CHAPTER VI

SUMMARY
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The occurrence of fluoride in drinking water is due to various natural processes like weathering of rocks, volcanic activity etc. and other sources like phosphatic sediments. It is estimated that about 80 to 90 % of the dissolved fluoride in river water is due to the cyclic process derived from the atmosphere. Much of the fluoride found in minerals, particularly in micas, enter the insoluble residue and hydrolyzates. Fluorosis, an endemic public health problem, is caused mainly by fluoride ingestion through drinking water. A direct correlation between the mean fluoride level in drinking water and the percentage of dental fluorosis has already been established.

The major objectives of this investigation include defluoridation studies using montmorillonite, kaolinite and illite clay mixture, calcium carbonate, dolomite and marble; the kinetics and mechanism of leaching of fluoride from chondrodite and toxicological studies of fluoride in albino rats. The influence of important factors like contact time, particle size, dosage, common anions, pH and temperature were experimentally verified by conducting batch experiments. The materials having the smallest particle size exhibited the maximum defluoridation efficiency and this was attributed to the larger surface area of the adsorbents. The significance of contact time was ascribed to the formation of a monolayer coverage of the fluoride ions on the surface of the adsorbent materials. The minimum
contact time required for the maximum removal of fluoride ions by montmorillonite, calcium carbonate, clay mixture and dolomite was 50 minutes while, in the case of marble, it was 60 minutes. The effect of pH on the adsorption of fluoride in all cases was significant. At pH values below the point of zero charge, the net surface charge of the materials was positive and adsorption of the anion was favoured. The positive charge density on the surface of the adsorbents decreased as pH increased and this led to lower adsorption of fluoride from water at higher pH ranges. The defluoridation property of all the five adsorbents was experimentally verified in the presence of excess chloride, sulphate, nitrate and bicarbonate ions. Chloride, sulphate and nitrate ions did not exhibit any change in the defluoridation process. However, the presence of bicarbonate ions significantly reduced the defluoridation efficiency of the materials. This specificity in the case of bicarbonate ions was due to its competition with fluoride ions for active sites on the surface of the adsorbents. The enhanced adsorption rate at higher temperature was due to the increased mobility of the fluoride ions and the swelling effect of the adsorbents. All the five systems adhered to Freundlich and Langmuir isotherms. The values of n, the intensity of adsorption between 1 and 10 represent favourable adsorption. The adherence to Freundlich and Langmuir isotherms by the systems indicated that the adsorption was governed by physisorption and/or chemisorption. The adsorption kinetics of all the adsorbents followed the
Laguerren first order expression. The dimensionless equilibrium factor, $R_L$, values, for the systems were found to be between 0 and 1, indicating favourable adsorption at all temperatures. The increasing values of equilibrium constants, $K_0$, with rise in temperature, showed that the adsorption increased with temperature. The values of thermodynamic functions indicated that the reactions were endothermic and spontaneous. The positive values of $AS^0$ showed increased randomness at the solid-solution interface during the adsorption of fluoride on adsorbent materials. The negative values of $AG^0$ for the adsorption reactions indicated the sorption process to be spontaneous. The time dependence on the fraction of adsorption was verified. It was found that an initial instantaneous adsorption stage was preceded by the intraparticle diffusion which is the rate determining step leading to an equilibrium. A steep rise in the adsorption, as evidenced by the intraparticle diffusion plots against the amount adsorbed, indicated the accelerated pore diffusion rates. A gradual increase in the $K_p$ values with temperature was observed in all the five systems, indicating an increase in the adsorption rate. The fluoride adsorption by the five adsorbents was also interpreted in terms of the results of X-ray diffraction, FTIR and SEM analysis. X-ray diffraction studies were carried out to understand the changes occurring on the crystal structures of the adsorbent materials due to the adsorption of fluoride on their surfaces. FTIR spectra of the raw and fluoride treated surfaces of the
adsorbents provided information on the molecular groups as well as small changes in the environment of the surface groups. The formation of a layer of fluoride on the surface of the adsorbents was further confirmed by the SEM analysis. Based on the experimental results, a probable mechanism was developed for the fluoride adsorption process. A comparison of the adsorption efficiencies of all the five adsorbents was made. The higher values of adsorption isotherms in the case of montmorillonite and clay mixture confirmed their greater adsorption efficiencies. The higher sorptive capacity of the two is due to the larger surface area and exchanging capacity with hydroxyl ions in solution. The order of preferential adsorption of the fluoride ions by the five adsorbents was montmorillonite > clay mixture > calcium carbonate > dolomite > marble.

The effect of contact time on the leaching of fluoride from chondrodite at different pH levels was studied. The results indicated an enhanced rate of leaching of fluoride at higher pH levels. There was a positive correlation between the fluoride concentration and the electrical conductivity in the leachate. The same trend was found in the case of total alkalinity also. The interdependence of water quality parameters on the dissolution of fluoride from the chondrodite was studied using correlation analysis. Ions like \( \text{OH}^- \) and \( \text{HC}0_3^- \) which are responsible for alkalinity, accelerated the exchanging capacity of fluoride and this led to higher dissolution of fluoride from the mineral.
The effect of fluoride on the right tibia and fibula bones of young albino rats was studied for 50 days by administering sodium fluoride. The reversibility of the induced toxicity in the animals was monitored by supplementing calcium, aluminium, copper and selenium ions as antidotes with sodium fluoride simultaneously and also after withdrawing the supply of sodium fluoride. The simultaneous administration of antidotes had a beneficial role in the body weight gain and locomotor activity of the fluoride treated animals. Similarly, a significant decline of fluoride concentration in the tibia and fibula bones and blood serum was observed after the supplementation of antidotes. This was further confirmed by the observations obtained in the remarkable changes in bone structures by radiological examination. Calcium, as calcium phosphate, has a beneficial role in mitigating the fluoride toxicity, compared to aluminium, copper and selenium.