Fluoride Removal from Water Environment by Acid Modified Fish Scale Biochar

Thesis submitted by

DISHA ASARAM KHANDARE

DOCTOR OF PHILOSOPHY (Engineering)

DEPARTMENT OF CIVIL ENGINEERING
FACULTY COUNCIL OF ENGINEERING & TECHNOLOGY
JADAVPUR UNIVERSITY
KOLKATA-700032, INDIA
2022

JADAVPUR UNIVERSITY

KOLKATA-700032

Index No. 75/19/E

Registration No. 1021903001

TITLE OF THE Ph.D. (Engg.) THESIS

Fluoride Removal from Water Environment by Acid Modified Fish Scale Biochar

NAME, DESIGNATION&INSTITUTION OF THE SUPERVISORS:

(i) **Prof. (Dr.) Somnath Mukherjee**

Professor, Department of Civil Engineering,
Jadavpur University, Kolkata – 700032
West Bengal, INDIA.

LIST OF PUBLICATIONS

- ***International Journal /National Journal***

1) Khandare, D. A., & Mukherjee, S. (2019), "Fish scale waste: potential low-cost adsorbent for fluoride removal", Journal of Indian Chemical Society, 96, 429-434.

2) Khandare, D. A., Mukherjee, S(2020), "Comparative assessment of Commercial activated carbon and fish scale derived activated carbon for adsorptive removal of fluoride from drinking water", Journal of Indian Chemical Society, 97-10b,1778-1783

3) Khandare, D. A., Mukherjee, S(2022), "Fixed bed column adsorption study for removal of fluoride by Acid modified Fish Scale Biochar", Positif Review Journal, Vol 22, Issue 7, 264-276

- **List of Patents – NIL**

- ***List of Presentations in National /International Conferences /Workshops***

1) Khandare, D., & Mukherjee, S. (2019). A review of metal oxide nanomaterials for fluoride decontamination from water environment. *Materials Today: Proceedings*, *18*, 1146-1155.

2) Khandare, D., & Mukherjee S., (2019), "Fish Scale Waste- a potential sustainable material for water pollution remediation", Proceedings of 9th International Conference on Sustainable Waste Management towards Circular Economy (ICON SWM CE -2019), International Society of Waste Management, Air and Water (ISWMAW), India **(Conference Proceeding)**

3) Khandare, D., Tembhurkar, A., & Mukherjee, S. (2021), "Adsorptive Removal of Fluoride from Water Using Non-conventional Adsorbents", In *Advances in Civil Engineering and Infrastructural Development* ,Springer, Singapore, 447-455 **(Springer Book Chapter)**

PROFORMA – 1

"Statement of Originality"

I, Disha Asaram Khandare registered on 30-04-2019; do hereby declare that this thesis entitled "Fluoride Removal from water Environment by Acid Modified Biochar" contains literature survey and original research work done by the undersigned candidate as part of Doctoral studies. All information in this thesis have been obtained and presented in accordance with existing academic rules and ethical conduct. I declare that, as required by these rules and conduct, I have fully cited and referred all materials and results that are not original to this work. I also declare that I have checked this thesis as per the "Policy on Anti Plagiarism, Jadavpur University, 2019", and the level of similarity as checked by iThenticate software is 05 %.

Signature of Candidate ……………………………………

Date: 04-04-2023

04/4/23

Certified by Supervisor(s):
(Signature with date, seal)

DR. S. N. MUKHERJEE
Professor
CIVIL ENGINEERING DEPT.
JADAVPUR UNIVERSITY
KOLKATA-700032, (W.B)

1. Dr. Somnath Mukherjee, Professor, Department of Civil Engineering, Jadavpur University, Kolkata-700032.

PROFORMA-II

CERTIFICATE FROM THE SUPERVISORS

*This is to certify that the thesis entitled "**Fluoride Removal from Water Environment by Acid Modified Fish Scale Biochar** " submitted by **Ms. Disha Asaram Khandares,** who got her name registered on **30th April, 2019** for the award of Ph.D. (Engg.) degree of Jadavpur University is absolutely based upon his own work under the supervision of Prof. (Dr.) Somnath Mukherjee, and that neither his thesis nor any part of the thesis has been submitted for any degree/diploma or any other academic award anywhere before.*

04/4/23

date with office Seal

DR. S. N. MUKHERJEE
Professor
CIVIL ENGINEERING DEPT.
JADAVPUR UNIVERSITY
KOLKATA-700032, (W.B)

Dedicated to my Family,

Teachers and Friends...

ACKNOWLEDGEMENT

Working for my Ph.D. has been an amazing and enriching experience to me. I am grateful to many people for making this journey to the completion of my Ph.D., a pleasant and memorable experience. The insight of this thesis is certainly due to the contribution of several outstanding persons.

“A great guru is one who can inspire hope, ignite the imagination,
and instill a love of learning”

Words in my vocabulary, fail to illuminate my deep sense of regard and gratitude to my guide and honorific supervisor ***Dr. Somnath Mukherjee,*** Professor, Department of Civil Engineering, Jadavpur University for furthering my research through his immense supervision and perception. Without his constructive and timely advice, this thesis would have not been progressed as smoothly as it did towards its completion.

Thanks are extended to the All India Council for Technical Education (AICTE), New Delhi for providing QIP (Poly) fellowship to me. I extend my heartiest thanks to the ***Director, Directorate of Technical Education***, Govt. of Maharashtra for permitting me to carry out my research work under QIP (Poly) scheme. I would also like to extend my sincere gratitude to respected ***Dr. C.S. Thorat,*** (Retd. Principal,Government Polytechnic, Nagpur***)*** and ***Prof. S.P. Lambhade*** (Principal, Government Polytechnic, Sakoli) and all the faculty members of Government Polytechnic, Nagpur and Government Polytechnic, Sakoli.

I would also take this opportunity to express my sincere gratitude to ***Prof. B. Bhattacharyya***, QIP-Coordinator, ***Head of Civil Engineering Department,*** Jadavpur University during my entire Ph. D. journey at the department for their helpful guidance while providing departmental facilities during every strata of my thesis work. I would like to thank profusely ***Prof. S.N. Chakarabarty, Dr. Amit Dutta , Dr. Anupam Deb Sarkar, , Dr. Tumpa Hazra, and Dr. Abhishek Roy***. They have been very generous and have always given me valuable suggestions and constant support throughout this journey.

Thanks are also extended to ***The Secretary*** and ***staff of F.E.T. office*** for their cordial assistance and administrative support. ***Special thanks goes to Mr. Subrata Bhattacharya of F.E.T. and Mr. Monojit Dey*** of research section for their timely guidance for administrative procedures.

I wish to express my heartfelt obligations and thanks to my parents, ***Mr. Asaram N. Khandare and Mrs. Seema A. Khandare*** for making me the person that I am today and the person who has yet to grow. Last but not the least; I would like to thank my husband ***Mr. Indrajit Wakde*** and my beloved son ***Rijul*** , for their utmost care , immense sacrifice , unlimited patience and constant endorsement at all stages of my Ph. D. work. This work would not have been possible without their support. I would like to extend my thanks to all my family members and friends for their constant encouragement and support in the pursuit of this research work.

Last, but not the least, there are limitless worth names, which deserve mention here, but it could not be possible to include in this section due to space constraints. I acknowledge all those people with gratitude who have helped me directly or indirectly to make this Ph.D. work complete.

Date : 04-04-2023

Disha Asaram Khandare

CONTENTS

Page No.

Abstract

List of Tables

List of Figures

Abbreviations

Nomenclature

1. Introduction **1-18**

1.1 Background **1**

1.2 Occurrence and sources of Fluoride **2**

1.3 Health effects and permissible limits of Fluoride **5**

1.4 Global scenario of fluoride contamination **9**

1.4.1 World scenario **9**

1.4.2 Indian scenario **9**

1.5 Control of fluoride toxicity **14**

1.6 Statement of the problem **15**

1.7 Motivation **16**

1.8 Organization of thesis **17**

2. Literature Review **19-55**

2.1 Defluoridation of water **19**

2.2 Fluoride removal technologies **20**

2.2.1 Precipitation/coagulation techniques **20**

2.2.2 Ion-exchange techniques **21**

2.2.3 Membrane techniques **21**

2.2.4 Adsorption techniques **22**

2.3 Adsorbents used for defluoridation **25**

2.3.1 Alumina and aluminium-based adsorbents **25**

2.3.2 Biochar and Carbon-based adsorbents **26**

2.3.3 Calcium-based adsorbent **29**

2.3.4 Oxides/hydroxides and layered double hydroxides **31**

2.3.5 Nanomaterials **33**

2.3.6 Natural materials **34**

2.3.7 Building material and waste based adsorbents **35**

2.4 Fish Scale for Water /Wastewater treatment **37**

2.4.1 Removal of Heavy metals **38**

2.4.2 Removal of Industrial Dye **41**

2.4.3 Removal of miscellaneous water pollutants **41**

2.5 Limitations of earlier work **43**

2.6 Critical Review of Literature **44**

3. Objective of Present Research Work 46

3.1 Objective of research work **46**

3.2 Scope of the proposed work **46**

4. Materials and Methods 47-58

4.1Materials **47**

4.1.1 Chemicals & Reagents **47**

4.1.2 Apparatus and Instruments used **47**

4.1.3 Preparation of adsorbent material **48**

4.1.3.1 Preparation untreated Fish scale biochar (FSB) **48**

4.1.3.2 Preparation of acid treated fish scale biochar (AMFSB) **54**

4.1.3.3 Preparation of Metal impregnated Fish Scale Biochar **54**

4.2 Surface chemical and physical characterization **54**

4.2.1Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) **54**

4.2.2 Fourier-transform infrared spectroscopy (FTIR) analysis **55**

4.2.3 X-Ray Diffraction Analysis (XRD) **55**

4.2.4 Moisture content **56**

4.2.5 Determination of Bulk Density **56**

4.2.6 Determination of surface area (BET method) **56**

4.3 Batch adsorption studies **57**

4.4 Fixed Bed Column Study **57**

5. Theoretical Consideration 59-66

5.1 General ideas about adsorption **59**

5.1.1 The Adsorption Process **59**

5.1.2 Adsorption isotherm **60**

5.1.2.1 Langmuir isotherm **60**

5.1.2.2 Freundlich isotherm **61**

5.1.3 Adsorption kinetics and mechanisms **61**

5.1.3.1Pseudo-First-Order Kinetics **62**

5.1.3.2 Pseudo-second-order kinetics **62**

5.1.3.3 Intra particle diffusion **62**

5.2 Column studies **63**

5.2.1 Column data analysis **64**

5.2.2 Modelling of column performance **64**

5.2.2.1 Thomas model **64**

5.2.2.2 Yoon-Nelson model **65**

5.2.2.3 Bed depth service time (BDST) model **65**

5.3 Response Surface Methodology **66**

6. Result Discussion **67-112**

6.1 Characterization of Fish Scale Biochar **67**

6.1.1 Physiochemical Characteristics **67**

6.1.2 SEM-EDS analysis **69**

6.1.3 FTIR analysis **73**

6.1.4 XRD analysis **75**

6.2 Preliminary investigation **76**

6.3 Batch operation **77**

6.3.1 Removal of Fluoride with Fish Scale Biochar **77**

6.3.2.1 Effect of contact time **77**

6.3.1.2 Effect of adsorbent dose **78**

6.3.1.3 The effect of initial pH: **79**

6.3.1.4 Effect of initial concentration of fluoride **80**

6.3.1.5 Effect of agitation speed **81**

6.3.2 Removal of Fluoride with Acid Modified Fish Scale Biochar (AMFSB) **82**

6.3.2.1 Effect of contact time **82**

6.3.2.2 Effect of adsorbent dose **82**

6.3.2.3 The effect of initial pH **83**

6.3.2.4 Effect of initial concentration of fluoride **84**

6.3.2.5 Effect of agitation speed **85**

6.3.2.6 Effect of co-ions **86**

6.4 Adsorption Isotherm **87**

6.4.1Langmuir Isotherm **87**

6.4.2Frendulich Isotherm **89**

6.5 Adsorption Kinetics **91**

6.6 Fixed-bed column adsorption study **94**

6.6.1 Effect of adsorbent bed depth **95**

6.6.2 Effect of flow rate **96**

6.6.3 Effect of initial F- concentration **96**

6.6.4 Breakthrough curve modelling **99**

6.6.4.1 Thomas model **99**

6.6.4.2 Yoon-Nelson model **100**

6.6.4.3 Bed depth service time (BDST) model **101**

6.7 Response Surface Methodology **103**

6.8 Comparison of fluoride removal using AMFSB with other adsorbent **111**

7. Conclusion **113-114**

7.1 Conclusions **113**

7.2 Future Scope of the study **114**

References **115-142**

Curriculum Vitae **143-144**

List of Publications

LIST OF TABLES

Table No.	Description	Page No.
Table 1.1	Effect of different fluoride concentration	8
Table 1.2	Standards for fluoride in drinking water	8
Table 1.3	Studies reported fluoride concentrations in groundwater and soil across India	12
Table 2.1	Comparison of fluoride removal technologies	24
Table 2.2	Fish scale based adsorbents for removing metal ions from water environment	39
Table 2.3	Fish scale based adsorbents for removing dyes from water environment	42
Table 2.4	Fish scale based adsorbents for removing miscellaneous pollutant from water environment	43
Table 4.1	Instruments Used	49
Table 6.1	Physical Characteristics of Fish Scale Biochar	68
Table 6.2	BET surface area for various Biochars used as an adsorbent	68
Table 6.3	Elemental composition of AMFSB	69
Table 6.4	Functional group identification-FTIR	74
Table 6.5	Langmuir adsorption constants for fluoride removal	89
Table 6.6	Frendulich adsorption parameters for fluoride removal	89
Table 6.7	Kinetic parameters for adsorption of fluoride on CAC and FSAC	94
Table 6.8	Experimental column parameters obtained from breakthrough curve	98

Table 6.9	Parameters of the Thomas model under different bed height using linear regression analysis	100
Table 6.10	Parameters of the Yoon-Nelson model under different F-Concentrations	101
Table 6.11	Parameters of the BDST model	102
Table 6.12	Experimental range and levels of the independent parameters	103
Table 6.13	Analysis of variance (ANOVA) for Response Surface Quadratic Model	104
Table 6.14	Fit Statistics for fluoride removal by AMFSB	105
Table 6.15	Comparison of fluoride removal capacity of different adsorbent	112

LIST OF FIGURES

Figure No.	Description	Page No.
Figure 1.1	Modified Schematic diagram of occurrence and movement of Fluoride in various environmental compartments	3
Figure 1.2	Industrial sources of Fluoride release in environment	4
Figure 1.3	Effects of Fluoride on Human Health	7
Figure 1.4	World map for fluoride distribution in different countries	10
Figure 1.5	India map for fluoride distribution in ground water (Central Groundwater Board, India, 2020:	11
Figure 4.1 (a)	Collection of fish scale from local market	50
Figure 4.1 (b)	Sorting of Fish Scales	50
Figure 4.1 (c)	Washing of Fish scales	51
Figure 4.1 (d)	Sun drying of Fish scales	51
Figure 4.1 (e)	Sun dried Fish scales	52
Figure 4.1 (f)	Fish scale biochar	52
Figure 4.2	Schematic diagram of FSB and AMFSB synthesis	53
Figure 4.3	Schematic of Column study	58
Figure 5.1	Schematic of adsorption column breakthrough curve and MTZ in fixed column	63
Figure 6.1	SEM of AMFSB before adsorption of F-	70
Figure 6.2	SEM of AMFSB after adorption F-	70

Figure 6.3	EDX before adsorption of fluoride	71
Figure 6. 4	EDX after adsorption of fluoride	72
Figure 6.5	FTIR of AMFSB before and after adsorption of F-	74
Figure 6.6	X-ray diffraction patterns for Acid modified Fish scale biochar before adsorption	75
Figure 6.7	X-ray diffraction patterns for Acid modified Fish scale biochar After adsorption	76
Figure 6.8	Effect of contact time on F- removal for prepared biochars	77
Figure 6.9	Effect of contact time on removal of Fluoride at various adsorbent dose	78
Figure 6.10	Effect of adsorbent dose on removal of Fluoride	79
Figure 6.11	Effect of pH on removal of Fluoride	80
Figure 6.12	Effect of Initial F- concentration on removal of Fluoride	81
Figure 6.13	Effect of agitation speed on removal of Fluoride	81
Figure 6.14	Effect of contact time on removal of Fluoride at various adsorbent dose	82
Figure 6.15	Effect of adsorbent dose on removal of Fluoride	83
Figure 6.16	Effect of pH on removal of Fluoride	84
Figure 6.17	Effect of initial F^- concentration on removal of Fluoride	85
Figure 6.18	Effect of agitation speed removal of Fluoride	86
Figure 6.19	Effect of co-existing ions removal of Fluoride	85
Figure 6.20 (a)	Langmuir isotherm for FSB	87
Figure 6.20 (b)	Langmuir isotherm for AMFSB	88

Figure 6.21 (a) Frendulich isotherm for FSB 88

Figure 6.21 (b) Frendulich isotherm for AMFSB 90

Figure 6.22 (a) Pseudo-first-order plot for FSB 90

Figure 6.22 (b) Pseudo first order plot for AMFSB 91

Figure 6.23 (a) Pseudo Second order plot for FSB 92

Figure 6.23 (b) Pseudo Second order plot for AMFSB 92

Figure 6.24 Intra-particle diffusion model for FSB and AMFSB 93

Figure 6.25 Breakthrough curve of fluoride removal at different bed height 95

Figure 6.26 Breakthrough curve of fluoride removal at different flow rate. 96

Figure 6.27 Breakthrough curve of fluoride removal at different F- ion concentration 97

Figure 6.28 Thomas model plot of ln(Co/Ct - 1) vs time (t) at different Bed Depth 99

Figure 6.29 Yoon-Nelson model plot at different F- ion concentration 101

Figure 6.30 BDST model plot at C/Co 102

Figure 6.31 (a) Response surface plot for effects of pH and contact time 106

Figure 6.31 (b) Response surface plot for effects of pH and adsorbent dose 106

Figure 6.31 (c) Response surface plot for effects of contact time and initial F^-concentration 107

Figure 6.31 (d) Response surface plot for effects of contact time and 107

	adsorbent dose	
Figure 6.31 (e)	Response surface plot for effects of adsorbent dose and initial F-concentration	108
Figure 6.32	Perturbation plot showing effect of parameters on fluoride removal	109
Figure 6.33	Plot showing the distribution of actual vs. predicted fluoride removal %	109
Figure 6.34	Normal plot of residuals showing % probability versus residual error	110
Figure 6.35	Desirability ramp for numerical optimization of process parameters	111

NOMENCLATURE

Symbol	**Description**
C_b	The desired concentration of solute at breakthrough (mg/L)
C_e	Equilibrium concentration of adsorbate in solution after adsorption
C_o	Initial solute concentration at $t = 0$
Ct	Solute concentration at time ‘t’ (mg/L)
d	The depth of the adsorbent (cm),
F	The fractional capacity of adsorbent
F_m	The flow rate (ml/min)
K	Adsorption rate constant (L/mg-h)
K_f	Freundlich constant related to adsorption capacity
K_1	Pseudo-first order reaction rate constant
K_2	Pseudo-second order reaction rate constant
M	Weight of adsorbent in g
N_0	Adsorption capacity
1/n	Adsorption intensity
Q	The maximum capacity of removal of adsorbate in the column
q_e	The amount of solute adsorbed per unit weight of adsorbent at equilibrium
q_t	The amount of solute adsorbed per unit weight of adsorbent at any time ‘t’
t	Service time of column (min)
t_e	The time required to establish Primary Adsorption Zone (min),
t_f	The time of formation of PAZ.
t_δ	Time required for movement of MTZ down the column (min)
$t_{1/2}$	Time to obtain 50% reduction of adsorbate in the solution
V	Linear flow velocity of feed to bed
V_b	The breakthrough volume (ml)
V_e	The exhaustion volume (ml)
Y	Predicted %removal of Fluoride
Xi	Coded independent variables
Xj	Un-coded independent variables
βo	Regression coefficient
β_i	Linear coefficient
β_{ii}	Quadratic coefficient

ABBREVIATIONS

AA	Activated alumina
AMFSB	Acid modified biochar
BBD	Box-Behnken design
BIS	Bureau of Indian Standards
CCD	Central composite design
CPHEEO	Central Public Health and Environmental Engineering Organisation
EDS	Energy dispersive X-ray spectroscopy
FSB	Fish scale biochar
FTIR	Fourier-transform infrared spectroscopy
ICMR	Indian Council of Medical Research
RSM	Response surface modeling
SEM	Scanning electron microscopy (SEM)
XRD	X-Ray diffraction analysis
WHO	World Health Organisaton

ABSTRACT

Fluoride ingress in sub surface water resources is widely found in many part of world including India. Concentration in groundwater over and above 1.5 mg/L- 2 mg/L is considered to be unsafe for human consumption. Dental carries, Skelton fluorosis are the common health issues for fluoride uptake in drinking water. Fluoride contamination of groundwater is also an important global water quality issue. Approximately 200 million people in 29 counties are suffering from fluoride contamination. Fluoride contamination through wastewater discharge s also found in some industrial effluent that releases from industries of fertiliser manufacturing, glass processing units, semiconductor manufacturing industries, etc.

In this connection various technologies are used presently for removal of fluoride from water environment. Among all available technologies, use of adsorption is very common. Adsorption is a technologically friendly and easily applicable engineering method for fluoride removal from water environment. Activated alumina is an excellent material for elimination of Fluoride from water, however this material is costly and is availability is also a concern. Moreover it is efficient technique at lower pH (5-6). The most important fact that, disposal of used Activated alumna is a cumbersome process. Due to limitation of usage of activated alumina uses scientist and engineers are actively involved in search of easily available low cost absorbent for removal of fluoride from water.

Earlier, Bhaumik et al.,(2017) used fish scale powder material for removal of fluoride. In India, many markets produces huge amount of fish scale waste and dispose them off indiscriminately causing aesthetics and physical pollution of soil and other environment. Moreover, fish scale derived active carbon contained some useful sorption site for removal of the above solute material. With this viewpoint a research study is undertaken for perusing Ph. D. Dissertation in environmental engineering laboratory to examine the potential application of fish scale derived activated carbon as biochar (FSB) with some surface modification for removal of Fluoride from water environment.

Successful use of Fish scale biochar (FSB) as an absorbent material is considered to be novel and not only groundwater treatment to be done by this material but at the same time solid waste problem to is curbed down particularly from fish market area. In the present research Fish scales in sizeable amount was collected from a local fish market and sundried in openly in air with subsequent heating at 600^0C in muffle furnace to remove moisture, volatile matter reduced for converting to carbonaceous material. The biochar thus formed is named as Fish Scale Biochar (FSB).This material was subsequently washed in ammonia free distilled water and exposed to acidic solution to remove fine foreign materials and other impurities. This acid laden Fish scale biochar was named as Acid modified fish scale biochar (AMFSB).FSB and AMFSB are tested with Fourier-transform infrared spectroscopy (*FTIR*) scanning electron microscope (SEM) Energy Dispersive X-ray and X-Ray Diffraction Analysis (XRD)to characterize its chemical and structural composition. A pre-determine amount of both the material have been taken in Fluoride spiked solution of known fluoride concentration is with varying adsorbent dose and stirred 150 rpm for contact time of 150 minute to examine its fluoride removal capacity.

To determine the feasibility and fluoride uptake capacity of absorbent batch Kinetic studies are conducted with the different initial fluoride concentration, pH, absorbent dose , contact time and agitation speed, as per standard absorption experiment flowed by previous researchers.The effect of various influencing parameters on fluoride removal efficiency of AMFSB are also observed. Various types of isotherm studies are carried out and plotting was done on the basis of experimental data. Kinetic Data reveals that it follows pseudo first order kinetic rate and Langmiur adsorption isotherm model, was reasonably fitted for FSB (R^2 =0.984) and AMFSB (R^2 =0.985). The result demonstrated that fish scale derived biochar is able to remove fluoride up to 92.2 % corresponding to an initial concentration 5mg/L and adsorbent dose of 6 gm/L. Both the materials followed adsorption phenomenon. It is also found that adsorption capacity of FSB and AMFSB is about 2.12 and 5.16 mg/g respectively. Which is comparable with many other adsorbents investigated earlier by other researchers for fluoride removal.

The batch experimental data also indicates that pH of the solution contributes maximum effect on removal mechanism. It was observed that for FSB maximum removal taken place at pH 5.5. Whereas, for AMFSB pH value was found to be 6.5 for optimum removal. Other parameter effects are not very predominant as compared to pH. It was found by various earlier researchers that percent fluoride removal by activated alumina took place at pH less than 4, i.e. in acidic condition.

After kinetic studies, fixed bed column study is conducted with perplex short column with column of 2 cm diameter and 40 cm length for different initial concentration of fluoride such as 5, 7, 10 mg/L. The bed height of column was varied between 1, 2 and 3cm,the application flow rate was also allowed to vary. The breakthrough service time was noted and plotted with c/co value. Column study results are also employed to examine validity of Thomas model, Yoon-Nelson and BDST model.The column study plot exhibit BDST model reasonably fitted well with service time 674 minutes for column of adsorbent depth of 3cm.

Some optimization too has been also exercised to predict the optimum condition for fluoride removal of AMFSB application for batch treatment. This optimization analysis was done by applying RSM analysis with Box-Behnken design model. The F-test ANOVA is used for explaining the significance of the regression model equations. The F-values and P-values gave the significance of each variable. The RSM analysis predicted maximum fluoride % removal efficiency of AMFSB to be 85% at optimum pH of 7.1, contact time of 165.885 min, initial fluoride concentration of 5.26912 mg/L. and adsorbent dose of 6.21 mg/L.

This present research investigation exhibits both Fish scale biochar (FSB) and Acid modified fish scale biochar (AMFSB) are significantly efficient for removal of fluoride from water environment and perhaps be new adsorption material for groundwater and wastewater treatment.

Chapter - 1

Introduction

Chapter 1
Introduction

1.1 Background

Water is abundantly available natural resource, essential for all living beings, plants and animals. About 75% of the matter of earth's crust contains water and is an essential constituent of all animal and vegetable matters existing ting on the earth surface. Though, there is plenty of water is available on the earth's surface very little of it is fit for direct consumption by to sustain living entities (Edmunds and Smedley 2013). Water is renewable but water fit for drinking is limited, so it is a vulnerable resource of prime importance. The rise in global industrialization, population explosion, modern agricultural practices and other environmental changes around the globe, has resulted in severe of drinking crisis of drinking water in many parts of the world (Amini et al. 2016; Lapworth et al. 2012). According to WHO report presented in 2019, 2.2 billion people of global population still don't have access to safe drinking water (WHO, 2019). Water pollution is a critical problem faced by developing countries where majority of the people depend on groundwater for drinking. A large section the world's population is already facing of water shortage. Pollution caused due to various wastes and contaminants from cities, industry and agriculture have deteriorated quality of water in rivers and underground. Natural water bodies have impurities from various sources. Colloidal materials, microorganisms, suspended particles, various dissolved metallic and non-metallic substances and pesticides are commonly found as contaminants in water. The anionic pollutants like fluoride and nitrate contamination in groundwater has been recognized as problem of concern worldwide (Sabti *et. al*. 2022). Fluoride is one such contaminant which is abundantly present in groundwater and creates serious toxicological effects on environment (Ahmad et al., 2022)

Fluoride is often described as a "double-edged sword". The improper intake of fluoride promotes dental caries, including dental, skeletal and soft tissue fluorosis. Fluorosis is becoming a global environmental toxicological problem and is most commonly found in water-stressed regions. (Fawell *et al*.,2000; Raju 2017). Fluoride contamination in drinking water sources has been a major problem in many countries, especially in several parts of Argentina, China, India, East Africa, part of South Africa South Africa, Sri Lanka Tanzania, Turkey and some part of South America. (Srimurali *et al.*, 1998; Barati *et al.*, 2014)

1.2 Occurrence and sources of Fluoride

Fluoride is the 13th most abundant element on earth. It exists in varying amount in earth crust, air, flora and fauna. Anthropogenically it is added in in soil and water and air. The fluoride is amply found in the earth crust in the form of fluoride bearing minerals s and rocks. Fluoride-bearing minerals and rocks are the geogenic source of fluoride ions (F−) is found in groundwater and soils. Various Fluoride-bearing minerals and rocks are. fluorite [CaF_2], fluorapatite [$Ca_5(PO_4)_3(F,Cl,OH)$], cryolite [Na_3AlF_6], actinolite [$Ca_2(Mg_{4.5-2.5}Fe^{2+}_{0.5-2.5})Si_8O_{22}(OH)_2$], muscovite [$(KF)_2(Al_2O_3)_3(SiO_2)_6(H_2O)$], topaz ($Al_2SiO_4(F,OH)_2$), asbestos [$Mg_3Si_2O_5(OH)_4$] chrysotile [$Mg_3Si_2H_4O_9$]), sphene ($CaTiSiO_5$), and villiaumite [NaF], etc., are a widespread source of fluoride in groundwater (Kundu et al., 2001; Biswas et al. 2017; Naaz, 2015; Adimalla and Venkatayogi, 2017; Kimambo et al. 2019;Adimalla et al., 2019, Ahmed et.al. 2022, Kumar,et al., 2022). Fluorides are liberated into the groundwater by the steady breaking up minerals and rocks (Biswas *et. al.*, 2009). Natural and manmade activities attribute fluoride esisnc in water.

Fluoride is an electronegative and reactive element having yellow-green color. Fluorine is an irritant and odors gas. Due to its electro-negativity and reactivity it does not exist in natural form. The source transportation of fluoride in various environmental compartments is schematically illustrated in **Figure 1.1** Natural water contains fluoride certain concentrations. The fluoride concentration in sea water was found to be 1mg/ l, where as in several lakes and rivers the concentrations of fluoride were found to be less than 0.5 mg/l(Khandare 2013; Ali et al. 2016; Biswas et al., 2017;). The fluoride is contributed in groundwater is mainly due to the chemical, geological, physical characteristics of the aquifer which contains fluoride bearing rocks and minerals. The fluoride in air is also present in quite low concentrations. Natural source of fluoride in air are coal mines and volcanic eruptions.

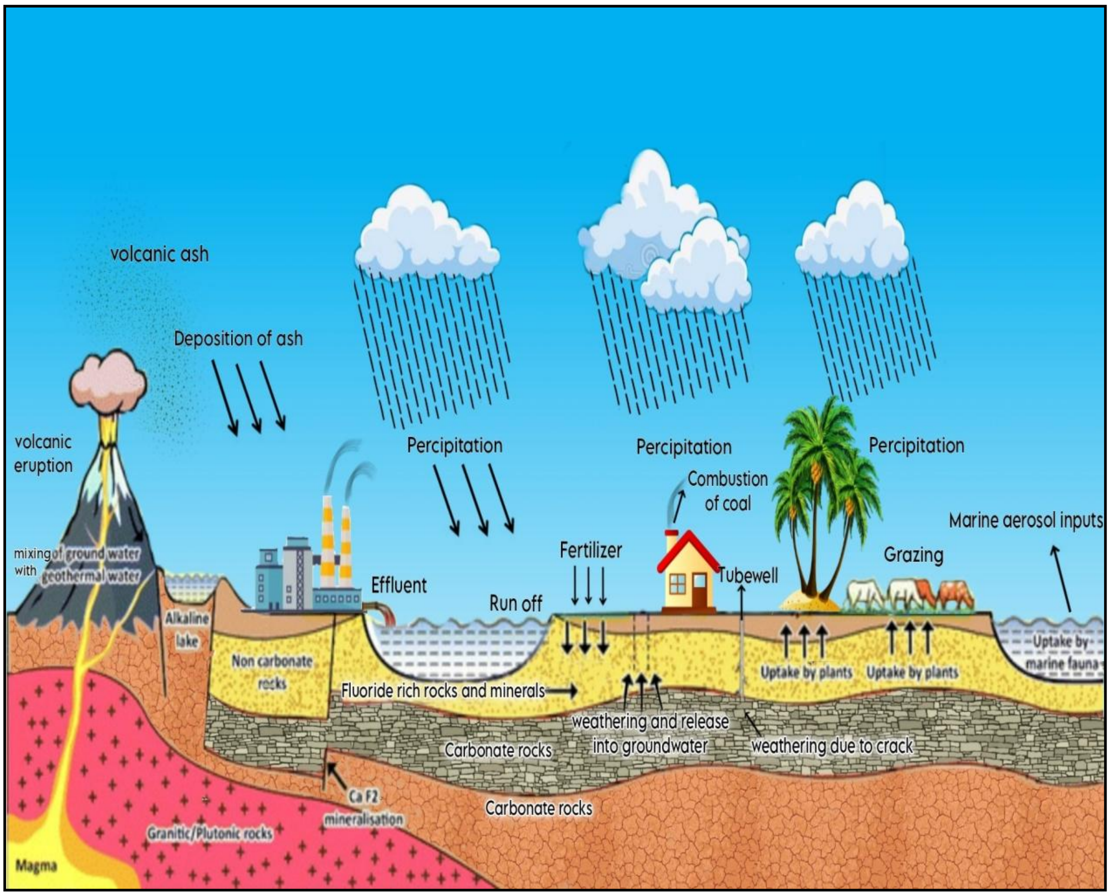

Figure 1.1 : Modified Schematic diagram of occurrence and movement of Fluoride in various environmental compartments (Edmunds and Smeldley, 2005)

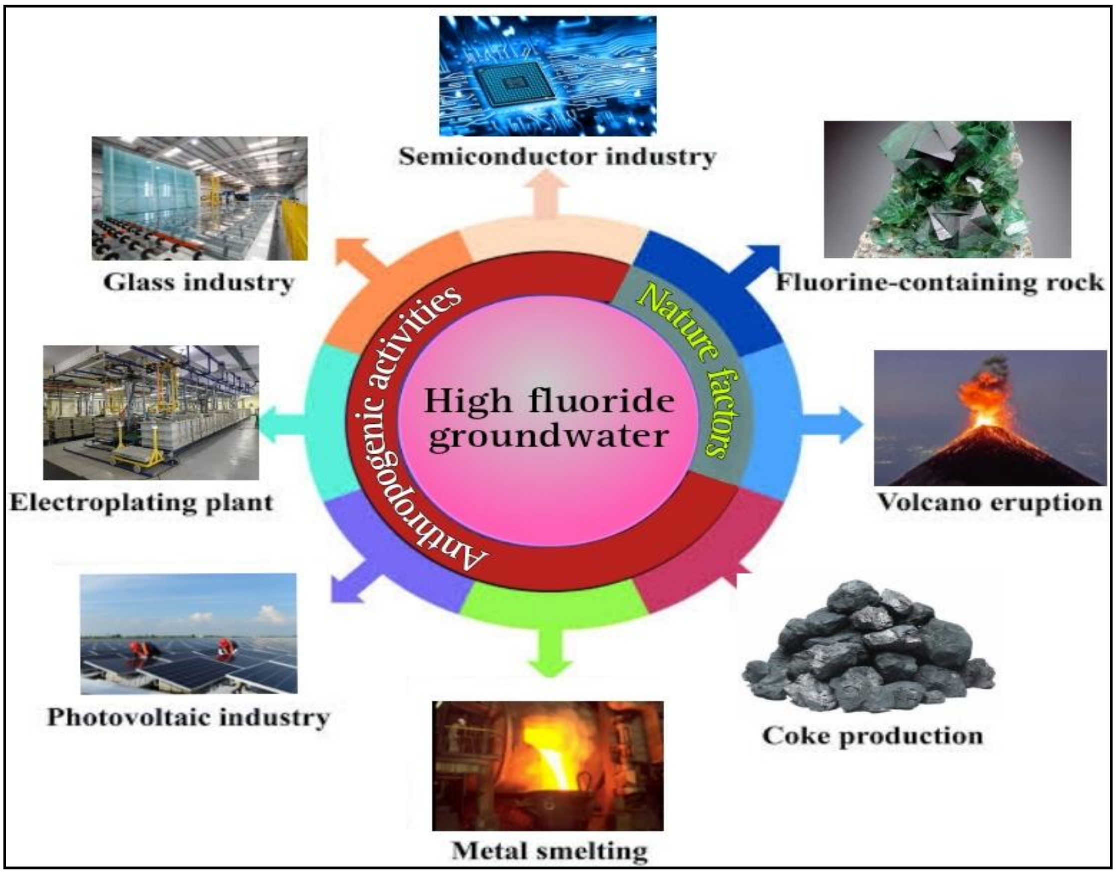

Figure 1.2 : Industrial sources of Fluoride release in environment

Figure 1.2 shows the various industries which are major anthropogenic source of fluoride in environment. The anthropogenic sources of fluoride includes industries related to glass manufacturing, coal-fired plants, electroplating plants, fertilizer manufacturing units, metal smelting units , phosphate manufacturing plants, , semiconductor industry, etc. (Jayarathne et. al., 2014; Singh et al. 2018). The many industries fluoride is widely used in the form of fluoride salts. The atmosphere is getting polluted by industrial production of phosphate fertilizers and coal ash. It releases fluoride into air, and there by increases its concentration. Modern agricultural practices are focused on the application of fertilizers and pesticides which contribute fluoride to groundwater(Kimambo et al. 2019).

1.3 Health effects and permissible limits of Fluoride

Fluoride is a persistent and non-biodegradable pollutant. Through various modes of transport it get accumulated in soil, plants, wildlife and in human beings (Tomar , 2013). Fluoride in low concentrations is considered a necessary for human health whereas, prolonged exposure of high concentrations of fluoride is leads to serious disease called fluorosis (Yadav *et. al.,* 2022, Sawangjang, and Takizawa, 2023). Consumption of Fluoride in small concentrations is beneficial to human health. The beneficial fluoride concentration range for human health is too narrow i.e between 0.5- 1.0 mg/L(Ahmad et al. 2022). Long term exposure of fluoride through consumption of fluoride laden water and other natural source is a matter of great concern regarding well being of mankind (Ahmed et.al. 2022, Kumar et al., 2022). **Table 1. 1** shows the effect of fluoride on human health at various concentrations of fluoride. Fluoride enters into the human body mostly through food and water consumed and dental products used. Fluoride ions in the stomach produce hydrofluoric acid (HF) combined with hydrogen ions in acidic conditions of gastrointestinal tract. Formation of hydrofluoric acid intestine leads to nausea, diarrhea, vomiting, and abdominal pains (Ahmad et al. 2022). When Fluoride get mixed in bloodstream, it reaches and reacts with calcium present in teeth and bones, which leads to bone deformities and dental fluorosis in children. There are two main kinds of fluorosis identified as dental fluorosis and skeletal fluorosis commonly found in fluoride affected areas (Ayoob and Gupta, 2006). Teeth mottling is mild dental fluorisis shows opaque white patches on the teeth, in moderate and severe stages of dental fluorosis it leads to display brown to black staining on teeth , followed by pitting of teeth surfaces. A skeleton fluorosis is caused due consumption of water having fluoride > 4 mg/L. In skeleton fluorosis, person suffers from deformation of bones and joints in association with muscle pain. The stiffness in joints, headache, and muscle weakness are the signs of skeleton fluorosis. (Yousefi *et. al*., 2018; Yadav *et. al.* 2022). The severe stage of skeleton fluorosis is called osteosclerosis and is characterized by damaged of nervous system, major joints and spine. Earlier the excess fluoride was considered only to affects bones and teeth (Vithanage and Bhattacharya, 2015). According to various literature published higher levels of fluoride(>4mg/L) in drinking water are responsible for arthritis, infertility, hypertension, neurotoxicological effects, skeletal cancer. It also damages to soft tissues organs like as liver, lungs, kidneys and testis (Sun et al., 2013; Yousefi *et al*., 2018; Fallahzadeh *et al*., 2018, Yadav, *et. al.*, 2022). **Figure 1.3** elaborates the effect of excessive fluoride consumption on various organs of human body.

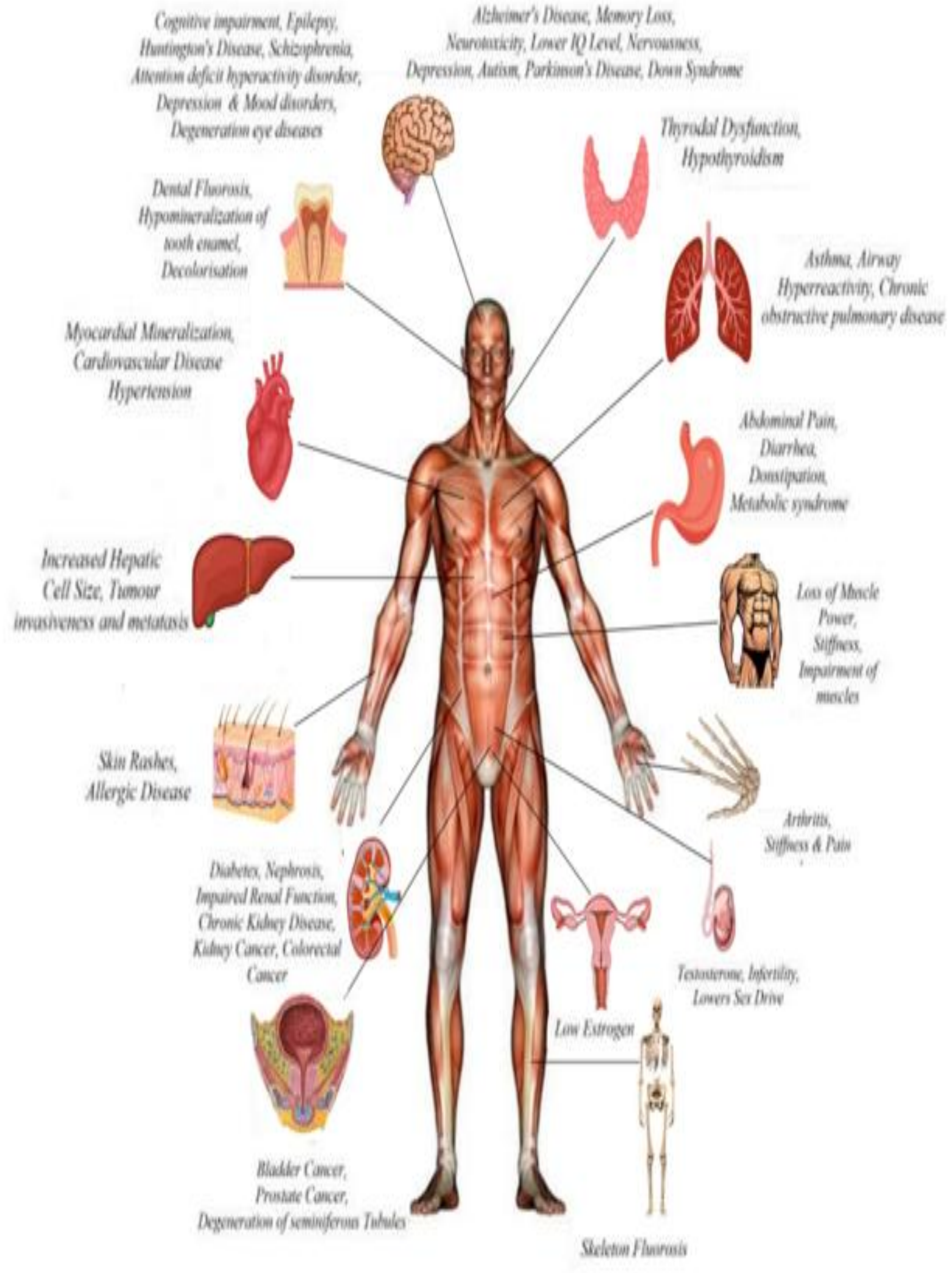

Figure 1.3: Effects of Fluoride on Human Health

Table 1.1 Effect of different fluoride concentration (Source: Biswas et al. 2017)

Fluoride (mg/L)	Effects on human body
Less than 0.5	Dental cavities
0.5–1.0	Protection against dental cavities. Care of bone and teeth
1.5–3.0	Dental fluorosis
3.0–10	Skeletal fluorosis (adverse changes in bone structure
10 or more	Crippling skeletal fluorosis and severe osteosclerosis

To mitigate the elevated fluoride consumption related health problems various organizations have specified the permissible limit for fluoride in drinking water. The standards for fluoride in drinking water are given in **Table 1.2.**

Table 1.2: Standards for fluoride in drinking water

Name of organization	Desirable limit (mg/L)	Reference
BIS	0.6–1.2	IS 10500: 2012
ICMR	1.0	Mohapatra et al., 2012 Upendra et al., 2015
CPHEEO	1.0	Bhagan et al,. 1996 ;Aldaco et al., 2005
WHO	1.5	Upendra et al., 2015;Mobeen *et al*., 2017

1.4 Global scenario of fluoride contamination

1.4.1 World scenario

Fluoride in drinking water is posing a serious problem across the world. About 200 million people worldwide are at risk due to of fluorosis. As reported by Cherukumilli et al., 2017 around 200 million people are using fluorinated water for drinking and about 70 million people are suffering through various stage of fluorosis complications. According to many research studies in past, more than 35 countries are facing problem of high fluoride water sources. India, China, Ethiopia, Kenya, Pakistan, Iran, Germany, Sri Lanka, Tanzania, Nigeria, and South Africa are few countries suffering from excessive fluoride concentrations in water (Biswas et al. 2017; Dheeraj Kumar et al. 2022; Dhillon, Prasad, and Kumar 2017; Jadhav et al. 2015; Mohapatra et al. 2009). **Figure 1.4** represents the world map of fluoride occurrence. In the tropical regions like Egypt, Pakistan, Malawi, Jordan, Ethiopia, South Africa, Mexico, Sri Lanka, India, water consumption from groundwater is more due to climate conditions, their fluoride levels in water are more (Mohan, Kumar and Srivastava 2014; Sivarajasekar et al. 2017). The problem associated with defluoridation of groundwater in such countries are high cost of fluoride removal technology, cost of the adsorbent or insufficient fluoride removal capacity of adsorbents. These problems need to be addressed in fluoride-affected countries.

1.4.2 Indian scenario

In India, 18 states have been identified as epidemic for fluorosis (Andezhath *et al*., 1999, Mondal *et al.*, 2014; Das 2017). The severe cases of fluorosis were reported in part of North-Western part of India exceeds fluoride concentration of 0.4-19 mg/L(Yadav et al., 2009; Dhiman and Kesari, 2006). Few literatures have reported fluoride concentration of 0.2-20 mg/L in parts South India(Shaji et al., 2007; Karthikeyn et al., 2010; Mamatha and Rao 2010). Central India and Deccan Province have also reported moderated fluorosis due to fluoride concentration of 0.2-10 and 0.4-8 mg/L respectively(Mobeen and Kumar 2017; Sivarajasekar et al. 2017; Yadav et al. 2019,) . Nearly 200 districts of 18 Indian states have reported fluoride associated problems affecting around with 200 million people (Mondal and George 2015; **Das 2017**). **Figure 1.5** shows India map for fluoride distribution in ground water given by Central Groundwater Board , India, 2020. Endemic fluorosis is a is observed in many parts of India. Andhra Pradesh, Gujarat, , Punjab, Maharashtra, Telangana, Rajasthan, Orissa, West Bengal etc are most affected states of India. (Edmunds and Smedley, 2013). Rajasthan has high fluoride content because of large deposits mica, Fluorspar, and Fluorapatite (Patel et al, 2012). Fluoride in groundwater is also reported in northern areas and Panchmahal districts of Gujarat where Cryolite, fluorspar and fluoropatite, are found in abundance. (Shah and Indu,2004). **Table 3** gives details the ranges of fluoride concentrations in water in various Indian states reported by researchers.

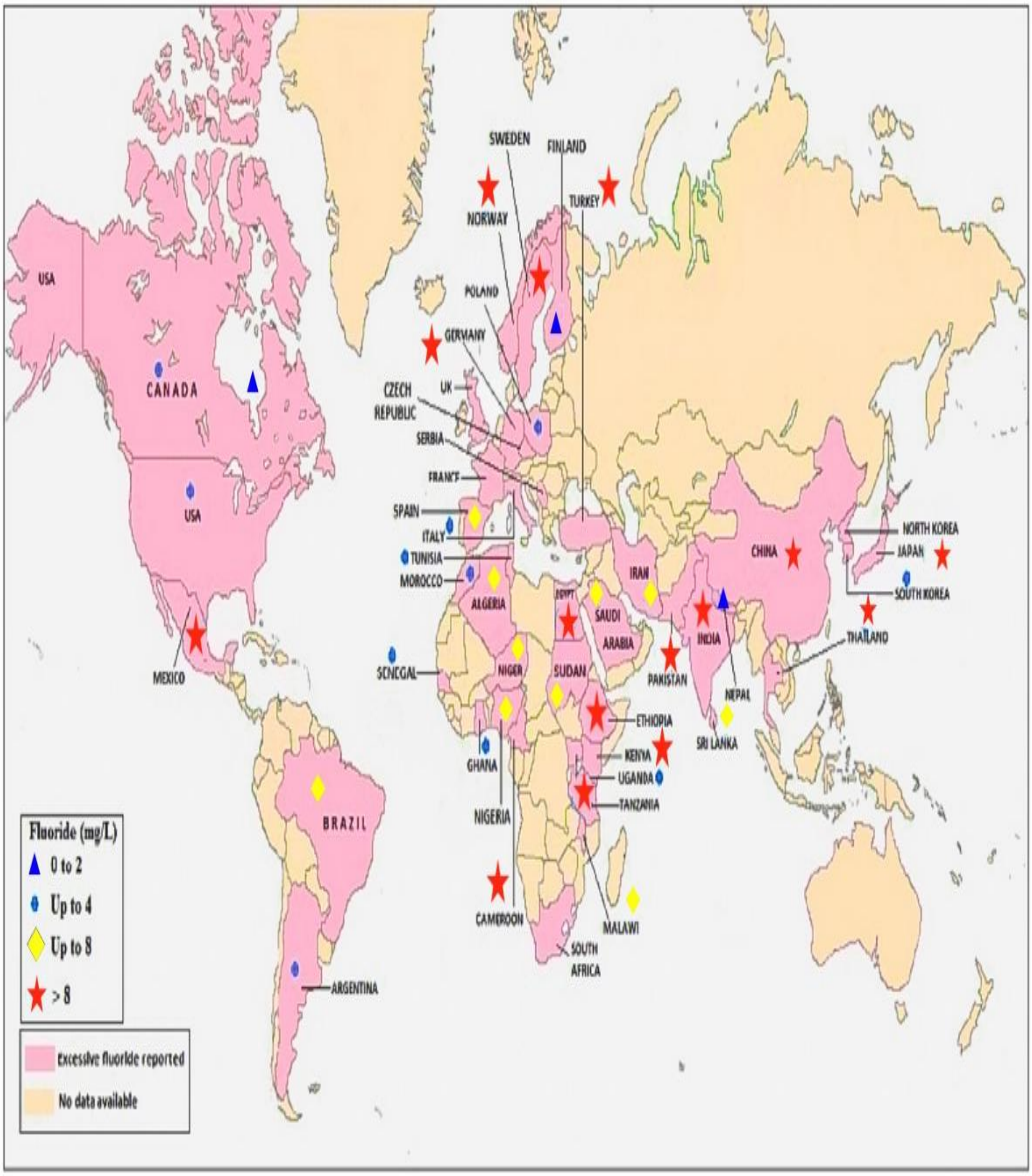

Figure 1.4 : World map for fluoride distribution in different countries.

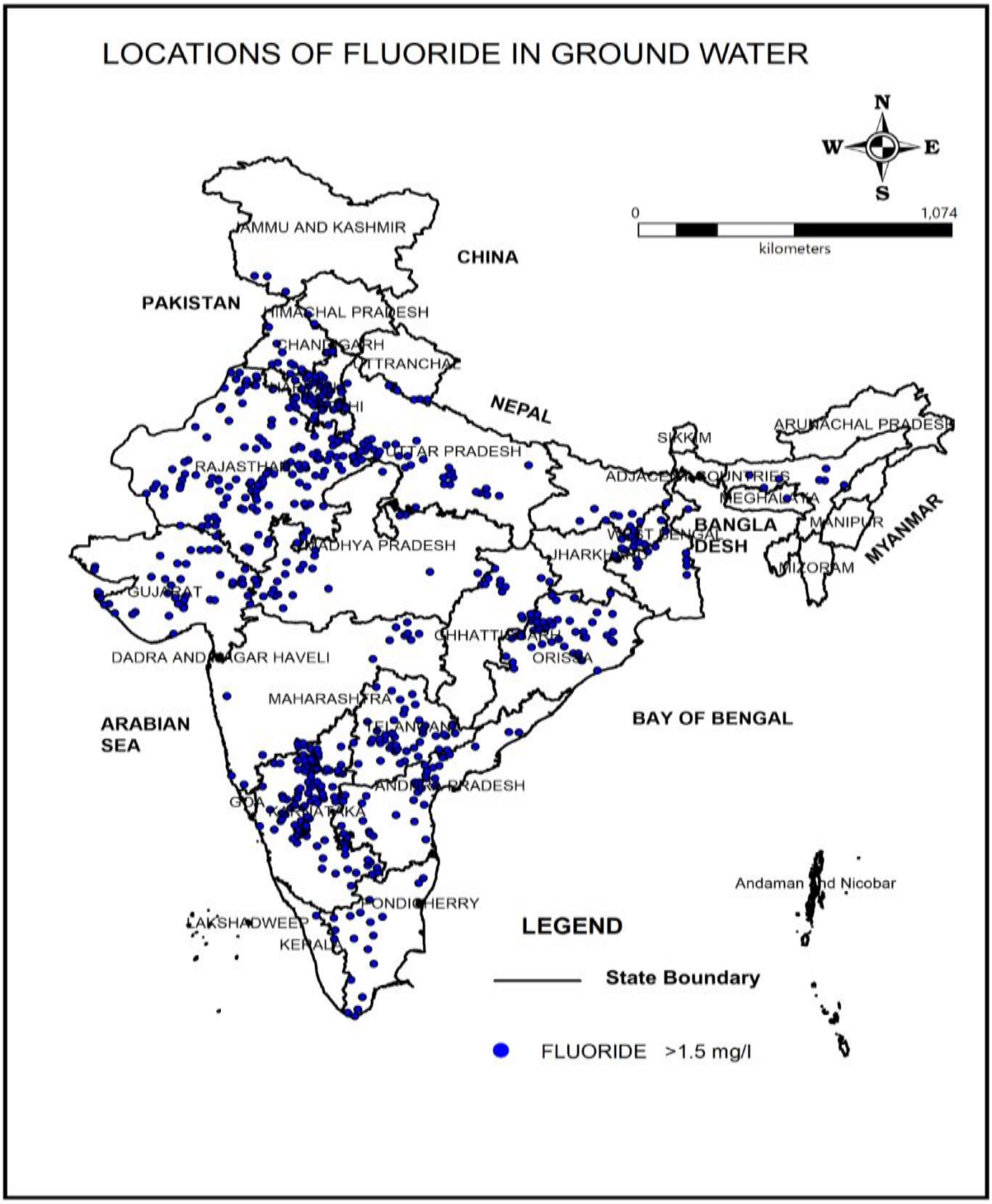

Figure 1.5 India map for fluoride distribution in ground water (Central Groundwater Board, India, 2020)

Table 1.3. Studies reported fluoride concentrations in groundwater and soil across India

State	FluorideConcentration (mg /L)	References
Andhra Pradesh	0.3 – 6.88	Rao and Devadas, 2003 Subba Rao, 2003 Ramanaiah et al., 2006 Asadi et al., 2007 Rao, 2009 Arveti et al., 2011 Brindha et al., 2011
Assam	> 1.5 High Concentration	Das et al., 2003 Dutta et al., 2006 Dar et al., 2011
Bihar	0.1-2.5	Ray et al., 2000
Chhattisgarh	0.6-8.8	Beg et al., 2011
Delhi	2.01-9.45	Srivastava and Ramanathan, 2008
Gujarat	0.14-5.6	Gupta et al., 2005 Dhiman and Keshari, 2006 Salve et al., 2008
Haryana	0.03-16.6	Kaushik et al., 2004 Bishnoi and Arora, 2007
Karnataka	0.02-3.5.35	Sujatha, 2003 Mamatha and Rao, 2010 Srinivasamoorthy et al., 2011 Singaraja et al., 2013
Kerala	0.2-5.75	Ravindra and Garg, 2006 Yadav et al., 2009 Srinivasamoorthy et al., 2012
Madhya Pradesh	61.4	Ramakrishnaiah et al., 2009 Avtar et al., 2013

State	FluorideConcentration (mg /L)	References
Maharashtra	0.3-13.41	Shaji et al., 2007 Madhnure et al., 2007 Raj and Shaji, 2017
Odissa	0-6.4	Kundu et al., 2001 Sankararamakrishnan et al., 2008 Dey et al., 2012
Panjab	0.02-1.61	Kumar et al., 2007 Vikas et al., 2009 Vikas et al., 2013
Rajasthan	0.1-16.9	Suthar et al., 2008 Singh et al., 2011 Arif et al., 2012 Hussain et al., 2012 Vikas et al., 2013
Tamil Nadu	0-8.5	Arumugam and Elangovan, 2009 Karthikeyan et al., 2010 Magesh et al., 2011 Chidambaram et al., 2013
Telangana	0.3-8.8	Singh and Mukherjee, 2015Adimalla and Venkatayogi, 2017 Narsimha and Sudarshan, 2017
Uttar Pradesh	0.1-14.8	Raju et al., 2009 Sharma et al., 2011 Raju et al., 2012
West Bengal	0.006-13.61	Gupta et al., 2006 Kundu and Mandal, 2009 Mondal et al., 2014

1.5 Control of fluoride toxicity

According to existing literature, developing countries are worst affected by endemic fluorosis. The rural areas and economically weaker sections of society are at risk due consumption of fluoride contaminated water. Access to safe drinking water is still a big challenge for millions of people across the world and in India. In fluoride affected areas with limited water resources substitution of water source is not practically viable solution. Defluoridation of drinking water is considered as the only means to prevent fluorosis (Fawell et al., 2006; Gandi 1.1et al., 2012, Bhaumik et al., 2017) .Current trends in water de-fluoridation techniques include chemical precipitation/coagulation, ion exchange, adsorption, reverse osmosis, and electro-dialysis. In addition to these physical and chemical defluoridation methods, few researchers have reported phytoremediation as biological processes defluoridation and bioremediation through microbes (Bhaumik 2017; Weerasooriyagedara et al., 2020) .These techniques are often perplexing to common people. Activated alumina is well known for its effective treatment of fluoride laden water. But this process functions better at low pH (4.5-5.5) (Ghorai S and Pant K, 2005) which requires necessary secondary pH correction. The chemical precipitation method is widely used for fluoride removal but it generates a large amount of sludge and its poses disposal problems. Other methods of fluoride removal such as ion exchange, electro-dialysis and reverse osmosis require high capital and operational costs (Gupta et al. , 2014; Zhang et al. , 2015).

Many of these methods have limitations for their practicle application at large scale due to critical factors like high operational and maintenance cost, generation of toxic byproducts (pollution) and sometimes to complex treatment. Among the available methods of defluoridation adsorption is considered as most suitable due to its simple operation and the availability of a wide range of adsorbents. (Srimurali *et al,* 1998; Suriyaraj *et al.* 2015; Thakre *et al*. 2015). In recent years use of waste based adsorbents is gaining lot of attention in water and wastewater treatment. The biomass are bluntly available in nature and can be easily converted into an adsorbent. Various sources of raw biomass are plants, agricultural wastes, animal waste and industrial by-products which can be used as an adsorbent for efficient fluoride removal. Application of such waste based adsorbents is not only useful for defluoridation of water but also addresses the problem associated with solid waste management and its disposal. Numerous studies have reported that, these low cost, waste based materials have great potential of fluoride removl nd can be used to substitute the expensive commercial adsorbent like activated carbon (Daifullah et al., 2007; Xue et al., 2009; Ganvir et al. , 2011; Mondal et al. 2012; Kumari et al. , 2013; Gupta et al. , 2014; Zhang et al. , 2015; Bhumik et al., 2017). Similarly, many studies have reported biochar as a universal sorbent for the removal of pollutants from soil and water environment. Biochar possesses relatively large specific surface area, high porosity and stable carbon matrix structure which make it a material of choice as an adsorbent. Existing literature reports, numerous biochar derived adsorbents have successfully removed fluoride for water environment (Khandare and Mukherjee 2019; Kumar et al., 2022; Khan et al., 2022)

1.6 Statement of the Problem

Consumption of water with high levels of fluoride is causing great concern across the globe. India has 29 states and more than 18 states are affected by fluorosis. The excessive consumption of Fluoride resulting in fluorosis. The disease caused due to excessive intake of fluoride has great impact on physical and mental health in persons affected by fluorosis. The health effects of fluoride in drinking water are not only irreversible but also detrimental. Preventing people from consumption of water laden with excessive fluoride is the only possible cure for this problem. Defluoridation of such contaminate water is the only sustainable approach. Among all the methods of defluoridation, adsorption is the most convenient method. Many adsorbents have been used by the adsorption method, but the they have limited use due to their high cost, less adsorption capacity and less regeneration capacity.

On the other hand consumption of fish and shrimp worldwide is increased over the last decade. As an outcome of these activities a huge production of fish scale is salvaged globally. In India, this waste is discarded as garbage and indiscriminately disposed without recovery of any useful product. This formed the base and need of the present study, focusing on using fish scale waste based adsorbent materials to remove fluoride ions from water which will give sustainable solution to the problem. In terms of the magnitude of fluoride contamination problem, exploring the novel, economic and environment friendly Fish scale Biochar and composite material will be a small attempt for a big problem. It will a veil some of the existing problem of Solid waste management, will also reduce the burden of environmental pollution due to fishery waste.

1.7 Motivation

Supply of safe drinking water purification is the biggest challenged the world is facing today. Groundwater remains the most important source for community/rural water supply. It is a scientific challenge to establish a techno-economical feasible method technology for remediation of ground water to save mankind and the environmental risks that fluoride induces. Among the technological options for abetment of excessive fluoride form groundwater, adsorption technique is considered appropriate; however, availability suitable and sustainable adsorbent remains a main challenge in real life situations. So, the development of potential Fluoride adsorbent is still on demand in many parts of developing countries.

Utilization of fish scale for water remediation is a recent innovation. The existing literature reveals that, Fish scales and their derivatives have been explored for removal of Heavy Metals and dyes from water environment but no such previous study has been performed to explore the potential of Fish Scale Biochar (FSB) for Fluoride removal from water environment. This has prompted and motivated for evaluation of waste based Fish Scale Biochar as an effective adsorbent for fluoride removal form water environment.

With the above viewpoint the present dissertation research is undertaken to examine the potential of fish scale derived biochar for abatement of fluoride contamination of groundwater.

1.8 Organization of thesis

Chapter 1 : Introduction

In this chapter statement of the problem, national and international scenario, genesis of the problem is discussed. It highlights occrance and sources of Fluoride in water environment. The toxicological health risks of fluoride in drinking water are dicussed in brief. The Chapter describes the motivation for the thesis problem. Finally the organization of the thesis is highlighted at the end of the chapter.

Chapter 2: Review of literature

This chapter explore the literature survey which are essential to understand available methods of defluoridation, previous extensive work and findings carried out by various researchers in past. The chapter includes most recent literature in the thematic field of fluoride removal with specials emphasis on fluoride removal by adsorption. It tries to highlight the conventional non-conventional, bio- origin based, waste based adsorbents used for fluoride removal. It highlights the least and most promising adsorbents developed and evaluated for fluoride removal in recent times. It also has a literature review regarding use of fish scale for removal of water contaminants. The chapter has the most recent and advanced literature in the thematic field of fluoride removal and use of fish scale as an adsorbent. The objective of the literature review is to find out an cost-effective, eco-friendly, sustainable and systematic approach for defluoridation of water environment. The chapter also critically evaluates and summarizes findings of existing literature studied in Chapter 2. The chapter briefly enlightens the research gaps of earlier work and need of present study.

Chapter 3: Objectives and scope

This chapter gives the specific objectives and scope of proposed research work.

Chapter 4: Materials and methods

The chapter includes detailed description of materials and methods used in the whole study. It also briefs about the various instruments along with their specifications required to conduct the present study. This chapter describes the experimental methods of adsorbent preparations, adsorbent characterization methods, conduct of batch and fixed bed column adsorption studies and optimization technique used in present research work.

Chapter 5: Theoretical considerations

The proposed work is based on the various theories related adsorption. This chapter briefly discusses those theoretical considerations based on which all experimental data were analyzed. It briefly elaborates the kinetic models, adsorption isotherms and mathematical modeling of batch and fixed bed column adsorption data. The chapter also briefly discusses the Response Surface Methodology and Box–Behnken design approach used for batch study experimental designs.

Chapter 6: Result and discussion

The chapter discusses the viability of the proposed waste based Fish scale biochar for the removal of fluoride. It discusses the observations made from characterization of adsorbent ie, FSB and AMFSB. The results and figures obtained for SEM, FTIR and XRD are explained in brief. It also elaborates the experimental data obtained for batch adsorption experiments and fixed bed column experiments. Further it describes the equilibrium, isotherm studies. It also discuses column studies, its breakthrough curve analysis and mathematical modeling of fixed bed column data. The Response surface Modeling was employed for statistical analysis of batch adsorption data. The chapter also includes the results obtained and its interpretation after employing BBD approach for statistical data analysis.

Chapter 7: Conclusion

This chapter summarizes the inference drawn from the complete research work done for removal of fluoride using fish scale biochar and its composites. The chapter briefly discusses the limitations of present study and suggestions towards future research.

Chapter - 2

Literatures Review

Chapter 2

Literatures Review

2.1. Defluoridation of water

Fluoride at excess level in drinking water is a posing a great threat to populations across the world. The severity of drinking water crisis is grave in developing country is an emerging problem There are mainly three possible options to overcome the risks caused due to consumption of excessive fluoride . these are : (i) Alternative water source, (ii) Better Nutrition (iii) Defluoridation of water (Harte et al. 1992). The option of using alternate water sources is not a viable solution due to some of its own limitations. Nutritious diet can help to minimize the ill effects of fluorosis to some extent. But for developing and economically backward countries it is a big challenge to provide better nutritional food due to the poverty and lack of resources. And so, defluoridation of water is the only viable option to overcome the problems associated with it (Meenakshi and Maheshwari 2006; Mohapatra et al. 2010; Tomar and Kumar 2013; Yadav et al. 2019). Extensive research has been done in this field of defluoridation of water and various are techniques are explored to bring the fluoride concentration of drinking water within the acceptable limits (Bhatnagar and Kumar 2012; Singh 2016). Defluoridation of water can be done by different methods. The technologies currently available to people are Precipitation/coagulation techniques, Ion-exchange techniques, Membrane techniques electrochemical treatments , Nano-filtration, and Adsorption techniques(CR Nagendra Rao 2003; Shen et al. 2003; Sujana et al. 2009; Khatibikamal et al. 2010; Bhatnagar, Kumar, and Sillanpää 2011 Diawara et al. 2011; Bhaumik and Mondal 2015;Jadhav et al. 2015; Waghmare et al. 2015; Mobeen and Kumar 2017; Yadav et al. 2018; Sabti, et al 2023).

Among them adsorption is preferred because of its easy availability of materials , low cost and ease of operation (Meenakshi and Maheshwari 2006; Tomar and Kumar 2013; Bhaumik and Mondal 2015; Mobeen and Kumar 2017; Yadav et al. 2018; Sabti, et al. 2023).

2.2 Fluoride removal technologies

Defluoridation of water can be done by different methods. The technologies currently available to people are Precipitation/coagulation techniques, Ion-exchange techniques, Membrane techniques electrochemical treatments , Nanofiltration, and Adsorption techniques(CR Nagendra Rao 2003; Shen et al. 2003; Sujana et al. 2009; Khatibikamal et al. 2010; Bhatnagar, Kumar, and Sillanpaa 2011; Diawara et al. 2011; Bhaumik and Mondal 2015;Jadhav et al. 2015; Waghmare et al. 2015; Mobeen and Kumar 2017; Yadav et al. 2018; Sabti, et al 2023). Among them adsorption is preferred because of its easy availability of materials , low cost and ease of operation (Meenakshi and Maheshwari 2006; Tomar and Kumar 2013; Bhaumik and Mondal 2015; Mobeen and Kumar 2017; Yadav et al. 2018; Sabti, et al. 2023) Extensive study has been reported for application of different technologies explored for defluoridation. This section discusses the existing fluoride removal technologies in brief.

2.2.1 Precipitation/coagulation techniques

Fluoride removal through Precipitaion / coagulation is widely achievd by using alum and lime as coagulants for defluoridation (Waghmare and Arfin, 2015; Kumar S., 2022). The Nalgonda technique developed by NEERI is an example of a coagulation/precipitation method. In this method, aluminium salts, lime, and bleaching powder are added to fluoride laden water. Then rapid mixing, flocculation, sedimentation is allowed to remove the fluoride flocs. During contact precipitation, addition of alluminium salts forms the insoluble aluminium hydroxide flocs. Lime added enhances the floc formation and helps to form bigger and denser flocs for fast settling. This floc then settles down by sedimentation. The insoluble aluminium hydroxide flocs when sediment they co-precipitate fluoride. The bleaching powder added ensures disinfection of water (Nawlakhe, 1975; Renuka and Pushpanjali, 2013; Gandhi and Shrishsa 2017; Shivarajsekharan, 2017). Nowadays, the precipitation technique is seldom used owing to e of its high chemical costs, formation of toxic sludge, toxic aluminium fluoride complex sludge causing secondary pollution , post treatment decrease in palatability of water and high residual aluminium concentration (Ayoob and Gupta 2009; Kumar et al. 2022; Meenakshi and Maheshwari 2006; Mondal, et al., 2015).

2.2.2 Ion-exchange techniques

Many researchers in past have explored the efficiency of fluoride removal by ion-exchange withother techniques (Onyango 2005, Bhatnagar 2011; Noori 2014; Raghav 2019). In ion exchange process, water flows through a bed of ion exchange media to separate the undesirable ions till the adsorbent bed gets exhausted. Ion exchange media i.e. ion exchangers are of two types: positively charged cation exchangers and negatively charged anion exchangers (Meenakshi 2007; Raghav 2019). A few materials behave as an ion exchanger known as natural and synthetic includes cellulose, living cells, proteins, and soil particles and synthetic materials can be membranes and beaded polymer resins (Noori 2014; Raghav 2019). The fluoride exchange capacity of these resins depends on the ratio of fluoride to total anions in water (Mobeen et al., 2017). Zeolites are positively charged ions and widely used for fluoride removal form water (Mohapatra et al. 2009; Bhatnagar and Kumar 2012; Raghav et al., 2019). In recent past, Chubar et al. (2005), Viswanathan and Meenakshi (2008), Solangi et al. (2010) have successfully used ion-exchanger for fluoride extraction. They reported that theese resins are efficient in fluoride removal and could be regenerated several times for its use. The resins used for defluoridation are costly and many times their regeneration creates large volume of fluoride containing waste causing secondary pollution(Tomar and Kumar 2013; Dhillon, Prasad, and Kumar 2017; Jadhav et al. 2015; Kumar et al. 2019).

2.2.3 Membrane techniques

Membrane technique is another advance method used in fluoride removal. In this method, membrane creates a selective barrier for the particles having smaller dimension than the pores of membrane to pass out. A potential difference between the two sides of the membrane is the driving force responsible for movement of ions across the membrane. Electro-dialysis, Reverse osmosis and nanofiltration are the membrane techniques used for deluoridation. The membrane motive force is applied on one side of the semi-permeable membrane to separate out the salts in the water behind the membrane (Assefa et al., 2006; Diawara et al., 2011). Many studies have been reported for utilizing RO technique for fluoride removal. Ndiaye et al., (2005) evaluated RO technique for fluoride removal from industrial wastewater. Assefa B., et al., (2006) experimented with RO membranes for fluoride removal in Ethiopian Rift Region. To remove fluoride and salinity from brackish water, Diawara et al.,(2011) used low pressure reverse at Senegal village. Gedam et al., (2012) have reported defluoridation of water at Moradgaon village of Chandrapur district by with the help of Polyamide RO membrane .

In electro-dialysis process, the ions are allowed to pass across the membrane but not the water. An electric current is the driving force in electro dialysis which carries the ions through the membranes (Tomar and Kumar 2013; Jadhav et al. 2015; Suneetha et al., 2015; Waghmare and Arfin 2015; Yadav et al. 2016; Dhillon et al. 2017).

Nano-filtration is recently developed advanced technology that uses the principal of reverse osmosis and ultra-filtration (Mobeen and Kumar 2017). Nano-filteration is considered as low energy consuming technology as it requires lower pressure than those for reverse osmosis. (Diawara et al. 2011) The nano-filtration membranes have reported higher permeability to those used in reverse osmosis. Nanoflteration is a promising method as membranes used have high and specific selectivity for fluoride ions (Tahaikt et al., 2007). Diawara et al. (2011) performed comparative study between nanofiltration and low pressure reverse osmosis (LPRO) membranes for its efficiency to remove fluoride and salinity from brackish drinking water. Hoinkiset al. (2011) examined fluoride removal potential of commercially available nano-filtration membranes, namely NF 90 and NF 270. Bejaoui et al.,(2014) used nano-filtter membrane (NF-90) and reverse osmosis (RO-SG) for fluoride decontamination a metal packaging industry effluent.

2.2.4 Adsorption techniques

Adsorption is the most widely used technology for removal of contaminants from water environment. It is a physiochemical method where physical/chemical forces make contaminant molecules to get attached with the surface of an adsorbent (Ayoob and Gupta 2009; Dhillon et al. 2017; Killedar 1993; Mohan et al. 2012; Mohapatra et al. 2009). This technique is quite popular among the researchers as due to its ease of application and availability of variety of adsorbents. Thus, making adsorption process as an effective solution to fluoride removal from water Extensive work has been done to explore the potential of various adsorbent materials for defluoridation. Adsorption has great gathered the attention of researchers around the world due to its cost effectiveness, simplicity of operation, efficient removal capacities, and possibility of reusing the adsorbent after its regeneration(Cai et al. 2015; Kumar et al. 2019; Meenakshi and Maheshwari 2006; Mobeen and Kumar 2017; Mondal 2012; Waghmare and Arfin 2016). Adsorption process involves external mass transfer, adsorption of fluoride ions onto particle surfaces and intra-particle diffusion (Mohapatra et al., 2009; Habuda-Stanic et al., 2014). Various adsorbents explored for defluoridation are discussed in details in the next section. Based on the literature available the comparison on different technologies used in removal of fluoride along with its advantages and disadvantage is presented in **Table 2.1.**

Table 2.1: Features merits and demerits of fluoride removal technologies.

Technology	Merits	Demerits	References
Coagulation /precipitation	High fluoride removal efficiency, commercially available chemicals	Cost is high , removal is affected by pH and presence of co-ions, pH corrections are required, sludge formation with high amount aluminium fluoride complex.	Mohapatra et al., 2009 Kumar et al. 2019
Membrane technology	High fluoride removal efficiency; efficient in removing other pollutants in water	High ooperating and maintenance costs, At end of treatment toxic liquid waste is produced.	Dhillon et al. 2017 Mobeen and Kumar 2017
Electrochemical treatments / Electro-coagulation	High efficiency; better fluoride ion selectivity	installation and maintenance cost is high	Tomar and Kumar 2013; Jadhav et al. 2015
Ion exchange	High efficiency Removes fluoride up to 90–95%. Retains the taste and colour of water intact	Expensive, vulnerable to interfering ions (Sulphate, phosphate, chloride etc.) Frequent regeneration is required Replacement of media is required Exhausted media contains toxic solid waste, regeneration creates toxic waste causing secondary pollution.	Singh et al., 1999; Tor, 2007
Adsorption	Great availability of materials , low cost simplicity of operation	High efficiency pH can affect the fluoride removal , co-ions can interfere fluoride removal	Bhantnagar et al 2011 Kumar et al. 2019

2.3 Adsorbents used for defluoridation

2.3.1 Alumina and aluminium-based adsorbents

Wu (1978) studied removal of fluoride ion using activated alumina without any pretreatment. The optimum conditions for fluoride removal were observed as, at pH 5. At this pH the rate of adsorption of fluoride was found to be dependent on initial fluoride concentration and activated alumina dose. The kinetic aspect of water defluoridation with activated alumina was by described Langmuir isotherm. the result showed adsorption capacity of to 637 μ mole of fluoride ion per gram of activated alumina.

Talnikar, et al. (2004) performed fluoride removal from synthetic waterusing indegeneous activated alumina. The comapirative study was done with the actual fluoride contaminated water and synthetic water samples. The performance of fixed bed column was evacuated. The fixed bed column could remove upto 94% fluoride at a pH value of 7. The real life samples had total dissolved solids (T.D.S.). upto 2114 mg/L which interfered with fluoride ions resulting the decreased in fluoride removal efficiency by 5%.

Maliyekkal and Sharma, (2006) explored magnesia-amended activated alumina (MAAA) for its potential to remove fluoride from water. The study reported > 95% removal of fluoride at adsorbent dose of 10 mg/L. The maximum removal was achieved at 3 hr of contact time at pH 7. The BET surface area of adsorbent was 193.5 m2/g. The adsorption followed pseudo-second-order kinetics.it was observed that adsorption was affected by presence of higher concentrations of bicarbonate and sulphate ions.

Ayoob et al. (2009) performed defluoridation synthetic and natural ground water using alumina cement granules (ALC).The fluoride adsorption capacity of 3.91 mg/g and 0.806 mg/g was found for synthetic and natural water respectively. It is reported that pH in range 3.0-11.5, have very little effect on fluoride removal. The adsorption had negligible effect of co-anions like chloride, biocarbonate, sulfate and nitrate ALC.

Jagtap et al.(2011) experimented with chitosan-based mesoporous alumina (MA450) for defluoridation of water. They reported that at initial fluoride concentration of 5 mg/L chitosan-based mesoporous alumina exhibited maximum adsorption capacity of 8.26 mg/g.

Lanas et al. (2016) studied the potential of mesoporous hierarchical alumina microspheres (HAM) for defluoridation of water. Potentiometry and isothermal titration calorimetry (ITC) were used to check fluoride adsorption. HAM was efficient enough to have fluoride uptake up to 26 mmol/g. The removal of fluoride by HAM followed the monolayer adsorption Langmuir isotherm model.

2.3.2 Biochar and Carbon-based adsorbents

Killedar and Bhargava (1993) utilized fishbone charcoal for the defluoridation of water. The moving media adsorption system was used for this study. They reported that fluoride removal occurred mainly due to presence of calcium phosphate in fishbone. Flow rate through media and initial was influencing parameter for fluoride adsorption. It was observed that Langmuir and Freudlich isotherms did not showed good correlation in the study.

Abe et al. (2004) have investigated six different carbonaceous materials for fluoride removal. The materials investigated are carbon block (CB), four kinds of coal charcoals (CC) and bone char (BC). They found that the fluoride removal efficiency of thse materials was in the order of BC > CC > CB > AC . the bone char reported highest fluoride removal of 82% at pH 4.6. The adsorption through BC flowed Freundlich isotherm with coefficient (r) 0.998. The adsorption was reported to be an ion exchange between fluoride and phosphate ions present in BC.

Kaseva (2006) has investigated bone char for the defluoridation of drinking water in Tanzania. He optimized the regeneration of bone char. It is reported that fine grain sze particle (0.5 -1.0 mm) of bone char carbon could remove upto 70.64%. Adsorption capacity of bone char regenerated at 500°C was found to be 0.75mg/g. Batch adsorption and column adsorption studies were also performed by him also.

Tembhurkar and Dongre (2006) studied commercial activated charcoal for defluoridation of water. Fluoride removal of 94 % at adsorbent dose of 20gm/L was observed at equilibrium time 120 minutes. It was observed that maximum removal occur at very low pH of 2.0. the experimental data fitted well Langmuir isotherm (R^2=0.984) as compared to Fruendlich isotherm (R^2=09634).

Karthikeyan G , et al., (2007) explored the fluoride removal potential of activated carbon prepared from Morringa indica bark. At the initial fluoride concentration of 2 mg/l and pH fluoride removal was found to be 71%. The experimental data followed Freundlich and Langmuir isotherms and pseudo-second-order kinetic model.

Alagumuthu and Rajan (2013) investigated cashew nut shell carbon and zirconium impregnated cashew nut shell for fluoride decontamination of water. It is observed that at equilibrium time of 180 minutes 80.33% and 72.67% removal of fluoride took place by using zirconium impregnated carbon and cashew nut shell carbon respectively.

Sivasankar et al. (2013) studied cerium-impregnated adsorbent for fluoride removal. The adsorbent was prepared with potato starch as carbon source. The adsorbent was used for defluoridation of synthetic water. The effects of process parameters i.e. adsorbent dose (25–150 mg/L), fluoride initial concentration (2.8–8.3 mg/L), pH (5.5–9.0) , temperature (25–45 °C) and coexisting anions such as Cl^-, HCO_3^-, NO_3^-, SO_4^{2-} and PO_4^{4-} were aslo investigated. At pH -7.75 , maximum adsorbent capacity of 29.1 mg/g was achieved. The removal efficiency was found to be decreased with increase in initial concentration of Fluoride in water.

Yadav et al. (2013) also examined s the feasibility of fluoride removal by three low-cost agricultural biomass based adsorbents. Three novel materials examined were activated bagasse carbon (ABC), sawdust raw (SDR), and wheat straw raw (WSR). The study was conducted at neutral pH range. Comparative evaluation with commercially available activated carbon (CAC) was done for their removal efficiency. The newly prepared adsorbents successfully removed fluoride in order CAC> ABC> SDR>WSR. . The highest removal of 57.6 % was observed for CAC. These result were observed at slightly acidic pH of 6 with exposure time of 60 min and adsorbent dose of 4 gm/L. The experimental data was tested for rate kinetic order and isotherm modeling and they found that both surface adsorption and intra-particle diffusion were responsible for the rate determining step.

Gourouza et al. (2014) prepared a char using beef shoulder blade bones. This char was used as an adsorbent for defluoridation of water. The batch experiments revealed that at optimum dose of 8 g/l and 10 mg/l of initial fluoride concentration the fluoride removal was 60.27% within 180 minutes. The experiment data was explained well with Freundlich isotherm and obeyed pseudo-second-order kinetic model confirming chemisorption of fluoride ions.

Rugayah et al. (2014), explored application of chicken bone waste charcoal. He investigated the potential of the adsorbent fluoride removal of groundwater in Indonesia. The chicken bone charcoal could remove 67% of fluoride removal. the higher adsorption capacity was achieved with dose of chicken bone char higher dose with 12 hours contact time.

Bandewar et al.(2015) synthesized activated carbon from coconut shell with particle size less than 150 mm. Fixed bed column were used to study the removal of fluoride from water.ed out. The maximum fluoride uptake was observed bed height of 6 cm and at flow rate was of 4 mL/min. The adsorbent could remove upto 72% of fluoride from drinking water. The effects of process parameter on fluoride removal in a fixed bed were evaluated in this study.

Brunson and Sabatini (2015) prepared eucalyptus wood char for fluoride removal. It was observed that adsorbent had the more removal capacity at burning temperature of 500 and 600 ^{o}C as compared to bone char. The eucalyptus wood char was improved the adsorption capacity from 0.11 to 0.72 mg/g when modified with aluminum oxides.

Guan et al. (2015) investigated Mongalian scotch pine tree saw dust char (MMSC) for fluoride removal. The adsorbent was prepared by using phosphoric acid and microwave heating treatment on Mongalian scotch pine tree saw dust. With optimum dose of 36 gm /L 82, 71 and 63% removal of fluoride were observed at initial

Fluoride concentration of 5, 10 and 20 mg/l respectively. The adsorption reaction followed Langmuir isotherm and exerted an endothermic reaction.

Zhou et al. (2019) utilized pristine and magnetic biochars prepared form peanut hull and bovine bone for defluoridation of water. The biochars developed were characterized by BET, FT-IR, SEM-EDS, VSM, XRD and XPS techniques. The experimental data demonstrated that the magnetic biochar modified with FeCl laden solution accelerated fluoride uptake in comparison of biochar modified with Fe^{2+}/Fe^{3+} solution with NaOH. They suggested both the materials excellent fluoride removal efficiency due to the presence of hydroxyapatite (HAP) and γ-Fe_2O_3 / g). It is also reported that bone-derived biochars could also remove the co-existing Cr(VI) was also removed simultaneously along with fluoride.

Sadhu et al. (2021) investigated Watermelon Rind (*Citrullus lanatus*) Biochar (WMRBC) for its defluoridation potential. Batch adsorption studies were conducted to see the effect of pH, adsorbent dosage, contact time, initial concentration. The experimental data was well described by Freundlich isotherm and pseudo-second-order model. It was observed that the maximum fluoride adsorption capacity of adsorbent was 9.5 mg/g. The fluoride adsorption process was a found to be spontaneous and exothermic in nature. Commonly existing co-ions such as CO_3^{2-}, Cl^-, HCO_3^-,SO_4^{2-}, and NO_3^- had negligible effect on fluoride removal efficiency at 50 mg/L. Characterization studies were conducted before and after fluoride adsorption. The results obtained from ATR, EDX , SEM, and XRD analysis revealed the adsorption of fluoride on WMRBC surface was due to electrostatic attraction and subsequent precipitation at the mineral sites. The authors concluded that use of developed adsorbent can be effectively used for fluoride decontamination of drinking water and industrial wastewater.

2.3.3 Calcium-based adsorbent

Larsen and Pearce (2002) explored calcite and brushite for their potential to remove fluoride . Equal amounts of brushite and calcite around 300–500 mg were mixed with 1 L of the fluoride-contaminated water. The mixed water was heated in an electric kettle for some time. After cooling, the sedimented calcium salts were. It is reported that, this process could remove sufficient amount of fluoride from water.

The water sample having initial fluoride concentration 5, 10 and 20 mg/L were reduced to 0.06, 0.4 and 5.9 mg/L, respectively.

Gao et al. (2009) have reported fluoride removal from water using synthetic hydroxyapatite. He reported that defluoridation was through synthetic hydroxyapatite has size-dependent properties. He observed that smaller the size of HAP particles had better the fluoride uptake capacity than bigger size particles. The experimental data obeyed pseudo-second-order kinetics and Freundlich isotherm models. The adsorption was found to be physisorption and endothermic in nature. The fluoride removal efficiency was also affected by adsorbent dose and contact time.

Sivasankar et al. (2012) *used Tamarindus indica* fruit shells (TIFSs) as calcium rich compounds to prepare the adsorbent. The tamrind seed were initially modified with ammonium carbonate impregnation and carbonization. The modification resulted to form ammonium carbonate activated carbon (ACA-TIFS). The XRD analysis revealed that presence of calcium oxalate and calcium carbonate mixture was responsible for uptake of fluoride. Batch studies were conducted to effect of pH, initial fluoride concentration, contact time and co-ion interference. Various kinetic models and adsorption isotherms models were evaluated. The ACA-TIFS carbon 83% removal efficiency at a pH of 7.05.

Prabhu et al. (2014) also performed investigation on surfactant modified hydroxyapatite (HAp) aiming fluoride decontamination of water. He performed batch studies to evaluate effect of various process parameters. The modified HAp powder showed good defluoridation capacity of 9.369 mg/g at 50 mg/l dose of adsorbent. It is reported that, electrostatic attraction and ion-exchange mechanism was responsible for fluoride removal. The experimental data was examined for different isotherm was found best fitted the pseudo-second-order kinetic and intra-particle diffusion kinetic models.

Jayarathne et al. (2015) synthesized new calcium aluminate (CA) adsorbent using natural crystalline apatite for fluoride removal. They reported that pH was governing process parameter for fluoride removal efficiency of adsorbent. The optimal pH for maximum removal was recorded at slightly acidic pH 6 and initial fluoride concentration of 15 mg/L and 10 min of contact time. The adsorption data followed Langmuir isotherm with adsorption capacity of 0.212 mg/g.

Gogoi and Dutta (2016) used modified limestone powder to prepared hydrothermally modified adsorbent. Hydroxyapatite was formed during the hydrothermal modification in presence of phosphoric acid. Various characterization techniques were used to understand the adsorption mechanism. The adsorption capacity of the hydrothermally modified adsorbent was 6.45 mg/g. The adsorption data was tested for rate order kinetics. An adsorption of fluoride on limestone powder was a endothermic, spontaneous, and irreversible process.

Shen et al. (2016) investigated calcium-based chitosan beads (MONs@CS) for fluoride removal. The adsorption of fluoride on MONs@CS adsorbent followed obeyed Langmuir adsorption isotherm and highest adsorption capacity was found to be of 50.01 mg/g, which was higher than many calcium-based adsorbents. The adsorbent performed well in wide pH range from 3 to 12. The removal has no effect on the F^- adsorption due to presence of coexisting.

Singh et al., (2020) performed comparative study between un-calcined hydroxyapatite and calcined hydroxyapatite for its potential of defluoridation. The physiochemical proposties of hydroxyapatite (HAP) were characterized by XRD, FEG-SEM, and XPS analysis. The experimental investigation has reported that fluoride uptake decreases with increasing calcinations temperature. The un-calcined HAP showed adsorbent capacity of 4.38 mg F^-/g HAP, it reduced to 3.53 mg/g and o 0.7 mg/g with increase in temperature. Equilibrium studies revealed that Langmuir isotherm and fluoride removal follows pseudo-second-order reaction kinetics was best suited for the adsorption mechanism. The defluoridation capacity decreased with an increase in pH (pH 5–9). Fixed bed column studies were also performed and obtained results follow a conventional bed depth service time (BDST) model.

2.3.4 Oxides/hydroxides and layered double hydroxides

Biswas *et.al.* (2010) also performed defluoridation studies on hydrous iron (III) – chromium (III) bimetal mixed oxide (HICMO). The maximum fluoride removal took place at pH 3 and with increase in pH removal decreased .The adsorption isotherm model and rate order kinetic study was done .They reported that removal of fluoride using HICMO was a spontaneous and endothermic process.

Wu ***et al.*** (2011) used co-precipitation method for fluoride removal. They experimented with tri-metal oxide as an adsorbent and co precipitation was done with Fe(II), Al(III.) and Ce(IV). The experiments were performed in alkaline conditions with molar ratio of 1:4:1. The adsorbent sowed high fluoride uptake capacity of 178 mg/g at neutral pH. The results showed that the adsorption of fluoride was affected by presence of high concentrations of phosphate or arsenate. Chloride, sulfate and nitrate has little or no effect on adsorption.

Zhang et al. (2012) studied a novel adsorbent layered double hydroxides (LDHs) for fluoride decontamination of water. The maximum efficiency of LDH was reported as 97.36%. The physical and chemical properties of synthesized materials were examined by TEM, XRD analysis, N2 adsorption/desorption analysis, and TGA. The result showed that synthesized adsorbent has highly crystalline structure with well-ordered layer structure. It has high specific surface areas of 37.24–51.27 m2/g. The adsorption equilibrium was achieved within 1 h. The experimental data was tested for rate order kinetics and found that it obeyed pseudo-second-order model and followed Freundlich adsorption isotherm model.

Sujana, et al. (2013) developed hydrous ferric oxide (HFO) and alginate based biopolymer beads defluoridation of water. Batch studies were conducted to determine optimum conditions for fluoride removal. Influence of operational operational parameters i.e. pH, contact time, initial fluoride concentration, adsorbent dose , co-ions and temperature. Authers have reported that pH is a operational parameter governing fluoride removal efficiency. The adsorbent performed efficiently in pH range from 3.5 to 5, at higher it efficiency was decreased.

Ganvir and Das (2011) explored possibility of fluoride removal using aluminum hydroxide coated rice husk ash. The batch adsorption experiments were conducted for initial fluoride concentrations range of 10–60 mg/L. The modified rice husk ash had exhibited fluoride uptake of 15.08 mg/g and fixed bed column reported to have adsorption capacity of 9.5 mg/g. The results confirmed that adsorption was pH-dependent and maximum fluoride removal was obtained at pH 5.0.

2.3.5 Nanomaterials

Pathak *et al.* (2003) used the nano-sized powder of inorganic oxides such as Fe_3O_4, Al_2O_3 and ZrO_2 for fluoride removal. An activated charcoal was prepared by chemical modification of oxides. The material was used in packed bed reactor for removal of trace of contaminants like fluoride, arsenite and arsenate from industrial wastewater.

Chen *et. al.* (2013) also used granulated Fe-Al-Ce nano-adsorbent for fluoride removal. The granulated Fe-Al-Ce nano-adsorbent was prepared with aluminium, silica sol, titanium and zirconium. They found that zirconium and titanium reduced fluoride removal efficiency of Fe-Al-Ce adsorbent whereas aluminium and silica sol accelerated fluoride removal. The granulated Fe-Al-Ce obtained by extrusion with aluminium sol showed higher fluoride removal over 90% .

Christina and Viswanathan (2015) prepared two different nanoadsorbents. He investigated Fe_3O_4 nanoparticle immobilized in sodium alginate matrix (FNPSA). He also used Fe_2O_3 nanoparticle and orange peel residue modified with odium alginate matrix (FNPSOPR) for defluoridation of water. The adsorption data was tested for adsorption isotherm modeling and rate order kineicts. It was found that both the adsorbents obeyed Langmuir isotherm and pseudo-first-order kinetic model. They reported FNPSA and FNPSOPR to have fluoride removal capacity of 58.24 and 80.33 mg/g respectively.

Dayananda *et. al*. (2015) used MgO nano-particle loaded with mesoporous alumina ($MgO@Al_2O_3$) for reducing fluoride level of water. 40 wt. %MgO nanoparticle loaded on mesoporous Al_2O_3 exhibited maximum fluoride removal of nearly 90%. The adsorption kinetics was studied with Langmuir and Freundlich isotherm models. The rate order kinetics was found to be pseudo second- order confirming chemisorptions of fluoride. The loaded mesoporous Al_2O_3 ($40Mg@Al_2O_3$) nanoparticles efficiently could reduced 5 and 10 mg/L of fluoride to approximately 1 mg/L

Kashyap et al. (2023) synthesized the cerium oxide nanoparticles from seed extract of *Litchi chinensis*. The characterization techniques like FT-IR, PXRD, HR-TEM. SEM, EDS and Raman spectrum were used for this study. The batch adsorption studies were conducted to evaluate the removal efficacy of fluoride ion different pH, contact duration, initial fluoride concentration and temperature. The experimental data was tested for isotherm modeling and rate order kinetics and reported to hae monolayer chemisorptions of fluoride. The results indicated that cerium oxide nanoparticles prepared from *Litchi chinensis*, had potential to remove fluoride from wastewater.

2.3.6 Natural materials

Pandey et al., (2012) prepared a biosorbent from Tinospora cordifoli plant for fluoride removal from water environment. It was observed that pH had a strong effect on of removal efficieny of adsorbent. The equilibrium was achieved within 120 min. The novel adsorbent had fluoride uptake capacity of 25 mg/g.

Togarepi et al. (2012) investigated sand for its ability to remove fluoride removal. The sand was treated thermally and chemically. Batch mode investigation was performed to understand effect of various parameters. viz., adsorbent dose, pH and initial fluoride concentration. The equilibrium data concluded that fluoride removal by sand was done by multilayer adsorption mechanism.

Dwivedi et al. (2014) utilized peepal leaf powder (Ficus religiosa) as an adsorbent for defluoridation of water. The peepal leaf powder at pH- 7 and contact time of 45 min exhibited maximum adsorption capacity of 2.24 mg/g. The removal was reported to follow multilayer adsorption mechanism.

Msagati et al., 2014 focused on a plant based restructured lignite (RSL) prepared from Cuminum cyminum. The adsorbent was characterized by BET, SEM, and XRD techniques. It was found that the RSL had 3.12 times greater BET surface area than that of lignite. The fluoride removal was reported as 15.8 mg/g and 13.8 mg/g for RSL and lignite respectively. Even after the fifth cycle of regeneration, RSL was found to be to remove up to 60% fluoride,. Desorption experiments were conducted using 0.01 M NaOH.

Getachew *et al.* (2015) investigated thermally activated banana peel and coffee husk for defluoridation of water. The maximum fluoride removal was reported as 85 and 86% by banana peel and coffee husk were respectively. The optimum removal took place at pH 2.0 for both the adsorbents. The fluoride removal capacity of coffee husk was higher than the banana peel. The adsorption process followed the Langmuir isotherm and pseudo-second-order kinetic model

Kumari et al. (2015) examined the sal (Shorea robusta) leaf powder as an adsorbent to reduce elevated fluoride level in water. The adsorbent was a characterized by SEM, FTIR, and EDX. The sal leaf powder showed excellent fluoride removal of 98.6%. The optimum pH and adsorbent dose was observed to pH 7.5 and 60 g/L respectively. The Freundlich isotherm fitted best with the experimental data.

Ranjeeta (2015) used fly ash generated at Chula and investigated its potential for fluoride decontamination of water. Maximum removal of fluoride occurred at higher dose of 100 g/L and 120 min exposure time. The fly ash showed good fluoride removal possibly due to the presence of unburnt carbon particles.

2.3.7 Building material and waste based adsorbents

Gupta et al., (2007) investigated waste carbon slurry for its potential of defluoridation. The carbon slurry was obtained from fertilizer companies. The adsorbent worked well at pH 7-8. The equilibrium was obtained at 1h with maximum adsorption capacity of 4.861 mg/g.

Kagne et al. (2008) also performed defluoridation studies with hydrated cement (HC). It is reprted that, post defluoridation the HC did not produce secondary chemical sludge. The adsorbent worked well within wide range of pH 3 to 10. The optimum condition of pH and dose are reported as 6.9 and 10g/L respectively. They have reported Langmuir adsorption capacity of HC as 2.68 mg/g. The defluoridation was effective at acidic pH range and chemisorption and precipitation were responsible for adsorption of fluoride.

Mohan et al., (2008) conducted experimental investigation on adsorbents derived from agricultural waste viz. coconut shell, coconut shell fibers and rice husk. These adsorbents were used to reduce spiked fluoride levels industrial wastewater. The fluoride removal capacity of adsorbents is found to be in order of coconut shell fiber carbon (ATFAC) > coconut shell carbon (ATSAC) > rice husk carbon (ATRHC).

Deshmukh et al., (2009) investigated adsorbent prepared from agricultural waste rice husk. Chemical impregnation by physical activation was used for adsorbent preparation. Batch studies were conducted to evaluate effect of pH, contact time, dose of adsorbent and initial adsorbate concentration. The optimum adsorbent dose was found to be 10g/L. Maximum fluoride removal was observed to be 75%.

Bhaumik *et al,.* (2015) investigated Eggshells waste based adsorbent for defluoridation of water. The dried eggshells were ground to different size particles and used to conduct batch study. The effect of process parameter was studied for achieving optimum condition. The experimental data fitted with the Langmuir isotherm model. These results indicate that eggshell powder can be used as an effect.
Bhaumik et al., (2017) investigated feasibility of fish scale dust for fluoride removal from aqueous solution. The fish scale dust prepared was characterized by SEM, FTIR and pH_{ZPC}. Various operating variables and their combined effect on removal of fluoride was assessed by using Response Surface Methodology (RSM) based on Box-Behnken design (BBD). It was found that adsorbent dose, contact time, initial concentration pH for fluoride adsorption were found as 2.26 g/100 mL, 179.72 min 8.49 mg/L and 9.93 respectively. The isotherm modeling of batch experimental data was performed and monolayer adsorption of fluoride was observed Kinetic studies confirmed pseudo-second-order rate kinetics. The results also suggest the thermodynamic feasibility of fluoride adsorption. They suggested that fish powder could succesfuuly used for reducing elevated fluoride concentrations in drinking water.

Meilani et al. (2021) derived aluminum-impregnated biochar from food waste and named as (Al-FWB). The adsorbent was studied for its ability to remove fluoride removal. The individual and interactive effects pyrolysis temperature, time and aluminum content were investigated. Box–Behnken-based response surface methodology model, was used to predict optimum conditions. The optimum conditions were found as 315 °C, 0.65 h , 5.89%. for temperature , time and aluminum content respectively. The Langmuir isotherm model and pseudo-second-order kinetics fitted well for the experiential data.

2.4 Fish Scale for Water /Wastewater treatment

Fish is a source of rich protein and consumed in large quantities across the world. It is cheaper sources of protein than many other animal and have high nutrition value (Kafle and Sung 2013; Othman and Zayadi 2016). Some varieties of fishes are scales over their skin while others are without scales. Large quantities of fish scale waste is produced and discarded as waste globally. Many studies in past have been performed to use fish scales for variety engineering ,industrial and medical applications thereby nuisance when it is just discarded as waste into the environment (Pathan et al., 2019; Shalaby et al., 2020; Lv et al., 2021; Fu et al., 2021; Qin et al., 2022).

Biosorption is a recent trend in wastewater treatment utilizing living and non-living biomaas (Demirbas, 2008) for adsorption of contaminants. Many researchers have fish scales to treat wastewaters having dyes, heavy metals and pharmaceuticals concentrations causing water pollution. Biosorbent derived from fish scales are reported to be easy to source and synthesize. The major source of fish scale are local fish markets, fish industries and large culinary establishments. Some researchers have used fish scales directly; some have modified them chemically, thermally while others have used as source for deriving hydroxyapatite.

The available scientific literatures reveals that fish scale waste based adsorbents have been successfully explored for removal of heavy metals (Cr, Cu, Mn, Pb, Se, U, Zn, etc), textile dyes, pharmaceutical compounds and inorganic pollutants like Arsenic and Fluoride. Applications of fish scale waste adsorbent have been divided into subsections on (2.4.1) for removal of heavy metals; (2.4.2) for removal of industrial dyes , (2.4.3) for miscellaneous pollutant. Recent findings on removal of these pollutants using fish scale based adsorbent are briefly discussed below.

2.4.1 Removal of Heavy metals

“Heavy metals” are metallic element having high density, high atomic weight and are toxic even at low concentration. Heavy metal toxicity is cause of concern for human health as it not only damages liver, lungs, kidneys, central nervous system and some vital organs but also Alzheimer's disease, Parkinson's disease and muscular dystrophy may occur due to its long term exposure (Verma & Dwivedi, 2013). Heavy metals may enter in the environment through natural sources like seepage from metal containing rocks, forest fires and volcanic eruptions. Whereas, anthropogenic source mainly includes effluent discharge from various industries (Kwaansa et al., 2019). **Table 2.2** given below summarizes the adsorption capacities of different fish scale based adsorbents in removing metal ions from water environment.

Table 2.2: Fish scale based adsorbents for removing metal ions from water environment.

Species of fish used for scales	Metal Ions removed	Uptake capacity (mg/gm)	% Removal	References
Oreochromis Niloticus (Mojarra Tilapia)	Cu	58	--	Espinosa et.al., (2001)
Atlantic cod	Pb	--	95%	Mustafiz et. al. (2002)
Atlantic cod Shouairi scale	Pb	---	--	Basu et. al.(2006)
Tilapia	Copper	0.25	--	Huang (2007)
Rohu (Labeo rohita)	Pb(II)	472	--	Nadeem et. al., (2007)
Emperor fish (Lethrinus nebulosus)	Pb Cd Mn Cd		97 to 93 for Pb and Cd 26 80	Amjad & Jamal (2008)
Catla catla(Labeo catla)	Cu	79.35	--	Das , et al (2008)
Catla catla(Labeo catla)	Cr	27.1	61	Srividyand Mohanty (2009)
Corvina fish	U		80	Costa et al., (2011)
Grass carp fish	Ni	120.9		Liu (2012)
Corvina fish (M. furnieri)	Cr	--	--	Moura (2012)
Croaker fish	Pb	14.58	--	Nkiko (2013)
Tilapia nilotica	Se	--	--	Kongsri, (2013)
Farming carp (cyprinus carpio)	Pb Cd As	62.5 69.0 32.1	94 98 71	Bajić (2013)
Mixed fish scales	Fe Zn	-- --	74 81	Darge and. Mane J. (2013)

Species of fish used for scales	**Metal Ions removed**	**Uptake capacity (mg/gm)**	**% Removal**	**References**
Tilapia and Merah	Pb			Bawadi (2014)
Labeo rohita Fish scale derived hydroxyapatite	Cu	209.732	91.77	Mandal et al. (2015)
Tilapia	Zn, Pb Fe	-- -- --	92.30 89.33 64.20	Zayadi et. al. (2015)
Dicentrarchus labrax	Cu	127.16	--	Uzunoglu and Ozer (2016)
Mozambique Tilapia	Zn Pb	--	82 78	Othman et.al., (2015)
Mozambique tilapia	Zn Fe	--	85 59	Othman et al. (2016)
Catla catla(Labeo catla)	Cu	79.35	--	Das *et. al.* (2016)
Mixed fish scale	Cr	27.27	50	Bamukyaye and Wanasolo (2017)
Mixed fish scale	Pb Zn	-- --	81.97 80.37	Stevens and Batlokwa (2017)
Hydroxyapatite scaffolds from Tilapia fish scale	Pb	344.8	99.9	Wen-Kuang et al. (2017)
Impregnated nano-magnetic Fe3O4 on Rutilus kutum fish scale.	Cu	--	76.5	Ahmadifar and Koohi (2018)
Oreochromis niloticus	Cu, Mn Fe	16.51, 50.46 96.29	--	Kwaansa et *al.*, (2018)

2.4.2 Removal of Industrial Dye

Presence of colour is a primary indication of water pollution. Industries processing leather, paper, paint, pulp, textile, and tannery are the main sources discharging huge amount of colored wastewater into the environment (Ahmadgurabi et. al.,2018). The colored wastewater not only reduces the action of photosynthesis by hindering the passage of sunlight but also toxic to aquatic life as well as humans (Javed, 2010). These days textile, paper and paint industries use low cost synthetic, non-biodegradable dyes. Most of these dyes contain heavy metals and chlorine. Chlorine containing dyes are carcinogenic and are responsible for respiratory diseases and skin allergies (Kabir , 2018). Therefore, removal of dyes is of primary concerns for environmental researchers worldwide. Though many removal technologies are present, industries demands more economical dye removal methods.

In last decade, verity of fish scale based adsorbent has been explored for removal of dyes from aqueous medium. The adsorption capacities and efficiency of these adsorbent are shown in **Table 2.3**

2.4.3 Removal of miscellaneous water pollutants

Large number of organic and inorganic pollutants along with microbial populations have been reported are contaminating water every day. In addition to heavy metals and industrial dyes contamination of water bodies through pollutants like Arsenic, Fluoride , pesticides, polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phenols, drug residues are also posing threat to humans and environment (Ali I. and Gupta V K., 2006). Few of these pollutants have been successfully removed from water using fish scale derived adsorbent. **Table 2.4** summarizes utilization of fish scale waste as adsorbent for removal of contaminants other than heavy metals and industrial dyes.

Table 2.3 : Fish scale based adsorbents for removing dyes from water environment

Species of fish used for scales	Dye removed	Uptake capacity (mg/gm)	Removal (%)	References
Redfish	Asthaxanthin	0.360	--	Stepnowski (2003)
Rohu (Labeo rohita)	Acid yellow	0.180	--	Iqbal (2010)
Rohu (Labeo rohita)	Crystal violet Methylene blue	74.39 58.67	--	Chakraborty et.al., (2012)
Leporinus elongates	Remazol dyes	--	--	Vieira et.al., (2012)
Labeo rohita	Malachite Green	38.46		Chowdhury et.al., (2012)
Leporinus elongates	Anionic dyes	--	--	Vieira et al. 2012)
Labeo rohita	Brilliant red	--	--	Begum and Kabir (2013)
Tilapia nilotica	Ponceau 4R	134.4	78	Zhu et al. (2013)
Tilapia nilotica fish scale-based porous carbon	Methylene blue	1050.72	--	Neves et al. 2018 Sheng et al. 2009
Oreochromis niloticus	Reactive blue 5G	241.20	--	Ribeiro et. al. (2015)
Mixed fish scales	COD and Color	--	90 %.	Musa (2015)
Carbonized Labeo rohita fish scale	Reactive orange 16	114.2	--	Marrakchi et al. 2016)
Carbonized Labeo rohita fish scales	Methylene blue	184.4	--	(Marrakchi et al. 2017)
Orechromis niloticus fish scale	Reactive dye	--	--	Ribeiro et al. (2015)
Mixed fish scale	Azo dye (AB113)	157.3	90	(Ooi et al. 2017)
Nanomagnetic Fe3O4@ Mixed Fish Scale	Methylene blue	60.87	--	Ahmadgurabi, et al. (2018)
Pogonias cromis	Acid dyes	2.7	89	(Fijul Kabir and M Fijul Kabir BS 2018)

Table 2.4: Fish scale based adsorbents for removing miscellaneous pollutant from water environment

Species of fish used for scales	Dye removed	Uptake capacity (mg/gm)	% Removal	References
Micropogonias furnieri (Corvina) fish	Dichlorophenol	--	--	Mota et al. (2012
Aatlantic cod	Arsenic (As)	--	--	Rahaman et al. (2015)
Fish waste derived adsorbent	Sulfamethoxazole and trimethoprim	--	--	Nielsen and Bandosz (2016)
Indian major carp Catla (Catla catla)	Fluoride (F)	4.69 mg/g	93.85%	Bhaumik et al (2017)
Labeo rohita scales	Fluoride (F)	2.82		Khandare and Mukherje. (2019)

2.5 Limitations of earlier work

- Though Fluoride removal by adsorption is hugely explored and exploited with various adsorbent, there exist a great gap between developed technology and its application where required
- Methods developed for defluoridation so far are either not sustainable or economical for various unfavorable factors.
- With a view to explore to achieve sustainable and low cost solution scientist and engineers still carrying out extensive research work in this area in pursuit of these objectives
- The existing literature reveals that, Fish scales and their derivatives have been explored for removal of Heavy Metals and dyes from water environment but no such previous study has been performed to explore the potential of Fish Scale Biochar (FSB) for Fluoride removal from water environment

2.6 Critical Review of Literature

Fluoride is recognized as emerging pollutant in water environment particularly for sub-surface water resources. Removal of Fluoride from water environment is utmost important for potable water supply. Developing an effective and robust technology for removal of excess fluoride from water environment becomes a challenging task especially for developing countries.

Most of the publications dealt with Fluoride removal with physicochemical methods predominantly with adsorption process. The serious drawback of all these methods leads into generation of secondary pollution mostly as sludge. Adsorption with activated alumina have reported higher fluoride adsorption capacity. Activated alumina is an expensive adsorbent fluoride removal is affected by presence of co-existing ions in water. Materials based on rare earth oxide reported to have high fluoride uptake in batch adsorption, but they too are very expensive. Carbon based adsorbents have hugely explored but limited application due to small adsorption capacities. Various natural materials are used to prepare adsorbents which have potential to remove fluoride from water but they are difficult to regenerate and have low efficiency. Application of biosorption is an environmentally friendly approach for fluoride removal. However, there are some limitations over its use in real life scenario and treatment of industrial waste containing fluoride. Recently nano-adsorbents have been attracted considerable attention for defluoridation of water. These adsorbents have reported to have higher fluoride uptake capacity. Many researchers have investigated influence process parameters like pH, adsorbent dose, agitation time, initial fluoride concentration, temperature, particle size, presence of co-ions for defluoridation with various adsorbents. Existing literature indicates that many adsorbents obeyed pseudo-second order or pseudo-first order of rate kinetics. The equilibrium data was also tested by many researchers for adsorption isotherm modeling.

A few literatures have addressed to treat Fluoride contaminated water by Biochars. Some literatures describes fluoride removal by Fish bone charcoal, however all the literatures already described in earlier section showed some limitations for engineering application. From the literature, it is also evident that biochar would be a preferred adsorbent in recent years in water pollution control and environmental remediation. Numerous biochars developed from natural resources played unique roles in field of defluoridation and water pollution control as they manifest the advantages of low cost and ease of operation. Many such literatures the column analysis, breakthrough studies and kinetic evaluation are not addressed to validate appropriate method of treatment. Literature back up also did not present / exhibit any relevant research work with fish scale charcoal or coupled with any kind of composite material. In spite the fact that previously studied adsorbents showed good performance, more studies are needed develop waste based adsorbent which can address two environmental issues simultaneously. So, the future must be focused on evaluating effectiveness of adsorbents in terms of its ease of operation, efficiency of removal, sustainability and cost of treatment. Hence it is felt by the researcher to carry out further study in details in the level of doctoral work for removal of fluoride from water environment by Fish Scale Biochar.

Chapter - 3

Objective of Present Research Work

Chapter 3

Objective of Present Research Work

3.1 Objective of research work

The objective of this research investigation is to explore and examine a novel, feasible and cost effective Fish Scale based Biochar and its composite forms for defluoridation. The major focus of the research is to develop an engineering reactor considering economics, efficiency, and environment friendly approach by using the above as an alternative and substitute of traditional adsorbent material for fluoride removal. In terms of the magnitude of fluoride contamination problem, exploring the novel, economic and environment friendly fish scale biochar and its composite forms will a veil some of the existing problem in drinking water treatment as well a the burden of environmental pollution.

3.2 Scope of the proposed work

The scopes of the present investigation work considered are as follows:

1. Selection and collection of appropriate Fish Scale for biochar synthesis and alternative chemicals for its surface modification for enhancing adsorptive capacities.
2. Synthesis of selected Fish scale biocahar and its composites.
3. Characterization of material with various standard techniques (BET, FITR, SEM, XRD, EDX etc).
4. Batch sorption studies with synthetic samples.
5. Study of different influencing process parameters.
6. Removal kinetics and adsorption isotherm studies.
7. Optimization of different process parameters.
8. Design of column determination of kinetics order.
9. Column performance study for determining breakthrough service time.
10. Mathematical modeling of reactor column kinetic data.
11. Optimization using statistical tool Response surface methodology (RSM) for batch experiments.

Chapter - 4

Materials and Methods

Chapter 4

Materials and Methods

4,1 Materials

4.1.1 Chemicals & Reagents

A stock solution of fluoride concentration (F^-) 1000 mg/L was prepared by dissolving 2.21 gm analytical grade Sodium fluoride (NaF) [Make Merck, India] in 1L of Double distilled water. Subsequent dilution of different strength of F spiked solutions with stock solution were made by addition of double distilled water with pre determined volume. All the solutions utilized throughout the experiments were prepared in double distilled water (DW).

For estimation of Chlorides in water Standard $AgNO_3$ solution (0.014N) was prepared by adding 2.397gm of $AgNO_3$ were dissolved in 1L double distilled water. The Potassium chromate (K2CrO4) indicator solution (5%) was prepared by adding 5g of K_2CrO_4 into 100 ml of double distilled water. Sodium chloride (0.0141N) was prepared b y dissolving 824.1mg NaCl was dissolve in 1000 mL distilled water.

Methyl orange indicator was used during estimation of Bicarbonates present in water. It was prepared by adding 0.5 g of indicator into 1000 ml of CO_2 free distilled water. Phenolphthalein indicator and Standard H_2SO_4 (0.02N) was used for titration.

For adding Sulphate as co-ion in water a standard stock solution of Na_2SO_4 was prepared mixing 1.47 gm Na_2SO_4 in 1L of distilled water. To prepare conditioning reagent, 25ml of glycerol was added 15 ml HCl and then it was mixed 50 ml of isopropyl alcohol (95%) along with 3.75 gm of NaCl in double distilled water.

4.1.2 Apparatus and Instruments used

i) For all experimental work glassware were used of Borosil India make.

ii) All the glassware were washed 1N HCL acid solution then after with distilled water. Tap water and distilled water was subsequently used for cleaning process along with chromic acid.

iii) A high precision electrical balance was used for weighing the reagents, chemicals and adsorbent during the experimental works.

iv) Digital pH meter (Deluxe , Model 101E,M.S. Electronics India Pvt Ltd.) was used for pH measurements.

v) A mechanical shaker, Remi India make was used for agitating the samples for conduction of batch studies.

vi) Polyethylene bottles (Torson Co. Ltd) of 250 ml capacity were used for all batch experiment studies.

vii) Hot Air Oven for drying the Adsorbent and glassware.

viii) A muffele furnace was used to prepare adsorbent biochar form fish scales.

ix) Neuro solution 5®, Thermo Scientific Orion Fluoride Ion Selective Electrode (Orion Star™ A214 pH/ISE Bench top Meter) was employed for the determination of fluoride ions. EPA-approved ISE test procedures for fluoride in drinking water and waste water (ASTM D1179-B) and Standard Methods (4500-F-C) was used for measurement of fluoride. The ISE instrument was calibrated daily before measurement of fluoride from aqueous solution and operated as and as recommended by the manufacturers.

x) A peristaltic pump of Rivotek™ supplied by Riviera Glass Private limited was used for conducting the fixed bed column studies. The fixed bed column studies were conducted in up-flow mode at varying flow rates.

4.1.3 Preparation of adsorbent material

4.1.3.1 **Preparation untreated Fish scale biochar (FSB)**

Labeo Rohita (Rohu) scales used were collected from the local fish market of Kolkata (India). The dust, dirt and soluble impurities from the surface of fish scales were removed by washing them thoroughly with tap water and distilled water. Then the scales were sun dried for 2 days and carbonized in muffle furnace at 600ºC for 3 h. The resulting fish scale biochar was pulverized to biochar powder using a grinder. The grinded powder was sieved to obtain particle size of 125–250µm and was used as adsorbent without any chemical modification. The biochar thus obtained was named as Fish scale biochar (FSB). The schematic representation of preparation of FSB is exhibited in **Figure 4.1 (a) though Figure 4.1(e).**

Table 4.1: Instruments Used

Process	Instrument	Make
pH determination	Digital pH meter	Deluxe , Model 101E,M.S. Electronics India Pvt Ltd.
Fluoride measurement	Ion Selective Electrode(ISE)	Orion Star™ A214 pH/ISE Bench top Meter
Weight measurements	High precision electrical balance	Wensar , Model PGB 300
Agitation of batch study samples	Orbital mechanical shaker	Remi , India make
Drying of washed adsorbent	Hot Air Oven	Scientific Industries, India
Carbonization of FSB	A muffle furnace	Sicco India furnace , India
BET surface area	BET surface analyser	Quantachrome NovaWin, Japan
Surface morphology and elemental composition	SEM (Scanning electron microscope), equipped with EDX	JSM-6490 V, JEOL, JAPAN)
FTIR analysis	Fourier Transform Infrared Spectrometer	Perkin Elmer Spectrum, United Kingdom
XRD analysis	X-ray diffract meter equipment	Bruker, D8 Advance, Germany
Fixed bed column study (up-flow mode)	A peristaltic pump	A peristaltic pump of Rivotek™ supplied by Riviera Glass Private limited

Figure 4.1 (a) Collection of fish scale from local market

Figure 4.1(b) Sorting of Fish Scales

Figure 4.1 (c) Washing of Fish scales

Figure 4.1 (d) Sun drying of Fish scales

x

Figure 4.1 (e) Sun dried Fish scales

Figure 4.1 (f) Fish scale biochar

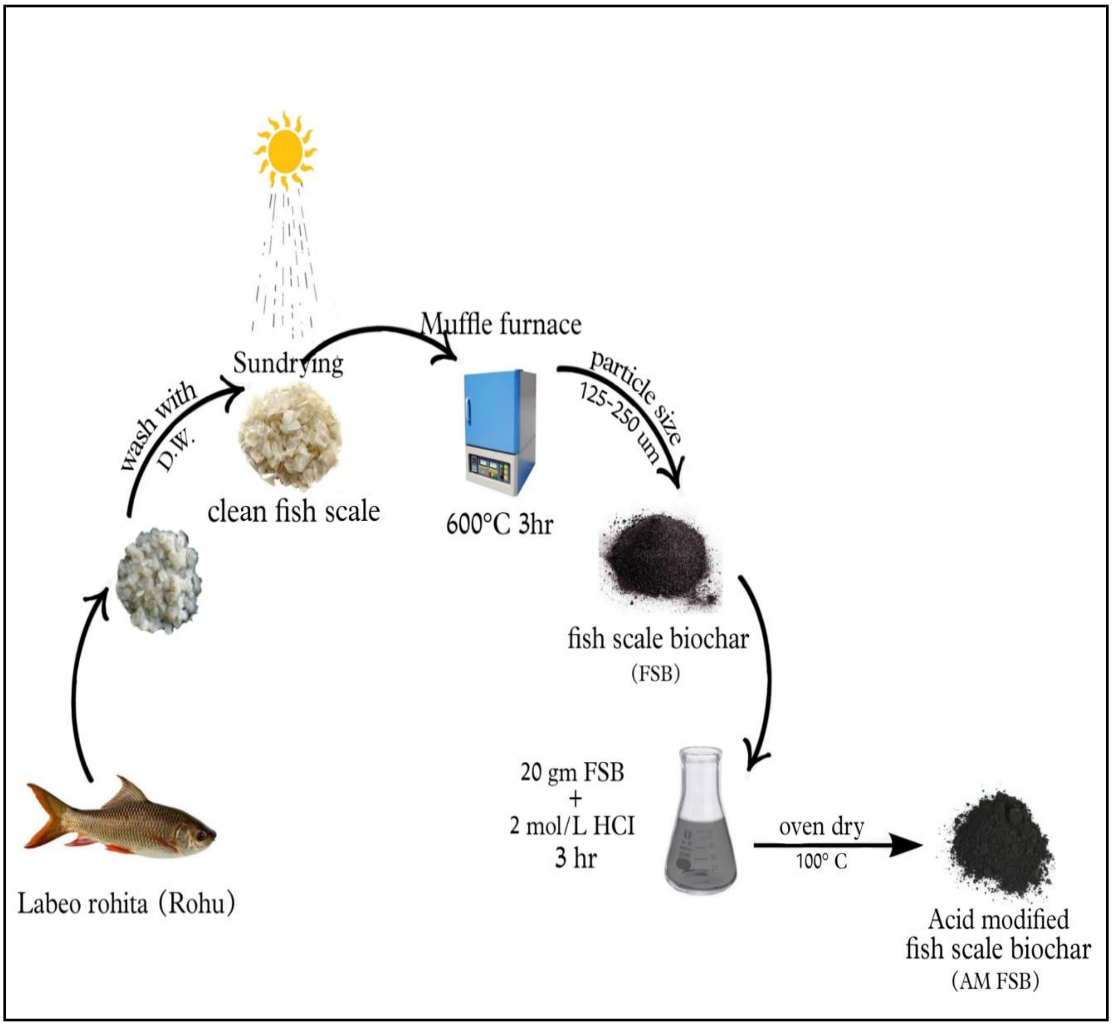

Figure 4.2: Schematic diagram of FSB and AMFSB synthesis

4.1.3.2 Preparation of acid treated fish scale biochar (AMFSB)

To prepare acid modified fish scale biochar, 20 gm of fish scale biochar(FSB) has been kept in diluted HCL solution (2 mol/L), and stirred for 3 h. After this the fish scale biochar was filtered and washed several times with distilled water till wash water reaches to neutral pH. The washed acid soaked biochar was then oven dried at 100^0 C till it reached to constant weight. This dry acid modified biochar was then stored in air tight container and used as adsorbent in fixed bed continuous column for fluoride removal studies. **The Figure 4.2** depicts the schematic of preparation of Acid modified fish scale biochar.(AMFSB)

4.1.3.3 Preparation of Metal impregnated Fish Scale Biochar

For preparation Aluminum (Al), Iron (Fe) and Manganese (Mg) impregnated Fish Scale Biochar of Aluminium nitrate($Al(NO_3)_3$), Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) and Magnesium chloride hexahydrate ($MgCl_2.6H_2O$) having 99.99% purity was purchased from Merck and used without further purification. For the $Al(NO_3)_3$ doped Biochar sample, 20gm of the previously prepared biochar was mixed thoroughly with 5gm of $Al(NO_3)_3$ in a mortar pestle. The mixture was then heated in a muffle furnace at 550°C for 4 hours at 5°C/min heating rate in air atmosphere. A black colored powder sample was obtained after cooling down to room temperature. This was named as Al –Fish scale biochar (Al-FSB). For the Iron and Magnesium impregnated biochar synthesis, the same procedure was followed with $FeCl_3.6H_2O$ and $MgCl_2.6H_2O$ as the precursor respectively. The black powder obtained in this case was named as Fe- fish scaled biochar (Fe-FAB) and Mg-fish scale biochar (Mg-FSB) respectively.

4.2 Surface chemical and physical characterization

4.2.1 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX)

A scanning electron microscope (SEM) is widely used advanced electron microscope which uses a focused beam of highly energetic electrons onto any surfaces to generate scanned images. In this method the Field emission gun produces electrons which are passed through high vacuum column. Low acceleration voltage is maintained at the vacuum column. The beam of generated electrons are passed and centered through electromagnetic lenses for converting it into narrow electron beam of range of 1–10 nm. This beam performs the raster scanning on the sample surface. The narrow range beam of electron interacts with the solid sample produces a secondary electron. This secondary electron thus formed escape from the sample into the column vacuum. These secondary electrons carry structural information of the sample under consideration. Energy Dispersive X-ray (EDX) is an integral part of SEM analysis. In EDX , a focused beam of electrons is bombarded on sample to obtain a localized chemical composition. EDX can detect all elements. For performing this SEM-EDX analysis the sample is coated with gold for making it electronically conducting medium.

4.2.2 Fourier-transform infrared spectroscopy (*FTIR*) analysis

Fourier-transform infrared spectroscopy (*FTIR*) analysis a powerful tool for the identification of various chemical bonds present in the sample. FTIR spectrometer generally used to measures the absorption of IR radiation by any materials. The technique identifies resonance frequency characteristics of functional groups present in the sample. This technique widely used for identification of functional groups of any mixtures or compounds to be analyzed. The incident infrared light (4000–400 cm^{-1}) when interacts with sample, the alterations in chemical bonds i.e. bending, rotation, stretching, twisting etc. vibration modes occurs for performing the analysis all samples were prepared using a KBr disc method. For performing the FTIR analysis on 2 mg of AMSB sample was mixed with 100 mg KBr and its the spectra was observed in an middle IR region between 4000–400 cm^{-1}.

4.2.3 X-Ray Diffraction Analysis (XRD)

X-Ray Diffraction Analysis (XRD) is an important analytical technique and widely used to examine crystalline material structure. This analysis evaluates the atomic arrangement, crystallite size of sample. X-ray diffraction (XRD) patterns of AMFSB was recorded using an advance X-ray diffractometer (Philips Analytical PW-1710) which was equipped with Cu-Kα radiation of λ=1.5418 Å. The equipment was operated at scanning speed 0.4° min/L and $2\Theta = 10$ and 70 . A potential current of 30 mA and 40 kV voltage was maintained throughout the XRD investigation process. applied current. The powder samples were pressed in a glass sample holder for performing the analysis. The analysis was carried out using a Bruker D8 Discover advanced X– ray diffractometer with Cu–Ka radiation over a range of 10–80° (based on 2 θ) at a scan speed of 5°/min.

4.2.4 Moisture content

The oven drying method was used to determine the Moisture content of fish scale biochar. A petridish with about 5.0 g of the adsorbent was weighed accurately in a and placed in an electric oven. The temperature at the oven was maintained at 110 ± 5 ºC for 4 hours after which the petridish was weighed again after cooling in desiccators. This procedure was repeated for three times and then average of the three observations was used to determine moisture content. The moisture content was calculated by using the equation (1)

$$\text{Moisture content (\%)} = \frac{(W_1 - W_2)}{W_1} \times 100 \qquad (1)$$

where, W_1 = Initial weight of the adsorbent taken for oven–drying (g);
W_2 = Final weight of the adsorbent after drying (g).

4.2.5 Determination of Bulk Density

To determine bulk density of FSBand AMFSB, a dry empty 10 ml centrifuge tube was cleaned and weighed (W_1). The same tubes were then filled with prepared adsorbent and weighed (W_2) again. The difference in the initial and final weights denoted the weight of adsorbent in tube. Equation (2) was used to calculate bulk density of FSB and AMFSB.

$$\text{Bulk Density} = \frac{(W_1 - W_2)}{V_{ct}}) \times 100 \qquad (2)$$

where, W_1 and W_2 are initial and final weight of sample (g) before and after respectively.

4.2.6 Determination of surface area (BET method)

Surface area and porosity are two important physical properties for any adsorbent. The Brunauer, Emmett, and Teller (BET) theory for gas adsorption was used for the measurement of surface area of FSB. The analysis was done at laboratory of Jadavpur University, Kolkata. The procedure involved determining the volume of a gas required to form a monolayer on the surface of FSB. BET analysis determined the specific surface areas of FSB sample by nitrogen monolayer adsorption measured as a function of relative pressure. Before start of the analysis the sample was heated to blow away adsorbed gas or vapors present if any from the surface of the sample. A fully automated analyzer, model Nova 2000e, (Quantachrome Instruments Limited, USA) was employed for this purpose.

4.3 Batch adsorption studies

A series of batch experiments were conducted to evaluate the effect of process influencing parameters viz., adsorbent dose, pH, initial fluoride concentration, contact time, agitation speed and co-existing ions. a series of batch adsorption process was carried out by mechanical agitation. All adsorption batch study experiments were performed in triplicate. One factor at a time (OFAT) approach was used for optimizing the process parameters. To determine optimum pH for removal of fluoride pH of water sample was varied from pH 2-12. The adsorbent dose was varied from 2-12 gm/L. The contact time for batch study was varied from 60 to 210 min. The initial fluoride ion concentration was varied from 2mg/L to 10 mg/L. To observe the effect of agitation speed ton fluoride removal the orbital mechanical shaker was rotated at varying speed from 60rpm to 180rpm. The effects of co–existing anions like bicarbonates, chlorides, sulphates and nitrates were also observed After every batch experiment the sample was allowed for the gravitational settlement of adsorbent and then the solution was filtered using Whatman filter paper (No 1). This sample was used for estimation of fluoride ion concentration The remaining fluoride ion concentration in the sample was estimated by an ISE meter(Orion fluoride ion selective electrode (Thermo Scientific Orion, USA). All the experiments were conducted at ambient temperature. The experimental data obtained was for adsorption isotherm analysis and to determine rate order kinetics. An empirical statistical technique Response surface methodology (RSM) was used with Box-Behnken design approach for designing experiments and finding the optimum conditions for various process parameters.

4.4 Fixed Bed Column Study

To evaluate the performance of the prepared acid modified fish scale biochar for removal of fluoride from water, continuous fixed bed column experiments were conducted. The effects of different bed depths, flow rate and initial F^- concentrations were analyzed using breakthrough curves. The adsorption experiments were conducted at a neutral pH 7.0 ± 0.1 and room temperature (30^0C). A vertical Acrylic column of 2cm diameter and 40cm height was used for performing the fixed bed column studies. The column study was conducted with synthetic fluoride water sample at ambient temperature. Acrylic columns were wet-packed with glass beads at the bottom. Then a thin layer of glass wool (Sigma Aldrich) was place just below and above acidified fish scale biochar as per experiment design. An influent tank of 10 lit capacity of the was used for the column to run in up-flow mode and the peristaltic pump was connected to it with pipe. The influent fluoride solution from the model water tank was allowed to pass through an inlet placed at the packed bed column in a up-flow direction at a design flow rates. At fixed interval, the treated effluent is collected at the outlet placed above the packed bed. The schematic diagram of the column experimental set-up is shown in **Figure 4.3** below. Breakthrough curve analysis was performed on the results obtained for fixed bed column study. Mathematical modeling of fixed bed column data was done by using Thomas model, Yoons – Nelson model and bed height service time (BDST) model.

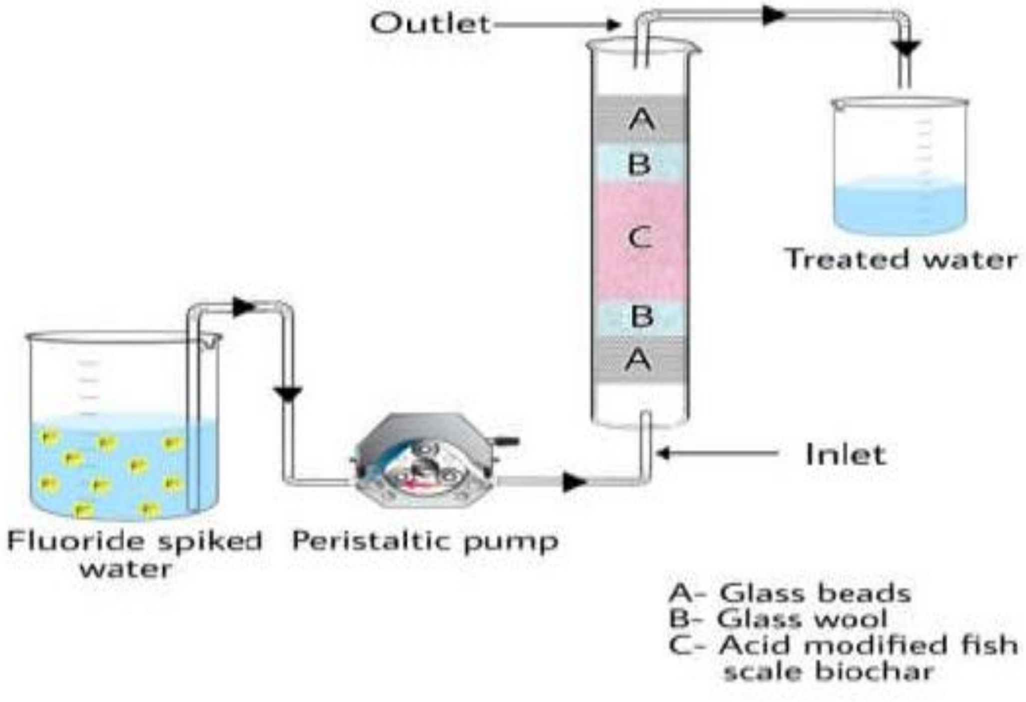

Figure 4 3 Schematic of Column study

Chapter - 5

Theoretical Consideration

Chapter 5

Theoretical Consideration

5.1 General ideas about adsorption

Adsorption, is an important surface interacting phenomenon, widely in engineering application of separation and purification of contaminant. The molecules or ions that have separated referred to as adsorbate and the medium of occurrence is called the adsorbent. The adhesive or cohesive forces are attributed inside the layers or films on the surface for such phenomenon. (Van-Vliet et al, 1980; Weber et al.,1985). Based on the interactions between adsorbent and adsorbent, the process of adsorption is classified into as follows

(i) **Physical adsorption**
(ii) **Chemical adsorption**
(iii) **Exchange adsorption**
(iv) **Specific adsorption**

In the last few decades, the adsorption science has become an increasingly important tool in removal of pollutants from water environment. This has stimulated a growing interest in research fraternity to look into adsorbate-adsorbent interactions. Thomas and Crittenden (1998) have evaluated history and development of the adsorption technology, for using it for commercial practice. In the early part of the twentieth century several scientists including Brunauer, Emmet and Teller, Langmuir and later by Barrer, had exerted sizeable exercise which resulted understanding of adsorption process mechanism. Adsorption is carried out by both batch and continuous flow system mode.

5.1.1 The Adsorption Process

The accumulation of a substance over a solid surface is a thermodynamic process where surface or pore attractive forces are predominant between adsorbate and adsorbent . The adsorption processes can be done in three modes as follows:

a) Batch process,
b) Fixed bed process, or

c) Moving bed process.

The adsorbents are assessed for equilibrium capacity (q_e) and rate of removal are governed by chief factors as given below:

a) The surface area

b) The physiochemical characteristics of adsorbent surface

c) The availability of active sites to adsorbate molecules or ions

d)The physical size and

e Form of the adsorbent particles

5.1.2 Adsorption isotherm:

The isotherm is a mathematical relationship between the adsorbate and sorbet in equilibrium at a constant temperature. The study of adsorption isotherm gives values of coefficients that quantitatively describe the adsorbate and sorbent interactions (Langmiur ,1918; Ho and McKay 1999). It indicates effectiveness of the absorbent for a specific adsorbate.

An adsorption isotherm model gives a better understanding of mechanism of adsorption. It also determines type of interaction between adsorbate and adsorbent at its equilibrium state. The batch experimental data obtained is analyzed using existing established isotherm models. For adsorption isotherm study Langmuir, Freundlich and Intra-particle diffusion models were studied.

5.1.2.1 Langmuir isotherm

Irving Langmuir in 1932, proposed an empirical isotherm for gases adsorbed on solids. The Langmuir isotherm models is expressed in linearized equation forms as equation (3) .

$$\frac{\mathrm{Ce}}{\mathrm{q_e}} = \frac{1}{K_l\, q_{max}} + \frac{Ce}{\mathrm{q_{max}}} \qquad (3)$$

where, $q_{e=}$ the amount of fluoride adsorbed per unit mass of Fish scale biochar (FSB) (mg/g)

C_e = equilibrium concentration of fluoride(mg/L)

q_{max} = maximum amount of the fluoride ions per unit mass of FSB

K_L = Langmuir constant representing the binding sites affinity (L/mg).

A dimensional equilibrium parameter (R_L) is a characteristic of Langmuir model and it is expressed as equation (Ho and McKay, 1999)

$$R_L = \frac{1}{(1+c_0 * k)} \qquad (4)$$

Where, *k* = constant (Langmuir) Co = concentration of fluoride (mg/l). When the R_L value is greater than 1, then it indicates the adsorption isotherm type supposedly to be unfavorable and if $R_L = 1$, then type is linear. When value of R_L ranges within 0 to 1 ($0< R_L <1$), it is considered as favorable and R_L equals to 0 then, its irreversible

5.1.2.2 Freundlich isotherm

Freundlich and Kuster earlier in 1894 suggested an empirical isotherm model known as Freundlich isotherm. Freundlich isotherm describes the non-ideal and reversible adsorption. It is mostly early applicable to physico-chemical adsorption on heterogeneous surfaces (Ho and McKay, 1998). It is based on the assumption that adsorbent surface is heterogeneous for adsorption of adsorbate. In this model, adsorption takes place at all active sites of adsorbent surface. Freundlich isotherm model is expressed as:

$$ln\, q_e \ln K_f \; + \frac{1}{n} ln\, C_e \qquad (5)$$

where, K_F ((mg g^{-1})(L mg^{-1})1/n) is a parameter of relative adsorption capacity of the adsorbent and 1/n gives an indication of the favorability of adsorption. Values of n > 1 represent favorable adsorption condition (Langmuir, 1918).

5.1.3 Adsorption kinetics and mechanisms

The kinetic behavior of an adsorbate removal or the absorption of a particular compound on to the adsorbent surface follows three main steps (Ho and McKay, 1999; Salameh et al. 2015)

(i) The molecular transfer from suspension to adsorbent surface
(ii) Internal diffusion of molecules of the sites of the adsorption on the adsorbent surface occurs.
(iii) Process adsorption is completed.

To evaluate the adsorption mechanism, the inspection of adsorption kinetics is very crucial. So, to implement this kinetic models that had been utilized viz , pseudo 1st order, pseudo 2nd order and intra-particle diffusion models. The sorption kinetics provides insight into mechanism of adsorption reaction, Pseudo first order kinetic model and pseudo second order were used in the present study.

5.1.3.1 Pseudo-First-Order Kinetics

Different kinetic reactor model are used to determine the mechanism of adsorption and estimating reactor order. Bhattacharyya and Sengupta, 2006 suggested Lagergren model is most useful. The pseudo-first-order kinetic model is based on the assumption that solute sorption process is first-order in nature and it is only dependent on the number of fluoride ions present in the solution at any specific time (Langmuir, 1918; Bellack 1971; Dayanada et al., 2014)

Pseudo first order kinetic model is expressed as:

$$\boldsymbol{Log(q_e - q_t) = log q_e - \frac{K_1 t}{2.303}} \qquad (6)$$

Where, qe and qt are uptake capacity (mg/g) at equilibrium and at any time t, respectively. K_1 is first order kinetic rate constant. (min/L)

5.1.3.2 Pseudo-second-order kinetics

A second order rate law considers that the rate of removal depends on the sorption capacity and not the concentration of the sorbate (Ho and Mackay, 1998; Singh et al, 2022) Pseudo-second-order kinetic model assumes that the fluoride adsorption process is dependent on the number of fluoride ions present in the solution as well as available adsorption sites on the adsorbent surface [6,10]. The Pseudo-second –order equation is expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

Where K_2 is rate constant, q_t is uptake capacity at any time t.

5.1.3.3 Intra particle diffusion:

In adsorption process, there are several steps that that enhances the movement of adsorbate from solution on the adsorbent surface. The steps are governed by various factors like surface diffusion, film or external diffusion, pore diffusion or combination of more than one step (Ho and McKay, 1999). This kinetic model had been suggested by Weber and Morris and possibility of intra-particle diffusion can be described using following formula:

$$q_t = k_d t^{0.5} + \mathrm{C} \qquad (8)$$

where, k_d = diffusion rate constant (mg/g. $h^{0.5}$), C = intercept and represents boundary layer thickness and qt = the amount of adsorbed compound (mg g/L) to the adsorbent at time t (min).

5.2 Column studies

The fixed bed column adsorption method allows the solute solution to flow continuously through a packed bed of adsorbent. The bed height, the rate of flow and initial concentration are varied to see their effect on adsorption. The performance of column adsorption is continuously monitored by measuring the effluent concentration with predetermined interval of time.

The efficiency of the column can be explained by means of the breakthrough curves (Onyangoa et al., 2004; Ofomaja et al., 2005).A breakthrough curve is plotted between column effluent concentration vs treated volume or treatment time (Fawell, 2004). The shape of breakthrough curve the graph is in general S- shaped.

Breakthrough is deemed to have occurred at some time t_b, break point time, when the concentration of the adsorbate leaving the bed increases to an arbitrarily defined value, C_e, break point concentration, which is often the minimum detectable or maximum allowable concentration of the component to be removed. In other words, the breakthrough point can be defined as the point at which the effluent concentration increases rapidly (Chen et al., 2001; Ramesh et al., 2012). The **Figure 5.1** shows a typical adsorption column breakthrough curve and movement of MTZ in fixed column

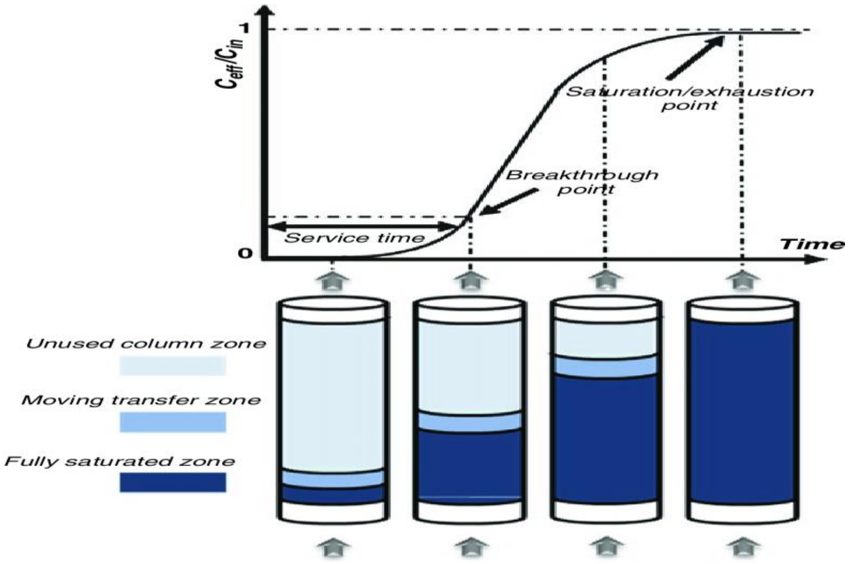

Figure 5.1 Schematic of adsorption column breakthrough curve and MTZ in fixed column

5.2.1 Column data analysis

Breakthrough curve can be used to evaluate the fixed bed-column adsorption performance. The breakthrough point was taken until the outlet fluoride concentration was reaches 90% of inlet fluoride concentration. The breakthrough curve is obtained by the graph of C_o/C_f against contact time (Fawell, 2004, Chen et al., 20011; Anirudhan et al., 20011). Where C_o and C_f represents initial and final fluoride concentration, respectively. Total outlet volume, V_{eff} can be determined by the following equation (9).

$$V_{total} = Q \times t_{total} \tag{9}$$

Where, Q =flow rate in volume(mL/min), t_{total} = total flow time (min) . Total adsorbed amount of fluoride q_{total} (mg) can be obtained by using the equation (10).

$$q_{total} = \frac{Q}{1000} \times \int_{t=0}^{t=total} C_{ad}\, dt \tag{10}$$

Adsorption capacity qe (mg/g) can be calculated from equation (11)

$$q_{e=\frac{q_{total}}{m}} \tag{11}$$

The empty bed contact time (EBCT) is calculated as ,

$$\text{EBCT} = \frac{\text{BV}}{\text{Q}} \tag{12}$$

where , BV is bed volume(ml) .

5.2.2 Modeling of column performance

Several models are used for predicting the performance studies of fixed bed adsorption columns. Thomas model, Yoon-Nelson model and BDST are employedb for analyzing the experimental data in the present work. Each these models are based on different type of adsorption isotherm, consideration of chemical reaction, mass transfer resistance and the type of rate law goverened.

5.2.2.1 Thomas model

Thomas model considers that the rate adsorption obeys Langmuir adsorption isotherm and second order reversible reaction kinetics (Tewari et al., 2009; Zhou et al., 2014). This model can explain well the adsorption process having extremely small external and internal diffusion resistances (Lippens et al., 1965). Thomas equation can be given as follows,

$$ln\left[\frac{C_o}{C}-1\right]=\frac{K_{th}q_om}{v}-K_{th}C_ot \tag{13}$$

where, C_0, C are influent and effluent concentration of adsorbate (mg/L), k_{th} is Thomas model constant (mL/min.mg), q_0 is equilibrium uptake (mg/g), m is mass of adsorbent (g) and is linear velocity (cm/min)

5.2.2.2 Yoon-Nelson model

Yoon and Nelson developed is a less complicated model, which requires no detailed data concerning the characteristics of the adsorbate, properties of the adsorption bed and the type of adsorbent. It is assumed that the rate of decrease in the probability of adsorption is proportional to the probability of adsorption and the probability of adsorbate breakthrough on the adsorbent [Noh et al., 1989; Aniruddhan et al., 2011). Linerized Yoon-Nelson equation written as

$$ln\left(\frac{C}{C_o-C}\right)=K_{yn}\ t-\tau K_{yn} \tag{14}$$

where, C_0, C are influent and effluent concentration of adsorbate (mg/L), K_{yn} is the Yoon Nelson rate constant (min^{-1}) and τ is the time required for 50% adsorbate breakthrough (min), t is the breakthrough (sampling) time (min).

5.2.2.3 Bed depth service time (BDST) model

Hutchins modified the Adams –Bohart model and the modified model is called the Bed depth Service Time Model. The bed depth service time model is another widely used mathematical model to describe the breakthrough curves parameters. (Ahamad and Jawed, 2012). The BDST model is significantly based on the theory of the surface reaction rate (Alagumuthu et al., 2010; Ramesh et al, 2012). The the simple mathematical expression of height of adsorbent bed (Z) and service time (t) is given as (Hutchins, 1973), which is given below,

$$t=\frac{N_oz}{C_ou}-\frac{1}{K_oC_o}\ln\left(\frac{C_o}{C_b}-1\right) \tag{15}$$

where, K_o is adsorption rate constant (L/mg/min), N_o represents adsorption capacity (mg/L), t (min), linear flow velocity is u (cm/min).

5.3 Response Surface Methodology

Response surface methodology (RSM) is an empirical statistical technique introduced by George E. P. Box and K. B. Wilson in 1951 usually employed for multiple regression analysis to explore the relationships between several descriptive variables and one or more response variables (Jaafari and Yaghmaeian, 2019). The first step of RSM is to focus on the optimum operating conditions for any given experimental system. It also finds true relationship between the set of independent variables (factors) and the dependent variable i.e., the response. Box–Behnken statistical experiment design (BBD) Central composite design (CCD), two– level full factorial design (FFD) are the most commonly adopted RSM techniques for interpretation of experimental data (Roy, 2014; Bhaumik et al, 2015). The parameters that affect the process are called dependent variables, while the responses are called dependent variables.

Box-Behnken design of response surface methodology (RSM) is helps to design the experiments and optimize input parameters. It also analyzes the interaction effects between independent variables. The coded values of independent variables Xi are coded the following equation (16),

$$X_i = \frac{X_i - X_o}{\Delta X} \tag{16}$$

where, X_i =coded value of independent variable.

X_i = uncoded value of independent variable

X_o= uncoded value of the same variable at the center point.

The relationship between the dependent variable and independent variables can be mathematically expressed by the equation(17)(Bhaumik et al, 2015; Massoudinejad, Ghaderpoori, Shahsavani, & Amini, 2016; Massoudinejad *et. al*., 2018; Jaafari & Yaghmaeian, 2019)

$$Y = \beta + \sum_i \beta_i X_i + \sum_{ii} \beta_{ii} X_i^2 + \sum_{ij} \beta_{ij} X_i X_j \tag{17}$$

where, Y = predicted %removal of fluoride

Xi , Xj = uncoded independent variables

βo =regression coefficient

β_i =linear coefficient

β_{ii} = quadratic coefficient

$\beta_i j$ = interaction coefficient

Chapter 6

Result Discussion

Chapter 6

Result Discussion

6.1 Characterization of Fish Scale Biochar

6.1.1 Physiochemical Characteristics

Bulk density, Moisture content and biochar yield of Fish scale biochar were determined by was determined by following standard method as discussed in **Chapter 4.** The physiochemical characteristics evaluation is presented in **Table 6.1**. The bulk density of Fish scale biochar (FSB) and Acid modified fish scale biochar (AMFSB) was found to be 1.25 and 1.18 respectively. pH of FSB and MSFB was found to be 7.84 and 6.62 respectively. pH is an important characteristics of biochar which influence the application of any adsorbent material (Roy & Das, 2016; Singh et al., 2017). The moisture content was determined for FSB and AMFSB as reported in Table 7.1. It is evident from previous works that yield and composition of any biochar varied with its feedstock, method of a pyrolysis and the temperature during thermal activation. The results indicated that FSB biochar yield was decreased with increase in temperatures from 400°C to 600°C. Yield decreased with increasing biochar production temperature (Jindo *et al.* 2014; Liu *et al.* 2015; Li *et al.* 2016). This may be due during pyrolysis the volatile matters get liberated as reported by Jindo *et al.(* 2014), Liu *et al.* (2015), Li *et al.* (2016) and Achieng, G. O., *et. al.*(2019). The adsorption performance gets greatly affected by pore size distribution of activated carbon (Oginni, *et al.*2019). The surface area and the pore volume were the most influential characteristics of the micro-porous structure. It indicated that the surface of the fish scale biochar has pore structure and large surface area. This is property of activated carbon/ adsorbent contributes to the physical adsorption (Ji et al. 2021). The BET surface area obtained for AMFSB was 37.976 m^2/g which is much higher than that of many biochars used for adsorption. The BET surface area for various activated carbons used for adsorption is given in **Table 6.2.** The pore volume 0.108 cc/g and pore diameter 3.618 nm reveals the meso-porosity of the produced AMFSC. The results observed in this study are very closer to the earlier reports by Marrakchi, (2017), Cortes et al., (2019) Ji, et. al., (2021), Islam et al., (2022)

Table 6.1 Physical Characteristics of Fish Scale Biochar

Parameter	FSB	AMFSB
Bulk density (g/ml)	1.08	1.02
pH	7.84	6.62
Moisture content (%)	0.982	1.14
Biochar yield (wt%)		
FSB @ 400	51	-
FSB @ 600	48	-
BET surface area(m^2/g)	--	37.967
Pore Volume(cc/g)	--	0.108
Pore Diameter(nm)	--	3.618

Table 6.2: BET surface area for various Biochars used as an adsorbent

Adsorbent	BET surface area(m^2/g)	Reference
Pine wood biochar	7.66	Mohan , *et. al.*, 2012
Rubber wood sawdust biochar		
C 300	1.930	Shaaban , *et al.*2013
C 700	5.493	
Magnetic corn stove biochar	4.11	Mohan *et. al.*, 2014
S. ravnnaue grass biochar	5.57	Saikia, *et. al.*,2017
Chemically reduced biochar Tea waste	11.33	Roy S. *et. al.*, 2018
Bovine bone biochar	5.05	Zhou J., *et. al.*, 2019
Fish scale based Porous carbon	30.94	Islam M., *et. al.*, 2022
Acid modified fish scale biochar	36.976	Present study

6.1.2 Scanning electron microscopy and Energy dispersive X-ray spectroscopy (SEM-*EDS*) analysis

Scanning electron microscope (SEM) equipped with Energy dispersive X-ray spectroscopy (EDS) (JSM-6490 LV, JEOL, JAPAN) was used to analyze the morphology of AMFSB. The Figure 6.1 (a) and (b) displays the SEM micrographs obtained for AMFSB before and after adsorption of Fluoride from water environment. The **Figure 6.1 (a)** revealed that the AMFSB biochar has a rough and uneven porous surface which results in adorption F^- on its surface from an aqueous solution. The **Figure 6.1(b**) vividly shows that surface pores almost disappeared due to deposition of F- . This is validated with the EDX analysis obtained for AMFSB. The **Figure 6.2 (a)** and **(b)** shows the EDX spectra of AMFSB before and after adsorption of Fluoride from water environment. It is observed that a peak showing the presence of F- is clearly seen in EDX spectra of AMFSB after its application for fluoride removal. Similar findings are reported by Ji *et al.* 2021; Li 2021 and Yang *et. al*. 2021. The **Table 6.6** gives elemental composition of AMFSB obtained through EDX analysis.

Table 6.3 Elemental composition of AMFSB

	Composition by wt %						
Element	**C**	**O**	**N**	**Ca**	**P**	**Mg**	**F**
AMFSB before adsorption	63.1	16.8	16.7	2.1	1.3	0.1	ND
AMFSB after adsorption	63.0	14.7	13.1	5.8	3.1	0.1	0.2

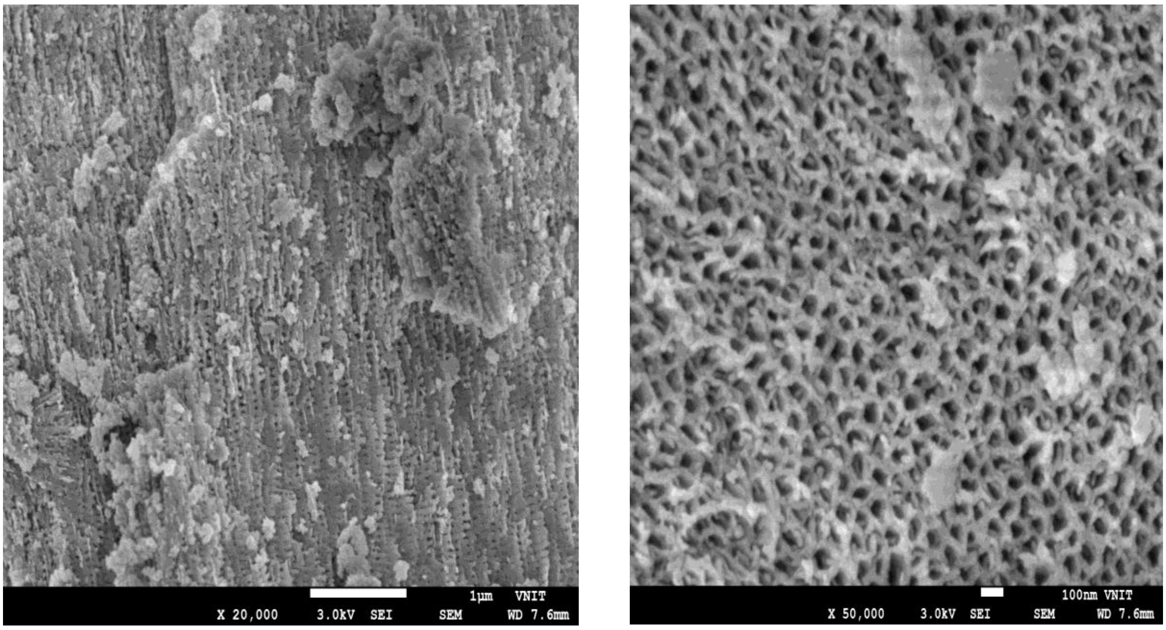

Figure 6.1 SEM of AMFSB before adsorption of F-

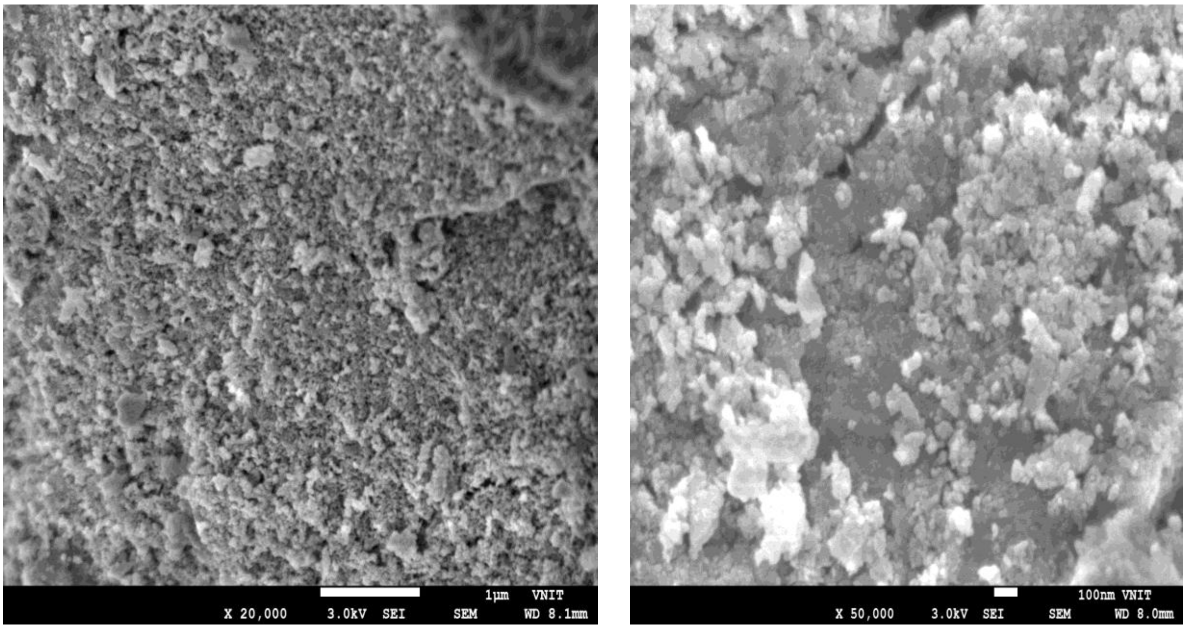

Figure 6.2 SEM of AMFSB after adorption F-

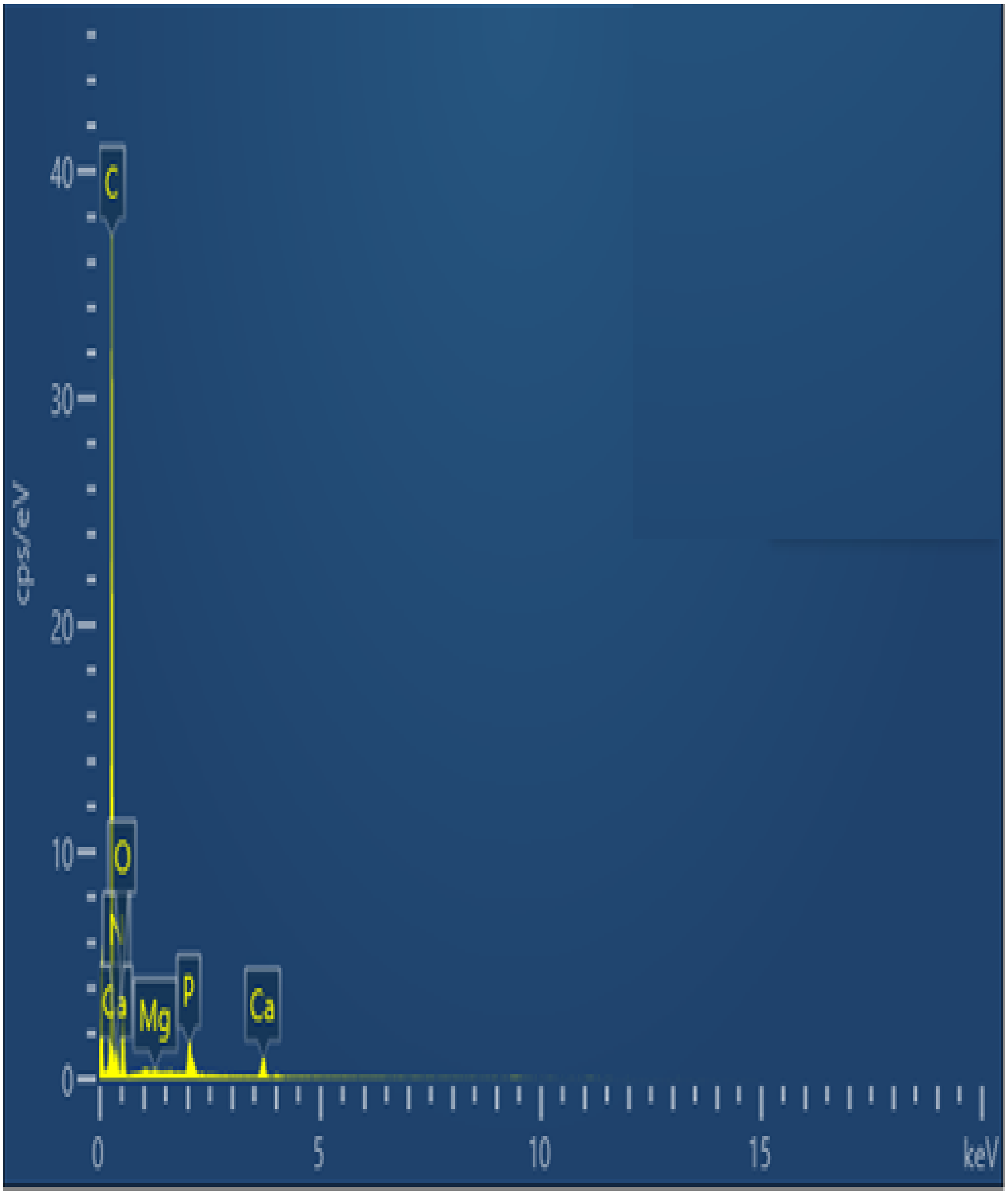

Figure 6.3: EDX before adsorption of fluoride

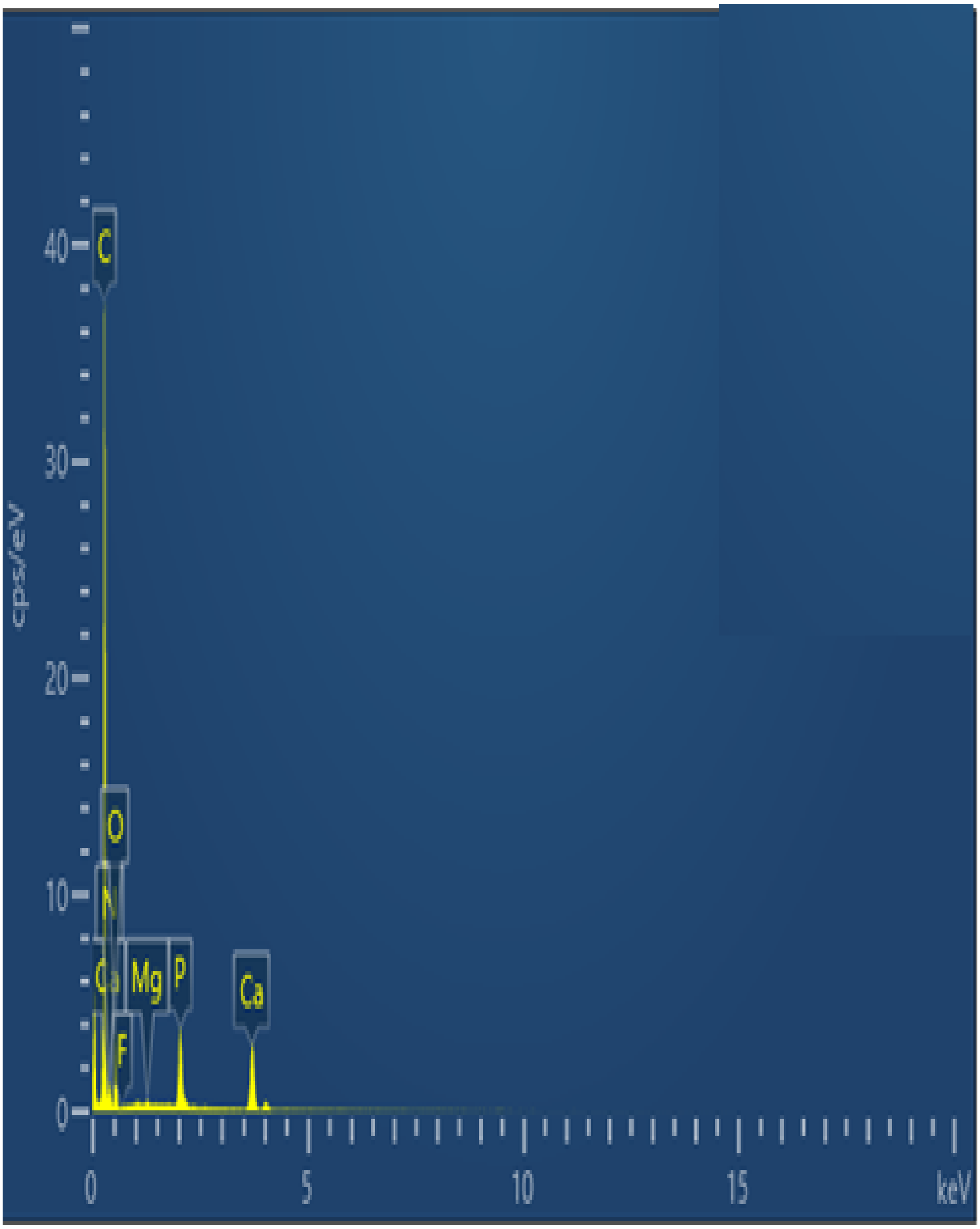

Figure 6. 4: EDX after adsorption of fluoride

6.1.3 FTIR

Fourier transform infrared spectroscopy (FTIR) illustrates the existence of surface functional groups present in the material. The **Figure 7.3** shows the FTIR spectra of AMFSB with wave number range 4000–400 cm^{-1}. The AMFSB is observed to majorly composed of C, O, Ca and P. It is observed that the FTIR spectrum of AMFSB has total nine bands clearly at 3175.5, 2309.26, 2204.51, 2012.3, 1465.76, 1040.36, 871.85, 607.68 and 566.69. As per the literarture available these bands relates to natural hydroxyapatite structure.(Younesi et al., 2011; Marrachki et al., 2017; ,Ji et al., 2021) The hydroxyapatite mainly contains hydroxyl and carbonyl groups(Markovic et al., 2004,. Bhumik et al., 2012, Chagas et al., 2012). The absorption bands of 3175.5 $cm{-}^{1}$ belong to strong O–H stretching vibrations are represented by the alcoholic functional group (Zainon, et al.; 2012, Paul et al. 2017). The peaks observed at 2309, 2204.51 and 2012.3 $cm{-}^{1}$ belong to -CH_3 group. The presence of other IR vibrations at and 1465.76 represent presence of Carbonate group stretching. The bands at 1,040 cm^{-1} and 1,014 cm^{-1} relates to C-O stretching vibrations, whereas the bands observed between 871.85 and 566.69 cm^{-1} relates to PO_4^{3-} groups of hydroxyapatite (Markovic et al., 2004 ; Zainon, et al.. 2012, Paul et al., 2017). Similar findings were also reported by Markovic, et al.(2004); Brunson et al.(2009) ;Wang et al., (2023) for bone char used as an adsorbent. There are no significant changes in FTIR of used and unused AMFSB except slight shift of band 607.68 cm^{-1} to 566.69 cm^{-1} . This is due to adsorption of F- on the surface of AMFSB replacing $CO_3{}^2$ and $PO_4{}^3$ anions . (Younesi 2011; Reynel, 2016)

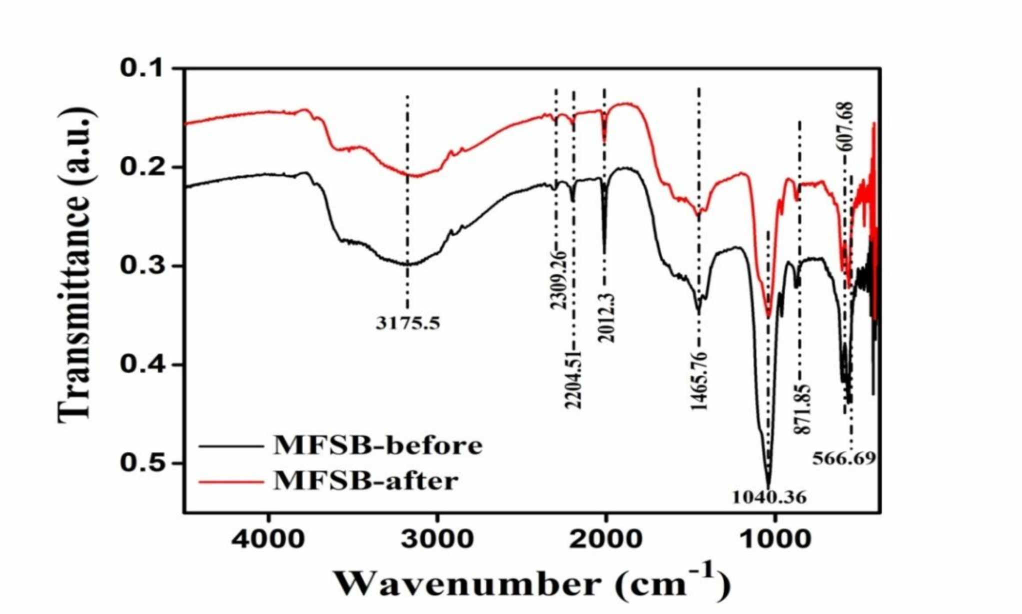

Figure 6.5: FTIR of AMFSB before and after adsorption of F-

Table 6.4: Functional group identification-FTIR

Peak wave number (cm^{-1})	**Assignment**
3175.5-- 2309.26,	Alcoholic hydroxyl group (OH) Acidic hydrogen of COOH stretching,
2204.51	CH2 symmetrical stretching
2012.3,	C=O stretch/hydrogen bond coupled with
1465	NH bending coupled with CN stretching and CO –double stretching.
1040.36--871.85	C-N stretch of amines
607.68 - 566.69	Inorganic phase representing P-O due to PO^{3}_{4}, mainly Hydroxyaptite.

6.1.4 X–ray diffraction analysis (XRD)

The XRD analysis gives insight into the phase compositions of the biochars. The XRD studies revealed the crystalline phase of the fish scale biochar. The **Figure 6.6** and **Figure 6.7** shows the XRD diffraction pattern for AMFSB before and after adsorption of Fluoride. The strong peaks located at 25.13°, 26.61°, 31.85°, 39.83°, 46.65°, 48.04°, 49.53°, and 53.24° related to the crystalline hexagonal structure. It is observed that after the adsorption of F- the peaks are 25.93°, 29.12°, 32.02°, 39.83°, 46.82°, 49.5°, and 53.41° showing with simultaneous decrease in the peak intensity. The results obtained are in agreement with the findings of Zainon, *et.al.,* (2012), Paul *et.al.,* (2017). The XRD data of AMFSB is in accordance with data of 2θ for hydroxyapatite indicating that the biochar samples mainly contains hydroxyapatite (Younesi *et al.*2011, Marrachki, *et al.,* 2017 ,Ji *et al.,* 2021).

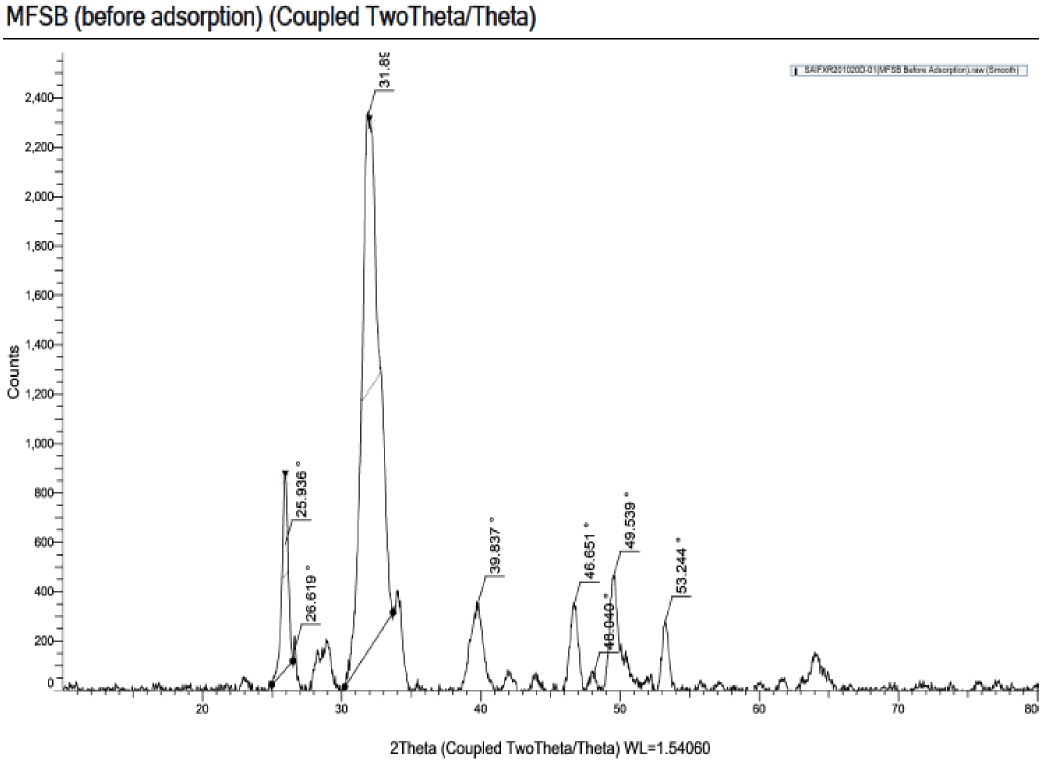

Figure 6.6 :X-ray diffraction patterns for Acid modified Fish scale biochar before adsorption

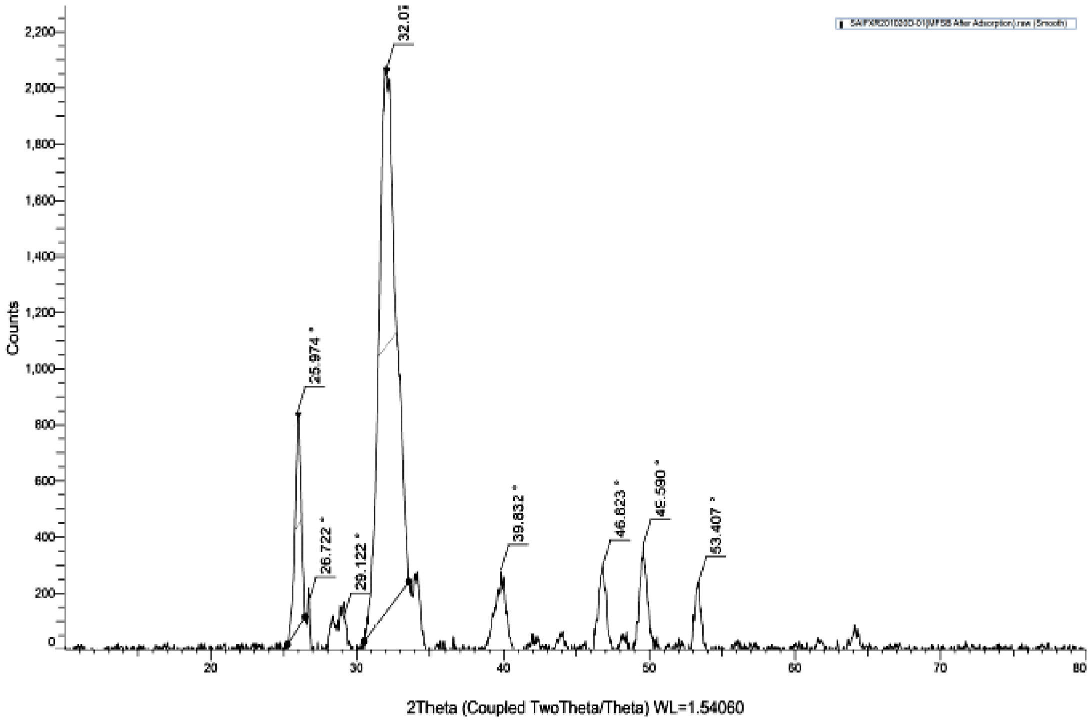

Figure 6.7: X-ray diffraction patterns for Acid modified Fish scale biochar aftre adsorption

6.2 Preliminary investigation

Preliminary batch studies were conducted to check the feasibility of adsorption of F- with various biochars prepared with Fish scale. As mentioned in chapter 4, 5 biochars prepared as Fish scale biochar (FSB) , Al –FSB, Fe-FSB , Mg-FSB and Acid modified fish scale biochar (AMFSB) were used as an adsorbent for removal of fluoride from water as a preliminary investigation. This study was done to select an appropriate adsorbent with optimum removal ease of synthesis and its possible scale up use. The batch operation was performed with ad adsorbent dose of 4g/L, Initial F- concentration was 5 mg/L and stirring rate of 120 RPM. The shaking the samples were agitated 270 min after which the samples were filtered for F- determination with the help of ISE. The **Figure 6.8** shows the plot of contact time vs. % Removal by various FSB prepared in this study. It is observed that highest removal of 84.1%5 was done by Al-FSB at contact time of 270 min whereas the AMFSB had removed 83.80 % almost close to that of Al-FSB . After contact time of 270 min the removal for FSB , Al –FSB, Fe-FSB , Mg-FSB and AMFSB was 69.13, 84.15, 73.12,72.34 and 83.80 % respectively.

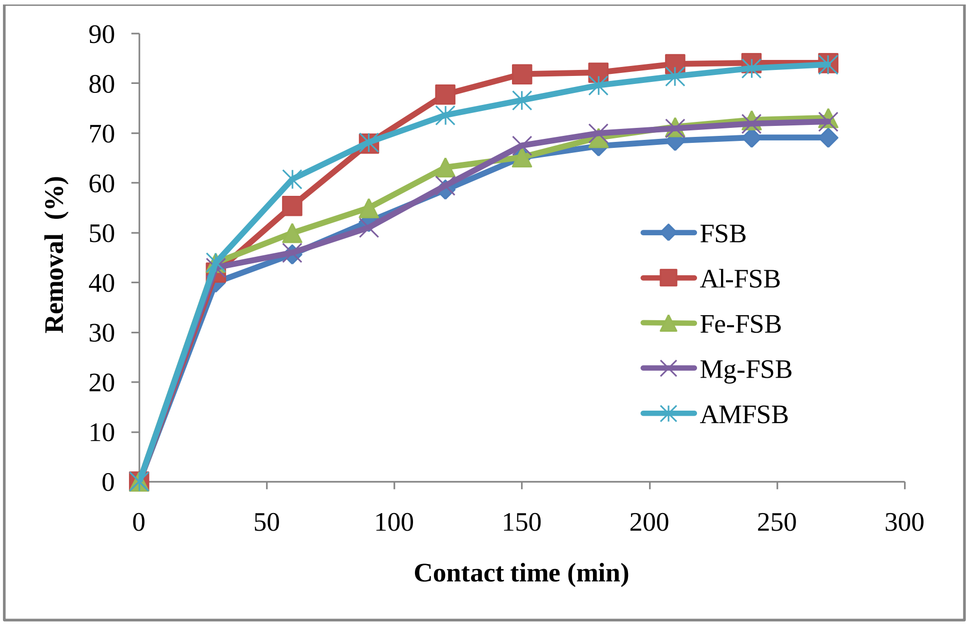

Figure 6.8 Effect of contact time on F- removal for prepared biochars

The earlier works have reported the concerns of leaching of metal ions into the environment form used metal doped biochars causing secondary pollution (Jianhua et al., 2022; Liu et al., 2022). As there was no significant difference in % Removal capacity of AMFSB than that of 20 % Al-FSAB, further detailed batch study for fluoride removal was investigated with FSB and AMFSB.

6.3 Batch operation

Batch equilibrium adsorption experiments were conducted under differing operating conditions to evaluate the adsorption potential of FSB and AMFSB for fluoride removal. The effect of process parameter i.e. contacts time, adsorbent dose, pH of solution and initial fluoride concentrations are further discussed in the following section.

6.3.1 **Removal of Fluoride with Fish Scale Biochar**

6.3.1.1 Effect of contact time

The effect of contact time on adsorption of fluoride onto FSB is depicted in **Figure 6.9** shows the. The batch studies illustrate that, the adsorption dynamics is greatly influenced by contact time. The effect of contact time for adsorbent dose varying from 2g/L to 12g/L was observed. Initial Fluoride ion concentration (F-) was kept 5mg/L and stirring rate was 120 rpm. As shown in **Figure 6.9** the adsorption rate of fluoride on FSB increases with time and eventually reaches to equilibrium after 180 min. At the start of FSB and F– interaction initial more number of active sites are available favorably for adsorption but with progress of time active adsorption sites was decreased and hence after equilibrium time no significant increase in removal of fluoride is observed. Similar trend of adsorptive removal were observed by (Meenakshi and Sukumar, 2008; Bhumik *et al.*, 2016; Marrakchi *et al.*, 2017; Ayalew A., 2023)

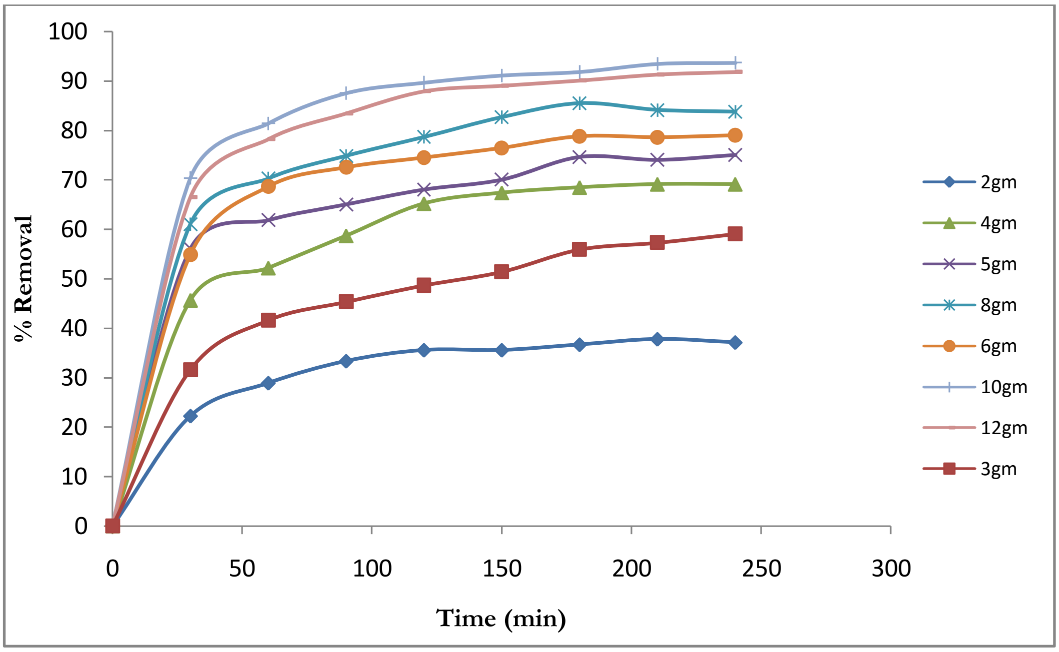

Figure 6.9 Effect of contact time on removal of Fluoride at various adsorbent dose

6.3.1.2 Effect of adsorbent dose

The effect of adsorbent dose on % removal of fluoride can be seen in **Figure 6.10**. The adsorbent doses were varied in the range of 2 to 12 g/L. It is observed that the percentage fluoride removal increased with increase in adsorbent dose. The maximum of removal was 97.41% at 10 g/L. At higher concentration of the sorbent amount percentage removal is increased as exchangeable sites present are more and remained constant as it reached towards equilibrium as reported by Bhumik et al., 2016; Ayalew et al., 2023 and Tolkou et al., 2023) It was observed that there was no significant increase in rate of fluoride removal after adsorbent dose of 8gm/L. These results obtained are inconsistent with the earlier experimental observations made done by Ye et al., 2018. This is due to over- lapping of active sit at higher dosage of adsorbent (Ayalew et al, .2023 and Tolkou,*et al.*, 2023)

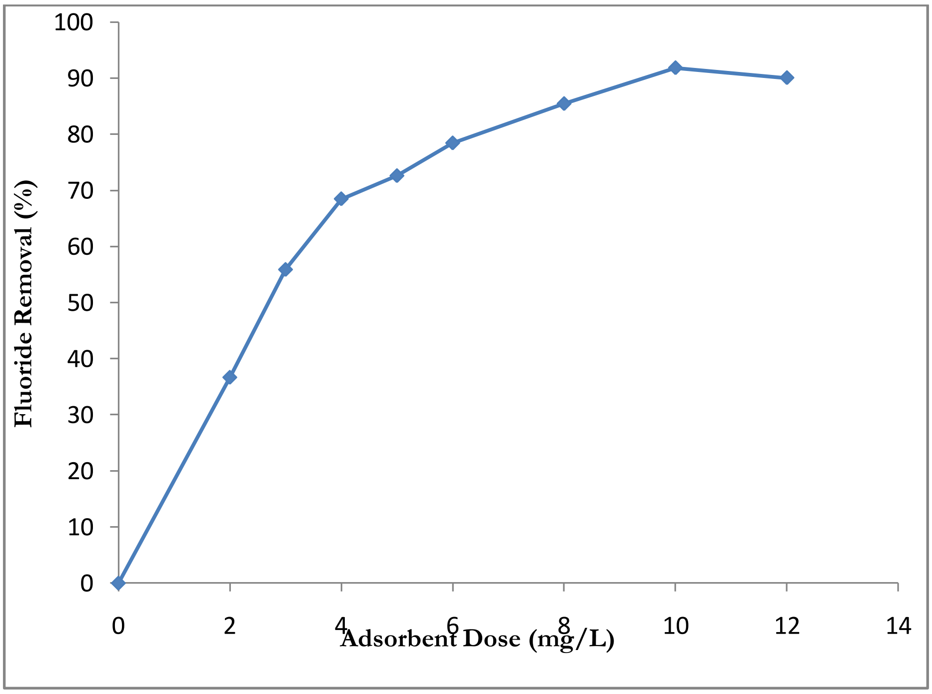

Figure 6.10 : Effect of adsorbent dose on removal of Fluoride

6.3.1.3 The effect of initial pH:

The pH of the solution is one of the major influencing process parameter in adsorptions as discussed in some literatures (Reynl 2016 ; Jianhua *et al.*,2022).The effect of pH on fluoride removal form water by FSB is plotted in **Figure 6.11.** The effects of initial pH on adsorption capacity of FSB was observed for pH range of 2.0–12.0 with 10 g/L of adsorbent dose at initial fluoride concentration at 5 mg/L for a contact time of 180 min. The 0.5 *N* HCl/0.1 *N* NaOH was used to maintain desired value of pH within ±0.2. The adsorption percentages decreased approximately from 92 to 80% with increasing initial pH from 5.0 to 12.0. The anions are better absorbed at a low pH in presence of H+. At a high pH, because of competition with OH–the fluoride surface by FSB found to be decreased due to electrostatic repulsion. A similar observation was recorded by Nabilah *et al*, 2013; Yadav *et al.*, 2013; Reynel 2016 and Sahu *et al.*, 2021. Increase in pH of solution results increase in number of negative charge sites relating to OH^-, as result decreased in the rate of defluoridation. This is a phenomenon occurs due to the competitive sorption between F- and OH^- at active site available at the surface of the adsorbent (Bhatnagar *et al.*, 2011; Patil et al., 2013, Sahu *et al.*, 2021)

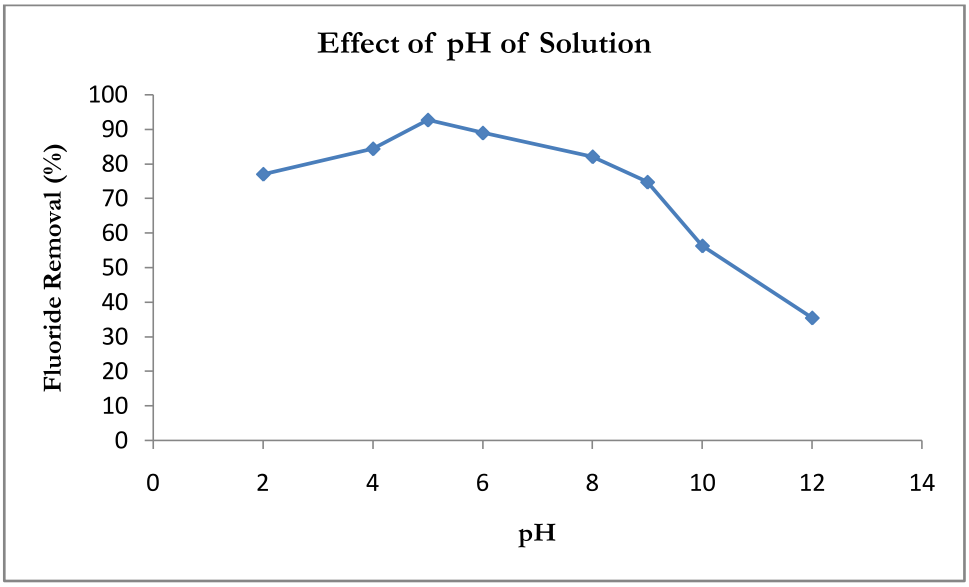

Figure 6.11: Effect of pH on removal of Fluoride

6.3.1.4 Effect of initial concentration of fluoride:

The **Figure 6.12** shows the effect of initial fluoride ion concentration on its removal efficiency by FSB. The fluoride ion concentration was varied in the range of 2–14 mg/L with 10 g/L adsorbent dose and contact time of 180 min it was observed that as fluoride concentration increases, the percentage removal of fluoride increased too. The results proved that at lower initial F- concentrations the sites available for adsorption are more whereas at higher F- concentrations most of the F- are left unabsorbed due unavailability of active adsorption sites onto the adsorbent surface. The obtained result concludes that % removal of F- was directly proportional to the initial F- concentration of water sample. This observation is in agreement with the reports by Patil *et al.*, 2013; Sahu *et al* , 2021 and Tan *et al.*, 2020.

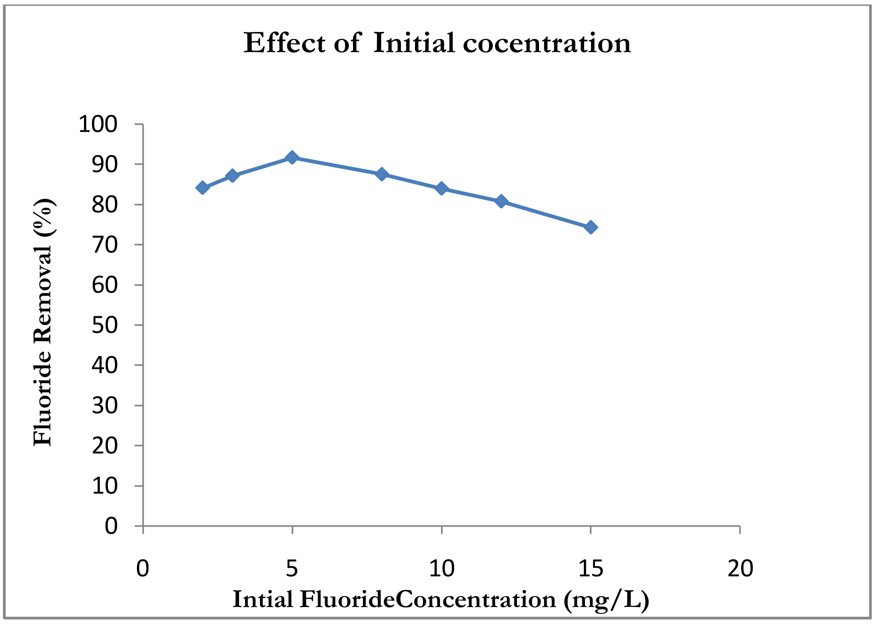

Figure 6.12 : Effect of Initial F- concentration on removal of Fluoride

6.3.1.5 Effect of agitation speed

The **Figure 6.13** shows the effect of agitation speed on removal of Fluoride removal by FSB. The effect of agitation was observed by varying speeds from 60 to 180 rpm with optimum adsorbent dose of 10.0 g/L, pH of 5 with, contact time of 180 min and initial concentration of 5 mg/L. Maximum Removal achieved was about 91.67 % for adsorbent dose of 10 gm/L at pH 5 with initial F^- concentration of 5 mg/L at 150 rpm. It was observed that at a given time, fluoride removal increases with the increase in the speed of agitation. This is because, at higher agitation speed adsorbate can make proper contact with adsorbent surface (Tembhurkar et al., 2006 ; Roy et al., 2013)

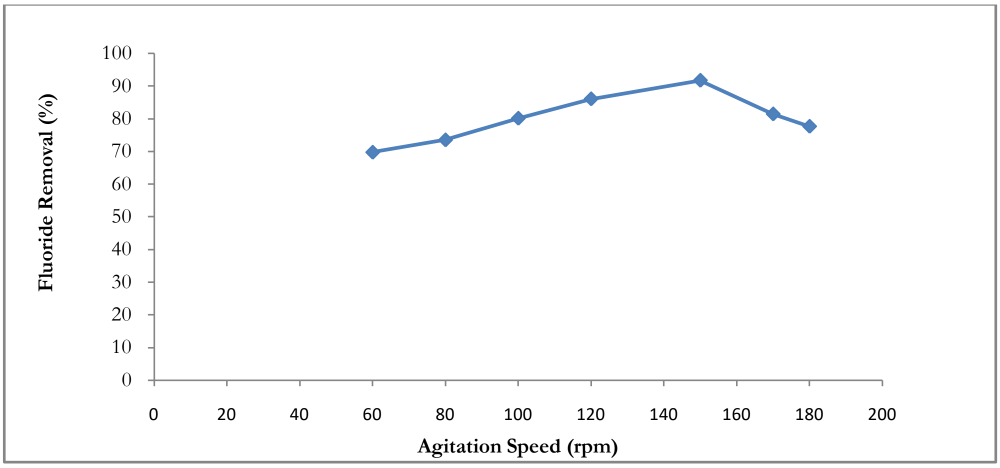

Figure 6.13 Effect of agitation speed on removal of Fluoride

6.3.2 **Removal of Fluoride with Acid Modified Fish Scale Biochar(AMFSB)**

6.3.2.1 Effect of contact time

Adsorption dynamics is greatly influenced by Contact time between the adsorbate and adsorbent (Bazrafshan et al., 2016) The effect of contact time on adsorption of fluoride onto AMFSB is shown in Figure 7.14. The effect of contact time for various adsorbent doses from 4-12 g/L was at initial fluoride concentration of 5 mg/L and stirring rate 120 rpm was studied by conducting batch study. As shown in **Figure. 6.14**, the adsorption rate of fluoride on AMFSB increases with time and eventually reaches to equilibrium after 180 min for all the varying doses. .there was no significant increase in % removal of fluoride after 180 min. In the beginning AMFSB and F– interaction , initial more number of active sites are available for adsorption but with progress of time active adsorption sites was decreased and hence after equilibrium time no significant increase in removal of fluoride is observed. Similar observations were made by Abe *et al.*, . (2004) and Janardhana, *et al.*(2007)

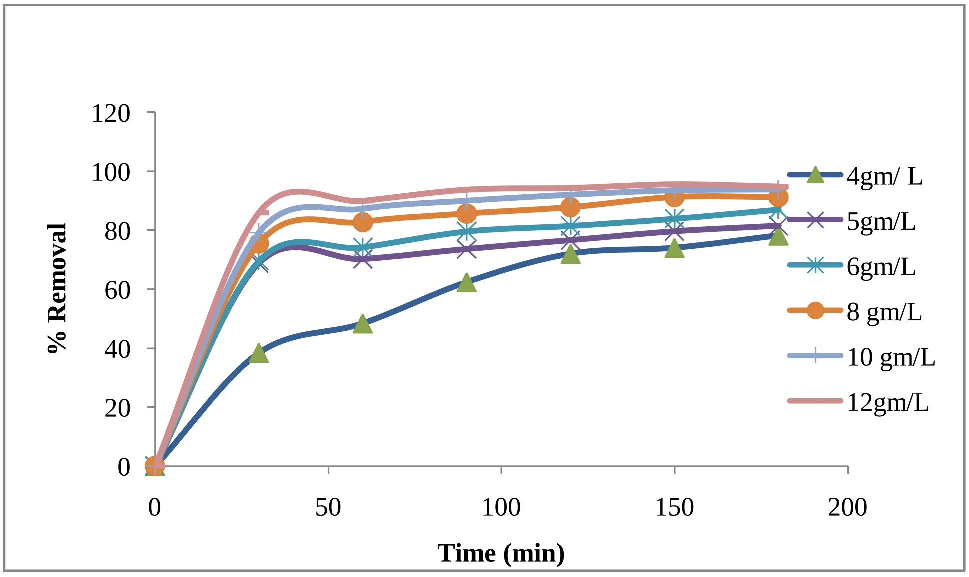

Figure 6. 14: Effect of contact time on removal of Fluoride at various adsorbent dose

6.3.2.2 Effect of adsorbent dose

The **Figure 6.15** shows the effect of adsorbent dose on removal of fluoride removal. During the experimentation the adsorbent dose was varied from 1 – 12 g/L. It is observed that % removal of fluoride increased from 70 to 93.5 % for an adsorbent dose of 1 and 6g/L respectively. This is due to with increase in dose the more number of active sites are available for adsorption of Fluoride ions. Whereas further increase of dose beyond 6g/L caused % removal to decrease and stabilize,. This is due to saturation of the adsorbent surface by adsorbate ions resulting in repulsion may have taken place between the fluoride ions and adsorbent surface (Bhumik et al., 2017; Roy et al., 2018). Therefore optimal dose of adsorbent was considered as 6g/L.

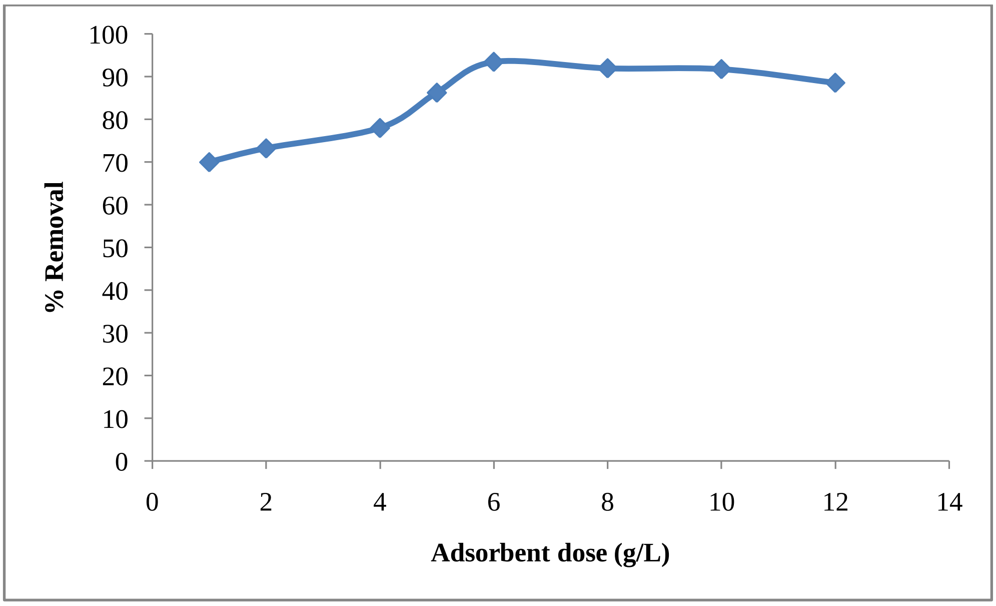

Figure 6.15 : Effect of adsorbent dose on removal of Fluoride

6.3.2.3 The effect of initial pH

The removal of any pollutant from water environment by adsorption is highly dependent on the pH of the solution. The ionization, dissociation nature, and surface properties of the sorbent are highly affected by the pH of the solution (Tembhurkar and Dongre 2006; Khaniabadi O., *et al.*, 2015). In present investigation, the effect of pH on % removal efficiency of fluoride was examined by varying the pH of solution from 3.5 to 11.5. The **Figure 6.16** shows the effect of pH on % removal of fluoride. The maximum removal 84.5 % was observed at 6.5 pH. It evident from the observations made that acid modified biochar has high adsorption efficiency at acidic pH as compared alkaline pH. As pH increased from 8.5 pH the adsorption capacity reduced rapidly. This may be due to presence of OH- ions at higher pH which may compete with negatively charged fluoride ion (Roy *et al.*, 2018; Sahu *et al.*, 2021). Thus, it can be concluded from the comparative study that removal efficiency of AMFSB was better than only FSB. The % removal of 84.5,80.0 and 71.87 % was observed at pH 6.5, 7.5 and 8.5 indicated usefulness of AMFSB for defluoridation of fluoride laden water.

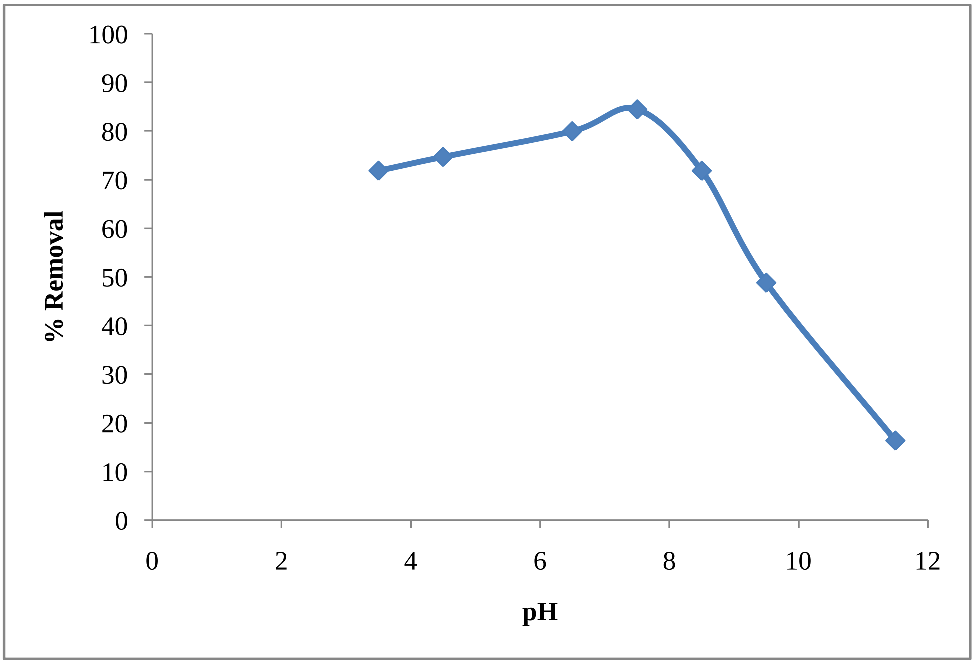

Figure 6.16: Effect of pH on removal of Fluoride

6.3.2.4 Effect of initial concentration of fluoride

The **Figure 6.17** depicts the sensitiveness of % removal efficiency of AMFSB in correspondance to initial fluoride concentration of fluoride. It was observed that similar to the results obtained for removal by FSB, the uptake of fluoride decreased considerably with increasing fluoride concentration. This decrease in removal efficiency is due to less availability of active sites (Sujana and Anand, 2011, Sahu *et al.*,2021) The experimental data reveals that with increase in the initial concentration, the % removal of fluoride subsequently decreased due to fluoride ion saturation of available active sites on the surface of AMFSB .Fluoride ions interact with the surface of AMFSB and occupy the active sites on its surface. The highest removal of 92. 2 % was observed at initial F- concentration of 5 mg/L which was decreased to 63.84 % at initial concentration of 12 mg/L.

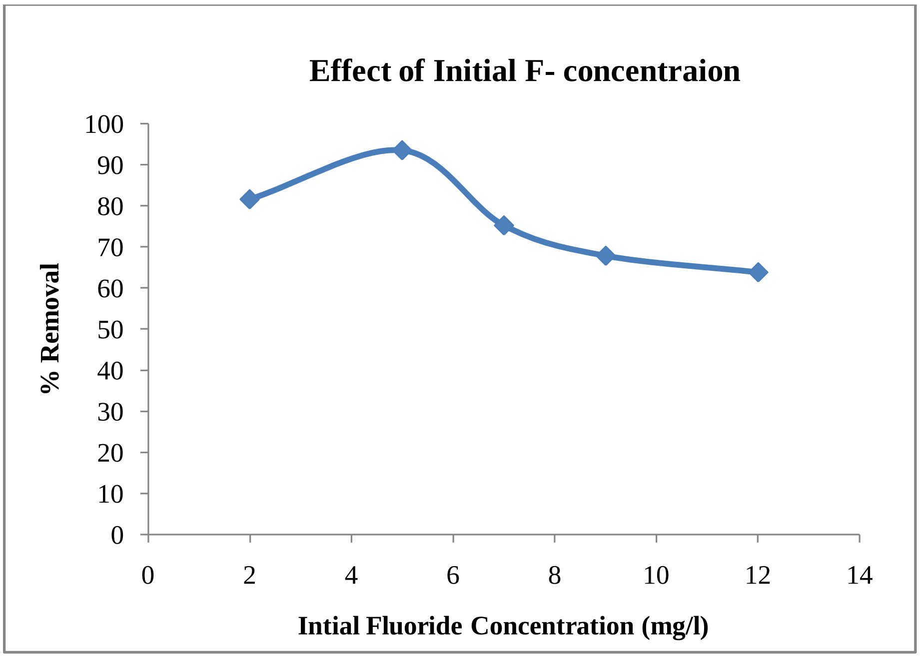

Figure 6.17: Effect of initial F^- concentration on removal of Fluoride

6.3.2.5 Effect of agitation speed

Agitation speed influences in the distribution of fluoride ions in sample waster. It can also accelerate the formation of the external boundary film. (Ghouti et al.,2009).The effect of stirring rate was observed by varying speeds from 60 to 180 rpm with optimum adsorbent dose of 10.0 g/L, pH of 5 with, contact time of 180 min and initial concentration of 5 mg/L. The **Figure 6.18** shows the effect of agitation speed on removal of Fluoride removal by FSB. Maximum Removal achieved was about 87.9 % for adsorbent dose of 6 gm/L at pH 7.5 with initial F^- concentration of 5 mg/L at 150 rpm. It was observed that at a given time, % removal of fluoride increased with the increase in the speed of agitation up to some extent after which it decreased considerably. This is because, at higher agitation speed adsorbate can make proper contact with adsorbent surface (Tembhurkar *et al.* 2006, Ghouti *et al.* 2009, Roy *et al.* 2013)

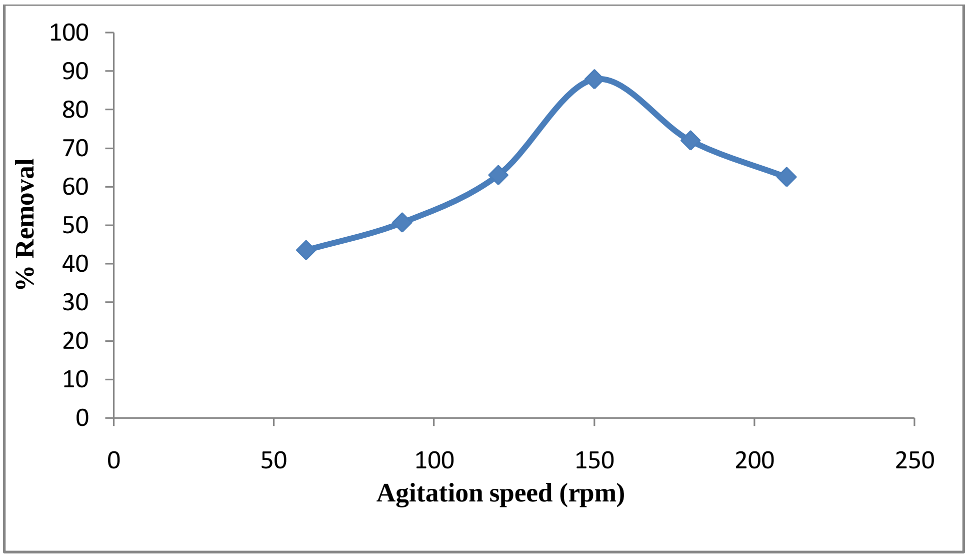

Figure 6.18 Effect of agitation speed removal of Fluoride

6.3.2.6 Effect of co-ions

A natural water source contains many co-existing ions that can compete with fluoride ions for active adsorption sites during an adsorption process. Bicarbonates calcium,, chlorides, phosphate, sulfates, and sodium ions are commonly found in groundwater (Tatawat and Chandel , 2008). To understand the effect of such existing co-ions on fluoride removal, batch adsorption studies were carried out at a single co-existing ion concentration of varying from 100 -250 mg/ L, and by keeping the other adsorption parameters constant. Figure 6.19 depicts the effect of co-ions on fluoride adsorption. It is observed that, the % removal efficiency of AMFSB decreased considerably in the presence for some co-ions in water. From the experimental results it is noted that high concentrations of nitrate and chloride ions up to (350 mg/L), had very marginal effect on fluoride removal efficiency as fluoride ions competed more than chloride and nitrate ions. Whereas, adsorption of F-was greatly affected by the presence of phosphate ions. In real life, groundwater with such high concentrations of ions are seldom present in drinking water. The experimental result showed that interference by competing ions followed the following order: nitrate <chloride <sulfate < bicarbonate <phosphate, from lower to higher concentrations in aqueous medium. The results obtained are in good agreement with results obtained for hydroxyapatite-based biochar materials reported by other authors to (Monal and George 2015, He, *et al.*, 2016).

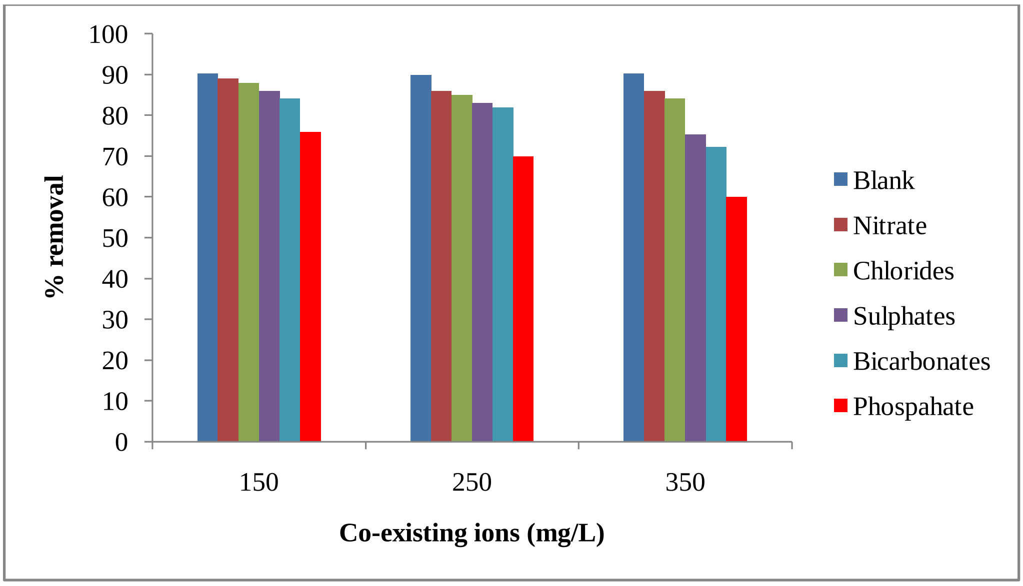

Figure 6.19: Effect of co-existing ions removal of Fluoride

6.4 Adsorption Isotherm

To recognize the adsorption potential and adsorption mechanism of FSB and AMFSB different adsorption isotherm models were employed in the present study. Langmuir and Freundlich are isotherm models were used to illustrate the surface properties and adsorption mechanism

6.4.1 Langmuir Isotherm

The Langmuir isotherm constants; q_m (mg/g) and K_L (L/mg) were obtained from the linear plot calculated using equation (**3)** are presented in **Table 6.7.** The value of R_L signifies the adsorption nature which can be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). **Figure 6.20(a) and (b)** shows the Langmiur isotherm plot for FSB and AMFSB.

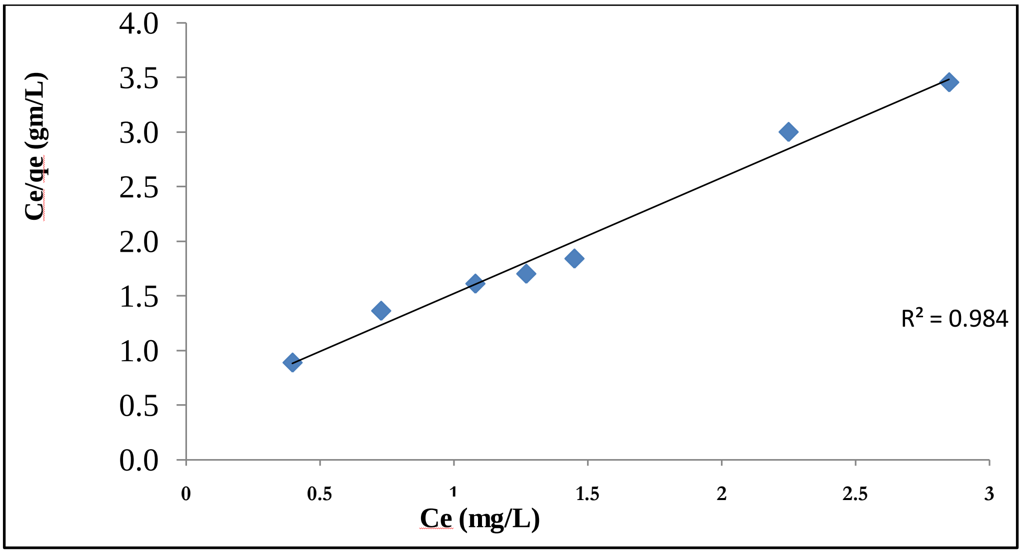

Figure 6.20 (a): Langmuir isotherm for FSB

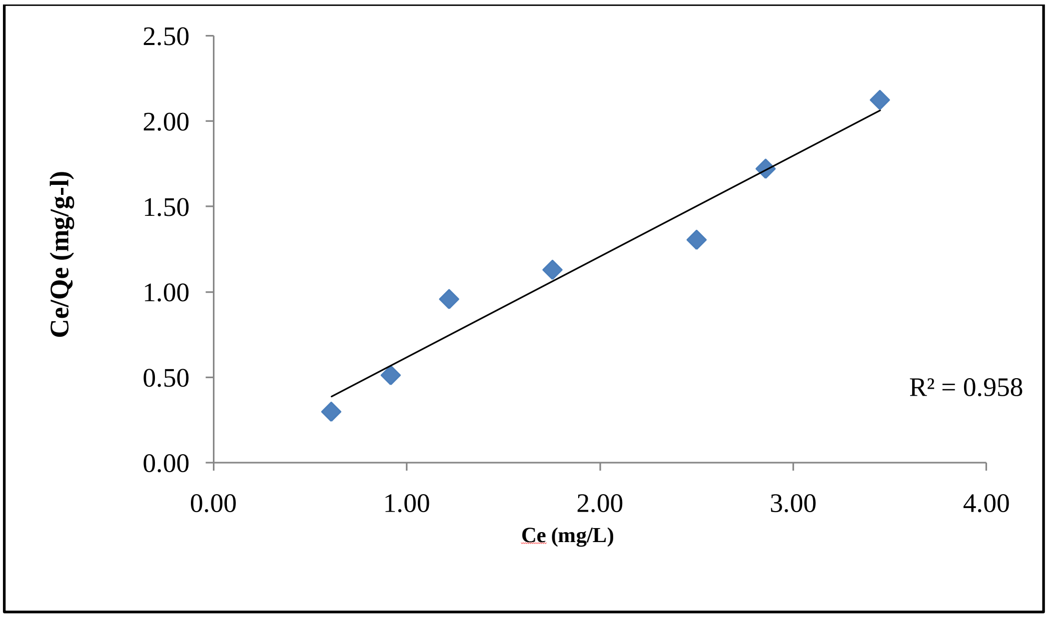

Figure 6.20(b): Langmuir isotherm for AMFSB

Table 6. 5: **Langmuir adsorption constants for fluoride removal**

Parameter	FSB	AMFSB
R^2	0.984	0.984
q_{max}(mg/gm)	2.16	6.12
b (L mg^{-1})	0.437	0.035
R_L	0.320	0.89

6.4.2 Frendulich Isotherm

The Frendulich isotherm is widely used to represent the relationship between the amount of adsorbate adsorbed per unit mass of the adsorbent and the adsorbate concentration in an aqueous solution at equilibrium. The logarithmic plot of the Freundlich isotherm is depicted in **Figure 6.21 (a) and (b).** The values of Freundlich constant (n and K_F) and regression coefficient (R^2) are calculated by using linear Freundlich isotherm equation (**5)** and and are given in **Table 6.6.** Based on values of regression coefficient (R^2), It was observed that FSB and AMFSB equilibrium data fitted well with Langmuir model than Frendulich model.

The plot for AMFSB with high R^2 values suggests the good applicability of the model as compared with R^2 value for FSB. The value of 1/n less than 1 obtained for confirmed that the adsorption of fluoride prepared FSB and AMFSB surface was favorable.

Table 6.6: Frendulich adsorption parameters for fluoride removal

Parameter	FSB	AMFSB
R^2	0.872	0.980
1/n	0.319	0.895
n	3.135	1.11
K_f	2.92	2.66

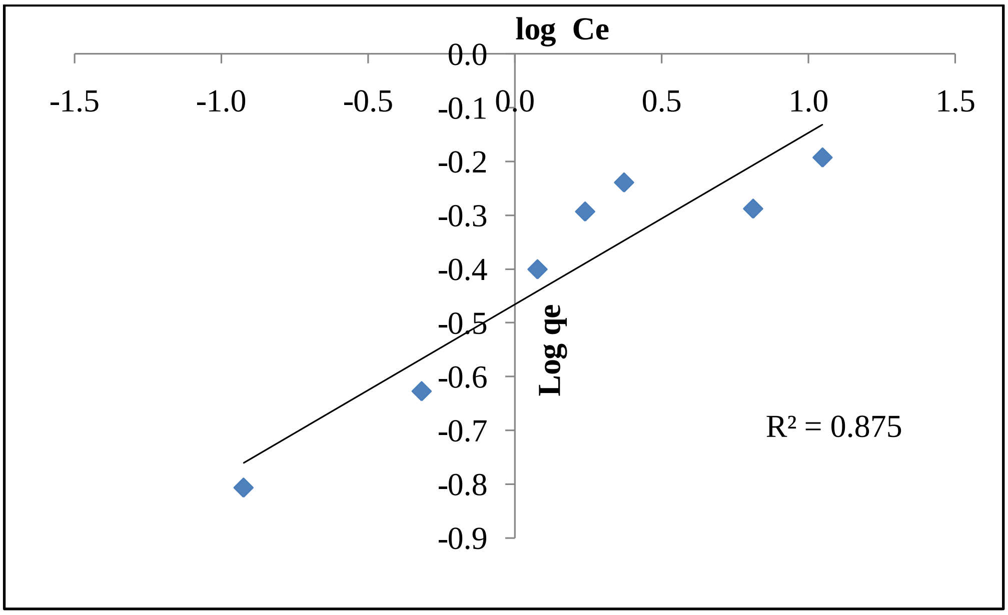

Figure 6.21(a): Frendulich isotherm for FSB

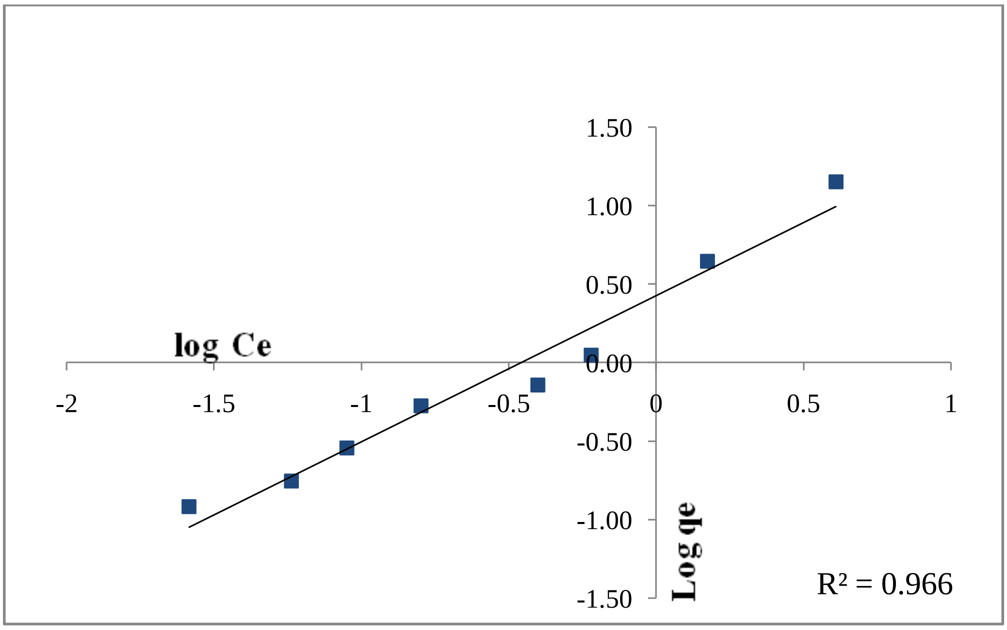

Figure 6.21(b) : Frendulich isotherm for AMFSB

6.5 Adsorption Kinetics

The applicability of a particular rate expression for the fluoride removal by FSB and AMFSB was examined from the goodness of data fit and regression coefficient value (R^2). Pseudo-first-order and pseudo-second-order model were used to elucidate rate limiting state of fluoride removal (Ho and McKay, 1998). It is observed that the pseudo-first-order equation gives a higher regression value of 0.964 and 0.990 for FSB and AMFSB confirming the adherence to the pseudo-first-order rate law. The excellent fit of experimental data into pseudo-first- order models suggest that the removal of fluoride onto the surface of FSB and AMFSB is favored by physisorption. The results indicated that the rate constant (K_1) and the fluoride concentration in water shares the direct linear relationship (Sarkar et al., 2006; Sundaram et al., 2008; Mariappan et al., 2015; Bhaumik *et. al.*, 2017). The linear plots for pseudo first order, pseudo second orderand intra-particle diffusion are shown as **Figure 6.26(a-b), Figure 6.27(a-b) and Figure 6.27** respectively. The results of pseudo first order kinetics are listed in **Table 6.7.** It is observed that (K_2) values of AMFSB are larger than that of the FSB ,these results are in good agreement with observations made by of Sundaram et al., 2008, Imtiaz et al., 2022; Chaudhari et al., 2023. the R2 value for intra-particle diffusion model was found to be 0.962 and 0.977 for FSB and AMFSB respectively. It confirms that intra-particle diffusion also attributed to the rate determining step of fluoride removal by FSB and AMFSB(Ghorai et al., 2005; Biswas et al., 2007; Gupta et al., 2013; Chaudhari et al.2023).

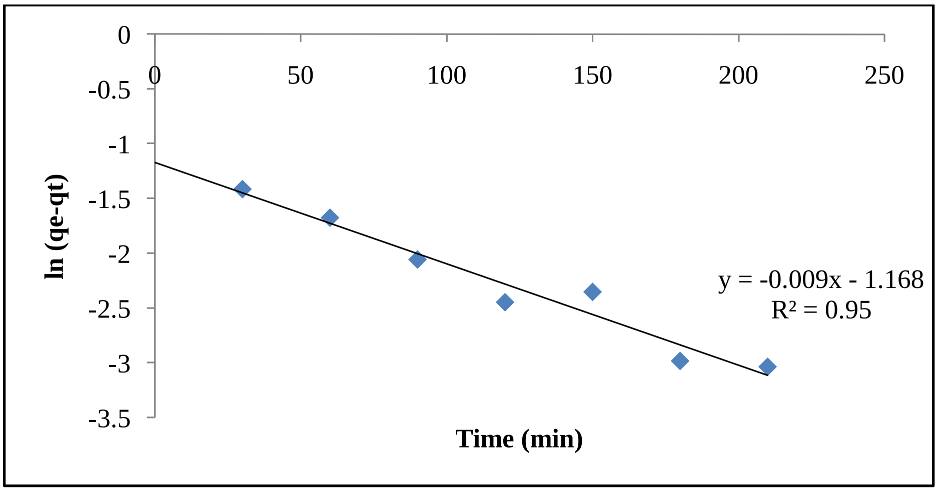

Figure 6. 22(a) : Pseudo-first-order plot for FSB

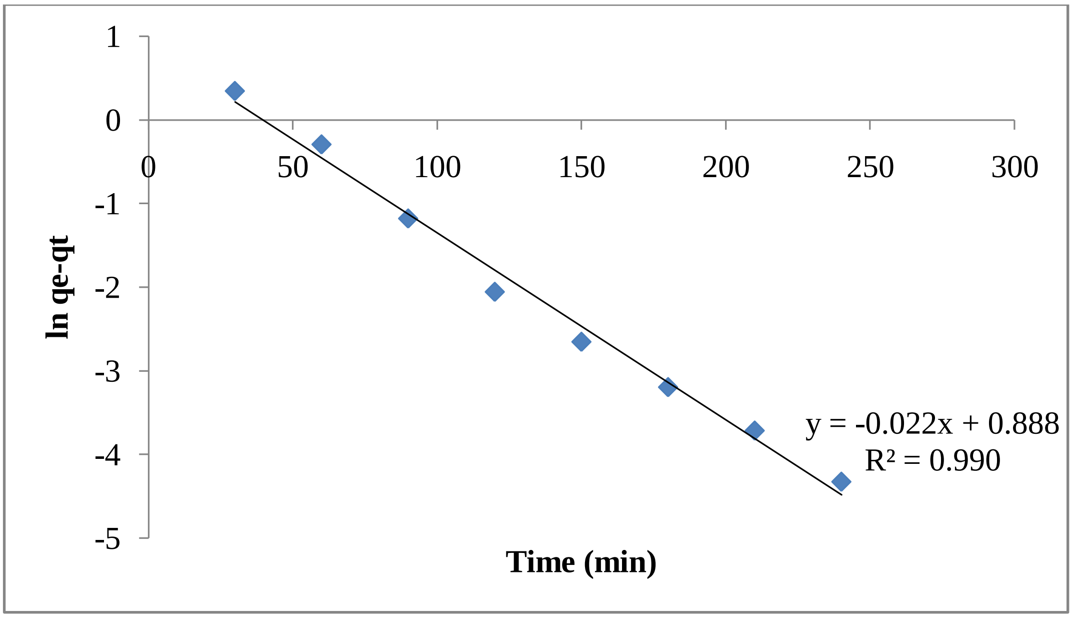

Figure 6.22 (b): Pseudo first order plot for AMFSB

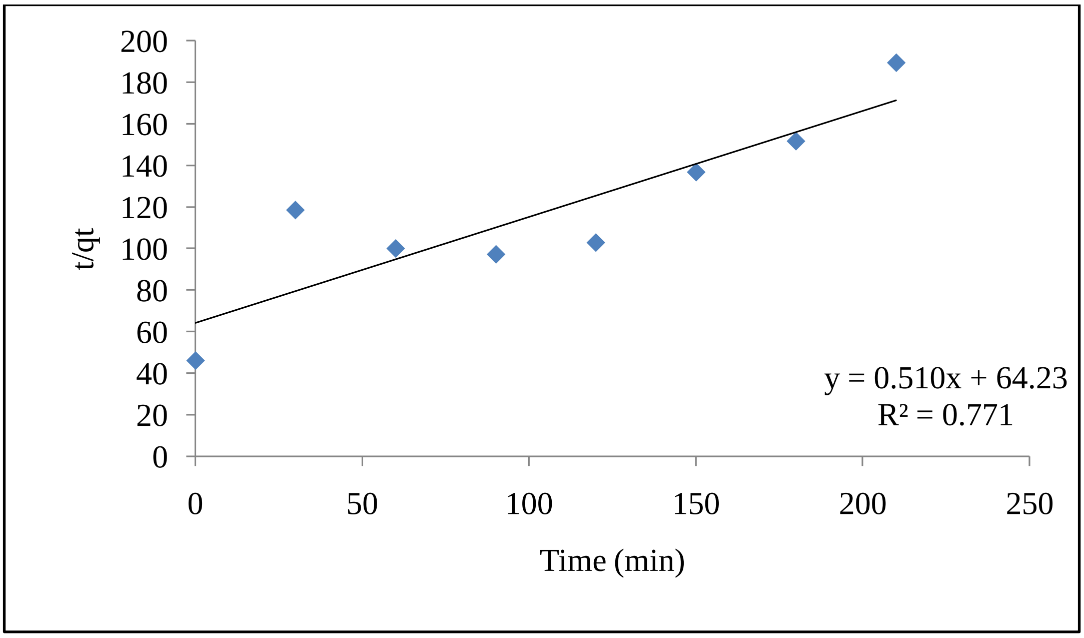

Figure 6.23 (a): Pseudo Second order plot for FSB

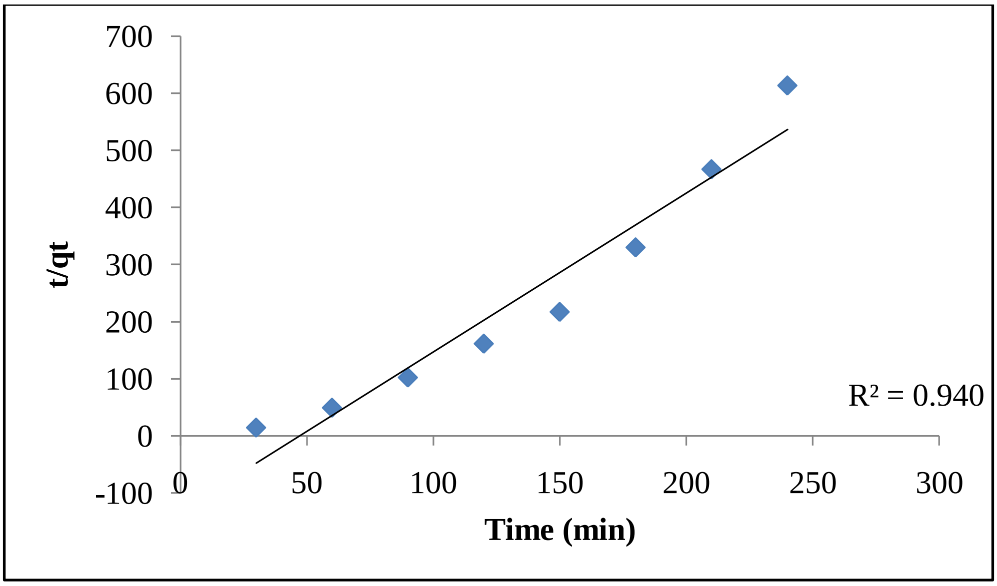

Figure 6.23 (b): Pseudo Second order plot for AMFSB

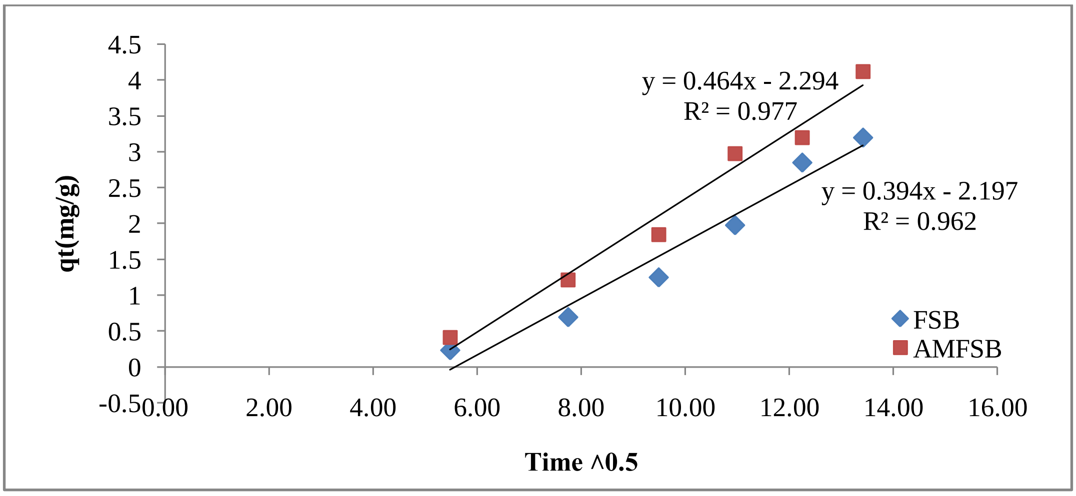

Figure 6.24 : Intra-particle diffusion model for FSB and AMFSB

Table 6.7 : Kinetic parameters for adsorption of fluoride on CAC and FSAC

Adsorbent	Pseudo-first-order model			Pseudo-second-order Model		
	Calculated q_e (mg/g)	K_1 (1/min)	R^2	Calculated q_e (mg/g)	K_2 (g/mg min)	R^2
FSB	2.01	0.021	0.964	1.53	0.0041	0.771
AMFSB	5.15	0.562	0.99	5.78	0.0082	0.940

6.6 Fixed-bed column adsorption study

Removal of fluoride by batch adsorption studies by many adsorbents have been reported in large, but the practical utility of an adsorbent in removing the fluoride from the water is mainly judge by column operation (Ghorai and Pant, 2004; Ghorai & Pant, 2005; Ma et al.,2008 ; Ku et al., 2011; Ramesh et al., 2012; Ghosh et al., 2015; Halder et al., 2015; He et al., 2017; Chatterjee et al., 2018). In the context of applicability, column operations are more competent mode of operation over batch adsorption process as these operations allows more efficient utilization of adsorbents.

The column experiments were also performed to evaluate the effect of column design parameter i.e. initial fluoride concentration, adsorbent bed height and flow rate. The column performance was explicated with breakthrough curves. A breakthrough curve can be obtained by plotting C_t/C_0 (the ratio of column effluent concentration at any time, t (min) and initial effluent concentration) versus either volume treated or time of treatment. The S-shaped breakthrough curves of were obtained for various fixed bed operating conditions. The various fixed bed parameter were calculated from data obtained from breakthrough curves. In this research work, the efficiency of AMFSB packed fixed-bed column for fluoride removal has been evaluated critically with varying range of column designing parameters. The kinetic modeling of the breakthrough curve was tested using Thomas model, Yoons – Nelson model and bed height service time (BDST) model.

6.6.1 Effect of adsorbent bed depth

To investigate the effect of bed height, there different bed heights i.e. 1, 2 and 3 cm maintaing F- concentration 7.5 mg/L and flow rate through fixed bed of 1.5 mL/min as constant. The breakthrough curves plotted is represented in **Figure 6.25.** It is observed that with increase in bed height, the breakthrough time and exhaustion time were increased. At initial stage, breakthrough curve showed gradual increase in slope and high fluoride removal. This gradual increase continued till the adsorbent bed got exhausted. At breakthrough point the concentration of fluoride in effluent increased more quickly so as the slope of the curve. The columns with minimum bed height got saturated earlier than the columns with more bed heights. **Table 6.5** gives the various column parameters evaluated. The volume of treated water also increased with increase in service time of fixed bed column. This is due to increase in bed height provides greater contact time between adsorbate and adsorbent, resulting in larger volume of treated water. (Rout et al, 2014; Patel 2020).

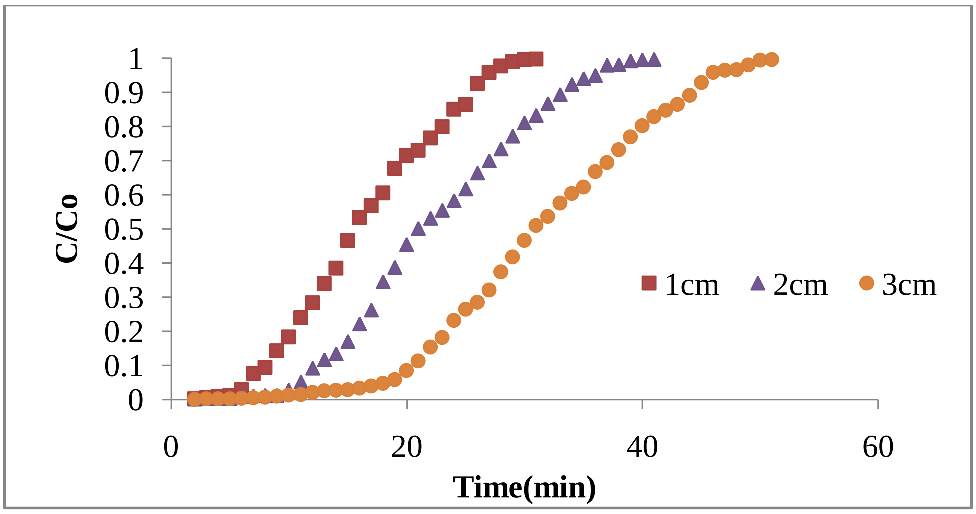

Figure 6. 25 :Breakthrough curve of fluoride removal at different bed height

The breakthrough volumes (V_b) of 425.46, 661.5 and 1010.3 ml were obtained for bed height 1.0, 2.0 and 3.0 cm were respectively at a fixed flow rate of 1.5 mL/min. It was noted that , with increased in bed height breakthrough volume (V_b) and empty bed contact time (EBCT) also increased(Ghosh *et al.*, 2015). The empty bed contact time (EBCT) was found to be 8.73, 16.75 and 25 .12 min for 1 .0, 2.0 and 3.0 cm of bed depth respectively.

6.6.2 Effect of flow rate

The effect of flow rate on fixed bed adsorption of fluoride by acidified fish scale biocar was accessed by , the flow rate was varied from 1.5 ml/min , 2.5ml/min and 3.5ml/min keeping the initial F- ion concentration (7.5 mg/L) and bed height (2 cm) constant. **Fig.6.26** demonstrates the influence of influent flow rate on fluoride removal breakthrough curve at a fixed bed height 2 cm of column. From the evaluation of breakthrough data it is observed that with increase in the flow rate, breakthrough time (t_b), exhaustion time (t_e) and uptake capacity (q_b) decreased whereas the treated volume was increased. This is due to, at lower flow rate F^- ions get longer contact time to diffuse with adsorbent surface (Maity, *et al.*2008; Mohan *et. al.*, 2017). Thus it is concluded that lower flow rates gives better column performance and treat large volume of water. The evaluated data also shows that adsorbent got exhausted earlier at higher flow rate. The various column parameters are listed in **Table 6.8**.

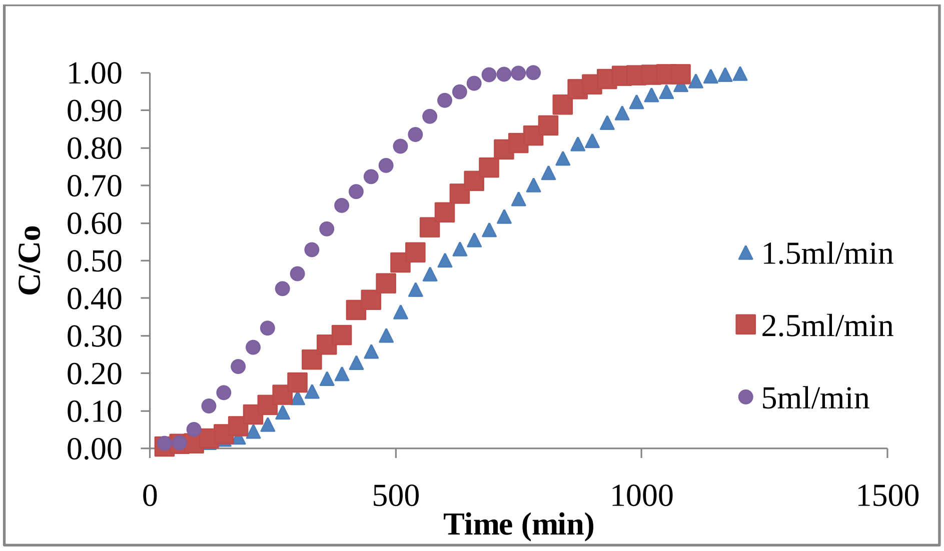

Figure 6.26 Breakthrough curve of fluoride removal at different flow rate.

6.6.3 Effect of initial F- concentration

To investigate the effect of F- concentration on the adsorption by acid modified fish scale biochar with a constant flow rate (2.5 mL/min) and bed depth (2 cm) , the F- ion concentration was varied 5 mg/L, 7.5 m/L and 10 mg/L. **Figure 6.27** shows the breakthrough curve at varying F-ion concentrations. The results obtained are summarized in Table 1. It is observed that, lower the initial concentration of influent adsorbate results in higher breakthrough time and larger V_e values. It is also observed that with higher F^- ion concentration the adsorbent bed het saturated in short time resulting in decrease in breakthrough time (t_b) and exhaustion time (t_e) (Murutu et al 2012; Mohan et al, 2017). The evaluated data reveals that maximum uptake capacity occurs at highest F- ion concentration. This is due to fact that in the aqueous phase higher initial F- ion concentration the creates higher gradient which results into greater driving force for the adsorption of F^- ion.(Ranjan et al., 2009; Mohan et al., 2017).

The results also showed that the plateau of the breakthrough curve reached faster with increasing flow rate, which was due to the decrease of contact time between the solute in mobile phase and the surface of the stationary phase making quicker appearance of adsorption zone at the bottom of the column.

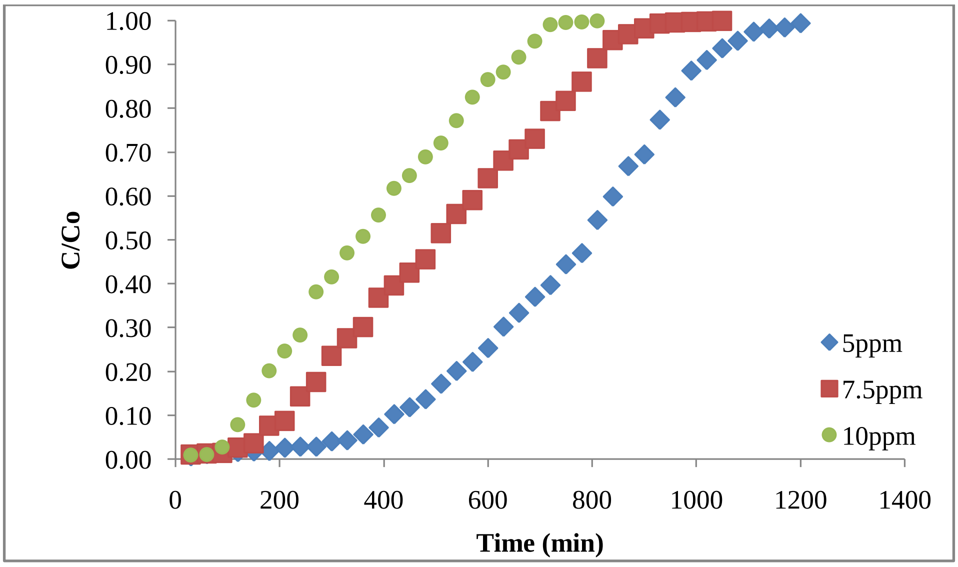

Figure 6.27 Breakthrough curve of fluoride removal at different F- ion concentration

Table 6.8 : Experimental column parameters obtained from breakthrough curve

Ci (mg/L)	Z (cm)	M (gm)	Q (ml/min)	t_b (min)	t_e (min)	t_z (min)	MTZ cm	V_b (ml)	V_e (ml)	q_b (mg/gm)	BV cm3	EBCT (min)
7.5	1	2	1.5	283.64	734.48	450.84	0.61	425.46	1101.72	1.60	12.56	8.373
7.5	2	4.12	1.5	441	966.21	525.21	1.09	661.5	1449.32	1.20	25.13	16.75
7.5	3	6.2	1.5	673.53	1297.12	623.59	1.44	1010.3	1945.68	1.22	37.69	25.12
7.5	2	4.12	1.5	394	990.05	596.05	1.20	591	1485.08	1.08	25.13	16.753
7.5	2	4.12	2.5	314.23	832.45	518.22	1.31	785.575	2081.13	1.18	25.13	10.052
7.5	2	4.12	3.5	174.08	577.3	403.22	1.41	609.28	2020.55	1.28	25.13	7.18
5	2	4.12	2.5	630	1020	390	1.02	1575	2550	1.91	25.13	10.052
7.5	2	4.12	2.5	316.72	832.78	516.06	1.24	791.8	2081.95	1.44	25.13	10.052
10	2	4.12	2.5	183.19	645.72	462.53	1.43	457.98	1614.3	1.11	25.13	10.052

6.6.4 Breakthrough curve modeling

6.6.4.1 Thomas model

The Thomas model is an extensively mathematical tool to describe the performance of fixed bed adsorption column. The model is significantly based on Langmuir kinetics of adsorption and 2nd order reversible kinetics of rate of driving force (Yahya *et al.*, 2020, Cruz *et. al.*, 2020, Kumari Usha *et al.*, 2021). The mathematical expression of Thomas model in its linear form is given below,

$$\ln\left(\frac{C_O}{C_t} - 1\right) = \frac{K_{th} \times q_{th} \times M}{Q} - K_{th} \times C_O \times t \qquad (18)$$

where, K_{Th} is the Thomas rate constant (l/mg. min), q_{th} (mg/g), represents maximum solid phase concentration. The plot of ln (C/C_0 - 1) vs time (t) yield a straight line with slope as K_{th}, Co and intercept as M .q_{th}. K_{th}/Q are the process parameters are evaluated from the Thomas model plot and values of K_{th} and $q_o$are summarized in **Table 6..9** . The plot showed the satisfactory correlation having R^2 values 0.96, 0.96 and 0.968 for 1cm, 2cm and 3 cm bed height respectively. Hence, it is evident that , Thomas model reasonably fits well and interpret the adsorption of fluoride on acid modified fish scale biochar (Ibrahim *et al.*, 2016, Cruz *et. al.*, 2020, Kumari *et. al.*,2021)

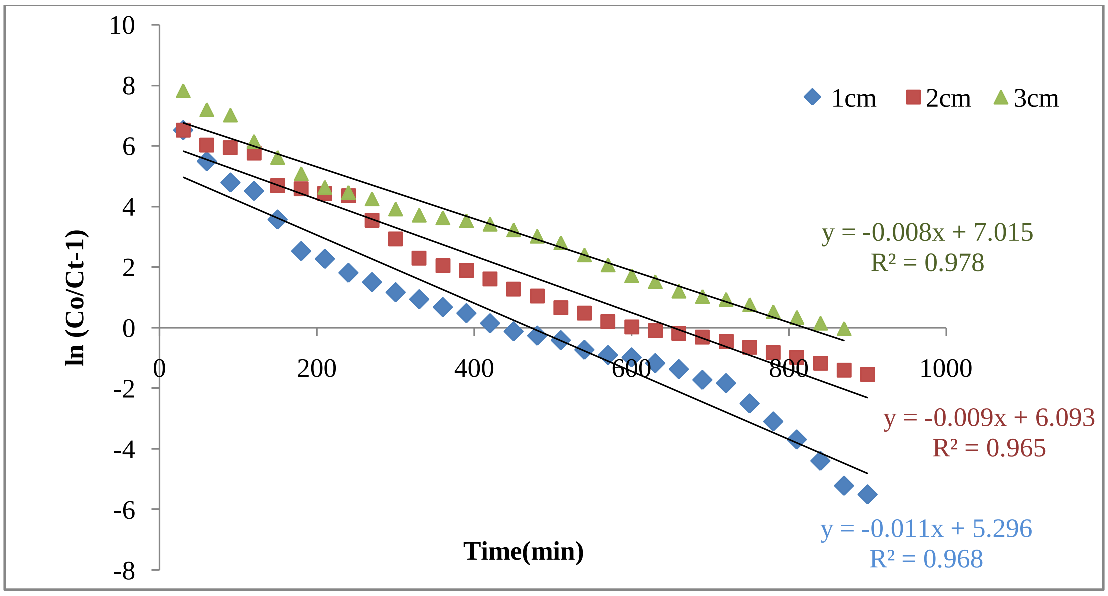

Figure 6.28: Thomas model plot of ln(Co/Ct - 1) vs time (t) at different Bed Depth

Table 6.9 : Parameters of the Thomas model under different bed height using linear regression analysis

Input parametr			**Thomas parameters**		
Co (mg/l)	Z (cm)	M (gm)	K_{th} (ml/mg min)	**q_o (mg/gm)**	**R^2**
7.5	1	2	1.1	3.97	0.968
7.5	2	4.12	1.2	3.75	0.965
7.5	3	6.2	1.8	4.84	0.978

6.6.4.2 Yoon-Nelson model

The Yoon–Nelson model is the simplest to predict the nature of adsorption process and exhaustion time (te) for given adsorbate concentration (Gupta and Garg, 2019, Bhan *et al.*2021). The expression of Yoon–Nelson model is given by,

$$\frac{C}{C_0} = \frac{1}{1 \pm \exp\left(K_{yn}\{\tau - t\}\right)} \tag{19}$$

This can also be expressed as,

$$ln\frac{C}{C_o - C} = K_{yn}(\tau - t) \tag{20}$$

where, the K_{yn} is rate constant and τ (min) time taken for adsorbate breakthrough. The Fig. 3 illustrates the plot of ln [C/(C$_0$- C)] against t is used to estimate the Ye-N constants (i.e., K_{yn} and τ). It is observed that the plots have good correlation coefficient 0.990, 0.96 and 0.98 for 5mg/L , 7.5 mg/L and 10 mg/L initial F- ion concentration. The Y-N parameters obtained are summarized in **Table 6.10** The result indicates that increase in initial concentration attributes to rise in the values of Y-N rate constant (K_{ny}) whereas the value of τ decreases subsequently. It his is due to fact that the fast saturation of adsorbent present in fixed bed column (Demarchi et al., 2015; Bhan et al., 2021).

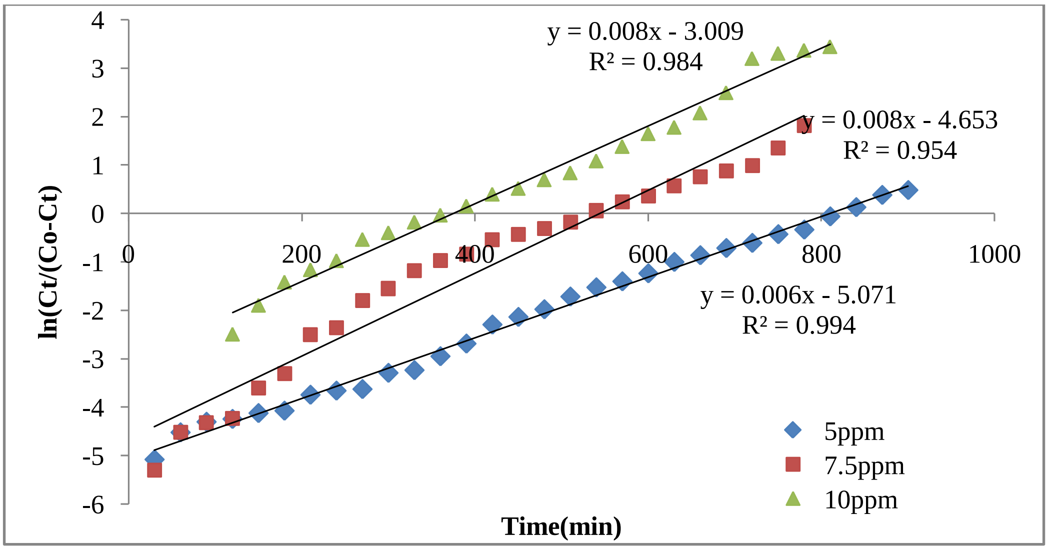

Figure 6.29 : Yoon-Nelson model plot at different F- ion concentration

Table 6.10 : Parameters of the Yoon-Nelson model under different F- Concentrations

Experimental conditions			Thomas parameters		
Co (mg/l)	Bed Height	M (gm)	K_{yn} (ml/min)	τ(min)	R^2
5	2	2	0.0061	845.17	0.99
7.5	2	4.12	0.0079	581.625	0.96
10	2	6.2	0.0087	376.125	0.98

6.6.4.3 BDST model

The bed depth service time model is another widely used mathematical model to describe the the breakthrough curves parameters. (Ahamad and Jawed, 2012). The BDST model is significantly based on the theory of the surface reaction rate (Ramesh et al , 2012). The simple mathematical expression of height of adsorbent bed (Z) and service time(t) is given as (Hutchins, 1973), which is given below,

$$t = \frac{N_o z}{C_o u} - \frac{1}{K_o C_o} \ln\left(\frac{C_o}{C_b} - 1\right) \qquad (21)$$

where, K_o is adsorption rate constant (L/mg/min), N_o represents adsorption capacity (g/L), t (min), linear flow velocity is u (cm/min). **Figure 6.30** depicts the BDST model plot for AMFSB.

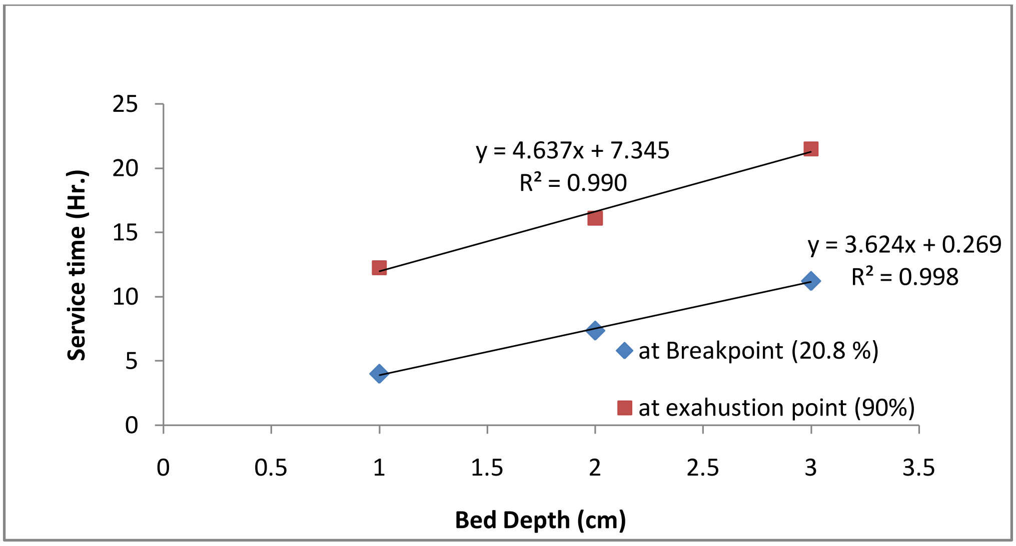

Figure 6.30: BDST model plot at C/Co

Table 6.11 : Parameters of the BDST model

Experimental conditions			**BDST parameters**		
Co (mg/l)	Bed Height	M (gm)	*K_o* (L/mg/min)	N_o (mg/L)	**R^2**
7.5	2	2	0.689	4.65	0.99
7.5	2	4.12	-0.045	8.31	0.99

The data fits well in a linear graph with good R^2 value of 0.998 and 0.990 for breakthrough and exhaustion point of adsorbent respectively. The adsorption rate constant (K_o) and the dynamic bed capacity per unit volume of bed at breakthrough were calculated as 0.689 (L/mg/min) and 4,65(mg/L) respectively. As reported by Vijayaraghavan *et al.*, 2004; Demarchi et al., 2015 and Bhan et al., 2021, at larger value of adsorption rate constant (K_o), breakthrough will occurs at lower bed heights whereas a smaller K_0 value requires higher bed height to avoid breakthrough. The evaluated co-efficient for that the potential of acid modified fish scale biochar to absorb F- ion increased with increase in C/C_O ratio which suggest that BDST model satisfactorily fits the fixed bed column data.(Mohan *et. al.*, 2017; De *et. al.*, 2018)

6.7 Response Surface Methodology

The Response Surface Methodology (RSM) is widely used statistical tool to understand the effect of individual and interactive effects of independent variables. The conventional methods of optimization of multiple variables requires performance of number of experiments and consumes time to perform. Changing a multiple variables at a time can be a solution to this. Designing experiments can be easily done using statistical techniques such as response surface methodology (RSM) (Chatterjee *et al.*2012; Thakur et al., 2016; Halder et al., 2016; Bhaumik 2017; Mittal et al., 2020; Ahmadi et al., 2021; Shekhawat et al., 2023) . RSM has can evaluate interaction between multiple input parameters which is not possible with one-factor-at-a-time (OFAT) method. (Alkhatib et al. 2015). In the present study, statistical analysis using Design-Expert (Stat-Ease Inc.,version7.0.3, Minneapolis, USA, trail version) was employed for designing the experiments, data analysis, and interpretation According to The Box–Behnken design, 27 experiments were carried out to determine simultaneously the interaction effects. Response Surface Methodology was also used to explore optimal condition for fluoride removal.

The **Table 6.12** gives experimental levels and ranges of the independent parameters used in fluoride removal experiments. The input factors were pH, contact time (min), initial fluoride concentration(mg/L), adsorbent dose (mg) .

Table 6.12 Experimental range and levels of the independent parameters

Coded variables	Code notation	Coded Levels		
		−1	0	+1
A	**pH**	2	6	10
B	**Time(min)**	60	120	180
C	**Initial F-(mg/L)**	2	7.5	10
D	**Dose(mg)**	2	5	8

The % of removal was treated as the response. In the present investigation the second-order polynomial equation by Box-Behnken design (BBD) was used to predict the response. Analysis of variance (ANOVA) was performed with a 95% confidence level. The fit of the model was determined by determination coefficient R^2 and adjusted R^2. (Ahmadi et al., 2021; Haldar et al., 2020; Mittal et al., 2020; Shekhawat et al., 2023; Buddharatna, 2016). **Table 6.13** shows the results obtained for ANOVA. F-test ANOVA was used for finding significance of the regression model equations. The F-values and P-values gave the significance of each variable (Ayoob et al., 2008; Bhaumik & Mondal, 2016; Roy & Das, 2016; Mourabet et al., 2017; Mukherjee & Halder, 2016; Roy et al., 2018). P-values for all independent variable are found to be < 0.05 showing that they are highly significant for adsorption of fluoride by AMFSB. The **Model F-value** of 36.89 confirms that the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. In removal of fluoride by AMFSB it is concluded that A, B, C, D, AB, BC, BD, B^2, C^2, D^2 are significant model terms. It was found that except for interaction between time and initial concentration i.e., BC all the interaction effects between input variables were statistically insignificant for AMFSB.

Table 6.13: Analysis of variance (ANOVA) for Response Surface Quadratic Model.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	8.26	14	0.5902	36.89	< 0.0001	significant
A-ph	0.0686	1	0.0686	4.29	< 0.0006	
B-time	3.59	1	3.59	224.43	< 0.0001	
C-F	0.6971	1	0.6971	43.57	< 0.0001	
D-Dose	0.8922	1	0.8922	55.76	< 0.0001	
AB	0.6576	1	0.6576	41.10	< 0.0001	
AC	0.0424	1	0.0424	2.65	0.1297	
AD	0.0000	1	0.0000	0.0019	0.9659	
BC	0.3853	1	0.3853	24.08	0.0004	
BD	0.1303	1	0.1303	8.14	0.0145	
CD	0.0040	1	0.0040	0.2510	0.6254	
A^2	0.0052	1	0.0052	0.3276	0.5777	
B^2	0.1868	1	0.1868	11.67	0.0051	
C^2	0.1155	1	0.1155	7.22	0.0198	
D^2	1.01	1	1.01	62.90	< 0.0001	
Residual	0.1920	12	0.0160			
Lack of Fit	0.1845	10	0.0184	4.91	0.1808	not significant
Pure Error	0.0075	2	0.0038			
Cor Total	8.46	26				

The RSM model equation obtained for fluoride removal by AMFSB in coded form is : *Removal (%) =* $8.33-0.756\,A++0.5470\,B-0.2410\,C+0.2727\,D-0.4055AB+0.1029AC-0.0028AD+0.3104BC+0.1805BD-0.0317\,CD-0.0313\,A^2-0.1871\,B^2+0.1472\,C^2+0.4344\,D^2$

It can also be written in input parameter form as:

Removal (%) =8.33-0.756 pH++0.5470 time -0.2410 Intial F^-*+ 0.2727 Dose - 0.4055pH.time+0.1029pH.intial* F^- *-0.0028pH.dose + 0.3104time. initial* F^- *+ 0.1805 time. Dose - 0.0317 Initial* F^-*Dose - 0.0313* pH^2*-0.1871* $time^2$ *+0.1472 initial* F^{-2} *+0.4344*$dose^2$

Table 6.14 gives the Fit statistics for fluoride removal by AMFSB. The RSM result showing higher values R^2 (0.9773), **Adjusted R^2 (0**.9508) and **Predicted R^2** (0.923) confirmed a good fitting of experimental data to model.

Table 6.14: Fit Statistics for fluoride removal by AMFSB

Std. Dev.	0.1265	**R^2**	0.9773
Mean	8.49	**Adjusted R^2**	0.9508
C.V. %	1.49	**Predicted R^2**	0.923
		Adeq Precision	25.3057

Figure 6.31(a) through Figure 6.31 (e) presents 3D surface plots showing various interactive effect of pH, contact time, initial fluoride concentration and adsorbent dose for percent removal efficiency of fluoride by using AMFSB.. Two independent variables were varied simultaneously to evaluate interactive effects of various parameters. The 3D plot can be interrelated as red color indicating high % removal and moving towards blue % removal decreases. It was found that % removal of fluoride was range between 50 and 91 %.

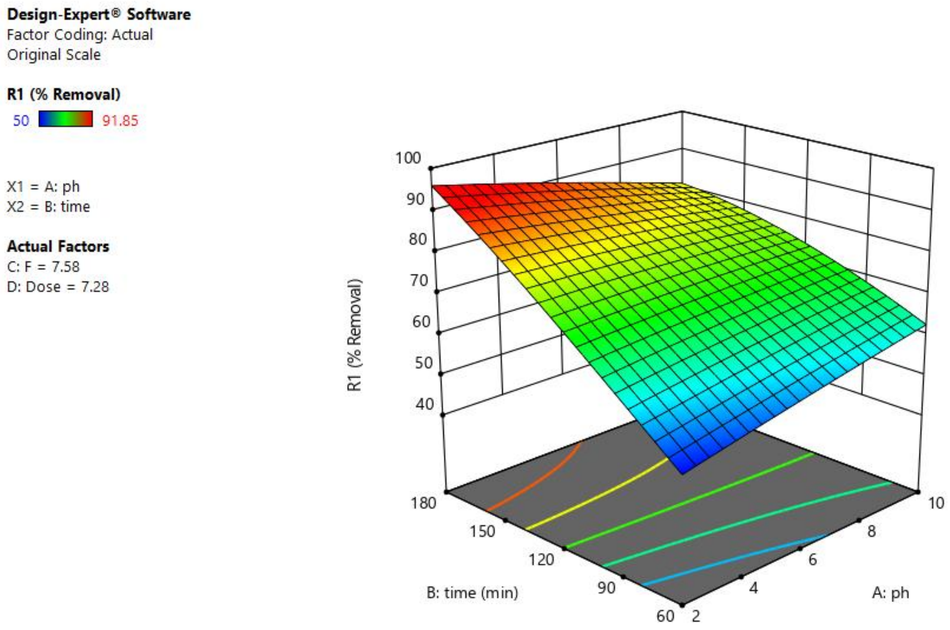

Figure 6.31 (a) : Response surface plot for effects of pH and contact time

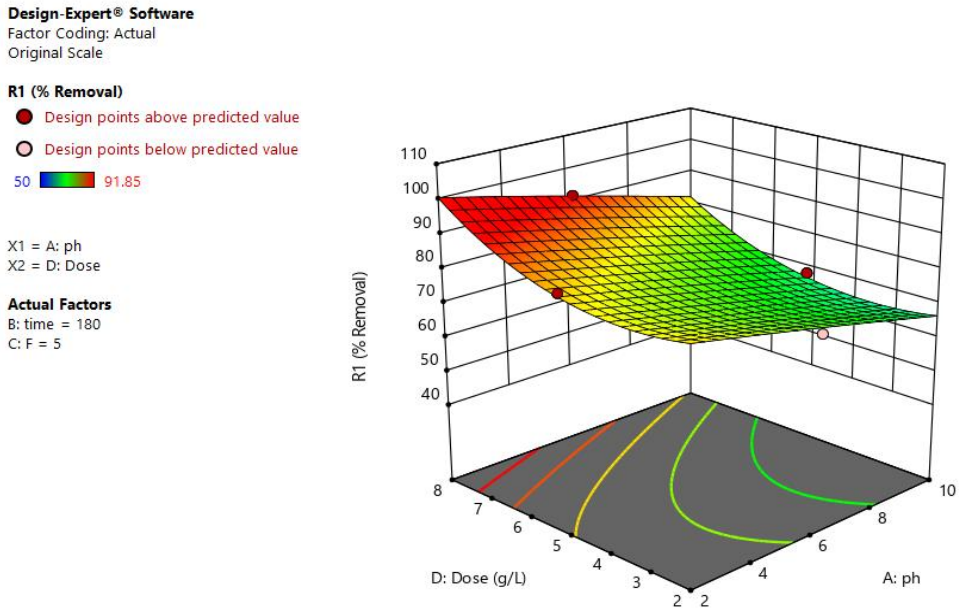

Figure 6.31 (b) : Response surface plot for effects of pH and adsorbent dose

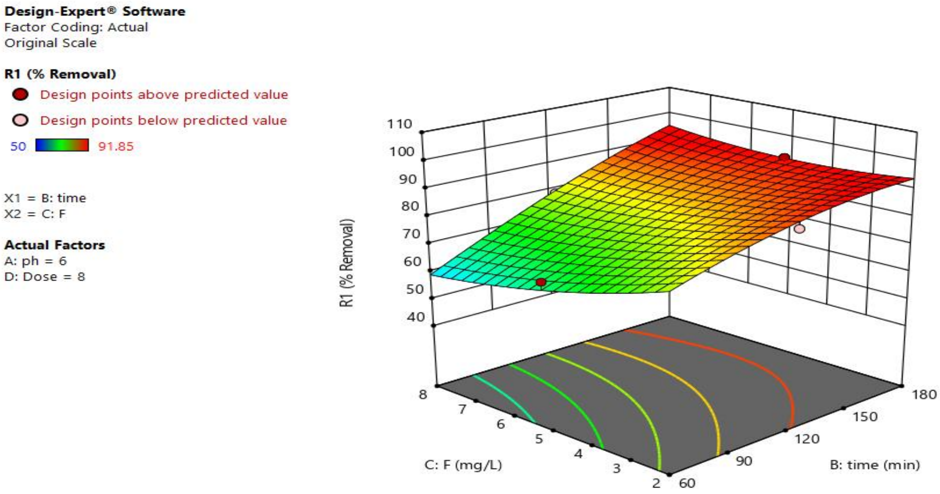

Figure 6.31 (c) : Response surface plot for effects of contact time and initial F^-concentration

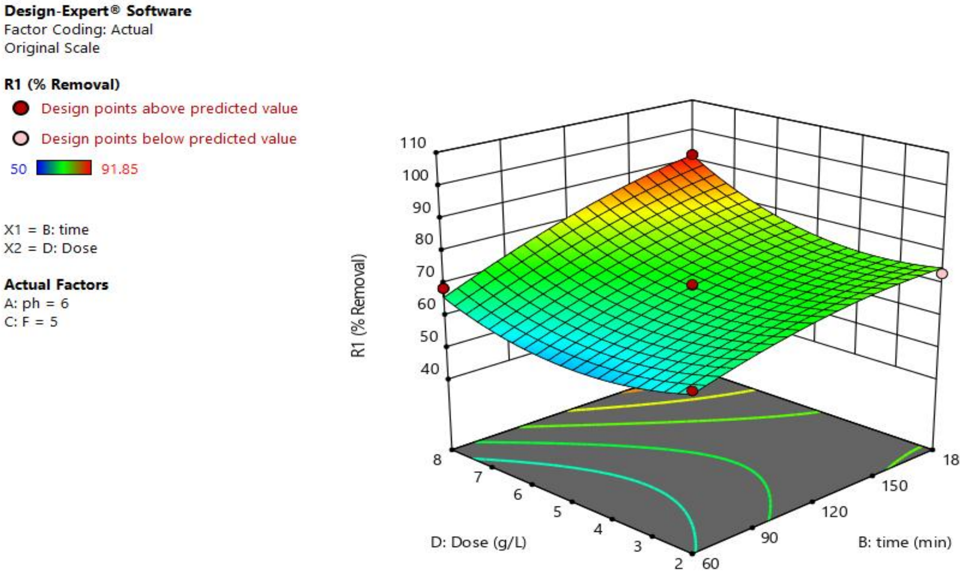

Figure 6.31 (d): Response surface plot for effects of contact time and adsorbent dose

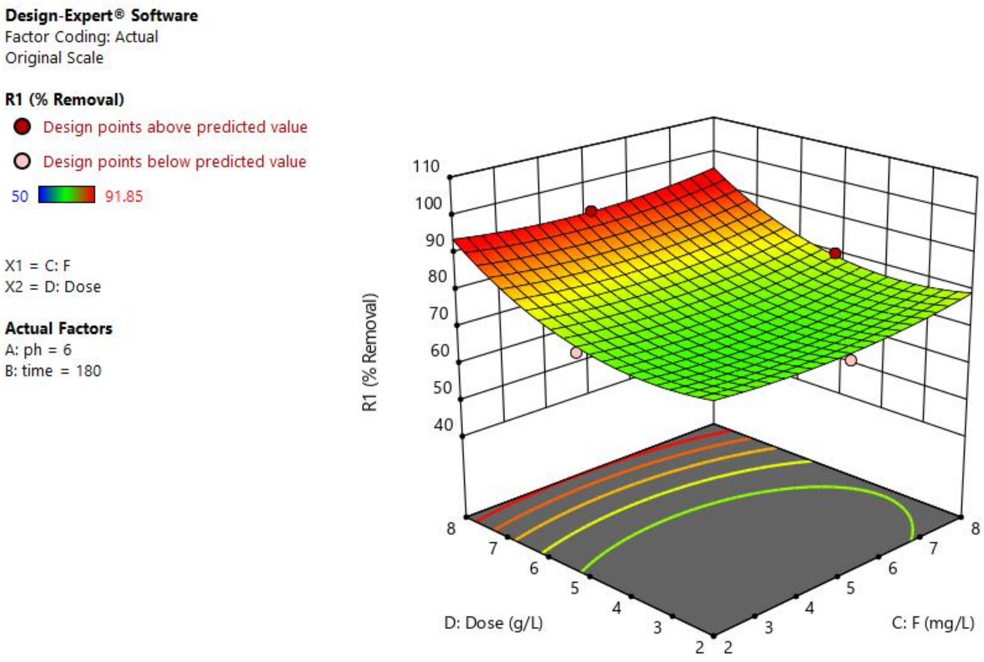

Figure 6.31 (e) : Response surface plot for effects of adsorbent dose and initial F^-concentration

Perturbation plot is shown **Figure 6.32** demonstrates the effect of all the factors at a particular point in the design space. Any steep slope or curvature is characterized as , the response is dependent on that factor. A relatively flat line shows that the factor has relatively little or no effect on response (Anderson & Whitcomb 2004).From the plot it is evident %removal of fluoride is dependent on all input parameters, viz. pH , contact time, initial fluoride concentration and adsorbent dose .

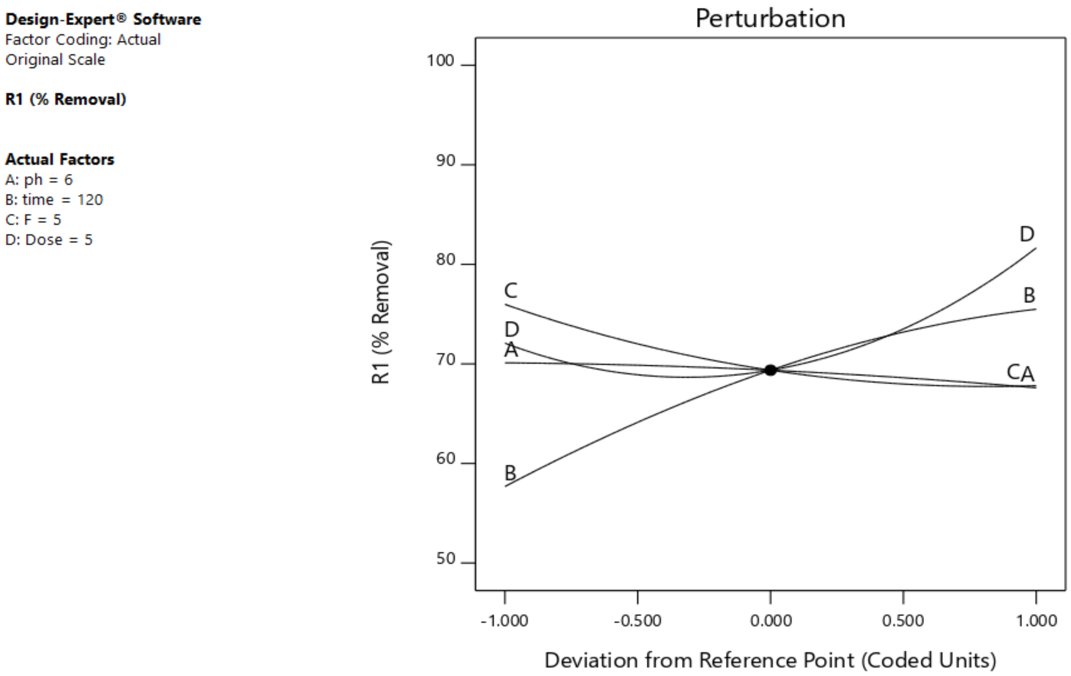

Figure 6.32: Perturbation plot showing effect of parameters on fluoride removal

.

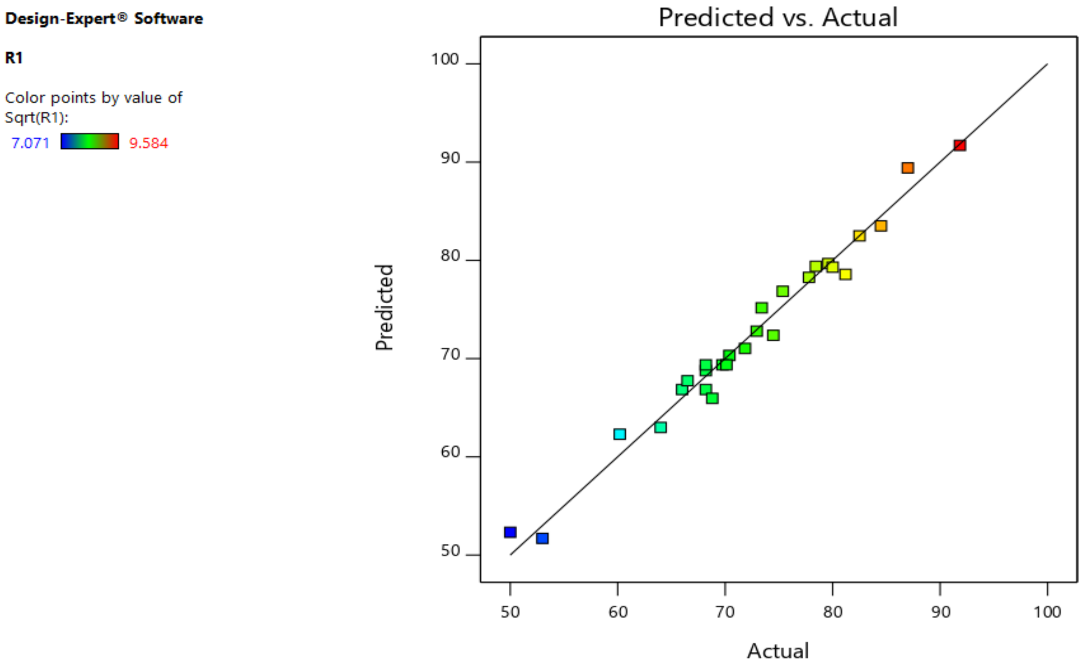

Figure 6.33: Plot showing the distribution of actual vs. predicted fluoride removal %

Figure 6.33 shows plot actual and predicted % removal of fluoride by AMFSB. The plot showed that all point falls closer to the straight line indicating both values are in reasonable agreement with each other. The plot implied good correlation between input and output variables could be drawn by the model developed. These observations are in good agreement with results reported by Halder et al., 2016; Bhaumik 2017; Mittal et al., 2020 and Ahmadi et al., 2021.

The normal plot of residuals showing % probability versus residual error is shown in **Figure 6.34** gives. The plot considers residuals with a 95% confidence. The graph confirmed that observations from experiments come from a normally distributed population as all points fall approximately nearer to the straight line (Ghosh et al., 2016)

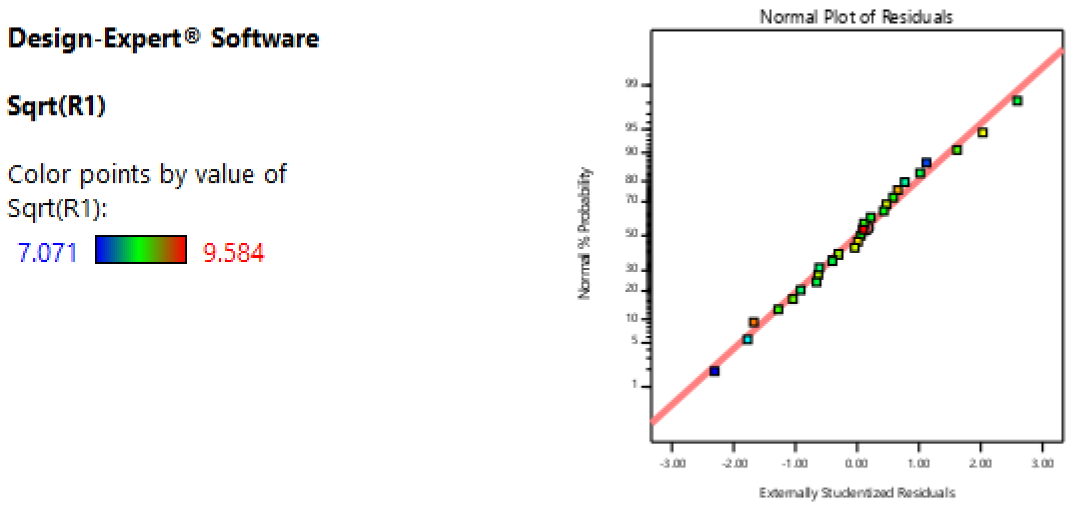

Figure 6.34: Normal plot of residuals showing % probability versus residual error

For fluoride removal using AMFB optimal conditions of parameters was predicted using Desirability ramp solutions. The RSM analysis predicted maximum % removal efficiency to be 85% at optimum pH of 7.1, contact time of 165.885 min, initial fluoride concentration of 5.26912 mg/L. and adsorbent dose of 6.21 mg/L. The results obtained by RSM were verified by batch adsorption experiments at obtained optimum conditions. Maximum 83.6 % removal of fluoride was obtained in batch study conducted with optimum variable conditions. The batch study revealed that actual % removal of fluoride was very near to the results of RSM analysis. It confirmed that RSM with BBD a design approach can be effectively employed to optimize input parameters for fluoride removal by Acid modified biochar.

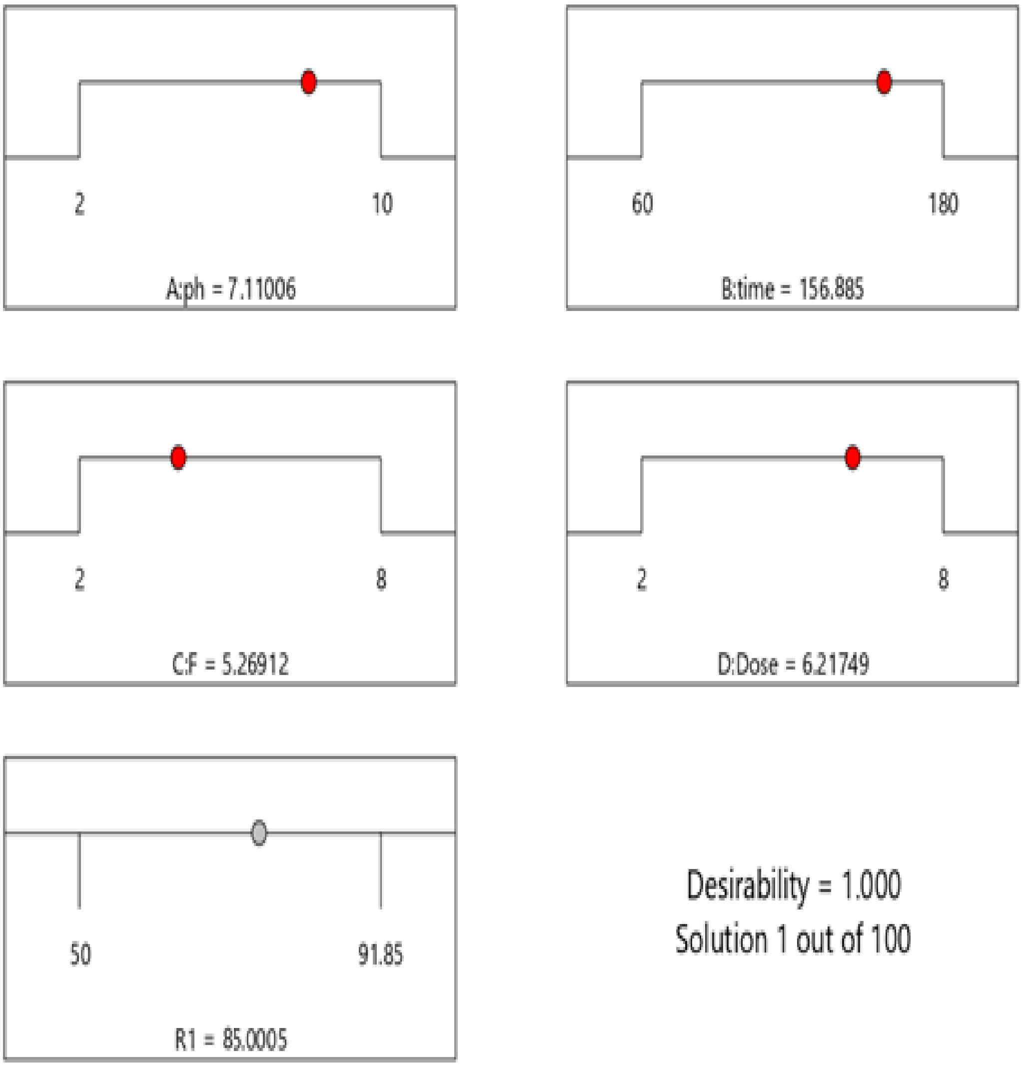

Figure 6.35: Desirability ramp for numerical optimization of process parametes

6.8 *Comparison of fluoride removal using AMFSB with other adsorbent*

Many adsorbents have been explored and proved to be efficient in fluoride removal from water environment. **Table 6.15** compares some of the previously reported adsorbents with Fish Scale biochar (FSB) and Acid modified fish scale biochar (AMFSB). The FSB and AMFSB showed relatively good adsorption capacity for fluoride as compared adsorbent reported below.

Table 6.15: Comparison of fluoride removal capacity of different adsorbent

Adsorbent	Adsorption capacity (mg/g)	Reference
Used tea leaves	0.51	Methodis et al.,
Rice straw activated carbon	15.90	Daifullah et al
Baggasee carbon	1.15	Yadav et al
Activated Eicbornia crassipes	0.027	Haldar et al
Granular ceramic	0.941	Chen et al., 2010
Carbon slurry	4.66	Gupta et al., 2007
Hydroxyaptite	3.12	Mourabet et al., 2015
Egg shell powder	1.09	Bhaumik et al. 2012
Fish scale dust	4.89	Bhaumik et al., 2017
Fish scale biochar	2.12	Present study
Acid modified biochar	5.15	Present study

Chapter - 7

Conclusion

Chapter 7

Conclusion

7.1 Conclusions

In this present investigation a waste based Fish scale biochar and its composites was studied for its potential to remove fluoride from water environment. The following conclusions are derived after detailed investigation of novel adsorbents prepared for fluoride removal.

- The detailed physiochemical characterization of adsorbent material was done. The BET surface analysis showed good surface area of 37.967 m2/ gm. The SEM-EDS , FTIR and XRD analysis confirmed the mesoporous structure of FSB and presence of Fluoride binding constituents in the prepared biochar.
- The batch studies were conducted to see the effect of process parameters. It was found that the removal of fluoride with FSB and AMFSB was greatly influenced by pH, initial concentration of Fluoride, contact time and adsorbent dose.
- Langmuir isotherm and Freundich isotherm models were studied and found to be favorable for both FSB and AMFSB. The coefficients obtained for isotherm indicated prominent mechanism of monolayer surface adsorption.
- The experimental data fitted well with Pseudo first order kinetic model and intra-particle diffusion model and confirmed that both attributed to rate limiting kinetic removal fluoride by FSB and AMFSB.
- Breakthrough column study indicated EBRT time as 25.12 min for AMFSB which is relatively higher than that of any adsorbents recently explored.
- The results have also been described by statistical tool RSM. The RSM analysis predicted maximum % removal efficiency to be 85% at optimum pH of 7.1 , contact time of 165.885 min, initial fluoride concentration of 5.26912 mg/L. and adsorbent dose of 6.21 mg/L.
- The optimum conditions of process parameters obtained by RSM are very close to the results obtained from batch studies conducted.

- Experimental study reveals the adsorption is favorable and Fish scale derived biochar is actively found for suitability of F- removal from water environment.
- The present work has demonstrated that the abundantly available fish scale waste biomass can be converted into excellent adsorbent for removal of fluoride. It will a veil some of the existing problem of Solid waste management as well as also reduce the burden of environmental pollution due to fishery waste
- In terms of the magnitude of fluoride contamination problem, exploring the novel and environment friendly Fish scale biochar seems to be a promising solution for fluoride deconatamination of drinking water.

7.2 Future Scope of the study

- Temperature dependent isotherm and kinetic parameters to be studied in detail.
- Hybrid process for the treatment of fluoride to be developed for further efficient removal of fluoride
- Desorption and regeneration studies to be undertaken to maximise the material usage.
- Real life sample would be used for for fluoride removal in real life scale..
- The experiment should be done taking the detailed investigation for effect of Iron , Hardness causing salts etc. for multispecies effect on fluoride remval.

References

Referances:

1. Abdullah B., Vo D.V., "An evaluation of fish scales as potential adsorbents: pH and concentration effect." Applied Mechanics and Materials, 625 (2014): 73-76.
2. Abe I., Iwasaki S., Tokimoto T., Kawasaki N., Nakamura T., Tanada S., "Adsorption of fluoride ions onto carbonaceous materials." Journal of colloid and interface science, 275.1 (2004): 35-39.
3. Achieng G.O., Kowenje C.O., Lalah J.O., Ojwach S.O., "Preparation, characterization of fish scales biochar and their applications in the removal of anionic indigo carmine dye from aqueous solutions." Water Science and Technology 80.11 (2019): 2218-2231.
4. Adimalla N., Venkatayogi S.J., "Mechanism of fluoride enrichment in groundwater of hard rock aquifers in Medak, Telangana State, South India." Environmental Earth Sciences, 76 (2017): 1-10.
5. 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 (2012): 345-351.
6. Ahmad M., Lee S.S., Dou X., Mohan D., Sung J.K., Yang J.E., Ok Y.S., "Effects of pyrolysis temperature on soybean stover-and peanut shell-derived biochar properties and TCE adsorption in water." Bioresource technology, 118 (2012): 536-544.
7. Ahmad S., Singh R., Arfin T., Neeti K., "Fluoride contamination, consequences and removal techniques in water: a review." Environmental Science: Advances, (2022).
8. Ahmadi S., Mesbah M., Igwegbe C.A., Ezeliora C.D., Osagie C., Khan N.A., Dotto G.L., Salari M., Dehghani M.H., "Sono electro-chemical synthesis of LaFeO3 nanoparticles for the removal of fluoride: Optimization and modeling using RSM, ANN and GA tools." Journal of Environmental Chemical Engineering, 9.4 (2021): 105320.
9. Ahmedna M., Clarke S.J., Rao R.M., Marshall W.E., Johns M.M., "Use of filtration and buffers in raw sugar colour measurements." Journal of the Science of Food and Agriculture, 75.1 (1997): 109-116.

10. Al Sabti B., Samayamanthula D.R., Dashti F.M., Sabarathinam C., "Fluoride in Groundwater: Distribution, Sources, Processes, Analysis, and Treatment Techniques: A Review." Hydrogeochemistry of Aquatic Ecosystems, (2023): 1-31.
11. Alagumuthu G., Rajan M., "Equilibrium and kinetics of adsorption of fluoride onto zirconium impregnated cashew nut shell carbon." Chemical Engineering Journal, 158.3 (2010): 451-457.
12. Al-Ghouti, M. A., Khraisheh, M. A., Ahmad, M. N., Allen, S., "Adsorption behaviour of methylene blue onto Jordanian diatomite: a kinetic study." Journal of hazardous materials, 165.1-3 (2009): 589-598.
13. Amini M., Mueller K.I., Abbaspour K.C., Rosenberg T., Afyuni M., Møller K.N., Sarr M., Johnson C.A., "Statistical modeling of global geogenic fluoride contamination in groundwaters." Environmental science &technology, 42.10 (2008): 3662-3668.
14. Anderson M.J., Whitcomb P.J., "RSM simplified: optimizing processes using response surface methods for design of experiments." Productivity press, 2016.
15. Arif M., Hussain I., Hussain J., Sharma S., Kumar S., "Fluoride in the drinking water of Nagaur Tehsil of Nagaur district, Rajasthan, India." Bulletin of environmental contamination and toxicology, 88 (2012): 870-875.
16. Arumugam K., Elangovan K., "Hydrochemical characteristics and groundwater quality assessment in Tirupur region, Coimbatore district, Tamil Nadu, India." Environmental geology, 58 (2009): 1509-1520.
17. Arveti N., Sarma M.R., Aitkenhead-Peterson J.A., Sunil K., "Fluoride incidence in groundwater: a case study from Talupula, Andhra Pradesh, India." Environmental monitoring and assessment, 172 (2011): 427-443
18. Asadi S.S., Vuppala P., Reddy M.A., "Remote sensing and GIS techniques for evaluation of groundwater quality in municipal corporation of Hyderabad (Zone-V), India." International journal of environmental research and public health, 4.1 (2007): 45-52.
19. Ashraf I., Li R., Chen B., Al-Ansari N., Rizwan Aslam M., Altaf A.R., Elbeltagi A., "Nanoarchitectonics and Kinetics Insights into Fluoride Removal from Drinking Water Using Magnetic Tea Biochar." International Journal of Environmental Research and Public Health, 19.20 (2022): 13092.

20. Assefa B., "Defluoridation of Ethiopian rift valley region water using reverse osmosis membranes." Zede Journal, 23 (2006): 1-6.

21. Avtar R., Kumar P., Surjan A., Gupta L.N., Roychowdhury K., "Geochemical processes regulating groundwater chemistry with special reference to nitrate and fluoride enrichment in Chhatarpur area, Madhya Pradesh, India." Environmental earth sciences, 70 (2013): 1699-1708.

22. Ayalew, A.A.,"Comparative adsorptive performance of adsorbents developed from kaolin clay and limestone for de-fluoridation of groundwater." South African Journal of Chemical Engineering, 44 (2023): 1-13.

23. Ayoob S., Gupta A. K., "Fluoride in drinking water: a review on the status and stress effects." Critical reviews in environmental science and technology, 36.6 (2006): 433-487

24. Ayoob S., Gupta A.K., Bhat V.T., "A conceptual overview on sustainable technologies for the defluoridation of drinking water." Critical reviews in environmental science and technology, 38.6 (2008): 401-470.

25. Bandewar S., Mane S. J.,Tirthakar S. N.," Removal of fluoride from drinking water by using low cost adsorbent." International Journal of Research in Engineering and Technology, 4.4 (2015): 349-351.

26. Barati A., Eskandari, Z., TaghiMiri, S., and Asgari,M., “Removal of Fluoride Ion from Aqueous Solution by Nanocomposite Hydrogel Based on Starch/Sodium Acrylate/Nano Aluminium Oxide.” Iranian Journal of Polymer Science and Technology, 26.5 (2014): 381 -391.

27. Bazrafshan, E., Balarak, D., Panahi A.H., Kamani H. and Mahvi A.H., "Fluoride removal from aqueous solutions by cupricoxide nanoparticles." Fluoride, 49.3 (2016): 233.

28. Beg M.K., Srivastav S.K., Carranza E.J., De Smeth J.B., "High fluoride incidence in groundwater and its potential health effects in parts of Raigarh District, Chhattisgarh, India." Current Science, (2011): 750-754.

29. Begum H.A., Kabir M.H., "Removal of brilliant red from aqueous solutions by adsorption on fish scales." Dhaka University Journal of Science, 61.1 (2013): 7-12.

30. Bejaoui I., Mnif A., Hamrouni B., "Performance of reverse osmosis and nanofiltration in the removal of fluoride from model water and metal

packaging industrial effluent." Separation Science and Technology, 49.8 (2014): 1135-1145.

31. Bhan C., Singh J., Sharma Y.C., Koduru J.R., "Synthesis of lanthanum-modified clay soil-based adsorbent for the fluoride removal from an aqueous solution and groundwater through batch and column process: mechanism and kinetics." Environmental Earth Sciences, 81.9 (2022): 253.

32. Bharali, R. K., Bhattacharyya K. G., "Kinetic Study on Fluoride Sorption using Silikha (Terminalia chebula) Leaf Powder as Biosorbent." International Journal of Research in Chemistry and Environment, 4.1 (2014): 114-119.

33. Bhatnagar A., Kumar E., Sillanpää M., "Fluoride removal from water by adsorption - a review." Chemical engineering journal, 171.3 (2011): 811-840

34. Bhaumik R., Mondal N.K., Das B., Roy P., Pal K.C., Das C., Baneerjee A., "Eggshell powder as an adsorbent for removal of fluoride from aqueous solution: equilibrium, kinetic and thermodynamic studies." E-Journal of Chemistry, 9.3 (2012): 1457-1480.

35. Bhaumik, R., Mondal, N. K., Chattoraj S., "An optimization study for defluoridation from synthetic fluoride solution using scale of Indian major carp Catla (Catlacatla): an unconventional biosorbent." Journal of Fluorine Chemistry, 195 (2017): 57-69.

36. Bishnoi M., Arora S., "Potable groundwater quality in some villages of Haryana, India: Focus on fluoride." Journal of Environmental biology, 28. 2 (2007): 291.

37. Biswas G., Kumari M., Adhikari K., Dutta S. A., "A critical review on occurrence of fluoride and its removal through adsorption with an emphasis on natural minerals." Current Pollution Reports, 3 (2017): 104-119.

38. Biswas K., Gupta K., Ghosh U.C., "Adsorption of fluoride by hydrous iron (III)–tin (IV) bimetal mixed oxide from the aqueous solutions." Chemical Engineering Journal, 149.1-3 (2009): 196-206.

39. Brindha K., Rajesh R., Murugan R., Elango L., "Fluoride contamination in groundwater in parts of Nalgonda District, Andhra Pradesh, India." Environmental Monitoring and Assessment, 172 (2011): 481-492.

40. Brunson L. R., Sabatini D. A., “An evaluation of fish bone char as an appropriate arsenic and fluoride removal technology for emerging regions.” Environmental engineering science, 26.12 (2009) 1777-1784.

41. Brunson L.R., Sabatini D.A., "Role of surface area and surface chemistry during an investigation of eucalyptus wood char for fluoride adsorption from drinking water." Journal of Environmental Engineering, 141.2 (2015): 04014060.

42. Chakraborty S., Chowdhury S., Saha P.D., "Fish (Labeorohita) scales as a new biosorbent for removal of textile dyes from aqueous solutions." Journal of Water Reuse and Desalination, 2.3 (2012): 175-184.

43. Chatterjee S., Mukherjee M., De S., “Defluoridation using novel chemically treated carbonized bone meal: batch and dynamic performance with scale-up studies.” Environmental Science and Pollution Research, 25.18 (2018): 18161-18178.

44. Chaudhari V., Patkar M., "Fluoride Removal from Aqueous Solution Employing Chicken Feathers: Isotherms, Kinetics and Thermodynamics Studies." International Journal of Environmental Research, 17.2 (2023): 23.

45. Chen N., Zhang Z., Feng C., Li M., Chen R., Sugiura N., "Investigations on the batch and fixed-bed column performance of fluoride adsorption by Kanuma mud." Desalination, 268.1-3 (2011): 76-82.

46. Chidambaram S., Bala Krishna Prasad M., Manivannan R., Karmegam U., Singaraja C., Anandhan P., Prasanna M.V., Manikandan S., "Environmental hydrogeochemistry and genesis of fluoride in groundwaters of Dindigul district, Tamilnadu (India)." Environmental Earth Sciences, 68 (Jan 2013): 333-342.

47. Chidambaram S., Manikandan S., Ramanathan A.L., Prasanna M.V., Thivya C., Karmegam U., Thilagavathi R., Rajkumar K., "A study on the defluoridation in water by using natural soil." Applied Water Science, 3 (Dec 2013): 741-751.

48. Choi A.L., Sun G., Zhang Y., Grandjean P., "Developmental fluoride neurotoxicity: a systematic review and meta-analysis." Environmental health perspectives, 120.10 (2012): 1362-1368.

49. Chubar N.I., Samanidou V.F., Kouts V.S., Gallios G.G., Kanibolotsky V.A., Strelko V.V., Zhuravlev I.Z., "Adsorption of fluoride, chloride, bromide, and bromate ions on a novel ion exchanger." Journal of colloid and interface science, 291.1 (2005): 67-74.

50. Cortes L.N., Druzian S.P., Streit A.F., Godinho M., Perondi D., Collazzo G.C., Oliveira M.L., Cadaval Jr. T.R., Dotto G.L., "Biochars from animal wastes as alternative materials to treat colored effluents containing basic red 9." Journal of Environmental Chemical Engineering, 7.6 (2019): 103446.
51. Cruz M.A., Guimarães L.C., da Costa Júnior E.F., Rocha S.D., Mesquita P.D., "Adsorption of crystal violet from aqueous solution in continuous flow system using bone char." Chemical Engineering Communications, 207.3 (2020): 372-381.
52. Dahiya S., Kaur A., "Studies on removal of fluoride by coconut coir pith carbon." Indian Journal of Environmental Protection, 19.11 (1999): 811-814.
53. Dar M.A., Sankar K., Dar I.A., "Fluorine contamination in groundwater: a major challenge." Environmental monitoring and assessment, 173 (2011): 955-968.
54. Das B., Talukdar J., Sarma S., Gohain B., Dutta R.K., Das H.B., Das S.C., "Fluoride and other inorganic constituents in groundwater of Guwahati, Assam, India." Current Science, (2003): 657-661.
55. Das S., Nag S.K., "Geochemical appraisal of fluoride-laden groundwater in Suri I and II blocks, Birbhum district, West Bengal." Applied Water Science, 7 (2017): 2559-2570.
56. De D., Santosha S., Aniya V., Sreeramoju A., Satyavathi B., "Assessing the applicability of an agro-industrial waste to Engineered Bio-char as a dynamic adsorbent for Fluoride Sorption." Journal of Environmental Chemical Engineering, 6.2 (2018): 2998-3009.
57. Dehghani M.H., Gholami S., Karri R.R., Lima E.C., Mahvi A.H., Nazmara S., Fazlzadeh M., "Process modeling, characterization, optimization, and mechanisms of fluoride adsorption using magnetic agro-based adsorbent." Journal of Environmental Management, 286 (2021): 112173.
58. Demarchi C.A., Campos M., Rodrigues C.A., "Adsorption of textile dye Reactive Red 120 by the chitosan–Fe (III)-crosslinked: Batch and fixed-bed studies." Journal of Environmental Chemical Engineering, 1.4 (2013): 1350-1358.
59. Demirbas, A., "Heavy metal adsorption onto agro-based waste materials: a review." Journal of hazardous materials, 157. 2-3 (2008): 220-229.

60. Dey R.K., Swain S.K., Mishra S., Sharma P., Patnaik T., Singh V.K., Dehury B.N., Jha U., Patel R.K., "Hydrogeochemical processes controlling the high fluoride concentration in groundwater: a case study at the Boden block area, Orissa, India." Environmental Monitoring and Assessment, 184 (2012): 3279-3291.
61. Dhanasekaran P., Sai P.S., Gnanasekar K.I., "Fixed bed adsorption of fluoride by Artocarpus hirsutus based adsorbent." Journal of Fluorine Chemistry, 195 (2017): 37-46.
62. Dhiman S.D., Keshari A.K., "Hydrogeochemical evaluation of high-fluoride groundwaters: a case study from Mehsana District, Gujarat, India." Hydrological Sciences Journal, 51.6 (2006): 1149-1162.
63. Diawara C.K., Diop S.N., Diallo M.A., Farcy M., DerataniA.,"Performance of nanofiltration (NF) and low pressure reverse osmosis (LPRO) membranes in the removal of fluorine and salinity from brackish drinking water." Journal of Water Resource and Protection, 3.12 (2011): 912.
64. Durmaz F., Kara H., Cengeloglu Y., Ersoz M., "Fluoride removal by Donnan dialysis with anion exchange membranes." Desalination, 177.1-3 (2005): 51-57.
65. Dutta R.K, Saikia G., Das B., Bezbaruah C., Das H.B., Dube S.N., "Fluoride contamination in groundwater of Central Assam, India." Asian Journal of Water, Environment and Pollution, 3.2 (2006): 93-100.
66. Edmunds W.M., Smedley P.L., "Fluoride in natural waters." Essentials of medical geology: Revised Edition, (2013): 311-336
67. Errico M., Desogus F., Mascia M., Tola G., Dendena L., "Soil adsorption defluoridation of drinking water for an Ethiopian rural community." Chemical Papers, 60 (2006): 460-465.
68. Fallahzadeh R.A., Miri M., Taghavi M., Gholizadeh A., Anbarani R., Hosseini-Bandegharaei A., Ferrante M., Conti G.O., "Spatial variation and probabilistic risk assessment of exposure to fluoride in drinking water." Food and Chemical Toxicology, 113 (2018): 314-321.
69. Fawell J., Bailey K., Chilton J., Dahi E., Fewtrell L., Magara Y., "Fluoride in drinking-water." Narrative, 1 (2003): 12.

70. Fox, K. R., "Removal of inorganic contaminants from drinking water by reverse osmosis." USEPA, Drinking Water Res. Div., Municipal Environmental Research Laboratory, Cincinnati (unpublished) (1981).

71. Fu B., Mei S., Su X., Chen H., Zhu J., Zheng Z., Lin H., Dai C., Luque R., Yang D.P., "Integrating waste fish scale-derived gelatin and chitosan into edible nanocomposite film for perishable fruits." International Journal of Biological Macromolecules, 191 (2021): 1164-1174.

72. Gai W.Z., Deng Z.Y., "A comprehensive review of adsorbents for fluoride removal from water: Performance, water quality assessment and mechanism." Environmental Science: Water Research & Technology, 7.8 (2021): 1362-1386.

73. Gandhi N., Sirisha D., Shekar K.C., Asthana S., "Removal of fluoride from water and waste water by using low cost adsorbents." International Journal of ChemTech Research, 4.4 (2012): 1646-1653.

74. Gandi N., Sirisha D., "Removal of fluoride by using Passiflora foetida fruits as natural coagulant." Discovery Nature, 13 (2014): 44-61.

75. Ganvir V., Das K., "Removal of fluoride from drinking water using aluminum hydroxide coated rice husk ash." Journal of hazardous materials, 185. 2-3 (2011): 1287-1294.

76. Gao S., Sun R., Wei Z., Zhao H., Li H., Hu F., “Size-dependent defluoridation properties of synthetic hydroxyapatite." Journal of Fluorine Chemistry, 130.6 (2009): 550-556.

77. Gedam V.V., Patil J.L., Kagne S., Sirsam R.S., Labhasetwar P., "Performance evaluation of polyamide reverse osmosis membrane for removal of contaminants in ground water collected from Chandrapur district." Journal of Membrane Science & Technology, 2.3 (2012): 2-5.

78. Getachew T., Hussen A., Rao V.M., "Defluoridation of water by activated carbon prepared from banana (Musa paradisiaca) peel and coffee (Coffea arabica) husk." International Journal of Environmental Science and Technology, 12 (2015): 1857-1866.

79. Ghimire K.N., "Effective removal of fluoride onto metal ions loaded orange waste." Journal of Nepal Chemical Society, 27 (2011): 61-66.

80. Ghorai S., Pant K.K., "Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina." Separation and purification technology, 42.3 (2005): 265-271.

81. Gogoi S., Nath S.K., Bordoloi S., Dutta R.K., "Fluoride removal from groundwater by limestone treatment in presence of phosphoric acid." Journal of Environmental Management, 152 (2015): 132-139.

82. Gourouza M., Natatou I., Boos A., "Elimination of fluoride ions from an aqueous solution with charred beef shoulder blade bones." J. Mater. Environ. Sci, 5.2 (2014): 416-425.

83. Guan X., Zhou J., Ma N., Chen X., Gao J., Zhang R., "Studies on modified conditions of biochar and the mechanism for fluoride removal." Desalination and Water Treatment, 55.2 (2015): 440-447.

84. Gupta A., Garg A., "Adsorption and oxidation of ciprofloxacin in a fixed bed column using activated sludge derived activated carbon." Journal of environmental management, 250 (2019): 109474.

85. Gupta S., Banerjee S., Saha R., Datta J.K., Mondal N., "Fluoride geochemistry of groundwater in Nalhati-1 block of the Birbhum district, West Bengal, India." Fluoride, 39.4 (2006): 318.

86. Gupta S.K., Deshpande R.D., Agarwal M., Raval B.R., "Origin of high fluoride in groundwater in the North Gujarat-Cambay region, India." Hydrogeology Journal, 13 (2005): 596-605.

87. Gupta V.K., Rastogi A., Nayak A., "Biosorption of nickel onto treated alga (Oedogonium hatei): application of isotherm and kinetic models." Journal of colloid and interface science, 342.2 (2010): 533-539.

88. Habuda-Stanić M., ErgovićRavančić M., Flanagan A., "A review on adsorption of fluoride from aqueous solution." Materials, 7.9 (2014): 6317-6366.

89. Haldar D., Duarah P., Purkait M.K., "MOFs for the treatment of arsenic, fluoride and iron contaminated drinking water: A review." Chemosphere, 251 (2020): 126388.

90. Halder G., Sinha K., Dhawane S., "Defluoridation of wastewater using powdered activated carbon developed from Eichhornia crassipes stem: optimization by response surface methodology." Desalination and Water Treatment 56.4 (2015): 953-966

91. He J., Zhang, K., Wu, S., Cai, X., Chen K., Li Y., Sun B., Jia Y., Meng F., Jin, Z., Kong, L., "Performance of novel hydroxyapatite nanowires in treatment of fluoride contaminated water." Journal of hazardous materials, 303 (2016): 119-130.

92. He J., Chen K., Cai X., Li Y., Wang C., Zhang K., Jin Z., Meng F., Wang X., Kong L., Liu J., "A biocompatible and novelly-defined Al-HAP adsorption membrane for highly effective removal of fluoride from drinking water." Journal of Colloid and Interface Science, 490 (2017): 97-107.

93. Hernández M. V., Ramírez-Montoya L.A., Bonilla-Petriciolet A., Montes-Morán M.A., “Optimizing the removal of fluoride from water using new carbons obtained by modification of nut shell with a calcium solution from egg shell.” Biochemical Engineering Journal, 62 (2012): 1–7.

94. Hettithanthri O., Rajapaksha A.U., Nanayakkara N., Vithanage M., "Temperature influence on layered double hydroxide tailored corncob biochar and its application for fluoride removal in aqueous media." Environmental Pollution, (2023): 121054.

95. Ho Y.S., McKay G., "The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat." The Canadian journal of chemical engineering, 76.4 (1998): 822-827.

96. Huang Z., Shao H., Huang B., Li C., Huang Y., Chen X., "High-performance fish-scale-based porous carbon for the removal of methylene blue from aqueous solution." RSC Advances, 4.36 (2014): 18737-18743.

97. Hussain I., Arif M., Hussain J., "Fluoride contamination in drinking water in rural habitations of Central Rajasthan, India." Environmental monitoring and assessment, 184.8 (2012): 5151-5158.

98. Hutchins R.A., "New method simplifies design of activated carbon systems." Chem. Eng., 80 (1973): 133-138.

99. Ibrahim W.M., Hassan A.F., Azab Y.A., "Biosorption of toxic heavy metals from aqueous solution by Ulva lactuca activated carbon." Egyptian journal of basic and applied sciences, 3.3 (2016): 241-249.

100. Islam M.A., Hameed B. H., Ahmed M. J., Khanday W. A., Khan M. A., Marrakchi, F., "Porous carbon–based material from fish scales for the adsorption of tetracycline antibiotics." Biomass Conversion and Biorefinery, (2022): 1-10.

101. Islam M., Patel RK., "Evaluation of removal efficiency of fluoride from aqueous solution using quick lime." Journal of Hazardous Materials, 143.1-2 (2007): 303-310.

102. Jain S., Jayaram R.V., "Removal of fluoride from contaminated drinking water using unmodified and aluminium hydroxide impregnated blue lime stone waste." Separation Science and Technology, 44.6 (2009): 1436-1451.

103. Jamode A.V., Sapkal V.S., Jamode V.S., "Defluoridation of water using inexpensive adsorbents." Journal of the Indian Institute of Science, 84.5 (2004): 163.

104. Jamwal K.D., Slathia D., "A review of defluoridation techniques of global and indian prominence." Curr. World Environ, 17 (2022): 41-57.

105. Janardhana C., Rao G.N., Sathish R.S., Kumar P.S., Kumar V.A., Madhav M.V., "Study on defluoridation of drinking water using zirconium ion impregnated activated charcoals.", Indian Journal of Chemical Technology, 14.4 (2007): 350-354.

106. Jayarathne T., Stockwell C.E., Yokelson R.J., Nakao S., Stone E.A., "Emissions of fine particle fluoride from biomass burning." Environmental science &technology, 48.21 (2014): 12636-12644.

107. Ji Q., Li H., Zhang J.,"Preparation and characterization of bio-based activated carbon from fish scales." BioResources ,16.1 (2021): 614.

108. Jindo K., Mizumoto H., Sawada Y., Sanchez-Monedero M.A., Sonoki T., "Physical and chemical characterization of biochars derived from different agricultural residues." Biogeosciences, 11.23 (2014): 6613-6621.

109. Kabir H., Gupta A.K., Tripathy S., "Fluoride and human health: Systematic appraisal of sources, exposures, metabolism, and toxicity." Critical Reviews in Environmental Science and Technology, 50.11 (2020): 1116-1193.

110. Kafle G.K., Kim S.H., Sung K.I., "Ensiling of fish industry waste for biogas production: a lab scale evaluation of biochemical methane potential (BMP) and kinetics." Bioresource technology 127 (2013): 326-336.

111. Kagne S., Jagtap S., Dhawade P., Kamble S.P., Devotta S., Rayalu S.S., "Hydrated cement: a promising adsorbent for the removal of fluoride from aqueous solution." Journal of hazardous materials, 154.1-3 (2008): 88-95.

112. Karthikeyan K., Nanthakumar K., Velmurugan P., Tamilarasi S., Lakshmanaperumalsamy P., "Prevalence of certain inorganic constituents in

groundwater samples of Erode district, Tamilnadu, India, with special emphasis on fluoride, fluorosis and its remedial measures." Environmental monitoring and assessment, 160 (2010): 141-155.

113. Kaseva M. E., "Optimization of regenerated bone char for fluoride removal in drinking water: a case study in Tanzania." Journal of water and health, 4.1 (2006): 139-147.

114. Kaushik A., Kumar K., Sharma I.S., Sharma H.R., "Groundwater quality assessment in different land-use areas of Faridabad and Rohtak cities of Haryana using deviation index." Journal of Environmental Biology, 25.2 (2004): 173-180.

115. Khan B.A., Ahmad M., Iqbal S., Bolan N., Zubair S., Shafique M.A., Shah A., "Effectiveness of the engineered pinecone-derived biochar for the removal of fluoride from water." Environmental Research, 212 (2022): 113540.

116. Khandare A.L., Rao G.S., "Uptake of fluoride, aluminum and molybdenum by some vegetables from irrigation water." Journal of Human Ecology, 19.4 (2006): 283-288.

117. Kimambo V., Bhattacharya P., Mtalo F., Mtamba J., Ahmad A., "Fluoride occurrence in groundwater systems at global scale and status of defluoridation–state of the art." Groundwater for Sustainable Development, 9 (2019): 100223.

118. Kondapalli S., Mohanty K., "Influence of temperature on equilibrium, kinetic and thermodynamic parameters of biosorption of Cr (VI) onto fish scales as suitable biosorbent." Journal of Water Resource and Protection, 3.6 (2011): 429.

119. Kongsri S., Janpradit K., Buapa K., Techawongstien S., Chanthai S., "Nanocrystalline hydroxyapatite from fish scale waste: Preparation, characterization and application for selenium adsorption in aqueous solution." Chemical engineering journal, 215 (2013): 522-532.

120. Ku Y., Chiou H.M., "The adsorption of fluoride ion from aqueous solution by activated alumina." Water, air, and soil pollution, 133 (2002): 349-361.

121. Ku Y., Chiou H.M., Chen H.W., "Removal of fluoride from aqueous solution by aluminum-loaded Duolite C-467 resin." Journal of the Chinese Institute of Engineers, 34.6 (2011): 801-807.

122. Kumar M., Kumari K., Ramanathan A.L., Saxena R., "A comparative evaluation of groundwater suitability for irrigation and drinking purposes in two intensively cultivated districts of Punjab, India." Environmental geology, 53 (2007): 553-574.

123. Kumar R., Sharma P., Yang W., Sillanpää M., Shang J., Bhattacharya P., Vithanage M., Maity JP., "State-of-the-art of research progress on adsorptive removal of fluoride-contaminated water environments using biochar-based materials: Practical feasibility through reusability and column transport studies." Environmental Research, (2022): 114043.

124. Kumari U., Mishra A., Siddiqi H., Meikap B.C., "Effective defluoridation of industrial wastewater by using acid modified alumina in fixed-bed adsorption column: experimental and breakthrough curves analysis." Journal of Cleaner Production, 279 (2021): 123645.

125. Kundu M.C., Mandal B.,"Assessment of potential hazards of fluoride contamination in drinking groundwater of an intensively cultivated district in West Bengal, India." Environmental monitoring and assessment, 152 (2009): 97-103.

126. Kundu N., Panigrahi M., Tripathy S., Munshi S., Powell M., Hart B., "Geochemical appraisal of fluoride contamination of groundwater in the Nayagarh District of Orissa, India." Environmental Geology, 41 (2001): 451-460.

127. Lanas S.G., Valiente M., Aneggi E., Trovarelli A., Tolazzi M., Melchior A., "Efficient fluoride adsorption by mesoporous hierarchical alumina microspheres." RSC advances, 6.48 (2016): 42288-42296.

128. Lapworth D.J., Baran N., Stuart M.E., Ward R.S., "Emerging organic contaminants in groundwater: a review of sources, fate and occurrence." Environmental pollution, 163 (2012): 287-303.

129. Larsen M.J., Pearce E.I., Jensen S.J., "Defluoridation of water at high pH with use of brushite, calcium hydroxide, and bone char." Journal of Dental research, 72.11 (1993): 1519-1525.

130. Lhassani A., Rumeau M., Benjelloun D., Pontie M., "Selective demineralization of water by nanofiltration application to the defluorination of brackish water." Water research, 35.13 (2001): 3260-3264.

131. Li C., Huang Q., Zhang H., Wang Q., Xue R., Guo G., Hu S., "Characterization of biochars produced by co-pyrolysis of hami melon (Cantaloupes) straw mixed with polypropylene and their adsorption properties of cadmium." International Journal of Environmental Research and Public Health, 18.21 (2021): 11413.

132. Li F., Shen K., Long X., Wen J., Xie X., Zeng X., Liang Y., Wei Y., Lin Z., Huang W., Zhong R., "Preparation and characterization of biochars from Eichornia crassipes for cadmium removal in aqueous solutions." PloS one, 11.2 (2016): e0148132.

133. Liu J., Cheng X.Z., Peng Y., Chen H.M., "The adsorption of nickel from wasterwater samples on grass carp scales." Advanced Materials Research, 573 (2012): 617-621.

134. Liu Y., Chen Y., Li Y., Chen L., Jiang H., Li H., Luo X., Tang P., Yan H., Zhao M., Yuan Y., "Fabrication, application, and mechanism of metal and heteroatom co-doped biochar composites (MHBCs) for the removal of contaminants in water: A review." Journal of Hazardous Materials, (2022): 128584.

135. Lopes C., Antelo L.T., Franco-Uría A., Alonso A.A., Pérez-Martín R., "Valorisation of fish by-products against waste management treatments–Comparison of environmental impacts." Waste management, 46 (2015): 103-112.

136. Lv S., Hu L., Xia C., Cabrera M.B., Guo Y., Liu C., You L., "Recycling fish scale powder in improving the performance of asphalt: A sustainable utilization of fish scale waste in asphalt." Journal of Cleaner Production, 288 (2021): 125682.

137. Ma W., Ya F.Q., Han M., Wang R., "Characteristics of equilibrium, kinetics studies for adsorption of fluoride on magnetic-chitosan particle." Journal of hazardous materials, 14.1-2 (2007): 296-302.

138. Ma W., Ya F., Wang R., Zhao Y., "Fluoride removal from drinking water by adsorption using bone char as a biosorbent." International Journal of Environmental Technology and Management, 9.1 (2008): 59-69.

139. Madhnure.P., Sirsikar D.Y., Tiwari A.N., Ranjan B., Malpe D.B., "Occurrence of fluoride in the groundwaters of Pandharkawada area, Yavatmal district, Maharashtra, India." Current Science, (2007): 675-679.

140. Magesh N.S., Krishnakumar S., Chandrasekar N., Soundranayagam J.P., “Groundwater quality assessment using WQI and GIS techniques, Dindigul district, Tamil Nadu, India." Arabian Journal of Geosciences, 6 (2013): 4179-4189.

141. Mahramanlioglu M., Kizilcikli I., Bicer I.O., "Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth." Journal of Fluorine Chemistry, 115.1 (2002): 41-47.

142. Mamatha P., Rao S.M., "Geochemistry of fluoride rich groundwater in Kolar and Tumkur Districts of Karnataka." Environmental Earth Sciences, 61 (2010): 131-142.

143. Mandal N., Mondal S., Mondal A., Mukherjee K., Mondal B., "Response surface modeling of Cu (II) removal from wastewater using fish scale-derived hydroxyapatite: application of Box–Behnken experimental design." Desalination and Water Treatment, 57.33 (2016): 15410-15423.

144. Mann S., Mandal A., "Performance of low-cost adsorbents for the removal of fluoride ions–An overview." International Journal of Engineering Science and Innovative Technology (IJESIT), 3 (2014): 437-443.

145. Mariappan R., Vairamuthu R., Ganapathy A., "Use of chemically activated cotton nut shell carbon for the removal of fluoride contaminated drinking water: kinetics evaluation." Chinese Journal of Chemical Engineering, 23.4 (2015): 710-721.

146. Markovic, M., Fowler, B. O., Tung, M. S., "Preparation and comprehensive characterization of a calcium hydroxyapatite reference material." Journal of research of the National Institute of Standards and Technology, 109.6 (2004): 553.

147. Márquez-Mendoza S., Jiménez-Reyes M., Solache-Ríos M., Gutiérrez-Segura E., "Fluoride removal from aqueous solutions by a carbonaceous material from pyrolysis of sewage sludge." Water, Air, & Soil Pollution, 223.5 (2012): 1959-1971.

148. Marrakchi F., Ahmed M.J., Khanday W.A., Asif M., Hameed B.H., "Mesoporous carbonaceous material from fish scales as low-cost adsorbent for reactive orange 16 adsorption." Journal of the Taiwan Institute of Chemical Engineers, 71 (Feb 2017): 47-54.

149. Marrakchi F., Auta M., Khanday W.A., Hameed B.H., "High-surface-area and nitrogen-rich mesoporous carbon material from fishery waste for effective adsorption of methylene blue." Powder Technology, 321 (Nov 2017): 428-434.

150. Meenakshi S., Maheshwari R. C., "Fluoride in drinking water and its removal." Journal of Hazardous materials, 137.1 (Sep 2006): 456-463.

151. Meenakshi S., Viswanathan N., "Identification of selective ion-exchange resin for fluoride sorption." Journal of colloid and interface science, 308.2 (Apr 2007): 438-450.

152. Meenakshi S., Sundaram C.S., Sukumar R., "Enhanced fluoride sorption by mechanochemically activated kaolinites." Journal of hazardous materials, 153.1-2 (May 2008): 164-172.

153. Meenakshi S., Viswanathan N., "Enhanced fluoride sorption using La (III) incorporated carboxylated chitosan beads." Journal of Colloid and Interface Science, 322.2 (Jun 2008): 375-383.

154. Mei L., Qiao H., Ke F., Peng C., Hou R., Wan X., Cai H., “One-step synthesis of zirconium dioxide-biochar derived from Camellia oleifera seed shell with enhanced removal capacity for fluoride from water." Applied Surface Science, 509 (2020): 144685.

155. Meilani V., Lee J.I., Kang J.K., Lee C.G., Jeong S., Park S.J., "Application of aluminum-modified food waste biochar as adsorbent of fluoride in aqueous solutions and optimization of production using response surface methodology." Microporous and Mesoporous Materials, 312 (2021): 110764.

156. Mittal Y., Srivastava P., Kumar N., Yadav A.K., "Remediation of fluoride contaminated water using encapsulated active growing blue-green algae, Phormidium sp." Environmental Technology & Innovation, 19 (2020): 100855.

157. Mohan D., Sharma R., Singh V. K., Steele, P., Pittman Jr. C. U.,"Fluoride removal from water using bio-char, a green waste, low-cost adsorbent: equilibrium uptake and sorption dynamics modeling." Industrial & Engineering Chemistry Research, 51.2 (2012): 900-914.

158. Mohan D., Kumar S., Srivastava A., "Fluoride removal from ground water using magnetic and nonmagnetic corn stover biochars." Ecological Engineering, 73 (2014): 798-808.

159. Mohan R., Dutta R.K., "A study of suitability of limestone for fluoride removal by phosphoric acid-crushed limestone treatment." Journal of Environmental Chemical Engineering, 8.6 (2020): 104410.

160. Mohan S., Singh D.K., Kumar V., Hasan S.H., "Effective removal of Fluoride ions by rGO/ZrO2 nanocomposite from aqueous solution: fixed bed column adsorption modelling and its adsorption mechanism." Journal of Fluorine Chemistry, 194 (2017): 40-50.

161. Mondal D., Gupta S., Reddy D.V., Nagabhushana P., “Geochemical controls on fluoride concentrations in groundwater from alluvial aquifers of the Birbhum district, West Bengal, India.” Journal of Geochemical Exploration, 145 (2014): 190 -206.

162. Mondal P., George S. "Removal of fluoride from drinking water using novel adsorbent magnesia-hydroxyapatite." Water, Air, & Soil Pollution, 2.26 (2015): 1-15.

163. Mourabet M., El Rhilassi A., El Boujaady H., Bennani-Ziatni M.R., El Hamri R., Taitai A., "Removal of fluoride from aqueous solution by adsorption on hydroxyapatite (HAp) using response surface methodology." Journal of Saudi Chemical Society 19.6 (2015): 603-615.

164. Msagati T.A., Mamba B.B., Sivasankar V., Omine K., "Surface restructuring of lignite by bio-char of cuminum cyminum–exploring the prospects in defluoridation followed by fuel applications." Applied surface science, 301 (2014): 235-243.

165. Muhammad N., Gao Y., Iqbal F., Ahmad P., Ge R., Nishan U., Rahim A., Gonfa G., Ullah Z., "Extraction of biocompatible hydroxyapatite from fish scales using novel approach of ionic liquid pretreatment." Separation and Purification Technology, 161 (2016): 129-135.

166. Mukherjee S., Halder G., "Assessment of fluoride uptake performance of raw biomass and activated biochar of Colocasia esculenta stem: optimization through response surface methodology." Environmental Progress & Sustainable Energy, 35.5 (2016): 1305-1316.

167. Murutu C., Onyango M.S., Ochieng A., Otieno F.A.., "Fluoride removal performance of phosphoric acid treated lime: Breakthrough analysis and point-of-use system performance." Water SA, 38.2 (2012): 279-286.

168. Naaz A., "Hydrogeochemistry of fluoride-rich groundwaters in semiarid region of Central India." Arabian Journal of Geosciences, 8 (2015): 10585-10596.

169. Narsimha A., Sudarshan V., "Contamination of fluoride in groundwater and its effect on human health: a case study in hard rock aquifers of Siddipet, Telangana State, India." Applied Water Science, 7 (2017): 2501-2512.

170. Nawlakhe W. G., Kulkarni D. N., Pathak B. N. ,Bulusu K. R.,"Defluoridation of water by Nalgonda technique.", Indian Journal of Environmental Health, 17 . 1 (1975): 26-65.

171. Ndiaye P.I., Moulin P., Dominguez L., Millet J.C., Charbit F., "Removal of fluoride from electronic industrial effluent by RO membrane separation." Desalination, 173.1 (2005): 25-32.

172. Oginni O., Yakaboylu G.A., Singh K., Sabolsky E.M., Unal-Tosun G., Jaisi D., Khanal S., Shah A., "Phosphorus adsorption behaviors of MgO modified biochars derived from waste woody biomass resources." Journal of Environmental Chemical Engineering, 8.2 (2020): 103723.

173. Onyango M.S., Kojima Y., Kuchar D., Osembo S.O., Matsuda H., "Diffusion kinetic modeling of fluoride removal from aqueous solution by charge-reversed zeolite particles." Journal of chemical engineering of Japan, 38.9 (2005): 701-710.

174. Onyango M.S., Kojima Y., Kumar A., Kuchar D., Kubota M., Matsuda H., "Uptake of fluoride by Al3+ pretreated low-silica synthetic zeolites: adsorption equilibrium and rate studies." Separation Science and Technology, 41.4 (2006): 683-704.

175. Patel H., "Batch and continuous fixed bed adsorption of heavy metals removal using activated charcoal from neem (Azadirachta indica) leaf powder." Scientific Reports, 10.1 (2020): 16895.

176. Pathan I.B., Munde S.J., Shelke S., Ambekar W., MallikarjunaSetty C., “Curcumin loaded fish scale collagen-HPMC nanogel for wound healing application: Ex-vivo and In-vivo evaluation." International Journal of Polymeric Materials and Polymeric Biomaterials, 68.4 (2019): 165-174.

177. Patil S., Renukdas S., Patel N., "Defluoridation of water using biosorbents: kinetic and thermodynamic study." International Journal of Research in Chemistry and Environment (IJRCE), 3.1 (2013): 125-135.

178. Prabhu S.M., Meenakshi S., "Synthesis of surface coated hydroxyapatite powders for fluoride removal from aqueous solution." Powder technology, 268 (2014): 306-315.

179. Qin D., Bi S., You X., Wang M., Cong X., Yuan C., Yu M., Cheng X., Chen X.G., “Development and application of fish scale wastes as versatile natural biomaterials." Chemical Engineering Journal, 428 (2022): 131102.

180. Qu J., Shi J., Wang Y., Tong H., Zhu Y., Xu L., Wang Y., Zhang B., Tao Y., Dai X., Zhang H., "Applications of functionalized magnetic biochar in environmental remediation: A review." Journal of Hazardous Materials, (2022): 128841.

181. Raghav S., Nair M., Kumar D., "Tetragonal prism shaped Ni-Al bimetallic adsorbent for study of adsorptive removal of fluoride and role of ion-exchange." Applied Surface Science, 498 (2019): 143785.

182. Raj D., Shaji E., "Fluoride contamination in groundwater resources of Alleppey, southern India." Geoscience Frontiers, 8.1 (2017): 117-124.

183. Raju N.J., Dey S., Das K., "Fluoride contamination in groundwaters of Sonbhadra district, Uttar Pradesh, India." Current science, (2009): 979-985.

184. Raju N.J., Dey S., Gossel W., Wycisk P., "Fluoride hazard and assessment of groundwater quality in the semi-arid Upper Panda River basin, Sonbhadra district, Uttar Pradesh, India." Hydrological Sciences Journal, 57.7 (2012): 1433-1452.

185. Raju N.J., "Prevalence of fluorosis in the fluoride enriched groundwater in semi-arid parts of eastern India: Geochemistry and health implications." Quaternary International, 443 (2017): 265-278.

186. Ramakrishnaiah C.R., Sadashivaiah C., Ranganna G., "Assessment of water quality index for the groundwater in Tumkur Taluk, Karnataka State, India." E-Journal of chemistry, 6.2 (2009): 523-530.

187. Ramanaiah S.V., Mohan S.V., Rajkumar B., Sarma P.N., "Monitoring of fluoride concentration in ground water of Prakasham district in India: correlation with physico-chemical parameters." Journal of Environmental science and Engineering, 48.2 (2006): 129.

188. Ramesh S.T., Gandhimathi R., Nidheesh P.V., Taywade M., "Batch and column operations for the removal of fluoride from aqueous solution using

bottom ash." Environmental Research, Engineering and Management, 60.2 (2012): 12-20.

189. Rao, N. S., "Fluoride in groundwater, varaha river basin, visakhapatnam district, Andhra Pradesh, India." Environmental Monitoring and Assessment, 152 (2009): 47-60.

190. Ravindra K., Garg V.K., "Distribution of fluoride in groundwater and its suitability assessment for drinking purpose." International Journal of Environmental Health Research, 16. 2 (2006): 163-166.

191. Ray D., Ravindar Rao R., Bhoi A.V., Biswas A.K., Ganguly A.K., Sanyal P.B., "Physico-chemical quality of drinking water in Rohtas district of Bihar." Environmental monitoring and assessment, 61 (2000): 387-398.

192. Razbe N, Razbe N., "Various options for removal of fluoride from drinking water." IOSR Journal of Applied Physics, 3 (2013): 40-47.

193. Reddy A.G., Reddy D.V., Rao P.N., Prasad K.M., "Hydrogeochemical characterization of fluoride rich groundwater of Wailpalli watershed, Nalgonda District, Andhra Pradesh, India." Environmental Monitoring and Assessment, 171.1-4 (2010): 561-577.

194. Reynel-Avila H.E., Mendoza-Castillo D.I., Bonilla-Petriciolet A., "Relevance of anionic dye properties on water decolorization performance using bone char: Adsorption kinetics, isotherms and breakthrough curves." Journal of Molecular Liquids, 219 (2016): 425-434.

195. Rout P.R., Dash R.R., Bhunia P., "Modelling and packed bed column studies on adsorptive removal of phosphate from aqueous solutions by a mixture of ground burnt patties and red soil." Adv. Environ. Res, 3.3 (2014): 231-251.

196. Roy P., Mondal N.K., Bhattacharya S., Das B., Das K., "Removal of arsenic (III) and arsenic (V) on chemically modified low-cost adsorbent: batch and column operations." Applied Water Science, 3 (2013): 293-309.

197. Roy S., Das P., "Assessment on the defluoridation using novel activated carbon synthesized from tea waste: batch, statistical optimization and mathematical modeling." Journal of Industrial Pollution Control, 32.2 (2016).

198. Roy S., Sengupta S., Manna S., Das P., "Chemically reduced tea waste biochar and its application in treatment of fluoride containing wastewater: batch and optimization using response surface methodology." Process Safety and Environmental Protection, 116 (2018): 553-563.

199. Rugayah N., Nuraini H., "Chicken bone charcoal for defluoridation of groundwater in Indonesia." International Journal of Poultry Science, 13.10 (2014): 591-596.

200. Sadhu M., Bhattacharya P., Vithanage M., Sudhakar P.P., "Adsorptive removal of fluoride using biochar–a potential application in drinking water treatment." Separation and Purification Technology, 278 (2021): 119106.

201. Sahu N., Bhan C., Singh J., "Removal of fluoride from an aqueous solution by batch and column process using activated carbon derived from iron infused Pisum sativum peel: characterization, Isotherm, kinetics study." Environmental Engineering Research, 26.4 (2021).

202. Saikia, R., Goswami R., Bordoloi N., Senapati K.K., Pant K.K., Kumar M. and Kataki, R., "Removal of arsenic and fluoride from aqueous solution by biomass based activated biochar: optimization through response surface methodology." Journal of environmental chemical engineering, 5.6 (2017): 5528-5539.

203. Sakhare N., Lunge S., Rayalu S., Bakardjiva S., Subrt J., Devotta S., Labhsetwar N., "Defluoridation of water using calcium aluminate material." Chemical Engineering Journal, 203 (2012): 406-414.

204. Salve P.R., Maurya A., Kumbhare P.S., Ramteke D.S., Wate S.R., "Assessment of groundwater quality with respect to fluoride." Bulletin of environmental contamination and toxicology, 81 (2008): 289-293.

205. Samadi M.T., Zarrabi M., Sepehr M.N., Ramhormozi S.M., Azizian S., Amrane A., "Removal of fluoride ions by ion exchange resin: kinetic and equilibrium studies." Environmental Engineering & Management Journal (EEMJ), 13.1 (2014).

206. Sankararamakrishnan N., Sharma A.K., Iyengar L., "Contamination of nitrate and fluoride in ground water along the Ganges Alluvial Plain of Kanpur district, Uttar Pradesh, India." Environmental monitoring and assessment, 146 (2008): 375-382.

207. Sarkar M., Banerjee A., Pramanick P.P., "Kinetics and mechanism of fluoride removal using laterite." Industrial & engineering chemistry research, 45.17 (2006): 5920-5927.

208. Sawangjang B., Takizawa S., "Re-evaluating fluoride intake from food and drinking water: Effect of boiling and fluoride adsorption on food." Journal of Hazardous Materials, 443 (2023): 130162.
209. Scheverin V.N., Horst M.F., Lassalle V.L., "Novel hydroxyapatite-biomass nanocomposites for fluoride adsorption." Results in Engineering, 16 (2022): 100648.
210. Sehn P., "Fluoride removal with extra low energy reverse osmosis membranes: three years of large scale field experience in Finland." Desalination, 223.1-3 (2008): 73-84.
211. Shaaban A., Se S.M., Mitan N.M., DiminM.F.,"Characterization of biochar derived from rubber wood sawdust through slow pyrolysis on surface porosities and functional groups." Procedia Engineering, 68 (2013): 365-371.
212. Shah T., Indu R., "Fluorosis in Gujarat: a disaster ahead." IWMI-Tata Program Annual Partner's Meet, Anand (2004).
213. Shaji E., Viju J., Thambi D.S., "High fluoride in groundwater of Palghat District, Kerala." Current Science, (2007): 240-245.
214. Shalaby M., Agwa M., Saeed H., Khedr S.M., Morsy O., El-Demellawy M.A., "Fish scale collagen preparation, characterization and its application in wound healing." Journal of Polymers and the Environment, 28 (2020): 166-178.
215. Sharma B.S., Agrawal J., Gupta A.K., "Emerging challenge: fluoride contamination in groundwater in Agra District, Uttar Pradesh." Asian J Exp BiolSci, 2.1 (2011): 131-134.
216. Shekhawat A., Jugade R., Kahu S., Saravanan D., Deshmukh S., "Mesoporous Cellulose assemblage Al-doped ferrite for sustainable defluoridation process based on parameters optimization through RSM." Inorganic Chemistry Communications, (2023): 110528.
217. Shen J., Schäfer A., "Removal of fluoride and uranium by nanofiltration and reverse osmosis: a review." Chemosphere, 117 (2014): 679-691.
218. Sidiras D., Batzias F., Schroeder E., Ranjan R., Tsapatsis M., "Dye adsorption on autohydrolyzed pine sawdust in batch and fixed-bed systems." Chemical Engineering Journal, 171.3 (2011): 883-896.
219. Singaraja C., Chidambaram S., Anandhan P., Prasanna M.V., Thivya C., Thilagavathi R., "A study on the status of fluoride ion in groundwater of

coastal hard rock aquifers of south India." Arabian Journal of Geosciences, 6 (2013): 4167-4177.

220. Singh B., Dolk M.M., Shen Q., Camps-Arbestain M., "Biochar pH, electrical conductivity and liming potential." Biochar: A guide to analytical methods, 23 (2017).

221. Singh C.K., Rina K., Singh R.P., Shashtri S., Kamal V., Mukherjee S., "Geochemical modeling of high fluoride concentration in groundwater of Pokhran area of Rajasthan, India." Bulletin of Environmental Contamination and Toxicology, 86 (2011): 152-158

222. Singh C.K., Mukherjee S., "Aqueous geochemistry of fluoride enriched groundwater in arid part of Western India." Environmental Science and Pollution Research, 22 (2015): 2668-2678.

223. Singh G., Kumari B., Sinam G., Kumar N., Mallick S., "Fluoride distribution and contamination in the water, soil and plants continuum and its remedial technologies, an Indian perspective–a review." Environmental Pollution, 239 (2018): 95-108.

224. Solangi I.B., Memon S., Bhanger M.I., "Removal of fluoride from aqueous environment by modified Amberlite resin." Journal of hazardous materials, 171.1-3 (2009): 815-819.

225. Solangi I.B., Memon S., Bhanger M.I., "An excellent fluoride sorption behavior of modified amberlite resin." Journal of Hazardous Materials, 176.1-3 (2010): 186-192.

226. Srimurali M., Pragathi A., Karthikeyan J., "A study on removal of fluorides from drinking water by adsorption onto low-cost materials." Environmental pollution, 99.2 (1998): 285-289.

227. Srinivasamoorthy K., Nanthakumar C., Vasanthavigar M., Vijayaraghavan K., Rajivgandhi R., Chidambaram S., Anandhan P., Manivannan R., Vasudevan S., "Groundwater quality assessment from a hard rock terrain, Salem district of Tamilnadu, India." Arabian Journal of Geosciences, 4,1 (2011): 91-102.

228. Srinivasamoorthy K., Vijayaraghavan K., Vasanthavigar M., Sarma S., Chidambaram S., Anandhan P., Manivannan R., "Assessment of groundwater quality with special emphasis on fluoride contamination in crystalline bed rock aquifers of Mettur region, Tamilnadu, India." Arabian Journal of Geosciences, 5.1 (2012): 83-94.

229. Srivastava S.K., Ramanathan A.L., "Geochemical assessment of groundwater quality in vicinity of Bhalswa landfill, Delhi, India, using graphical and multivariate statistical methods." Environmental Geology, 53 (2008): 1509-1528.

230. Subba Rao, N. "Groundwater quality: focus on fluoride concentration in rural parts of Guntur district, Andhra Pradesh, India." Hydrological Sciences Journal, 48.5 (Oct 2003): 835-847.

231. Subba Rao N., John Devadas D., "Fluoride incidence in groundwater in an area of Peninsular India." Environmental Geology, 45 (Dec 2003): 243-251.

232. Sujana M.G., Anand S.,"Fluoride removal studies from contaminated ground water by using bauxite." Desalination, 267. 2-3 (2011): 222-227.

233. Sujatha D., "Fluoride levels in the groundwater of the south-eastern part of Ranga Reddy district, Andhra Pradesh, India." Environmental Geology, 44 (2003): 587-591.

234. Sun L., Gao Y., Liu H., Zhang W., Ding Y., Li B., Li M., Sun D., "An assessment of the relationship between excess fluoride intake from drinking water and essential hypertension in adults residing in fluoride endemic areas." Science of the Total Environment, 443 (2013): 864-869.

235. Sundaram C.S., Viswanathan N., Meenakshi S.,"Defluoridation chemistry of synthetic hydroxyapatite at nano scale: equilibrium and kinetic studies." Journal of Hazardous Materials, 155.1-2 (Jun 2008): 206-215.

236. Sundaram C.S., Viswanathan N., Meenakshi S., "Defluoridation of water using magnesia/chitosan composite." Journal of Hazardous Materials, 163.2-3 (Apr 2009): 618-624.

237. Sundaram C.S., Meenakshi S., "Fluoride sorption using organic–inorganic hybrid type ion exchangers." Journal of Colloid and Interface Science, 33.1 (May 2009): 58-62.

238. Suthar S., Garg V.K., Jangir S., Kaur S., Goswami N., Singh S., "Fluoride contamination in drinking water in rural habitations of Northern Rajasthan, India." Environmental Monitoring and Assessment, 145 (2008): 1-6.

239. Tahaikt M., El Habbani R., Haddou A.A., Achary I., Amor Z., Taky M., Alami A., Boughriba A., Hafsi M., Elmidaoui A., "Fluoride removal from groundwater by nanofiltration." Desalination, 212.1-3 (2007): 46-53.

240. Tan T.L., Nakajima H., Rashid S.A., "Adsorptive, kinetics and regeneration studies of fluoride removal from water using zirconium-based metal organic frameworks." RSC advances, 10.32 (2020): 18740-18752.

241. Tatawat R.K., Chandel C.S., "A hydrochemical profile for assessing the groundwater quality of Jaipur City." Environmental monitoring and assessment, 143 (2008): 337-343.

242. Tembhurkar A. R., Dongre S., "Studies on fluoride removal using adsorption process." Journal of environmental science & engineering, 48.3 (2006): 151-156.

243. Thakre D., Jagtap S., Sakhare N., Labhsetwar N., Meshram S., Rayalu S., "Chitosan based mesoporous Ti–Al binary metal oxide supported beads for defluoridation of water." Chemical Engineering Journal, 158.2 (2010): 315-324.

244. Thakre D., Dixit P., Waghmare S., Manwar S. , Labhsetwar N., Rayalu S. , “Synthesis optimization and fluoride uptake properties of high capacity composite adsorbent for defluoridation of drinking water.” Environmental Progress & Sustainable Energy, 34.6 (2015): 1576-1585.

245. Thakur L.S., Mondal P., "Techno-economic evaluation of simultaneous arsenic and fluoride removal from synthetic groundwater by electrocoagulation process: optimization through response surface methodology." Desalination and Water Treatment, 57.59 (2016): 28847-28863.

246. Thakur S., Govender P.P., Mamo M.A., Tamulevicius S., Thakur V.K., "Recent progress in gelatin hydrogel nanocomposites for water purification and beyond." Vacuum, 146 (2017): 396-408.

247. Tolkou A.K., Trikalioti S., Makrogianni O., Trikkaliotis D.G., Deliyanni E.A., Kyzas G.Z., Katsoyiannis I.A., "Magnesium modified activated carbons derived from coconut shells for the removal of fluoride from water." Sustainable Chemistry and Pharmacy, 31 (2023): 100898.

248. Tomar V., Kumar D., “A critical study on efficiency of different materials for fluoride removal from aqueous media.” Chemistry Central Journal, 7 (2013): 1–15.

249. Turner B.D., Binning P., Stipp S.L., "Fluoride removal by calcite: evidence for fluorite precipitation and surface adsorption." Environmental science & technology, 39.24 (2005): 9561-9568.

250. Upendra R.S., Khandelwal P., Amiri Z.R., Achar A., Kumari B.G., Sowmaya M., Tejaswini J., "Optimization of fluoride removal system using Ocimum sp. Leaves and ragi seed husk by applying bio-statistical tools." Journal of Environmental Research and Development, 9.4 (2015): 1109.

251. Van Vliet B.M., Weber Jr. W.J., Hozumi H., "Modeling and prediction of specific compound adsorption by activated carbon and synthetic adsorbents." Water Research, 14.12 (1980): 1719-1728.

252. Vardhan C.V., Karthikeyan J., "Removal of fluoride from water using low-cost materials." Fifteenth International Water Technology Conference IWTC, 15 (2011): 1-14.

253. Vieira E.F.S., Cestari A.R., Carvalho W., Oliveira A., Chagas R.A., "The use of freshwater fish scale of the species Leporinus elongatus as adsorbent for anionic dyes: An isothermal calorimetric study." Journal of thermal analysis and calorimetry, 109. 3 (2012): 1407-1412.

254. Vijayaraghavan K., Jegan J., Palanivelu K., Velan M., "Removal of nickel (II) ions from aqueous solution using crab shell particles in a packed bed up-flow column." Journal of hazardous materials, 113.1-3 (2004): 223-230.

255. Vikas C., Kushwaha R.K., Pandit M.K., "Hydrochemical status of groundwater in district Ajmer (NW India) with reference to fluoride distribution." Journal of the Geological Society of India, 73 (2009): 773-784.

256. Vikas C., Kushwaha R., Ahmad W., Prasannakumar V., Reghunath R., "Genesis and geochemistry of high fluoride bearing groundwater from a semi-arid terrain of NW India." Environmental earth sciences, 68 (2013): 289-305.

257. Viswanathan N., Meenakshi S., "Synthesis of Zr (IV) entrapped chitosan polymeric matrix for selective fluoride sorption." Colloids and Surfaces B: Biointerfaces, 72.1 (2009): 88-93.

258. Vithanage M., Bhattacharya P., "Fluoride in drinking water: health effects and remediation." CO2 sequestration, biofuels and depollution, (2015): 105-151

259. Wang J., Lin X., Luo X., Long Y., "A sorbent of carboxymethyl cellulose loaded with zirconium for the removal of fluoride from aqueous solution." Chemical Engineering Journal, 252 (2014): 415-422

260. Wang M., Ye H., Zheng X., Chen S., Xing H., Tao X., Dang Z., Lu G., "Adsorption behaviors and mechanisms of simultaneous cadmium and fluoride removal on waste bovine bone from aqueous solution." Journal of Environmental Chemical Engineering, 11.1 (2023): 109035.

261. Weerasooriyagedara M., Ashiq A., Rajapaksha A.U., Wanigathunge R.P., Agarwal T., Magana-Arachchi D., Vithanage M., "Phytoremediation of fluoride from the environmental matrices: A review on its application strategies." Groundwater for sustainable development, 10 (2020): 100349.

262. Weginwar N., Takarkhede A. and Kamble R.., "Ground Water Fluoride in Chandrapur city in Maharashtra." Indian Journal of Environmental Protection, 28.7 (2008): 648-653.

263. World Health Organization. Progress on household drinking water, sanitation and hygiene 2000-2017: special focus on inequalities. World Health Organization, 2019.

264. Wu H. X., Wang, T. J., Chen L., Jin, Y., Zhang Y., Dou, X. M., "Granulation of Fe–Al–Ce hydroxide nano-adsorbent by immobilization in porous polyvinyl alcohol for fluoride removal in drinking water." Powder Technology, 209.1-3 (2011): 92–97.

265. Yadav A.K., Abbassi R., Gupta A., DadashzadehM.,"Removal of fluoride from aqueous solution and groundwater by wheat straw, sawdust and activated bagasse carbon of sugarcane." Ecological engineering, 52 (2013): 211-218.

266. Yadav J.P., Lata S., Kataria S.K., Kumar S., "Fluoride distribution in groundwater and survey of dental fluorosis among school children in the villages of the Jhajjar District of Haryana, India." Environmental geochemistry and health, 31 (2009): 431-438.

267. Yadav T. K., Prasad B., Singh D., Suranjit Prasad K., "Calcium pretreated Pinus Roxburghii wood biochar for adsorptive removal of fluoride from aqueous solution." Bionterface Research in Applied Chemistry, 12.4 (2022): 4307-4316.

268. Yahya M.D., Muhammed I.B., Obayomi K.S., Olugbenga A.G., Abdullahi U.B., "Optimization of fixed bed column process for removal of Fe (II) and Pb (II) ions from thermal power plant effluent using NaoH-rice husk ash and Spirogyra." Scientific African, 10 (2020): e00649.

269. Yang Z., Yang X., Wang T., Hu R., Wu J., "Oxygen-functionalized Typha angustifolia biochars derived from various pyrolysis temperatures: Physicochemical properties, heavy metal capture behaviors and mechanism." Colloids and Surfaces A: Physicochemical and Engineering Aspects, 628 (2021): 127259.

270. Younesi M., Javadpour S., Bahrololoom M.E., "Effect of heat treatment temperature on chemical compositions of extracted hydroxyapatite from bovine bone ash." Journal of Materials Engineering and Performance, 20 (2011): 1484-1490.

271. Yousefi M., Ghoochani M., Mahvi A.H., "Health risk assessment to fluoride in drinking water of rural residents living in the Poldasht city, Northwest of Iran." Ecotoxicology and environmental safety 148 (2018): 426-430.

272. Yu T., Chen Y., Zhang Y., Tan X., Xie T., Shao B., Huang X., "Novel reusable sulfate-type zirconium alginate ion-exchanger for fluoride removal." Chinese Chemical Letters, 32.11 (2021): 3410-3415.

273. Zainol I., Alwi N.M., Abidin M.Z., Haniza H.M., Ahmad M.S., Ramli A., "Physicochemical properties of hydroxyapatite extracted from fish scales." Advanced Materials Research, 545 (2012): 235-239

274. Zayadi, N., and Norzila O., "Characterization and optimization of heavy metals biosorption by fish scales." Advanced Materials Research, 795 (2013): 260-265.

275. Zhang G., Yang H., Fu P., Li Z., Ma W., "Evaluation of straw ash as a cost–effective adsorbent for the removal of phosphate and fluoride from aqueous solution." Groundwater for Sustainable Development, 14 (2021): 100626.

276. Zhou J., Liu Y., Han Y., Jing F., Chen J., "Bone-derived biochar and magnetic biochar for effective removal of fluoride in groundwater: Effects of synthesis method and coexisting chromium." Water environment research, 91.7 (2019): 588-597.

277. Zhou N., Guo X., Ye C., Yan L., Gu W., Wu X., Zhou Q., Yang Y., Wang X., Cheng Q., "Enhanced fluoride removal from drinking water in wide pH range using La/Fe/Al oxides loaded rice straw biochar." Water Supply, 22.1 (2022): 779-794

278. Zuo H., Chen L., Kong M., Qiu L., Lü P., Wu P., Yang Y., Chen, K., "Toxic effects of fluoride on organisms." Life sciences, 198 (2018): 18-24.

(Disha A Khandare)

04/4/23

DR. S. N. MUKHERJEE
Professor
CIVIL ENGINEERING DEPT.
JADAVPUR UNIVERSITY
KOLKATA-700032, (W.B)

Curriculum Vitae

CURRICULUM VITAE

Name	:	Disha Asaram Khandare
Date of Birth	:	16th May 1982
Correspondence Address	:	103, Laxmi Plaza, Opposite to Alexis Hospital, Mankapur Road, Nagpur-440030

❖ **Current designation and Affiliation:**

1) Lecturer (Selection Grade) , Civil Engineering Department, Government Polytechnic , Sakoli (M.S.)
2) QIP-Research Scholar , Civil Engineering Department Jadavpur Universit, Kolkata(W.B.)

❖ **Academic Qualification**:

Sr No.	**Qualification**	**Institute/ University**	**Year**	**Subject and area specialization**
1	S.S.C.	Maharashtra State Board	1998	Math, Science , Social Science, Language - Marathi
2	H.S.C.	Maharashtra State Board	2000	Science
3	B. E. (Civil)	R.T.M.Nagpur University	2005	Civil Engineering
4	M. Tech.	V.N.I.T., Nagpur	2008	Environmental Engineering
5	Ph.D. (pursuing)	Jadavpur University, Kolkata	Pursuing	Water Treatment

❖ ***Professional Experience :***

- Contributing to society through teaching profession for past 14 years. During these years gotopportunity to work as Asst. Professor at UG and PG level of Civil Engineering Department.

- Worked as Asst. Professor at renowned NBA accridiated institutes like Shri Ramdeobaba College of Engineering and Management(RKNCE), Nagpur and Yeshwantrao Chavan College of Engineering (YCCE), Nagpur form December 2006 to July 2011.
- From August – 2011, working as Lecturer at Government Polytechnic(M.S.) selected through MPSC.
- Worked as Research Scholar under QIP –Poly scheme at Jadavpur University, Kolkata fromDecember, 2017 to June , 2021.

❖ **Professional Membership:**

Member of Indian Society for Technical Education
Member of Institute of Engineers
Member of Indian Water Works Association.

❖ **Award/Prize/Certificate:**

1. Academic Excellence Award for highest Cumulative Performance at M.Tech - 2008
2. Bhide Memorial Prize -2008 for best performer M. Tech.
3. Purna Award for First order of Merit -2008
4. Honored as Youth Icon -2010 by NG0-NNBY, India for contributing inducation for underprivileged program
4. Best Performer of the year 205-16 for exceptional contribution to Institute Development.
5. Honored as Inspirational Women Teacher 2017 by Womens wing GovernmentPolytechnic, Nagpur.
6. Received Best paper award at an International Conference at NIT, Durgapur forInnovative Sustainable Research-Development Idea - 2020

PAPERS PUBLISHED

April-4- p65

J. Indian Chem. Soc.,
Vol. 96, April 2019, pp. 429-434

Fish scale waste: Potential low-cost adsorbent for fluoride removal

Disha A. Khandare and Somnath Mukherjee*

Environmental Engineering Division, Civil Engineering Department, Jadavpur University, Kolkata-700 032, India

E-mail: mukherjeesomnath19@gmail.com

Manuscript received online 31 January 2019, accepted 25 March 2019

Wastes generated at fish industry are considered as an important pollutant having a serious impact on the environment. Fish waste generally has high biological oxygen demand (BOD) and typically possesses strong offensive smell. Fish scales constitute major part of fishery waste and usually be disposed as a waste with no commercial value. The feasibility of using fish scale derived biochar is investigated as a low-cost adsorbent for defluoridation. A batch removal and kinetic study was performed to examine the efficiency of fluoride removal from simulated spiked water sample. Some influencing parameters such as adsorbent dose contact time, agitation speed etc. on the fluoride removal kinetics are also evaluated. Experimental outcome reveals that fish scale biochar (FSB) can successfully be used as an effective adsorbent in water environment for fluoride removal.

Keywords: Fishery waste, fish scales, adsorption, biochar, fluoride removal.

Introduction

Consumption of fish and shrimp worldwide is increased over the last decade. As an outcome of these activities a huge production of fish scale is salvaged globally. In India, this waste is discarded as garbage and indiscriminately disposed without recovery of any useful product[1]. About 18–30 million tons of fish wastes is generated at fish processing industry of which 4% are fish scales[2]. Depending on the fish species, the yield of scales from fish is around 4–10%[3]. In last few decades, variety of low-cost adsorbents were derived from different types of waste/by-products of agricultural, municipal and industrial sources which were reported as effective pollutant removal from water and wastewaters[4]. Many conventional methods like membrane filtration, precipitation, ion-exchange, electro-coagulation, reverse osmosis, nanofiltration and adsorption are widely used for defluoridation. These methods so far are either not sustainable or economical for various unfavorable factors.

In past few decades, many biosorbents from various trees and animal sources have been tried as defluoridation agents. leaf powder[5–7], activated rice husk[8,9], barks[10,11], tamarind seeds[12], seed extracts of *Moringa oleifera*[13], tea ash[14,15], egg shell powder[16], treated powdered corn cob[17], chitin, chitosan[18] are few among them. In recent times, adsorbent produced from industrial waste have attracted many researchers for using as relatively less costly, renewable and abundantly available materials. Similarly, many studies have reported biochar as a universal sorbent for the removal of pollutants from soil and water environment. Biochar possesses relatively large specific surface area, high porosity and stable carbon matrix structure which make it a material of choice as an adsorbent[19]. A few studies have shown fish scales are used as effective biosorbent for removal of lead, chromium, arsenic and many such heavy metals. Table 1 shows recent studies made on fish scale as an adsorbent for removal of heavy metals from water environment.

This study is conducted to examine the use of Rohu Fish (Labeo Rohita) scales (FS) waste collected from fish market as a raw material to produce fish scale biochar (FSB) as a novel inexpensive adsorbent for defluoridation of drinking water and industrial wastewater. The primary emphasis of this present investigation was to reduce the high amount environmental burden related to fish waste disposal. This will also result in value addition of usages of waste materials. Few researchers have evaluated the potential of fish scale to remove heavy metals from water environment as listed in Table 1. The existing literature reveals that, no previous study has been done to explore the potential of fish scale biochar (FSB) for fluoride removal from water environment which

DR. S. N. MUKHERJEE
Professor
CIVIL ENGINEERING DEPT.
JADAVPUR UNIVERSITY
KOLKATA-700032, (W.B)

(Disha A. Khandare)

WEES-2020 Special Issue

J. Indian Chem. Soc.,
Vol. 97, No. 10b, October 2020, pp. 1778-1783

Comparative assessment of commercial activated carbon and fish scale derived activated carbon for adsorptive removal of fluoride from drinking water

Disha A. Khandare* and Somnath Mukherjee

Civil Engineering Department, Jadavpur University, Kolkata-700 032, India

E-mail: dishakhandare@gmail.com

Manuscript received online 22 May 2020, revised and accepted 18 September 2020

Excessive fluoride concentration above WHO (2011) standard (> 1.5 mg/L) is observed worldwide in groundwater. Considering its serious concern a laboratory based investigation was undertaken to find the fluoride elimination potential by the Commercial Activated Carbon (CAC) and indigenously developed Fish Scale Activated Carbon (FSAC) from water solution. Batch sorption studies were carried out to observe some important process parameters such as adsorbent dose, contact time, pH etc. on removal kinetics. At pH 2, CAC could remove upto 75% of fluoride wheras FSAC could remove up to 92.68% of fluoride at pH 6. The percent removal of fluoride enhanced with the increase in sorbent mass. The equilibration state was found to be achieved within 2 and 3 h for CAC and FSAC respectively. Both CAC and FSAC exhibit reasonably well fluoride uptake capacity for initial fluoride level of 7 and 5 mg/L respectively. The equilibrium data fitted well into Freundlich as well as Langmuir isotherms models. The experimental investigations suggest that both Commercially Available Activated Carbon (CAC) and Fish Scale Derived Activated Carbon (FSAC) can be adopted as adsorbent for defluridation purpose in the treatment of drinking water. Fish scale derived activated carbon (FSAC) showed more fluoride uptake capacity than commercially available activated carbon (CAC).

Keywords: Adsorption, fluoride, commercial and fish scale carbon, removal kinetics.

Introduction

Water is elixir of all forms of life. Presence of undesirable element in excess in water makes the water unfit for consumptive use. Fluoride is one such kind of pollutant of concern. Excessive fluoride concentration above WHO standard (i.e. > 1.5 mg/L) is observed in groundwater throughout the globe. Prolonged consumption of water with excess fluoride (> 1.5 mg/L) is responsible for fluorosis in human beings. Prolonged exposure of fluoride through drinking water is being contributed to a serious health hazard of dental and skeletal fluorosis. The fluorine-containing rocks are main natural geological sources of elevated fluoride levels in groundwater. Besides this, anthropogenic sources like discharges from aluminium smelters, ceramic production units, and coal fired power stations, electroplating processes, fertilizer manufacturing industries, glass manufacturing and processing industries, and semiconductor manufacturing industries are contributing to fluoride contamination of water environment[1]. Numerous endeavours are attempted earlier to establish a sustainable engineering method of fluoride removal under different constraints in developing countries. A surge of conventional engineering methods are used and practiced for defluoridation of water with various physico-chemical unit operation[2]. Membrane filtration techniques are broadly comprised of electro-dialysis, nano-filtration and reverse osmosis[3]. The challenges in adopting most of these methods are their limited fluoride removal capacities, high operational and maintenance cost, post-treatment alterations of water quality, generation of toxic sludge and its disposal into the environment[4].

Among these techniques of defloration, adsorption method is most favoured method due to its ease of operation, greater accessibility to variety of adsorbents, lower cost of treatment. In water purification and industrial wastewater treatment, activated carbons are widely used an important and efficient commercial adsorbents[5]. In recent years, many defluoridation studies have foucused on preparion and use of carbons derived from naturally available materials. The

4/4/23

DR. S. N. MUKHERJEE
Professor
CIVIL ENGINEERING DEPT.
JADAVPUR UNIVERSITY
KOLKATA-700032, (W.B)

POSITIF

Fixed bed column adsorption study for removal of fluoride by Acid modified Fish Scale Biochar.

Khandare D. A.[a], Mukherjee S.[b]

[a] Rresearch scholar, Civil Engineering Department, Jadavpur University, Kolkata-700 032, India
[b] Professor, Civil Engineering Department, Jadavpur University, Kolkata-700 032, India

Abstract:
Fluoride (F$^-$) is well known geogenic water contaminant and found in many parts of the world in subsurface water. It is element of concern due to its harmful effects on human health. In the present use of study a waste based biochar i.e. acid modified fish scale biochar was investigated for its potential to remove fluoride from water through a modified fish scale biochar packed continuous column adsorption. The influence of some salient effect of process parameter such as bed height, flow rate and initial F$^-$ ion concentration was investigated through breakthrough curves and the relevant well known breakthrough models were examined. For bed height of 1, 2 and 3 cm the breakthrough time was observed as 283.64, 441 and 673.53 min respectively. The highest breakthrough adsorption capacity (q_b) was found to 1.91 mg/gm at 5mg/L initial fluoride concentration and 1 cm bed height. To further analyze the breakthrough curves, i.e. Bed Depth Service Time (BDST), Thomas and Yoon–Nelson were applied on experimental data. From the experimental data it is evident that the BDST model significantly demonstrates the fixed bed adsorption with high R^2 values as compared to other mathematical models. The breakthrough service time was observed as 283.64, 441 and 673.53 min for bed height 1, 2 and 3cm respectively. The breakthrough curves were also successfully analyzed and described by both Thomas and Yoon–Nelson models.

Keywords: Fluoride removal, Biochar, Fixed bed column, Breakthrough modeling

4/4/23

DR. S. N. MUKHERJEE
Professor
CIVIL ENGINEERING DEPT.
JADAVPUR UNIVERSITY
KOLKATA-700032, (W.B)

(Disha A. Khandare)

Conference Attended

ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Materials Today: Proceedings 18 (2019) 1146–1155

materialstoday: PROCEEDINGS

www.materialstoday.com/proceedings

ICN3I-2017

A Review of Metal oxide Nanomaterials for Fluoride decontamination from Water Environment

Ms. Disha Khandare[a], Dr. Somnath Mukherjee[b]

[a] *Civil Engineering Department, Government Polytechnic, Nagpur-440030, India.*
[b] *Civil Engineering Department, Jadavpur University, Kolkata-700032, India.*

Abstract

Fluoride pollution in water emerges a challenging problem to environmental researchers especially in regions where people depend on groundwater for drinking. Natural water bodies are experienced Fluoride impurities from geogenic and anthropogenic sources. Fluoride contamination in drinking water sources has been recognized as a major problem in many countries worldwide especially in several parts of India, China, Sri Lanka, South Africa, Tanzania, Argentina, East Africa, part of South Africa, Turkey and some part of South America. Intrusion of Fluoride with drinking water manifests several health effects such as dental caries and teeth mottling besides skeletal fluorosis. Due to clinical manifestations caused by drinking Fluoride contaminated water, the World Health Organization (WHO) has recommended 1.5 mg L-1. Hence, it is very much needed to supply water with safe F^-. Various physico-chemical methods are available for defluoridation of water, out of which adsorption method is common and widely be used .to remove fluoride from water. Till date, activated alumina is most conventional adsorbing material that are conveniently being used for this purpose. However, activated alumina performed well in acidic environment and regeneration issue poses a complex problem. Other traditional adsorbents though are able to uptake Fluoride from water environment the low sorption capacities and efficiencies restricted their wide application. A major breakthrough took place in recent years due to application of nanomaterial in water purification. As compared with traditional materials used, nanostructure based adsorbents exhibited much higher

Corresponding author. Tel.:+ 91 9422819119; fax: +91-712-256-4483.
E-mail address: dishakhandare@gmail.com

Selection and/or Peer-review under responsibility of International Conference on Nanotechnology: Ideas, Innovations & Initiatives-2017 (ICN:3i-2017).

4/4/23

DR. S. N. MUKHERJEE
Professor
CIVIL ENGINEERING DEPT.
JADAVPUR UNIVERSITY
KOLKATA-700032, (W.B)

(Disha A. Khandare)

Adsorptive Removal of Fluoride from Water Using Non-conventional Adsorbents

Disha Khandare, Ajay Tembhurkar, and Somnath Mukherjee

Abstract The rapid industrialization and ever-growing population have led to degradation of water quality and reduction in availability safe drinking water. Presence of priority and secondary pollutants in underground water is posing serious health concerns. Fluoride in drinking water is referred as a two-edge sword for its beneficial (up to 1 mg/L) and detrimental effects (>1.5 mg/L). In the present study, an attempt is made to assess the fluoride removal efficiencies of some waste material as well as the naturally occurring substances. In the present study, fly ash, modified neem bark powder and fish scale biochar were investigated for their feasible use as adsorbent for fluoride removal from water environment. Batch sorption experiments were employed to examine the effect of influencing parameters like adsorbent dose, contact time, pH, initial fluoride concentration and agitation speed, etc. The batch sorption data showed non-conventional adsorbents can be used effectively in fluoride removal and simultaneously also renders to reduce refuse disposal problem of human settlement.

(Disha A. Khandare)

Keywords Adsorption · Non-conventional adsorbent · Fluoride removal · Batch studies

1 Introduction

The presence of fluoride contamination of drinking water source is a serious concern worldwide. Many countries like Sri Lanka, parts of South Africa, China, Turkey

---

D. Khandare (✉)
Civil Engineering Department, Jadavpur University, Kolkata 700032, India
e-mail: dishakhandare@gmail.com

A. Tembhurkar
Civil Engineering Department, VNIT, Nagpur 440010, India
e-mail: artembhurkar@civ.vnit.ac.in

S. Mukherjee
Civil Engineering Department, Jadavpur University, Kolkata 700032, India
e-mail: mukherjeesomnath19@gmail.com

4/4/23
DR. S. N. MUKHERJEE
Professor
CIVIL ENGINEERING DEPT.
JADAVPUR UNIVERSITY
KOLKATA-700032, (W.B)

L. M. Gupta et al. (eds.), *Advances in Civil Engineering and Infrastructural Development*, Lecture Notes in Civil Engineering 87,
https://doi.org/10.1007/978-981-15-6463-5_42

Waste Management
towards Circular Economy
www.iswmaw.com

Fish Scale Waste- a potential sustainable material for water pollution remediation

D. A. Khandare*, S. N. Mukherjee

Civil Engineering Department. Jadavpur University, Kolkata, India
**Corresponding Author: Email - dishakhandare@gmaill.com*

ABSTRACT *An enormous quantity of non-edible by-products of fishery waste including fish scales are generated at fish markets and fish-processing industries. At the end of the day this fish waste is generally dumped in-land or hauled into water bodies haphazardly without any commercial recovery and valorization of product. Though some components of fish waste are utilized as animal feed, fish silage, fish-meal and in production of surgical products, biodiesel, biogas, fertilizers, natural pigments, ornaments, cosmetics and in pharmaceutical industries still the main bulk as scale is discarded as waste leading major concern of environmental pollution. A fish yields scales around 4-10 % of its biomass depending on its species, which constitute major part of fishery waste. Non utilization of industrial by-products like fishery waste has great impact on the environmental pollution and economy of the country. In recent years use of waste based adsorbents is gaining lot of attention in water and wastewater treatment. Use fish scales as an adsorbents for removal of dyes, heavy metals and other inorganic pollutants from water and wastewaters is a very recent innovation and a value added sustainable material can be used for waste management. Fish scale based adsorbents have shown excellent adsorbent capacities in removal of heavy metals, industrial dyes and various inorganic pollutants. Researchers have mainly studied effect of influencing process parameters, optimization, equilibrium, kinetics and thermodynamics of adsorption. The present review aims to provide succinct information regarding use of Fish scale as an adsorbent for water remediation, furthermore identifying limitations and future scope of its application. Utilization of fish scale waste for removal of pollutants from water environment can be innovative waste minimization option for Fishery waste management.*

Keywords: *Fish scale, adsorption, pollutants remediation, sustainable waste management*

4/9/23

DR. S. N. MUKHERJEE
Professor
CIVIL ENGINEERING DEPT.
JADAVPUR UNIVERSITY
KOLKATA-700032, (W.B)

(Disha A. Khandare)