IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

FLUORIDE REMOVAL FROM WATER BY MIXED METAL OXIDE ADSORBENT MATERIALS: A STATE-OF-THE-ART REVIEW

Sanghratna S. Waghmare*, Tanvir Arfin
* Environmental Materials Division, National Environmental Engineering Research Institute (CSIR),
Nehru Marg, Nagpur-440020, India

ABSTRACT

Fluoride is a vital element, essential for support of dental wellbeing. However, fluoride concentrations in drinking water above 1.5 mg/L may be inconvenient to human wellbeing. Numerous approaches have been established for removing extreme fluorid from drinking water. The current manuscript reviews demonstrate the capability of mixed metal oxide, in a constant flow for removal of fluoride ions from industrial wasterwater and drinking water request to to give helpful data about the distinctive advancements. At the point when conceivably the adsorption capacity of metal oxide under diverse experimental condtions is accounted for to help to think about the fluoride's adequacy removal process.

KEYWORDS: Fluoride removal, metal oxide, adsorption, Langmuir, pseudo-order kinetic

INTRODUCTION

Water is one of the five eleements mentioned in the "Hindu Scriptures"to structure life. The inquiry of life in universe with the hunt of water. Ground water is the most suitable and generally utilized foundation for drinking water [1].Fluoride is named as a follow element, however is, truth be told pervasive, and may vigorous among the more simple lements in the biosphere. Most surface waters contain under 0.1 mg F/L, while ground waters may, contingent on the neighborhood base rock, contan quite high concentrations of fluoride ion. Defluoridation of water has been taken as an vital community implementation. While ceaseless endeavors have been coordinated towards adsorptive removal of fluoride from water test utilizing various minimal effort adsorptive materials i.e. the modest option and biodegradable materilas. The present study was done with the target of comprehensive the pattern of circulation of mixed metal oxide and their likely sources.The retrieval and safe exchange of mixed metal oxide adsorbents have been furthermore reviewed in this paper.

MIXED METAL OXIDES ADSORBENTS

CERIUM BASED

Xiuru et al. (1998) prepared CeO_2-TiO_2/SiO_2 surface composite by sol-gel method to coating CeO_2-TiO_2 on SiO_2 substrate for defluoridation of water and adsorption capacity was found to be 21.4 mg/g and percentage removal was observed 85.6% [2].

Xu et al. (2001) prepared cerium (IV) oxide coated SiMCM-41 ((Ce)SiMCM-41) adsorbent for removal of fluoride from drinking water. The optimum ratio of Ce/Si and calcination temperature was 1/30 and 540°C respectively. The maximum fluoride adsorption capacity was found to be 5.64 mg/g at $pH \leq 5.0$. The Langmuir adsorption capacity of (Ce)SiMCM-41 was observed to be 6.02 mmol/g due to anion exchange between the hydroxyl groups existing on the surface of (Ce)SiMCM-41 and F^- ions [3].

Zhongzhi et al. (2004) used an inorganic cerium based adsorbent (CTA) for defluoridation of drinking water. Adsorption process has followed by Freundlich isotherm model at low pH. The maximum fluoride adsorption was mainly governed by hydroxyl group of CTA [4].

Liu et al. (2010) prepared Al-Ce hybrid adsorbent by co-precipitation method using 0.2 mol L^{-1} $AlCl_3$ and 0.05 mol $L^{-1}Ce(NO_3)_3$ and it precipitate was dried at 80°C . The pHpzc and optimum pH of Al-Ce hybrid adsorbent was 9.6 and 6.0 respectively. The Langmuir adsorption capacity was 91.4 mg/g and the adsorbent had a high adsorption capacity upto 27.5 mg/g where the equilibrium fluoride concentration of 1mg/l . It was much higher than other conventional adsorbents. The adsorption process was spontaneous and endothermic in nature. Their effects on fluoride sorption has followed the decreasing order of HPO_4^{2-}>SO_4^{2-}> SiO_3^{2-}>HCO_3^{-}>Cl^{-}. The presence of phosphate ions has reduced highly. The presence of hydroxyl groups and protonated hydroxyl groups were highly responsible for fluoride removal from water [5]. Ping et al. (2010) prepared Ce-La binary hydroxide (CLH) adsorbent for defluoridation of industrial wastewater. The optimum pH range was found to be 4 – 8. The adsorption capacity of 77.4 - 89.5 mg/g was maintained upto pH 8.0. The equilibrium was reached after 120 minutes. The experimental data was fitted well with Langmuir isotherm model and followed the pseudo-second-order kinetic model. The Langmuir maximum adsorption capacity was 84.2 mg/g at pH 7.0. The presence of co-anions had affected the adsorption in the order of HPO_4^{2-}>HCO_3^{-} ≥ SiO_3^{2-} > SO_4^{2-}> Cl^{-}, NO_3^{-} [6].

Deng et al. (2011) prepared Mn-Ce oxide adsorbent by co-precipitation method. The granulation was prepared by process of calcining the Mn-Ce powder and pseudo-boehmite. The optimum Ce/Mn ratio was 1:1 and calcined at 300ºC with an adsorption efficiency of 85.1 mg/g. The Langmuir maximum adsorption capacity of fluoride on powdered and granulated Mn-Ce oxide adsorbent was 137.5 and 103.1 mg/g respectively. The adsorption capacity of powder and granular Mn-Ce adsorbent were 79.5 and 45.5 respectively at the fluoride equilibrium concentration of 1mg/l. The adsorption on granulate Mn-Ce oxide was very fast in first 1h and reached in equilibrium after 3h. The hydroxyl groups present on adsorbent surface was responsible for fluoride adsorption. The sorption of fluoride on Mn-Ce adsorbent was mainly governed by anion exchange and electrostatic interaction [7].

Deng et al. (2012) synthesized the cerium impregnated fibrous protein (CeFP) for adsorption of fluoride , arsenate and phosphate from aqueous solution. The pH_{pzc} of CeFP was increased upto 9.0. The maximum adsorption of fluoride, arsenate and phosphate was 5.59 mmol/g, 2.3 mmol/g and 2.11 mmol/g at pH of 3.0, 3.0-7.0 and 4.0-7.0 respectively at 303K. The experimental data were fitted well with the Langmuir isotherm model and followed pseudo-second-order kinetic model by three anions. According to thermodynamics study, the adsorption of fluoride was spontaneous and exothermic, while arsenate and phosphate adsorption were endothermic in nature. The CeFP had a strong affinity toward arsenate than fluoride and phosphate. The adsorption was governed ion exchange of fluoride ions by hydroxyl group of CeFP [8].

Sivasankar et al. (2013) synthesized a hybrid adsorbent by cerium dispersed in carbon (CeDC) via carbonization of ammonium cerium sulfate impregnated starch. The experimental data were fitted well with Langmuir isotherm model. The Langmuir sorption capacity of CeDC was observed to be 209 mg/g with a high R_L value of 0.699. The maximum defluoridation capacity of CeDC was 52 mg/g at pH 8.07 and 29.1 mg/g at pH 7.75 respectively. The adsorption was followed pseudo-second-order kinetic model, spontaneous and endothermic in nature. The regeneration of exhausted CeDC adsorbent was done by washing with an alkaline solution and then it was activated by acidic solution [9].

Zhang et al. (2013) used non-thermal plasma modified CeO_2/Al_2O_3 composite adsorbent for defluoridation of water. The CeO_2/Al_2O_3 composite was synthesized by a simple chemical co-precipitation method. The Ce/Al molar ration and calcination temperature for the development of optimum CeO_2/Al_2O_3 composite was 1/20 and 250ºC respectively. The non-thermal plasma (NTP) modified adsorbent had the higher adsorption capacity than pristine composites. The optimum fluoride adsorption was obtained at a pH range of 3-10. The presence of co-anions affected fluoride efficiency decreased in the order of Cl^{-}< NO_3^{-}< SO_4^{2-}< CO_3^{2-}< $C_2O_4^{2-}$< HPO_4^{2-}. The kinetic of adsorption was well described by the pseudo-second-order kinetic model and adsorption isotherm was best fitted by Redlich-Peterson model. The defluoridation capacity of unmodified and NTP modified CeO_2/Al_2O_3 composite was 24.1 mg/g and 37.0 mg/g respectively for initial fluoride concentration of 120mg/l with an adsorbent dose of 2g/l and adsorption time of 24 h. The adsorption was governed by chemisorption [10].

Ghosh et al. (2015) studied defluoridation performance of agglomerated (140-290µm) Ce(IV)-Zr(IV) mixed oxide nanoparticle (~50 nm) from ground water in packed bed column. Throughput volume has increased at breakthrough point (1.0 mg/l) with increased bed volume, decreasing initial concentration and effluent rate. The breakthrough was well described by Thomas kinetic model and the ground water with initial fluoride concentration of 3.0 mg/l was treated effectively by bed capacity (542.43 mg/cm^3) and length of mass transfer zone (0.6039cm) as calculated by bed depth service time model [11].

IRON BASED

Wu et al. (2007) used Fe-Al-Ce trimetal oxide for defluoridation of water in both of batch and column study. The tri-metal oxide was developed by co-precipitation process of Fe(II), Al(III) and Ce(IV) salt solution with a molar ratio of 1:4:1 under alkaline condition. More than 90% of fluoride removal was obtained for tri-metal oxide calcined below 600ºC. The optimum pH was observed to be in the range of 6-6.5 and higher adsorption was also taking place in the pH range of 5.5-7.0. A high adsorption capacity of 178 mg/g was obtained at pH of 7.0. for equilibrium fluoride concentration of 84.5 mg/l and adsorbent dose of 150mg/l. The adsorption was well explained by the Langmuir two-site adsorption. The Langmuir maximum defluoridation capacity was 185 mg/g and 229 mg/g for one-site and two-site adsorption model respectively. The presence of phosphate or arsenate has reduced adsorption efficiency highly. The presence of sulphate and chloride did not significantly affected defluoridation whereas nitrate above 50mg/l affected defluoridation efficiency. Desorption of 97% was obtained by treating spent adsorbent with NaOH solution at pH of 12.2. Column study of 1 mm pellets of tri-metal oxide adsorbent with a space velocity of 5h-1, pH of 5.8 and 2240 bed volume reduced the influence of 5.5 mg/l of fluoride solution to 1.0 mg/l in effluent [12]. Biswas et al. (2007) synthesized crystalline and hydrous iron (III)-zirconium(IV) hybrid oxide (IZHO) material for defluoridation of water. The optimum pH range for fluoride adsorption was 4-7. The equilibrium data were fitted well with Redlich-Peterson than the Langmuir isotherm model. The adsorption process was spontaneous and took place with an increase of entropy. The kinetic of adsorption was well described by the pseudo-first order and reversible first order than pseudo-second-order equation at pH 6.8±0.1 and 303±2 K respectively. The kinetics of fluoride adsorption on the mixed oxide was founded to take place not so clear with boundary layer diffusion. External mass transport with intra-particle diffusion phenomena was controlled by rate limiting process, which has been confirmed from Boyd poor non-linear kinetic plot [13].

Streat et al. (2008) studied the adsorption performance of hydrous ferric oxide adsorbent for removal of arsenic, phosphorous, fluorine and cadium ions in both batch and mini-column modes. The anionic species (arsenate, phosphate and fluoride) were effectively removed in the pH range of 4-9. The optimum pH for anionic species was 4.0 since surface had positive charges. The cadmium removal was maximum at pH 9.0. The adsorption capacity of anionic species was found in the order of fluoride (1.8 mmol/g) > arsenate (0.9-1 mmol/g) > phosphate (0.65-0.75 mmol/g). The cadmium uptake was less than fluoride but more than arsenate and phosphate on granular ferric hydroxide depending on the system pH. Fluoride was desorbed to 85-100% by 0.1M NaOH solution [14]. Wu et al. (2008) developed Fe-Al-Ce trimetal hydroxide adsorbent with acrylic-styrene copolymer latex as binder for spray coating on sand to remove fluoride from drinking water. The stable coating of 75 µ was done by latex/Fe-Al-Ce ratio of 0.8 and its defluoridation capacity was 3.46 mg/g at pH7.0 and initial fluoride concentration of 50 mg/l. This sand coated Fe-Al-Ce adsorbent was used effectively in a packed bed column for defluoridation from drinking water [15]. Kumar et al. (2009) studied the defluoridation capability of granulated ferric hydroxide (GFH) from aqueous solution in batch mode. The adsorption process was rapid and 95% of adsorption were completed within 10 minutes and equilibrium was achieved within 60 minutes. The maximum defluoridation capacity of GFH was 7.0 mg/g. The optimum pH range was found to be 4-8. The adsorption has followed the both pseudo-second-order kinetic model and Langmuir isotherm model. The adsorption process was endothermic in nature. The co-anion was reduced the fluoride in order of phosphate > carbonate > sulphate. The adsorption process was mainly governed by ion exchange mechanism [16].Tang et al. (2009) used granular ferric hydroxide for defluoridation of water in batch study. Ionic strength did not affect equilibrium adsorption at the pH range of 2-11. The optimum pH range was 3-6.5 where maximum fluoride removal took place. The experimental data were followed both of Freundlich isotherm model and pseudo-second-order kinetic model. Desorption of fluoride was carried out at alkaline solution and 65% of fluoride release at pH of7.0. The presence of co-anions were affected fluoride removal efficiency in the order of $H2PO_4^{-}>HCO_3^{-}>SO_4^{2-}>Cl^{-}$ [17]. Sujana et al. (2009) studied the defluoridation potential of amorphous Fe/Al mixed hydroxides from aqueous solution. The optimum pH was observed to be 4-5 with molar ratio of 1:0, 3:1 and 2:1. The adsorption rate was very high and equilibrium was reached within 2 h. The experimental data were fitted well to both Langmuir and Freundlich isotherm model and adsorption followed the pseudo-first order kinetic with intra-particle diffusion model. The maximum Langmuir adsorption capacity of 91.7 mg/g was obtained with molar ratio of 1:0. The phosphate , sulphate and arsenate ions were affected the fluoride adsorption. A maximum regeneration of 80.5% was achieved with 0.5M NaOH [18]. Biswas et al. (2009) prepared synthetic iron (III)-tin(IV) mixed oxide (HITMO) for defluoridation of water. The adsorption capacity of HITMO was found constant in the pH range of 5-7.5. The experimental equilibrium data were fitted well with both Langmuir isotherm and the Pseudo-second-order kinetic model. The Langmuir adsorption capacity of HITMO was 10.50 mg/g and mean adsorption energy by Dubinin–Redushkevich isotherm was 9.05 kJ/mol. The adsorption process was spontaneous and endothermic in nature. The presence of bicarbonate ions only reduce the fluoride adsorption. The regeneration of nearly 75% of HITMO was achieved by solution of pH 13.0. The natural water with initial fluoride concentration of 2.97 mg/g was reduced to 1.5 mg/l with the 2 g/l of adsorbent dose [19].

Biswas et al. (2010) synthesized hydrous iron(III) –chromium (III) bimetal mixed oxide (HICMO) adsorbent for defluoridation of water. The optimum pH for maximum fluoride adsorption was 3.0 and then adsorption declined in the pH range of 3-5. The equilibrium data fitted well with the Langmuir isotherm model and followed the pseudo-second-order kinetic model. The maximum Langmuir adsorption capacity of HICMO was 16.34 mg/g. The thermodynamic study revealed that the adsorption process was spontaneous and endothermic in nature. The adsorption was mainly governed by an ion-exchange mechanism. The bicarbonate ions reduced the fluoride adsorption capacity strongly. Desorption of 91% was achieved by 0.5M NaOH solution. The column breakthrough capacity of HIMCO at a flow rate of 1 to 2 ml/min was 7.47 mg/g. The HIACMO dose of 0.2 g/50 ml reduced the fluoride solution of 10mg/l to 1.5 mg/l [20].

Chen et al. (2011) studied the fluoride removal capability of iron impregnated granular ceramics (GC) from aqueous solution. The ceramic granules made by Kanuma mud, zeolite, starch and $FeSO_4.7H_2O/Fe_2O_3$ mixed at a ratio of 4:3:2:1 by granulation method at room temperature. The granular ceramic (GC) with $FeSO_4$ was more effective than the granular ceramic with Fe_2O_3. The optimum pH for GC with $FeSO_4$ and GC with Fe_2O_3 was 7.0 and 4.0 respectively. The adsorption was described well with both Langmuir and Freundlich isotherm models for GC with $FeSO_4$ and GC with Fe_2O_3 and followed the pseudo-second-order kinetic with intra-particle diffusion as the rate determining step. Both these adsorption processes showed thermodynamically spontaneous and endothermic in nature [21]. Wu et al. (2011) prepared 3-5 mm granulated nano-adsorbent of Fe-Al-Ce tri-metal hydroxide (FAC) immobilized in porous polyvinyl alcohol (PVA) matrix via cross-linking with boric acid. The mechanically sound and good adsorbent were developed by a FAC concentration of 12% and PVA concentration of 7.5% resulted into fluoride adsorption capacity of 4.46 mg/g at pH of 6.5 with an initial fluoride concentration of 19mg/l and dose of 2.0g/l for 100ml fluoride solution [22]. Dou et al. (2011) used granular zirconium-iron oxide (GZI) composed of amorphous and nano-scale oxides particles prepared by extrusion method for defluoridation of water. The maximum equilibrium adsorption capacity of GZI was 9.80 mg/g for 10mg/l of fluoride solution at pH of 7.0. The GZI performed well at pH of 6-8. The batch experiment data were fitted well with Freundlich isotherm model and was followed the pseudo-second-order kinetic model. The Langmuir adsorption capacity of GZI was 22.82 mg/g at neutral pH and more than activated alumina (7.728m/g at same pH). The bicarbonate ions were affected the defluoridation capacity of GZI whereas the presence of others co-anions did not affect adsorption. The toxicity characteristic leaching procedure (TCLP) leachability results revealed that spent GZI was not toxic and can dispose directly. The successful regeneration of GZI was done by 0.01M NaOH solution. The ground water was treated about 370, 239 and 128 bed volumes before breakthrough was reached under space velocity of 0.5, 1 and 3 h^{-1} respectively for influent fluoride concentration of 3.59 mg/l, pH of 8.3 and TOC of 7.6 mg/l [23]. Chen et al. (2011) studied defluoridation capability of Fe-Al-Ce (FAC) trimetal oxides sprayed onto glass beads with acrylic-styrene copolymer latex. The maximum fluoride removal of 2.77 mg/g was obtained when the granules were coated at 65ºC using a latex/FAC ratio of 0.5:1 for 0.001M of initial fluoride concentration at pH of 7.0 and a granule dose of 5g/l for adsorption time of 36 h. The Langmuir maximum adsorption capacity of adsorbent was found to be 5.9 mg/g [24].Huang et al. (2011) used waste iron oxide materials (BT3), a by-product of fluidized bed Fenton reaction (FBR-Fenton) for defluoridation of an aqueous system after thermal treatment between 200 and 900ºC. The maximum defluoridation was obtained at 300ºC and the optimum pH was found to be 4.0. The maximum adsorption capacity was increased from 12 mg/g to 20.4 mg/g as the initial fluoride concentration increased from 1.5mm to 6.0mm. The presence of co-anions at pH 3.9 ±0.2 founded in order of $PO_4^{3-} > SO_4^{2-} > Cl^- > NO_3^-$ [25]. Chen et al. (2011) prepared porous granular ceramic containing dispersed aluminum and iron oxides for defluoridation of water. The 1M $FeCl_3$ and 1M $AlCl_3$ treated porous ceramic granules (knar clay:zeolite:wheat starch = 1:1:1) and calcined at 600ºC. The surface area of adsorbent was 50.69 m^2/g. The optimum fluoride removal was obtained at a pH range of 4-9. The maximum defluoridation capacity of adsorbent was 1.79 mg/g at pH 6.0. The experimental data were well described by both Langmuir and Freundlich isotherm models and adsorption followed the pseudo-second-order kinetic model [26]. Chang et al. (2011) developed a nano-sized super-magnetic zirconia material (SPMZ) ($ZrO_2/SiO_2/Fe_3O_4$) for defluoridation of water and simulated industrial wastewater. The SPMZ was showed chemical stability at moderate acidic and basic conditions. Sorption and desorption was developed very fast so that the equilibrium was attained in a few minutes. Fluoride sorption capacity increased with decreasing the pH value. The monolayer adsorption capacity of 14.7 mg/g was obtained at pH of 4.0. The regeneration with 10^{-3}N NaOH was found excellent [27].

Chen et al. (2012) synthesized Fe(II)-Ti(IV) oxide nano-adsorbent by co-precipitation using ammonia titration at room temperature. The optimized adsorbent was obtained at Fe/Ti molar ratio of 2:1 and calcined at 200°C after ethanol washing and drying in microwave has the maximum adsorption capacity of 47.0 mg/g. The fluoride ions interacted with Fe-O-Ti bond available on the surface of adsorbent to form Fe-O-Ti-F bond and mainly responsible for adsorption [28]. Mohapatra et al. (2012) used Mg-doped nano ferrihydrite for defluoridation of water. The fluoride removal was increased from 66% to 91% when Mg doping on nano-ferrihydrite was varying from 0.39% -0.98%. The experimental data were fitted well with the Langmuir adsorption isotherm model. The highest defluoridation capacity of 0.98%. Mg-doped nano-ferrihydrate was 64 mg/g at optimum condition (pH=5.75, initial fluoride concentration=30 mg/l, dose=1g/l, contact time=5h and temperature=30ºC). The adsorption was followed the pseudo-second-order kinetic model and the adsoprion process was spontaneous and endothermic in nature. The presence of sulphate and chloride reduced the defluoridation efficiency from 91.2% to 53.8% and 72.5% as their concentration was increased from 5 to 50mg/l. Desorption of 89% was done by 1M NaOH solution [29]. Zhao et al. (2012) prepared granular Fe-Al-Ce tri-metal oxides (GFAC) extruded with cross-linked poly (vinyl alchohol) (PVA) as a binder and used for defluoridation of water. The optimum ratio of binder/FAC powder, cylinder granule diameter and drying temperature were observed to be 1.4, 1.6 mm and 65ºC respectively. The Langmuir adsorption capacity of GFAC was 51.3 mg/g at pH of 7.0. The column adsorption capacity at breakthrough point (1.0mg/g) for F-spiked tap water (pH=7.8±0.2) and F-bearing groundwater (pH=8.2±0.2) was 5.7 and 3.2 mg/g respectively. The regeneration of spent GFAC was done by NaAlO2 with near 60% recovery of adsorption capacity after four cycles of adsorption-regeneration [30]. Poursaberi et al. (2012) synthesized zirconium (IV)-metalloporphyrin grafted Fe_3O_4 nanoparticles for removal of fluoride from wastewater. Fe_3O_4 nanoparticles were synthesized by co-precipitation of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions in an ammonia solution and then surface modified with 3-aminopropyl triethoxysilane (APTES) and zirconium (IV) porphyrin complex [Zr(TCPP)]. The fluoride removal of 92% was obtained at optimum conditions (Initial fluoride concentration: 10mg/l; contact time: 20 min; pH: 5.5 and nano-sorbent dose: 100mg). The regeneration of adsorbent was carried out after washing with a basic solution and it is reused upto five life cycles [31]. Liu et al. (2012) used iron and aluminum binary oxide (FeAlO*x*H*y*), aluminum oxyhydroxide (AlO*x*H*y*) and iron oxyhydroxide (FeO*x*H*y*) for simultaneous removal of arsenate and fluoride and the competitive adsorption between them. Iron oxyhydroxide (FeO*x*H*y*) showed a high removal capacity toward arsenate (As (V)) than fluoride (F) especially at pH above 6.5 whereas aluminum oxyhydroxide (AlO*x*H*y*) showed good adsorption capability toward As(V) and F but maximum removal was found at weak acidic pH of 6.0. To overcome the drawback of pH and competition between As(V) and F, combine iron oxyhydroxide (FeO*x*H*y*) with aluminum oxyhydroxide (AlO*x*H*y*) to form iron and aluminum binary oxide (FeAlO*x*H*y*). In comparison to FeO*x*H*y* and AlO*x*H*y*, FeAlOxHy showed superior performance for simultaneously remove As (V) and F. The removal of fluoride by FeAlOxHy, AlO*x*H*y* and FeO*x*H*y* were 64.5%, 29.4% and 18.4% respectively [32].

Chai et al. (2013) prepared sulphate doped Fe_2O_4/Al_2O_3 nanoparticle with magnetic separability for defluoridation of drinking water. The adsorption reaction was very fast and 90% of removal was achieved within 20 minutes and the remaining was occurred within 8 hours. The adsorption isotherm was well described by the Elovich model. The Langmuir adsorption capacity was found to be 70.4 mg/g at pH 7.0 and the optimum pH was observed in the range of 4-10. The fluoride removal of 90% and 70% was obtained in the pH range of 4-10 for initial fluoride concentration of 10 mg/l and 50 mg/l respectively. Except phosphate ions affected the defluoridation capacity whereas the presence of other co-anions (NO_3^-, Cl^- and SO_4^{2-}) not affected adsorption [33]. Sanchez et al. (2013) studied the defluoridation capacity of aluminum modified iron oxides in a fixed bed column for simulated water and drinking water. The experiment was carried out in borosilicate glass column of 9 mm diameter with fluoride solution of 4 mg/l at pH 6.4 for aqueous solution and at pH 7.4 for drinking water. The experiment was run for 2, 4 and 6 g of aluminum modified iron oxides with a bed depth of 3.5, 7 and 10.5 cm at flow rate of 1 ml/min. The column study observed that the maximum adsorption of 0.509 mg/g was obtained at bed height of 3.5cm and 2g of adsorbent after 254.3 minutes for aqueous solution whereas adsorption capacity of 0.296 mg/g was obtained at same condition after 148 minutes for drinking water. The pH of water was 7.2 and 7.3 for model solution and drinking water respectively. The experimental data of breakthrough curve was fitted well with Thomas, Bohart-Adams and bed depth service time (BDST) model for both model solution and drinking water [34]. Kang et al. (2013) prepared calcined Mg/Fe layered double hydroxide (Mg/Fe-CLDH) by co-precipitation method for simultaneous fluoride and arsenate removal from aqueous solution. The maximum adsorption capacity of 50.91 and 50.24 mg/g for fluoride and arsenate was obtained at optimum condition with a M^{2+}/M^{3+} ratio of 5, calcined at 400 °C and pH of 7.0. The experimental data for equilibrium was best fitted with the Langmuir isotherm model and pseudo-second-order kinetic model and the adsorption mechanism was involved surface adsorption and ion-exchange interaction [35]. Zhang et al. (2013) studied defluoridation capacity of non-thermal plasma modified CeO_2/Mg-Fe layered double hydroxides. The Langmuir maximum adsorption capacity was 60.4 mg/g and adsorption followed the pseudo-second-order kinetic model and the adsorption process was spontenous and exothermic in nature [36].Chen et al. (2013) prepared Fe-Al impregnated granular ceramic adsorbent for defluoridation from aqueous solution. The fluoride removal was achieved more than 98% at neutral pH with an initial fluoride solution of 10 mg/l within 48h. The experimental data were fitted well with the Langmuir isotherm model and adsorption followed the pseudo-second-order kinetic model. The Langmuir maximum adsorption capacity was observed to be 3.56 mg/g in the pH range between 4-9. The presence of carbonate and phosphate ions in aqueous solution reduced the adsorption capacity. The intra-particle diffusion and pore diffusion were played an important role for adsorption of fluoride [37]. Su et al. (2013) prepared granulation of Fe-Al-Ce nano-adsorbent for fluoride removal from drinking water. The granulation of Fe-Al-Ce nano-adsorbent was synthesized by using aluminium, zirconium, titanium and silica sol. The inorganic binders like zirconium and titanium reduced the adsorption capacity of Fe-Al-Ce adsorbent whereas aluminium and silica sol. showed enhanced adsorption capacity. The granulation of Fe-Al-Ce by extrusion with aluminium sol. calcined at 500ºC had maximum fluoride removal over 90% and much higher than granulation by acrylic-styrene copolymer latex as a binder [38].

Woyessa et al. (2014) synthesized hydrous aluminium (III)-Iron (III)-Manganese (IV) ternary mixed oxide by co-precipitation method for defluoridation of water. The maximum adsorption was achieved by Al:Fe:Mn sample of ratio 75:15:10. The optimum pH range was found to be 6-7. The kinetic data was described well with the pseudo-second-order equation and equilibrium data was fitted well with the Freundlich isotherm model. The adsorption process was spontaneous and endothermic in nature with ahigh degree of randomness. The maximum adsorption capacity of hydrous Al-Fe-Mn was 23.99 mg/g at pH 6-7 and a temperature of 25ºC with initial fluoride concentration of 20 mg/l. The presence of phosphate ions reduced the fluoride adsorption capacity greatly whereas carbonates, sulphate, nitrate and chloride ions effected on adsorption capacity was not significant [39]. Nur et al. (2014) used hydrous ferric oxide (HFO) for defluoridation of drinking water in both batch and fixed bed column experiments. The fluoride uptake of HFO was founded more than four anion exchange resins and three multivalent metal oxides. The adsorption data of HFO was best fitted with both the Langmuir and Freundlich models. The Langmuir maximum adsorption capacity of HFO was 6.71 mg/g at pH 6.5. The pH_{pzc} of HFO was found to be 5.0. Desorption of HFO was done by 0.1M NaOH. The column adsorption capacity of adsorbents (10% or 20% HFO + 90% or 80% anthracite) was observed to be 3.26 mg/g after three consecutive adsorption-desorption cycles. The breakthrough data of column experiment was well described by Thomas model. The artificial neural network was used to improve the model capability [40]. Qiao et al. (2014) prepared Al-Fe (hydr)oxides with different Al/Fe molar ratios of co-precipitation method for simultaneous removal of arsenate and fluoride from water in the pH range of 5.0-9.0. The removal of fluoride was more at acidic pH and maximum at pH 6.0 and deceased onward. The fluoride removal was preliminary due to ligand exchange and the surface hydroxyl group density of Al-Fe (hydr)oxides beside its largest pH_{pzc}. The adsorption capacity of both fluoride and arsenate were in order of 4Al:Fe> Al: Al:Fe > Al:4Fe > Fe at pH 6.5±0.3 [41].

Gitari et al. (2015) used Fe^{3+}-modified bentonite clay and raw bentonite for defluoridation of aqueous solution. The optimum loading was obtained at 30 min by mixing with 100 ppm of Fe^{3+} solution. The modified bentonite had a large surface area and micropore area than raw bentonite. The modified bentonite removed fluoride more efficiently than raw bentonite. The fluoride removal of ≈ 100% was achieved over wide pH range of 2-10 by Fe^{3+}-modified bentonite clay whereas raw bentonite released fluoride at alkaline pH > 10. The adsorption capicity of Fe^{3+}-modified bentonite clay was 2.91 mg/g. The experimental data were fitted well with the Langmuir isotherm model indicating a monolayer coverage of the adsorption. The Fe^{3+}-modified bentonite clay removed the fluoride from groundwater at neutral and optimum pH well below the WHO guidelines but pH of treated water was became acidic in nature (pH drop) and need pH adjustment. The Fe^{3+}-modified bentonite clay used effectively for treatment of borewell water with high fluoride concentration [42]. Yu et al. (2015) synthesized Fe-Mg-La tri-metal amorphous composite by co-precipitation method for defluoridation of water. The optimum pH was found to be 4.0. The adsorption isotherm was well described by Langmuir model. The Langmuir maximum adsorption capacity of adsorbent was 270.3 mg/g and found much higher than reported adsorbents. The adsorption was very fast in first 1 h and reached an equilibrium within 5 h. The presence of natural organic matters, chloride and bicarbonates did not affect fluoride uptake. The adsorption mechanism was governed by ion-exchange between sulphate ions on adsorbent and fluoride ions in the solution [43].

LANTHANUM BASED

Wasay et al. (1996) used lanthanum impregnated silica gel for removal of fluoride , phosphate and arsenate ions from the drinking water. The removal of fluoride and arsenate ions were more than 99.9% at neutral pH from the initial concentration of 0.55 mmol/L and 0.2 mmol/L respectively. The removal of phosphate was 95% at neutral pH from the initial concentration of 0.5 mmol/L. The adsorption of each anion were fitted well with Langmuir isotherm model and adsorption process followed first-order reaction. The Langmuir adsorption capacity for fluoride, phosphate and arsenate ions were 0.200, 0.111 and 0.118 mmol/g respectively and found much more than reported value of activated alumina except for fluoride. The presence of co-anions like chloride, sulphate, nitrate, bromide and iodide did not affect defluoridation capacity [44].

Na and Park (2010) used lanthanum hydroxide for defluoridation of water. The optimum pH for maximum fluoride removal was observed in the pHeq≤7.5. The equilibrium data were fitted well with Langmuir isotherm model and maximum monolayer adsorption was observed to be 242.2 mg/g at pHeq≤7.5 and 24.8 mg/g at pHeq>10.0 respectively. The adsorption kinetics was well described by the pseudo-second-order equation. The adsorption process was spontaneous and endothermic in nature and the spent adsorbent was regenerated to 85% by 1 M NaOH solution [45].

Zhang et al. (2014) used La(III)-Al(III) loaded scoria for removal of fluoride from groundwater. The adsorption equilibrium was reached within 5 minutes. The adsorption followed the pseudo-second-order kinetic model. The equilibrium data were fitted well with both Langmuir (R^2=0.97) and Freundlich (R^2=0.98) isotherm models. The large amount of La-Al-O composite oxide existed on the surface of La-Al Scoria was found responsible for excellent removal of fluoride and the Langmuir adsorption capacity of La-Al Scoria was 23.91 mg/g [46]. Yu et al. (2014) prepared Mn-La metal bimetal composite for removal of fluoride from water. The optimum pH of adsorbent was found to be 5.0. The adsorption data were fitted well with Langmuir isotherm model and the Langmuir maximum adsorption capacity was 292.9 mg/g at pH 5.0. The adsorption was fast in first 60 min and equilibrium was reached within 8 h. The phosphate ions affected fluoride removal efficiency whereas chloride, sulphate and humic acid did not affect fluoride efficiency. The adsorption process was mainly occurred due to ion-exchange between sulphate and fluoride as well as presence of weak acid functional groups. The intra-particle diffusion model was rate determining step [47].

LAYERED DOUBLE HYDROXIDES

Diaz-Nava et al. (2003) used thermally treated hydrocalcite for defluoridation of well water. The fluoride solution of 5 mg/l was reduced to 0.15 mg/l at pH 5 with 10 g/l dose of calcined hydrocalcite (500°C) [48]. Das et al. (2003) synthesized calcined Zn/Al hydrocalcite like compound (HTlc) for defluoridation of drinking water. The maximum fluoride removal more than 85% was obtained at pH 6 with 4 hours. The maximum adsorption capacity of 13.43 mg/g obtained for fluoride solution of 10 mg/l at pH 6, dose of 0.2g/l and 30°C. The adsorption data were fitted well with the Langmuir isotherm model and pseudo-first order equation. The adsorption process was exothermic in nature and the adsorption efficiency was reduced due to presence of sulpahte and phosphate co-anions drastically. The regeneration was done by 0.01M NaOH in 6h [49].

Lv et al. (2006) studied the calcination effect of Mg/Al LDH on the defluoridation capacity. The defluoridation capacity of Mg/Al- LDH (CLDH) calcined at 200 °C, 400 °C, 500 °C and 600°C was observed to be 65, 70, 80 and 62 mg/l respectively and showed maximum adsorption efficiency when calcined at 500 °C. The calcined Mg/Al with molar ratio of 2 was given maximum adsorption capacity. The adsorption capacity of Mg/Al LDH was higher than Ni/Al LDH and Zn/Al LDC since atomic weight of Ni and Zn was higher than Mg. The maximum fluoride adsorption capacity of 213 mg/g was obtained at pH 6. The 98 % of fluoride removal was achieved at pH 6 with fluoride solution of 50 mg/l. The fluoride solution of 20 mg/l was reduced to 0.4 mg/l by calcined Mg/Al LDH. The equilibrium data were fitted with both Freundlich and Langmuir adsorption isotherms and the fluoride removal efficiency with co-anions increased in order $PO_4^{3-} < Cl^- \approx SO_4^{2-} < Br^- \ll NO_3^-$ [50]. Lv et al. (2006) prepared calcined Mg/Al LDH (CLDH) for defluoridation of water. The maximum adsorption was obtained by LDH with Mg/Al molar ratio of 2 calcined at 500°C at pH 6.0. The experimental data were fitted well with the Langmuir isotherm model and adsorption process was spontaneous and exothermic in nature. The maximum fluoride adsorption capacity of 213 mg/g was obtained at pH 6 [51]. Lv et al. (2006b) studied the kinetics of calcined Mg/Al-CO_3 (CLDH) in batch mode. The adsorption was followed the pseudo-second-order kinetic model and the activation energy (E_a) value of 39.73 kJ/mol indicated that the process was reaction controlled [52].

Lv et al. (2007) studied the defluoridation potential of Mg/Al-CO3 layered double hydroxide (LDH). The adsorption of fluoride decreased with increase in pH of aqueous solution. The presence of co-anions reduced the adsorption of fluoride in the order of $HCO_3^- > Cl^- > H_2PO_4^- > SO_4^{2-}$. The adsorption data was described well with Langmuir-Freundlich isotherm model and adsorption followed the pseudo-second-order kinetic equation. The maximum adsorption capacity of LDH was 319.8±5.7 mg/g and the adsorption process was spontaneous and endothermic [53].

Wang et al. (2007) synthesized Mg-Al/CO3 hydrotalcite compound (HT) and its calcined product (HTC) for defluoridation of water. The adsorption efficiency of HTC was higher than HT due to increase in surface area and formation of LDH like structure. The adsorption capacity increased with temperature in case of HTC whereas fluoride removal efficiency decreased in case of HT precursor. The removal efficiency was inversely proportional to the initial fluoride concentration for HTC. The HTC130 (synthesized at 130°C) reduced fluoride solution of 5 mg/l to 1 mg/l at pH 7. The HTC130 did not follow Langmuir isotherm model (k=0.46 L/g) [54].

Mandal and Mayadevi (2008) prepared Zn/Al layered double hydroxide (LDH) for defluoridation of water. The Zn/Al molar ratio of 0.97 showed a higher defluoridation capacity (1.14-4.16mg/g). The adsorption increased after calcination upto 500°C. The equilibrium data were fitted well with Langmuir, Freundlich and Temkin equation and followed the pseudo-second-order kinetic model [55].

Mandal et al. (2009) synthesized Zn/Al/Cl anionic clay for defluoridation of water. The equilibrium data were fitted well to Langmuir isotherm model and adsorption was well explained by two-steps first-order kinetic model. The adsorption process was feasible and exothermic in nature. Adsorption capacity of ZA-13 clay was not much influenced in the pH range of 5.2 to 6.4. The regeneration of adsorbent was carried out by 0.01M NaOH solution and used successfully for five cycles without loss of fluoride adsorption capacity and the 28% loss of adsorption capacity was occurred after five cycles of regeneration [56]. Yang et al. (2009) synthesized magnetic Mg-Fe-Al hydrotalcite compound (MgAlFe HTlc) for defluoridation of water by co-precipitation method. The molar ratio of Mg^{2+}:Fe^{3+}:Al^{3+} was 1:0.8:0.2. The adsorption capacity of HTlc was 3.31 mg/g at pH 6.0 for fluoride solution of 10 mg/l with 200 min. Further increased in pH above 6.0 reduced the adsorption capacity. The HTlc calcined at 500ºC had increased the adsorption capacity. The experimental data were fitted well with Langmuir isotherm model and adsorption process followed pseudo-first order kinetic model. The Langmuir maximum adsorption capacity of HTlc500 was 14.92 mg/g. The field sample of 10mg/l was reduced to 1.26 mg/l and 5.87 mg/l by HTlc and commercial adsorbent at pH 8.3, 293K temperature and contact time of 5h [57].

Warsakoon et al. (2010) prepared Mg-Al-hydroxide LDH (Mg-Al-OH) for defluoridation by co-precipitation method. The 2 g/100 ml dose of adsorbent (Mg-Al-OH) reduced the fluoride solution of 8.04 mg/l to 1.05 mg/l and was found suitable for drinking purpose. The regeneration of spent LDH was carried out by calcination where the fluoride removes as a gas. This fluoride gas was absorbed into a $Ca(OH)_2$ solution to form CaF_2 precipitate. This precipitate CaF_2 can be used as an ingredient in the toothpaste industry [58].

Lv et al. (2012) studied the Mg-Ca-Al (NO_3) hydrocalcite like structure for defluoridation of water. The NO_3-HTlcs with Mg/Ca/Al molar ratio of 2.5/0.5/1 gave maximum defluoridation capacity of 82.35 mg/g and 72.69 mg/g at pH 5.0 and 40ºC in BSA and LSZ system. The losses of both BSA and LSZ were low (<1.5%) during the whole experiment. The presence of co-anions was reduced the fluoride adsorption in the order of bicarbonate > sulphate > chloride > nitrate. The equillibrium adsorption data fitted well with the Langmuir isotherm model and pseudo-second-order kinetic model. The adsorption process was spontaneous and endothermic in nature and the physisorption was responsible for fluoride adsorption [59]. Manda et al. (2012) synthesized Mg-Cr-Cl layered double hydroxide for defluoridation of ground water and wastewater. The adsorption experiment was well described by Langmuir isotherm model and adsorption process followed the first order kinetic model. The fluoride removal of 88.5% and 77.4% at neutral pH was obtained with adsorbent dose of 0.6 g/l with initial fluoride concentration of 10 and 100 mg/l respectively. The equilibrium was achieved in 40 min. The thermodynamic study revealed that the adsorption process was spontaneous and endothermic in nature. The presence of co-anions reduced the fluoride adsorption in the order of phosphate > sulphate > nitrate. The regeneration of material was not possible [60]. Cai et al. (2012) prepared calined Mg-Al-CO3 layered double hydroxide (CLDH) for removal of fluoride and phosphate from water. The optimum pH and equilibrium time for CLDH was 6 and 24 h. The adsorption of fluoride and phosphate was decreased in presence of each other. Kinetics of CLDH was well described by pseudo-second-order equation. The experimental data were fitted well with Langmuir isotherm model and the Langmuir maximum adsorption capacity of F, P, F(P) and P(F) was 1.94, 1.79, 0.63 and 1.42 mg/g respectively [61].

Koilraj and Kannan (2013) used nitrate containing zirconium/chromium layered double hydroxides ($ZnCr_3$-NO_3-LDH) with Zn/Cr ratio of 2.0, 3.0 and 4.0 synthesized by co-precipitation method for defluoridation of water in batch mode. The maximum adsorption capacity was observed to be 31 mg/g and fluoride uptake was increased with an increase in layered double hydroxide loading. The fluoride removal was constant over pH range of 3-10. The polysulfone/ZnCr-LDH composite material with varying amount of LDH was used in column study showed higher performance in wet state than dry state and the defluoridation capacity of hybrid adsorbent were get affected by presence of co-anions in water [62].

MAGNESIUM BASED

Goswami and Das (2005) used dual bed system with fly ash in Bed I and ferric alum and $MgCl_2$ modified fly ash in Bed II (15g) for effective removal of fluoride solution of 100ppm and reduce to 0 ppm. The first bed was used to maintain the pH of influent to 7.5. The pH of effluent from Bed II was 5.4-5.5 and suitable for drinking [63].

Maliyekkal et al. (2006) studied the defluoridation capacity of manganese oxide coated alumina (MOCA) and activated alumina (AA). The defluoridation capacity of MOCA and AA was 2.85 and 1.08 mg/g respectively. The adsorption process by MOCA was followed Langmuir isotherm model and Pseudo-second-order kinetic model. The optimum pH was ranged between 4-7. The presence of sulphate, nitrate and bicarbonate ions did not affected defluoridation efficiency. The desorption was carried out by using 2.5% NaOH solution. The column performance was studied by bed-depth-service time BDST model. MOCA bed was found to be 1.25gl1, which is around 2.5 times greater than that of AA [64].

Zhu et al. (2009) prepared magnesia-amended silicon dioxide granules (MAS) by modification of silicon dioxide with wet impregnation of magnesium chloride and used for defluoridation of water. The maximum fluoride was obtained at pH range of 3-4 and declined at pH above10.0. The maximum defluoridation capacity of MAS was 12.6 mg/g at pH 3.0. The order of reduction of fluoride adsorption was bicarbonate > sulphate > phosphate. The reduction of fluoride adsorption was due to the competition for active sites between these ions or due to change in pH or combination of both [65]. Yue et al. (2009) have used manganese oxides coated granular activated carbon (GAC-MnO_2) by using redox process as adsorbent for defluoridation of water. The fluoride removal efficiency of GAC-MnO_2 obtained by coating 0.3M $MnCl_2$ on granular activated carbon was observed to be at least three times greater than plain GAC. The optimum pH for maximum removal of fluoride was observed to be 3.0. The experimental data were followed the Freundlich isotherm and pseudo-second-order kinetic model. The adsorption process was involved both boundary layer diffusion and intra-particle diffusion. The fluoride removal of GAC-MnO_2 coated adsorbent was higher than uncoated MnO_2 since the surface area of MnO_2 coated GAC and uncoated GAC was 914.17 m^2/g and 850.60 m^2/g respectively [66].

Kang et al. (2011) used calcined magnesia/pullan (cMgOP) composite for defluoridation of water. The surface area and adsorption micro pore size of cMgOP were 33 m^2/g and 30 nm whereas 7.6 m^2/g and 14 nm for pure MgO. The presence of bicarbonate ions reduced the fluoride efficiency while chloride, sulphate and nitrate ions had negligible effect on defluoridation capacity. The defluoridation capacity of cMgOP was 4537 mg/kg at pH 7 and 30°C with 10 mmol/l of fluoride solution and was found ten times than that of MgO (457 mg/kg). The maximum fluoride removal of 97.6% was obtained at pH of 5.0. The experimental data were fitted well with Langmuir isotherm model and followed pseudo-second-order kinetic model and the adsorption process was spontaneous and endothermic in nature [67]. Sivasankar et al. (2011) used manganese dioxide modified disposed earthware (DEW) for defluoridation of water. The Manganese dioxide concentration was varied from 0.01 to 0.025%. The defluoridation was done in static condition at pH range of 5-11 and contact time of 35 minutes. The defluoridation capacity of DEW dispersed with 0.025% of manganese dioxide increased from 1198 to 1888 mg/kg at pH 5-7. The presence of sulphate ions reduced adsorption greatly as compare to presence of bicarbonate, chloride and phosphate ions. The exhausted adsorbent was regenerated by NaOH solution. In the simulating equilibrium data, simple kinetic models namely, pseudo I and II order, particle and pore diffusion, Elovich and isothermal models of Langmuir and Freundlich were used [68]. Xu et al. (2011) prepared magnesia-loaded fly ash cenospheres (MLC) by wet impregnation of magnesium chloride on fly ash cenosphere for defluoridation of water. The adsorption process was described well by Langmuir isotherm model and pseudo-second-order kinetic model. The value of ΔG, ΔH and ΔS were observed to be -0.409 $kJmol^{-1}$, 20.04 $kJmol^{-1}$ and 63.80 $Jmol^{-1}K^{-1}$ respectively at 318K. The maximum adsorption capacity of MLC was about 6.0 mg/g with 100 mg/l of fluoride solution and dose of 2.5 mg/l at pH 3.0 and 318K. The presence of co-anion was influenced fluoride adsorption in the order of dihydric phosphate > nitrate > sulphate [69].

Sasaki et al. (2012) studied the chemical regeneration of magnesium oxide used for defluoridation of water. The calcination of $MgCO_3$ at 1273 K for 1 hour produced the MgO. The sorption of fluoride by MgO was 9.82 mM on the calcined product. The solid residue after adsorption was further calcined and used for adsorption repeatedly for five times to determine trends in sorption density of fluoride and stability of chemical regeneration of MgO. The sorption density of fluoride on the calcined product was the greatest for MgO-I and the smallest for MgO-II. This difference was occurred due to increasing of the crystal size observed by transmission electron microscopy. The CO_2-TDP analysis showed the positive correlation between the sorbed mass of F^- per SBET (Q_o) and the sorption capacity of CO_2 indicate basicity. The basicity on the surface of the MgO affects its hydration and found responsible for sorption of fluoride during co-precipitation of fluoride with $Mg(OH)_2$. The number of weak base sites was calculated from the peak intensity at 373K in CO_2-TDP. Large quantity of $NaMgF_3$ and elemental Mg were evaporated by the calcination at 1273K of the solid residues formed after sorption of fluoride [70].

Mondal and George (2013) prepared a novel calcium-aluminium-magnesium (CAM) based adsorbent for defluoridation of water. The adsorption capacity was equivalent to activated alumina. The optimum pH and equilibrium time were 7.0 and 180 minutes respectively. The adsorption process was followed Freundlich isotherm model and pseudo-second-order kinetic model. The leaching of calcium and magnesium were negligible in water. The regeneration of exhausted CAM was done by alkaline washing with NaOH followed by acid washing with HCl or H_2SO_4 [71]. Dash et al. (2013) used manganese oxide modified aluminium oxy(hydroxide) (MOAOH) adsorbent by sol-gel method for defluoridation of water. The fluoride removal of 94.8% was obtained at pH range of 5-7. The equilibrium was reached after 15 min. The experimental data were fitted well with Langmuir isotherm model and adsorption process followed pseudo-second-order kinetic model. The Langmuir maximum adsorption capacity was observed to be 18.62 mg/g. The energy value of 9.71kJ/mol represented that the adsorption process was mainly due to chemisorption. Desorption of 86.20% was achieved by using 1% NaOH solution in 3 h [72].

Suzuki et al. (2013) used commercial-grade MgO for immobilization of fluoride in the water-kaolinite-MgO system. The commercial grade MgO was a good immobilized agent for soil treatment against fluoride and found durable with permissible leaching against the acid rain test for several years [73].

Margandan et al. (2014) had optimized MgO dose in MgO-$CaCl_2$-Lime-HCl defluoridation system. The optimum dose of MgO was found to be 0.8 g/l to obtained fluoride removal of 67.5%. The TDS of water was 1240 ppm and found within the permissible limit of 2000 ppm. The chloride ion concentration of HCl treated water was 665 ppm and was well within permissible limit of 1000 ppm. The residual $Mg^{+2}$was 78 ppm within the permissible limit of 100 ppm. The residual Ca^{+2} in water was minimum at 0.7-0.8 ppm. The total hardness (Ca^{+2}+ Mg^{+2}) was 108 ppm and less than permissible limit of 600 ppm. The total alkalinity value was 260 ppm well within the permissible limit of 600 ppm [74]. Devi et al. (2014) used nano-sized magnesium oxide (nano-MgO) for fluoride removal from water. The surface area of adsorbent was 92.46 m^2/g. The maximum fluoride removal of 90% was obtained with 0.6 g/l dose of adsorbent. The influence of pH on adsorbent was negligible. The experimental data were fitted well with Freundlich isotherm model which indicated that the adsorption was multilayer. The adsorption followed the pseudo-second-order kinetic model. Desorption of 95% was achieved by 1M HCl. The presence of co-anions on reduction of adsorption was found in order of hydroxide (76%) < sulphate (83%) < bicarbonate (84%) < chloride (89%) [75]. Alemu et al. (2014) synthesized aluminium oxide – manganese oxide (AOMO) composite adsorbent for defluoridation of water in batch experiment. 11% manganese oxide in AOMO had better adsorption capacity. The pH_{pzc} of AOMO was 9.54. The adsorption was increased with increase in initial fluoride concentration. The optimum pH range and equilibrium time of AOMO were 5-7 and 120 min. The adsorption capacity of AOMO was observed to be 18.6 mg/g. The experimental data were fitted well with Freundlich isotherm model and adsorption followed pseudo-second-order kinetic model and the Langmuir maximum adsorption capacity of AOMO was 191.19 mg/g [76]. Li et al. (2014) prepared porous hollow MgO microsphere for defluoridation of water. The adsorption capacity of adsorbent was more than 120 mg/g at pH 7.0. The MgO reacted with water to form $Mg(OH)_2$which in-turn responsible for attracting fluoride ions and the presence of phosphate ions greatly reduced fluoride uptake [77]. Minju et al. (2015) prepared magnesium oxide (MgO) coated magnetite (Fe_3O_4) nanoparticle by sol-gel method for defluoridation of aqueous solution. The maximum fluoride removal of 98.6% was obtained in the initial fluoride concentration of 13.6 mg/l at optimum conditions (pH=6, dose = 2g/l, contact time=120 min). The adsorption was very fast and equilibrium was reached within 180 min. The adsorption equilibrium data were fitted well with the Langmuir isotherm model and adsorption followed the pseudo-second-order kinetic model and the Langmuir monolayer adsorption capacity was observed to be 10.96 mg/g [78].

TITANIUM BASED

Ishihara et al. (2002) studied the titanium hydroxide [$Ti(OH)_4$] as fluoride ion exchanger. The titanium hydroxide was saturation capacity of 1.60 m.mol/g. The capacity of adsorbent was not changed over four time repetition for ion-exchange and desorption. The presence of $H_2PO_4^-$ reduced the defluoridation capacity drastically whereas nitrate, chloride and sulphate ions had negligible effect on fluoride efficiency. The leaching of Ti was found negligible. The ion exchange was performed at pH of 5 whereas desorption was carried out at pH of 12. $Ti(OH)_4$ had more defluoridation capacity than TiO_2 [79] .

Wajima et al. (2009) used gel like titanium hydroxide-derived adsorbent from titanium oxysulfate, $TiO(SO_4)$. Maximum fluoride adsorption was occurred at pH of 3.0. The experimental data were fitted well with the Freundlich isotherm than the Langmuir isotherm model. The adsorbent could remove fluoride in actual wastewater below 0.8mg/l. The regenerated adsorbent was used three times after repeated adsorption and desorption without changing the adsorption capacity [80].

Gopal et al. (2010) used magnesium titanate for defluoridation of water. The defluoridation capacity of 0.029 mg/g was obtained from 4 mg/l of fluoride solution. The defluoridation was carried out in wide pH range of 3 -11 and temperature range of 30–50°C. The presence of co-anions did not affect defluoridation capacity. The adsorption followed Langmuir isotherm model and adsorption process was endothermic in nature and the mechanism of fluoride adsorption by magnesium titanate was physisorption [81]. Li et al. (2010) prepared Ti-Ce, Ti-La and TiO_2 by hydrolysis-precipitation and hydrolysis for defluoridation of water. The defluoridation capacity of Ti-Ce, Ti-La and TiO_2 were 9.6, 15.1 and 1.7 mg/g respectively. The equilibrium for three adsorbent was achieved within 4 hours. The sorption capacity was decreased with increasing pH from 3 to 9.5. The experimental data were fitted well with the Langmuir isotherm model and adsorption followed the pseudo-second-order kinetic model and the adsorption of fluoride took place by hydroxyl group available on the surface of adsorbents [82].

Babaeivelni and Khodadoust (2013) used anatase TiO2 with specific surface area of 56 m^2/gm to remove fluoride from water. The adsorption kinetic showed that the maximum adsorption of fluoride was occurred within 3 h and followed the pseudo-second-order kinetic model. The experimental data were fitted well with the Langmuir isotherm model and Dubinin-Radushkevich model indicated the physical adsorption of fluoride. The maximum defluoridation was occurred in pH range of 2-5, while approximately 75% of fluoride adsorption achieved at pH 7.0. and adsorption declined when pH > 9.0. Higher bicarbonate concentration reduced the adsorption efficiency due to increase in alkalinity of solution [83].

ZIRCONIUM BASED

Swain et al. (2010) synthesized the zirconium (IV)-propanolamine (ZrPA) hybrid adsorbent for defluoridation of water. The optimum proportion of Zr:PA was 1:1. The fluoride removal of above 95% was achieved at pH 7. The experimental data were fitted well with Dubinin-Radushkevich (D-R) isotherm model (R^2=0.997) and the pseudo-second-order kinetic model. The Langmuir maximum adsorption capacity of ZrPA was 32.25 mg/g. The adsorption process was spontaneous and endothermic in nature. The value of energy per mole of adsorbate (E) was found to be 10 indicating the ion-exchange process. The presence of sulphate, phosphate and nitrate ions did not affect fluoride adsorption. The ZrPA was effectively used upto ten consecutive cycles but reduced fluoride removal from 98% to 80%. The regeneration of spent ZrPA to 95% was achieved by 0.1M NaOH solution [84].

Swain et al. (2011) used meso-structured zirconium phosphate (MZrP) for defluoridation of drinking water. The maximum fluoride uptake was obtained at pH of 6.0. The fluoride removal of 96% was achieved with a dose of 3.0 g/l. The presence of other co-anions did not affect the adsorption. The adsorption was governed by ion-exchange mechanism. The kinetic study was followed the pseudo-second-order kinetic model. The value of enthalpy (ΔH) and entropy (ΔS) factors were evaluated to be 44.79 kJ mol^{-1} and 0.223 kJ mol^{-1} K^{-1}, respectively. The adsorption process was spontaneous in nature. The regeneration of MZrP was successfully used for adsorption upto five cycles with reduced adsorption capacity [85].

Dey et al. (2012) prepared zirconium (IV) – ethylenediamine (ZrEDA) hybrid adsorbent by sol-gel method for defluoridation from drinking water. The maximum fluoride removal by ZrEDA at neutral pH was 99% and adsorption equilibrium was attained within 14 minutes. The kinetic of adsorption was well described by the pseudo-second-order equation and adsorption process was spontaneous and endothermic in nature. The regeneration of spent adsorbent was achieved by 0.1M NaOH solution and regenerated adsorbent was tested upto ten cycles without significant loss of adsorption efficiency [86]. Dou et al. (2012) studied the defluoridation of water using synthesized hydrous zirconium oxide in batch mode. The maximum defluoridation capacity was found to be 124 and 68 mg/g at pH 4 and 7 respectively. The adsorption process was followed the pseudo-second-order kinetic model. The adsorption was occurred by exchange of surface hydroxyl groups with fluoride and by the electrostatic interaction between charging surface and fluoride. The presence of phosphate, arsenate and bicarbonate ions affected the adsorption capacity whereas nitrate, chloride and sulfate showed slight effects on adsorption [87]. Swain et al. (2012) prepared zirconium (IV) – ethylenediamine (ZrEDA) hybrid adsorbent by sol-gel method for defluoridation of water. The fluoride removal of 99% was obtained at optimum condition (initial fluoride concentration of 10mg/l, pH of 7, dose of 0.1g/100ml and contact time of 60 min). The equilibrium was attained in 14 minutes. The adsorption followed a pseudo-second-order kinetic. The adsorption reaction was spontaneous and endothermic in nature. Desorption was done by using 0.1M NaOH solution and adsorbent could be used for 10 cycles without significant loss of adsorption efficiency. The presence of co-anions did not affect defluoridation capacity [88].

Wang et al. (2013) used Ce_2O_3-ZrO_2 nano-cages prepared by Kirkendall effect for defluoridation of water. The optimum pH range was 3.5-4.5. The experimental data were fitted well with the Langmuir isotherm than Freundlich isotherm model. The Langmuir maximum capacity of the Ce_2O_3-ZrO_2 was found to be 175 mg/g at pH of 4.0. The presence of chloride and arsenate in high concentration affected fluoride adsorption. The groundwater of 2.820 mg/l of fluoride concentration was reduced to 1.39 mg/l after treatment with 0.4g/l dose of Ce_2O_3-ZrO_2. The kinetics of adsorption was well described by the pseudo-second-order rate equation [89].Tomar et al. (2013) prepared Zr-Mn composite adsorbent for defluoridation of water. The fluoride removal of 90% was achieved at adsorbent dose of 1.2g/50mL, pH 7, temperature 29°C and the contact time 145 min. The removal of fluoride ions from distilled water (90%) was more than natural water (82-87%). The experimental data were fitted well with the Freundlich isotherm model. The fluoride adsorption was mainly governed by anion exchange and electrostatic interaction in the adsorption process [90].

Yang et al. (2014) prepared mesoporous ZrO_2 nanomaterials in an agarose gel medium by a bio-inspired approach and then calcined at 600ºC for 2 h followed by removal of agarose gel for defluoridation of water. The surface area and pore volume of adsorbent was 40.14 m^2/g and 0.091 cm^3/g respectively that increased with increase of gel concentration and decreased with increase of initial $ZrOCl_2$ concentration. The fluoride adsorption capacity of ZrO_2 sample synthesized in agarose gel was more than that synthesized in aqueous solution [91].

Saha et al. (2015) prepared β-Cyclodextrin modified hydrous zirconium oxide (CY-HZO) for defluoridation from aqueous solution. The particle size and surface site concentration of CY-HZO was 150 nm and 6300 nm^{-2} and more than pristine HZO (60 nm and 26 nm^{-2}). The fluoride adsorption over HZO was improved by modification with β-CD by adding abundance OH^- groups. Fluoride adsorption onto CY-HZO was increased upto pH 5.0 and declined sharply at pH 6.0. The adsorption data were fitted well with the Langmuir isotherm model and followed the pseudo-second-order kinetic model for both CY-HZO and HZO respectively. The adsorption process for both CY-HZO and HZO were spontaneous but endothermic with CY-HZO and exothermic with HZO. The Langmuir adsorption capacity of CY-HZO and HZO were 31.45 mg/g and 22.45 mg/g at 303K. Fluoride adsorption by CY-HZO based on ion-exchange process. Desorption of 95% was achieved for CY-HZO by 3.0 M NaOH solution [92].

OTHERS

Eskandarpour et al. (2008) studied the defluoridation of wastewater by using schwertmannite. The schwertmannite adsorbent had ability to lower the fluoride concentration to desirable level and re-generable in nature and mostly applied to polish wastewater after a precipitation/coagulation process. The optimum pH range was 3-3.7 where the maximum defluoridation was obtained and adsorption was decreased after pH > 3.7. The defluoridation capacity of schwertmannite was very high (50-80 mg/g) with different isotherm models such as two-site Langmuir, Freundlich, Langmuir-Freundlich, Redlich-Peterson, Toth, Dubbinin-Radushketvich at 296.5, 303 and 313 K respectively. The experimental equilibrium data were fitted well with all model except the Freundlich isotherm and Dubinin-Radushlkevitch isotherm model was overestimated the adsorption capacity [93].

Karthikeyan et al. (2009) used conductive polypyrrole for defluoridation of water. The adsorption capacity was founded to be 6.37 mg/g with fluoride solution of 10 mg/l at 30ºC. The adsorption process was dependent on pH and temperature. The experimental data were fitted well with Freundlich and Dubinin-Radushkevick (D-R) isotherm models. The kinetic study revealed that the adsorption was spontaneous and exothermic in nature. The chemisorption played an important role for adsorption of fluoride [94].

Sakhare et al. (2012) has used calcium aluminate (CA) for fluoride uptake from aqueous solution. The fluoride removal of 85% was obtained by dose of 3.0 g/l for 8.9 mg/l of initial fluoride concentration at neutral pH. The adsorption process involved both physisorbent (alumina) and chemisorbent (calcium) mechanisms. The experimental data were fitted well with Langmuir adsorption isotherm and followed the pseudo-second-order kinetics. The intra-particle diffusion was contributed to the rate determining step. The thermodynamic study revealed that the adsorption reaction was spontaneous and endothermic in nature. The chemisorption was the main governing phenomenon for adsorption as per thermodynamic study. The regeneration of CA upto 84% was achieved by 5% NaOH and 0.5% H_2SO_4. The bicarbonate only decreased the fluoride removal in small amount at higher concentration (400-600 mg/l) [95].

Srivastav et al. (2013) studied the defluoridation of water by using bismuth trioxide (Bi_2O_3) and three hydrous bismuth oxides (HBO_1, HBO_2 and HBO_3) were synthesized by varying amount of NaOH in the Bi_2O_3-HCl solution. HBO_1 showed high fluoride removal efficiency. The fluoride removal of 65% was obtained by HBO_1 for 5-10 mg/l of fluoride solution. The adsorption potential (q_e) varied from 0.136 mg/g to 0.092 mg/g as pH increased from 4 to 12 and defluoridation was decreased beyond pH of 9. The optimum dose and contact time were 50g/l and 3 h with initial fluoride concentration of 10 mg/l. The XRD of HBO_1 showed crystalline and high peak of bismuth hydroxide and bismuth oxychloride in the material. FTIR revealed presence of Bi-O and OH groups in HBO_1. The SEM image reveals a rough surface and cotton like spongy structure. The data of adsorption were fitted well with the Langmuir isotherm model. The Langmuir adsorption capacity varied from 0.60 to 1.93 mg/g with different temperature and maximum of 1.93 mg/g at 293K. The kinetic study revealed that adsorption followed the pseudo-second-order kinetic model. The adsorption process was endothermic in nature. The defluoridation was done by physical adsorption as per Dubinin–Radushkevich (D–R) isotherm. The presence of sulphate and chloride ions had greater impact on defluoridation efficiency than bicarbonate ions [96].

Rafique et al. (2014) used trimetal-oxide (refractory ceramic waste) from a local steel mill for defluoridation from aqueous solution in batch study. The kinetics of adsorption was well described by pseudo-first-order as well as the pseudo-second-order equations. The adsorption data was best fitted with the Langmuir isotherm and the pseudo-second-order kinetic model. The Langmuir maximum adsorption capacity was found to be 2.199 mg/g. The fluoride uptake of 78% was achieved at pH range of 6-7. The main constituents of trimetal oxides was Al_2O_3 (40.40%), CaO(30.65%), MgO(22.10%) as well as diaspora (43.60%), calcite (30.20%) and dolomite (20.90%) as dominant phases. The adsorption was chemisorption. The adsorbent was low cost and used for defluoridation from groundwater of Thar Desert of Pakistan [97]. Barathi et al. (2014) prepared aluminium oxy hydroxide modified graphene oxide [GO-Al-O(OH)] by chemical precipitation method for defluoridation of water. The adsorption data were fitted well with the Langmuir isotherm and the pseudo-second-order kinetic model. The Langmuir maximum adsorption capacity of adsorbent was 51.42 mg/g. The fluoride solution of 5 mg/l was treated to obtain 2.0 L of water with concentration less than 1.5 mg/l by using oxide [GO-Al-O(OH)]. The regeneration of adsorbent was done using ammonium hydroxide [98].

Jia et al. (2015) prepared bayerite/boehmite nano-composite by a facile one pot hydrothermal method for defluoridation of water. The maximum adsorption capacity of adsorbent was 56.80 mg/g at pH 7.0. The presence of bicarbonates and sulphate ions inhibited the fluoride removal at high concentration. The hydroxide groups and nitrate ions present on surface adsorbent were participated for fluoride adsorption by ion-exchange process [99].

CONCLUSIONS AND FUTURE PERSPECTIVES

The fundamental marvel that may be effective in the fluoride removal from water is a sorption/precipitatin onto cpmposite oxide materilas. It can expect that metal oxides may be fascinating materilas in the defluoridation of water.The metal oxide material as an adsorbent for fluoride removal from was effectively utilized. The metal oxide material opens a opportunity for an efficient removal of fluoride from industrial wastewaters and crude water of the drinking water supply. The metal oxide material has a great affinity for fluoride. There is no sorption of other mono-valence anions. Because of the small particle size, the rate of sorption is high point. Accordingly, metal oxide material have the improves of high mass transfer rates, good selectivity of fluoride, and physicochemical stability. The present study determined that metal oxide material as a minimal effort adsorbents have demonstrated a decent effectiveness in fluoride removal from aqueous solution and can be actually utilized for waste management and environmental security persistences.

REFERENCES

[1] Waghmare S.S., Arfin T., Manwar N., Lataye D.H., Labhsetwar N., and Rayalu S., “Preparation and characterization of polyalthia longifolia based alumina as a novel adsorbent for removing fluoride from drinking water”, Asian J. Basic Sci., Vol. 4, No. 1, pp. 12-24, 2015.

[2] Xiuru Y., Kuanxiu S., Jianping W., Liuchang H., and Zhaohui Z., “Preparation of CeO_2-TiO_2/SiO_2 and its removal properties for fluoride ions”, J. Rare Earths, Vol. 16, No. 4, pp. 279–280, 1998.

[3] Xu Y.M., Ning A.R., and Zhao J., “Preparation and defluorination performance of activated cerium(IV) oxide/SiMCM-41 adsorbent in water”, J. Colloid Interface Sci., Vol. 235, Issue 1, pp. 66–69, March 2001.

[4] Zhongzhi J., Zhonglin C., Min Y., Yu Z., and Guibai L., “Adsorption of fluoride ion by inorganic cerium based adsorbent”, High Technol Lett. Vol.10, No. 4, pp.83–86, 2004.

[5] Liu H., Deng S., Li Z., Yu G., and Huang J., “Preparation of Al-Ce hybrid adsorbent and its application for defluoridation of drinking water”, J. Hazard Mater., Vol. 179, Issues 1-3, pp. 424–430, July 2010.

[6] Zhang P., Tong O., Shanshan C., Ruoshuang L., and Limin L., Fluoride adsorption onto a Ce-La binary hydroxide adsorbent as recovery of ceria glass polishing wastes, 4th Int. Conf. IEEE on Bioinformatics and Biomedical Engineering, pp 1-4, 18-20 June 2010.

[7] Deng S., Liu H., Zhou W., Huang J., and Yu G., “Mn-Ce oxide as a high-capacity adsorbent for fluoride removal from water”, J. Hazard Mater., Vol 186. Issues 2-3, pp.1360–1366, Feb. 2011.

[8] Hui D., Xili Y., “Adsorption of fluoride, arsenate and phosphate in aqueous solution by cerium impregnated fibrous protein”, Chemical Engineering Journal, Vol.184, pp. 205– 212, March 2012.

[9] Sivasankar V., Murugesh S., Rajkumar S., and Darchen A., Cerium dispersed in carbon (CeDC) and its adsorption behavior: A first example of tailored adsorbent for fluoride removal from drinking water, Chemical Engineering Journal, Vol. 214, pp. 45–54, Jan. 2013.

[10] Zhang, T., Qiurong L., Zhenyu M., Haiyan X., Hongxiao L., Yuming Zho., “Adsorption of fluoride ions onto non-thermal plasma-modified CeO2/Al2O3 composites”, Desalination and Water Treatment, Vol. 52, Issues 16-18, pp. 3367-3376, April 2014.

[11] Ghosh A., Chakrabartib S., Biswas K., and Ghosh U.C., “Column performances on fluoride removal by agglomerated Ce(IV)–Zr(IV) mixed oxide nanoparticles packed fixed-beds”, Journal of Environmental Chemical Engineering Vol.3, Issue 2, pp. 653–661, June 2015.

[12] Wu X., Zhang Y., Dou X., and Yang M., “Fluoride removal performance of a novel Fe–Al–Ce trimetal oxide adsorbent”, Chemosphere, Vol.69, Issue 11, pp.1758–1764, Nov. 2007.

[13] Biswas K., Bandhoyapadhyay., Ghosh U.C., "Adsorption kinetics of fluoride on iron(III)-zirconium(IV) hybrid oxide", Adsorption, Vol.13, pp. 83–94, 2007.

[14] Streat M., Hellgardt K, Newton N.L.R., "Hydrous ferric oxide as an adsorbent in water treatment: Part 3: Batch and mini-column adsorption of arsenic, phosphorus, fluorine and cadmium ions", Process Safety Environ Protect., Vol. 86, Issue 1, pp. 21–30, Jan. 2008.

[15] Wu H.-X., Wang T.-J., Dou X.-M., Zhao B., Chen L., and Jin Y.,"Spray Coating of Adsorbent with Polymer Latex on Sand Particles for Fluoride Removal in Drinking Water", Ind. Eng. Chem. Res. Vol. 47, Issue 14, pp. 4697–4702, 2008.

[16] Kumar E., Bhatnagar A., Minkyu J., Jung W., Lee S., Kim S., Lee G., Song H., Choi J., Yang J., and Jeon B., "Defluoridation from aqueous solutions by granular ferric hydroxide (GFH)", Water Res., Vol. 43, Issue 2, pp. 490–499, Feb. 2009.

[17] Yulin T., Xiaohong G., Jianmin W., Naiyun G., Martin R. M., and Charles C. C., "Fluoride adsorption onto granular ferric hydroxide: Effects of ionic strength, pH, surface loading, and major co-existing anions", Journal of Hazardous Materials Vol. 171, Issues 1-3, pp. 774–779, Nov. 2009.

[18] Sujana M.G., Soma G., Vasumathi N., and Anans S., "Studies on fluoride adsorption capacities of amorphous Fe/Al mixed hydroxides from aqueous solutions", J. Fluorine Chem., Vol. 130, Issue 8, pp. 749–754, August 2009.

[19] Biswas K., Gupta K., and Ghosh U.C., "Adsorption of fluoride by hydrous iron(III)- tin(IV) bimetal Mixed oxide from the aqueous solutions", Chem. Eng. J., Vol. 149, Issues 1-3, pp. 196–206, July 2009.

[20] Biswas K., Debnath S., and Ghosh U.C.,"Physicochemical Aspects on Fluoride Adsorption for Removal from Water by Synthetic Hydrous Iron(III) –Chromium(III) Mixed Oxide", Separ. Sci.Technol., Vol.45, pp. 472–485, 2010.

[21] Chen N., Zhang Z., Feng C., Li M., Zhu D., and Sugiura N., "Studies on fluoride adsorption of ironimpregnated granular ceramics from aqueous solution", Mater. Chem. Phys. Vol. 125, Issues 1-2, pp. 293–298, Jan. 2011.

[22] Wu H.-X., Wang T.-J., Chen L., Jin Y., Zhang Y., and Dou X.-M.,"Granulation of Fe–Al–Ce hydroxide nano-adsorbent by immobilization in porous polyvinyl alcohol for fluoride removal in drinking water", Powder Technol., Vol. 209, Issues 1-3, pp. 92–97, May 2011.

[23] Dou X., Zhang Y., Wang H., Wang T., and Wang Y., "Performance of granular zirconium-iron oxide in the removal of fluoride from drinking water", Water Res. , Vol. 45, Issue 12, pp. 3571–3578, June 2011.

[24] Chen L., Wang T.-J., Wu H.-X., Jin Y., Zhang Y., and Dou X.-M.,"Optimization of a Fe–Al–Ce nano-adsorbent granulation process that used spray coating in a fluidized bed for fluoride removal from drinking water", Powder Technol., Vol. 206, Issue 3, pp.291–296, Jan. 2011.

[25] Huang Y.H., Shih Y.J., and Chang C.C., "Adsorption of fluoride by waste iron oxide: The effects of solution pH, major coexisting anions, and adsorbent calcination temperature", J. Hazard. Mater., Vol. 186, Issues 2-3, pp. 1355–1359, Feb. 2011.

[26] Chen N., Zhang Z., Feng C., Zhu D., Yang Y., and Sugiura N., "Preparation and characterization of porous granular ceramic containing dispersed aluminum and iron oxides as adsorbents for fluoride removal from aqueous solution", J. Hazard. Maters., Vol. 186, Issue 1, pp. 863–868, Feb. 2011.

[27] Chang C.F., Chang C.Y., and Hsu T.L., "Removal of fluoride from aqueous solution with the superparamagnetic zirconia material", Desalination Vol. 279, Issues 1-3, pp. 375–382, Sept. 2011.

[28] Chen L., He B.Y., He S., Wang T.J., Su C.L, and Jin Y., "Fe–Ti oxide nano-adsorbent synthesized by co-precipitation for fluoride removal from drinking water and its adsorption mechanism", Powder Technol. Vol. 227, pp. 3–8, Sept. 2012.

[29] Mohapatra M., Hariprasad D., Mohapatra L., Anand S., and Mishra B.K, "Mg-doped nano ferrihydrite—A new adsorbent for fluoride removal from aqueous solutions", Appl. Surface Sci., Vol. 258, Issue 10, pp. 4228–4236, March 2012.

[30] Zhao X., Wang J., Wu F., Wang T., Cai Y., Shi Y., and Jiang G., "Removal of fluoride from aqueous media by Fe_3O_4@$Al(OH)_3$ magnetic nanoparticles", J. Hazard. Mater., Vol. 173,Issues 1-3, pp. 102–109, Jan. 2010.

[31] Poursaberi T., Hassanisadi M., Torkestani K,; and Zare M., "Development of zirconium (IV)-metalloporphyrin grafted Fe_3O_4 nanoparticles for efficient fluoride removal", Chem. Eng. J., Vol. 189–190, pp. 117–125, May 2012.

[32] Liu R., Gong W., Lan H., Yang T., Liu H., and Qu J., “Simultaneous removal of arsenate and fluoride by iron and aluminum binary oxide: Competitive adsorption effects”, Sep. Purif. Technol., Vol. 92, pp. 100–105, May 2012.

[33] Chai L., Wang Y., Zhao N., Yang W., and You X., “Sulfate-doped Fe3O4/Al2O3 nanoparticles as a novel adsorbent for fluoride removal from drinking water”, Water Res. Vol. 47, Issue 12, pp. 4040–4049, August 2013.

[34] García-Sánchez J.J., Solache-Ríos M., Martínez-Miranda V., and Solís Morelos C., “Removal of fluoride ions from drinking water and fluoride solutions by aluminum modified iron oxides in a column system”, J. Colloid Interface Sci. Vol. 407, pp. 410–415, Oct. 2013.

[35] Kang D., Yu X., Tong S., Ge M., Zuo J., Cao C., and Song W., “Performance and mechanism of Mg/Fe layered double hydroxides for fluoride and arsenate removal from aqueous solution”, Chem. Eng. J., Vol. 228, pp. 731–740, July 2013.

[36] Zhang T., Li Q., Xiao H., Mei Z., Lu H., and Zhou Y., “Enhanced fluoride removal from water by non-thermal plasma modified CeO2/Mg–Fe layered double hydroxides”, Appl. Clay Sci., Vol. 72, pp.117–123, Feb. 2013.

[37] Chen N., Feng C., Miao L., “Fluoride removal on Fe–Al-impregnated granular ceramic adsorbent from aqueous solution”, Clean Techn. and Environ. Policy, Vol.16, Issue 3, March 2014.

[38] Chao-Li S., Chen L., Ting-Jie W., Li-Xin Y., and Jin Y.,“Granulation of Fe-Al-Ce nano-adsorbent for fluoride removal from drinking water using inorganic binder”, Water Science & Technology: Water Supply, Vol. 136, pp. 1309-1316, Sept. 2013.

[39] Woyessa G.W., Srivastava B.B.L., and Demissie E.G., “Synthesis of Hydrous Aluminum (III) -Iron (III)-Manganese (IV) Ternary Mixed Oxide for Fluoride Removal”, Int. J. Sci. Eng. Res., Vol. 5, Issue 3, pp. 885-892, March-2014.

[40] Nur T., Loganathan P., Nguyen T.C., Vigneswaran S., Singh G., and Kandasamy J., “Batch and column adsorption and desorption of fluoride using hydrous ferric oxide: Solution chemistry and modelling”, Cical Eng. J., Vol. 247, pp. 93-102, 2014.

[41] Qiao J., Cui Z., Sun Y., and Hu Q., “Simultaneous removal of arsenate and fluoride from water by Al-Fe (hydr)oxides”, Front. Environ. Sci. Eng., Vol. 8, Issue2, pp. 169–179, April 2014.

[42] Gitari W.M., Ngulube T., Masindi V., and Gumbo J.R., “Defluoridation of groundwater using Fe3+-modified bentonite clay: optimization of adsorption conditions”, Desalination Water Treat. Vol. 53, pp. 1578–1590, 2015.

[43] Yu Y., Yu L., and Chen J.P., “Adsorption of fluoride by Fe–Mg–La triple-metal composite: Adsorbent preparation, illustration of performance and study of mechanisms” Chem. Eng. J., Vol. 262, pp. 839–846, Feb. 2015.

[44] Wasay S.A., Haron M.J., and Tokunaga S., “Adsorption of fluoride, phosphate, and arsenate ions on lanthanum-impregnated silica gel”, Water Environ. Res., Vol. 68, No. 3, pp. 295–300, May-June 1996.

[45] Na C., and Park H., “Defluoridation from aqueous solution by lanthanum hydroxide”, J. Hazard Mater., Vol. 183, Issue 1-3, pp.512–520, Nov. 2010.

[46] Zhang S., Lu Y., Lin X., Su X., and Zhang Y., “Removal of fluoride from groundwater by adsorption onto La(III)-Al(III) loaded scoria adsorbent”, Applied Surface Science Vol. 303, pp. 1-5, June 2014.

[47] Yu Y., and Paul C.J., “Fabrication and performance of a Mn-La metal composite for remarkable decontamination of fluoride”, J. Mater.Chem.A , Vol.2, pp. 8086–8093, 2014.

[48] Diaz-Nava C., Solache-Rios M., and Olguin M.T., “Sorption of fluoride ions from aqueous solutions and well drinking water by thermally treated hydrotalcite”, Sep. Sci. Technol., Vol. 38, No. 1, pp. 131–147, 2003.

[49] Das D.P., Das J., and Parida K., “Physicochemical characterization and adsorption behaviour of calcined Zn/Al hydrotalcite-like compound (HTlc) towards removal of fluoride from aqueous solution”, J. Colloid Interface Sci. Vol. 261, Issue 2, pp. 213–220, May 2003.

[50] Lv L., He J., Wei M., Evans D.G., and Duan X., “Factors influencing the removal of fluoride from aqueous solution by calcined Mg–Al–CO3 layered double hydroxides”, J. Hazard. Mater. Vol. 133, Issues 1-3, pp. 119–128, May 2006.

[51] Lv L., “Adsorption behaviour of calcined layered double hydroxides towards removal of fluoride from aqueous solution, Journal of Water Supply: Res.Technol.”, AQUA, Vol. 55, Issue6, pp. 413-418, Sept. 2006.

[52] Lv L., He J., Wei M., and Duan X., “Kinetic studies on fluoride removal by calcined layered double hydroxides”, Ind. Eng. Chem. Res. Vol. 45, Issue 25, pp. 8623–8628, Nov. 2006.

[53] Lv L., He J., Wei M., Evans D.G., Zhou Z., "Treatment of high fluoride concentration water by Mg-Al–CO_3 layered double hydroxides: kinetic and equilibrium studies", Water Res. Vol. 41, Issue 7, pp. 1534–1542, April 2007.

[54] Wang H., Chen J., Cai Y., Ji J., Liu L., and Teng H.H., "Defluoridation of drinking water by Mg/Al hydrotalcite-like compounds and their calcined products", Appl. Clay Sci., Vol. 35, Issues 2-3, pp. 59–66, Jan. 2007.

[55] Mandal S., and Mayadevi S., "Adsorption of fluoride ions by Zn–Al layered double hydroxides", Appl. Clay Sci. Vol. 40, Issue 1-4, pp. 54–62, June 2008.

[56] Mandal S., and Mayadevi S., "Defluoridation of water using as-synthesized Zn/Al/Cl anionic clay adsorbent:Equilibrium and regeneration studies", J. Hazard. Mater., Vol. 167, Issue 1-3, pp. 873–878, Aug. 2009.

[57] YangG., Wang R., Ma W., Tian L., and Cheng Z.,"Layered double hydroxides for the adsorption of fluoride from aqueous solution", The 3rd International Conference on Bioinformatics and Biomedical Engineering , ICBBE, IEEE, pp. 1-4, 2009.

[58] Warsakoon E., Gunawardene,N., Kalahe, H., Munaweera I., Madusanka N., and Kottegoda N., "Defluoridation of drinking water using layered double hydroxides", International Conference on Sustainable Built Environment (ICSBE-2010) Kandy, pp. 63-68, 13-14 December 2010.

[59] Lv T., Ma W., Xin G., Wang R., Xu J., Liu D., Liu F., and Pan D., "Physicochemical characterization and sorption behavior of Mg–Ca–Al (NO3) hydrotalcite-like compounds toward removal of fluoride from protein solutions", J. Hazard. Mater., Vol. 237– 238, pp. 121– 132, Oct. 2012.

[60] Manda S., Tripathy S., Padhi T., Sahu M.K., Patel R.K.,"Removal efficiency of fluoride by novel Mg-Cr-Cl layered double hydroxide (LDH) by batch process from water", J. Environ. Sci., Vol. 24, No. 5, pp. 1-6, 2013.

[61] Cai P., Zheng H., Wang C., Ma H., Hu J., Pu Y., and Liang P.,"Competitive adsorption characteristics of fluoride and phosphate on calcined Mg–Al–CO3 layered double hydroxides", J. Hazard. Mater., Vol. 213– 214, pp. 100–108, April 2012.

[62] Koilraj P., and Kannan S., "Aqueous fluoride removal using Zn-Cr layered double hydroxides and their polymeric composites: Batch and column studies", Chem. Eng. J., Vol. 234, pp. 406–415, Dec. 2013.

[63] Goswami D., and Das A.K., "Removal of fluoride from drinking water using a modified fly ash adsorbent", J. Sci. Ind. Res., Vol. 65, pp. 77-79, January 2006.

[64] Maliyekkal S.M., Sharma A.K.,. and Philip L, "Manganese-oxide-coated alumina: a promising sorbent for defluoridation of water", Water Res., Vol. 40, Issue 19, pp. 3497–3506, Nov. 2006.

[65] Zhu P., Wang H., Sun B., Deng P., Hou S., and Yu Y., "Adsorption of fluoride from aqueous solution by magnesia–amended silicon dioxide granules", J. Chem. Technol. Biotech. Vol. 84, Issue 10, pp. 1449–1455, Oct. 2009.

[66] Ma Y., Wang S.-G., Fan M., Gong W.-X., and Gao B.-Y., "Characteristics and defluoridation performance of granular activated carbons coated with manganese oxides", J. Hazard. Mater., Vol. 168, Issue 2-3, pp. 1140–1146, Sept. 2009.

[67] Kang J., Li B., Song J., Li D., Yang J., Zhan W., and Liu D., "Defluoridation of water using calcined magnesia/pullulan composite", Chem. Eng. J. Vol. 166, Issue 2, pp. 765–771, Jan. 2011.

[68] Sivasankar V., Ramachandramoorthy T., and Darchen A., "Manganese dioxide improves the efficiency of earthenware in fluoride removal from drinking water", Desalination, Vol. 272, Issue 1-3, pp. 179–186, May 2011.

[69] Xu X., Li Q., Cui H., Pang J., Sun L., An H., and Zhai J., "Adsorption of fluoride from aqueous solution on magnesia-loaded fly ash cenospheres", Desalination , Vol. 272, Issue 1-3, pp. 233–239, May 2011.

[70] Sasaki K., Fukumoto N., Moriyama S., Yu Q., and Hirajima T., "Chemical regeneration of magnesium oxide used as a sorbent for fluoride", Sep. Purif. Technol., Vol. 98, pp. 24–30, Sept. 2012.

[71] Mondal P., and George S., "Fluoride Removal by Using Calcium-Aluminium-Magnesium Powder as Adsorbent", Proceedings of International Conference on Materials for the Future - Innovative Materials, Processes, Products and Applications – ICMF, pp. 562-564, 2013.

[72] Dash N., Dasb S., Patnaik T., Patel S.B., and Dey R.K., "Development of a new manganese oxide modified aluminium oxy(hydroxide) for the effective removal of fluoride from drinking water", Adv. Appl. Sci. Res., Vol. 4, Issue 4, pp. 387-399, 2013.

[73] Suzuki T., Nakamura A., Niinae M., Nakata H., Fujii H., Tasaka Y., “Immobilization of fluoride in artificially contaminated kaolinite by the addition of commercial-grade magnesium oxide”, Chem. Eng. J., Vol. 233, pp. 176–184, Nov. 2013.

[74] Margandan K., Agrawal R., Singh K., Acharya R., Sharma S.and Qanungo K., “Optimization of MgO Dosage in MgO-CaCl2-Lime-HCl Based Defluoridation Technique”, Chem. Sci. Trans., Vol. 3, Issue 1, pp. 79-86, 2014.

[75] Devia R.R., Umlong I.M., Raul P.K., Das B., Banerjee S., and Singh L., “Defluoridation of water using nano-magnesium oxide”, J. Exp. Nanosci., Vol. 9, No. 5, pp. 512-524, 2014.

[76] Alemu S., Mulugeta E., Zewge F., and Chandravanshi B.S.,“Water defluoridation by aluminium oxide–manganese oxide composite material”, Environ.Technol., Vol. 35, No. 15, pp. 1893–1903, 2014.

[77] Li L.-X., Xu D., Li X.-Q., Liu W.-C., and Jia Y., “Excellent fluoride removal properties of porous hollow MgO microspheres”, New J. Chem., Vol. 38, pp. 5445-5452, 2014.

[78] Minju N., Venkat S. K., Haribabu K., Sivasubramanian V., and Senthil K. P., “Removal of fluoride from aqueous media by magnesium oxide-coated Nanoparticles”, Desalination Water Treat., Vol. 53, pp. 2905–2914, 2015.

[79] Ishihara T., Shuto Y., Ueshima S., Ngee H.L., Nishiguchi H., and Takita Y., “Titanium hydroxide as a new inorganic fluoride ion exchanger”, J. Ceram. Soc. Japan., Vol. 110,No. 1285, pp. 801–803, 2002.

[80] Wajima T., Umeta Y., Narita S., and Sugawara K., “Adsorption behaviour of fluoride ions using a titanium hydroxide- derived adsorbent”, Desalination, Vol. 249, Issue 1, pp. 323–330, Nov. 2009.

[81] Gopal V., and Elango K.P., “Studies on defluoridation of water using magnesium titanate”, Ind. J. Chem. Tech. Vol. 17, pp. 28–33, Jan. 2010.

[82] Li Z., Deng S., Zhang X., Zhou W., Huang J., and Yu G., “Removal of fluoride from water using titanium-based adsorbents”, Front Environ. Sci. Engg. China,Vol. 4, Issue 4, pp. 414–420, Dec. 2010.

[83] Babaeivelni K., and Khodadoust A.P., “Adsorption of fluoride onto crystalline titanium dioxide: Effect of pH, ionic strength, and co-existing ions”, J. Colloid Interface Sci., Vol. 394, p. 419–427, March 2013.

[84] Swain S.K., Mishra S., Sharma P., Patnaik T., Singh V.K., Jha U., Patel P.K., and Dey R.K., “Development of a New Inorganic-Organic Hybrid Ion-Exchanger of Zirconium(IV)-Propanolamine for Efficient Removal of Fluoride from Drinking Water”, Ind. Eng. Chem. Res., Vol. 49, Issue 20, pp. 9846–9856, Sept. 2010.

[85] Swain S.K., Patnaik T., Singha V.K., Jha U. Patel R.K., and Dey R.K., “Kinetics, equilibrium and thermodynamic aspects of removal of fluoride from drinking water using meso-structured zirconium phosphate”, Chem. Eng. J., Vol. 171, Issue 3, pp. 1218–1226, July 2011.

[86] Dey R.K, Swain S.K., Patnaik T., Novel hybrid sorbent for the removal of fluoride from drinking water, Int. J. Eng. Soc. Sci., Volume3, Issue3, pp. 1-6, 2012.

[87] Dou X., Mohan D., Pittman C.U., and Yang S., “Remediating fluoride from water using hydrous zirconium oxide”, Chem. Eng. J., Vol. 198–199, pp. 236–245, August 2012.

[88] Swain S.K., Mishra S., Patnaik T., Patel R.K., Jha U, and Dey R.K., “Fluoride removal performance of a new hybrid sorbent of Zr(IV)–ethylenediamine”, Chem. Eng. J., Vol. 184, pp. 72–81, March 2012.

[89] Wang J., Xu W., Chen L., Jia Y., Wang L., Huang X.J., and Liu J., “Excellent fluoride removal performance by CeO2–ZrO2 nanocages in water environment”, Chem. Eng. J., Vol. 231, pp.198–205, 2013.

[90] Tomar V., Prasad S., Kuamr D.,“Adsorptive removal of fluoride from water samples using Zr–Mn composite material”, Microchem. J., Vol.111, pp. 116–124, July 2013.

[91] Yang D., Li Y., Wang Y., and Jiang Z.,“Bioinspired synthesis of mesoporous ZrO_2 nanomaterials with elevated defluoridation performance in agarose gels”, RSC Adv., Vol. 4, pp. 49811-49818, 2014.

[92] Saha I., Ghosh A., Nandi D., Gupta K., Chatterjee D., and Ghosh U.C., “β-Cyclodextrin modified hydrous zirconium oxide: Synthesis, characterization and defluoridation performance from aqueous solution”, Chem. Eng. J., Vol. 263, pp. 220–230, March 2015.

[93] Eskandarpour A., Onyango M.S., Ochieng A., and Asai S., “Removal of fluoride ions from aqueous solution at low pH using schwertmannite”, J. Hazard. Mater., Vol. 152, Issue 2, pp. 571–579, April. 2008.

[94] Karthikeyan M., Elango K.P., “Removal of fluoride ions from aqueous solution by conducting polypyrrol”, J Hazard Mater, Vol. 167, Issues 1-, pp. 300–305, Aug. 2009.

[95] Sakhare N., Lunge S., Rayalu S., Bakardjiva S., Subrt J., Devotta S., Labhsetwar N.,“Defluoridation of water using calcium aluminate material”, Chem. Eng. J., Vol. 203, pp. 406–414, 2012.

[96] Srivastav A.L., Singh P.K., Srivastava V., and Sharma Y.C., “Application of a new adsorbent for fluoride removal from aqueous solutions”, J. Hazard. Mater., Vol. 263, Part 2, pp. 342–352, Dec. 2013.

[97] Rafique T., Chadhar K.M., Usmani T.H., Memon S.Q., Shirin K., Kamaluddin S., Soomro F.,“Adsorption behavior of fluoride ion on trimetal-oxide adsorbent”, Desalination Water Treat., pp. 1–12, 2014.

[98] Barathi M., Kumar A.S. K., Kumar C.U., and Rajesh N., “Graphene oxide–alu-minium oxyhydroxide interaction and its application for the effective ad-sorption of fluoride”, RSC Adv., Vol. 4 (96) pp. 53711–53721, 2014.

[99] Jia Y., Zhu B.-S., Jin Z., Sun B., Luo T., Yu X.-Y., Kong L.-T., Liu J.-H.,“Fluoride removal mechanism of bayerite/boehmite nanocomposites: Roles of the surface hydroxyl groups and the nitrate anions”, J. Colloid Interface Sci., Vol. 440, pp 60–67, Feb. 2015.

.

AUTHOR BIBLIOGRAPHY

Sanghratna S. Waghmare is a working as a Senior Scientist at Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), Nagpur. He has experience in condition assessment of RCC buildings and bridges using NDT and PDT techniques also engaged in development of building materials from wastes, design and development of instant houses and polymer composites from sisal fibers. Currently, Waghmare has been involved in defluoridation and carbon dioxide sequestration.

Tanvir Arfin is currently working as a Scientist at Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), India. Dr. Arfin has been actively engaged in research related to various fields of electrochemistry, defluoridation, platinum group materials, polymer science, membrane, hybrid materials, graphite oxides and biomass energy. He has published more than 25 scientific peers reviewed journal papers and 9 book chapters.