Chapter 4

Conclusions and future scope

4. Conclusions and Future Scope

The conclusions of the entire thesis work along with some suggested scopes for future studies have been presented here.

4.1 Conclusions

Fluoride removal from groundwater and industrial wastewater using limestone has been investigated by many researchers. Though limestone can precipitate and adsorb fluoride up to some extent, it requires a long treatment time due to the slow dissolution of limestone in water which gives a poor fluoride removal capacity of limestone[246]. Fluoride removal efficiency of limestone can be enhanced by adding acid or by passing CO_2 through limestone column during the treatment process[246, 247]. In the present work, the author has chosen PA in the limestone treatment process in order to increase the fluoride removal capacity of the limestone. The study has been carried out in five stages, *viz*., fluoride removal by limestone powder in presence of PA, hydrothermal modification of limestone powder in presence of PA and fluoride removal by the modified materials, fluoride removal by PA-crushed limestone treatment (PACLT) in continuous-flow mode, a laboratory-scale pilot test of fluoride removal by PACLT in plug-flow mode and a field trial of fluoride removal by PACLT in plug-flow mode at fluoride affected villages. The main findings of the work described in the thesis are mentioned below.

4.1.1 Fluoride removal by limestone powder in presence of PA

- Addition of PA to fluoride containing water increases the fluoride removal by limestone powder. About 92% of fluoride can be removed from initial 5 mg/L [F^-] in presence of 0.10 M initial [PA].
- The fluoride removal increases with increase in contact time and reaches equilibrium at 3 h.
- The final pH of water by this method is found to be within the range of 6.00-6.50. The added PA is neutralized due to reaction with limestone powder.
- The kinetics of fluoride adsorption follows pseudo-second order kinetics. The kinetics of the fluoride removal by the present method fits to various models in

the order: pseudo second-order > pseudo first-order > Elovich > intra-particle diffusion.

- The fluoride removal in the present method conforms to sorption of fluoride by the adsorbent. The sorption fits to various adsorption isotherms in the order: Temkin > Freundlich > D-R > Langmuir.
- It has been suggested that the fluoride sorption occurs on HAP formed due to the reaction between PA and limestone powder.
- The best fit with the Temkin model indicates that sorption of fluoride takes place through ion-exchange between OH^- of HAP and F^- ions.
- The adsorption of fluoride on limestone powder in presence of PA takes place through physisorption as indicated by better fitting of the Freundlich model than the Langmuir model.
- The maximum monolayer adsorption capacity of limestone has been found as 4.38 mg F^-/g which is higher than the reported value for limestone alone[107].
- The fluoride removal by limestone powder in presence of PA is a spontaneous, endothermic and irreversible process.

4.1.2 Fluoride removal by hydrothermally modified limestone powder using PA

- HAP is formed in the hydrothermal modification of limestone powder in presence of PA. Maximum fluoride removal has been obtained by using the modified limestone modified using 0.90M PA, M9. About 93% fluoride removal from 150 mL of 10 mg/L fluoride containing water has been achieved with 0.5 g the modified material M9.
- The adsorption of fluoride on modified limestone follows the pseudo-second order kinetics.
- The various isotherm models for fluoride adsorption on modified limestone powder reveals that fluoride adsorption takes place through exchange of OH^- ions of HAP by F^-. The adsorption of fluoride in the process is physisorption.
- The maximum fluoride adsorption capacity of M9 sample, calculated from Langmuir isotherm model has been found as 6.45 mg/g.
- The fluoride loaded-adsorbent can be regenerated by alkali treatment.

- The present fluoride adsorption process is spontaneous, endothermic and irreversible.

4.1.3 Fluoride removal by phosphoric acid-crushed limestone treatment in continuous-flow mode

- The phosphoric acid-crushed limestone treatment (PACLT) in continuous-flow mode can remove fluoride from initial 5-10 mg/L [F^-] to 0.1-1.5 mg/L in presence of 0.01, 0.03 and 0.05 M $[PA]_0$ at the flow rate of 100 mL/h.
- Fluoride removal has been found to increase with increase in $[PA]_0$.
- The breakthrough occurs sooner on increasing the flow rate from 100 mL/h to 300 mL/h.
- The pH of the effluent water has been found to be in the range of 6.5-5.2.
- The effect of co-existing ions has little effect on fluoride removal by this method.
- Both precipitation of calcium fluoride and sorption of fluoride on HAP, produced in situ in the process, contribute to the fluoride removal. However, the saturation index of fluorite suggests that the sorption is the dominant mechanism.
- The relevant water quality parameters of effluent water remain within the WHO guideline values/acceptable range.
- Treatment of the exhausted limestone by NaOH shows about 73% regeneration of activity.
- The actual fluoride removal capacity of limestone has been estimated as 3.84 mg/g.
- The recurring cost of the present method has been estimated as INR 0.03 (US$ 0.00041) per litre of treated water.

4.1.4. Fluoride removal by phosphoric acid-crushed limestone treatment: *A laboratory pilot test*

- The present PACLT in laboratory-scale pilot experiment of the PACLT in plug-flow mode of influent fluoride-containing water pre-mixed with PA efficiently removes fluoride from water. Fluoride can be removed from an initial concentration of 10 mg/L to about 0.01-0.10 mg/L in a residence time of 3 h with 0.01 M $[PA]_0$.

- The exhausted limestone regenerated by simply scrubbing and rinsing with water and by $Ca(OH)_2$ and NaOH treatment shows about 50% regeneration of activity towards fluoride removal.
- The results of the analysis of the relevant water quality parameters of the treated water shows that treated water is safe for drinking.
- The presence of competing ions, *viz.*, NO_3^-, Cl^-, Br^- and SO_4^{2-} ions has little effect in the present method.
- The present method is efficient, safe and has an advantage as it does not involve any sophisticated or energy-intensive technology.

4.1.5. Field study of fluoride removal by phosphoric acid-crushed limestone treatment: *Fluoride Nilogon*

- The field trial has shown the PACLT in plug-flow mode (*Fluoride Nilogon*) to be an excellent and consistent fluoride removal technique at domestic ad small community level.
- The method removes fluoride from initial 2.8-20 mg/L to 0.5-0.8 mg/L with a dose of just 0.68 mM PA. The removal is almost independent of initial fluoride concentration.
- In this method, the precipitation rapidly brings down the fluoride concentration from any high level up to at least 20 mg/L to a moderate level of 1-2 mg/L controlled by solubility product, thereafter sorption removes the rest fluoride to finally give the desired 0.5-0.8 mg/L in the effluent water.
- The relevant water quality parameters after treatment remain within the WHO guideline values for drinking water. The pH of the treated water also remains within the range of 7.4-7.8 which is in the middle of the acceptable range for drinking water, i.e., 6.5-8.5.
- The pre-assessment with the replica test gave 83 L of treated fluoride-free water per kg of crushed limestone but the field small community unit has been giving more treated water than that. The regenerated limestone shows almost 45% and 57% activity using simple scrubbing-rinsing and lime solution treatment, respectively, as found from the replica test. There is no need for frequent replacement or replenishment of limestone in the units.

- The actual fluoride removal capacity of limestone in the PACLT in plug-flow mode has been found to be 1.20 mg/g from the pre-assessment experiment with the replica unit. The recurring cost of the PACLT method including the costs of limestone and PA has been estimated to be INR 0.016 (US$ 0.00023) per liter of water.
- The acceptance of the method by the rural users and the ability of the rural people to use the method shows its simplicity of the method which can be operated without electricity.
- The field trial has clearly proven the PACLT in plug-flow mode method as an efficient, low-cost, safe, environment-friendly and user-friendly method suitable for rural applications in fluoride affected areas.

4.2 Future scope

After carrying out the work described in this thesis, some more related interesting things as mentioned below appear which need to be addressed.

- The pH of keeps changing during fluoride removal in the reactor in PACLT due to the continuously changing concentration of PA. Study of the detailed mechanism of fluoride removal as a function of time and pH will be interesting considering the excellent fluoride removal by the method.
- The author has noticed variations in fluoride removal performance in PACLT of limestone collected from different sources. A detail study of performance of limestone of different sources with respect to their exact composition and physical properties will be useful.
- Field trial of the PACLT in plug-flow mode for large community piped drinking water schemes and developing automated device for domestic use of the PACLT in plug-flow mode will be interesting.
- Excess fluoride in agricultural water is known affect crops. A field trial of the PACLT in plug-flow mode for agricultural use in large scale may be carried out.
- The PACLT in continuous-flow mode has also been found to have potential for application. Further application oriented works on the PACLT in continuous-flow mode may be worthwhile.

References

1. Amini, M., et al. Statistical modeling of global geogenic fluoride contamination in groundwaters, *Environ. Sci. Technol.* **42**, 3662--3668, 2008.
2. Edmunds, W.M., & Smedley, P. Fluoride in natural waters, in *Essentials of smedical geology: impacts of the natural environment on public health*, Selinus O., et al. eds., Academic Press, US, 2005, 301--329.
3. Bhatnagar, A., et al. Fluoride removal from water by adsorption-A review, *Chem. Eng. J.* **171**, 811--840, 2011.
4. Frencken, J.E. (ed). *Endemic Fluorosis in developing countries: causes, effects and possible solutions*, NIPG-TNO, Leiden, Netherlands, 1992.
5. Parikh, P. *Fluoride contamination in fluorsper mine of Kadipani, Gujrat, India,* Laxmi book publication, Maharastra, India, 2015.
6. Preedy, V.R. (ed.). *Fluorine: Chemistry, Analysis, Function and Effects*, RSC, UK, 2015.
7. Lide, D.R. *CRC Handbook of Chemistry and Physics*, 76^{th} ed., CRC Press, US, 1995.
8. Breach, B. (ed.). *Drinking water quality management from catchment to consumer: A practical guide for utilities based on water safety plans*, IWA, London, 2012.
9. Weinstein, L.H., & Davison, A. *Fluorides in the environment: Effects on plants and animals*, CABI, UK, 2004.
10. Shen, F., et al. Electrochemical removal of fluoride ions from industrial wastewater, *Chem. Eng. Sci.* **58**, 987--993, 2003.
11. Sahoo, N., et al. Fluorosis in sheep around an aluminium factory, *Indian Vet. J.* **80**, 617--621, 2003.
12. Susheela, A.K. *A Treatise on Fluorosis, Fluorosis Research and Rural Development Foundation*, New Delhi, 2001.
13. Mohapatra, M., et al. Review of fluoride removal from drinking water, *J. Environ. Manage.* **91**, 67--77, 2009.
14. Das, B., et al. Fluoride and other inorganic constituents in groundwater of Guwahati, Assam, India, *Curr. Sci.* **85**, 657--661, 2003.
15. Meenakshi, S., & Maheswari, R.C. Fluoride in drinking water and its removal, *J. Hazard. Mater.* **137**, 456--563, 2006.

16. Segreto, V.A., et al. A current study of mottled enamel in Texas, *J. Am. Dent. Assoc.* **108**, 56--59, 1984.
17. Zhang, B., et al. Distribution and risk assessment of fluoride in drinking water in the west plain region of Jilin Province, *China. Environ. Geochem. Health* **25**, 421--431, 2003.
18. Wang, S.X., et al. Arsenic and fluoride exposure in drinking water: children's IQ and growth in Shanyin county, Shanxi province, China, *Environ. Health Perspect.* **115**, 643--647, 2007.
19. Groundwater quality: Tanzania, British Geological Survey, https://www.bgs.ac.uk/downloads/start.cfm?id=1291
20. Ghiglieri, G., et al. Hydrogeology and hydrogeochemistry of an alkaline volcanic area: the NE Mt. Meru slope (East African Rift–Northern Tanzania), *Hydrol. Earth Syst. Sci.* **16**, 529--541, 2012.
21. Gaciri, S.J., & Davies, T.C. The occurrence and geochemistry of fluoride in some natural waters of Kenya, *J. Hydrol.* **143**, 395--412, 1993.
22. Muller, W.J., et al. Finding the optimum: fluoridation of potable water in South Africa, *Water SA* **24**, 21--27, 1998.
23. Rango, T., et al. Groundwater quality and its health impact: an assessment of dental fluorosis in rural inhabitants of the Main Ethiopian Rift, *Environ. Int.* **43**, 37--47, 2012.
24. Azbar, N., & Turkman, A. Defluoridation in drinking waters, *Water Sci. Technol.* **42**, 403--407, 2000.
25. Ayoob. S., et al. A conceptual overview on sustainable technologies for the defluoridation of drinking water, *Crit. Rev. Env. Sci. Technol.* **38**, 401--470, 2008.
26. Paoloni, J.D., et al. Fluoride contamination of aquifers in the southeast subhumid pampa, Argentina, *Environ. Toxicol.* **18**, 317--320, 2003.
27. Díaz-Barriga, F., et al. Endemic fluorosis in Mexico, *Fluoride* **30**, 233--239, 1997.
28. Queste, A., et al. High concentrations of fluoride and boron in drinking water wells in the Muenster region-results of a preliminary investigation, *Int. J. Hyg. Environ. Health* **203**, 221--224, 2001.
29. Shah, M.T., & Danishwar, S. Potential fluoride contamination in the drinking water of Naranji area, Northwest Frontier Province, Pakistan, *Environ. Geochem. Health* **25**, 475--481, 2003.

30. Wang, L.F., & Huang, J.Z. Outline of control practice of endemic fluorosis in China, *Soc. Sci. Med.* **41**, 1191--1195, 1995.
31. Dissanayake, C.B. The fluoride problem in the groundwater of Sri Lanka– environmental management and health, *Int. J. Environ. Stud.* **19**, 195--203, 1991.
32. Ishii, T., & Suckling, G. The severity of dental fluorosis in children exposed to water with a high fluoride content for various periods of time, *J. Dent. Res.* **70**, 952--956, 1991.
33. Shortt, H.E., et al. Endemic fluorosis in the Madras Presidency, *Indian J. Med. Res.* **25**, 553--561, 1937.
34. Thangarajan, M. (ed). *Groundwater: resource evaluation, augmentation, contamination, restoration, modeling and management*, Springer, New York, 2007.
35. Ghosh, G.K. *Water of India: Quality and Quantity,* A.P.H. publishing corporation, New Delhi, 2002.
36. Teotia, S.P., & Teotia, M. Endemic fluorosis in India: A challenging national health problem, *J. Assoc. Physicians India* **32**, 347--352, 1984.
37. Pangare, G., et al. *Springs of Life: India's Water Resources*, Academic foundation, New Delhi, India, 2006.
38. Sengupta, A. In workshop on groundwater pollution and protection, Central Groundwater Board, Science City, Calcutta, 69--70, 1999.
39. Dutta, R.K., et al. Fluoride contamination in groundwater of central Assam, India, *Asian J. Water Environ. Poll*. **3**, 93--100, 2006.
40. Kotoky, P., et al. Fluoride and endemic fluorosis in the Karbianglong District, Assam, India, *Fluoride* **41**, 42--45, 2008.
41. Sarma, R., et al. Hydrogeochemical study of groundwater fluoride contamination: A case study from Guwahati city, *Asian J. Water Environ. Poll.* **2**, 47--54, 2005.
42. Chakraborti, D., et al. Fluorosis in Assam, India, *Curr. Sci.* **78**, 1421--1423, 2000.
43. Taher, M., & Ahmed, P. *Geography of North-East India,* Mani Manik Prakash, 2nd ed., Guwahati, 2001.
44. Karbi Anglong district at a glance, http://karbianglong.nic.in/at%20a%20glance.html
45. WHO, *Guidelines for Drinking-water Quality: Second Addendum, Vol. 1, Recommendations,* 3rd ed., IWA (International Water Association), Geneva, 2008.
46. Ranjan, R., & Ranjan, A. *Fluoride toxicity in animals,* Springer, New York, 2015.

47. Preedy, V.R., & Watson, R.R. (eds.). *Reviews in food and nutrition toxicity,* CRC press, Taylor and Francis group, Boca Raton, 2005.
48. Welch, A.H., et al. Arsenic in ground water of the United States-occurrence and geochemistry, *Ground Water* **38**, 589--604, 2000.
49. WHO (World Health Organization), *Guidelines for Drinking-water Quality,* 4^{th} ed., IWA (International Water Association), Geneva, 2011.
50. BIS (Bureau of Indian Standards), *Indian standard: drinking water specification*, IS: 10500, New Delhi, 2003.
51. Wen, D., et al. Arsenic, fluoride and iodine in groundwater of China, *J. Geochem. Explor.* **135**, 1--21, 2013.
52. 2012 Edition of the Drinking Water Standards and Health Advisories, EPA 822-S-12-001, Office of Water U.S. Environmental Protection Agency Washington, DC, https://rais.ornl.gov/documents/2012_drinking_water.pdf
53. Selinus, O., et al. *Essentials of Medical Geology*, Revised ed., Springer, New York, 2013.
54. Chaturvedi, A.K., et al. Defluoridation of water by adsorption on fly ash, *Water Air Soil Poll*. **49**, 51--61, 1990.
55. Choubisa, S.L., & Sompura, K. Dental fluorosis in tribal villages of Dungerpur district (Rajasthan), *Poll. Res.* **15**, 45--47, 1996.
56. Pendrys, D.G., & Katz, R.V. Risk of enamel fluorosis associated with fluoride supplementation, infant formula, and fluoride dentifrice use, *Am. J. Epidemiol.* **130**, 1199--1208, 1989.
57. Dean, H.T., et al. Domestic water and dental caries V. Additional studies of the relation of fluoride domestic waters to dental caries experience in 4,425 white children aged 12-14 years in 13 cities in 4 states, *Public Health Rep.* **57**, 1155--1179, 1942.
58. Richards, A., et al. Enamel fluoride in unerupted fluorotic human teeth, *Caries Res.* **23**, 103, 1989.
59. Fejerskov, O., et al. The nature and mechanism of dental fluorosis in man. *J. Dent. Res.* **69**, 692--700, 1990.
60. Thylstrup, A., & Fejerskov, O. Clinical appearance of dental fluorosis in permanent teeth in relation to histological changes, *Community Dent. Oral Epidemiol.* **6**, 315--328, 1978.

61. Richards, A., et al. Enamel fluoride in relation to severity of human dental fluorosis, *Adv. Dent. Res.* **3**, 147--153, 1989.
62. Gupta, A.K., et al. Quadriparesis–A Rare Presentation of Skeletal Fluorosis, *J. Ind. Acad. Clini. Med*. **9**, 201--204, 2008.
63. Jolly, S.S., et al. Endemic fluorosis in India, *J. Assoc. Physicians India* **18**, 459--471, 1970.
64. Pandit, C.G., et al. Endemic Fluorosis in South India; A study of factors involved in the production of mottled enamel in children and severe bone manifestations in adults, *Indian J. Med. Res.* **28**, 533--558, 1940.
65. Ozsvath, D., Fluoride and environmental health: a review. *Rev. Environ. Sci. Biotechnol.* **8**, 59--79, 2009.
66. Choi, A.L., et al. Developmental fluoride neurotoxicity: a systematic review and meta-analysis, *Environ. Health Perspect.* **120**, 1362--1368, 2012.
67. Zhou, Y., et al. Adsorption of fluoride from aqueous solution on La^{3+} impregnated crosslinked gelatin, *Sep. Purif. Technol.* **36**, 89--94, 2004.
68. Islam, M., & Patel, R.K. Thermal activation of basic oxygen furnace slag and evaluation of its fluoride removal efficiency, *Chem. Eng. J.* **169**, 68--77, 2011.
69. Perumal, E., et al. A brief review on experimental fluorosis, *Toxicol. Lett.* **223**, 236--251, 2013.
70. Harte, J., et al. *Toxics A to Z: A guide to everyday pollution hazards*, University of California press, Oxford, England, 1991.
71. Fazlul Hoque, A.K.M., et al. Fluoride levels in different drinking water sources in Bangladesh, *Fluoride* **36**, 38--44, 2003.
72. Dinesh, C. Fluoride and human health-cause for concern, *Ind. J. Environ. Protec.* **19**, 81--89, 1998.
73. Susheela, A.K., *Prevention and Control of Fluorosis, Vol. II–Health Aspects*, Rajiv Gandhi National Drinking Water Mission, Govt. of India, 1993.
74. Chandrasekharan, H. Sharma, R.K., & Sundaram, K.V. *Water resources development and management,* Mital Publications, New Delhi, India, 2004.
75. IISc method, civil.iisc.ernet.in/~msrao/files/applicationIIScmethod.pdf
76. Nawlakhe, W.G., et al. Defluoridation using the Nalgonda Technique in Tanzania, *Ind. J. Environ. Health.* **17**, 26--65, 1975.

77. Apparao, B.V., & Kartikeyan, G. Permissible limits of fluoride on in drinking water in India in rural environment, *Ind. J. Environ. Protec.* **6**, 172--175, 1986.
78. Nayak, P. Aluminium: impacts and disease, *Environ. Res.* **89**, 101--115, 2002.
79. Loeb, J.J. Donnan equilibrium and the physical properties of proteins III. Viscosity, *Gen. Physiol.* **3**, 827--841, 1921.
80. Hichour, M., et al. Fluoride removal from diluted solutions by Donnan dialysis with anion-exchange membranes, *Desalination* **122**, 53--62, 1999.
81. Shen, J., & Schafer, A. Removal of fluoride and uranium by nanofiltration and reverse osmosis: A review, *Chemosphere* **117**, 679–691, 2014.
82. Schneiter, R.W., & Middlebrooks, E.J. Arsenic and fluoride removal from groundwater by reverse osmosis, *Environ. Int.* **9**, 289--291, 1983.
83. Fu, P., et al. A pilot study on groundwater natural organics removal by low-pressure membranes, *Desalination* **102**, 47--56, 1995.
84. Ndiaye, P.I., et al. Removal of fluoride from electronic industrial effluent by RO membrane separation, *Desalination* **173**, 25--32, 2005.
85. Arora, M., et al. Use of membrane technology for potable water production, *Desalination* **170**, 105--112, 2004.
86. Richards, L.A., et al. Renewable energy powered membrane technology: salt and inorganic contaminant removal by nanofiltration/reverse osmosis, *J. Membr. Sci.* **369**, 188--195, 2011.
87. Sehn, P. Fluoride removal with extra low energy reverse osmosis membranes: three years of large scale field experience in Finland, *Desalination* **223**, 73--84, 2008.
88. Diawara, C.K. Nanofiltration process efficiency in water desalination, *Sep. Purif. Rev.* **37**, 303--325, 2008.
89. Lhassani, A., et al. Selective demineralization of water by nanofiltration: application to the defluoridation of brackish water, *Water Res.* **35**, 3260--3264, 2001.
90. Drioli, E., et al. Integrated membrane operations in desalination processes, *Desalination* **122**, 141--145, 1999.
91. Tahaikt, M., et al. Fluoride removal from groundwater by nanofiltration, *Desalination* **212**, 46--53, 2007.

92. Tahaikt, M., Comparison of the performances of three commercial membranes in fluoride removal by nanofiltration. Continuous operations, *Desalination* **225**, 209--219, 2008.

93. Malaisamy, R., et al. Polyelectrolyte modification of nanofiltratiom membrane for selective removal of monovalent anions, *Sep. Purif. Technol.* **77**, 367--374, 2011.

94. Hichour, M., et al. Fluoride removal from waters by Donnan dialysis, *Sep. Purif. Technol.* **18**, 1--11, 2000.

95. Garmes, H., et al. Defluoridation of groundwater by a hybrid process combining adsorption and Donnan dialysis, *Desalination* **145**, 287--291, 2002.

96. Elazhar, F., et al. Defluoridation of Moroccan Groundwater by Nanofiltration and Electrodialysis: Performances and Cost Comparison, *World Appl. Sci. J.* **22**, 844--850, 2013.

97. Durmaz, F., et al. Fluoride removal by Donnan dialysis with anion exchange membranes, *Desalination* **177**, 51--57, 2005.

98. Annouar, S., et al. Defluoridation of underground water by adsorption on the chitosan and by electrodialysis, *Desalination* **165**, 437--438, 2004.

99. Sahli, M.A., et al. Fluoride removal for underground brackish water by adsorption on the natural chitosan and by electrodialysis, *Desalination* **212**, 37--45, 2007.

100. Kabay, N., et al. Separation of fluoride from aqueous solution by electrodialysis: effect of process parameters and other ionic species, *J. Hazard. Mater.* **153**, 107--113, 2008.

101. Lahnid, S., et al. Economic evaluation of fluoride removal by electrodialysis, *Desalination* **230**, 213--219, 2008.

102. Onyango, M.S., et al. Diffusion kinetic modeling of fluoride removal from aqueous solution by charge-reversed zeolites, *J. Chem. Eng. Jpn.* **38**, 701--710, 2005.

103. Onyango, M.S., et al. Uptake of fluoride by Al^{3+} pretreated low-silica synthetic zeolites: adsorption equilibrium and rate studies, *Sep. Sci. Technol.* **41**, 683--704, 2006.

104. Meenakshi, S., & Viswanathan, N. Identification of selective ion-exchange resin for fluoride sorption, *J. Colloid Interf. Sci.* **308**, 438--450, 2007.

105. Viswanathan, N., & Meenakshi, S. Enhanced fluoride sorption using La(III) incorporated carboxylated chitosan beads, *J. Colloid Interface Sci*. **322**, 375--383, 2008.

106. Viswanathan, N., & Meenakshi, S. Synthesis of Zr(IV) entrapped chitosan polymeric matrix for selective fluoride sorption, *Colloids Surf. B: Biointerfaces* **72**, 88--93, 2009.

107. Chubar, N.I., et al. Adsorption of fluoride, chloride, bromide, and bromate ions on a novel ion exchanger, *J. Colloid Interface Sci.* **291**, 67--74, 2005.

108. Solangi, B., et al. Removal of fluoride from aqueous environment by modified Amberlite resin, *J. Hazard. Mater.* **171**, 815--819, 2009.

109. Solangi, B., et al. An excellent fluoride sorption behavior of modified amberlite resin, *J. Hazard. Mater.* **176**, 186--192, 2010.

110. Miretzky, P., & Cirelli, A.F. Fluoride removal from water by chitosan derivatives and composites: A review, *J. Fluorine Chem.* **132**, 231--240, 2011.

111. Bharali, R.K., & Bhattacharyya, K.G. Biosorption of fluoride on Neem (*Azadirachta indica*) leaf powder, *J. Environ. Chem. Eng.* **3**, 662--669, 2015.

112. Fan, X., et al. Adsorption kinetics of fluoride on low cost materials, *Water Res.* **37**, 4929--4937, 2003.

113. Farrah, H., et al. Fluoride interactions with hydrous aluminium oxides and alumina, *Aust. J. Soil Res.* **25**, 55--69, 1987.

114. Ku, Y., & Chiou, H.M. The adsorption of fluoride ion from aqueous solution by activated alumina, *Water Air Soil Pollut.* **133**, 349--361, 2002.

115. Ghorai, S., & Pant, K.K. Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina, *Sep. Purif. Technol.* **42**, 265--271, 2005.

116. Wasay, S.A., et al. Removal of hazardous anions from aqueous solutions by La(III)- and Y(III)-impregnated alumina, *Sep. Sci. Technol.* **31**, 1501--1514, 1996.

117. Tripathy, S.S., et al. Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina, *Sep. Purif. Technol.* **50**, 310--317, 2006.

118. Maliyekkal, S.M., et al. Manganese-oxide-coated alumina: A promising sorbent for defluoridation of water, *Water Res.* **40**, 3497--3506, 2006.

119. Cheng, J., et al. La^{3+}-modified activated alumina for fluoride removal from water, *J. Hazard. Mater.* **278**, 343--349, 2014.

120. Shimelis, B., et al. Removal of excess fluoride from water by aluminum hydroxide, *Bull. Chem. Soc. Ethiopia* **20**, 17--34, 2006.

121. Eskandarpour, A., et al. Removal of fluoride ions from aqueous solution at low pH using schwertmannite, *J. Hazard. Mater.* **152**, 571--579, 2008.
122. Streat, M., et al. 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.* **86**, 21--30, 2008.
123. Kumar, E., et al. Defluoridation from aqueous solutions by granular ferric hydroxide (GFH), *Water Res.* **43**, 490--498, 2009.
124. Mohapatra, M., et al. Facile synthesis of additive-assisted nano goethite powder and its application for fluoride remediation, *J. Nanopart. Res.* **12**, 681--686, 2010.
125. Liu, Q., et al. Adsorption of fluoride on synthetic siderite from aqueous solution, *J. Fluorine Chem.* **131**, 635--641, 2010.
126. Bhargava, D.S., & Killedar, D.J. Fluoride adsorption on fishbone charcoal through a moving media adsorber, *Water Res*. **26**, 781--788, 1992.
127. Kaseva, M.E. Optimization of regenerated bone char for fluoride removal in drinking water: A case study in Tanzania, *J. Water Health* **4**, 139--147, 2006.
128. Janardhana, C., et al. Study on defluoridation of drinking water using zirconium ion impregnated activated charcoals, *Indian J. Chem. Technol.* **14**, 350--354, 2007.
129. Gupta, A.K., et al. Adsorptive removal of fluoride by micro-nanohierarchal web of activated carbon fibers, *Ind. Eng. Chem. Res.* **48**, 9697--9707, 2009.
130. Karthikeyan, M., & Elango, K.P. Removal of fluoride from aqueous solution using graphite: A kinetic and thermodynamic study, *Indian J. Chem. Technol.* **15**, 525--532, 2008.
131. Li, Y.H., et al. Adsorption of fluoride from water by amorphous alumina supported on carbon nanotubes, *Chem. Phys. Lett.* **350**, 412--416, 2001.
132. Li, Y.H., et al. Adsorption of fluoride from water by aligned carbon nanotubes, *Mater. Res. Bull.* **38**, 469--476, 2003.
133. Li, Y.H., et al. Removal of fluoride from water by carbon nanotube supported alumina, *Environ. Technol*. **24**, 391--398, 2003.
134. Sivasamy, A., et al. M. Maruthamuthu, Studies on defluoridation of water by coal-based sorbents, *J. Chem. Technol. Biotechnol.* **76**, 717--722, 2001.
135. Borah, L., & Dey, N.C. Removal of fluoride from low TDS water using low grade coal, *Indian J. Chem. Technol.* **16**, 361--363, 2009.

136. Piekos, R., & Paslawaska, S. Fluoride uptake characteristic of fly ash, *Fluoride* **32**, 14--19, 1999.
137. Xu, X., et al. Adsorption of fluoride from aqueous solution on magnesia-loaded fly ash cenospheres, *Desalination* **272**, 233--239, 2011.
138. Moges, G., et al. Preliminary investigations on the defluoridation of water using fired clay chips, *J. African Earth Sci.* **22**, 479--482, 1996.
139. Coetzee, P.P., et al. Characterisation of selected South African clays for defluoridation of natural waters, *Water SA* **29**, 331--338, 2003.
140. Gogoi, P.K., & Baruah, R. Fluoride removal from water by adsorption on acid activated kaolinite clay, *Indian J. Chem. Technol.* **15**, 500--503, 2008.
141. Kamble S.P., et al. Defluoridation of drinking water using chemically modified bentonite clay, *Desalination* **249**, 687--693, 2009.
142. Thakre, D., et al. Magnesium incorporated bentonite clay for defluoridation of drinking water, *J. Hazard. Mater.* **180**, 122--130, 2010.
143. Ramdani, A., et al. Removal of excess fluoride ions from Saharan brackish water by adsorption on natural materials, *Desalination* **250**, 408--413, 2010.
144. Sujana, M.G., & Anand, S. Fluoride removal studies from contaminated groundwater by using bauxite, *Desalination* **267**, 222--227, 2011.
145. Das, N., et al. Defluoridation of drinking water using activated titanium rich bauxite, *J. Colloid Interface Sci.* **292**, 1--10, 2005.
146. Thole, B., et al. Groundwater defluoridation with raw Bauxite, Gypsum, Magnesite, and their composites, *Clean–Soil Air Water,* **40**, 1222--1228, 2012.
147. Thole, B. Defluoridation kinetics of 200°C calcined bauxite, gypsum, and magnesite and breakthrough characteristics of their composite filter, *J. Fluorine Chem.* **132**, 529--535, 2011.
148. Sarkar, M., et al. Use of laterite for the removal of fluoride from contaminated drinking water, *J. Colloid Interface Sci.* **302**, 432--441, 2006.
149. Sarkar, M., et al. Design and operation of fixed bed laterite column for the removal of fluoride from water, *Chem. Eng. J.* **131**, 329--335, 2007.
150. Maiti, A., et al. Chemical treated laterite as promising fluoride adsorbent for aqueous system and kinetic modeling, *Desalination* **265**, 28--36, 2011.
151. Sujana, M.G., et al. Studies on fluoride sorption on some geomaterials. *J. Hazard. Mater.* **161**, 120--125, 2009.

152. Onyango, M.S., et al. Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9, *J. Colloid. Interface Sci.* **279**, 341--350, 2004.

153. Onyango, M.S., et al. Breakthrough analysis for water defluoridation using surface-tailored zeolite in a fixed bed column, *Ind. Eng. Chem. Res.* **48**, 931--937, 2009.

154. Samatya, S., et al. Removal of fluoride from water by metal ions (Al^{3+}, La^{3+} and ZrO^{2+}) loaded natural zeolite, *Sep. Sci. Technol.* **42**, 2033--2047, 2007.

155. Cai, Q. The kinetics of fluoride sorption by zeolite: Effects of cadmium, barium and manganese, *J. Contam Hydrol* **177–178**, 136--147, 2015.

156. Onar, A.N., & Ozturk, B. Adsorption of phosphate onto pumice powder, *Environ. Technol.* **14**, 1081--1087, 1993.

157. Kitis, M., Adsorption of natural organic matter from waters by iron coated pumice, *Chemosphere* **66**, 130--138, 2007.

158. Asgari, G., et al. The investigation of kinetic and isotherm of fluoride adsorption onto functionalize pumice stone, *J. Hazard. Mater.* **217–218**, 123--132, 2012.

159. Mandal, S., & Mayadevi, S. Adsorption of fluoride ions by Zn–Al layered double hydroxides, *Appl. Clay Sci.* **40**, 54--62, 2008.

160. Pavan, P.C., et al. Sorption of anionic surfactants on layered double hydroxides, *J. Coll. Inter. Sci.* **229**, 346--352, 2000.

161. Lv, L., et al. Factors influencing the removal of fluoride from aqueous solution by calcined Mg–Al–CO_3 layered double hydroxides, *J. Hazard. Mater.* **133**, 119--128, 2006.

162. Das, D.P., et al. Physicochemical characterization and adsorption behaviour of calcined Zn/Al hydrotalcite-like compound (HTlc) towards removal of fluoride from aqueous solution, *J. Colloid Interface Sci.* **261**, 213--220, 2003.

163. Jiménez-Núñez, M.L., et al. Fluoride removal from aqueous solutions by magnesium, nickel, and cobalt calcined hydrotalcite-like compounds, *Sep. Sci. Technol.* **42**, 3623--3639, 2007.

164. Kamble, S.P., et al. Defluoridation of drinking water using chitin, chitosan and lanthanum-modified chitosan, *Chem. Eng. J.* **129**, 173--180, 2007.

165. Yao, R., et al. Defluoridation of water using neodymium-modified chitosan, *J. Hazard. Mater.* **165**, 454--460, 2009.

166. Viswanathan, N., & Meenakshi, S. Enriched fluoride sorption using alumina/chitosan composite, *J. Hazard. Mater.* **178**, 226--232, 2010.

167. Viswanathan, N., & Meenakshi, S. Selective fluoride adsorption by a hydrotalcite/chitosan composite, *Appl. Clay Sci.* **48,** 607--611, 2010.

168. Viswanathan, N., & Meenakshi, S. Development of chitosan supported zirconium (IV) tungstophosphate composite for fluoride removal, *J. Hazard. Mater.* **176**, 459--465, 2010.

169. Sundaram, C.S., et al. Defluoridation of water using magnesia/chitosan composite, *J. Hazard. Mater.* **163**, 618--624, 2009.

170. Swain, S.K., et al. Removal of fluoride from aqueous solution using aluminum-impregnated chitosan biopolymer, *Sep. Sci. Technol.* **44**, 2096--2116, 2009.

171. Sundaram, C.S., et al. Fluoride sorption by nanohydroxyapatite/chitin composite, *J. Hazard. Mater.* **172**, 147--151, 2009.

172. Bansiwal, A., et al. Fluoride removal using lanthanum incorporated chitosan beads, *Colloids Surf. B: Biointerfaces* **74**, 216--224, 2009.

173. Thakre, D., et al. Synthesis of La-incorporated chitosan beads for fluoride removal from water, *J. Fluorine Chem*. **131**, 373--377, 2010.

174. Jagtap, S., et al. New modified chitosan-based adsorbent for defluoridation of water, *J. Colloid Interface Sci.* **332**, 280--290, 2009.

175. Mohan, S.V., et al. Removal of fluoride from aqueous phase by biosorption onto algal biosorbent Spirogyra sp.-IO2: Sorption mechanism elucidation, *J. Hazard. Mater.* **141**, 465--474, 2007.

176. Mohan, S.V., et al. Biosorption of fluoride from aqueous phase onto algal Spirogyra IO1 and evaluation of adsorption kinetics, *Bioresour. Technol.* **98**, 1006--1011, 2007.

177. Bhatnagar, M., et al. Interactive biosorption by microalgal biomass as a tool for fluoride removal, *Biotechnol. Lett.* **24**, 1079--1081, 2002.

178. Ramanaiah, S.V., et al. Adsorptive removal of fluoride from aqueous phase using waste fungus (Pleurotus ostreatus 1804) biosorbent: Kinetics evaluation, *Ecol. Eng.* **31**, 47--56, 2007.

179. Miretzky, P., et al. Fluoride removal from aqueous solution by Ca-pretreated macrophyte biomass, *Environ. Chem.* **5**, 68--72, 2008.

180. Yadav, A.K., et al. Defluoridation of groundwater using brick powder as an adsorbent, *J. Hazard. Mater.* **128**, 289--293, 2006.
181. Oguz, E. Adsorption of fluoride on gas concrete materials, *J. Hazard. Mater.* **117**, 227--233, 2005.
182. Oguz, E. Equilibrium isotherms and kinetics studies for the sorption of fluoride on light weight concrete materials, *Colloids Surf. A: Physicochem. Eng. Aspects* **295**, 258--263, 2007.
183. Kagne, S., et al. Hydrated cement: A promising adsorbent for the removal of fluoride from aqueous solution, *J. Hazard. Mater.* **154**, 88--95, 2008.
184. Ayoob, S., et al. Investigations on the kinetics and mechanisms of sorptive removal of fluoride from water using alumina cement granules, *Chem. Eng. J.* **140**, 6--14, 2008.
185. Hammari, L.E.L., et al. Retention of fluoride ions from aqueous solution using porous hydroxyapatite: Structure and conduction properties, *J. Hazard. Mater.* **114**, 41--44, 2004.
186. Badillo-Almaraz, V.E., et al. Elimination of fluoride ions in water for human consumption using hydroxyapatite as an adsorbent, *J. Radioanal. Nucl. Chem.* **271**, 741--744, 2007.
187. Nie, Y., et al. Enhanced fluoride adsorption using Al (III) modified calcium hydroxyapatite, *J. Hazard. Mater.* **233–234**, 194--199, 2012.
188. Prabhu, S.M., & Meenakshi, S. Synthesis of surface coated hydroxyapatite powders for fluoride removal from aqueous solution, *Powder Technol.* **268**, 306--315, 2014.
189. Gao, S., et al. Study on the fluoride adsorption of various apatite materials in aqueous solution, *J. Fluorine Chem.* **130**, 1035--1041, 2009.
190. Gao, S., et al. Size-dependent defluoridation properties of synthetic hydroxyapatite, *J. Fluorine Chem.* **130**, 550--556, 2009.
191. Sundaram, C.S., et al. Defluoridation chemistry of synthetic hydroxyapatite at nano scale: Equilibrium and kinetic studies, *J. Hazard. Mater.* **155**, 206--215, 2008.
192. Poinern, G.E.J., et al. Defluoridation behavior of nanostructured hydroxyapatite synthesized through an ultrasonic and microwave combined technique, *J. Hazard. Mater.* **185**, 29--37, 2011.

193. Wang, Y., et al. Enhanced adsorption of fluoride from aqueous solution onto nanosized hydroxyapatite by low-molecular-weight organic acids, *Desalination* **276**, 161--168, 2011.
194. Pandi, K., & Viswanathan, N. In situ precipitation of nano-hydroxyapatite in gelatin polymatrix towards specific fluoride sorption, *Int. J. Biol. Macromol.* **74**, 351--359, 2015.
195. Zhang, H., et al. An efficient method to synthesize carbonated nano hydroxyapatite assisted by poly(ethylene glycol), *Mater. Lett.* **75**, 26--28, 2012.
196. Sanosh, K.P., et al. Synthesis of nano hydroxyapatite powder that simulate teeth particle morphology and composition, *Curr. Appl. Phys.* **9**, 1459--1462, 2009.
197. Chaudhry, A.A., et al. Instant nano-hydroxyapatite: a continuous and rapid hydrothermal synthesis, *Chem. Commun.* **21**, 2286--2288, 2006.
198. Liu, J., et al. Rapid formation of hydroxyapatite nanostructures by microwave irradiation, *Chem. Phys. Lett.* **396**, 429--432, 2004.
199. Sadat-Shojai, M., et al. Synthesis methods for nanosized hydroxyapatite with diverse structures, *Acta Biomater.* **9**, 7591--7621, 2003.
200. Catros, S., et al. Physico-chemical and biological properties of a nano-hydroxyapatite powder synthesized at room temperature, *IRBM* **31**, 226--233, 2010.
201. Liu, Y., et al. A simple wet chemical synthesis and characterization of hydroxyapatite nanorods, *Mater. Chem. Phys*. **86**, 69--73, 2004.
202. Zhang, H.G., & Zhu, Q. Surfactant-assisted preparation of fluoride-substituted hydroxyapatite nanorods, *Mater Lett.* **59**, 3054--3058, 2005.
203. Fathi, M., et al. Preparation and bioactivity evaluation of bone-like hydroxyapatite nanopowder, *J. Mater. Process. Tech.* **202**, 536--542, 2008.
204. Montazeri, N., et al. Synthesis of fluorapatite–hydroxyapatite nanoparticles and toxicity investigations, *Int. J. Nanomedicine* **6**,197--201, 2011.
205. Hsieh, M.F., et al. Phase purity of sol–gel-derived hydroxyapatite ceramic, *Biomaterials* **22**, 2601--2607, 2001.
206. Rajabi-Zamani, A., et al. Synthesis of nanocrystalline carbonated hydroxyapatite powder via nonalkoxide sol–gel method, *Mater. Sci. Eng. C* **28**, 1326--1329, 2008.
207. Weng, W., et al. The effect of citric acid addition on the formation of sol–gel derived hydroxyapatite, *Mater. Chem. Phys.* **74**, 92--97, 2002.

208. Fang, Y., et al. Fabrication of porous hydroxyapatite ceramics by microwave processing, *J. Mater Res.* **7**, 490--494, 1992.
209. Ruban, K.A., et al. Microwave assisted synthesis of hydroxyapatite nano strips, *Cryst. Res. Technol*. **45**, 776--778, 2010.
210. Sarig, S., & Kahana, F. Rapid formation of nanocrystalline apatite, *J. Cryst. Growth.* **237**, 55--59, 2002.
211. Zyman, Z., et al. Nanocrystalline calcium-deficient hydroxyapatite prepared by a microwave-assisted solvent-free reaction, *Mat-wiss. u. Werkstofftech*. **42**, 154--157, 2011.
212. Park, Y., et al. Preparation of whisker-shaped hydroxyapatite/b-tricalcium phosphate composite, *Mater. Chem. Phys.* **109**, 440--447, 2008.
213. Jalota, S., et al. Microwave-assisted synthesis of calcium phosphate nanowhiskers, *J. Mater. Res.* **19**, 1876--81, 2004.
214. Zhang, G., et al. Preparation of amino-acid regulated hydroxyapatite particles by hydrothermal method, *Mater. Lett.* **65**, 572--574, 2011.
215. Zhang, H., & Darvell, B.W. Morphology and structural characteristics of hydroxyapatite whiskers: effect of the initial Ca concentration, Ca/P ratio and pH, *Acta Biomater.* **7**, 2960--2968, 2011.
216. Earl, J., et al. Hydrothermal synthesis of hydroxyapatite, *Phys: Conf. Ser.* **26**, 268--271, 2006.
217. Yoshimura, M., et al. Hydrothermal conversion of calcite crystals to hydroxyapatite, *Mater. Sci. Eng. C* **24**, 521--525, 2004.
218. Loo, S.C.J., et al. Synthesis and hydrothermal treatment of nanostructured hydroxyapatite of controllable sizes, *J. Mater. Sci: Mater. Med.* **19**, 1389--1397, 2008.
219. Sadat-Shojai, M., et al. Hydroxyapatite nanorods as novel fillers for improving the properties of dental adhesives: synthesis and application, *Dent. Mater.* **26**, 471--482, 2010.
220. Zhang, H., et al. Plate-like hydroxyapatite nanoparticles synthesized by the hydrothermal method, *J. Phys. Chem. Solids.* **70**, 243--248, 2009.
221. Jagdale, P.N., & Bamane, S.R. Calcium hydroxyapatite bioceramics and evaluation of their in vitro biocompatibility, *Res. J. Pharm., Biol. Chem. Sci.* **2**, 180--186, 2011.

222. Bose, S., & Saha S.K. Synthesis and characterization of hydroxyapatite nanopowders by emulsion technique, *Chem. Mater.* **15**, 4464--4469, 2003.

223. Spinelli, M.A., et al. Mechanism of fluoride uptake by hydroxyapatite, *Arch. of Oral Bio.***16**, 187--203, 1971.

224. Dahi, E. Development of the contact precipitation method for appropriate defluoridation water, in 2nd International Workshop on Fluorosis Prevention and Defluoridation of Water, Nazreth, Ethiopia, 1997.

225. Lin, J., et al. The adsorption of fluoride ions by hydroxyapatite from aqueous solution, *Coll. Surf.* **3**, 357--370, 1981.

226. Duff, E.J. Orthophosphates. Part II. The transformations brushite→fluoroapatite and monetite→fluoroapatite in aqueous potassium fluoride solution, *J. Chem. Soc. A: Inorganic, Physical, Theoretical* 33--38, 1971.

227. Duff, E.J. Orthophosphates. Part IV. Stability relationships of orthophosphates within the systems $CaO-P_2O_5-H_2O$ and $CaF_2-CaO-P_2O_5-H_2O$ under aqueous conditions, *J. Chem. Soc. A: Inorganic, Physical, Theoretical* 921--926, 1971.

228. Duff, E.J. Orthophosphates. Part V. Phase equilibria in the system calcium oxide–phosphorus pentoxide-calcium fluoride-water along the fluoroapatite-hydroxyapatite join under aqueous conditions, *J. Chem. Soc. A: Inorganic, Physical, Theoretical* 1895--1898, 1971

229. Duff, E.J. Fluorite formation in biological and mineralogical systems. Part I. The transformation calcite→fluorite in aqueous fluoride solutions, *J. Chem. Soc. A:Inorganic, Physical, Theoretical* 2779--2781, 1971.

230. Duff, E.J. Orthophosphates. Part III. The hydrolysis of secondary calcium orthophosphates, *J. Chem. Soc. A:Inorganic, Physical, Theoretical* 917--921, 1971.

231. Duff, E.J. Orthophosphates. Part VIII. The transformation of newberryite into bobierrite in aqueous alkaline solutions, *J. Chem. Soc. A:Inorganic, Physical, Theoretical* 2736--2740, 1971.

232. Duff, E.J. Orthophosphates-XIII. Thermal decomposition of secondary calcium orthophosphate ($CaHPO_4$) and secondary calcium orthophosphate dehydrate ($CaHPO_4.2H_2O$), *J. Appl. Chem. Biotechnol.* **21**, 233--235, 1971.

233. Duff, E.J. Orthophosphates-VII: Thermodynamical considerations concerning the stability of oxyapatite, $Ca_{10}O(PO_4)_6$, in aqueous media, *J. Inorg. Nuclear Chem.* **34**, 853--857, 1972.

234. Duff, E.J. Orthophosphates-IX: Chloroapatite: Phase relationships under aqueous conditions along the $Ca_5F(PO_4)_3$---$Ca_5Cl(PO_4)_3$ and $Ca_5OH(PO_4)_3$---$Ca_5Cl(PO_4)_3$ joins of the system CaO---$CaCl_2$---CaF_2---P_2O_5---H_2O, *J. Inorg. Nuclear Chem.* **34**, 859--871, 1972.
235. Duff, E.J. Orthophosphates-X: The stability of the magnesium analogues of fluoro- and hydroxyapatite under aqueous conditions, *J. Inorg. Nuclear Chem.* **34**, 95--100, 1972.
236. Duff, E.J. Orthophosphates-XI Bromoapatite: Stability of solid solutions of bromoapatite with other calcium apatites under aqueous conditions, *J. Inorg. Nuclear Chem.* **34**, 101--108, 1972.
237. Duff, E.J. The transformation: Brushite→calcium monofluorophosphate under aqueous conditions, *J. Appl. Chem. Biotechnol.* **22**, 475--481, 1972.
238. Duff, E.J. The transformation of secondary calcium orthophosphates into apatites under aqueous alkaline fluoride conditions, *J. Inorg. Nuclear Chem.* **37**, 503--506, 1975.
239. Gasser, P., et al. Surface reactions on hydroxyapatite in the presence of fluoride ions 1. Saturated and congruent conditions, *Coll. Surf. A:Physicochem. Eng. Asp.* **74**, 275--286, 1993.
240. Gasser, P., et al. Mechanism of action of adsorbed fluoride ions on the dissolution kinetics of apatite powder, *J. Coll. Inter. Sci.* **168**, 465--472, 1994.
241. Kanazawa, T., et al. Uptake of fluoride ion by amorphous calcium phosphate, *J. Chem. Technol. Biotechnol. Chem. Technol.* **33A**, 435--438, 1983.
242. Aoba, T., et al. Fluoride and apatite formation in vivo and in vitro, *J. Elect. Microsc.* **52**, 615--625, 2003.
243. Tafu, M., & Chohji, T. Reaction between calcium phosphate and fluoride in phosphogypsum, *J. Euro. Cera. Soc.* **26**, 767--770, 2006.
244. Li, L., et al. Adsorption of fluoride ions on a Ca-deficient hydroxyapatite, *Huan Jing Ke Xue.* **311**, 554--1559, 2010.
245. Jiménez-Reyes, M., & Solache-Ríos, M. Sorption behaviour of fluoride ions from aqueous solutions by hydroxyapatite, *J. Hazar. Mater.* **180**, 297--302, 2010.
246. Reardon, E.J., & Wang, Y. A Limestone Reactor for Fluoride Removal from Wastewaters, *Environ. Sci. Technol*. **34**, 3247--3253, 2000.

247. Turner, B.D., et al. Fluoride removal by calcite: evidence for fluoride precipitation and surface adsorption, *Environ. Sci. Technol.* **39**, 9561--9568, 2005.

248. Jain, S., & Jayaram, R.V. Removal of fluoride from contaminated drinking water using unmodified and aluminium hydroxide impregnated blue limestone waste, *Sep. Sci. Technol.* **44**, 1436--1451, 2009.

249. Murutu, C., et al. Fluoride removal performance of phosphoric acid treated lime: Breakthrough analysis and point-of-use system performance, *Water SA* **38**, 279--285, 2012.

250. Murutu, C.S., et al. Investigation on limestone-derived apatite as a potential low cost adsorbent for drinking water defluoridation, http://www.ewisa.co.za/literature/files/148_101%20Murutu.pdf

251. Sivasankara, V., et al. Tamarind (Tamarindus indica) fruit shell carbon: A calcium-rich promising adsorbent for fluoride removal from groundwater, *J. Hazard. Mater.* **225–226**, 164--172, 2012.

252. Kanno, C.M., et al. Novel Apatite-Based Sorbent for Defluoridation: Synthesis and Sorption Characteristics of Nano-micro-crystalline Hydroxyapatite-Coated-Limestone, *Environ. Sci. Technol.* **48**, 5798--5807, 2014.

253. Mourabet, M., et al. Defluoridation of water using Brushite: Equilibrium, kinetic and thermodynamic studies, *Desalination* **278**, 1--9, 2011.

254. Husain J., & Jha, R.C. Fluoride distribution and occurrence of fluorosis in central Rajasthan and alternative low cost defluoridation technique by the use of marble slurry, World water week, Stockholm, September, 2010.

255. Mehta, D., et al. Utilization of marble waste powder as a novel adsorbent for removal of fluoride ions from aqueous solution, *J. Environ. Chem. Eng.* **4**, 932--942, 2016.

256. Gandhi, N., et al. Adsorption of fluoride from aqueous solution by using chalk powder, *World J. Pharm. Pharm. Sci*. **2**, 3897--3914, 2013.

257. Karthikeyan, G., et al. Kinetic and thermodynamic studies on adsorption of fluoride by dolomite, *Indian J. Chem. Technol.* **9**, 397--401, 2002.

258. Sasaki, K., et al. Sorption of fluoride on partially calcined dolomite, *Colloids Surf. A: Physicochem. Eng. Aspects* **435**, 56--62, 2013.

259. Chaudhary, V., & Prasad, S. Rapid removal of fluoride from aqueous media using activated dolomite, *Anal. Methods* **7**, 8304--8314, 2015.

260. Toshiyuki, K., et al. Influence of Mg components in hydroxylated calcined dolomite to (co-)precipitation of fluoride with apatites, *Chem. Eng. J.* **285**, 487--496, 2016.

261. Islam, M., & Patel, R.K. Evaluation of removal efficiency of fluoride from aqueous solution using quick lime, *J. Hazard. Mater.* **143**, 303--310, 2007.

262. Grayson, J.F. The conversion of calcite to fluorite, *Micropaleontology* **2**, 71--78, 1956.

263. Bear, N.S., & Lewin, S.Z. The replacement of' calcite by fluorite: A kinetic study, *Am. Mineral.* **55**, 466--476, 1970.

264. Augustyn, W., et al. Studies of the reaction of crystalline calcium carbonate with aqueous solutions of NH_4F, KF and NaF, *J. Fluorine Chem.* **12**, 281--292, 1978.

265. Trautz, O.R., & Zapanta, R.R. Experiments with calcium carbonate phosphates and the effect of topical application of sodium fluoride, *Arch. Oral Bio.* **4**, 122--133, 1961.

266. Simonsson, D. Reduction of fluoride by reaction with limestone particles in a fixed bed, *Ind. Eng. Chem. Process Des. Dev.* **18**, 288--292, 1979.

267. Sato, S., et al. Practical application of fluoride recovery and processing technology to existing waste water treatment systems, In Proceedings of Conference on Semiconductor Pure Water and Chemicals, *Place,* Santa Clara, California,1995.

268. Sato, S. A fluoride regeneration technology from wastewater by using granular $CaCO_3$, *J. Soc. Water Environ.* **20**, 391--396, 1997.

269. Majima, T., & Takatsuki, H. Fluoride removal from smoke-washing wastewater by using CaF_2 separating method, *Water Purif. Liq. Wastes Treat.* **28**, 433--443, 1987.

270. Ekdunge, P., & Simonsson, D. Treatment of ammonium fuoride solutions in a semicontinuous fixed bed process, *J. Chem. Tech. Biotechnol.* **34A**, 1--9, 1984.

271. Yang, M., et al. Fluoride removal in a fixed bed packed with granular calcite, *Water Res.* **33**, 3395--3402, 1999.

272. Lee, M.S., Liao, C.C., Shao, H. and Chang, W.K. *Process for removing fluoride from wastewater,* **US Patent No. 6210589,** April 3, 2001.

273. Aldaco, R., et al. Fluidized bed reactor for fluoride removal, *Chem. Eng. J.* **107**, 113--117, 2005.

274. Aldaco, R., et al. Particle growth kinetics of calcium fluoride in a fluidized bed reactor, *Chem. Engin. Sci.* **62**, 2958--2966, 2007.

275. Broeck, K.V., et al. Sustainable treatment of HF wastewaters from semiconductor industry with a fluidized bed reactor, *IEEE Trans. Semicond. Manuf.* **16**, 423--428, 2003.

276. Turner, B.D., et al. Impact of phosphate on fluoride removal by calcite, *Environ. Eng. Sci.* **27**, 643--650, 2010.

277. Nath, S.K., & Dutta, R.K. Fluoride removal from water using crushed limestone, *Indian J. Chem. Technol.* **17**, 120--125, 2010.

278. Nath, S.K., & Dutta, R.K. Enhancement of limestone defluoridation of water by acetic and citric acids in fixed bed reactor, *Clean—Soil, Air, Water* **38**, 614--622, 2010.

279. Nath, S.K., & Dutta, R.K. Acid-enhanced limestone defluoridation in column reactor using oxalic acid, *Process Saf. Environ. Prot.* **90**, 65--75, 2012.

280. Nath, S.K. *Development of de-fluoridation methods for water by enhancement of calcium ion activity in filter bed or column of lime materials*, Ph. D. Thesis, Tezpur University, Assam, India, 2010.

281. Ben Nasr, A., et al. Precipitation and adsorption during fluoride removal from water by calcite in the presence of acetic acid, *Desalin. Water Treat.* **52**, 2231--2240, 2014.

282. Mahadevaiah, M.S.Y.K., et al. A simple spectrophotometric determination of phosphate in sugarcane juices, water and detergent samples, *E-J. Chem.* **4**, 467--473, 2007.

283. U.S. Environmental Protection Agency, http://www.epa.gov/osw/hazard/wastetypes/wasteid/inorchem/docs/phosphor.pdf

284. George, D., & Mallery, P. *SPSS for windows step by step: A simple guide and reference, 17.0 update,* 10th ed., Pearson, India, 2011.

285. Kumar, E., et al. Defluoridation from aqueous solutions by nano-alumina: Characterization and sorption studies, *J. Hazard. Mater.* **186**, 1042--1049, 2011.

286. Ming-Cheng, S. Kinetics of the batch adsorption of methylene blue from aqueous solutions onto rice husk: Effect of acid-modified process and dye concentration, *Desalin. Water Treat.* **37**, 200--214, 2012.

287. Weber, W.J., & Morris J.C. Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* **89**, 31--60, 1963.

288. Aharoni, C., & Tompkins, F.C. Kinetics of adsorption and desorption and the Elovich equation, in *Advance in Catalysis and Related Subjects*, D.D. Eley, et al. eds., Academic press, New York, NY, 1970, 1--49.
289. Huang, R., et al. Removal of fluoride ions from aqueous solutions using protonated cross-linked chitosan particles, *J. Fluorine Chem.* **141**, 29--34, 2012.
290. Nigussie, W., et al. Removal of excess fluoride from water using waste residue from alum manufacturing process, *J. Hazard. Mater.* **147**, 954--963, 2007.
291. Temkin, M.I., & Pyzhev, V. Kinetics of ammonia synthesis on promoted iron catalysts, *Acta Physiochim. U.R.S.S.* **12**, 327--356, 1940.
292. Ismail, O., et al. Kinetic, thermodynamic, and equilibrium studies for adsorption of azo reactive dye onto a novel waste adsorbent: charcoal ash, *Desalin. Water Treat.* **52**, 6091--6100, 2013.
293. Halim, A.A., et al. Ammoniacal nitrogen and COD removal from semi-aerobic landfill leachate using a composite adsorbent: Fixed bed column adsorption performance, *J. Hazard. Mater.* **175**, 960--964, 2010.
294. Ahamad, K.U., & Jawed, M. Breakthrough studies with mono- and binary-metal ion systems comprising of Fe(II) and As(III) using community prepared wooden charcoal packed columns, *Desalination* **285**, 345--351, 2012.
295. U.S. Environmental Protection Agency (USEPA), Method 1311: Toxicity characteristic leaching procedure, 1992.
296. Islam, M., et al. Physicochemical characterization of hydroxyapatite and its application towards removal of nitrate from water, *J. Environ. Manage.* **91**, 1883--1891, 2010.
297. Tahir, H. Comparative trace metal contents in sediments and the removal of chromium using Zeolite-5A, *Electron. J. Environ. Agric. Food Chem.* **4**, 1021--1032, 2005.
298. Beniash, E., et al. Transient amorphous calcium phosphate in forming enamel, *J. Struct. Biol.* **166**, 133--143, 2009.
299. Khunur, M.M., et al. Synthesis of fluorite (CaF_2) crystal from gypsum waste of phosphoric acid factory in silica gel, *Bull. Chem. Eng. Catal.* **7**, 71--77, 2012.
300. Aldaco, R., et al. Fluoride recovery in a fluidized bed: Crystallization of calcium fluoride on silica sand, *Ind. Eng. Chem. Res.* **45**, 796--802, 2006.

301. Boyd, G.E., et al. Heat capacity changes in ion-exchange reactions. The exchange of tetra-n-butylammonium with sodium ion in cross-linked polystyrenesulfonatel, *J. Phys. Chem.* **72**, 2651--2654, 1968.

302. Li, Y., et al. Adsorption of fluoride from aqueous solution by graphene, *J. Colloid Interface Sci.* **363**, 348--354, 2011.

303. Atasoy, A.D., & Sahin, M.O. Adsorption of fluoride on the raw and modified cement clay, *Clean–Soil, Air, Water* **42**, 415--420, 2014.

304. Agarwal, M., et al. Deflouridation of water using amended clay, *J. Clean Prod.* **11**, 439--444, 2003.

305. Mawaniki, D.L., et al. Fluoride binding capacity of bone charcoal and its effects on selected micro-organisms, *East Afr. Med. J.* **67**, 427--431, 1990.

306. Ji, J., et al. Rapid identification of dolomite using Fourier Transform Infrared Spectrophotometer (FTIR): A fast method for identifying Heinrich events in IODP Site U1308, *Mar.Geol,* **258**, 60--68, 2009.

307. Babou-Kammoe, R., et al. Synthesis of $CaCO_3$ nanoparticles by controlled precipitation of saturated carbonate and calcium nitrate aqueous Solutions, *Can. J. Chem. Eng.* **90**, 26--33, 2012.

308. Rusu, V.M., et al. Size-controlled hydroxyapatite nanoparticles as self-organized organic–inorganic composite materials, *Biomaterials* **26**, 5414--5426, 2005.

309. Bongo, G., et al. Treatment of aluminium plant hazardous wastes containing fluoride and PAH, *J. Environ. Eng*. **135**, 159--166, 2009.

310. Heughebaert, J.C., et al. The growth of nonstoichiometric apatite from aqueous solution at 37°C. I. Methodology and growth at pH 7.4. *J. Colloid Interface Sci.* **135**, 20--32, 1990.

311. Sathish, R.S. A Quantitative Study on the Chemical Composition of Renal Stones and Their Fluoride Content from Anantapur District, Andhra Pradesh, India, *Curr. Sci.* **94**, 104, 2008.

312. Standard methods for the examination of water and wastewater, APHA/AWWA/WEF, 19^{th} ed., 1995.

313. Christofferson, J., et al. Kinetics of dissolution and growth of calcium fluoride and effects of phosphate, *Acta. Odontol. Scand.* **46**, 325--336, 1988.

314. Narasaraju, T.S.B., et al. Determination of solubility products of hydroxylapatite, chlorapatite, and their solid solutions, *Can. J. Chem.* **57**, 1919-1922, 1979.

315. Ramos, R.L., et al. Adsorption of fluoride from aqueous solution on aluminum-impregnated carbon, *Carbon* **37**, 609--617, 1999.