.31%, respectively, in the case of a fluoride concentration of 40 mg/l.

Alginate (SA) and carboxymethyl cellulose (CMC) have a large number of active groups (*viz.* hydroxyl, carboxyl) and have the ability to adsorbents with high removal efficiency [26]. Alginate/carboxymethyl cellulose sodium composite loaded with calcium and aluminium (SA/CMC–Ca–Al) developed the defluoridation abilities. Ca(II) and Al(III) were incorporated into SA/CMC through sodium ion exchange. The maximum adsorption amount for fluoride was 35.98 mg/g at pH 2.0, 298.15 K concentration 100 mg/l. Na-alginate is well-focused for its high dispersion, biocompatibility, relatively low cost, and porous structure. The alginate-based adsorbent had been shaped in different forms. 3D yttrium-based graphene oxide-sodium alginate hydrogel is one of the forms explored. It is a 3D macroporous structure composed of 2D sheets of graphene oxide with the uniform dispersion of Y(III) onto the gels. The 3D network structure prevented aggregation and facilitated mass transport to the internal system. The inclusion of graphene oxide nanosheets supported the large specific and abundant functional groups *viz.*, –COOH, –OH, and epoxy groups. The maximum adsorption capacity of the hydrogel regarding defluoridation was 288.96 mg/g at pH 4.0 [27]. Alginate-based adsorbent by entrapping trimetallic (Fe–La–Ni) oxide into the matrix was helpful in the defluoridation of water. The natural anionic alginate biopolymer is composed of two different monomers (1→4) linked α–L–guluronate (G) and β–D–mannuronate (M) [28]. The presence of di-tri valent metal ions facilitated the formation of rigid, ordered, and strong structures. It helped to immobilize the nanopowder for the adsorption of ions. The polymeric matrix showed a very high fluoride ion adsorption capacity, *i.e.*, 333 mg/g.

Carboxymethylcellulose (CMC), a biopolymer with a supramolecular structure, possess metal binding sites [29]. It is a linear one with carboxymethyl ($CH_2COO–$) substituent of negative surface charges. It has excellent coordination abilities with metal ions (Al^{3+}, Fe^{3+}). The hydrated state of ions enriched with OH^- ions and water molecules can attach F^- ions. CMC-*g*-2-acrylamido-2-methyl propane sulfonic acid (AMPS) /Fe/Al composite hydrogel impregnated with activated charcoal [30] was one of the excellent examples in this part. The maximum defluoridation efficiency of metal oxide incorporated was 84.67% at pH 6 at an initial F^- concentration of 5 mg/l.

Iron-impregnated pectin-*g*-poly(amidoxime) was based on low-cost natural polymer [31]. The presence of –COOH functionalities in the unit of α–(1–4′)-linked-D-galacturonic acid of pectin made it unique for the chelating agent [32]. It possessed metal ion enrichment capabilities and fluoride ions sorption in acidic conditions. The modification through the grafting of poly(amidoxime) and derivatization reactions enhanced the potential of defluoridation. Amidoxime functionalization was tethered pectin-Ca beads to achieve better removal capabilities. The synthesized amidoxime functionalized Ca-pectinate beads were also immobilized with iron to increase their efficiencies. Pectin-*g*-poly(amidoxime)-Fe complex (Figure 1) showed ~70% adsorption ability at pH 5.0.

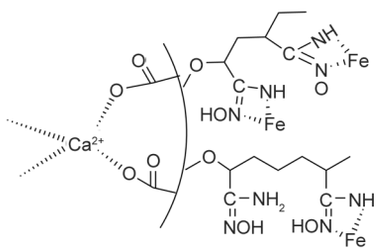

Figure 1. Proposed chemical structure of pectin-*g*-poly(amidoximes)-Fe complex [31].

3.2. Synthetic polymers

The polymers generated from the synthetic route are called synthetic polymers. The crosslinked polyvinil alcohol (PVA)-bimetallic systems *viz.* Ca–Zr–PVA polymer composites were particular adsorbents as the significance of the presence of two metals (Ca/Zr) in terms of selectivity of ions and synergistic effect. The choice of polymer films had a larger surface area. Moreover, a polymer like PVA is always advantageous because of its non-toxic and degradable nature. The fluoride adsorption of the Ca–Zr–PVA polymer composite was 97.14%, compared to pure crosslinked PVA (32%) [33].

Crosslinked PVA gels form due to acetal bridges between the PVA chains. The hydrogels feature their porous network and easy diffusability of ions across the surface. PVA-iron-zirconium hydrogel (PFZH) and PVA-copper-zirconium hydrogel (PCZH) showed promising defluoridation capabilities (100%) [34]. The defluoridation by the systems was pH-independent and least affected by commonly interfering ions (HCO_3^-, PO_4^{3-}, Cl^-, NO_3^-, SO_4^{2-}).

Hydrophilic hyper-crosslinked porous polymer networks, having high surface areas of 2000 m^2/g and robust chemical and thermal stabilities [35, 36], were synthesized from 2,2-biphenol (HHCP1) and bisphenol A (HHCP2) monomers [37]. Ca-loaded networks of the porous polymer resulted in a defluorinating adsorbent. Two monomers had different Ca-loading capacities. Both Ca-loaded networks were effective in defluoridation. Ca-loaded HHCP1 showed the ability of (267±34 mg/g), whereas HHCP2-Ca had a lower power of 96.2±10 mg/g with faster uptake kinetics.

The adsorbents prepared in the in situ polymerization method were also explored. Crosslinked porous polymeric adsorbent poly(zirconyl methacrylate-*co*-methylmethacrylate) (p(ZrDMA-*co*-MMA)) is one of the examples in this area. Due to its non-toxic nature, zirconium is well-accepted in the polymeric adsorbent field, especially defluoridation. The maximum fluoride adsorption was found to be 96.54% at neutral pH. The possibility of metal ions leaching was avoided [38]. Crosslinked ZrVAc adsorbents were prepared using zirconyl methacrylate (ZrDMA) and vinyl acetate (VAc), ethylene glycidyl methacrylate (EGDMA), through the suspension polymerization method. The maximum fluoride adsorption capacity was found to be 138 mg/g at pH 7.0 [39]. Gupta *et al*. [40] prepared the polymeric adsorbent based on zirconium dimethacrylate (ZrDMA) and lauryl methacrylate (LMA). The covalently co-ordinated metallic-polymeric moiety brings a stable network. During the adsorption process, it did not leach out any trace elements (Zr, F^-). The crosslinked polymer based on the combination of organometallic vinyl monomers (ZrDMA and AgMA), vinyl monomers (MMA), and (EGDMA) showed the highest adsorption capacities (q_{max}) were obtained as 64 mg/g [41]. The three-dimensional metallopolymer microsphere quaternized poly(zirconyl dimethacrylate-*co*-vinylbenzyl chloride)] (ZrVBZ) was reported by Gupta *et al*. [42]. The free radical polymerization in the presence of crosslinker (ethylene glycol dimethacrylate) and porogen (toluene) formed the porous network polymer. The schematic presentation for the polymer synthesis is shown in Figure 2. The maximum adsorption capacity of the polymer for fluoride was 116.5 mg/g. Recently, a similar compound based on poly(zirconyl dimethacrylate-*co*-vinyl imidazole)] was also reported. The maximum fluoride adsorption capacity was 109.6 mg/g [43].

Magnetic adsorbents are now familiar in this arena to increase separation efficiency. As fluoride is a hard base with a small size and high, electronegativity magnetic hydrogels have good separation abilities, which were strengthened by lanthanum loading in lanthanum-loaded magnetic cationic hydrogel (MCH-La) [44]. The hydrogels are prepared by crosslinking (3-acrylamidopropyl) trimethylammonium chloride (APTMACl), *N*,*N*-methylene bisacrylamide (MBA), *N*,*N*,*N*′,*N*′-tetramethylethylene-diamine (TEMED) in the presence of γ-Fe_2O_3. The maximum fluoride adsorption capacity for MCH-La was 136.78 mg F^-/g at an equilibrium fluoride concentration of 29.3 mg/l and pH 7.0.

Generally, triaryl boron-containing π-conjugated systems are known for their electronic and photophysical properties. But, these systems *viz.* (boron based conjugated microporous polymer) were also explored in defluoridation and F^- ion sensors [45]. It was the

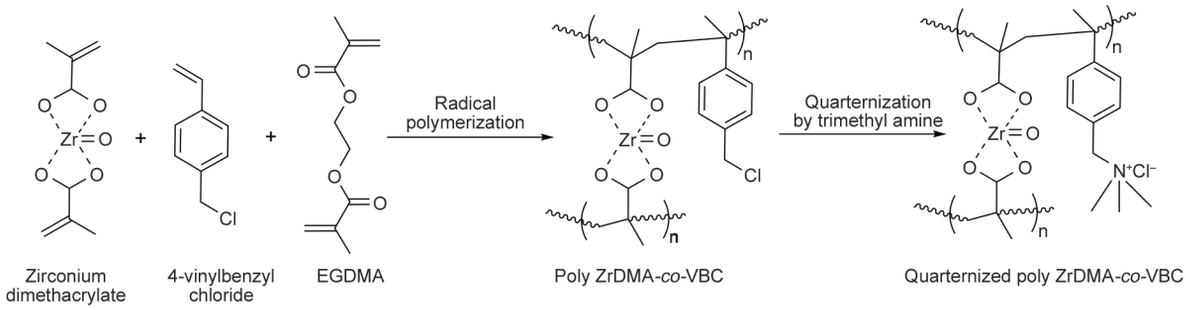

Figure 2. Schematic presentation of synthesis of ZrVBZ adsorbent [42].

product of polycondensation of tris(4-bromo-2,6-dimethylphenyl)borane and tris(4-dihydroxyboranylphenyl)amine (TBPA). The conjugated polymer showed an excellent adsorption capacity of up to 24 mg/g at equilibrium fluoride concentrations of 16 mg/l and a temperature of 298 K.

Crosslinked chitosan-polyvinyl alcohol (Ch-PVA) materials were used for defluoridation [46]. The crosslinking materials used were ethylene glycol diglycidyl ether (EGDE) and sodium tripolyphosphate pentabasic (TPP). The presence of epoxy groups bridged the condensation reaction between chitosan and PVA. The ionic crosslinking occurred between TPP and chitosan chains. The maximum fluoride adsorption capacity of the crosslinked material was 12.64 mg/g at pH 7 and 30 °C.

The adsorbent iron-aluminium-cerium tri-metal hydroxide (Fe–Al–Ce) with a polymer latex acrylic-styrene binder coated on the sand by spraying technique. The system showed fluoride adsorption of 3.46 mg/g at pH 7.0 and 50 mg/l fluoride concentration [47]. Polysulfone/$ZnCr_3$-NO_3-layered double hydroxides (PS/$ZnCr_3$-NO_3-LDH) composites were prepared by phase inversion and investigated for defluoridation by Koilraj and Kannan [48].

3.3. Conducting polymers

The loss of activities due to agglomeration, low adsorption capacities, reduced selectivity, and difficulty in isolation from an aqueous medium prompted separation researchers to prepare hybrid materials consisting of polymers having large active porous surfaces. In this direction, one of the approaches is adsorbents in conducting polymers domain. Conducting polymers are in conjugation and charge carriers. The charge carriers have gained the freedom to move over the entire chain. It has exchangeable counter ions from the oxidative solution. Thus, it can adsorb the ions on its surface. They exhibit desired properties like large surface area, chemical stabilities, modifiable surface chemistry, and high affinity for anionic pollutants [49, 50].

The conducting polymer-based materials have four categories, *viz.* (a) conducting polymer, (b) conducting polymer/adsorbents, (c) conducting polymer/clay minerals, and (d) conducting polymer/inorganic matrices. Hydrous TiO_2/polypyrrole hybrid nanocomposite showed fluoride's synergistic effect in adsorption capacity. The maximum adsorption capacity gained is 31.93 mg/g [51]. Polypyrrole (PPy)/HSnO (% loading, Pyrrole = 47.41, HSnO = 52.59) exhibited the best defluoridation performance and the maximum adsorption capacity 28.98±0.37 mg/g at 328 K. The hybrid materials possessed good regeneration properties and high desorption efficiency of 95.81% up to three cycles [52]. Fe_3O_4/PPy nanohybrid composite showed its excellence in adsorption even after 20 recycles [53]. The adsorption was enhanced in a rotating magnetic field. The maximum removal rate was 78.2% for fluoride (10 mg/l) aqueous solution [54].

The hydrous CeO_2-Fe_3O_4 decorated polyaniline fibers gained a maximum capacity was 93.46–117.64 mg/g in a broad pH of 3–10 [55]. Hydrous ZrO_2-polyaniline (PANI) nanofibers showed the potential of high adsorption capacity towards F^- ions [49, 56]. Cellulose nanofiber-PANI-templated ferrihydrite nanocomposite, the unique hybrid material, showed an adsorption capacity of 50.80 mg/g [57].

The synergistic effect of polyaniline/alumina (PANI/AlO) and PPy/AlO composite in terms of defluoridation (Figure 3)was reflected in the study of Karthikeyan *et al*. [50]. The maximum amount of adsorption was 6.6 and 8 mg/g for polyaniline/alumina and polypyrrole/alumina, respectively. The removal of fluoride ions by alumina occurs through the formation of an aluminium-fluoro complex, whereas for conducting polymer, it is through ion exchanging of dopant ions.

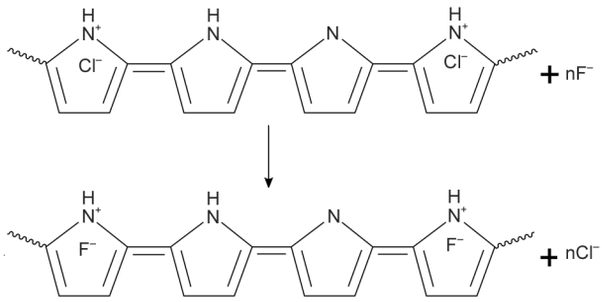

Figure 3. Ion exchange phenomena of doped ionizable chloride ions with fluoride ions [50].

Clay-based conducting polymer, polypyrrole-montmorillonite (PPy–MMT) composite, had the potential for defluoridation activities [58]. The maximum adsorption was 5.10 mg/g compared to 2.66 mg/g alone. The physical adsorption and ion exchange mechanistic pathways developed a synergetic approach to fluoride removal. Polypyrrole with attapulgite (magnesium aluminium silicate material) formed a composite showing defluoridation potential from an aqueous solution [59]. The adsorption efficiency was 74.71% at a sorbent dose of 0.18 g.

3.4. Ion exchange resin

It is another important class of materials used in this defluoridation arena. The aluminium form of each aminomethyl phosphonic acid-type ion exchanger based on the copolymerization of two monomers (*i.e.*, methyl methacrylate-ethylene glycol dimethacrylate) showed selectivity and excellent capacity for fluoride separation. The uptake was better than that of the commercially available strongly acidic cation exchanger Indion 225 and aminomethyl phosphonic acid-type chelating ion exchanger Duolite ES 467 [60]. Samatya *et al*. [61] prepared the Zr-immobilized resin based on Diolely phosphoric acid (DOLPA) and divinyl benzene (DVB) through surface template polymerization. The preparation was carried out w/o/w an emulsion. PVA was taken as an emulsion stabilizer. Polystyrene was used as porogen to immobilize more adsorption sites. The schematic illustration of the prepared resin is presented in Figure 4. The removal of fluoride ions using the Zr(IV) complex and phosphate functionality as a recognition site.

Modification by ethylenediamine of synthetic copolymeric resin *viz.* vinylbenzyl chloride/divinylbenzene (VBC/DVB), styrene/divinylbenzene/vinylbenzylchloride (ST/DVB/VBC) and acrylonitrile/divinylbenzene/vinylbenzylchloride (AN/DVB/VB) examined for defluoridation experiment. The resin's mechanistic aspects are presented as follows (Figure 5). AN/DVB/VBC-ED resin possessed higher defluoridation capacity (DC) than ST/DVB/VBC-ED and VBC/DVB-ED resins among all the synthetic resins [62].

Cai *et al*. [63] prepared nanocrystalline Li/Al-based layered hydroxide (LALDH-201) impregnating Li/Al inside a commercial polystyrene anion exchanger D201. The fixed-bed adsorption of LALDH-201 of the Fluoride contaminated groundwater was 4.1 mg/l, ~11 times compared to the anion exchanger D201. A similar study was also carried out using nanosized hydrous zirconium oxide (HZO) within anion exchanger D201. It showed 7–14 times capacity compared to D-201 [64]. ZrO_2 nanoparticles on polymeric anion exchanger resin. Hybrid anion exchange resin was reported by Singh *et al*. [65]. The maximum fluoride uptake capacity of the resin resulted in 12.0 mg/g. Nanosized cerium oxides (NCO) inside a porous polystyrene anion exchanger (PAE) functionalized with positive quaternary amine groups ($[–N(CH_3)^{3+}]$) showed the ability for efficient fluoride removal from wastewater [66].

Robshaw *et al*. [67] had shown the defluoridation potential of Purolite® S950+ loaded with lanthanum ions [67]. Purolite® S950+ commercial resin is a macroporous, weak acid, chelating one. It consisted of a styrene/divinylbenzene main chain with amino

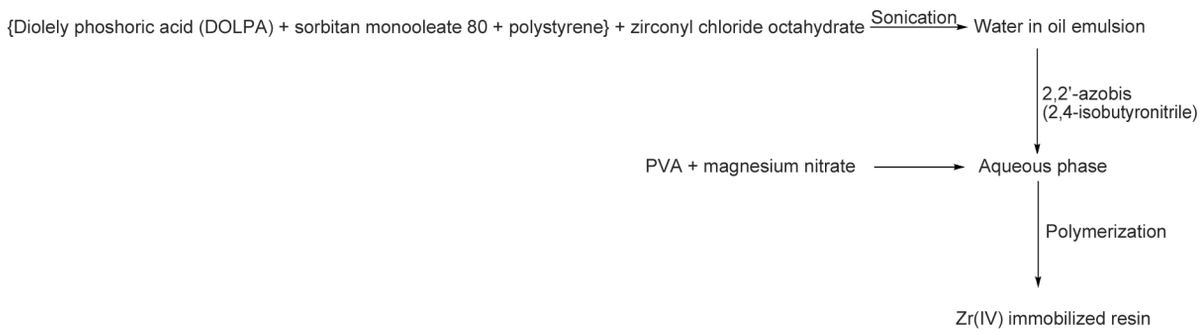

Figure 4. Schematic presentation of surface template polymerization with water/oil/water emulsions [61].

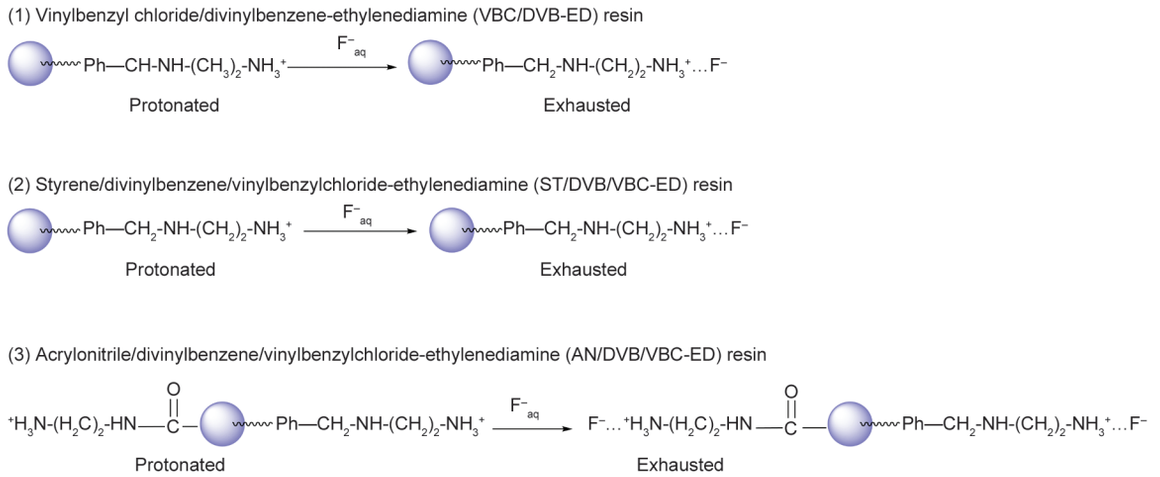

Figure 5. Reaction scheme of fluoride sorption onto different resins (VBC/DVB-ED, ST/DVB/VBC-ED, and AN/DVB/VBC-ED) [62].

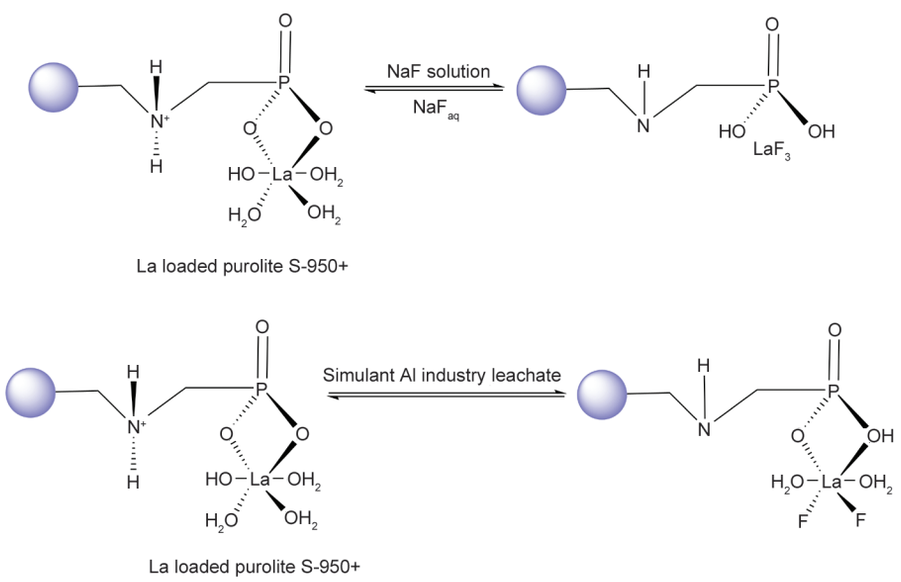

Figure 6. Schematic presentation of fluoride adsorption by La-Purolite S 950+ [67].

phosphonic acid functional groups. The La-modified one exhibited a large maximum defluoridation capacity of 187±15 mg/g from the NaF solution and 126±10 mg/g from the leachate. The schematic diagram of the fluoride uptake is represented in Figure 6.

Meenakshi and Viswanathan [68] experimented with Indion FR 10 (IND), crosslinked polystyrene, the chelating resin. The results showed that chelating resin was more selective than an anion-exchange resin for fluoride removal. The mechanistic aspect is in the following figure (Figure 7).

The incorporation of aluminium(hydr)oxide material inside the pores of Purolite A520E (strong-base ion-exchange resin) made it promising for fluoride removal. Purolite A 520E is macroporous polystyrene

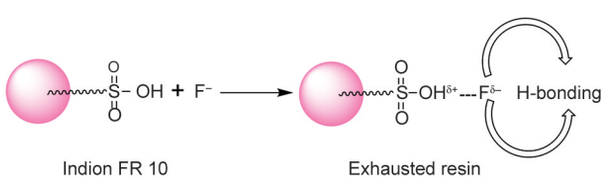

Figure 7. Adsorption of fluoride ions by Indion FR 10 resin [68].

crosslinked with divinylbenzene with a quaternary ammonium functional group [69].

The pulverized spent resins were loaded with Zr(IV) ions to develop adsorption sites, which effectively adsorb fluoride ions. The acidic cation exchange resin (MUROMAC MBX8-WH was polystyrene crosslinked by divinyl benzene and contains sulfonic acid groups [70]. At first, Zr(IV) was adsorbed following the cation exchange reaction. Consequently, the –OH

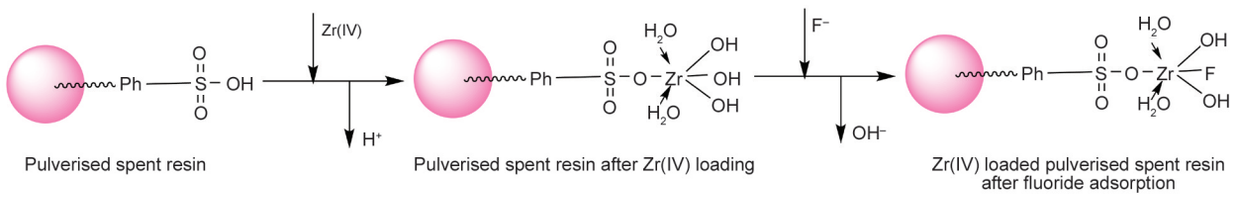

Figure 8. Zr(IV) Adsorption mechanism onto spent cation exchange resin powder and that of fluoride ions on the Zr(IV)-loaded spent exchange resin powder [70].

functional group was replaced by fluoride ion respectively (Figure 8).

Amberlite XAD-4TM (styrene-divinyl benzene) had been modified by introducing amino functionality onto the aromatic ring for its application in fluoride remediation [71]. An Al(III)-loaded and $Al(OH)_3$-coated chelating resin Lewatit TP 260 (Crosslinked polystyrene, aminomethylphosphonic acid) was prepared. Both the modified forms of the resin showed their abilities to remove F^-. The maximum adsorption capacity of $Al(OH)_3$-coated resin and Al(III)-loaded resin was 0.55 and 0.40 mg/g, respectively [72]. Lanxess TP208 (crosslinked polystyrene with chelating diamino acetate group), a weakly acidic macroporous cation exchange resin exchanged with Al^{3+} ions, showed a selective mode of removing fluoride ions [73]. Amberlite IRA400Cl anion resin, polystyrene divinyl benzene copolymer matrix, and chloride as mobile ions showed 76% fluoride removal [74].

4. Membrane materials

There are unequivocal shreds of evidence that membranes are the best water purification solution. The membrane system can be tailor-made per the people's requirements by making it compatible with water sources and demand. The 'fluoride in water' crisis challenges us to develop solutions for a very urgent issue. The membrane sector is vital as a driver of defluoridation techniques and time-to-market development [75–78]. The membranes have unique specialities in separation science as no need of chemicals are needed and have the capabilities to work under a wide pH range. The relevant membrane processes include nanofiltration, reverse osmosis, membrane distillation, and electrodialysis.

The defluoridation activities are mostly fit for nanofiltration as low-pressure RO membranes. Nanofiltration is a separation process positioned between ultrafiltration and reverse osmosis. It replaces conventional methods of water softening with more low pressure than reverse osmosis. The molecular weight cut off's (MWCO) for the membranes is generally 300 to 1000 Da (diameter in ~1 nm) [79–81]. It showed selectivity in ionic species, with weaker monovalent ions retention than bivalent ions. The process is applicable for total solid retention for salts with low concentrations. The high negative charge of fluoride makes it better retention through the nanofiltration process.

Polymers have flexibility in the preparation of membranes as it inherits the property of pores and charge generation. The breadth of polymers available for membranes has grown in the past few decades. The polymer research echoed this aspect of their behaviours because of its trouble-free processibility, ability to last, and lower price than the other parallel materials. The 'in-built' configurations make it feasible for the separation of ions. Moreover, they are flexible in terms of blending, composite, and surface modification as necessary. Of course, compatibility issues are to be considered. Thin film composite (polymer-based) membranes marked their position in defluoridation.

The composite signifies that different polymers are put together to be useful in applications. In the membrane arena, thin-film composite is a revolutionary technology. It consists of two polymer layers (*i.e.*, support and selective layer). The schematic presentation is as in Figure 9. The significance of the polymer support layer is to bring mechanical strength to sustain higher pressure in its engineering shape. The polymeric support layer was embedded in nonwoven polyester support, which imparted mechanical strength so that

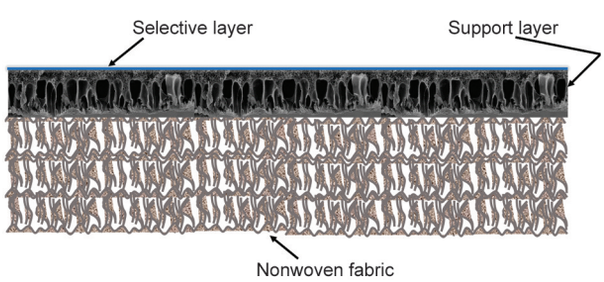

Figure 9. Schematic presentation of thin film composite membrane.

the membrane could be artfully worked out in shape and endure higher pressure. The support layer was chosen that fits in phase separation. The wet phase separation technique forms the pores on support layers. It means that diffusive transport of solvent-non-solvent takes place in polymeric matrices. In this regard, a few polymers (*viz.* polysulfone, polyether sulfone, polyvinylidine difluoride) are commonly used. The selective layer controls performance (flux and rejection), whereas the porous support layer is for the sustainability of the selective layer with a minimum resistance in permeate flow. Thus, the composites have specialities, and two important layers can be tuned for different functions.

The selective layer is polyamide considering the importance of –CONH– in biological systems. The polyamide formation occurs in situ through an interfacial polymerization reaction between diamines and acids/acid chlorides. The chemistry is represented in Figure 10. It is a straightforward reaction to form a polymer network structure consisting of two/more monomers in different solvents at the interface. The selective layer controls performance (flux and rejection), whereas the porous support layer is for the sustainability of the selective layer with a minimum resistance in permeate flow. Thus, the composite has a speciality, and two important layers can be tuned for different functions. Different amines and acid chlorides are used in interfacial polymerization to form polyamides [82]. Literature reports regarding the various commercial polyamide nanofiltration/low-pressure RO membrane exist. However, the detail of the chemistry of the membrane preparation is not revealed.

Extensive study has been done regarding the use of commercial membranes in defluoridation. As the report mentioned, we intend to unveil the membranes' chemistry and defluoridation potential. BW30 and NF270 (Dow FilmTech™, Minneapolis, MN, USA) are polyamide thin film composite (TFC) membrane. BW30 is a fully aromatic polyamide-based RO membrane, whereas NF270 is a piperazine-based polyamide NF membrane with semi-aromatic, weakly acidic COO^- groups [83]. NF 270 is rather a loose membrane, whereas BW30 is a tight one [84, 85]. The fluoride rejection of NF 270 was lower than BW30. Filmtec NF70-2540 membrane (DOW Chemical, Denmark) having MWCO 180 Da used a thin-film polyamide composite on a polysulfone support designed for tangential filtration [86]. The fluoride rejection was >94% for 6 bar pressure. Choi *et al.* [87] experimented with NTR-7250 (polyvinyl alcohol- piperazine based) membrane and compared the performances with NTR-7450 (Nitto Denko) (polysulfone based). NTR-7450 (–10 mV) has a higher surface potential than NTR-7250 (–5 mV at around pH 7). It showed a higher rejection rate than the NTR-7250. The rejection rate of fluoride was 72% for NTR-7450 whereas for NTR-7250 it was 70.4% (5 ppm).

The separation of fluoride with the Osmonics spiral module containing the HL 2514 T membrane was carried out. The membrane featured molecular weight cut-off (MWCO) for the organic compounds of about 150 to 300 Da. The module was ~64 mm in diameter and 356 mm in length. The HL membrane showed maximum >80% fluoride retention [88]. In a different experiment, two commercial polyamide membranes (NF90 and NF400) had different MWCOs, 90 and 400. NF90 rejected all the fluoride ions practically. There was no influence of feed concentration on fluoride, whereas NF400 showed no remarkable performances [89]. Three polyamide nanofiltration membranes (NF70 (Film Tec), DESAL 5DL (Osmonics), and MT 08(PCI)) were used for the defluoridation in natural brackish water from Senegal [90]. The efficiencies of these membranes were closely linked to the nature of the feed solution. The composite membranes were shaped into spiral wounds of a standard size (2540). The rejection rate [%] was 91, 83, and 90%, respectively, for 5 mg/l, at 8 bar pressure and pH 6 for these membranes [90, 91]. Valentukeviciene *et al.* [91] experimented with polyamide NF270 (piperazine based polyamide)

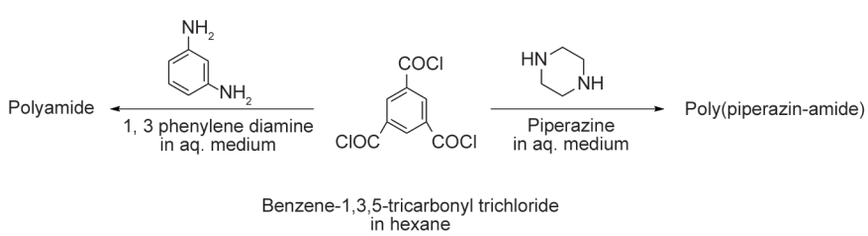

Figure 10. Chemistry of selective layer in thin film composite.

and NF90 (aromatic polyamide, Filmtec Dow) membranes. The NF90 can be regarded as a 'dense' and the NF270 as a 'loose' NF membrane. Both membranes are negatively charged (MWCO of NF90: 200 Da, NF270: 300 D [92]. NF270 represented lower roughness than NF90 [93]. The roughness of the membrane depends on the nature of monomers in interfacial polymerization, support polymers, and preparative conditions. The characteristic features influenced defluoridation performance. NF90 polyamide membrane retained 92% of fluoride ions, whereas NF270 polyamide kept 67%. The permeability results revealed that the NF270 membrane was more productive than the NF90 membrane, as evidenced by Hoinkis *et al*. [92] reported. NF270 could keep the fluoride level below the maximum contaminant level (MCL) (1.5 mg/l) up to 10 mg/l feed concentration. In contrast, the NF90 could keep fluoride permeate concentration below MCL for <20 mg/l feed concentration.

Commercial spiral wound RO-SG-2514 (Osmonics) and NF90-2540 (Dow-Filmtec) were used for the defluoridation of water and metal packaging industrial effluent [94]. Both were thin film polyamide composite membranes. The removal efficiency for fluoride was influenced by several parameters: feed concentration, transmembrane pressure, ionic strength, nature of cation associated with fluoride, and pH [95]. NF90-2540 membrane showed maximum rejection (>97.6%), whereas it was 92–97% for RO-SG. Diwara *et al*. [96] experimented with nanofiltration (NF) and low-pressure reverse osmosis (LPRO), both from Dow Chemical, in a membrane filtration plant constructed by Pall Corporation. The NF membrane resulted in a fluoride retention rate of 63.3–71%, whereas the low-pressure reverse osmosis (LPRO) membrane rejected 97–98.9%. Gedam *et al*. [97] experimented with defluoridation using Filmtec Spiral wound with a composite polyamide membrane module (model no. TW30-1812-75) with an effective area of 0.1054 m^2, module length of 300 mm and diameter of 40 mm. The spiral-wound membrane module was based on a polyamide membrane with an effective area of 2.5 m^2 (RE 2540, Saehan) [98]. It retained fluoride ions (retention factor >98%). Shen & Schäfer used six commercial membranes (BW30, BW30-LE, NF90, NF270, TFC-SR2 and TFC-SR3) [99]. All these membranes are thin film composite (TFC) membranes with a polyamide-based active layer [100–102]. Some details of the commercial membranes are summarised in Table 1. Chakrabortty *et al*. [104] experimented with three thin film polyamide composite nanofiltration membranes (NF-1, NF-2, and NF-20), Sepro Membranes Inc. (USA) for defluoridation. The fluoride rejection [%] was 95, 78, and 86, respectively. The separation performances depended on the difference in characteristics of the membranes. The features depend on the polymers and the membranes' preparation conditions. Three polyamide nanofiltration thin-film composite (TFC) membranes SR-1 (Koch Fluid System), DS-5-DL (DL) (Osmonics), and DS-51-HL (HL) (Osmonics) were used for the defluoridation performance [105]. The defluoridation performance increased with the higher solution flux and the lower feed concentration. Table 2 depicts the membrane's physical parameters (pore radius, pure water permeability, and surface electrical potential). The various

Table 1. Some details of some commercial membranes.

Membrane	Type	Diamine	Reference
A-15 (Permasep)	Polyamide	1, 3 phenylene diamine	[103]
NF90 (Dow filmtech)	Polyamide	1, 3 phenylene diamine	[102]
NF270 (Dow filmtech)	Poly(piperazine-amide)	Piperazine	
HL (GE Osmonics)	Poly(piperazine-amide)	Piperazine	
DL (GE Osmonics)	Poly(piperazine-amide)	Piperazine	
BW30 (Dow filmtech)	Polyamide	1, 3 phenylene diamine	

Table 2. Some parameters of different commercial membranes [105].

Membrane	Pure water permeability, $L_p \cdot 10^9$ [$m^3/(m^2 \cdot s \cdot kPa$]	Membrane pore radius, r_P [nm]	Membrane electrical potential, Ψ [mV]
SR-1	24.47±0.24	0.70±0.29	35.1±0.27
DS-5-DL (DL)	21.20±0.32	0.58±0.18	35.0±0.63
DS-51-HL (HL)	25.04±0.22	0.41±0.02	53.5±6.83

parameters (*viz.*, the support polymer rejecting polymer layer, reaction conditions) influenced the characteristics.

Researchers [106, 107] experimented with the four RO/NF polyamide membrane systems BW30, LE, NF90, and NF270. The first two were for brackish water, whereas NF90 and NF270 were for nanofiltration applications. NF90 membrane exhibited the best overall performance in water quantity and quality among the four. It was a pilot-scale solar-powered membrane system and employed high-fluoride brackish water in northern Tanzania. Throughout a typical solar day, the NF90 membrane system produced 1582 l of drinking water in permissible fluoride limits, with an average recovery of 27.8% and average specific energy consumption (SEC) of 1.6 kWh/m^3. Filmtec XLE-440 RO element was used for defluoridation [108]. The composition is unknown. The blending strategies were adopted to make it economical. The RO permeate water with a fluoride concentration of <0.03 mg/l was blended with the artificial groundwater to ensure a fluoride level below 1.3 mg/l in the drinking water.

The exciting study of Saxena *et al*. [109] showed the performance variation of poly(piperazine-amide) coating on different recycled stages of polysulfone (Ps) membranes(I^{st} to $VIII^{th}$). The ~15% increase in separation for 10 mg/l fluoride from Memb.-I-Pip to Memb.-VIII-Pip. The maximum separation of fluoride is 84.9% for Memb.-VIII-Pip.

Another attempt had been made to study the consequence of salt in a gelation bath and interfacial polymerization regarding the behaviour of poly(piperazine-amide) TFC membranes to separate fluoride from water. The flux through the polysulfone (Ps) membrane decreased with total dissolved salts (TDS). The increase in salt concentration in the aqueous phase of the interfacial reaction influenced the salt separation abilities of the TFC membranes. The maximum separation of fluoride was ~88% for the prepared membrane in which the salt concentration of the aqueous medium was 5 mg/l in the interfacial polymerization [110].

Apart from the thin film polyamide composite membranes, a few other membranes were experimented with. Iron(III) oxide (Fe_2O_3) nanoparticles modified polyethersulfone (PES)/cellulose acetate (CA) blend membranes were one of them [111]. Composite membranes were prepared by incorporating various amounts of Fe_2O_3 nanoparticles. The defluoridation potential was confirmed of the Fe_2O_3 nanoparticles for blended PES/CA membranes. The maximum fluoride removal efficiency of 70.3% was observed for a single run.

The hydrophobic nature of the polymers and polymer membranes played a role in membrane distillation. Plattner *et al*. [112] used commercial polytetrafluoroethylene (PTFE) membrane (General Electric, USA) in membrane distillation (MD). The key feature is the vapour-driven force compared to other pressure-driven technologies in membranes [113]. Direct contact MD produced high-quality water permeate (96–99% F rejection). Coupling with vacuum-enhanced DCMD (VEDCMD), the permeate flux increased by 42%. Hydrophobic polyvinylidene fluoride (PVDF) hollow fiber membranes in membrane distillation [114]. Direct contact membrane distillation (DCMD) is one of the techniques where the hydrophobic membrane directly partitions the feed and the distillate. It was simple, and the condensation occurred inside the membrane module. The maximum permeate flux was 35.6 kg/(m^2·h).

The ion exchange membranes can remove fluoride ions from water. It shows ion permselectivity and is classified into cation and anion exchange membranes. The positively charged groups are fixed to the anion exchange membrane, and cations are rejected by the positive charge and cannot permeate through anion exchange membranes. This is because anion exchange membranes are only permeable by anions. The electro dialyzer controls selective permeation. The ion exchange membranes have advantages over the ion exchange granules regarding regeneration. The regeneration is not required as it allows ions to permeate by direct current in an electro dialyzer.

The ion exchange membranes are polymer-based. Mostly anion-exchange membranes *viz.* DSV, AFX, AMX, ACS, AFN, AHA, and SB-6407) had the defluoridation potential [115–117]. AFX anion exchange membrane (polystyrene-divinyl benzene-polyvinyl chloride) was used in a diluted solution [118]. The ion exchange group associated with it was $–N(R)_3^+$. It was based on the chemical potential difference between the two compartments partitioned by an ion-exchange polymer. The plasma-modified membranes showed better flux and recovery values compared to pristine membranes. Tor [119] used Neosepta-ACM (anion-exchange membrane) (Tokuyama Soda Co. Ltd.) in the Donnan dialysis

condition. ACM membrane possesses quaternary ammonium as functionality. The membrane was in the chloride ion form. The transport of fluoride ions was maximum at pH 6 of the feed phase and pH 1 of the receiver phase. Durmaz *et al*. [117] experimented with anion exchange membranes used to remove fluoride. The nature of membranes was homogeneous and contained quaternary ammonium bases as ionic groups. They (AFN, AHA, SB-6407) were different from each other in the degree of crosslinking. The fluoride transport order was as follows: AFN>AHA>SB-6407.

Polyvinylidene fluoride (PVDF) blend poly(methyl methacrylate)-*co*-poly(chloromethyl styrene) (PMMA-*co*-PCMSt) membranes prepared through a nonsolvent induced phase separation process (Figure 11). Post-treatment with a tertiary diamine (tetramethyl diamino hexane, TMDAH) of the membranes made it fit for defluoridation. The membrane containing 69.5% w/w copolymer and 30.5% w/w PVDF exhibited excellent fluoride removal efficiency [120].

Membrane capacitive deionization (MCDI) is an advanced technique developed by Lee *et al*. [121]. In the MCDI technique, the counterions (ions with a different charge from the local electrode) are more fully depleted through electrode desorption [122]. Capacitive membrane deionization (MCDI) combined with a monovalent anion permselective exchange membrane (PSM) was the technique for defluoridation [78]. The MCDI unit cell comprised an acrylic plate, anode electrode, cation exchange membrane (NeoceptaCMX, Tokuyama, Japan), nylon spacer, anion exchange membrane (NeoceptaAMX, Tokuyama, Japan, and SelemionASV, Asahi Glass, Japan), a cathode electrode, and acrylic plate.

Porous membrane composites based on poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) with adsorbents (*viz*. montmorillonite (MMT), zeolites (NaY), bayerite (BAY) and hydroxyapatite (CaHAp)) were prepared by thermally induced phase separation [123]. A maximum fluoride separation of 68% was obtained after 6 filtrations for the CaHAp/P(VDF-HFP) composite membranes.

Cellulose acetate-based mixed matrix membrane (MMM) using mixed metal oxides nanoparticles-polymer composite (Fe-Al-Mn@chitosan) as nanofiller was used in defluoridation [124]. The total fluoride ion rejection (11 096 mg F^-/m^2) by the M8 membrane (CA: Fe-Al-Mn@chitosan 92:8) was found to be much higher compared to calculated fluoride rejection, which may be expected through adsorption only (92 mg F/m^2). The two mechanistic ways proposed were electrostatic repulsion between F^- and negatively charged MMM surface and the

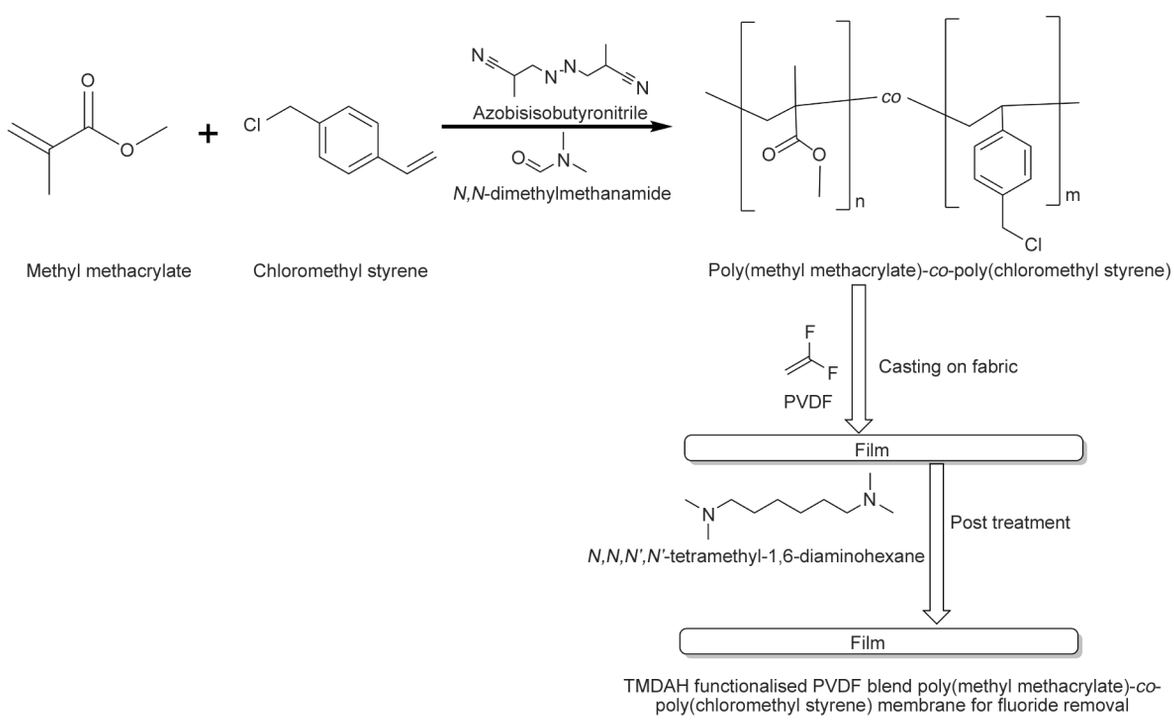

Figure 11. Schematic presentation of PMMA-*co*-PCMSt copolymer synthesis and preparation of blend membrane using the nonsolvent induced phase separation and post-treatment with TMDAH [120].

water-swelling nature of chitosan. The swelling nature of chitosan-cellulose acetate pores might create more resistance to water flow.

5. Conclusions

The growing global need for water and water treatment has driven the widespread development of Polymeric materials. The researcher's creative power brings forth modified polymers, revealing the possibilities to defluorinate water. The inherent characteristics of polymers made it possible to achieve the requisite properties. The polymeric adsorbent and membrane have paved their water in defluoridation. The other direction of polymeric materials is macrocycles (via the crown ether, cyclodextrin, porphyrins) based compounds in which flexible design for specific structures and functions showed many possibilities. It may be promising in the recognition of ions through host-guest chemistry and non-covalent interactions [125, 126]. The stupendous research efforts of polymeric development show people's confidence in the future.

Acknowledgements

Financial support from the Gujarat Council of Science and Technology (GUJCOST), India, is acknowledged. The manuscript has the CSIR-CSMCRI communication number 222/2022.

References

[1] Carrard N., Foster T., Willetts J.: Groundwater as a source of drinking water in southeast Asia and the Pacific: A multi-country review of current reliance and resource concerns. Water, **11**, 1605 (2019). https://doi.org/10.3390/w11081605

[2] Katsanou K., Karapanagioti H. K.: Surface water and groundwater sources for drinking water. in 'Applications of advanced oxidation processes (AOPs) in drinking water treatment' (eds.: Gil A., Galeano L. A., Vicente M. Á.) Springer, Cham, Vol. 67, 1–19 (2017). https://doi.org/10.1007/698_2017_140

[3] Podgorski J., Berg M.: Global analysis and prediction of fluoride in groundwater. Nature Communications, **13**, 4232 (2022). https://doi.org/10.1038/s41467-022-31940-x

[4] Jagtap S., Yenkie M. K., Labhsetwar N., Rayalu S.: Fluoride in drinking water and defluoridation of water. Chemical Reviews, **112**, 2454–2466 (2012). https://doi.org/10.1021/cr2002855

[5] Meenakshi, Maheshwari R. C.: Fluoride in drinking water and its removal. Journal of Hazardous Materials, **137**, 456–463 (2006). https://doi.org/10.1016/j.jhazmat.2006.02.024

[6] Mohapatra M., Anand S., Mishra B. K., Giles D. E., Singh P.: Review of fluoride removal from drinking water. Journal of Environmental Management, **91**, 67–77 (2009). https://doi.org/10.1016/j.jenvman.2009.08.015

[7] García M. G., Borgnino L.: Fluoride in the context of the environment. in 'Fluorine: Chemistry, analysis, function and effects' (ed.: Preedy V.) Royal Society of Chemistry Publishing, London, 3–21 (2015).

[8] Sharma S., Bhattacharya A.: Drinking water contamination and treatment techniques. Applied Water Science, **7**, 1043–1067 (2017). https://doi.org/10.1007/s13201-016-0455-7

[9] Kumar H., Patel M., Mohan D.: Simplified batch and fixed-bed design system for efficient and sustainable fluoride removal from water using slow pyrolyzed okra stem and black gram straw biochars. ACS Omega, **4**, 19513–19525 (2019). https://doi.org/10.1021/acsomega.9b00877

[10] Adimall N., Li P., Venkatayogi S.: Hydrogeochemical evaluation of groundwater quality for drinking and irrigation purposes and integrated interpretation with water quality index studies. Environmental Processes, **5**, 363–383 (2018). https://doi.org/10.1007/s40710-018-0297-4

[11] Haritash A. K., Aggarwal A., Soni J., Sharma K., Sapra M., Singh B.: Assessment of fluoride in groundwater and urine, and prevalence of fluorosis among school children in Haryana, India. Applied Water Science, **8**, 52 (2018). https://doi.org/10.1007/s13201-018-0691-0

[12] Bundschuh J., Maity J. P., Mushtaq S., Vithanage M., Seneweera S., Schneider J., Bhattacharya P., Khan N. I., Hamawand I., Guilherme L. R. G., Reardon-Smith K., Parvez F., Morales-Simfors N., Ghaze S., Pudmenzky C., Kouadio L., Chen C-Y.: Medical geology in the framework of the sustainable development goals. Science of the Total Environment, **581–582**, 87–104 (2017). https://doi.org/10.1016/j.scitotenv.2016.11.208

[13] Kimambo V., Bhattacharya P., Mtalo F., Mtamba J., Ahmad A.: Fluoride occurrence in groundwater systems at global scale and status of defluoridation – State of the art. Groundwater for Sustainable Development, **9**, 100223 (2019). https://doi.org/10.1016/j.gsd.2019.100223

[14] Bansiwal A., Thakre D., Labhshetwar N., Meshram S., Rayalu S.: Fluoride removal using lanthanum incorporated chitosan beads. Colloids and Surfaces B: Biointerfaces, **74**, 216–224 (2009). https://doi.org/10.1016/j.colsurfb.2009.07.021

[15] Karthikeyan M., Kumar K. K. S., Elango K. P.: Batch sorption studies on the removal of fluoride ions from water using eco-friendly conducting polymer/bio-polymer composites. Desalination, **267**, 49–56 (2011). https://doi.org/10.1016/j.desal.2010.09.005

[16] Li X., Li Y., Zhang S., Ye Z.: Preparation and characterization of new foam adsorbents of poly(vinyl alcohol)/chitosan composites and their removal for dye and heavy metal from aqueous solution. Chemical Engineering Journal, **183**, 88–97 (2012).
https://doi.org/10.1016/j.cej.2011.12.025

[17] Viswanathan N., Sundaram C. S., Meenakshi S.: Sorption behaviour of fluoride on carboxylated cross-linked chitosan beads. Colloids and Surfaces B: Biointerfaces, **68**, 48–54 (2009).
https://doi.org/10.1016/j.colsurfb.2008.09.009

[18] Swain S. K., Dey R. K., Islam M., Patel R. K., Jha U., Patnaik T., Airoldi C.: Removal of fluoride from aqueous solution using aluminum-impregnated chitosan biopolymer. Separation Science and Technology, **44**, 2096–2116 (2009).
https://doi.org/10.1080/01496390902881212

[19] Preethi J., Meenakshi S.: Fabrication of La^{3+} impregnated chitosan/β-cyclodextrin biopolymeric materials for effective utilization of chromate and fluoride adsorption in single systems. Journal of Chemical and Engineering Data, **63**, 723–731 (2018).
https://doi.org/10.1021/acs.jced.7b00889

[20] Chaudhary M., Rawat S., Jain N., Bhatnagar A., Maiti A.: Chitosan-Fe-Al-Mn metal oxyhydroxides composite as highly efficient fluoride scavenger for aqueous medium. Carbohydrate Polymers, **216**, 140–148 (2019).
https://doi.org/10.1016/j.carbpol.2019.04.028

[21] Ma J., Shen Y., Shen C., Wen Y., Liu W.: Al-doping chitosan–Fe(III) hydrogel for the removal of fluoride from aqueous solutions. Chemical Engineering Journal, **248**, 98–106 (2014).
https://doi.org/10.1016/j.cej.2014.02.098

[22] Zhou Y., Yu C., Shan Y.: Adsorption of fluoride from aqueous solution on La^{3+}-impregnated cross-linked gelatin. Separation and Purification Technology, **36**, 89–94 (2004).
https://doi.org/10.1016/S1383-5866(03)00167-9

[23] Thakur N., Kumar S. A., Wagh D. N., Das S., Pandey A. K., Kumar S. D., Reddy A. V. R.: Matrix supported tailored polymer for solid phase extraction of fluoride from variety of aqueous streams. Journal of Hazardous Materials, **201–202**, 193–201 (2012).
https://doi.org/10.1016/j.jhazmat.2011.11.065

[24] Wang J., Lin X., Luo X., Yao W.: Preparation and characterization of the linked lanthanum carboxymethylcellulose microsphere adsorbent for removal of fluoride from aqueous solutions. RSC Advances, **5**, 59273–59285 (2015).
https://doi.org/10.1039/C5RA07024D

[25] Viswanathan N., Meenakshi S.: Role of metal ion incorporation in ion exchange resin on the selectivity of fluoride. Journal of Hazardous Materials, **162**, 920–930 (2009).
https://doi.org/10.1016/j.jhazmat.2008.05.118

[26] Wu L., Lin X., Zhou X., Luo X.: Removal of uranium and fluorine from wastewater by double-functional microsphere adsorbent of SA/CMC loaded with calcium and aluminum. Applied Surface Science, **384**, 466–479 (2016).
https://doi.org/10.1016/j.apsusc.2016.05.056

[27] He J., Cui A., Ni F., Deng S., Shen F., Yang G.: A novel 3D yttrium based-graphene oxide-sodium alginate hydrogel for remarkable adsorption of fluoride from water. Journal of Colloid and Interface Science, **531**, 37–46 (2018).
https://doi.org/10.1016/j.jcis.2018.07.017

[28] Sapna, Raghav S., Nair M., Kumar D.: Trimetallic oxide entrapped in alginate polymeric matrix employed for adsorption studies of fluoride. Surfaces and Interfaces, **13**, 112–132 (2018).
https://doi.org/10.1016/j.surfin.2018.08.005

[29] Dogsa I., Tomšič M., Orehek J., Benigar E., Jamnik A., Stopar D.: Amorphous supramolecular structure of carboxymethyl cellulose in aqueous solution at different pH values as determined by rheology, small angle X-ray and light scattering. Carbohydrate Polymers, **111**, 492–504 (2014).
https://doi.org/10.1016/j.carbpol.2014.04.020

[30] Sinha V., Chakma S.: Synthesis and evaluation of CMC-*g*-AMPS/Fe/Al/AC composite hydrogel and their use in fluoride removal from aqueous solution. Environmental Technology and Innovation, **17**, 100620 (2020).
https://doi.org/10.1016/j.eti.2020.100620

[31] Sharma P., Sen K., Thakur P., Chauhan M., Chauhan K.: Spherically shaped pectin-*g*-poly(amidoxime)-Fe complex: A promising innovative pathway to tailor a new material in high amidoxime functionalization for fluoride adsorption. International Journal of Biological Macromolecules, **140**, 78–90 (2019).
https://doi.org/10.1016/j.ijbiomac.2019.08.098

[32] Zhu J., Lin X., Wu P., Luo X.: Pectin/Al_2O_3–ZrO_2 core/shell bead sorbent for fluoride removal from aqueous solution. RSC Advances, **6**, 27738–27749 (2016).
https://doi.org/10.1039/C5RA26404A

[33] Bhandari R., Janardhana C.: Calcium–zirconium–polyvinyl alcohol polymer composite film as a promising adsorbent for removal of fluoride from aqueous solution. Desalination and Water Treatment, **57**, 9437–9443 (2016).
https://doi.org/10.1080/19443994.2015.1027961

[34] Mani S. K., Bhandari R., Nehra A.: Self-assembled cylindrical Zr(IV), Fe(III) and Cu(II) impregnated polyvinyl alcohol-based hydrogel beads for real-time application in fluoride removal. Colloids and Surfaces A: Physicochemical and Engineering Aspects, **610**, 125751 (2021).
https://doi.org/10.1016/j.colsurfa.2020.125751

[35] Wood C. D., Tan B., Trewin A., Niu H., Bradshaw D., Rosseinsky M. J., Khimyak Y. Z., Campbell N. L., Kirk R., Stöckel E., Cooper A. I.: Hydrogen storage in microporous hypercrosslinked organic polymer networks. Chemistry of Materials, **19**, 2034–2048 (2007). https://doi.org/10.1021/cm070356a

[36] Tan L., Tan B.: Hypercrosslinked porous polymer materials: Design, synthesis, and applications. Chemical Society Reviews, **46**, 3322–3356 (2017). https://doi.org/10.1039/C6CS00851H

[37] Robshaw T. J., James A. M., Hammond D. B., Reynolds J., Dawson R., Ogden M. D.: Calcium-loaded hydrophilic hypercrosslinked polymers for extremely high defluoridation capacity *via* multiple uptake mechanisms. Journal of Materials Chemistry A, **8**, 7130–7144 (2020). https://doi.org/10.1039/C9TA12285K

[38] Khan H., Sharma C. R., Sharma S.: Fabrication of sustainable organometallic polymeric adsorbents for remediation of fluoride from water: A novel approach. Journal of Water Process Engineering, **20**, 149–159 (2017). https://doi.org/10.1016/j.jwpe.2017.10.009

[39] Khan H., Gupta A. R., Sharma S.: Organometallic adsorbent for mitigating fluoride from water: An environment-friendly approach. ChemistrySelect, **3**, 11765–11774 (2018). https://doi.org/10.1002/slct.201802406

[40] Gupta A. R., Yadav A., Sharma S.: Scavenging fluoride from the aqueous system with porous organometallic three-dimensional architecture: An emerging adsorbent. Environmental Science and Pollution Research, **28**, 19166–19178 (2021). https://doi.org/10.1007/s11356-020-11916-4

[41] Gupta A. R., Ranawat B., Singh A., Yadav A., Sharma S.: Zirconium-silver nano organo-bimetallic network for scavenging hazardous ions from water and its antibacterial potentiality: An environment-friendly approach. Journal of Environmental Chemical Engineering, **9**, 105356 (2021). https://doi.org/10.1016/j.jece.2021.105356

[42] Gupta A. R., Joshi V. C., Yadav A., Sharma S.: Synchronous removal of arsenic and fluoride from aqueous solution: A facile approach to fabricate novel functional metallopolymer microspheres. ACS Omega, **7**, 4879–4891 (2022). https://doi.org/10.1021/acsomega.1c05456

[43] Gupta A. R., Chavda D., Mondal M., Manna M., Sharma S.: Strategic design of advanced sustainable Quaternized poly(zirconyl dimethacrylate-*co*-vinyl imidazole) microsphere as a potential adsorbent for the mitigation of fluoride from aqueous solution. Journal of Water Process Engineering, **50**, 103290 (2022). https://doi.org/10.1016/j.jwpe.2022.103290

[44] Dong S., Wang Y.: Characterization and adsorption properties of a lanthanum-loaded magnetic cationic hydrogel composite for fluoride removal. Water Research, **88**, 852–860 (2016). https://doi.org/10.1016/j.watres.2015.11.013

[45] Li Z., Li H., Xia H., Ding X., Luo X., Liu X., Mu Y.: Triarylboron-linked conjugated microporous polymers: Sensing and removal of fluoride ions. Chemistry A European Journal, **21**, 17355–17362 (2015). https://doi.org/10.1002/chem.201502241

[46] Valdez-Alegría C., Fuentes-Rivas R., García-Rivas J., Arce R. E. Z., de la Luz Jiménez Núñez M., García-Gaitán B.: Synthesis of chitosan-polyvinyl alcohol biopolymers to eliminate fluorides from water. Biomolecules, **10**, 156 (2020). https://doi.org/10.3390/biom10010156

[47] Wu H-X., Wang T-J., Dou X-M., Zhao B., Chen L., Jin Y.: Spray coating of adsorbent with polymer latex on sand particles for fluoride removal in drinking water. Industrial and Engineering Chemistry Research, **47**, 4697–4702 (2008). https://doi.org/10.1021/ie800278b

[48] Koilraj P., Kannan S.: Aqueous fluoride removal using ZnCr layered double hydroxides and their polymeric composites: Batch and column studies. Chemical Engineering Journal, **234**, 406–415 (2013). https://doi.org/10.1016/j.cej.2013.08.101

[49] Parashar K., Ballav N., Debnath S., Pillay K., Maity A.: Hydrous ZrO_2 decorated polyaniline nanofibres: Synthesis, characterization and application as an efficient adsorbent for water defluoridation. Journal of Colloid and Interface Science, **508**, 342–358 (2017). https://doi.org/10.1016/j.jcis.2017.08.044

[50] Karthikeyan M., Satheesh Kumar K. K., Elango K. P.: Conducting polymer/alumina composites as viable adsorbents for the removal of fluoride ions from aqueous solution. Journal of Fluorine Chemistry, **130**, 894–901 (2009). https://doi.org/10.1016/j.jfluchem.2009.06.024

[51] Parashar K., Ballav N., Debnath S., Pillay K., Maity A.: Hydrous TiO_2@polypyrrole hybrid nanocomposite as an efficient selective scavenger for the defluoridation of drinking water. RSC Advances, **6**, 99482–99495 (2016). https://doi.org/10.1039/C6RA20151B

[52] Parashar K., Ballav N., Debnath S., Pillay K., Maity A.: Rapid and efficient removal of fluoride ions from aqueous solution using a polypyrrole coated hydrous tin oxide nanocomposite. Journal of Colloid and Interface Science, **476**, 103–118 (2016). https://doi.org/10.1016/j.jcis.2016.05.013

[53] Wang M., Yan W., Kong W., Wu Z., An X., Wang Z., Hao X., Guan G.: An electroactive and regenerable Fe_3O_4@polypyrrole nanocomposite: Fabrication and its defluorination in an electromagnetic coupling system. Industrial and Engineering Chemistry Research, **56**, 12738–12744 (2017). https://doi.org/10.1021/acs.iecr.7b02601

[54] Aigbe U. O., Onyancha R. B., Ukhurebor K. E., Obodo K. O.: Removal of fluoride ions using a polypyrrole magnetic nanocomposite influenced by a rotating magnetic field. RSC Advances, **10**, 595–609 (2020). https://doi.org/10.1039/C9RA07379E

[55] Chigondo M., Paumo H. K., Bhaumik M., Pillay K., Maity A.: Hydrous CeO_2-Fe_3O_4 decorated polyaniline fibers nanocomposite for effective defluoridation of drinking water. Journal of Colloid and Interface Science, **532**, 500–516 (2018). https://doi.org/10.1016/j.jcis.2018.07.134

[56] Wang X., Pan S., Zhang M., Qi J., Sun X., Gu C., Wang L., Li J.: Modified hydrous zirconium oxide/PAN nanofibers for efficient defluoridation from groundwater. Science of the Total Environment, **685**, 401–409 (2019). https://doi.org/10.1016/j.scitotenv.2019.05.380

[57] Mukherjee S., Ramireddy H., Baidya A., Amala A. K., Sudhakar C., Mondal B., Philip L., Pradeep T.: Nanocellulose-reinforced organo-inorganic nanocomposite for synergistic and affordable defluoridation of water and an evaluation of its sustainability metrics. ACS Sustainable Chemistry and Engineering, **8**, 139–147 (2020). https://doi.org/10.1021/acssuschemeng.9b04822

[58] Karthikeyan M., Satheesh Kumar K. K., Elango K. P.: Studies on the defluoridation of water using conducting polymer/montmorillonite composites. Environmental Technology, **33**, 733–739 (2012). https://doi.org/10.1080/09593330.2011.592224

[59] Chen Y., Li J., Xu H.: Removal of F from water using PPyCl/ATP composites. in 'Proceedings of the 2016 4th International Conference on Renewable Energy and Environmental Technology (ICREET 2016), Paris, France' 636–640 (2017).

[60] Popat K. M., Anand P. S., Dasare B. D.: Selective removal of fluoride ions from water by the aluminium form of the aminomethylphosphonic acid-type ion exchanger. Reactive Polymers, **23**, 23–32 (1994). https://doi.org/10.1016/0923-1137(94)90107-4

[61] Samatya S., Mizuki H., Ito Y., Kawakita H., Uezu K.: The effect of polystyrene as a porogen on the fluoride ion adsorption of Zr(IV) surface-immobilized resin. Reactive and Functional Polymers, **70**, 63–68 (2010). https://doi.org/10.1016/j.reactfunctpolym.2009.10.004

[62] Viswanathan N., Prabhu S. M., Meenakshi S.: Development of amine functionalized *co*-polymeric resins for selective fluoride sorption. Journal of Fluorine Chemistry, **153**, 143–150 (2013). https://doi.org/10.1016/j.jfluchem.2013.04.002

[63] Cai J., Zhang Y., Pan B., Zhang W., Lv L., Zhang Q.: Efficient defluoridation of water using reusable nanocrystalline layered double hydroxides impregnated polystyrene anion exchanger. Water Research, **102**, 109–116 (2016). https://doi.org/10.1016/j.watres.2016.06.030

[64] Pan B., Xu J., Wu B., Li Z., Liu X.: Enhanced removal of fluoride by polystyrene anion exchanger supported hydrous zirconium oxide nanoparticles. Environmental Science and Technology, **47**, 9347–9354 (2013). https://doi.org/10.1021/es401710q

[65] Singh S., German M., Chaudhari S., Sengupta A. K.: Fluoride removal from groundwater using zirconium impregnated anion exchange resin. Journal of Environmental Management, **263**, 110415 (2020). https://doi.org/10.1016/j.jenvman.2020.110415

[66] Dong H., Tang H., Shi X., Yang W., Chen W., Li H., Zhao Y., Zhang Z., Hua M.: Enhanced fluoride removal from water by nanosized cerium oxides impregnated porous polystyrene anion exchanger. Chemosphere, **287**, 131932 (2022). https://doi.org/10.1016/j.chemosphere.2021.131932

[67] Robshaw T., Tukra S., Hammond D. B., Leggett G. J., Ogden M. D.: Highly efficient fluoride extraction from simulant leachate of spent potlining *via* La-loaded chelating resin. An equilibrium study. Journal of Hazardous Materials, **361**, 200–209 (2019). https://doi.org/10.1016/j.jhazmat.2018.07.036

[68] Meenakshi S., Viswanathan N.: Identification of selective ion-exchange resin for fluoride sorption. Journal of Colloid and Interface Science, **308**, 438–450 (2007). https://doi.org/10.1016/j.jcis.2006.12.032

[69] Markovski J., Garcia J., Hristovski K. D., Westerhoff P.: Nano-enabling of strong-base ion-exchange media *via* a room-temperature aluminum (hydr)oxide synthesis method to simultaneously remove nitrate and fluoride. Science of the Total Environment, **599–600**, 1848–1855 (2017). https://doi.org/10.1016/j.scitotenv.2017.05.083

[70] Paudyal H., Inoue K., Kawakita H., Ohto K., Kamata H., Alam S.: Removal of fluoride by effectively using spent cation exchange resin. Journal of Material Cycles and Waste Management, **20**, 975–984 (2018). https://doi.org/10.1007/s10163-017-0659-4

[71] Solangi I. B., Memon S., Bhanger M. I.: Removal of fluoride from aqueous environment by modified Amberlite resin. Journal of Hazardous Materials, **171**, 815–819 (2009). https://doi.org/10.1016/j.jhazmat.2009.06.072

[72] Demirkalp G., Alamut S., Arar Ö., Yüksel Ü., Yüksel M.: Removal of fluoride from water by Al(III)-loaded and $Al(OH)_3$-coated chelating resin. Desalination and Water Treatment, **57**, 15910–15919 (2015). https://doi.org/10.1080/19443994.2015.1074117

[73] Millar G. J., Couperthwaite S. J., Wellner D. B., Macfarlane D. C., Dalzell S. A.: Removal of fluoride ions from solution by chelating resin with imino-diacetate functionality. Journal of Water Process Engineering, **20**, 113–122 (2017). https://doi.org/10.1016/j.jwpe.2017.10.004

[74] Joshi S., Jana S.: Interaction of aqueous phase fluoride and Amberlite IR400Cl resin: Evaluation of batch process. Chemical Data Collections, **32**, 100643 (2021). https://doi.org/10.1016/j.cdc.2020.100643

[75] Gangani N., Joshi V. C., Sharma S., Bhattacharya A.: Fluoride contamination in water: Remediation strategies through membranes. Groundwater for Sustainable Development, **17**, 100751 (2022). https://doi.org/10.1016/j.gsd.2022.100751

[76] Grzegorzek M., Majewska-Nowak K., Ahmed A. E.: Removal of fluoride from multicomponent water solutions with the use of monovalent selective ion-exchange membranes. Science of the Total Environment, **722**, 137681 (2020). https://doi.org/10.1016/j.scitotenv.2020.137681

[77] Damtie M. M., Woo Y. C., Kim B., Hailemariam R. H., Park K-D., Shon H. K., Park C., Choi J-S.: Removal of fluoride in membrane-based water and wastewater treatment technologies: Performance review. Journal of Environmental Management, **251**, 109524 (2019). https://doi.org/10.1016/j.jenvman.2019.109524

[78] Pan J., Zheng Y., Ding J., Gao C., van der Bruggen B., Shen J.: Fluoride removal from water by membrane capacitive deionization with a monovalent anion selective membrane. Industrial and Engineering Chemistry Research, **57**, 7048–7053 (2018). https://doi.org/10.1021/acs.iecr.8b00929

[79] Cadotte J., Forester R., Kim M., Petersen R., Stocker T.: Nanofiltration membranes broaden the use of membrane separation technology. Desalination, **70**, 77–88 (1988). https://doi.org/10.1016/0011-9164(88)85045-8

[80] Chen S-H., Chang D-J., Liou R-M., Hsu C-S., Lin S-S.: Preparation and separation properties of polyamide nanofiltration membrane. Journal of Applied Polymer Science, **83**, 1112–1118 (2002). https://doi.org/10.1002/app.2282

[81] Mehiguene K., Garba Y., Taha S., Gondrexon N., Dorange G.: Influence of operating conditions on the retention of copper and cadmium in aqueous solutions by nanofiltration: Experimental results and modelling. Separation and Purification Technology, **15**, 181–187 (1999). https://doi.org/10.1016/S1383-5866(98)00096-3

[82] Mehta R., Bhattacharya A.: Diamines as tunable chemicals in thin film composite membrane formation. in 'Advances in chemistry research' (ed.: Taylor J. C.) Nova Science, New York, Vol. 62, 201 (2020).

[83] Khan M. M. T., Stewart P. S., Moll D. J., Mickols W. E., Nelson S. E., Camper A. K.: Characterization and effect of biofouling on polyamide reverse osmosis and nanofiltration membrane surfaces. Biofouling, **27**, 173–183 (2011). https://doi.org/10.1080/08927014.2010.551766

[84] Owusu-Agyeman I., Shen J., Schäfer A. I.: Renewable energy powered membrane technology: Impact of pH and ionic strength on fluoride and natural organic matter removal. Science of the Total Environment, **621**, 138–147 (2018). https://doi.org/10.1016/j.scitotenv.2017.11.111

[85] Owusu-Agyeman I., Reinwald M., Jeihanipour A., Schäfer A. I.: Removal of fluoride and natural organic matter from natural tropical brackish waters by nanofiltration/reverse osmosis with varying water chemistry. Chemosphere, **217**, 47–58 (2019). https://doi.org/10.1016/j.chemosphere.2018.10.135

[86] Lhassani A., Rumeau M., Benjelloun D., Pontie M.: Selective demineralization of water by nanofiltration application to the defluorination of brackish water. Water Research, **35**, 3260–3264 (2001). https://doi.org/10.1016/S0043-1354(01)00020-3

[87] Choi S., Yun Z., Hong S., Ahn K.: The effect of *co*-existing ions and surface characteristics of nanomembranes on the removal of nitrate and fluoride. Desalination, **133**, 53–64 (2001). https://doi.org/10.1016/S0011-9164(01)00082-0

[88] Mnif A., ben Sik Ali M., Hamrouni B.: Effect of some physical and chemical parameters on fluoride removal by nanofiltration. Ionics, **16**, 245–253 (2010). https://doi.org/10.1007/s11581-009-0368-7

[89] Tahaikt M., el Habbani R., Ait Haddou A., Achary I., Amor Z., Taky M., Alami A., Boughriba A., Hafsi M., Elmidaoui A.: Fluoride removal from groundwater by nanofiltration. Desalination, **212**, 46–53 (2007). https://doi.org/10.1016/j.desal.2006.10.003

[90] Diawara C. K., Paugam L., Pontié M., Schlumpf J. P., Jaouen P., Quéméneur F.: Influence of chloride, nitrate, and sulphate on the removal of fluoride ions by using nanofiltration membranes. Separation Science and Technology, **40**, 3339–3347 (2005). https://doi.org/10.1080/01496390500423706

[91] Valentukeviciene M., Zurauskiene R., Boussouga Y. A.: Fluoride removal from groundwater by technological process optimization. Ecological Chemistry and Engineering S, **26**, 133–147 (2019). https://doi.org/10.1515/eces-2019-0010

[92] Hoinkis J., Valero-Freitag S., Caporgno M. P., Pätzold C.: Removal of nitrate and fluoride by nanofiltration – A comparative study. Desalination and Water Treatment, **30**, 278–288 (2011). https://doi.org/10.5004/dwt.2011.2103

[93] Chung H-K., Kim W-H., Park J., Cho J., Jeong T-Y., Park P-K.: Application of Langmuir and Freundlich isotherms to predict adsorbate removal efficiency or required amount of adsorbent. Journal of Industrial and Engineering Chemistry, **28**, 241–246 (2015). https://doi.org/10.1016/j.jiec.2015.02.021

[94] Bejaoui I., Mnif A., Hamrouni B.: Performance of reverse osmosis and nanofiltration in the removal of fluoride from model water and metal packaging industrial effluent. Separation Science and Technology, **49**, 1135–1145 (2014). https://doi.org/10.1080/01496395.2013.878956

[95] Richards L. A., Vuachère M., Schäfer A. I.: Impact of pH on the removal of fluoride, nitrate and boron by nanofiltration/reverse osmosis. Desalination, **261**, 331–337 (2010). https://doi.org/10.1016/j.desal.2010.06.025

[96] Diawara C. K., Diop S. N., Diallo M. A., Farcy M., Deratani A.: Performance of nanofiltration (NF) and low pressure reverse osmosis (LPRO) membranes in the removal of fluorine and salinity from brackish drinking water. Journal of Water Resource and Protection, **3**, 912–917 (2011). https://doi.org/10.4236/jwarp.2011.312101

[97] Gedam V. V., Patil J. L., Kangne S., Sisram R. S., Labhasetwar P.: Performance evaluation of polyamide reverse osmosis membrane for removal of contaminants in ground water collected from chandrapur district. Journal of Membrane Science and Technology, **02**, 1000117 (2012). https://doi.org/10.4172/2155-9589.1000117

[98] Ndiaye P. I., Moulin P., Dominguez L., Millet J. C., Charbit F.: Removal of fluoride from electronic industrial effluentby RO membrane separation. Desalination, **173**, 25–32 (2005). https://doi.org/10.1016/j.desal.2004.07.042

[99] Shen J., Schäfer A. I.: Factors affecting fluoride and natural organic matter (NOM) removal from natural waters in Tanzania by nanofiltration/reverse osmosis. Science of the Total Environment, **527–528**, 520–529 (2015). https://doi.org/10.1016/j.scitotenv.2015.04.037

[100] Freger V., Gilron J., Belfer S.: TFC polyamide membranes modified by grafting of hydrophilic polymers: An FT-IR/AFM/TEM study. Journal of Membrane Science, **209**, 283–292 (2002). https://doi.org/10.1016/S0376-7388(02)00356-3

[101] Pontié M., Dach H., Leparc J., Hafsi M., Lhassani A.: Novel approach combining physico-chemical characterizations and mass transfer modelling of nanofiltration and low pressure reverse osmosis membranes for brackish water desalination intensification. Desalination, **221**, 174–191 (2008). https://doi.org/10.1016/j.desal.2007.01.075

[102] Tang C. Y., Kwon Y-N., Leckie J. O.: Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes: I. FTIR and XPS characterization of polyamide and coating layer chemistry. Desalination, **242**, 149–167 (2009). https://doi.org/10.1016/j.desal.2008.04.003

[103] Lee K. P., Arnot T. C., Mattia D.: A review of reverse osmosis membrane materials for desalination – Development to date and future potential. Journal of Membrane Science, **370**, 1–22 (2011). https://doi.org/10.1016/j.memsci.2010.12.036

[104] Chakrabortty S., Roy M., Pal P.: Removal of fluoride from contaminated groundwater by cross flow nanofiltration: Transport modeling and economic evaluation. Desalination, **313**, 115–124 (2013). https://doi.org/10.1016/j.desal.2012.12.021

[105] Hu K., Dickson J. M.: Nanofiltration membrane performance on fluoride removal from water. Journal of Membrane Science, **279**, 529–538 (2006). https://doi.org/10.1016/j.memsci.2005.12.047

[106] Shen J., Richards B. S., Schäfer A. I.: Renewable energy powered membrane technology: Case study of St. Dorcas borehole in Tanzania demonstrating fluoride removal *via* nanofiltration/reverse osmosis. Separation and Purification Technology, **170**, 445–452 (2016). https://doi.org/10.1016/j.seppur.2016.06.042

[107] Boussouga Y-A., Richards B. S., Schäfer A. I.: Renewable energy powered membrane technology: System resilience under solar irradiance fluctuations during the treatment of fluoride-rich natural waters by different nanofiltration/reverse osmosis membranes. Journal of Membrane Science, **617**, 118452 (2021). https://doi.org/10.1016/j.memsci.2020.118452

[108] Sehn P.: Fluoride removal with extra low energy reverse osmosis membranes: Three years of large scale field experience in Finland. Desalination, **223**, 73–84 (2008). https://doi.org/10.1016/j.desal.2007.02.077

[109] Saxena M., Sharma S., Bhattacharya A.: Impacts of recycled polysulfone on the salt separation performance of thin film poly(piperazine-amide) membranes. Journal of Environmental Chemical Engineering, **9**, 105869 (2021). https://doi.org/10.1016/j.jece.2021.105869

[110] Saxena M., Bhattacharya A.: Innate connection between salts on preparation and separation performance of thin-film poly(piperazinamide) composite membrane. Materials and Manufacturing Processes, **37**, 1756–1765 (2022). https://doi.org/10.1080/10426914.2022.2049301

[111] Evangeline C., Pragasam V., Rambabu K., Velu S., Monash P., Arthanareeswaran G., Banat F.: Iron oxide modified polyethersulfone/cellulose acetate blend membrane for enhanced defluoridation application. Desalination and Water Treatment, **156**, 177–188 (2019). https://doi.org/10.5004/dwt.2018.23174

[112] Plattner J., Naidu G., Wintgens T., Vigneswaran S., Kazner C.: Fluoride removal from groundwater using direct contact membrane distillation (DCMD) and vacuum enhanced DCMD (VEDCMD). Separation and Purification Technology, **180**, 125–132 (2017). https://doi.org/10.1016/j.seppur.2017.03.003

[113] Alkhudhiri A., Darwish N., Hilal N.: Membrane distillation: A comprehensive review. Desalination, **287**, 2–18 (2012). https://doi.org/10.1016/j.desal.2011.08.027

[114] Hou D., Wang J., Zhao C., Wang B., Luan Z., Sun X.: Fluoride removal from brackish groundwater by direct contact membrane distillation. Journal of Environmental Sciences, **22**, 1860–1867 (2010). https://doi.org/10.1016/S1001-0742(09)60332-6

[115] Hichour M., Persin F., Molénat J., Sandeaux J., Gavach C.: Fluoride removal from diluted solutions by Donnan dialysis with anion-exchange membranes. Desalination, **122**, 53–62 (1999). https://doi.org/10.1016/S0011-9164(99)00027-2

[116] Hichour M., Persin F., Sandeaux J., Gavach C.: Fluoride removal from waters by Donnan dialysis. Separation and Purification Technology, **18**, 1–11 (1999). https://doi.org/10.1016/S1383-5866(99)00042-8

[117] Durmaz F., Kara H., Cengeloglu Y., Ersoz M.: Fluoride removal by Donnan dialysis with anion exchange membranes. Desalination, **177**, 51–57 (2005). https://doi.org/10.1016/j.desal.2004.11.016

[118] Alkan E., Kır E., Oksuz L.: Plasma modification of the anion-exchange membrane and its influence on fluoride removal from water. Separation and Purification Technology, **61**, 455–460 (2008). https://doi.org/10.1016/j.seppur.2007.12.012

[119] Tor A.: Removal of fluoride from water using anion-exchange membrane under Donnan dialysis condition. Journal of Hazardous Materials, **141**, 814–818 (2007). https://doi.org/10.1016/j.jhazmat.2006.07.043

[120] Mondal R., Pal S., Bhalani D. V., Bhadja V., Chatterjee U., Jewrajka S. K.: Preparation of polyvinylidene fluoride blend anion exchange membranes *via* non-solvent induced phase inversion for desalination and fluoride removal. Desalination, **445**, 85–94 (2018). https://doi.org/10.1016/j.desal.2018.07.032

[121] Lee J. B., Park K-K., Eum H-M., Lee C-W.: Desalination of a thermal power plant wastewater by membrane capacitive deionization. Desalination, **196**, 125–134 (2006). https://doi.org/10.1016/j.desal.2006.01.011

[122] Li H., Zou L.: Ion-exchange membrane capacitive deionization: A new strategy for brackish water desalination. Desalination, **275**, 62–66 (2011). https://doi.org/10.1016/j.desal.2011.02.027

[123] Nunes-Pereira J., Lima R., Choudhary G., Sharma P. R., Ferdov S., Botelho G., Sharma R. K., Lanceros-Méndez S.: Highly efficient removal of fluoride from aqueous media through polymer composite membranes. Separation and Purification Technology, **205**, 1–10 (2018). https://doi.org/10.1016/j.seppur.2018.05.015

[124] Chaudhary M., Maiti A.: Fe–Al–Mn@chitosan based metal oxides blended cellulose acetate mixed matrix membrane for fluoride decontamination from water: Removal mechanisms and antibacterial behavior. Journal of Membrane Science, **611**, 118372 (2020). https://doi.org/10.1016/j.memsci.2020.118372

[125] Chen W., Chen P., Zhang G., Xing G., Feng Y., Yang Y-W., Chen L.: Macrocycle-derived hierarchical porous organic polymers: Synthesis and applications. Chemical Society Reviews, **50**, 11684–11714 (2021). https://doi.org/10.1039/D1CS00545F

[126] Skorjanc T., Shetty D., Trabolsi A.: Pollutant removal with organic macrocycle-based covalent organic polymers and frameworks. Chem, **7**, 882–918 (2021). https://doi.org/10.1016/J.CHEMPR.2021.01.002