Contents

Contents	Page No.
List of Abbreviations	**i**
List of Tables	**ii-iii**
List of Figures	**iv-xvi**
Chapter-1: Geochemical Appraisal of fluoride in Environment and Its Existing Treatment Technologies	1-41
1.1. Fluoride in Groundwater: An Environmental Threat	1-2
1.2.Fluoride contamination: Probable Sources and Contamination Mechanism	2-9
1.3.Distribution of Fluoride: An Appraisal	9-20
1.4.Fluoride Toxicity and Health Impacts	21-23
1.5. Existing Fluoride Removal Technologies: A critical Overview	23-37
1.5.1. Conventional Methods with Their Own Merits and Demerits	23-28
1.5.2. Adsorption as Cost Effective Environment Friendly Treatment Technique	29-37
1.6. Aims and Objectives of Present Work	37-38
1.7. Summary of the Present Research Work	38-41
Chapter-2: Experimental Methods and Procedures	42-76
2.1. Reagents and Apparatus	42
2.2.Preparation of Standard Solutions	42-43
2.2.1. Fluoride Solution	42
2.2.2. Preparation of Phosphate Solution	43
2.2.3. Preparation of Sulphate Solution	43
2.2.4. Preparation of bicarbonate solution	43

2.2.5. Preparation of chloride solution 43

2.3. Analytical Processes 44-45

2.3.1. Fluoride analysis 44

2.3.2. Hardness Estimation (Titrimetric method) 44

2.3.3. Total Dissolved Solid (TDS) 44

2.3.4. Estimation of pH_{ZPC} 45

2.4. Instrumental and Software Used 45

2.5. Synthesis of Proposed Adsorbents 46-49

2.5.1. Preparation of Ce (IV)-incorporated hydrous Fe (III) oxide named as (CIHFO) HFO and HCO 46

2.5.2. Surface modification of Ce (IV)-incorporated hydrous Fe (III) oxide (CIHFO) with graphene oxide and named as GO-CIHFO 47-48

2.5.2.1. Preparation of graphene oxide (GO) 47

2.5.2.2. Preparation of Graphene Oxide tweaked Ce(IV)-incorporated hydrous Fe(III) oxide (GO-CIHFO) 48

2.5.3. Synthesis of β-cyclodextrin modified Ce (IV)-incorporated hydrous Fe (III) oxide (βC-CIHFO) 49

2.6. Adsorbent Characterisation 49-56

2.6.1. Surface Morphology Study 49-52

2.6.1.1. Optical Microscope and Scanning Electron Microscope (SEM) Study with EDX Analysis. 49-51

2.6.1.2. Transmission Electron Microscope (TEM) with EDX Analysis 51

2.6.1.3. Atomic Force Microscope (AFM) Study 51-52

2.6.1.4. Surface Area Analysis 52-54

2.6.2. X-ray Powder Diffraction (XRD) Analysis 54

2.6.3. Thermogravimetric (TG)and Differential thermal Analysis (DTA) 54

2.6.4. Infrared (IR) Spectroscopy Study 54-56

2.6.5. Raman Spectroscopy Study 56

2.6.6. X-ray Photoelectron Spectroscopy (XPS) study 56

2.7. Experimental Design for Batch Study 57

2.7.1. Adsorption Kinetics Study 58

2.7.1.1. Adsorption Kinetics modelling 58-65

2.7.1.1.1. Pseudo First Order Kinetics Equation 59-60

2.7.1.1.2. Pseudo-Second Order Kinetics Equation 60-61

2.7.1.1.3. Mass Transfer 61-62

2.7.1.1.4. Diffusion Kinetics (Intra-particle Diffusion Model) 62-63

2.7.1.1.5. Elovich Model 63-64

2.7.1.1.6. Richenberg Model 64-65

2.7.2. Adsorption isotherm models 66-68

2.7.2.1. Langmuir Isotherm 66-67

2.7.2.2. Freundlich Isotherm 67

2.7.2.3. Dubinin - Radushkevich (D-R) isotherm 67-68

2.7.3. Thermodynamics Studies 68-69

2.7.4. Activation Energy 69-70

2.8. Fixed bed column adsorption models 70-71

2.8.1. Conventional mathematical modeling: Thomas model 70

2.8.2. Bed Depth Service Time (BDST) model 71

2.8.3. Statistical model 72-76

2.8.3.1. Artificial neural network (ANN) modeling 72-74

2.8.3.2. Response surface methodology (RSM) 74-76

Chapter-3: Synthesis, Characterisation and Application of Lab Bench Scale Prepared Chemically Modified Low–Cost Adsorbents for Removal of Fluoride from Groundwater by Batch Operation Technology 77-205

3.1. Introduction 77-79

3.2. Characterisation of Lab Bench Scale Prepared CIHFO, GO-CIHFO and βC-CIHFO 79-120

3.3. Batch Adsorption Study 121-125

3.3.1. Influence of Cerium Content in CIHFO on Fluoride Adsorption 121

3.3.2. Influence of Percentage of Graphene Oxide Content in CIHFO on Fluoride Adsorption 123-124

3.3.3. Influence of Molar Concentration Variation of Beta Cyclodextrin Solution for Synthesis of βC-CIHFO and Its Impact on Fluoride Adsorption 124-125

3.4. Effect of Adsorbent dose 125-127

3.5. Effect of pH upon Fluoride Adsorption Capacity of CIHFO, GO-CIHFO and βC-CIHFO 128-132

3.6. Effect of Contact Time on Adsorption Process and Kinetic Modelling 132-170

3.7. Equilibrium Analysis 171-181

3.8. Thermodynamics Studies 182-185

3.9. Activation Energy 186-187

3.10. Effect of Co-occurring ions on Fluoride Adsorption 187-190

3.11. Desorption and Re-usability of Proposed Adsorbents 190-194

3.12. Removal of Fluoride from a Natural Groundwater Sample 194-196

3.13. Proposed Mechanism of Fluoride Adsorption over CIHFO, GO-CIHFO and βC-CIHFO 197-202

3.13.1. Proposed Mechanism for CIHFO 197-198

3.13.2. Proposed Mechanism for GO-CIHFO 198-199,201

3.13.3. Proposed Mechanism for βC-CIHFO 199-200,202

3.14. Conclusion 203-205

Chapter-4: Continuous Fixed-Bed Column Study and Adsorption Modelling to Evaluate Fluoride Removal performance of Cerium (IV)-incorporated Hydrous Iron(III) Oxide (CIHFO) nanoaggregates from Groundwater 206-251

4.1. Introduction 206-207

4.2. Column Design for Adsorption Experimental Set-up 207-208

4.2.1. Water Sample Collection 208-210

4.2.2. Column Adsorption Concept under Transient Conditions 211-213

4.2.3. Designing of Fixed Bed Absorber Packed with CIHFO 214-220

4.3. Application of Cerium (IV)-Incorporated Hydrous Iron(III) Oxide (CIHFO) in Column Operation 221-225

4.3.1. Effect of Bed Depth (adsorbent mass) on Breakthrough Curve 221-222

4.3.2. Effect of Flow Rate on Breakthrough Curve 222-223

4.3.3. Effect of Concentration Variation on Breakthrough Curve 224-225

4.4. Fitting of Different Models on Breakthrough Curve 225-230

4.4.1. Thomas Kinetic Model 225-228

4.4.2. Bed depth service time (BDST) model 229-230

4.5. Modelling of the Adsorptive Removal of Fluoride by Artificial Neural Networking (ANN) Model: A Statistical Approach 231-233

4.6.Modelling of the Adsorptive Removal of Fluoride by Response Surface Methodology (RSM): A Fitting Process Model 234-242

4.6.1. Fitting of RSM Model 234-239

4.6.2. Interaction in-between the Independent Variables 239-241

4.6.2.1.Contour Plot 239-241

4.6.2.2. Perturbation Plot 241

4.6.3. Utilization of Desirability Functions for Optimization 241-242

4.7. Performance Indicator 247-248

4.8. Proposed Design of "Prototype" Filter Unit 248-249

4.9. Conclusion 250-251

5. Chapter -5: Conclusions and Future Scope of Work 252-255

6. References 256-286