

Defluoridation by Nano-Materials, Building Materials and Other Miscellaneous Materials: A Systematic Review

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ABSTRACT:The ground and surface water sources are getting polluted by various hazardous contaminants added in them due to industrial wastewater and leaching of harmful metals from surrounding rocks and layer presents around it. The fluoride is one of the pollutants focused worldwide due to its hazardous effects on human, plants and animals. The fluoride in present in less concentration helps in the development of teeth and enamels whereas in large amount causes dental fluorosis, skeletal fluorosis and non-skeletal fluorosis like muscle fibre degeneration, low haemoglobin levels, deformities in RBCs, excessive thirst, headache, skin rashes, nervousness, neurological manifestations, depression, gastrointestinal problems, urinary tract malfunctioning, nausea, abdominal pain, tingling sensation in fingers and toes, reduced immunity, repeated abortions or still births, male sterility, etc. The problems caused by fluoride on large extent are spread widely in many parts of the world where the fluorosis is epidemic in more than 20 countries across the globe. In India, ground water of around 19 states is affected by fluoride pollution. The limitation of fluoride in drinking water as per World Health Organization is 1 and 1.5 mg/l. The defluoridation of water through adsorption process is well known economical method apart from coagulation-precipitation, ion-exchange, membrane processes, electro dialysis and electrocoagulation. The present paper deals with the short review on defluoridation of water by adsorption using nanomaterials, building materials and other miscellaneous materials as high fluoride uptake and low-cost adsorbents.

KEYWORDS:Nano materials, Building materials, Defluoridation, Health effect, Kinetic.

I. INTRODUCTION

Water is essentially required for all forms of life for their survivals, well-beings, societal up- liftmen and sustainable growth and everyday needs to fulfil their desires. The water covers almost 75 percent of surface of the earth. The water availability on earth crust is broadly classified into surface water, sub-surface and ground water. The major source of water available for competing the needs is surface water whereas ground water contributes only 0.6 percentage but the developing countries like India are mostly dependent on ground water to satisfy their daily requirements starting from drinking to agricultural purposes. Since few decades ground water have been found as safest the source of drinking water on the globe. But at present it is not regarded as safest source because it is being polluted day by day due to human activities for their urbanization and industrialization as well as dissolution and mixing of chemical elements from natural mineral resources available in the earth crust itself. Fluoride is one of the basic chemical pollutants available in water that comes into water by dissolution of fluoride containing rocks by their weathering and leaching or discharge by agricultural and industrials activities during manufacturing glass, electronics, steel, aluminium, bricks, tiles, ceramics, pesticide and fertilizer [1-3].

Fluoride is an anion which is reduced form of fluorine. It is the most reactive and electronegative element of halogen family and it is the thirteenth most abundant element by weight in the earth crust and accounts to about 0.3 g/kg of Earth's crust in minerals like topaz, fluorite, fluorapatite, cryolite, phosphorite, theorapatite etc [4]. In India, the major source of fluoride from fluorite and topaz minerals are widespread. Fluoride never exists in element state due to

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its high reactivity property. It is mostly associated with monovalent cations like NaF, HF and KF and divalent cations such as CaF_2 and PbF_2 . The oxidation state of fluoride ion is -1. The fluoride compounds present in an environment occurs mostly in inorganic form when compared to the organic compound.

The presence of fluoride in groundwater for the purpose of drinking purposes may be beneficial or detrimental depending on its concentration and amount indigested. The drinking water with low concentration of fluoride in the range of 0.4 to 1.0 mg/L is beneficial as it promotes calcification of dental enamel and protects teeth against tooth decay, whereas if it is present in excess amount, it causes multiple health problems ranging from mild dental fluorosis to crippling skeletal fluorosis [5]. According to the World Health Organization (WHO) [6], the maximum acceptable concentration of fluoride is 1.5 mg/l, while India's permissible limit of fluoride in drinking water is 1 mg/l [7]. Keeping in view the climatic condition of the hot and humid region, the US Public Health Service have reduced the permissible limit of fluoride from 1.7 to 0.8 mg/l with an increases in the average maximum daily air temperature [8]. High F intake have been suspected to be involved in a wide range of adverse and severe health problems in addition to fluorosis such as cancer, impaired kidney function, digestive and nervous disorders, reduced immunity, Alzheimer's disease, nausea, adverse pregnancy outcomes, respiratory problems, lesions of the endocrine glands, thyroid, liver and other organs [9-14].

The crises of fluoride is still more critical and increasing with full pace as per the survey carried out world-wide basis. The fluorosis is epidemic at least 28 countries namely Bangladesh, Bhutan, India, Pakistan, Sri Lanka and so on [5]. According to estimates of UNESCO more than 200 million people in the whole world rely on drinking water with fluoride concentration more than the limit as prescribed by WHO guideline value [15]. In India, alone 66 million people were affected by fluorosis and this problem was prevalent in 20 out of the 35 States, especially Rajasthan, Madhya Pradesh, Andhra Pradesh, Tamil Nadu, Gujarat and Uttar Pradesh [16-17]. The major source of fluoride in majority of countries are due to minerals existing in rocks and soil with which water interact.

The mitigation of fluorosis is most essential to prevent their hazardous impact on human beings, animals and plants. Most of the research works are still going on to remove or reduce the concentration of fluoride to make it fit for drinking purpose by various treatment methods since the alternative source of drinking water are limited or not available in most of the countries.

Our main objective is to provide a comprehensive review dealing with the recent developments. We wish that this article could serve a wide interest and inspire for amazing development in the field of research. Latest development for the use of various nano materials as an adsorbent to remove fluoride from water in many years are reported elaborately.

II. NANO MATERIALS ADSORBENTS

Li *et al.* (2001) prepared Al_2O_3 in amorphous form assisted supported on carbon nanotubes ($\text{Al}_2\text{O}_3/\text{CNTs}$) for the defluoridation of water. The optimum calcined temperature was noted as 450°C and aluminium loading was of 30% respectively where the maximum fluoride adsorption was attained at pH 5.0 to 9.0. At equilibrium concentration of 12 mg/l, the adsorption capacity of $\text{Al}_2\text{O}_3/\text{CNTs}$ was approximately 13.5 times higher than of AC-300, 4 times higher than $\gamma\text{-Al}_2\text{O}_3$. At the pH of 6.0, the adsorption capacity of $\text{Al}_2\text{O}_3/\text{CNTs}$ was 28.7 mg/g and equilibrium concentration of 50 mg/l was observed [18].

Li *et al.* (2003) who prepared aligned carbon nanotubes (ANTs) by catalytic decomposition of xylene using ferrocene as the basic catalyst. At pH of 7, the maximum adsorption capacity of ANTs was 4.5 mg/g and equilibrium concentration of 15 mg/l was attained. The adsorption of fluoride was authorized by the surface and inner cavities of ANTs. It was noticed the adsorption was very rapid and equilibrium was reached in 180 min. It proves that the experimental data was quiet sufficient for Freundlich isotherm model [19].

Li *et al.* (2003) used the prepared carbon nanotube supported alumina ($\text{Al}_2\text{O}_3/\text{CNTs}$) for fluoride removal from drinking water. Freundlich model was capable enough to desire the isotherm and adsorption was followed pseudo-second-order rate equation. The maximum fluoride removal took place by the $\text{Al}_2\text{O}_3/\text{CNTs}$ synthesized with calcined temperature of 450°C and 30% of alumina loading and possessed the largest adsorption capacity of 9.6 mg/g where the optimum pH range was between 6.0 and 9.0. When the surface was positively charged, fluoride sorption occurred by ligand exchange and when the surface was neutral it occurred through ion exchange mechanism [20].

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Pathak *et al.* (2003) prepared the nano-sized powder of inorganic oxides such as Fe_3O_4 , Al_2O_3 and ZrO_2 and sonicated them in water and combined all the inorganic oxides in the matrix of activated charcoal through adsorption and finally used it as the adsorbing bed for the removal of trace of fluoride/arsenite and arsenate generally noticed with concentration upto 0.01-0.02 ppm) from industrial wastewater and aldehyde from perfume grade alcohol respectively. The oxides was prepared by the process of thermolysis of polymeric based aqueous precursor solution of sucrose and polyvinyl alcohol mixed with respective cations homogeneously and calcined the precursor powder at 200-500°C for 2 h to produced desired inorganic oxide phase of particle diameter (20 and 38nm) with 200 m^2/g surface area [21].

Chang *et al.* (2006) used the super magnetic nano-scale adsorbent of bayerite/ $\text{SiO}_2/\text{Fe}_3\text{O}_4$ or adsorbent for defluoridation of water. The adsorbent was synthesized through the three sequential steps such as chemical precipitation of Fe_3O_4 , coating of SiO_2 on Fe_3O_4 and finally coating of bayerite ($\text{Al}(\text{OH})_3$) on $\text{SiO}_2/\text{Fe}_3\text{O}_4$ by adopting the sol-gel (MASG) or homogeneous precipitation (MAHP) methods. Among the other defluoridation study, the MASG was found to be most effective adsorbent with the adsorption capacity of 38 g/kg at pH 6.0 as compared to adsorption capacity of CA at pH of 3.5. The sorbent possess physicochemical stability at pH range of 6-8 [22].

Patel *et al.* (2009) used CaO nanoparticle synthesized by the sol-gel method for defluoridation of water. The removal of 98% fluoride was achieved within 30 min at 0.6 g/l dose of sorbent for fluoride solution of 100mg/l. The adsorption process followed the Freundlich isotherm and pseudo-first-order kinetic equation where the maximum Langmuir adsorption capacity was noted as 163.3 mg/g. The thermodynamic study revealed that the adsorption process was spontaneous, endothermic in nature increasing randomly. It was also clear from the study that the fluoride adsorption mainly take place due to ion-exchange mechanism to form CaF_2 by replacing hydroxide ions with fluoride ions as hydroxide is effect. The sulphate and nitrate ions had no effect on adsorption. Desorption process was carried out up to 50% by maintaining the pH value between the range of 2 -12 by addition of 0.1M NaOH or 0.1M HCL solution [23].

Chen *et al.* (2009) used Fe-Al-Cenano-adsorbent coated with sand by spraying trimetallic oxides on sand in a fluidized bed with the polymer latex as binder. The particle of 2-3mm size with the uniform coating of 200 μm thickness was obtained by the method applied by them. The coating of 27.5% was noted to be optimized and adsorption capacity of 2.22 mg/g was achieved at neutral pH 7 for initial fluoride concentration of 0.001M. The fluoride solution of 5.5 mg/l has been treated in a packed bed column with adsorbent granules at pH 5.5. The SV of 5 h^{-1} has given to be 300 bed volume of treated water with fluoride concentration which is less than 1 mg/l and 500 bed volumes with concentration of 1.5 mg/l has indicated the on-field suitability of adsorbent [24].

Maliyekkalet *et al.* (2010) synthesized nano-magnesia by self-propagated combustion of magnesium nitrate trapped in cellulose fiber. The nanoparticle so obtained was crystalline with phase purity and particle of 3-7 nm size. The adsorption process followed pseudo-second-order equation and equilibrium data fitted well with Freundlich isotherm model and the maximum Langmuir adsorption capacity of nanomagnesia was 267.82 mg/g. The sorption capacity was negligibly sensitive to pH variations but at higher pH, the adsorption decreases slightly. Phosphate showed great competitive study of fluoride followed by bicarbonate and nitrate. The fluoride removal took place through isomorphic substitution of fluoride in brucite. The nanomagnesia employed in the household defluoridation and was treated with drinking water [25].

Zhang *et al.* (2012) used hydroxyapatite nanoparticle (nHAp) synthesized by waste phosphogypsum (PG) for defluoridation of water. The experimental data fitted well with Langmuir-Freundlich isotherm model and adsorption followed pseudo-second-order kinetic equation. The Langmuir-Freundlich maximum adsorption capacity of nHAp was 19.742, 26.108, 36.914 and 40.818 mg/g for the temperature of 298, 308, 318 and 328K respectively. The electrostatic interaction and hydrogen bond were actively responsible for fluoride removal through nHAp derived from PG [26].

Suriyaraj (2012) prepared hybrid $\text{Al}_2\text{O}_3/\text{Bio-TiO}_2$ nanocomposite impregnated on thermoplastic polyurethane membrane for defluoridation of water. The maximum adsorption capacity of nanocomposite impregnated membrane was observed to be 1.9 mg/g and was followed Langmuir isotherm and pseudo-second-order-kinetic model [27].

Baratiet *et al.* (2014) studied the defluoridation potential of nanocomposite hydrogel based on starch/sodium acrylate/nanoaluminum oxide from drinking water. The optimum pH range was between 5 and 7. It was noticed that the removal efficiency was increased with an increase in initial fluoride concentration. The fluoride removal of 60% was attained by nanocomposite hydrogel with 4 wt. % of nanoaluminum oxide along with fluoride solution of 5 ppm at pH

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6.8, temperature of 25°C and contact time of 4 hrs. The equilibrium data fitted well with Langmuir isotherm model and adsorption followed pseudo-second-order kinetic model. Under the same condition of temperature and pH, the equilibrium adsorption of fluoride for fluoride solution of 5 and 10 ppm was observed to be 85% and 68% respectively [28].

Wei *et al.* (2014) used nanosized fluorapatite (nFAP) for fluoride removal from aqueous solution. The adsorption data was briefly studied by Langmuir isotherm model and was followed by pseudo-second-order model and the adsorption process was spontaneous and endothermic in nature. The maximum defluoridation capacity of nFAP was 7.45 mg/g for 150 mg/l initial fluoride concentration at pH 5.0 and 25 °C, which was same as that of nanosized hydroxyapatite (7.75mg/g). The defluoridation from aqueous solution was highly suggested to be used due to its low costing and ease of regeneration of nFAP adsorbent [29].

He *et al.* (2014) used zirconium-based nanoparticle for the defluoridation from drinking water. The optimum pH was found to be 4 when the fluoride removal was carried out at pH range between 3.0 and 10.0. The adsorption process was found to be rapid and reached the equilibrium within 4hrs and it was noticed that the equilibrium data fitted well with Langmuir isotherm model. The intraparticle surface diffusion model well fitted the adsorption kinetics. The maximum adsorption capacity was observed as 97.48 and 78.56 mg/g at the optimal pH and neutral pH respectively. The adsorption capacity was found to be decreasing due to the presence of HCO_3^- and SiO_2^{3-} whereas phosphate, nitrate and organic matters had no effect on fluoride removal. The regeneration of adsorbent enhanced the reusability for defluoridation. The study revealed that the ion-exchange mechanism was equally responsible for adsorption of fluoride by zirconium-based nanoparticle [30].

He *et al.* (2014) prepared Zr-based nanoparticle embedded with polysulfone (PSF) blend hollow fiber membrane for the removal of fluoride from water. The adsorption of fluoride was carried out eventually in both static and dynamic state. The fluoride removal by membrane was attained at the pH range between 3 and 10, where the maximum adsorption capacity of optimized membrane was 60.65 mg/g at neutral pH found to be higher than the commercial adsorbent. The adsorption equilibrium was attained within 24 h of contact time. The fluoride removal was reduced due to the presence of bicarbonate and phosphate ions whereas nitrate, sulphate and HA had no effect on adsorption capacity. The membrane was regenerated and water was also treated in continuous filtration at the presence of organic matter. An intraparticle diffusion model was suitable to describe the adsorption kinetics. The adsorption of fluoride was mainly governed by ion-exchange between sulphate and fluoride ions [31].

Adenoet *al.* (2014) used nanoscale aluminium oxide hydroxide as nano- AlOOH for defluoridation from water. The adsorption was very fast as most of the adsorption took place during the first 30 min and equilibrium was attained within 60 min. with an optimum adsorbent dose of 1.6g/l for initial fluoride concentration of 20mg/l. It was noticed that the removal of fluoride increases with an increase in adsorbent dose. The fluoride removal efficiency was increased at pH range between 3 and 8 and further it decreases with increase in pH but the optimum pH was found at 7.0. The experimental data fitted well with Langmuir isotherm model and followed pseudo-second-order rate equation. The Langmuir maximum adsorption capacity was 62.5 mg/g with initial fluoride concentration of 20 mg/l. There was no action of intra-particle diffusion as it was not a rate-controlling step for the adsorption process. The adsorption process was enhanced due to chemisorption as the value of mean free energy (13.15 kJmol^{-1}) was found to be determined by D-R isotherm model [32].

Govhaet *al.* (2014) studied the kinetic process of fluoride adsorption on mixed oxide nanocomposites. The kinetics of adsorption was suited considerably with pseudo-second-order equation. The adsorption process followed the chemisorption to control the kinetics [33].

Jahin (2014) used nanoscale zero-valent iron (nZVI) for removal of fluoride from drinking water. The fluoride removal efficiency increases with an increase in dose of adsorbent and contact time and it showed gradual with an increase in initial concentration and pH of fluoride solution. The fluoride removal of 84% was achieved within 35 min at 0.6 g/l dose of nZVI and pH 4.0. The adsorption data fitted well with Freundlich isotherm model and the Langmuir maximum adsorption capacity of nZVI was 18.91 mg/g [34].

Teimouri (2015) used Chitosan/Montmorillonite/ ZrO_2 nanocomposites for defluoridation of water and has an adsorption capacity of 23 mg/g at pH 4.0, 30°C and a fluoride solution of 20 mg/l. The adsorption process was described well by Langmuir isotherm and pseudo-second-order equation [35].

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Dayananda *et al.* (2015) used MgO nano-particle loaded with mesoporous alumina ($\text{MgO}@ \text{Al}_2\text{O}_3$) for defluoridation from water. The maximum fluoride removal was obtained by 40 wt. % MgO nanoparticle loaded on mesoporous Al_2O_3 and denoted as $40\text{MgO}@ \text{Al}_2\text{O}_3$. The maximum fluoride removal of nearly 90% was attained by $40\text{MgO}@ \text{Al}_2\text{O}_3$ with initial fluoride concentration of 10 mg/l. The adsorption data fitted well with both Langmuir and Freundlich isotherm models. The kinetics of adsorption was noted as pseudo-second-order rate equation and the adsorption process was based on chemisorption. The fluoride samples with 5 and 10 mg/l was reduced to approximately 1 mg/l less by using mesoporous MgO nanoparticle loaded mesoporous Al_2O_3 ($40\text{Mg}@ \text{Al}_2\text{O}_3$) [36].

Dhillon and Kumar (2015) prepared a hybrid Fe-Ce-Ni nanoporous adsorbent for defluoridation of water. The maximum defluoridation capacity of 285.7 mg/g and removal of 98.7% was obtained at pH 7 with dose of 0.4g/l, contact time of 30 min and initial fluoride concentration of 10mg/l. The experimental data fitted well with Freundlich and Dubinin-Radushkevich isotherm models. The adsorption followed pseudo-second-order kinetic model. The adsorption reaction was spontaneous, endothermic, stable and irreversible in nature. The presence of co-anions has a significant effect on defluoridation capacity in the order of phosphate > bicarbonates > carbonate > sulphate > nitrate > chloride. Desorption of 95% was achieved by 4% NaOH solution. The adsorption capacity was reduced from 98.7% to 48% after the fifth cycle of adsorption-desorption [37].

Balarak (2015) used SiO_2 nanoparticle for defluoridation of water with maximum adsorption capacity of 49.95 mg/g at pH of 6 with a contact time of 20 minutes and initial fluoride concentration of 25 mg/l. Defluoridation data were fitted well with Langmuir isotherm and pseudo-second-order-kinetic models [38].

Pandi and Viswanathan (2015) prepared composite beads with n-HAp powder mixed into alginate polymer and cross-linked by La^{3+} ions for defluoridation of water. N-HApAlgLa beads have the maximum adsorption capacity of 3.72 mg/g in acidic pH. The adsorption process was followed the Langmuir isotherm model and pseudo-second-order as well as intraparticle diffusion models. The sorption reaction was spontaneous and endothermic in nature [39].

Wei (2015) used aluminum carbonate $[(\text{AlOH})\text{CO}_3]$ nanospheres having a maximum adsorption capacity of 59 mg/g in neutral solution and adsorption was not affected by common anions in water [40].

Dhillon (2015) has made hydrous hybrid Fe-Ca-Zr oxide nanoadsorbent for defluoridation of water and has the maximum adsorption capacity of 250 mg/g at pH 7.0 with an optimal dose of 0.25 mg/l. The adsorption process was well described by Freundlich and D-R isotherms and pseudo-second-order kinetic model. This composite adsorbent was also removed E-coli strain from water [41].

Minju (2015) used magnesium oxide coated magnetite nanoparticles for defluoridation of water. The fluoride removal of 98.6% for 13.6 mg/l of fluoride solution was achieved at optimum conditions of pH 6.0, contact time of 120 minutes and the adsorbent dose of 2 g/l. The experimental data fitted well with Langmuir isotherm and pseudo-second-order kinetic model [42].

Christina and Viswanathan (2015) were used two adsorbents viz. Fe_3O_4 nanoparticle immobilized in sodium alginate matrix (FNPSA) and Fe_2O_3 nanoparticles and saponified orange peel residue immobilized in sodium alginate matrix (FNPSOPR) for defluoridation of water. The adsorption process for both the adsorbent was fitted well with Langmuir isotherm and pseudo-first-order kinetic model. The maximum adsorption capacity of FNPSA and FNPSOPR were 58.24 and 80.33 mg/g respectively [43].

Malana (2015) prepared nanocomposites of MgAl_2O_4 with the polymer network for removal of fluoride from water. The maximum removal of 96% was achieved by using nanocomposite and adsorption reaction was well fitted with Langmuir isotherm and pseudo-second-order-kinetic model. The adsorption process was spontaneous in nature [44].

Pandi and Viswanathan (2015) used nano-hydroxyapatite (n-HAp) incorporated gelatin bio-composite (n-HAp@Gel) having adsorption capacity of 4.16 mg/g. The sorption data fitted well with Langmuir isotherm and pseudo-second-order as well as intraparticle diffusion kinetic models. The adsorption reaction was spontaneous and endothermic [45].

Wan (2015) prepared $\gamma\text{-AlOOH}@ \text{CS}$ (pseudoboehmite and chitosan shell) magnetic nanoparticles (ACMN) for defluoridation of water. The maximum adsorption capacity of ACMN was 67.5 mg/g at neutral pH. The adsorption data fitted well with Langmuir-Freundlich isotherm and pseudo-second-order and Elovich kinetic models. The sorption reaction was spontaneous and endothermic in nature [46].

Cai (2015) investigated defluoridation capacity of tea waste supported hydrous aluminium oxide (Tea-APAM-Al) with the help of polyacrylamide (APAM). The maximum adsorption of 42.14 was achieved in the pH range of 4.0 to 9.0 and

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contact time of 3 hours. The experimental data fitted well with Langmuir isotherm and Lagergren pseudo-second-order kinetic model [47].

Islam (2015) has used Polyaniline/Basic oxygen furnace slag nanocomposite for removal of fluoride from water. The maximum adsorption capacity of nanocomposite was observed to be 9.143 mg/g at 45°C. The maximum fluoride removal was occurred at pH range of 6 to 10. The adsorption data fitted well with Langmuir isotherm. The adsorption reaction was spontaneous and endothermic in nature [48].

Prathibha (2015) used nano calcium-aluminum mixed oxide (NCAMO) that was prepared by molar ratio of 1:1 of calcium and aluminum nitrate with urea as fuel. The equilibrium adsorption capacity of NCAMO was observed to be 23.7 mg/g at pH 4.0, contact time 4 hours, dose of 1 g/l and temperature at 25°C. The experimental data fitted well with Langmuir isotherm and pseudo-second-order-kinetic model. The thermodynamic study revealed that the process was spontaneous and endothermic in nature [49].

Thakkar (2015) used nanostructure diatom-ZrO₂ composite for defluoridation of water. The maximum Langmuir adsorption capacity was found to be 15.53 mg/g. The adsorption reaction was followed the pseudo-second-order-kinetic model. The maximum fluoride removal was obtained at a pH range of 2 to 6 [50].

III. BUILDING MATERIALS ADSORBENTS

This category of adsorbents is broadly divided into the four sub-parts like fluoride removal potential of cement pastes and granules, broken concrete, brick powder and sands.

1. CEMENT PASTE AND GRANULES

Kang *et al.* (2007) used paste made of cement for fluoride removal from water. The optimum pH range taken into account for cement slurry was found to be between 7.0 and 11.5. The fluoride removal mainly took place through the adsorption and precipitation as CaF₂ due to the presence of portlandite, calcium silicate hydrate (CSH) and ettringite in cement slurry. The real hydrofluoric acid wastewater with 1150 mg/l of fluoride concentration was reduced to 15 mg/l less by cement slurry filled with packed bed column [51].

Ayoobet *et al.* (2007) studied the feasibility of alumina cement granules (ALC) by the batch and column study for defluoridation of water. The fluoride solution of 8.65 mg/l was found to reduce from 1.0 mg/l by 2 g/l dose of alumina cement granules in batch study. The isotherm was significantly described well by Freundlich. The maximum monolayer capacity of ALC was 10.215 mg/g. According to column studies, the maximum adsorption capacity of ALC at breakthrough was 2.27 mg/g with a flow rate of 4 ml/min [52].

Ayoobet *et al.* (2008) studied the kinetics and mechanism of fluoride adsorption from water using alumina cement granules (ALC). The kinetics of adsorption was indigenously explained by pseudo-second-order equation. ALC indicated the biphasic kinetic with initial rapid uptake phases generally a slow and gradual phase. The activation energy of the system was 17.67 kJ/mol, referring the importance of intra particle diffusion in adsorption process. The surface of ALC was heterogeneous bonding site. The dominant mechanism of fluoride removal was found to be as a chemisorptive ligand exchange reaction engulfing the formation of inner-sphere complexation of fluoride with ALC [53].

Ayoobet *et al.* (2008) studied the adsorption potential of hard ALC for fluoride adsorption through isotherm study. The maximum monolayer adsorption capacity was noted as 34.36 mg/g and was reduced to 10.215 mg/g with the dose variation study and further reduced to 0.9358 mg/g in natural ground water. The experimental data was quite suitable for Freundlich isotherm model and adsorption process was endothermic in nature. The Freundlich adsorption parameter increased from 0.5589 to 0.99391 g⁻¹ in natural water and 3.980 to 7.51981 g⁻¹ in synthetic water systems when temperature was increased from 290K to 310K [54].

Ayoobet *et al.* (2009) have investigated the defluoridation capacity of alumina cement granules (ALC) from synthetic as well as the natural ground water. The 2 g/l dose of ALC was capable enough to reduce the fluoride concentration in water from 8.65 mg/l to 1.0 mg/l low level under optimal conditions. The maximum adsorption capacity was found to be 2.27 mg/g at flow rate of 4ml/min. The co-anions like sulfate, nitrate, chloride and bicarbonates had no effect on the fluoride adsorption whereas higher concentration of silicates and phosphates reduced the fluoride uptake by ALC. The adsorption process was spontaneous and endothermic in nature. The chemisorptive ligand exchange reaction involved

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the inner-sphere complexes of F^- with ALC. The adsorption of fluoride onto ALC clearly described by Thomas model with consistent vigour in all the consequent stages [55].

2. BROKEN CONCRETE

Oguzet *al.* (2005) used gas concrete for defluoridation from water. The optimum pH and contact time was 6.9 and 60 minute for maximum adsorption. The removal of 96% was attained for fluoride solution of 120mg/l at 40-60°C respectively. The regeneration of gas concrete was carried out at pH ranging between 1 and 3.9. The adsorption process mainly occurred due to adsorption and precipitation of Al^{3+} and Ca^{2+} salts (F^-) in a prominent order [56].

Oguzet *al.* (2007) suggested about the adsorption capability of light weight concrete for removal of fluoride from water. The fluoride adsorption on light weight concrete mainly occurred due to the presence of high content of aluminium and silica. The maximum fluoride removal was obtained at pH 6.9 and the adsorption reached to equilibrium in 60 min. The Langmuir maximum adsorption capacity was found to be 5.15 mg/g followed by pseudo-second-order kinetic model. The adsorption process was found to be endothermic in nature [57].

Bandyopadhyay *al.* (2009) reported about the use of broken concrete cubes for defluoridation of aqueous solution in column mode. The fluoride removal of 80% was achieved in 120 min. of contact time. It was found that percentage removal was increased with the dose of adsorbent. The maximum fluoride removal was attained at neutral pH. The column study for fluoride solution of 8 mg/l was reached to 1.5 mg/l at 26L cumulative flow of breakthrough point at the neutral pH. The field water with 8 mg/l was reduced to 1-1.23 mg/l by using broken concrete cube filled column for achieving safe drinking water of 25 litre from the contaminated water [58].

Hongoet *al.* (2014) synthesized ettringite, metaettringite and Ca-Al layered double hydroxide from concrete sludge for removal of borate, fluoride and chromate from the solution. The removal of borate from solution of 100 mg/l was done by CS-ettringite, CS-metaettringite and Ca-Al layered double hydroxide (CS-LDH) was 98.4, 6.3 and 84.1 mg/l with adsorption capacity of 0.13, 2.97 and 0.71 mg B/g and with pH of 10.2, 9.9 and 12.0 of treated water and contact time of 240 respectively. The removal of fluoride from 300 mg/l of initial concentration by CS-ettringite, CS-metaettringite and CS-LDH after 240 min. was 73.9, 14.5 and 14.1 mg/l with fluoride adsorption capacity of 114, 146 and 138 mg/g and with pH of 11.5, 11.4 and 12.0 of treated water respectively [59].

3. BRICK POWDER

Wijesundara *et al.* (2004) used broken bricks as defluoridating agent for development of a low cost domestic defluoridator for rural area. The reaction rate parameter (k) and capacity parameter (fm) was noted as 0.001 to 0.0005 $Lmg^{-1}h^{-0.5}$ and 0.10 mg/g respectively. The low cost defluoridator was used field water with low concentration of fluoride upto 2.0 mg/l. The capacity parameter depends on quality of bricks showing the characteristics properties as firing temperature of brick and optimal range was between 500 to 700°C. The rate of removal was far better in small piece of broken bricks than the large piece of brick [60].

Yadav *et al.* (2006) used brick powder (BP) as adsorbent for removal of fluoride from water and compared the result with commercial activated charcoal (CAC). The maximum adsorption of BP was found to be 51.0-56.8% in pH range between 6.0 and 8.0 found suitable for drinking purpose and the adsorption equilibrium time was 60 minutes. The removal of fluoride increased from 29.8 to 55.4% for BP and from 47.6 to 80.4% for CAC when the contact time was increased from 15 to 120 min. The fluoride removal of 48.73 and 56.4% was obtained for ground water sample with initial fluoride concentration of 3.14 and 1.21 mg/l respectively. The adsorption process was well described by Freundlich isotherm and pseudo first order rate mechanism. The surface adsorption and intra-particle diffusion was responsible for rate determining step as it was used as controlling agent. The presence of co-anions had no effect on the fluoride removal efficiency. The adsorption of fluoride by BP was mainly due to chemical interaction of fluoride with the metal oxides under suitable condition and pH. The availability and ease of brick powder was abundant when compared to that of CAC. The removal of fluoride by CAC occurred at pH in acidic condition [61].

Singh *et al.* (2008) used brick powder for removal of fluoride from aqueous solution and ground water. The 29.8 to 54.4% of fluoride was removed by brick powder at pH of 6-8 and adsorbent dose of 0.6-1.0g/l when the contact time was increased from 15 to 120 min [62].

Rani *et al.* (2012) suggested about the use of brick powder for removal of fluoride from aqueous solution and ground water. The removal of fluoride from aqueous solution was increased from 29.8 to 54.4% by using brick powder and

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increased from 47.6 to 80.4% by commercial activated charcoal at pH range of 6 to 8 and adsorbent dose of 0.6 to 1.0 g/100ml when the contact time was increased from 15 to 120 min. The fluoride removal of 48.73 and 56.4% was obtained for ground water with initial fluoride concentration of 3.14 and 1.21 mg/l respectively. The adsorption of fluoride from brick powder occurred due to interaction of fluoride with the metal oxides under suitable condition of pH [63].

Jain and Singh (2014) used alum impregnated brick powder (AIBP) for defluoridation of water. The removal of fluoride by AIBP was 4.0-5.0% higher than that of brick powder (BP). The optimum pH was found to be 6.0-8.0 and adsorption equilibrium time noted was found to be 60 min. The fluoride removal of 55-59% was achieved by AIBP in the pH range of 6-8. The adsorption of fluoride by AIBP occurred due to chemical interaction of fluoride with the metal oxides under suitable condition of pH and contact time. The adsorption process was indiscriminately explained first order equation and Langmuir isotherm model [64].

Bibi (2015) used hydrated cement, Brick powder and Marble powder wastes for fluoride and arsenic removal from water. Hydrated cement has the maximum adsorption capacity of 1.92 mg/g and 1.72 mg/g of arsenic and fluoride respectively at neutral pH. The experimental data fitted well with the Langmuir isotherm model [65].

4. SAND

Togarepiet *et al.* (2012) used activated sand with 10% Fe₂O₃ under the contact time of 3h and pH around 6.0 for defluoridation to water. The adsorption increased with an increase in initial fluoride concentration and dose of adsorbent. The fluoride removal of 90% was achieved for the fluoride solution of 10 mg/l with adsorbent dose of 12g in 50 ml (0.24mg/l) and optimum pH range of 5.7 to 6.3. The adsorption process was described Freundlich isotherm with Langmuir maximum adsorption capacity of modified sand as 10.3 mg/g [66].

IV. OTHERS AND MISCELLANEOUS ADSORBENTS

Sundarama and Meenakshi (2009) prepared a novel organic – inorganic hybrid type of ion exchanger for fluoride removal from water. The defluoridation capacity of polyacrylamide Ce (IV) phosphate (Ce-Ex), polyacrylamide Al (III) phosphate (Al-Ex) and polyacrylamide Zr (IV) phosphate (Zr-Ex) exhibited the fluoride adsorption capacity of 2.14, 2.29 and 2.17 mg/g respectively and the maximum fluoride removal occurred at acidic pH for all the synthesized materials [67].

Chen *et al.* (2010) used granular ceramic adsorption for defluoridation from water. The porous granular ceramic was developed by using Kanuma mud, starch, zeolite and FeSO₄.7H₂O and calcined. The surface area of adsorbent and total pore volume was 73.67m²/g and 0.14cm³/g respective and the optimum pH was between 5.0 and 8.0. The experimental data was quite suitable with Freundlich isotherm model and followed pseudo-second-order kinetics equation along with intra-particle diffusion model. The minimum adsorption capacity of granular ceramic was 12.12 mg/l at 20°C and found more than granular red mud which was 0.85mg/g. The mechanism of fluoride adsorption was reduced in presence of phosphate and sulphate ions but it increased in presence of chloride and nitrate ions. The fluoride uptake was governed by ion exchange of fluoride with hydroxides ions available on the granular ceramic [68].

Kaufholdet *et al.* (2010) used clay mineral allophane for fluoride removal from water and compared it with Fluorolith. The allophane had high adsorption capacity in comparison with kaolinite and goethite. The adsorption capacity of allophane was between 3 to 5 mg/g. The optimum pH was found to be in the range of 8-9. Fluorolith used mostly for fluoride adsorption at low concentration by ion exchange of F⁻ with OH⁻. Allophanewas employed as an alternate adsorbent for removal of fluoride similar to that of Fluorolith [69].

Goswami *et al.* (2011) used pyrophyllite for defluoridation from water. The adsorption reaction was rapid in first 20 min and equilibrium reached in about 120 min. The optimum pH was 4.9. The fluoride removal of 85% was achieved at dose of 4g/l within 2 h for initial fluoride concentration of 10 mg/l. The adsorption data was considerably fit with Langmuir isotherm model and pseudo-second-order kinetic model with the Langmuir maximum adsorption capacity as 2.2 mg/g. Intra-particle diffusion model was taken into account as the rate limiting step of the adsorption process. It was found that adsorption process was spontaneous and exothermic in nature. The sulphate ions had significant effect on the fluoride adsorption and reduced the fluoride efficiency by 5% [70].

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Malakootianet *et al.* (2011) reported about the prepared regenerated spent bleaching earth (RSBE) with acid and alkaline treatment and used it for defluoridation from water. The SBE was generally the waste generated from oil industry. The optimum pH and equilibrium time was 7 and 180 min respectively. The fluoride removal decreased with an increase in fluoride initial concentration. The maximum defluoridation capacity of RSBE was 0.6 mg/g at neutral pH and 10g/l dose of adsorbent with fluoride solution of 2.5-8 mg/l. The rate of fluoride adsorption by RSBE was 0.64 mg/g.min^{0.5} according to the kinetic study. The 10 g/l dose of RSBE had treated Kuhbonan water and brought down fluoride level of water on the basis of guideline given by WHO [71].

Islam *et al.* (2011) prepared a hybrid thorium phosphate composite with cinnamamide, thorium nitrate and phosphoric acid by co-precipitation method for removal of fluoride from drinking water. Polycinnamamide thorium (IV) phosphate resemble the good specific surface area of 101.2m²/g. The fluoride removal of 87.6, 83.9 and 80.2 % was obtained with 1 g/l dose of adsorbent for 100 ml of sample with initial fluoride concentration of 1, 5 and 10 mg/l respectively. The adsorption data suited exclusively well with Langmuir isotherm model and followed pseudo first order kinetics. The Langmuir adsorption capacity was 4.749 mg/g at optimum condition of concentration. The adsorption process was spontaneous and exothermic in nature. The adsorption was took place by ion exchange mechanism with phosphate ions present as adsorbent in addition to electrostatic attraction and hydrogen bonding [72].

Nunez *et al.* (2012) investigated nickel and magnesium hydrotalcite compound of NiAlHT, MgAlHT for removal of fluoride from an aqueous solution. They reported that NiAlHT was more efficient than MgAlHT for fluoride uptake. The grain size of 25-50 mesh gave maximum adsorption and equilibrium was reached in about 600 min. The kinetics of adsorption was explained eventually by Elovich rate equation model and indicated that the adsorption was chemisorption process. The presence of chloride, sulphate and arsenate had effect on fluoride uptake was also studied [73].

Wang *et al.* (2013) studied the defluoridation capability of carboxylated aerobic granules containing Ce (III) (Ce (III)-MAG) from water. The experimental data was quite suitable with Redlich-Peterson isotherm model and adsorption followed pseudo-first-order kinetic model. The optimum pH was found to be between 3.0-5.0. The presence of cations like potassium, magnesium, calcium and sodium ions increased defluoridation efficiency whereas anions like nitrate, chloride, sulphate, and bicarbonate and phosphate ions reduce the fluoride uptake. The adsorbent used in fixed bed treated fluoride solution of 10 mg/l to obtain 790 bed volumes with effluent concentration below 1.0 mg/l [74].

Pandi and Viswanathan (2015) synthesized carboxylatedalginate acid (CAA) and metal ions coordinated CAA (M-CAA) for defluoridation of water in batch mode. The CAA was obtained by oxidation of alginate acid with KMnO₄ and La³⁺ and Zr⁴⁺ metal was coordinate with CAA to obtain La-CAA and Zr-CAA. The defluoridation capacity was found in the order of Zr-CAA (4.064 mg/g) > La-CAA (3.137 mg/g) > CAA (0.880 mg/g). The adsorption data fitted well with Freundlich isotherm model. It was found that the adsorption reaction was spontaneous and endothermic in nature. The kinetic exclusively explained by pseudo-second-order kinetic and intra-particle diffusion models. The fluoride uptake mechanism was studied and elaborated by electrostatic adsorption and complexation. The M-CAA was used extensively for defluoridation due to the properties such as low cost, eco-friendly, biodegradable and biocompatible nature [75].

Srivastav (2015) used hydrous bismuth oxide (HBO₂) for defluoridation of water. The fluoride removal of 27 % was achieved for fluoride solution of 10 mg/l in contact time 3hrs and pH of treated water was observed to be 7.3. The Langmuir adsorption capacity of HBO₂ was 0.32 to 0.34 mg/g and obeyed pseudo-second-order-kinetic model [76].

Jha (2015) used Zirconium (IV) – loaded carboxylated orange peel (ZCOP) for removal of fluoride from water. The adsorption capacity of ZCOP was observed to be 5.605 mg/g at pH 6.0. The adsorption process was followed pseudo-second-order kinetic model and D-R isotherm model. The presence of phosphate and carbonate ions were reduced the fluoride removal capacity to some extent [77].

Deng and Yu (2015) used Zirconium impregnated fibrous protein (ZrFP) adsorbent for defluoridation of water. The maximum adsorption capacity of ZrFP was observed to be 12.6 mg/g at pH 5.0 and equilibrium concentration of 1.0 mg/l. The adsorption reaction was followed the pseudo-second-order-kinetic and Langmuir isotherm model [78].

V. CONCLUSION& OUTLOOK

The recent problem dealing with excess amount of fluoride in drinking water in most part of the world made people to look forward the cost effective as well as efficient adsorbents [79 – 89]. This paper briefly described the defluoridation

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capabilities of nanomaterials, building material and other miscellaneous related adsorbent as published in various journals. Nano-adsorbent has good affinity for fluoride with high adsorption capacity. Building materials based adsorbents had good removal efficiency by replacing commercial adsorbents and is available at low cost. The literature review summarizes that the fluoride uptake of adsorbents are significantly dependent on the factors such as pH of aqueous media, the dose of adsorbent, initial fluoride concentration, agitation speed, contact time, temperature, presence of co-anions, particle size etc. The adsorbents follow the pseudo-first-order or pseudo-second-order kinetic models and equilibrium data is suitable with Langmuir or Freundlich isotherm models. There are numerous option methods for taking care of the issue of high fluoride content in drinking water. Individuals settle on their own choice, contingent upon their bears, their insight, their qualities and their way of life. The innovation to identify and to lessen the fluoride in drinking water ought to be sufficiently straightforward to be taken care of by the villagers and simple to discover in the business sector. The national standard of fluoride in drinking water ought to be sufficiently low to shield individuals from fluoride poisonous quality. The future studies would be focussing on the techno-economic viability of adsorbents for field performances following the option of reuse and recycle. The above adsorbent has spacious exceptional opportunities in adjoining future that have been existing by the nanotechnology are regarded for improvement in the current world.

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