## Acknowledgment

I am thankful to the Almighty God, who showed me the path to through. It is very difficult to name all the sources of inspiration; moreover, words are often too weak a mode of revealing one's sentiments and feelings of indebtedness.

I express my deep sense of thankfulness to my supervisor, Prof. Prabhat Kumar Singh, for his valuable guidance, encouragement and help throughout my dissertation work. I had the privileges of being associated with Prof. Singh, not only in the context of this work but otherwise also. His myriad suggestions followed by free confabulation prevented me from being strayed. My gratitude's can well be understood, although expressing my indebtedness towards Prof. Singh is beyond my writing and words.

I am thankful to Prof. Prabhat Kumar Singh Dikshit, Head, Department of Civil Engineering, IIT (BHU) Varanasi for giving his kind consent for encouragement and support in the form of facilities provided by the Department.

I owe sincere gratitude to my esteemed Dr. Arun Lal Srivastav, Assistant Professor, School of Engineering and Technology, Chitkara University, for helping me all my journey on this topic and under whose caring environment I had the privilege of carrying out my M. Tech. dissertation work.

I express my gratitude to Er. Ramesh Singh, Visiting Faculty, Department of Civil Engineering, IIT(BHU) Varanasi for his valuable suggestions and guidance.

I am also thankful to Prof. Goutam Banerjee, Department of Civil Engineering, IIT (BHU) Varanasi for time to time guidance and also for their valuable suggestion which paved the easy way to achieve the goal.

I also express my profound gratitude to my Research Program Committee member Prof. Shyam Bihari Dwivedi, Department of Civil Engineering and Prof. Y.C. Sharma, Department of Chemistry, IIT (BHU) Varanasi for their keen interest, valuable guidance, continuous encouragement and inspiration. Thanks are also due to Research Scholars Dr. Sonali Saxena, Dr. Satya Prakash Maurya, Mrs. Shruti Singh, Mr. Abjijit Debnath, Mr. Nitin Ranjan, and Miss Ria Ranjan Srivastav, Environmental Engineering Divison, Department of Civil Engineering, IIT(BHU) Varanasi.

Here, I would like to mention that this research work would have been really difficult without the active help of Mr. Hira Lal Singh, Mr. Shankar Ram and Mr. Jai Singh Yadav of Environmental Engineering Laboratory, Department of Civil Engineering, IIT(BHU) Varanasi

I shall be failing in my duty if I do not express my thanks to my father Shree Haribansh Kumar and my mother Mrs. Malti Devi. I express my sincere sense of gratitude towards my parents and my other family members for their love, affection and support.

I thank to all of my friends and well-wishers, whose names could not be brought on this piece of paper for extending their cooperation without reservation.

I never forget the constant encouraging endeavors and generosity bestowed by my wife Mrs. Sujata Kumari and my son Master Rishaan Kashyap without whose love and affections this work would not have come into reality.

I would also like to thank the authorities of Water Resources Department, Govt. of Bihar for allowing me a Study Leave. I should thankfully acknowledge the moral support given by my Executive Engineers Shri Dr. Ishwar Chandra Thakur, Dr. Murlidhar Singh, and Shri Pramod Kumar. I am indebted with the love and affection shown by Mrs. Gita Singh for her supportive goodwill gestures. I also appreciate the help of Dr. Parvez Akhtar during the completion of this work.

#### MANISH RANJAN

## CONTENTS

Chapters	Title	Page No.
TITLE		i
CERTIFIC	CATES	ii
DECLAR	ATION BY THE CANDIDATE	iii
COPYRIC	GHT TRANSFER CERTIFICATE	iv
ACKNOW	VLEDGEMENT	v-vi
TABLE O	FCONTENTS	vii-x
LIST OF I	FIGURES	vi-vii
	ADDELUATIONS	x111-XV 
LIST OF A	ABBREVIATIONS	XV1-XV11
LIST OF S	SYMBOLS	xviii-xix
ABSTRA	CT	XX-XXX
1. CHAP	FER 1: INTRODUCTION	1-33
1.1 Water:	A basic natural resource	1
1.2 Safe w	ater for drinking	2
1.3 Groun	dwater	3
1.4 Contai	mination of groundwater	4
1.4.1	Nitrate contamination in groundwater	4
1.4.2	Fluoride contamination in groundwater	6
1.4.3	Arsenic contamination in groundwater	7
1.5 Global	scenario of contamination	9
1.5.1	Nitrate contamination in groundwater: Global scenario	9
1.5.2	Fluoride contamination in groundwater: Global scenario	9
1.5.3	Arsenic contamination in groundwater: Global scenario	10
1.6 Indian	scenario of contamination	12
1.6.1	Nitrate contamination in groundwater: Indian scenario	12
1.6.2	Fluoride contamination in groundwater: Indian scenario	14
1.6.3	Arsenic contamination in groundwater: Indian scenario	16
1.7 Standa	rds for nitrate, fluoride and arsenic in drinking water	18
1.7.1	Standards of nitrate in drinking water	18
1.7.2	Standards of fluoride in drinking water	18
1.7.3	Standards of arsenic in drinking water	19
1.7.4	Globally accepted standards of nitrate, fluoride and arsenic in	19
	drinking water	

1.8	Sim	Iltaneous presence of more than one contaminant in groundwater	20
1.0	IOP O	rinking in India	20
1.9	Need	1 of the study	30
1.10	Obje	ctives of the present study	31
1.11	Stru	cture of the thesis	31
2 (	CHAI	TER 2: LITERATURE REVIEW	34-83
2.1 0	Groun	dwater contamination	34
2.2 7	Techn	ologies for nitrate removal from water	36
2.3 T	Techn	ologies for fluoride removal from water	44
2.4 7	[echn	ologies for arsenic removal from water	57
2.5 F	Remov	al of nitrate, fluoride and arsenic in coexisting conditions	68
2.6 S	Select	on of adsorbent	76
2	2.6.1	Hydrous bismuth oxides (HBOs) in nitrate, fluoride and arsenic removal from water	77
2.7 S	Summ	ary of Literature Review and Objectives of the present study	80
2.8 0	Chara	cterization techniques of selected inorganic adsorbent (HBO)	81
2.9 F	Resear	rch aim	82
2.10	Scope	e of the present study	82
3.	CHA	PTER 3: MATERIALS AND METHODS	84-100
3.1	Mater	ial/Glassware	84
3.2 0	Chemi	cals and Reagents	84
3.3 I	nstrui	nent	84
3.4 I	Deterr	nination of pH, nitrate, fluoride, arsenic and others parameters	87
3.5 0	Gener	al experiment	90
3	3.5.1	Stock solutions for nitrate fluoride and arganic	
3		Stock solutions for intrate, nuoride, and arsenic	90
	8.5.2	Batch adsorption experiment	90 91
	3.5.2	Batch adsorption experiment 3.5.2.1 Effect of adsorbent dosage	90 91 91
	3.5.2	Batch adsorption experiment 3.5.2.1 Effect of adsorbent dosage 3.5.2.2 Effect of contact time	90 91 91 92
3	3.5.2 3.5.3	Batch adsorption experiment 3.5.2.1 Effect of adsorbent dosage 3.5.2.2 Effect of contact time Column adsorption experiment	90 91 91 92 92
3	3.5.2 3.5.3 3.5.4	Batch adsorption experiment 3.5.2.1 Effect of adsorbent dosage 3.5.2.2 Effect of contact time Column adsorption experiment Regeneration studies	90 91 91 92 92 94
3 3 3.6 A	3.5.2 3.5.3 3.5.4 Adsor	Batch adsorption experiment 3.5.2.1 Effect of adsorbent dosage 3.5.2.2 Effect of contact time Column adsorption experiment Regeneration studies	90 91 91 92 92 94 95
3 3 3.6 A 3.7 A	8.5.2 8.5.3 8.5.4 Adsor	Batch adsorption experiment 3.5.2.1 Effect of adsorbent dosage 3.5.2.2 Effect of contact time Column adsorption experiment Regeneration studies ption kinetics studies ption isotherm studies	90 91 92 92 94 95 95
3 3 3.6 A 3.7 A 3.8 C	3.5.2 3.5.3 3.5.4 Adsorj Comp	Batch adsorption experiment 3.5.2.1 Effect of adsorbent dosage 3.5.2.2 Effect of contact time Column adsorption experiment Regeneration studies btion kinetics studies btion isotherm studies eting anions studies	90 91 92 92 94 95 95 95
3 3 3.6 A 3.7 A 3.8 C 3.9 C	3.5.2 3.5.3 3.5.4 Adsorj Comp Calcul	Batch adsorption experiment 3.5.2.1 Effect of adsorbent dosage 3.5.2.2 Effect of contact time Column adsorption experiment Regeneration studies ption kinetics studies ption isotherm studies eting anions studies ation of adsorption potential (mg/g) and percentage removal of	90 91 92 92 94 95 95 95 96 96
3 3.6 A 3.7 A 3.8 C 3.9 C n	3.5.2 3.5.3 3.5.4 Adsorj Comp Calcul nitrate	Batch adsorption experiment 3.5.2.1 Effect of adsorbent dosage 3.5.2.2 Effect of contact time Column adsorption experiment Regeneration studies ption kinetics studies ption isotherm studies eting anions studies ation of adsorption potential (mg/g) and percentage removal of , fluoride and arsenic	90 91 92 92 94 95 95 96 96
3 3.6 A 3.7 A 3.8 C 3.9 C m 3.10	3.5.2 3.5.3 3.5.4 Adsor Comp Calcul nitrate Chai	Batch adsorption experiment 3.5.2.1 Effect of adsorbent dosage 3.5.2.2 Effect of contact time Column adsorption experiment Regeneration studies ption kinetics studies ption isotherm studies eting anions studies ation of adsorption potential (mg/g) and percentage removal of , fluoride and arsenic acterization of adsorbents	90 91 92 92 94 95 95 96 96 96
3 3.6 A 3.7 A 3.8 C 3.9 C 3.9 C 3.10 3.11	3.5.2 3.5.3 3.5.4 Adsor Comp Calcul aitrate Char Dete	Batch adsorption experiment 3.5.2.1 Effect of adsorbent dosage 3.5.2.2 Effect of contact time Column adsorption experiment Regeneration studies ption kinetics studies ption isotherm studies eting anions studies ation of adsorption potential (mg/g) and percentage removal of , fluoride and arsenic acterization of adsorbents rmination of bismuth concentration in treated water	90 91 92 92 94 95 95 96 96 96 97 99

3.13 Selection of adsorbent

99

3.14 P	reparations of Hydrous Bismuth Oxide (HBO) media	100
4. CH	APTER 4: RESULTS AND DISCUSSION 10	)1-179
4.1 HB	Os as possible sorbent for arsenic removal from aqueous	101
SOII	utions	102
4.2 Sin	iuitaneous removal of nitrate, fluoride and As(v) by HBOs	102
froi	m the mixed solution in batch adsorption experiment	105
4.2	.1 Effect of adsorbents dosage	105
4.2	2 Effect of mixed powder dosage	108
4.2	.3 Effect of contact time	111
4.2	.4 Preference of adsorption	112
4.2	.5 Simultaneous removal of nitrate, fluoride and As(V) from mixed	113
	solution in presence of competitive anions	
	4.2.5.1 Effect of bicarbonate	113
	4.2.5.2 Effect of sulfate	114
4.3 Ad	sorption kinetics studies	116
4.3	.1 First order kinetic model	117
4.3	.2 Second order kinetic model	118
4.3	.3 Weber-Morris (WM) kinetic model	119
4.4 Ad	sorption isotherm studies	130
4.4	.1 Langmuir isotherm model	130
4.4	.2 Freundlich isotherm model	131
4.4	.3 Dubinin-Redushkevich (DR) isotherm model	132
4.5 The	ermodynamic studies	145
4.6 Sin	nultaneous removal of nitrate, fluoride and As(V) by HBO <sub>12mix</sub>	147
fro	m mixed solution in column adsorption experiment	
4.6	1 First cycle of contaminants removal	148
4.7 Res	generation and reuse of HBO <sub>12mix</sub>	152
47	1 First regeneration of the HBO $_{12mix}$ bed	152
47	2 Second cycle of contaminants removal	152
4.7	3 Second regeneration of the $HBO_{12}$ bed	152
4.7	$\Lambda$ Third cycle of contaminants removal	155
4 8 Tes	sting of experimental results by mathematical empirical models	160
4.8	3.1 Bohart-Adams model	161
4.8	3.2 Thomas model	161
4.8	3.3 Yoon Nelson model	162
4.9 Per	formance of HBO12mix powder in real ground water of IIT (BHU)Varanas	si
spil	ked with nitrate, fluoride and As(V) contaminants	163
4.9	.1 Batch experiments	163
4.9	.2 Column experiments	164
4.10	Bismuth in treated water	168

4.11 Characterizations of adsorbent		169	
	4.11.1	X-Ray Diffraction (XRD) of HBO <sub>12mix</sub>	169
	4.11.2	Scanning Electron Microscopy (SEM)	171
	4.11.3	Energy-Dispersive X-ray Spectroscopy (EDS)	172
	4.11.4	Fourier Transform Infrared Spectroscopy (FTIR)	174
	4.11.5	pH at Point of Zero Charge (pHpzc)	176
	4.12 Pros	pect and challenges of using HBO as an adsorbent for	177
	grou	ndwater treatment in POU system	
	4.13 Cost	analysis of HBO <sub>12mix</sub>	178
5. CH	APTER 5: S	UMMARY AND CONCLUSIONS	180-187
5.1 St	immary		180
5.2 Co	onclusions		185
5.3 St	uggestions for	future work	187
R	EFERENCE	S	188-240
L	IST OF PUB	LICATIONS	

## LIST OF FIGURES

Figure No.	Title	Page No
Figure 1.1	Water on earth	2
Figure 1.2	Quality deterioration of ground water	4
Figure 2.1	Different classes of adsorbents used for the removal of nitrate from water	39
Figure 3.1	Ion meter for measuring pH	85
Figure 3.2	Ion meter for measuring nitrate and fluoride concentrations	86
Figure 3.3	Arsenator set up for measuring arsenic concentrations	86
Figure 3.4	Wagtech Digital Arsenator Kit	87
Figure 3.5	Grain size distribution of adsorbent	93
Figure 3.6	Experiment set up for column adsorption	94
Figure 4.1	Effect of adsorbent dosages on simultaneous removal of contaminants from mixed solution	104
Figure 4.2	Effect of mixed powder (a) HBO <sub>12mix</sub> and (b) HBO <sub>13mix</sub> on simultaneous removal of nitrate, fluoride and As(V) from mixed solution	110
Figure 4.3	Effect of contact time on contaminants removal and sorption potentials of HBO <sub>12mix</sub> powder from mixed solution	112
Figure 4.4	Effect of bicarbonate and sulfate ions on simultaneous removal of nitrate, fluoride and As(V) from mixed solution	115
Figure 4.5	Linearized kinetic plots of pseudo first order model for nitrate, fluoride and As(V) sorption from mixed solution	121
Figure 4.6	Linearized kinetic plots of pseudo second order model for nitrate, fluoride and As(V) sorption from mixed solution	122
Figure 4.7	Linearized kinetic plots of Weber-Morris model for nitrate, fluoride and As(V) sorption from mixed solution	123
Figure 4.8	Langmuir isotherm linearized plots for nitrate, fluoride and $As(V)$ sorption on $HBO_{12mix}$	134
Figure 4.9	Freundlich isotherm linearized plots for nitrate, fluoride and As (V) sorption on HBO <sub>12mix</sub>	135
Figure 4.10	DR model isotherm linearized plots for nitrate, fluoride and $As(V)$ sorption on $HBO_{12mix}$	136
Figure 4.11	Removal of nitrate, fluoride and As(V) by HBO <sub>12mix</sub> adsorbent in column mode of operation in first cycle; (a) Breakthrough curves for nitrate, fluoride and As(V);	150

	<ul><li>(b)Variation of pH with increasing volume of effluent;</li><li>(c) Changing concentrations of chloride in effluent</li></ul>	
Figure 4.12	Chloride uptake by HBO <sub>12mix</sub> adsorbent during first regeneration	152
Figure 4.13	Removal of nitrate, fluoride and As(V) by HBO <sub>12mix</sub> adsorbent in column mode of operation in second cycle; (a) Breakthrough curves for nitrate, fluoride and As(V); (b) Variation of pH with increasing volume of effluent; (c) Changing concentrations of chloride in effluent.	154
Figure 4.14	Chloride uptake by HBO <sub>12mix</sub> adsorbent during second regeneration	155
Figure 4.15	Removal of nitrate, fluoride and As(V) by HBO <sub>12mix</sub> adsorbent in column mode of operation in third cycle; (a) Breakthrough curves for nitrate, fluoride and As(V); (b) Variation of pH with increasing volume of effluent; (c) Changing concentrations of chloride in effluent.	157
Figure 4.16	Breakthrough curves for nitrate, fluoride and $As(V)$ through $HBO_{12mix}$ powder in down flow mode of operation in three cycles	158
Figure 4.17	Variation of effluent pH through HBO <sub>12mix</sub> powder in column mode of operation in three cycles	159
Figure 4.18	Characteristics of effluents from column using sand with HBO <sub>12mix</sub> in the bed and ground water of IIT(BHU) spiked with nitrate, fluoride and As(V) as influent; (a)Breakthrough curves for nitrate, fluoride and As(V); (b) Variation of pH with increasing volume of effluent; (c) Changing concentrations of chloride in effluent; (d) Concentration of sulphate in the effluent, and (e)	166
Figure 4.19	XRD patterns of $HBO_{12mix}$ (a) in original form (b) after adsorption of nitrate, fluoride and arsenic onto the material	170
Figure 4.20	SEM micrographs of $HBO_{12mix}$ (a) in original form and (b) after adsorption of nitrate, fluoride and arsenic from solution	172
Figure 4.21	EDS patterns of $HBO_{12mix}$ (a) in original form and (b) after adsorption of nitrate, fluoride and arsenic from solution	173
Figure 4.22	FTIR Spectra patterns of HBO <sub>12mix</sub> (a) in original form and (b) after adsorption of nitrate, fluoride and arsenic from solution	174

Table No	Title	Page No
Table 1.1	Nitrate contamination in water: Global scenario	9
Table 1.2	Fluoride contamination in water: Global scenario	10
Table 1.3	Arsenic contamination in water: Global scenario	11
Table 1.4	Districts in India with high nitrate concentrations in groundwater	12
Table 1.5	Districts in India with high fluoride concentrations in groundwater	14
Table 1.6 (a)	Districts in India with high arsenic concentrations in groundwater	16
Table 1.6 (b)	Districts in India with Arsenic (>0.05 mg/L) in ground water	17
Table 1.7	Anions standards in drinking water	20
Table 1.8	State wise names of the districts (partly) in India affected	21
	by nitrate, fluoride and arsenic contamination of ground waters	
Table 1.9	Districts of India reported with presence of more than	26
	one contaminant (nitrate, fluoride or arsenic) in groundwater beyond permissible limits for drinking	
Table 2.1	Common groundwater contaminants	34
Table 2.2	Comparative analyses of the removal technologies applicable for anionic contaminants removal from water	35
Table 2.3	Important features of some major nitrate removal technologies	38
Table 2.4	Important characteristics of different adsorbents examined for nitrate removal from water	40
Table 2.5	Important characteristics of different adsorbents	48
	examined for fluoride removal from water	
Table 2.6	Important characteristics of different adsorbents	59
	examined for arsenic removal from water	
Table 2.7	Characteristics of adsorbents used for simultaneous	68
	removal of more than one contaminant (nitrate, fluoride	
	and arsenic) coexisting in water	

## LIST OF TABLES

Table 2.8	Characteristics of hydrous bismuth oxides (HBOs) and	79
	their preparation methods for nitrate, fluoride and arsenic	
	removal from water	
Table 2.9	Techniques for characterization of inorganic adsorbents	81
Table 4.1	Arsenic removal efficiencies of hydrous bismuth oxides (HBO <sub>1</sub> )	101
Table 4.2	Effect of adsorbent dosage on simultaneous removal of contaminants from mixed solution	105
Table 4.3	Sorptive Potentials of HBOs for nitrate, fluoride and As(V) from water	106
Table 4.4	Simultaneous removal of nitrate, fluoride and As(V) from mixed solution using HBO <sub>12mix</sub> powder	108
Table 4.5	Simultaneous removal of nitrate, fluoride and As(V) from mixed solution using HBO <sub>13mix</sub> powder	109
Table 4.6	Preferential Sorptive Characteristics of HBO <sub>12mix</sub>	112
Table 4.7	Kinetic parameters for adsorption of nitrate, fluoride and $As(V)$ on $HBO_{12mix}$ powder	124
Table 4.8	Trend analysis for kinetic parameters of nitrate, fluoride and arsenic sorption from the solution on HBO <sub>12mix</sub> powder	129
Table 4.9	Initial and final parameters of adsorption isotherm on HBO <sub>12mix</sub> powder	137
Table 4.10	Isotherm parameters of adsorption for adsorption of nitrate, fluoride and As(V) on HBO <sub>12mix</sub> powder	138
Table 4.11	Trend analysis for isotherm parameters of nitrate, fluoride and arsenic sorption from the solution on HBO <sub>12mix</sub> powder	143
Table 4.12	Effect of temperature on nitrate, fluoride and As(V) sorption process on HBO <sub>12mix</sub> based on mean adsorption energy ( <i>E</i> ) of D-R isotherm studies	144
Table 4.13	Trend analysis of maximum adsorption capacity $(q_o)$ of HBO <sub>12mix</sub> for nitrate, fluoride and As(V) from aqueous solutions	144
Table 4.14	Thermodynamic parameters for simultaneous removal of nitrate, fluoride and As(V) by HBO <sub>12mix</sub> powder	147
Table 4.15	Relation between anions sorbed and chloride released from HBO <sub>12mix</sub> in first cycle of column experiment	151

Table 4.16	Relation between anions sorbed and chloride released	155
	from HBO <sub>12mix</sub> in second cycle of column experiment	
Table 4.17	Relation between anions sorbed and chloride released	158
	from HBO <sub>12mix</sub> in third cycle of column experiment	
Table 4.18	Parameter of different mathematical models used on	162
	Column study data	
Table 4.19	Characteristics of initial and final solutions in batch	163
	experiments with ground water spiked contaminants	
Table 4.20	Relation between anions sorbed and chloride released	167
	from HBO <sub>12mix</sub> in ground water column experiment	
Table 4.21	Determination of Bismuth in treated water	168
Table 4.22	XRD patterns of (a) Original HBO <sub>12mix</sub> and (b) Spent	171
	HBO <sub>12mix</sub>	
Table 4.23	FTIR Spectroscopic Analyses of HBO12mix before	175
	(original form) and after adsorption	
Table 4.24	pHpzc of different forms of HBOs	177
Table 4.25	Cost of production of some adsorbents	179

## LIST OF ABERVIATIONS

AAS	Atomic Absorption Spectrophotometer
AgNO <sub>3</sub>	Silver nitrate
As (III)	Arsenite/Arsenic (III)
As (V)	Arsenate/Arsenic (V)
BaCl <sub>2</sub>	Barium chloride
Bi(OH) <sub>3</sub>	Bismuth hydroxide
Bi <sub>2</sub> O <sub>3</sub>	Bismuth trioxide
BiOOH	Bismuthyl hydroxide
BIS	Bureau of Indian Standard
CER	Chloride exchange ratio
EC	European commission
EDS	Energy dispersive X-ray spectroscopy
FT-IR	Fourier Transform Infra-red spectroscopy
GV	Guidelines value
HBO <sub>1</sub>	Hydrous Bismuth Oxide 1(1:1 v/v)
HBO <sub>2</sub>	Hydrous Bismuth Oxide 2 (1:2 v/v)
HBO3	Hydrous Bismuth Oxide 3 (1:3 v/v)
HBO <sub>12mix</sub>	HBO <sub>1</sub> +HBO <sub>2</sub>
HBO <sub>13mix</sub>	HBO <sub>1</sub> +HBO <sub>3</sub>
HCl	Hydrochloric acid
HCO <sub>3</sub> <sup>-</sup>	Bicarbonate (alkalinity)
НМО	Hydrous metal oxide
JCPDS	International Centre for Diffraction Data 12 Campus Boulevard, Newtown Square, PA 19073-3273 U.S.A.

KCrO4	Potassium chromate
MCL	Maximum contamination level
ML	Mandatory limit
Na2HAsO4.7H2O	Sodium arsenate dibasic heptahydrate
Na2SO4	Sodium sulfate
NaBH4	Sodium borohydride
NaCl	Sodium chloride
NaF	Sodium fluoride
NaHCO3	Sodium bicarbonate
NaNO3	Sodium nitrate
NaOH	Sodium hydroxide
NH <sub>2</sub> .SO <sub>3</sub> H	Sulphamic acid
NO <sub>3</sub> <sup>-</sup>	Nitrate
PL	Permissible limit
rpm	Revolution per minute
SEM	Scanning Electron Microscope
<b>SO</b> <sub>4</sub> <sup>2-</sup>	Sulphate/ Sulfate
TISAB	Total Ionic Strength Adjustment Buffer
USEPA	United States Environmental Protection Agency
WHO	World health organization
XRD	X-ray diffraction

## LIST OF SYMBOLS

°C	Degree Celsius
μg/g	Microgram/gram
μg/L	Microgram/Liter
b	Adsorption equilibrium constant (L/mg)
с	Constant related to the Weber and Morris model
С	Effluent or final concentration (mg/L)
Ce	Concentration at equilibrium (mg/L)
Co	Influent or initial concentration (mg/L)
Cu	Coefficient of uniformity
<b>D</b> 10	Effective particle size in mm
<b>D</b> <sub>60</sub>	Effective size through which 60% particle will pass in mm
Ε	Mean free energy of adsorption (kJ/mol)
$\mathbf{F}^{-}$	Fluoride
g	Mass in gram
н	Hight of column
K	Constant related to adsorption energy
<b>K</b> 1	Pseudo-first-order rate constant (min <sup>-1</sup> )
<b>K</b> <sub>2</sub>	Pseudo-second-order rate constant (min <sup>-1</sup> )
<b>K</b> 3	Weber Morris rate constant (min <sup>-1/2</sup> )
Kba	Bohart adam rate constant [mL/(min mg)]
Kth	Thomas rate constant [mL/(min mg)]
Kyn	Yoon Nelson rate constant (1/h);
m	Mass of adsorbent per liter of solution (g/L)
Μ	Molarity (moles/Liter)

mg/g	Milligram/gram		
mg/L	Milligram/Liter		
n	Freundlich constant		
Ν	Normality (moles equivalent/Liter)		
Р	Standard thermodynamic equilibrium constant (L/g)		
pHpzc	Point of zero charge		
<b>Q</b> a	Theoretical adsorption capacity (mg/g)		
<b>Q</b> ba	Bohart adam maximum concentration of solute (mg/g)		
<b>q</b> e	Adsorption capacity at equilibrium (mg/g)		
qo	Maximum adsorption capacity (mg/g)		
qt	Adsorption capacity at any time t (mg/g)		
<b>Q</b> th	Thomas maximum concentration of solute (mg/g)		
R	Gas constant (8.314 J/mol K)		
t	Service time of column under the above conditions (h)		
Т	Absolute temperature in Kelvin (K)		
v	Linear flow velocity of feed to bed (mL/cm <sup>2</sup> )		
X	Relative cost of operation		
ΔG°	Change in Gibbs free energy		
ΔH°	Change in enthalpy		
ΔS°	Change in entropy		
3	Polanyi potential		
Г	Time (t) when C/ $C_o = 0.5$ .		
K <sub>f</sub>	Isotherm constant related to adsorption capacity		

### ABSTRACT

Contamination of groundwater for drinking purpose is a worldwide challenge that has economic and human health impacts (WHO, 2004). Such contamination is caused normally by dissolved chemical constituents, such as nitrate, fluoride and arsenic and other heavy metals in it, which may either be geogenic or anthropogenic in origin. A significant proportion of human population suffers from the problems of such anionic contaminants.

Among the various metal oxides used for anionic contaminants removal, very few have been examined for simultaneous removal of three commonly found anionic contaminants, namely nitrate (NO<sub>3</sub><sup>-</sup>), Fluoride (F<sup>-</sup>) and Arsenic (Arsenite: H<sub>2</sub>AsO<sub>3</sub><sup>-</sup> or Arsenate: H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>) from aqueous solution. Hydrous Bismuth Oxides (HBOs) have been indicated to have such potentials. Accordingly in the present study HBOs have been investigated with the objective to evaluate sorption efficiency for nitrate, fluoride, and arsenic simultaneously from aqueous solutions.

HBOs were synthesized using bismuth trioxide (Bi<sub>2</sub>O<sub>3</sub>) solution in 2N HCl with 2N NaOH in increasing volumetric proportions of 1:1, 1:2, 1:3 and the materials thus obtained were designated as HBO<sub>1</sub>, HBO<sub>2</sub> and HBO<sub>3</sub>. While HBO<sub>1</sub> is visibly white, HBO<sub>2</sub> and HBO<sub>3</sub> are yellow in color. After 1 h of reaction time, the supernatants were decanted and the precipitate was centrifuged to remove all unreacted chemicals. Finally, the precipitates were washed several times with distilled water till pH of the supernatant indicates neutral solution and chloride content is minimal. The materials were dried at 103+2°C and stored in dry bottles to be used. Mix of HBO<sub>1</sub> and HBO<sub>2</sub> in equal proportion is designated as HBO<sub>12mix</sub>.

### HBOs as possible sorbent for Arsenic species from aqueous solutions

In the present study, among the two species of Arsenic, arsenite  $(H_2AsO_3^-, HAsO_3^{-2} - and AsO_3^{-3})$  has been expressed as As(III) and arsenate  $(H_2AsO_4^-, HAsO_4^{-2} - and AsO_4^{-3})$ . as As(V). Based on initial studies, all the three forms of HBOs, i.e., HBO<sub>1</sub>, HBO<sub>2</sub> and HBO<sub>3</sub> were found giving more than 91 % of removal with respect to initial concentrations. Hence, HBO1 was selected for As(III) as well as As(V) sorption study. Also, for a 3h contact time, the removal efficiency for As(V) is higher (91%) than As(III) (74%). Hence for testing, As(V) was chosen for further experiments. HBO<sub>1</sub> is expected to work with higher efficiency in groundwaters obtained from oxidizing environment.

# Simultaneous removal of nitrate, fluoride and As(V) by HBO<sub>12mix</sub> from the mixed solution in batch adsorption experiment

All the batch and column experiments were carried out with synthetic mixed solution containing 1.5 meq/L ( $\approx$ 95 mg/L) of nitrate, 0.25 meq/L ( $\approx$ 5 mg/L) of fluoride and 0.001 meq/L ( $\approx$ 0.08 mg/L) of As(V) in distilled water.

#### Effect of single adsorbents dosage:

From the mixed solution, at equal dosage of 100 g/L of single adsorbent and 3h contact time, a maximum of 60-61% of nitrate by HBO2 and HBO3, 68% of fluoride and 91% of As(V) by HBO1 are observed. Thus, it appears that for simultaneous removal of all the three contaminants: nitrate, fluoride and As(V) from water, mixed media of (HBO<sub>1</sub>+HBO<sub>2</sub>) or (HBO<sub>1</sub>+HBO<sub>3</sub>) may be a good option. Accordingly, experiments were conducted to check the potentials of mixed powder media, i.e. HBO<sub>1</sub>+HBO<sub>2</sub>, designated as HBO<sub>12mix</sub> and HBO<sub>1</sub> +HBO<sub>3</sub>, designated as HBO<sub>13mix</sub>.

#### Effect of mixed powder dosage:

With increasing dosage from 10 g/L to 150 g/L of  $HBO_{12mix}$ , the removal of nitrate increased from 11% to 52% at 110 g/L, beyond which there is no further improvement. Fluoride removal increased from 22% to 71% at 130 g/L and then stabilized. As(V) removal increased from 81% at 10 g/L dosage to 92% at 20 g/L and remained constant there after.

With HBO<sub>13mix</sub> (HBO<sub>1</sub>+HBO<sub>3</sub>) as adsorbent, the nitrate removal increased from 20% to 53% at a dosage of 120 g/L, the fluoride removal increased from 28% at 20 g/L to 71% at 140 g/L and As(V) removal was 92% at 20 g/L which remained constant on all dosages.

Based on these observations  $HBO_{12mix}$  was selected as the media of preference and a dosage of 130 g/L of adsorbent was considered appropriate for further experiments.

#### **Effect of contact time:**

The percentage removal of nitrate, fluoride and As(V) generally increase with increasing time of contact and attain a stable level after around 180 min. onwards. Hence 180 min. contact time is considered optimum for the simultaneous removal of these contaminants using HBO<sub>12mix</sub> powder.

# Simultaneous removal of nitrate, fluoride and As(V) from mixed solution in presence of competing anions

A concentration range of 1-5 meq/L sulfate and bicarbonate were tested on simultaneous removals of 1.5 meq/L nitrate ( $\approx 95 \text{ mg NO}_3^-/\text{L}$ ), 0.25 meq/L fluoride ( $\approx 5 \text{ mg F}/\text{L}$ ) and 0.001 meq/L As(V) ( $\approx 0.08 \text{ As}(\text{V}) \text{ mg/L}$ ). Hence in presence of competitive anions (HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>).

Hence in presence of competitive anions (HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>)

- For nitrate removal by HBO<sub>12mix</sub>, the preference series of anions appear as: Bicarbonate >Sulfate> Nitrate.
- For fluoride and As(V) removal by HBO<sub>12mix</sub>, preference is as follows: Sulfate> Bicarbonate> Fluoride/ As(V).

Hence, HBO<sub>12mix</sub> is found potentially useful for sorption of As(V), Fluoride and Nitrate below an alkalinity of around 150 mg/L as CaCO<sub>3</sub> and Sulphate concentration of 140 mg/L.

#### Adsorption kinetic studies

Pseudo first order, Pseudo second order, Weber-Morris models were applied with the experimental data of the present study to understand the anions sorption on adsorbent. Pseudo first order kinetic model was found to give relatively higher correlation coefficient. Hence, these observations indicate that probably pseudo-first order kinetics is more dominant and governing than the pseudo-second order kinetics for all the three selected anionic contaminants in the present study.

In the solid-liquid adsorption system, the help of Weber-Morris model was taken to illustrate the diffusion mechanism and rate-controlling process of adsorption. The regression coefficient of process lies in between 0.913 to 0.985 suggesting that the rate-controlling steps were not governed by a single process.

#### Adsorption isotherm studies

The Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were used to conduct equilibrium studies for the removal of nitrate, fluoride and arsenate from water.

Inspection of the data revealed that the agreement of isotherm data fit well with Freundlich isotherm for nitrate. Arsenic adsorption data on HBO<sub>12mix</sub> appears to follow D-R isotherm equation more closely than others. Increased temperature leads to

increase the threshold energies of solute particle which result in more molecular collision at higher temperature.

The value of adsorption energy constant (*K*) derived from D-R isotherm can be further used to differentiate the process govern by the physisorption, ion exchange or chemisorption by calculating adsorption energy. From the D–R equation and according to the value *E* values indicated that the anions sorption by HBO<sub>12mix</sub> is the dominated by ion exchange phenomena followed by physical adsorption.

#### **Thermodynamics studies**

The values of  $\Delta G^{\circ}$  were found to be negative at all temperatures which indicated about the spontaneous nature of the anions adsorption onto HBO<sub>12mix</sub>. The positive value of  $\Delta H^{\circ}$  suggests that adsorption of anions over HBO<sub>12mix</sub> is endothermic in nature. The magnitude of  $\Delta H^{\circ}$  if lies between 2.1–20.9 kJ/mol the adsorption process can be accounted as physical while chemical adsorption generally falls into a range of 80–200 kJ/mol. In this case  $\Delta H^{\circ}$  value corresponds to intermediate range between physical and chemical adsorption.

## Simultaneous removal of nitrate, fluoride and As(V) by HBO<sub>12mix</sub> from the mixed solution in column adsorption experiment

Particle sizes of hydrous bismuth oxide powder are very fine in nature. In order to use it in column adsorption study, HBO<sub>1</sub>+HBO<sub>2</sub>: 50 g+200 g powders and 150 g sand were mixed to get observable results. The sand to be used was initially cleaned by keeping it in 0.1 N HCl for 24 h and then washed with sufficient distilled water. A glass column (Internal Diameter = 30 mm) was filled up to a height of around 51 cm with the mixed media consisting of sand and sorbents ( $D_{10} = 0.18$  mm,  $C_u = D_{60}/D_{10} = 2.4$ ). A synthetic mix solution of 1.5 meq/L (≈95 mg/L) nitrate, 0.25 meq/L (≈5 mg/L) fluoride and 0.001 meq/L (≈0.08 mg/L) As(V) with pH~7, which is representative of the field samples of anionic contaminated groundwaters in affected part of the country was taken for column study. The contaminants spiked water was passed at a flow rate of ~1.2-1.5 mL/min. Samples of effluent were collected at an interval of every 30 min and measurements of pH, nitrate, fluoride, As(V) and chloride were made.

In continuous mode of study, it is observed that  $C/C_o$  for all the three contaminants remains zero till around 520 mL effluent volume. The breakthrough for nitrate occurs first, followed by fluoride and then As(V). The breakthrough ( $C/C_o=0.1$ ) for these anions occurs at around 720, 1000 and 3680 mL cumulative volume respectively (Figure 1). Total anions sorbed upto zero concentration in the effluent and the breakthrough points are found to be around 0.99 and 1.33 meq respectively.

Concentrations of these anions exceed their respective permissible limits for drinking after treating around 1320, 1960 and 3680 mL of nitrate, fluoride and As(V) in first cycle. Similarly, effluent exceed their respective permissible limits just after treating around 480, 780 and 1240 mL of solution in the second cycle and consequently cumulative effluent volume of 380, 580 and 1000 mL third cycle respectively. The breakthrough of nitrate occurs first, followed by fluoride and As(V). Chloride Exchange Ratio (CER) for the anions sorbed and chloride released from HBO<sub>12mix</sub> powder was calculated as around 0.7, 0.6 and 0.5 for first, second and third cycle respectively.

The pH of effluent varied in the range 7.34-7.98 and chloride level in effluents keeps decreasing with time and further diminishes as the adsorbent reaches towards exhaustion. Ion exchange of contaminants with chloride embedded in the powder could be a possibility based on the results observed.



Figure 1: Removal of nitrate, fluoride and As(V) by HBO<sub>12mix</sub> adsorbent in column mode of operation in first cycle; (a) Breakthrough curves for nitrate, fluoride and As(V); (b)Variation of pH with increasing volume of effluent; (c) Changing concentrations of chloride in effluent

#### **Regeneration studies**

Regeneration of HBO<sub>12mix</sub> was also attempted for its further use in anions removal with 0.1 N NaOH and 0.1 N NaCl solutions. 60% anions content was obtained in desorption and further regenerated adsorbent was used up to 3 consecutive cycles of anions removal (Figure 2).





Figure 2: Removal of nitrate, fluoride and As(V) by  $HBO_{12mix}$  adsorbent in column mode of operation in second and third cycle; (a) Breakthrough curves for nitrate, fluoride and As(V); (b) Variation of pH with increasing volume of effluent; (c) Changing concentrations of chloride in effluent

Concentration of bismuth ion was also not detected in the treated water by Atomic Absorption Spectrophotometer (AAS) which indicated that no bismuth ions are present in treated water as already reported by Srivastav et al. (2014).

# Performance of HBO<sub>12mix</sub> in real ground water of IIT(BHU) Varanasi spiked with nitrate, fluoride and arsenic contaminants

#### **Batch experiments:**

Table 1 compiled the inlet and outlet qualities from groundwater after batch experiment.

Parameter	Influent	Effluent	Change
рН	7.4	7.9	Slight increase
Chloride (mg/L)	16	32.5	>50% increase
Alkalinity (as mg/L CaCO <sub>3</sub> )	305	80	Around 73% decrease
Sulphate (mg/L)	18	12	Around 33 % decrease
Nitrate (mg/L)	72.5	49.1	32% decrease
Fluoride (mg/L)	5.5	1.5	72% decrease
Arsenic (V) (mg/L)	0.080	0.007	91% decrease

Table 1: Inlet and Outlet qualities from groundwater after batch experiment

The experimental data from the above table could deduce the idea of alkalinity being more dangerous and competing anions for nitrate. As nitrate removal being hindered by high level of bicarbonate (alkalinity) at inlet level. But pH remains in limiting zone and chloride level quite variable at outlet.

#### **Column experiments:**

Hence, higher concentrations of alkalinity and sulfate put the limitation on concurrent removal of nitrate, fluoride and As(V) (Figure 3(a)). Slight release of hydroxide (Figure 3(b)) was observed as a result of nitrate, fluoride and As(V) on the surface of HBO<sub>12mix</sub> at initial flow. High concentration gradient of bicarbonate in influent leads to dumping of nitrate and fluoride by HBO<sub>12mix</sub> leads to rise in nitrate and fluoride appears at effluent.



Figure 3: Characteristics of effluents from column using sand and HBO<sub>12mix</sub> in the bed and ground water of IIT(BHU) spiked with nitrate, fluoride and As(V) as influent;(a) Breakthrough curves for nitrate, fluoride and As(V); (b) Variation of pH with increasing volume of effluent

Figure 4(b), (c) show the reduction in residual alkalinity and sulphate at effluent. Hence alkalinity and sulphate are being adsorbed by  $HBO_{12mix}$ . Whereas chloride concentrations were observed as incremental variable at effluent as shown in Figure 4(a). Priority of affinity was changed due the bicarbonate and chloride on the surface of adsorbent. Bicarbonate seems to be more unstable and get itself replaced with chloride. The elevated level of chloride at effluent and reduction in bicarbonate and sulfate concentrations, in themselves point towards chloride exchange by  $HBO_{12mix}$ .



Figure 4: Effluent quality from HBO<sub>12mix</sub> column with contaminants spiked groundwater (a) Changing concentrations of chloride in effluent; (b) Concentration of sulphate in the effluent, and (c) Concentration of alkalinity in the effluent

#### **Characterization of adsorbent**

#### X-Ray Diffraction (XRD) of HBO<sub>12mix</sub>

Presences of multiple peaks in XRD patterns indicate the broadly crystalline character of adsorbent. The 2 $\theta$  peak values (26.3°, 30.5°, 33.4°) for the XRD peak corresponds to Bi<sub>12</sub>O<sub>15</sub>Cl<sub>16</sub> (29-0237) by using X-pert high score software. The additional 2 $\theta$  peaks values of (23.92°, 30.16°), (29.94, 32.84) and 33.42 refer to Bi<sub>6</sub>O<sub>7</sub>FCl<sub>13</sub> (70-0854), Bi<sub>19</sub>AsO<sub>31</sub> (46-0192), Bi(ClO<sub>4</sub>)NO<sub>2</sub> (43-0759) respectively were observed after adsorption on the surface of adsorbent.

#### Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) analysis has been done to know the surface morphology of adsorbent. SEM spectrum initially (before adsorption) indicates the granular and spongy formation which later (after adsorption) becomes exhausted with heterogeneous and rough surface. SEM micrograph of HBO<sub>12mix</sub> in original and spent forms. The SEM analyses show granular irregular surface morphology of the adsorbent.

#### **Energy-dispersive X-ray spectroscopy (EDS)**

Energy-dispersive X-ray spectroscopy (EDS) spectrum analysis reflects the broad elemental analysis of the material. From EDS analysis, it is observed that HBO<sub>12mix</sub> is broadly composed of Bi, O and Cl. After the adsorption of nitrate, fluoride and As(V) from the solution, the EDS of spent material shows peaks corresponding to N, F and As, confirming the adsorption of anionic contaminants on the material. The percentage of Cl<sup>-</sup> appears to have decreased in spent material with respect to original one.

Hence, existence of nitrate, fluoride and arsenic(V) on the surface of exhausted adsorbent in addition to bismuth and chloride were detected from EDS analysis which is in agreement with our data findings in XRD analysis as well.

#### Fourier Transform Infra-red spectroscopy (FT-IR)

FT-IR spectrum of prepared adsorbent before and after adsorption has been done. The broad absorption peaks of 530 and 846 due to Bi-O bond. Further water molecule and hydroxide were spotted at peak of 1380, 1620 and 3430 respectively. Bervas et al. (2006) and Escudero et al. (2014) specified absorption bands corresponding to wave numbers 441 cm<sup>-1</sup> and 530 cm<sup>-1</sup> only as characteristics of Bi-F bond. The sharp peak at 1274 cm<sup>-1</sup> and 1310 cm<sup>-1</sup> could be due to the existence of BiNO<sub>3</sub>. In addition, the frequency at 675 cm<sup>-1</sup> to 1045 cm<sup>-1</sup> show characteristics of As-O bond. The distinctive absorptions bands corresponding to nitrate, fluoride and arsenic in additions to those of bismuth and hydroxyl ions indicate that the target anions have become integral part of the adsorbents. FT-IR analysis of tested materials supports the results obtained through XRD and EDS analysis.

#### pH at point of zero charge (pHpzc)

The pH at represents a condition in which the surface hold equal electrical charge density of positive and negative ions because of neutral condition. Whereas, the pH is lower than the pzc value, the system is said to be "below the pzc." Below the pzc, the acidic water donates more protons than hydroxide groups, and so the adsorbent surface gets positively charged (attracting anions) and hence, it favored the sorption of target anions.

The pH of point of zero charge of adsorbent was determined using fast alkalimetric titration method. In our experiment, the net titration curve for different ionic strengths of electrolyte meets at different levels giving a range of pHpzc rather than a single point. The pH<sub>PZC</sub> of HBO<sub>12mix</sub> is found to be in the range of 8.0-8.2. This may be due to possible interaction between the media and the chloride solution used as electrolyte. The pH<sub>PZC</sub> of HBO<sub>12mix</sub> is found to be 8.0-8.2 where the net surface charge becomes zero as surface of adsorbent becomes neutral attributing to equal density of negative and positive charge. Hence suitability and possibility of anionic uptake (nitrate, fluoride and arsenic) favors only with the condition of pH< pH<sub>PZC</sub> (8.0-8.2) due to columbic forces of attraction. Similarly force of repulsion will act as pH> pH<sub>PZC</sub> (8.0-8.2).

### CONCLUSIONS

Presence of high concentrations of nitrate, fluoride and arsenic in groundwater for drinking is a recognized problem in many parts of India and the world. Hydrous bismuth oxides (HBOs) have been shown to have sorptive properties for anionic contaminants. The present study focused on simultaneous removal of these contaminants from coexisting condition by HBOs. Central Ground Water Board (CGWB) of India has reported many districts in the country where all the three contaminants are found in the groundwater sources.

Three HBOs, designated as HBO<sub>1</sub>, HBO<sub>2</sub> and HBO<sub>3</sub> have been examined for removal of nitrate, fluoride and arsenic under coexisting condition of presence in water intended for drinking. A 1:1 weight basis mix of HBO<sub>1</sub> and HBO<sub>2</sub> powders has been designated as HBO<sub>12mix</sub> and that of HBO<sub>1</sub> and HBO<sub>3</sub> as (HBO<sub>13mix</sub>).

Conclusions recorded in the present study may be summarized as follows:

- Hydrous Bismuth Oxides (HBOs) appear to have significant sorptive potentials for removal of nitrate, fluoride as well as arsenic from contaminated ground water.
- 2. In coexisting conditions, at the levels mostly present in groundwater, arsenic is the most preferred anionic contaminant followed by fluoride and nitrate for HBOs in terms of removal potentials.
- 3. Among the three forms of HBOs, designated as HBO<sub>1</sub>, HBO<sub>2</sub> and HBO<sub>3</sub> examined during this study while HBO1 shows preferential adsorption of As(V), followed by fluoride, HBO<sub>2</sub> and HBO<sub>3</sub> prefer As(V) followed by nitrate.
- 4. A 1:1 mix of HBO<sub>1</sub> and HBO<sub>2</sub> (designated as HBO<sub>12mix</sub>) appears a potential material for simultaneous removal of nitrate, fluoride and arsenic from ground water in coexisting conditions.
- 5. While pHpzc of HBO<sub>1</sub> is around 6.5, for HBO<sub>12mix</sub>, it is around 8.0-8.2. The increased  $pH_{pzc}$  of HBO<sub>12mix</sub> appears to make it a more suitable for anionic contaminants removal from water in normal pH range.
- 6. Chloride embedded in the polymeric structure of material appears to be the exchange anion in the sorptive removal of contaminants and competitive anionic species from water.
- 7. Alkalinities followed by sulfate are the major competitive anions for nitrate, fluoride and arsenic removal by such media.

- 8. Regeneration of sorptive material can be done using NaOH and NaCl solutions, followed by bed washing with water.
- 9. In order to reduce the contaminants level to within limits for drinking, a pretreatment of water for alkalinity and sulfate reduction appears desirable and increasing proportional HBO<sub>2</sub> is essential.
- 10. HBO<sub>12mix</sub> may be used as a potential sorbent for developing a point of use (POU) treatment unit for removal of arsenic and fluoride coexisting in groundwater. Removal of nitrate remains low.