

## ***Contents***

---

<b>Contents</b>	<b>Pages</b>
<b>Abstract</b>	<b>i-v</b>
<b>Preface</b>	<b>viii</b>
<b>Acknowledgement</b>	<b>ix-x</b>
<b>Contents</b>	<b>xi-xviii</b>
<b>List of Tables</b>	<b>xix-xxiv</b>
<b>List of Figures</b>	<b>xxv-xxx</b>
<b>Abbreviations and acronyms</b>	<b>xxxi-xxxiii</b>
<b>Chapter 1</b>	
<b>1. Introduction</b>	<b>1-42</b>
1.1 Fluoride, the element	1
1.2 Fluoride contamination in groundwater	1
1.2.1 Natural geological sources	2
1.2.2 Industrial sources	3
1.3 Global scenario of fluoride contamination	4
1.3.1 Fluoride contamination in India	5
1.3.2 Fluoride contamination in Assam	6
1.4 Drinking water criteria for fluoride	8
1.5 Fluoride toxicity and its health effects	9
1.5.1 Dental fluorosis	9
1.5.2 Skeletal fluorosis	9
1.5.3 Other effects	10
1.6 Mitigation of fluoride menace	10
1.6.1 Alternate water sources	10
1.6.2 Better nutrition	11
1.6.3 Defluoridation of water	11
1.7 Existing fluoride removal techniques	12
1.7.1 Coagulation/precipitation	12

## **Contents**

---

1.7.2	Membrane process	14
1.7.2.1	Reverse osmosis	14
1.7.2.2	Nanofiltration	15
1.7.2.3	Dialysis and Electrodialysis	15
1.7.3	Ion-exchange	17
1.7.4	Adsorption	18
1.7.4.1	Activated alumina	18
1.7.4.2	Modified activated alumina	19
1.7.4.3	Iron-based sorbents for defluoridation of water	20
1.7.4.4	Carbon based sorbents for defluoridation of water	21
1.7.4.4.1	Carbon nanotubes	21
1.7.4.4.2	Alumina-impregnated carbon nanotubes	22
1.7.4.5	Natural materials as sorbents for defluoridation of water	22
1.7.4.6	Bauxite, magnesite and gypsum	22
1.7.4.7	Laterite	23
1.7.4.8	Zeolite	23
1.7.4.9	Pumice stone	23
1.7.4.10	Layered double hydroxides (LDHs)	24
1.7.4.11	Biosorbents for defluoridation of water	24
1.7.4.12	Building materials as sorbents for defluoridation of water	25
1.7.4.13	Hydroxyapatite	25
1.7.4.14	Nano-hydroxyapatite	26
1.7.4.14.1	Chemical precipitation method	27
1.7.4.14.2	Sol-gel method	27
1.7.4.14.3	Microwave assisted route	27
1.7.4.14.4	Hydrothermal method	28
1.7.4.14.5	The mechanism of fluoride removal by HAP	28

## ***Contents***

---

1.7.4.15 Other calcium-based sorbents for defluoridation of water	30
1.8 Limestone for fluoride removal	32
1.9 Limestone defluoridation and its mechanism	33
1.10 Limestone defluoridation in presence of acid	35
1.11 Acid-enhanced limestone defluoridation	36
1.12 Phosphoric acid-enhanced limestone defluoridation	37
1.13 The lacuna	38
1.14 Aim of the present work	39
1.15 Objectives	39
1.16 The strategy	41

## **Chapter 2**

<b>2. Materials and Methods</b>	<b>43-67</b>
2.1 Materials	43
2.1.1 Limestone	43
2.1.2 Chemicals	43
2.1.3 Water	43
2.1.3.1 Preparation of synthetic feed water	43
2.2 Analytical measurements	44
2.3 Statistical Analysis	45
2.4 Methods	45
2.4.1 Methods of fluoride removal by limestone powder in presence of PA	45
2.4.1.1 Batch study	45
2.4.1.2 Effects of process parameters	46
2.4.1.3 Adsorption kinetics	46
2.4.1.3.1 The pseudo first-order	47
2.4.1.3.2 The pseudo second-order	47
2.4.1.3.3 Intra-particle diffusion model	47
2.4.1.3.4 Elovich model	48
2.4.1.4 Adsorption isotherms	48
2.4.1.4.1 Freundlich isotherm	48

## **Contents**

---

2.4.1.4.2	Langmuir isotherm	48
2.4.1.4.3	Dubinin-Radushkevich (D-R) isotherm	49
2.4.1.4.4	Temkin isotherm	49
2.4.1.5	The thermodynamic of adsorption	50
2.4.2	Methods of fluoride removal by hydrothermally modified limestone powder using PA	50
2.4.2.1	Hydrothermal modification of limestone powder	50
2.4.2.2	Batch experiments of fluoride adsorption	51
2.4.2.3	Desorption study	51
2.4.2.4	Characterization of the modified limestone	51
2.4.2.5	Fluoride removal by modified limestone	51
2.4.2.6	Effect of process parameters	52
2.4.2.7	Adsorption kinetics	52
2.4.2.8	Adsorption isotherms	52
2.4.2.9	The thermodynamics study of fluoride sorption	52
2.4.3	Methods of continuous-flow column experiment	53
2.4.3.1	Effect process parameters	53
2.4.3.2	The effect of co-existing ions	55
2.4.3.3	Mechanism of fluoride removal	55
2.4.3.4	Column regeneration	55
2.4.3.5	Toxicity characteristics leaching procedure (TCLP) test	55
2.4.4	Methods of the laboratory-scale pilot test of PACLT	56
2.4.4.1	Regeneration of used limestone	57
2.4.4.2	Study of the relevant water quality parameters before and after PACLT treatment	57
2.4.5	Field trial	57
2.4.5.1	Selection of site	58

## ***Contents***

---

2.4.5.2	Methods of fluoride removal from groundwater model unit	58
2.4.5.3	Dose optimization and pre-assessment of performance	59
2.4.5.4	Regeneration and disposal of used limestone	59
2.4.5.5	TCLP test	60
2.4.5.6	User training and demonstration	60
2.4.5.7	Design and fabrication of Fluoride Nilogon systems of different capacities	65
2.4.5.8	Monitoring of user trial	67

### **Chapter 3**

#### **3. Results and discussion**

<b>3.1 Fluoride removal by limestone powder in presence of PA</b>	<b>69-91</b>
3.1.1 Batch study	69
3.1.1.1 Effect of adsorbent dose on fluoride removal	69
3.1.2 Role of sorption in the fluoride removal	70
3.1.2.1 FTIR evidence	71
3.1.2.2 XRD evidence	72
3.1.3 Kinetics of neutralization of PA by limestone powder	74
3.1.4 Effect of contact time on fluoride removal	75
3.1.5 Adsorption kinetics	77
3.1.5.1 Pseudo-first-order equation	78
3.1.5.2 Pseudo-second-order equation	78
3.1.5.3 Intra-particle diffusion model	79
3.1.5.4 Elovich model	81
3.1.6 Adsorption isotherms	81
3.1.6.1 Freundlich isotherm	82
3.1.6.2 Langmuir isotherm	82
3.1.6.3 Dubinin-Radushkevich (D-R) isotherm	85
3.1.6.4 Temkin isotherm	86

## **Contents**

---

3.1.7	Impact of calcium and phosphate ions on fluoride removal	87
3.1.8	The thermodynamic of adsorption	88
3.1.9	Competitiveness of the present adsorbent	90
3.1.10	Summary	91
<b>3.2</b>	<b>Fluoride removal by hydrothermally modified limestone powder using PA</b>	<b>93-116</b>
3.2.1	Characterization of the modified limestone	93
3.2.1.1	FTIR analysis	93
3.2.1.2	XRD analysis	95
3.2.1.3	SEM-EDX analysis	95
3.2.2	Batch study on fluoride removal	98
3.2.2.1	Fluoride removal by modified limestone	98
3.2.2.2	Effect of initial fluoride concentration	99
3.2.2.3	Effect of adsorbent dose	100
3.2.2.4	Effect of pH	102
3.2.3	Adsorption kinetics	103
3.2.3.1	Pseudo-first-order equation	103
3.2.3.2	Pseudo-second-order equation	104
3.2.3.3	Intra-particle diffusion model	104
3.2.3.4	Elovich model	105
3.2.4	Adsorption isotherm	106
3.2.4.1	Freundlich isotherm	107
3.2.4.2	Langmuir isotherm	108
3.2.4.3	Dubinin-Radushkevich (D-R) isotherm	110
3.2.4.4	Temkin isotherm	111
3.2.5	Thermodynamic investigation	111
3.2.6	Desorption of fluoride	113
3.2.7	Disposal of sludge	114
3.2.8	Competitiveness of the present adsorbent	114
3.2.9	Summary	115
<b>3.3</b>	<b>Fluoride removal by phosphoric acid-crushed limestone treatment in continuous-flow mode</b>	<b>116-140</b>
3.3.1	Effect of influent PA concentration	117

## ***Contents***

---

3.3.2	Effect of influent fluoride concentration	120
3.3.3	Effect of flow rates	122
3.3.4	The pH of effluent water	123
3.3.5	The effect of co-existing ions	126
3.3.6	Column regeneration	127
3.3.7	Mechanism of fluoride removal	130
3.3.7.1	FTIR analysis	131
3.3.7.2	XRD analysis	132
3.3.7.3	SEM-EDX analysis	133
3.3.7.4	Saturation index	133
3.3.7.5	The removal efficiency and the mechanism	137
3.3.8	Suitability Analysis	137
3.3.8.1	Safety	138
3.3.8.2	Capacity of limestone and cost-benefits analysis	139
3.3.9	Summary	139
<b>3.4</b>	<b>Fluoride removal by phosphoric acid-enhanced limestone treatment: <i>A laboratory pilot test</i></b>	<b>141-158</b>
3.4.1	The fluoride removal performance	141
3.4.2	The pH of treated water	146
3.4.3	Effect of co-existing ions	146
3.4.4	Mechanism of fluoride removal	146
3.4.4.1	Saturation index	147
3.4.4.2	FTIR analysis	149
3.4.4.3	XRD analysis	150
3.4.5	The schematic mechanism of PACLT method	151
3.4.6	Regeneration of used limestone	151
3.4.7	Suitability analysis	154
3.4.7.1	Safety	154
3.4.7.1.1	Other water quality parameters of treated water	155
3.4.7.1.2	Toxicity characteristic leaching procedure (TCLP) test	156

## **Contents**

---

3.4.7.2	Capacity	156
3.4.7.3	Cost estimation	156
3.4.8	Summary	157
<b>3.5</b>	<b>Field study of fluoride removal by phosphoric acid-crushed limestone treatment: <i>Fluoride Nilogon</i></b>	<b>159-186</b>
3.5.1	Optimization of PA dose	159
3.5.1.1	Influence of pH on fluoride removal	163
3.5.2	Pre-assessment of limestone capacity	163
3.5.3	Regeneration of used limestone	166
3.5.4	Performance of the small community unit	175
3.5.5	Performance of the domestic units	179
3.5.6	A remark on the mechanism of fluoride removal	183
3.5.7	Potability of treated water	184
3.5.8	Suitability of the method	185
3.5.8.1	Capacity	185
3.5.8.2	Cost estimation	185
3.5.9	Summary	186
<b>Chapter 4</b>		
<b>4.</b>	<b>Conclusions and future scope</b>	<b>187-191</b>
4.1	Conclusions	187
4.2	Future scope	191
<b>References</b>		<b>193-215</b>
<b>List of publications</b>		<b>217-219</b>