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

4. CHAPTER 4: RESULTS AND DISCUSSION 101-179

LIST OF FIGURES

LIST OF TABLES

LIST OF ABERVIATIONS

AAS	Atomic Absorption Spectrophotometer
$AgNO_3$	Silver nitrate
As (III)	Arsenite/Arsenic (III)
As (V)	Arsenate/Arsenic (V)
$BaCl_2$	Barium chloride
$Bi(OH)_3$	Bismuth hydroxide
Bi_2O_3	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_1	Hydrous Bismuth Oxide 1(1:1 v/v)
HBO_2	Hydrous Bismuth Oxide 2 (1:2 v/v)
HBO_3	Hydrous Bismuth Oxide 3 (1:3 v/v)
HBO_{12mix}	HBO_1+HBO_2
HBO_{13mix}	HBO_1+HBO_3
HCl	Hydrochloric acid
HCO_3^-	Bicarbonate (alkalinity)
HMO	Hydrous metal oxide
JCPDS	International Centre for Diffraction Data 12 Campus Boulevard, Newtown Square, PA 19073-3273 U.S.A.

$KCrO_4$	Potassium chromate
MCL	Maximum contamination level
ML	Mandatory limit
$Na_2HAsO_4.7H_2O$	Sodium arsenate dibasic heptahydrate
Na_2SO_4	Sodium sulfate
$NaBH_4$	Sodium borohydride
NaCl	Sodium chloride
NaF	Sodium fluoride
$NaHCO_3$	Sodium bicarbonate
$NaNO_3$	Sodium nitrate
NaOH	Sodium hydroxide
$NH_2.SO_3H$	Sulphamic acid
NO_3^-	Nitrate
PL	Permissible limit
rpm	Revolution per minute
SEM	Scanning Electron Microscope
SO_4^{2-}	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)
c	Constant related to the Weber and Morris model
C	Effluent or final concentration (mg/L)
C_e	Concentration at equilibrium (mg/L)
C_o	Influent or initial concentration (mg/L)
C_u	Coefficient of uniformity
D_{10}	Effective particle size in mm
D_{60}	Effective size through which 60% particle will pass in mm
E	Mean free energy of adsorption (kJ/mol)
F^-	Fluoride
g	Mass in gram
H	Hight of column
K	Constant related to adsorption energy
K_1	Pseudo-first-order rate constant (min^{-1})
K_2	Pseudo-second-order rate constant (min^{-1})
K_3	Weber Morris rate constant ($min^{-1/2}$)
K_{ba}	Bohart adam rate constant [mL/(min mg)]
K_{th}	Thomas rate constant [mL/(min mg)]
K_{yn}	Yoon Nelson rate constant (1/h);
m	Mass of adsorbent per liter of solution (g/L)
M	Molarity (moles/Liter)

mg/g	Milligram/gram
mg/L	Milligram/Liter
n	Freundlich constant
N	Normality (moles equivalent/Liter)
P	Standard thermodynamic equilibrium constant (L/g)
pH_{PZC}	Point of zero charge
q_a	Theoretical adsorption capacity (mg/g)
q_{ba}	Bohart adam maximum concentration of solute (mg/g)
q_e	Adsorption capacity at equilibrium (mg/g)
q_o	Maximum adsorption capacity (mg/g)
q_t	Adsorption capacity at any time t (mg/g)
q_{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)
T	Absolute temperature in Kelvin (K)
v	Linear flow velocity of feed to bed (mL/cm^2)
X	Relative cost of operation
$\Delta G°$	Change in Gibbs free energy
$\Delta H°$	Change in enthalpy
$\Delta S°$	Change in entropy
ε	Polanyi potential
г	Time (t) when $C/ C_o = 0.5$.
K_f	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_3^-), Fluoride (F^-) and Arsenic (Arsenite: $H_2AsO_3^-$ or Arsenate: $H_2AsO_4^-$) 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_2O_3) 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_1, HBO_2 and HBO_3. While HBO_1 is visibly white, HBO_2 and HBO_3 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_1 and HBO_2 in equal proportion is designated as HBO_{12mix}.

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_1, HBO_2 and HBO_3 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_1 is expected to work with higher efficiency in groundwaters obtained from oxidizing environment.

Simultaneous removal of nitrate, fluoride and As(V) by HBO_{12mix} 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 (≈95 mg/L) of nitrate, 0.25 meq/L (≈5 mg/L) of fluoride and 0.001 meq/L (≈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_1+HBO_2) or (HBO_1+HBO_3) may be a good option. Accordingly, experiments were conducted to check the potentials of mixed powder media, i.e. HBO_1+HBO_2, designated as HBO_{12mix} and HBO_1 +HBO_3, designated as HBO_{13mix}.

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_{13mix} (HBO_1+HBO_3) 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_{12mix} 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 (≈ 95 mg NO_3^-/L), 0.25 meq/L fluoride (≈5 mg F^-/L) and 0.001 meq/L As(V) (≈ 0.08 As(V) mg/L). Hence in presence of competitive anions (HCO_3^- and SO_4^{2-}).

Hence in presence of competitive anions (HCO_3^- and SO_4^{2-})

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

Hence, HBO_{12mix} is found potentially useful for sorption of As(V), Fluoride and Nitrate below an alkalinity of around 150 mg/L as $CaCO_3$ 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_{12mix} 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_{12mix} is the dominated by ion exchange phenomena followed by physical adsorption.

Thermodynamics studies

The values of ΔG^o were found to be negative at all temperatures which indicated about the spontaneous nature of the anions adsorption onto HBO_{12mix}. The positive value of ΔH^o suggests that adsorption of anions over HBO_{12mix} is endothermic in nature. The magnitude of ΔH^o 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 ΔH^o value corresponds to intermediate range between physical and chemical adsorption.

Simultaneous removal of nitrate, fluoride and As(V) by HBO_{12mix} 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_1+HBO_2: 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_{12mix} 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.

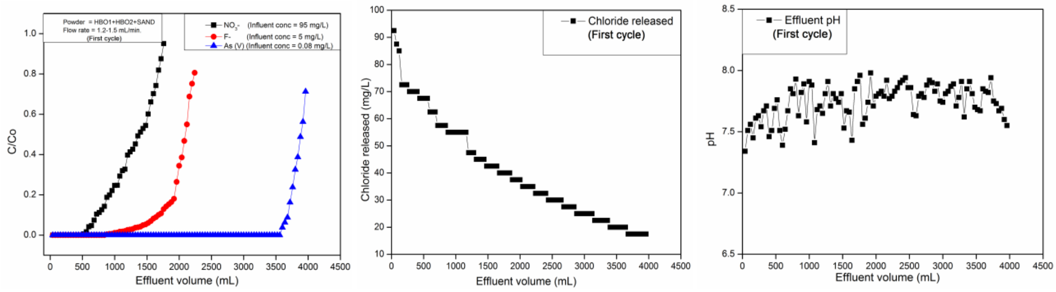
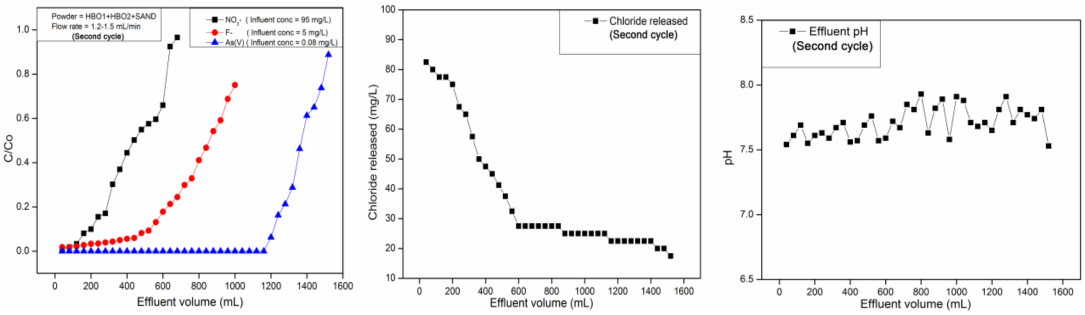


Figure 1: Removal of nitrate, fluoride and As(V) by HBO_{12mix} adsorbent in column mode of operation in first cycle; (a) Breakthrough curves for nitrate, fluoride and As(V); (b)Variation of pH with increasing volume of effluent; (c) Changing concentrations of chloride in effluent

Regeneration studies

Regeneration of HBO_{12mix} 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).



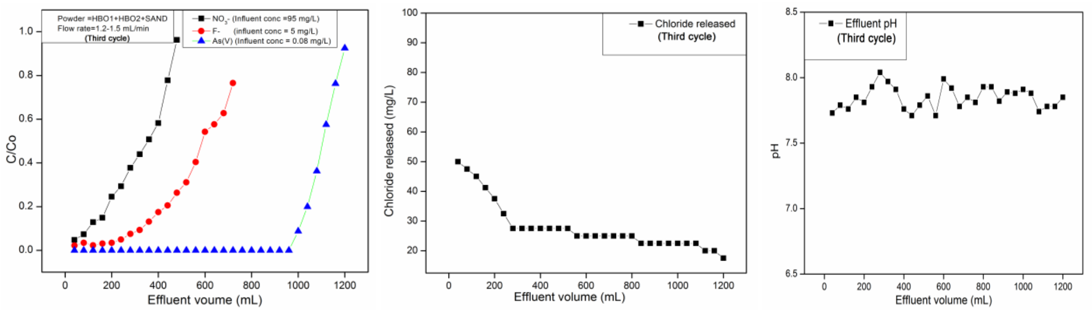


Figure 2: Removal of nitrate, fluoride and As(V) by HBO_{12mix} adsorbent in column mode of operation in second and third cycle; (a) Breakthrough curves for nitrate, fluoride and As(V); (b) Variation of pH with increasing volume of effluent; (c) Changing concentrations of chloride in effluent

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_{12mix} 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.

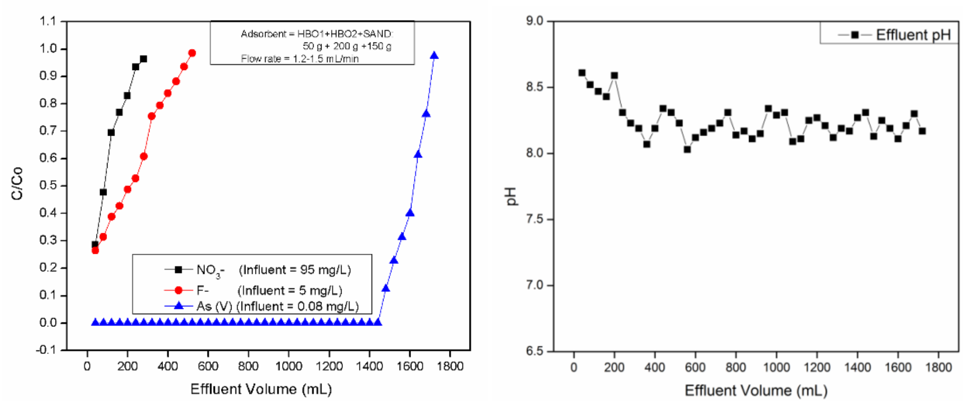
Table 1: Inlet and Outlet qualities from groundwater after batch experiment

Parameter	Influent	Effluent	Change
pH	7.4	7.9	Slight increase
Chloride (mg/L)	16	32.5	>50% increase
Alkalinity (as mg/L $CaCO_3$)	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

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:

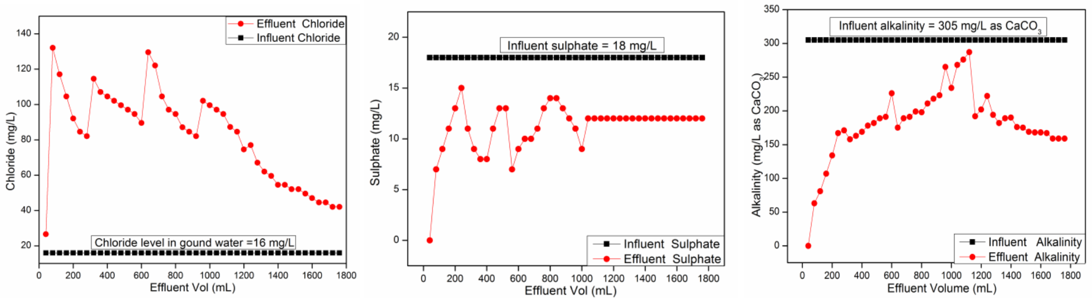
Hence, higher concentrations of alkalinity and sulfate put the limitation on concurrent removal of nitrate, fluoride and As(V) (Figure 3(a)). Slight release of hydroxide (Figure 3(b)) was observed as a result of nitrate, fluoride and As(V) on the surface of HBO_{12mix} at initial flow. High concentration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



(a) **(b)**

Figure 3: Characteristics of effluents from column using sand and HBO_{12mix} 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}.



(a) (b) (c)

Figure 4: Effluent quality from HBO$_{12mix}$ 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$_{12mix}$

Presences of multiple peaks in XRD patterns indicate the broadly crystalline character of adsorbent. The 2θ peak values (26.3°, 30.5°, 33.4°) for the XRD peak corresponds to $Bi_{12}O_{15}Cl_{16}$ (29-0237) by using X-pert high score software. The additional 2θ peaks values of (23.92°, 30.16°), (29.94, 32.84) and 33.42 refer to $Bi_6O_7FCl_{13}$ (70-0854), $Bi_{19}AsO_{31}$ (46-0192), $Bi(ClO_4)NO_2$ (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$_{12mix}$ 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$_{12mix}$ is broadly composed of Bi, O and Cl. After the adsorpotion 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^- 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^{-1} and 530 cm^{-1} only as characteristics of Bi-F bond. The sharp peak at 1274 cm^{-1} and 1310 cm^{-1} could be due to the existence of $BiNO_3$. In addition, the frequency at 675 cm^{-1} to 1045 cm^{-1} 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_{PZC} of HBO_{12mix} 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_{PZC} of HBO_{12mix} 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 $pH < pH_{PZC}$ (8.0-8.2) due to columbic forces of attraction. Similarly force of repulsion will act as $pH > pH_{PZC}$ (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_1, HBO_2 and HBO_3 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_1 and HBO_2 powders has been designated as HBO_{12mix} and that of HBO_1 and HBO_3 as (HBO_{13mix}).

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

1. 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_1, HBO_2 and HBO_3 examined during this study while HBO1 shows preferential adsorption of As(V), followed by fluoride, HBO_2 and HBO_3 prefer As(V) followed by nitrate.
4. A 1:1 mix of HBO_1 and HBO_2 (designated as HBO_{12mix}) appears a potential material for simultaneous removal of nitrate, fluoride and arsenic from ground water in coexisting conditions.
5. While pHpzc of HBO_1 is around 6.5, for HBO_{12mix}, it is around 8.0-8.2. The increased pH_{pzc} of HBO_{12mix} 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_2 is essential.
10. HBO_{12mix} 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.