

# Concurrent removal of nitrate, fluoride and arsenic by mixed hydrous bismuth oxide from water

Manish Ranjan and Prabhat Kumar Singh

## ABSTRACT

Clean and safe drinking water for all is an essential requirement for the world in which we want to live, but a majority of the population has been dependent on groundwater for its daily needs. Toxic contamination of such water could result in large-scale health effects. A great proportion of groundwater suffers from the problems of nitrate, fluoride, and arsenic contamination. Thus, the present research was aimed to remove these contaminants from the water. Hydrous bismuth oxide based adsorbents exhibited high adsorption capacities towards nitrate, fluoride and arsenic. However, As (V) removal was found to be more effective as compared to nitrate and fluoride. The removal efficiencies are 52, 72 and 92% for nitrate, fluoride and As (V), respectively, during concurrent removal of the same. Ion exchange with chloride ions was the probable mechanism for the concurrent removal of the above three anions from water. Scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR) were used for the characterization of HBO<sub>12mix</sub> adsorbents. The results of the present study indicated that HBO<sub>12mix</sub> has the potential for concurrent removal of nitrate, fluoride, and As (V) from groundwater. Hence, hydrous bismuth oxide can be used in the drinking water treatment process at a domestic level.

**Key words** | adsorption potential, arsenic, fluoride, FTIR, nitrate, XRD

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## HIGHLIGHTS

- New adsorbent for concurrent removal of nitrate, fluoride and arsenic.
- Displayed best capacity for the concurrent removal of nitrate, fluoride and arsenic.
- Affinity towards arsenic uptake in addition of nitrate and fluoride from water.
- The process of removal has been optimized.

## INTRODUCTION

The availability of safe drinking water has become a real challenge, especially in urban areas, and the majority of the population depends on groundwater for direct consumption. However, in recent years, the quality of groundwater that is used for drinking has degraded due to the addition of toxic elements (Velizarov *et al.* 2004). Thirty per cent of people are unable to access safe drinking water across the globe; hence providing safe drinking water has become a Sustainable Development Goal (SDG) which is set by the United Nations (Pradhan *et al.* 2017). However, there are

some places where high levels of contaminants make the water unfit for direct human consumption. In the category of contaminants arsenic, fluoride and iron are naturally added, whereas the generation of nitrates, phosphates, heavy metals, etc., are due to human activities. Moreover, nitrate, fluoride, and arsenic have been reported as the most common and widespread contaminants of the groundwater. High concentrations of contaminants like nitrate, fluoride, and arsenic have been found increasingly in ground water, making it unfit for drinking purposes (Liu

*et al.* 2012). The severe health hazard of arsenic is observed due to its extreme toxicity even at low concentrations (Sarkar & Paul 2016). Direct consumption of highly contaminated water is more hazardous to human beings because of toxicity. Hence, there is a dire need to maintain the quality of drinking water to avoid the ill effects of contaminants on human beings. Attention has been given to reduce the toxic influence of nitrate, fluoride and arsenic separately by several researchers but not on the concurrent removal of them (Jain *et al.* 2015; Kolomiyets *et al.* 2017; Mukhopadhyay *et al.* 2017).

Nitrate is one of the key ingredients used in nitrogenous fertilizers to increase the yield of the agricultural industry (Singh & Singh 2004). The elevated level of nitrate concentration in groundwater is directly correlated to the leaching effect of nitrate from intensive farming. The excessive nitrate in surface water bodies leads to eutrophication and degrades the quality of water which may have serious threats to human health including methaemoglobinaemia, cancer, increased infant mortality, gastrointestinal disturbances, etc. (Fewtrell 2004). A restriction of 10 mg/L  $\text{NO}_3^-$ -N in drinking water was prescribed by the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) due to its toxic health effects.

The occurrence of fluoride in groundwater is natural. Fluorine is the most electronegative element that is unstable and found in the elemental state. Due to its high reactivity, fluoride can attach with many naturally occurring minerals and erosion leads to an increase in the concentration of fluoride in groundwater. Excessive intake of fluoride usually has an adverse effect on the body metabolism, and also causes dental problems and skeletal fluorosis (Parashar *et al.* 2016). Fluorosis is an endemic public health problem which prevails in 32 nations around the globe (Mukhopadhyay *et al.* 2017). Acceptable fluoride concentration should be maintained in drinking water, especially among children below eight years of age. The beneficial and detrimental effects of fluoride in drinking water depend upon its concentration in aqueous solution. The permissible and acceptable provisions established by WHO for fluoride in drinking water is 1.5 and 1 mg/L, respectively.

Arsenite (As (III)) and arsenate (As (V)) are the two common forms of arsenic in water which exists naturally in groundwater. Arsenic is recognized by WHO as a first priority pollutant due to its toxicity and carcinogenic nature

(Sarkar & Paul 2016). Various types of skin manifestations/disorders and other arsenic toxicity were observed such as melanosis, keratosis, hyperkeratosis, dorsal keratosis, and cancer (Cantu *et al.* 2016). The regulation of 0.10 mg/L of the arsenic level has been set by WHO. Also, USEPA reduced the maximum arsenic contaminant level from 0.05 to 0.10 mg/L in response to the serious known adverse health effects in 2001 (Luther *et al.* 2012). Based on the toxic and deleterious nature of nitrate, fluoride and arsenic, the following standards have been set for drinking water, as given below in Table 1.

To overcome the above-mentioned problem of anionic water contamination, massive efforts have been made. Various treatment processes are being used to remove these pollutants, and to procure safe drinking water (Bhatnagar & Sillanpää 2011; Habuda-Stanić *et al.* 2014; Lata & Samadder 2016). However, neither of these methods was able to remove the entire nitrate, fluoride, and arsenic from water. Water treatment by various methods can remove partial nitrate, fluoride and arsenic contaminants with varying efficiencies. Comparatively, the ion exchange or adsorption process has been considered as the most promising technique for the removal of the toxic anions from water based on their simplicity, effectiveness, recovery and relatively low cost (Leigen *et al.* 2019). Adsorption technology has been found to be successful in removing inorganic anions like nitrate (Teimouri *et al.* 2016), fluoride (Parashar *et al.* 2016) and arsenic (Kolomiyets *et al.* 2017) from water by using various adsorbents.

The adsorption properties of inorganic materials/hydrous metal oxides have been used in drinking water treatment applications. Hydrous metal oxides have been used for the removal of nitrate such as hydrous zirconium

**Table 1** | Standards in drinking water

S. no.	Contaminants	PL (mg/L)	GV (mg/L)	ML	MCL (mg/L)
		BIS	WHO	(mg/L) EC	USEPA
1	Nitrate ( $\text{NO}_3^-$ )	45	50	50	50
2	Fluoride ( $\text{F}^-$ )	1.0–1.5	1.5	1.5	1.5
3	Arsenic (total As)	0.01	0.01	0.01	0.01

BIS = Bureau of Indian Standards, WHO = World Health Organization, EC = European Commission, USEPA = United States Environmental Protection Agency, PL = permissible limit, MCL = maximum contamination level, GV = guidelines value, ML = mandatory limit.

oxide (Dou *et al.* 2012), MgO nano-flakes (Zhang *et al.* 2012), ferric oxide (Mehrabi *et al.* 2015), hydrous bismuth oxide (Srivastav *et al.* 2014; Singh *et al.* 2015), magnesium oxide, cerium oxide, zinc oxide (Mahdavi *et al.* 2018), Zn/Fe LDH (Karthikeyan & Meenakshi 2020) etc., whereas activated alumina, manganese-oxide-coated alumina (Wang *et al.* 2007), Fe–Al–Ce tri-metal oxide (Delorme *et al.* 2007), hydrous-manganese-oxide-coated alumina (Teng *et al.* 2009), hydrous bismuth oxides (Srivastav *et al.* 2013; Singh *et al.* 2015), MgO (Jin *et al.* 2016), hydrous tin oxide (Parashar *et al.* 2016), MnO<sub>2</sub> (Mudzielwana *et al.* 2017), cerium(IV)-incorporated hydrous iron(III) (Mukhopadhyay *et al.* 2017), Mg/Ce/Mn oxide (Gitari *et al.* 2020) etc. have shown high affinity towards fluoride uptake from aqueous solution. Similarly, zirconium oxide (Suzuki *et al.* 2001), sand coated with iron oxide (Vaishya & Gupta 2002), ferric hydroxide (Daus *et al.* 2004), MnO<sub>2</sub> (Lenoble *et al.* 2004), alumina activated (Singh & Pant 2004), alumina coated by iron hydroxide (Hlavay & Polyak 2005), hydrous stannic oxide (Manna & Ghosh 2007), ferric hydroxide (Zhang *et al.* 2010), hydrous titanium dioxide (Pirilä *et al.* 2011), iron(III)-copper(II) binary oxide (Zhang *et al.* 2013), Mn-incorporated iron(III) oxide (Ghosh *et al.* 2014), TiO<sub>2</sub> (Yan *et al.* 2015), hydrous zirconium oxide (Pérez *et al.* 2016), iron cerium bimetal oxides (Wen *et al.* 2020) etc., are found to be efficient in the reduction of arsenic concentration.

However, activated alumina and activated carbon are the most widespread adsorbents and famous for their selectivity towards water contaminants. However, due to poor regeneration and incompetency for the concurrent removal of nitrate, fluoride and arsenic contaminants, it is imperative to develop new adsorbents which could give the higher as well as concurrent removal efficiency for all of these contaminants. However, an intense review of the literature was carried out for the compilation of anion exchange properties of these hydrous metal oxides which indicated that neither concurrent removal of nitrate, fluoride, and arsenic anions have been reported, nor have much of the reported materials shown concurrent sorptive properties towards nitrate, fluoride and arsenic. Hence, concurrent removals of these anions have been given the most priority in the present study.

Bismuth-based inorganic media have shown sorptive properties for nitrate, fluoride and arsenic. The hydrous

bismuth oxide is the promising sorptive media for the removal of major anionic contaminants like nitrate and fluoride from ground water (Srivastav *et al.* 2013; Singh *et al.* 2015). Both forms of arsenic were tested and the removal capacity for As (V) was found to be higher than the As (III) in the pH range of drinking water condition. However, the maximum removal efficiency of As (III) could be achieved at higher pH (>9) which makes the water unfit for drinking. Hence, As (V) was taken for further experiments. High removal capability of hydrous bismuth oxide was observed for As (V) and fluoride with respect to nitrate where all three anions exist together. Hence, in the present study, hydrous bismuth oxide was investigated with the aim to evaluate the sorption efficiency for nitrate, fluoride, and arsenic (V) concurrently.

## MATERIALS AND METHODS

### Standard solutions for nitrate, fluoride, and As (V)

All the chemicals used in this study were of analytical grade. NaNO<sub>3</sub>, NaF, and Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O (E.Mark, Germany) salts were used for preparations of 1,000 mg/L stock solutions in deionized water (DI), respectively. Further, a working solution containing all three water contaminants of 95 mg/L of nitrate, 5 mg/L of fluoride and 0.08 mg/L of As (V) was prepared based on the average value of contaminants reported in groundwater (Delorme *et al.* 2007; Devi *et al.* 2008; Bibi *et al.* 2015).

### Synthesis of adsorbent

Hydrous bismuth oxide (HBO) was made using bismuth trioxide (Bi<sub>2</sub>O<sub>3</sub>, MW = 466.0, Loba Chemie, Mumbai) powder of AR grade at a cost of 8,000 INR per kg in the Indian market. In the preparation of adsorbent, firstly 'yellow bismuth hydroxide' was synthesized as per the method reported by Fritsche (1993). The precipitate formed under the volumetric proportion of 1:1 (v/v) in Bi<sub>2</sub>Cl<sub>3</sub> (0.1 M Bi<sub>2</sub>O<sub>3</sub> dissolved 2 N HCl) with 2 N NaOH was designated as HBO1 (white color) and for HBO2, HBO3 (yellow color) in the ratio of 1:2 and 1:3 (v/v) was taken, respectively. A further reaction time of 1 h was given for

homogenous mixing. Excess hydroxide and chloride ions were removed from the obtained precipitate by washing with double distilled water. Further precipitates were dried in an oven at  $103 \pm 2$  °C for 24 h and powdered forms of HBO1, HBO2 and HBO3 were obtained which were subsequently used in the adsorption experiments.

### Determination of nitrate, fluoride, and arsenic

The instruments used during the determination of nitrate and fluoride concentration are an ion-meter (HANNA HI 4222, Hanna Equipments Pvt., Navi, India) with an ion-selective electrode (ISE) as per standard methods (Clesceri *et al.* 2005). Arsenic concentration of the samples was measured by an Arsenator (Model no: Wag-WE10500 made by Wag-Tech, UK). pH measurement was carried out with the help of a digital pH meter (ITS 201, ISO-TECH system PVT, Varanasi, India). All experiments were carried out at standard temperatures ( $25 \pm 2$  °C).

### Batch adsorption study

Sodium nitrate, sodium fluoride and sodium arsenate (AR grade) were used for preparation of all working solutions. Three hours of contact time were given at room temperature ( $25 \pm 2$  °C) to adsorbent with the solution in a 100 mL Erlenmeyer flask with a 130 g/L dose of HBO<sub>12mix</sub>. The contents were continuously stirred and further filtered using filter paper. The residual filtrates were then analyzed for the remaining concentration of anions. Initially, during contact time, the adsorbent dosage was optimized. Moreover, other parameters such as the effect of competitive anions on their removal were also investigated. Observations based on three triplicate samples were reported.

The amount of ions adsorbed, i.e. adsorption capacity ( $q_e$  in mg/g) and adsorption efficiency (%) were calculated as follows:

$$\text{Adsorption potential } (q_e) = \frac{C_o - C_e}{m} \quad (1)$$

$$\text{Adsorption efficiency } (\%) = \frac{C_o - C_e}{C_e} \times 100 \quad (2)$$

where  $C_o$  and  $C_e$  are the initial concentration (mg/L) and final residual concentration (mg/L),  $m$  is the mass (g) of adsorbent per liter of solution.

### Column adsorption study

To avoid the choking condition in the column test, a mixture of sand and hydrous bismuth oxide (HBO1 + HBO2) was taken as adsorbent. To achieve the best result, a mixture of adsorbent with sand was taken, based on trial and error, into the column with a 3 cm internal diameter. The deionized water was passed through the column until all free chloride was released. Influent water contained a synthetic solution of 95 mg/L NO<sub>3</sub><sup>-</sup>, 5 mg/L F<sup>-</sup> and 0.08 mg/L As (V). A flow rate of 1.2–1.5 mL/min was maintained while passing the influent through the column. A fraction of effluent (40 mL) was collected at regular intervals of 30 min for the determination of the residual concentration of pH, nitrate, fluoride, As (V) and chloride ions.

### Adsorption kinetics study

Adsorption kinetics was performed for a mixture of nitrate, fluoride and As (V) ions and was studied at room temperature. One hundred mL of anion solution was taken and 130 g/L of adsorbent (HBO<sub>12mix</sub>) was added to the solution. The samples were collected at an interval of 5, 10, 20, 30, 45, 60, 75, 90, 120, 150, 180, 210, 240 min and the remaining nitrate, fluoride, As (V) were analyzed in treated water samples. Pseudo first order, pseudo second order, and Weber–Morris models were applied to the experimental results to generate kinetic parameters.

### Adsorption isotherm study

Adsorption isotherm was conducted by mixing 130 g/L of adsorbent (HBO<sub>12mix</sub>) with 100 mL of anions solution with varying concentrations ranging from 70 to 95 mg/L for nitrate, 3–5 mg/L for fluoride and 0.08–0.10 mg/L for As (V). All the experiments were conducted at 250 rpm agitating condition with a contact time of 3 h at constant temperature (298, 308, and 318 K) to reach equilibrium. Langmuir, Freundlich, as well as DR isotherm models,

were applied to the experimental results to understand the feasibility of the experiments.

### Material characterization

Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) techniques were used to understand the mechanism of adsorption. The  $pH_{PZC}$  value was determined by the fast alkalimetric titration method as used by Srivastav *et al.* (2014). An FTIR spectrometer (Nicolet iS5, THERMO Electron Scientific Instruments LLC, USA) and an X-ray diffractometer (1710, Philips, The Netherlands) were used for FTIR spectrum and XRD patterns of hydrous bismuth oxide ( $HBO_{12mix}$ ). The information regarding texture morphology and elemental analysis was obtained from a SEM and EDS (ZEISS EVO 18, Model-2045, Industrial Measurements and Medical Devices, Germany).

## RESULTS AND DISCUSSION

### Arsenic removal possibilities of hydrous bismuth oxide

The literature suggests that hydrous bismuth oxide has a greater affinity for nitrate or fluoride, both in the drinking water pH range; but hydrous bismuth oxides have not been tested for arsenic sorption. HBO is expected to have a greater affinity for arsenic. Hence, to explore the simultaneous removal of nitrate, fluoride and arsenic it is imperative to determine the possibilities of arsenic sorption by hydrous bismuth oxide. Both forms of arsenic were tested and it was found that the removal capacity for As (V) was higher than As (III) from water in the given contact time. However, the maximum arsenic elimination required can be achieved by the removal of As (III), which needs to be dissociated in ionic form ( $H_2AsO_3^-$ ) at higher pH ( $pH > 9$ ) or oxidation into As (V). Hence oxidation of As (III) into As (V) could lead to the best result in concurrent removal at higher pH. However, increments in pH ( $>9$ ) make it unfit for drinking purposes. Lesser efficiency will be achieved by selected adsorbents in contaminant removal when drinking water obtained from groundwater aquifers in

a reducing environment. Groundwater obtained from an oxidizing environment could be used as an adsorbent for higher removal efficiency. Hence, arsenate was chosen for further experiments.

Table 2 summarizes the affinity of hydrous bismuth oxide in the individual removal of water contaminants.

### Concurrent removal of nitrate, fluoride and As (V) ions by different hydrous bismuth oxide (HBO1 or HBO2 or HBO3)

#### Batch experiments for nitrate, fluoride and As (V) adsorption

The concurrent removal of nitrate, fluoride, and As (V) from water using different HBOs powder was performed through batch experiments. It was observed that HBO1 did not show a good capability to remove nitrate from water in comparison to fluoride and As (V) removals. Only 19.07% of nitrate removal was achieved at a dosage of 100 g/L by HBO1 with 95 mg/L initial concentration, whereas 60% of nitrate removal was observed by using HBO2 and HBO3, respectively, as an adsorbent with the same conditions at an adsorbent dose of 100 g/L. No inference of hydroxide ion was observed in treated water samples as pH falls in the range of drinking water standards from 6.5 to 8.5. Hence, it can be understood that due to nitrate adsorption, no significant release of hydroxide ions from adsorbent was observed.

**Table 2** | Comparative study of hydrous bismuth oxide in individual removal of water contaminants

Media Hydrous bismuth oxides	Earlier results reported		Present study Affinity towards arsenic (V)
	Affinity towards nitrate	Affinity towards fluoride	
HBO1	Low (Singh 1999)	High (Srivastav <i>et al.</i> 2013)	High
HBO2	High (Srivastav <i>et al.</i> 2014)	Low (Srivastav <i>et al.</i> 2015)	High
HBO3	High (Singh <i>et al.</i> 2015)	Low (Srivastav <i>et al.</i> 2013)	High

Similarly, the use of HBO1 was found to be beneficial in the removal of fluoride as compared with HBO2. A maximum of 67% of fluoride removal was achieved at the dosage of 100 g/L with an initial concentration of 5 mg/L, whereas 24 and 17% were observed with HBO2 and HBO3, respectively, at the dosage of 100 g/L. Further, the pH variation of treated water was recorded in the permissible range of 7.0–8.5. Hence, again hydroxides were not observed as a caustic agent for fluoride sorption.

All HBO adsorbents have good capability to remove As (V) with comparisons to nitrate and fluoride from water. HBOs (HBO1, HBO2 and HBO3) were found to be equally efficient in As (V) removal with an average of 91.49% efficiency. Likewise, for the nitrate and fluoride removal, no significant changes in hydroxide ion were observed and hence hydroxide could not be responsible for As (V) sorption.

Figure 1 indicates that HBO1 was found to be efficient for both fluoride as well as As (V) removal with high dosages, whereas HBO2 and HBO3 have more affinity towards nitrate and As (V). Hence, based on the above observations, the mixture of HBO1 and HBO2 (or HBO3) seem a good adsorbent for the concurrent removal of nitrate, fluoride and arsenic (As (V)) from the water. Cost analyses in the preparation of adsorbent restrict us to select HBO3 as both adsorbents (HBO2 and HBO3) reflect approximately the same adsorption capacities. Hence, further studies have been carried out by taking a mixture of HBO1 and HBO2 (HBO<sub>12mix</sub>) as a single adsorbent for the concurrent removal of major anionic contaminants (nitrate, fluoride and As (V)) from aqueous solution.

## Concurrent removal of nitrate, fluoride and As (V) ions by HBO<sub>12mix</sub>

### Batch study

An equal mixed proportion of HBO1 and HBO2 were taken as HBO<sub>12mix</sub> for further experiments. Dosage was varied from 10 to 150 g/L for 3 h of contact time with continuous stirring at 250 rpm. After 3 h of contact time, filtered water samples were analyzed for residual pH, chloride, nitrate, fluoride, and As (V) concentrations. The removal of all three anions with HBO<sub>12mix</sub> was tested and a maximum removal efficiency of 52% for nitrate, 72% for fluoride and 92% for As (V) was found with a marginal increment of pH from 7.34 to 8.23 after treatment. The nitrate concentration was reduced from 95 to 45.6 mg NO<sub>3</sub><sup>-</sup>/L, whereas the fluoride concentration decreased from 5.11 to 1.43 mg/L and the As (V) concentration dwindled from 0.1 to 0.008 mg/L with 92% removal efficiency. Almost similar results were observed by using HBO<sub>13mix</sub> as adsorbent in concurrent removal of three anions. Maximum uptake was reported at a dosage of 130 g/L for nitrate and fluoride, whereas for As (V), 20 g/L was observed as the optimum dosage for maximum sorption (Figure 2). Further increase of the dosage had no significant effect on removal efficiency. Also, major changes of hydroxide ion concentration were not observed in treated water but the final value of chloride concentration reached 53.7 mg/L which has been marked as a major change from 16.3 mg/L as initial chloride concentration. Hence, elution of chloride could be considered as a reason for the sorption of anions on HBO<sub>12mix</sub> media.

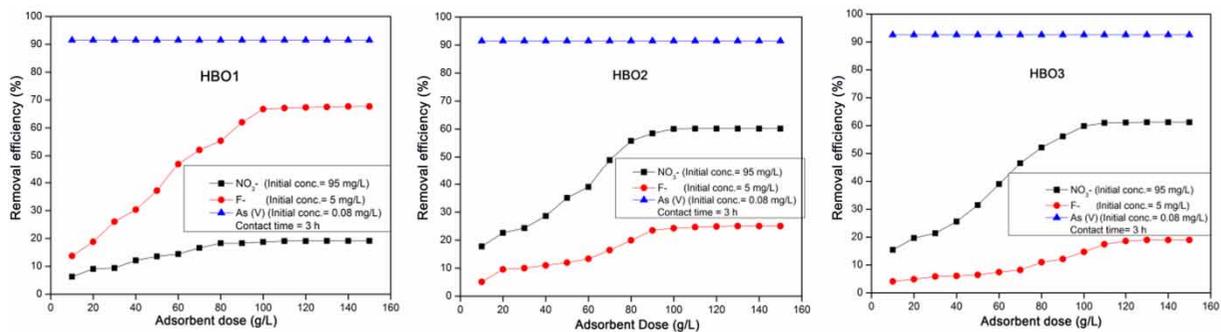


Figure 1 | Effect of adsorbent dosages on concurrent removal of nitrate, fluoride and As (V) by HBOs.

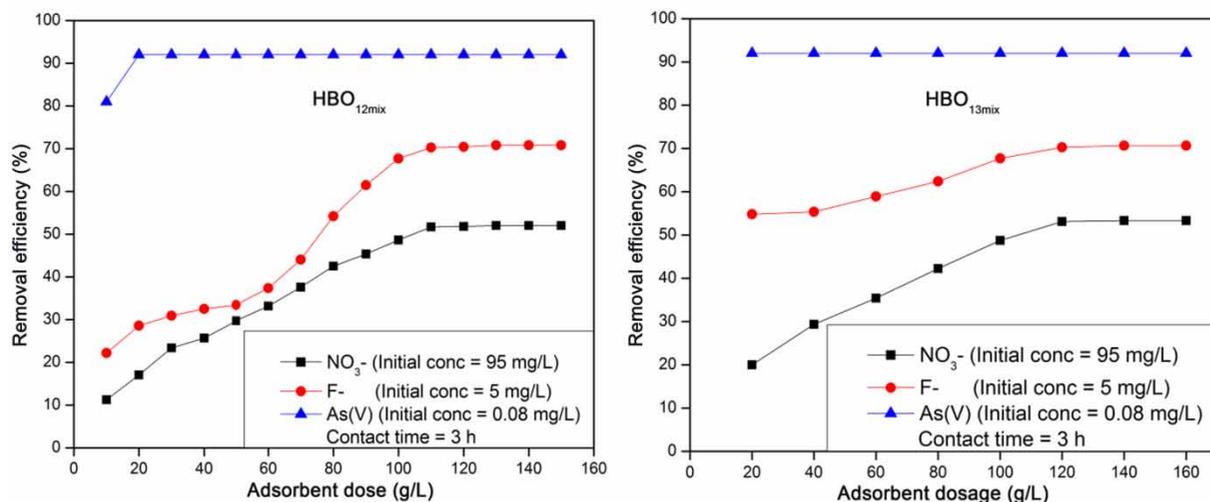


Figure 2 | Effect of adsorbent dosage on concurrent removal of nitrate, fluoride and As (V).

After adsorbent ( $\text{HBO}_{12\text{mix}}$ ) dosages of 130 g/L, there was no gain observed in the adsorption capacity of nitrate, fluoride, as well as As (V) from water. Similar findings were also reported by some authors including Swain *et al.* (2012) and Srivastav *et al.* (2013) during the adsorption of fluoride from water. The saturation of active adsorption sites could be due to them overlapping on themselves (Swain *et al.* 2012) and, because of that, afterwards insignificant removals were observed. Therefore, 130 g/L of adsorbent was considered as the optimum dose for further experiments.

### Effect of contact time

The effect of time has also been included during the present study. The effect of contact time was studied for a total of 5 h and samples were collected at regular intervals of 1 h (Figure 3). The enhanced removal efficiency was observed with increments in initial contact time up to 3 h; 32.44, 45.53 and 53% of removal percentage for nitrate were recorded along with 47.55, 62.23 and 72% of removal efficiency for fluoride and 51.25, 80 and 92% of As (V) removal at regular intervals of 1, 2 and 3 h. Initially, up to 3 h, the uptake of anionic contaminants was very high as the pore site was active and unsaturated. The percentage removal of 53% nitrate, 72% fluoride and 92% As (V) were recorded at the time up to 3 h. The slope in Figure 3

shows a steep negative slope up to 3 h and further as the time progress slope becomes constant, which concludes the non-availability of the adsorbent site for uptake ions and it could be due to the availability of an abundant number of adsorption active sites during the initial phases of adsorption (Khan *et al.* 2009). Hence, after 3 h the marginal changes in uptake could be noticed as the pore site became saturated and exhausted.

However, after an optimum time period, development of repulsive force between the adsorbate and bulk phase takes place which discourages the rate of further adsorption.

### Column studies

Particle sizes of hydrous bismuth oxide powder are very fine in nature. In order to use in column adsorption study, hydrous bismuth oxide powder ( $\text{HBO}_1 + \text{HBO}_2$ : 50 g + 200 g) and sand (150 g) was mixed in different proportions to obtain efficient results. The sand to be used was initially cleaned by keeping it in 0.1 N HCl for 24 h and then washing it with sufficient distilled water. A glass column (diameter of 30 mm) was filled up to a height of around 51 cm with the mixed media ( $D_{10} = 0.18$ ,  $C_u = D_{60}/D_{10} = 2.4$ ,  $\text{pH} \sim 7.0$ ). A synthetic solution of 95 mg/L nitrate, 5 mg/L fluoride and 0.08 mg/L As (V) was taken for column study which is representative of the field samples of anionic contaminated groundwater in parts of the

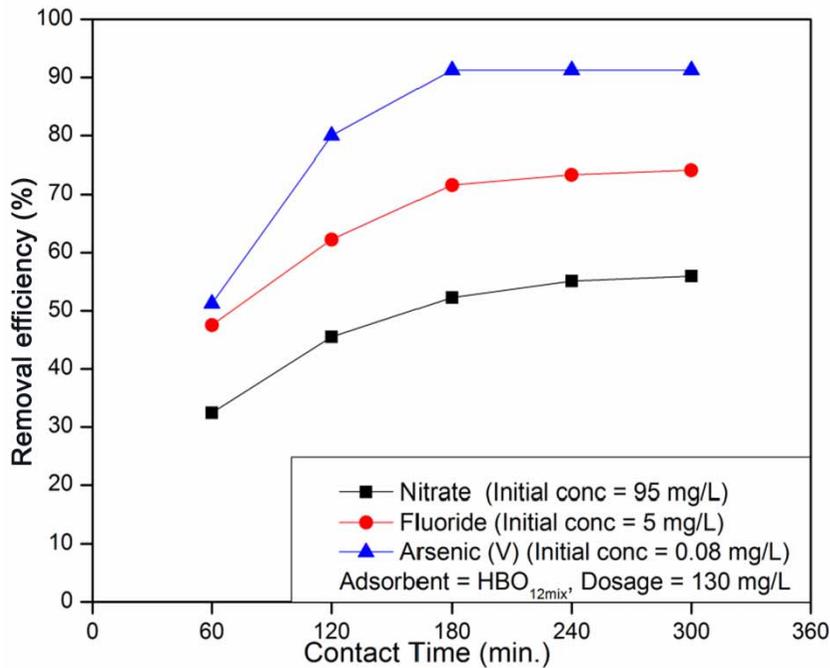


Figure 3 | Effect of time variation on removal efficiencies of anionic contaminants.

country. The contaminants spiked water samples were passed with a flow rate of  $\sim 1.2\text{--}1.5$  mL/min. Samples of effluents were collected at an interval of every 30 min. pH, nitrate, fluoride, As (V), and chloride were measured to understand the mechanism of removal.

As shown in Figure 4, zero effluent concentration was found as the synthetic anionic contaminated water passed through the column for 6 h, then the nitrate concentration rapidly rose to 90.23 mg/L at 1,320 min after the passage of 1,040 mL of influent, which means the column is saturated by nitrate ions first. Consequently, at the treatment

time of 1,680 and 2,970 min, the concentrations of fluoride and As (V) in the effluent reached 4 and 0.071 mg/L after the passage of 2,160 and 3,920 mL of influent, respectively. The column adsorption experiment shows that approximately 750 mL of contaminant free drinking water could be used by the consumer, whereas 1,180 mL (fluoride and arsenic free) and 3,512 mL (arsenic free) of drinking water could be used by the household. The column adsorption experiment shows that dynamic adsorption capacities of nitrate, fluoride, and As (V) ions onto the adsorbent are 46, 4.3 and 0.29 mg/g respectively. A marginal change in

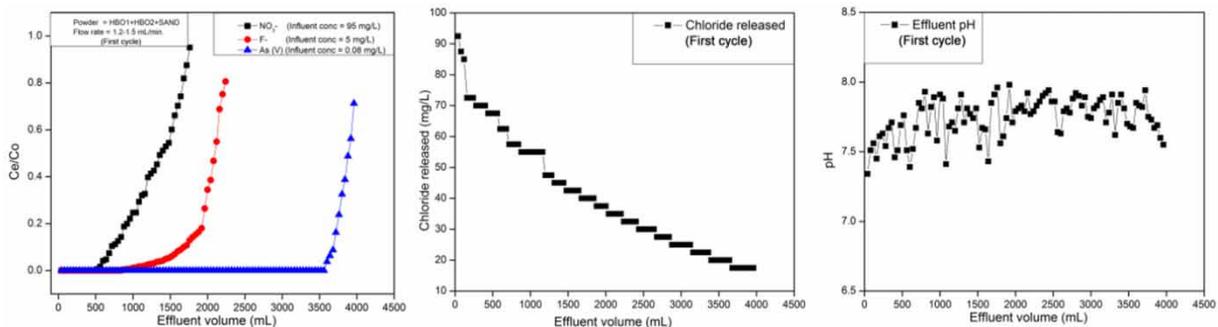


Figure 4 | Removal of anions in column mode through HBO<sub>12mix</sub> adsorbent.

pH could be observed but continued elution of chloride was monitored which diminishes as the adsorbent becomes exhausted. An indication of ion exchange could be predicted based on the results observed above.

Fritsche (1993) detected the simultaneous removal of nitrate and other anions by yellow bismuth hydroxide and also reported that  $\text{OH}^-$  is the caustic agent responsible for nitrate sorption through ion exchange mechanism. The earlier work of Ruixia *et al.* (2002) on the removal of fluoride, phosphate and As (V) by ion exchange fiber elucidates the dynamic adsorption capacities of 45.0, 155.5, and 96.0 mg/g. The ion exchange of chloride is the dominant sorption mechanism for fluoride and phosphate in synthetic wastewater. Park *et al.* (2008) conducted a series of experiments for the simultaneous removal of fluoride, phosphate and nitrate by cement paste column. The cement paste column could treat fluoride and phosphate to remarkably low levels with removal capacities of 1.67 and 1.96 meq/g, but nitrate entrapment is difficult as it makes it complex with cement cations but significant removal of nitrate was achieved by ion exchange with sulfate released. A similar attempt was made by Streat *et al.* (2008) for the adsorption of arsenic, phosphorus, and fluorine by hydrous ferric oxide as an adsorbent in water treatment. Greater adsorption of arsenate and phosphate was observed than of fluoride due to protonation. Singh *et al.* (2012) considered hydrous bismuth oxide (HBO1, HBO2 and HBO3) as adsorbents and studied the removal of nitrate in the presence of bicarbonate and sulfate. The authors concluded that HBO2 and HBO3 are found still very well in the nitrate removal, even in the presence of bicarbonate and sulfate but the removal percentage of alkalinity significantly dwindled by HBO1 from 77 to 22% in the column test.

### Regeneration studies

Regeneration of hydrous bismuth oxide was also attempted for its further use in anion removal with 0.1 N NaOH followed by 0.1 N NaCl solutions, although only by passing the 0.1 NaOH through media leads to elution of sorbed anions. Also, it has been observed that chloride is the exchange anion responsible for anion uptake by media. Hence it was expected to regenerate the media by passing through the 0.1 NaCl solutions. With respect to regeneration

experiments two significant changes have been marked down: first, the media has been dehydrated and secondly the regenerant has been changed from 0.1 NaOH to 0.1 NaCl. The elution of sorbed anions by chloride during regeneration may be due to higher preferences and concentration gradient effects. Sodium hydroxide has the advantage of affecting the pH ( $>9$ ) of the water environment, thereby affecting the sorbed ions and consequently the empty and active sites are occupied by sodium chloride. Sixty per cent anion content was obtained in desorption and further regenerated adsorbent was used in up to two consecutive cycles of anion removal (Figure 5).

It is important to note that effluent qualities exceed their respective permissible limits after treating around 200, 520 and 1,200 mL of nitrate, fluoride and As (V) in the second cycle, whereas 120, 320 and 1,000 mL quantity of nitrate, fluoride and As (V) were achieved before exceeding the permissible limits in the third cycle.

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

### Effect of competing anions on removal of nitrate, fluoride and As (V)

To simulate the real field conditions, it is important to access the properties of adsorbent in the presence of competitive anions. Sulfate and bicarbonate are the most common ions present in groundwater. Hence, these ions were considered as a hindrance and the effect of sulfate and bicarbonate ion presence was studied on the sorption capacity of HBO<sub>1,2,mix</sub> with an adsorbent dose of 110 g/L with 3 h contact time. A concentration range of 1–5 meq/L sulfate (44–220 mg/L as  $\text{SO}_4^{2-}$ ) and bicarbonate (50–250 mg/L as  $\text{CaCO}_3$ ) were tested on concurrent removals of nitrate (95 mg  $\text{NO}_3^-/\text{L}$ ), fluoride (5 mg  $\text{F}^-/\text{L}$ ) and As (V) (0.08 mg/L As (V)). It can be observed from Figure 6 that the bicarbonate ions imposed a relatively greater negative impact on nitrate removal whereas sulfate ions affected the removal of fluoride and As (V). The pH of the solution was greatly affected by increased bicarbonate concentration which could be related to the lower adsorption of nitrate in aqueous solution

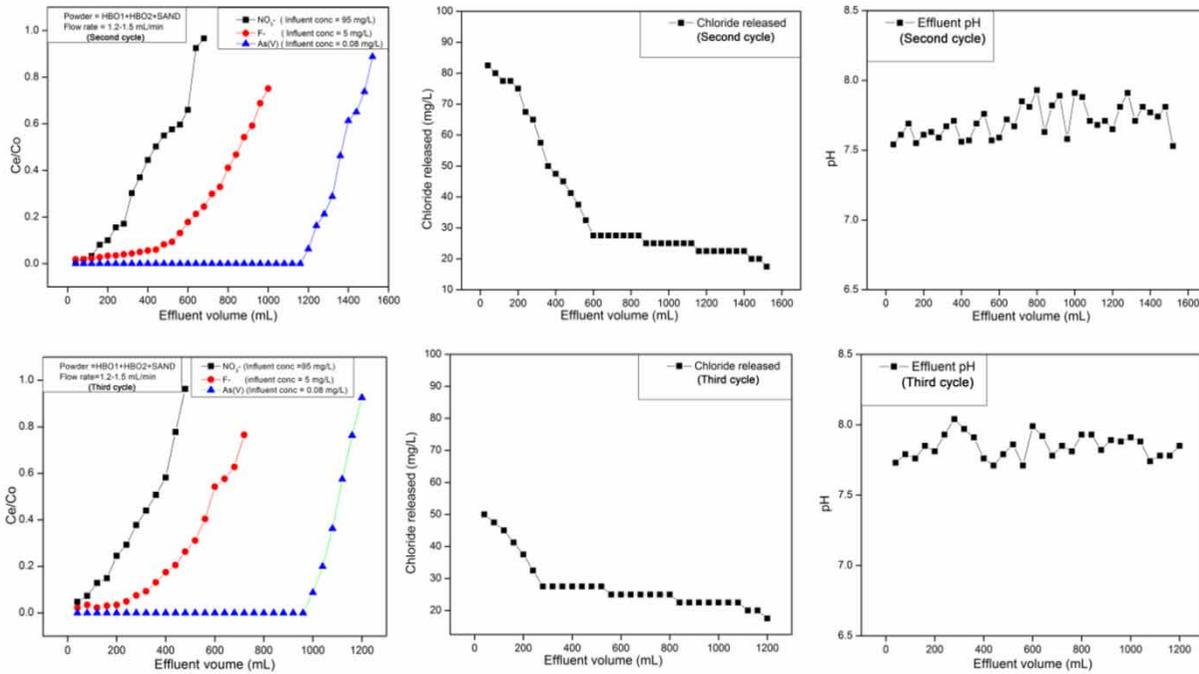


Figure 5 | Regeneration experiments.

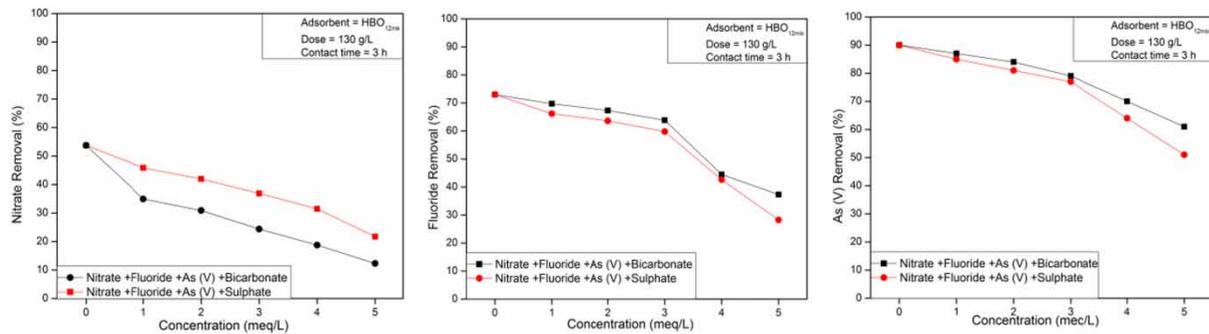


Figure 6 | Effect of competing anions on removal of targeted anions.

(Goswami & Purkait 2012). During adsorption, the multi-valent nature of sulfate anions has been preferred over monovalent anions (Mohapatra *et al.* 2012). The nitrate removal efficiency of  $\text{HBO}_{12\text{mix}}$  was remarkably decreased from 55 to 12% whereas fluoride and As (V) removal efficiency decreased from 72 to 25% and 90 to 50%, respectively, at 5.0 meq/L of each anion concentration. Hence, in the presence of competitive anions ( $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$ ), the preference of adsorption has been changed which reduces the outcomes of preference series of anions appear as: bicarbonate > sulfate > nitrate, whereas for fluoride and As (V) removal  $\text{HBO}_{12\text{mix}}$ , the preference is sulfate > bicarbonate > fluoride/As (V).

Thus,  $\text{HBO}_{12\text{mix}}$  is found potentially useful for the sorption of nitrate, fluoride and As (V) below an alkalinity of around 150 mg/L as  $\text{CaCO}_3$  and sulfate concentration of 140 mg/L.

#### Performance of hydrous bismuth oxide ( $\text{HBO}_{12\text{mix}}$ ) in real ground water of IIT (BHU), Varanasi, India, spiked with high nitrate, fluoride and As (V)

A batch experiment was carried out by taking water samples from the IIT (BHU), Varanai, India, added with nitrate conc. = 95 mg/L, fluoride conc. = 5 mg/L, As (V) conc. = 0.08 mg/L. The initial concentration of solution was applied

for the batch adsorption experiment with adsorbent as HBO<sub>12mix</sub> dose of 130 g/L for 3 h of reaction time. The outlet quality was analyzed for pH, nitrate, fluoride, As (V), alkalinity, sulfate and chloride. Table 3 provides the inlet and outlet qualities from ground water after the batch experiment.

A major reduction in alkalinity could be seen by HBO<sub>12mix</sub> in real ground water conditions. However, fluoride and As (V) removal efficiencies have not been affected but a high reduction in nitrate sorption was observed. pH remained in the desired range and the chloride level was quite variable in the treated water. The experimental data from Table 3 deduces the idea of alkalinity being more dangerous and competing anions for nitrate as nitrate removal is being hindered by a high level of alkalinity.

### Kinetic studies

Pseudo first order (Lagergren 1898), pseudo second order (Ho & McKay 1999), and Weber–Morris models (Weber & Morris 1963) were applied with the experimental results in the present study to understand the anions sorption on adsorbent. The mathematical expressions of kinetic models are expressed as follows (Equations (3)–(5)):

$$\text{Pseudo first order: } \log(q_e - q_t) = \log q_e - (K/2.303)t \quad (3)$$

$$\text{Pseudo second order: } \frac{t}{q_t} = \frac{1}{K q_e^2} + (1/q_e)t \quad (4)$$

$$\text{Weber and Morris: } q_t = k\sqrt{t} + c \quad (5)$$

**Table 3** | Batch adsorption experiment from real ground water of IIT (BHU), varanasi spiked with high nitrate, fluoride and arsenic (V)

Parameter	Influent	Effluent	Change
pH	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
Sulfate (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
As (V) (mg/L)	0.080	0.007	91% decrease

where  $q_e$  and  $q_t$  are the amount of anions adsorbed per unit gram (mg/g) at equilibrium and at any time  $t$  (min), respectively. The  $K_1$  (L/min),  $K_2$  (g/mg/min),  $K_3$  (mg/g/ $\sqrt{\text{min}}$ ) are the adsorption rate constants respectively for the three kinetic model mentioned above and  $c$  is the constant related to the Weber and Morris model.

In order to perform the kinetics study, the nitrate, fluoride and As (V) concentrations were varied on three levels (Table 4) and kinetic parameters were evaluated by keeping the reaction of 3 h and adsorbent dosage of 130 g/L of HBO<sub>12mix</sub>.

The linear plot of kinetic data and parameter of pseudo first order, pseudo second order, and Weber–Morris models are demonstrated in Table 4 and Figure 7. Based on higher correlation coefficients, the process of sorption on HBO<sub>12mix</sub> is governed by the pseudo first order reaction. The rate constant determined by the pseudo first order reaction for fluoride and As (V) was found to be higher than that of the nitrate. The rate constant ( $K_1$ ) increases with a decrease in initial concentration except for nitrate, while the higher rate constant ( $K_2$ ) was achieved by pseudo second order for fluoride sorption.

In the solid–liquid adsorption system, the Weber–Morris model was taken to illustrate the diffusion mechanism and rate-controlling process of adsorption. The regression coefficient of the process lies in between 0.913 to 0.954, suggesting that the rate-controlling steps were not governed by a single process.

Further, from the straight line and non-zero intercept plot from the Weber–Morris model, it can be interpreted that the adsorption of anions on the surface of HBO<sub>12mix</sub> is a complex process and is governed by surface adsorption as well as intraparticle diffusion (Ayooob & Gupta 2008; Gupta & Bhattacharyya 2011).

### Adsorption isotherm models

The Langmuir (Coulson *et al.* 1991), Freundlich (Milmile *et al.* 2011) and Dubinin–Radushkevich isotherm (Islam *et al.* 2010) models were used to conduct equilibrium studies for the removal of nitrate, fluoride and As (V) from water. The linear forms of the above equations can be expressed

**Table 4** | Kinetic parameter of adsorption

Initial conc. (mg/L)	Pseudo-first order model			Pseudo-second order model			Weber–Morris model	
	$K_1$ ( $\text{min}^{-1}$ )	$q_e$ (mg/g)	$R^2$	$K_2$ (g/mg/min)	$q_e$ (mg/g)	$R^2$	$K_3$ (mg/g/ $\sqrt{\text{min}}$ )	$R^2$
Nitrate								
95.0	0.018	0.458	0.987	0.012	0.667	0.882	0.031	0.941
80.0	0.016	0.463	0.995	0.013	0.743	0.754	0.033	0.954
70.0	0.013	0.510	0.989	0.015	0.784	0.977	0.037	0.953
Fluoride								
5.1	0.018	0.037	0.975	0.169	0.050	0.930	0.002	0.942
4.0	0.018	0.024	0.993	0.115	0.049	0.899	0.001	0.943
3.0	0.020	0.017	0.966	0.103	0.043	0.981	0.001	0.985
As (V)								
0.10	0.020	0.0008	0.964	0.024	0.0005	0.882	0.040	0.946
0.09	0.022	0.0007	0.992	0.013	0.0006	0.752	0.033	0.913
0.08	0.023	0.0006	0.985	0.012	0.0008	0.946	0.033	0.917

as follows (Equations (6)–(9)):

$$\text{Langmuir isotherms model: } \frac{1}{q_e} = \frac{1}{q_0 b C_e} + 1/q_0 \quad (6)$$

$$\text{Freundlich isotherm model: } \log q_e = \log K_F + (\log C_e) 1/n \quad (7)$$

$$\text{Dubinin–Radushkevich isotherm model: } \ln q_e = \ln q_m - K\varepsilon^2 \quad (8)$$

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (9)$$

where  $q_0$  and  $b$  are the Langmuir constants related to the adsorption capacity (mg/g) and the energy of the adsorption (L/mg) respectively,  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of anions (mg/L) and  $n$  is the Freundlich constant indicating the degree of favorability of adsorption and  $K_F$  is the Freundlich isotherm constant.  $R$  is the universal rate constant (8.314 kJ/mol·K) and  $T$  stands for temperature in kelvin. Theoretical adsorption capacity and adsorption energy constant is denoted by  $q_m$  and  $K$  respectively.

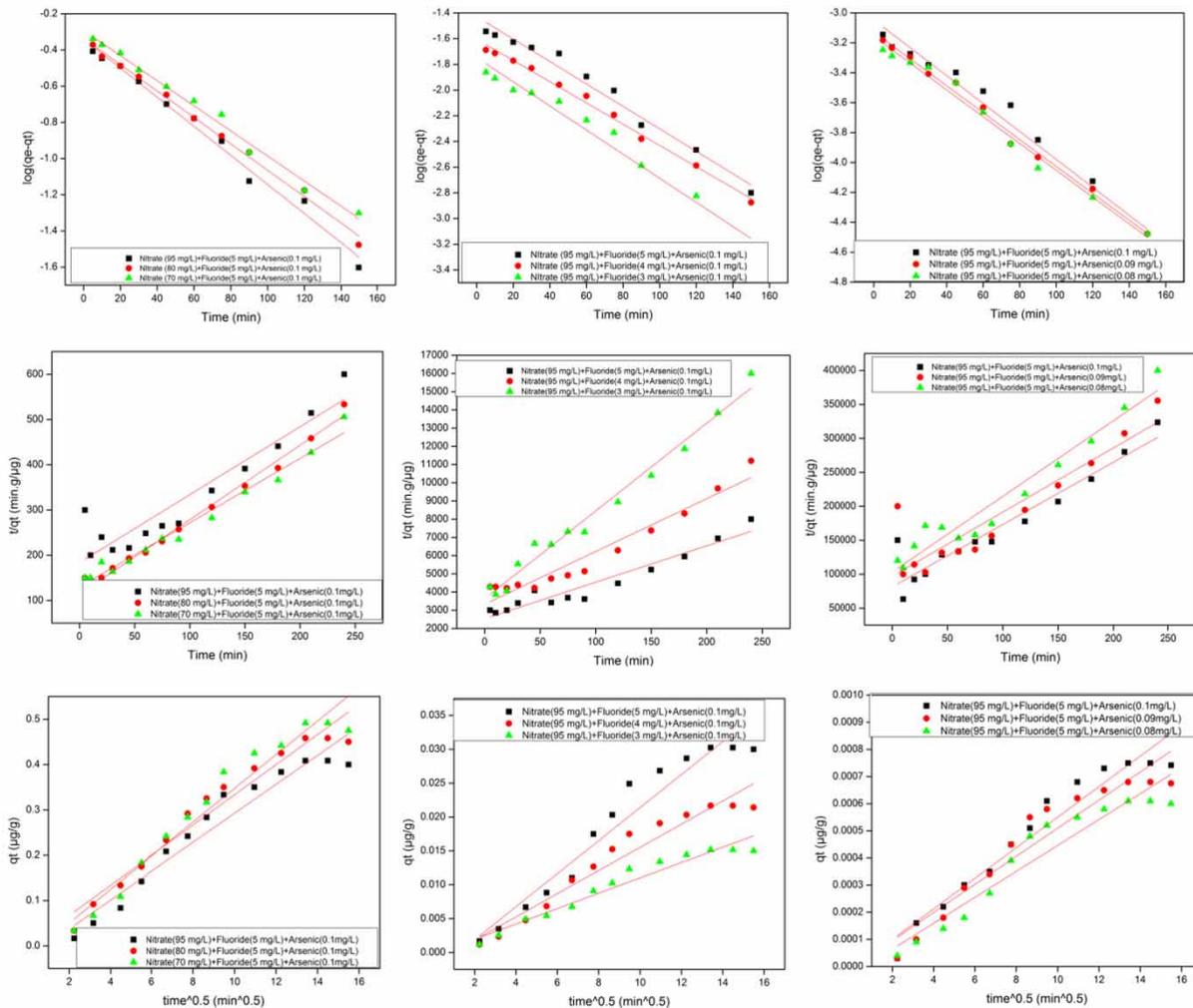
In order to perform the isotherm study, mixed solution of nitrate, fluoride and As (V) concentrations were varied at different temperatures (298, 308 and 318 K) (Table 5) at a reaction time of 3 h with an adsorbent dosage of 130 g/L.

Equilibrium data and isotherm data plot for the adsorption of anions on  $\text{HBO}_{12\text{mix}}$  at temperatures of 298, 308, and 318 K are shown in Table 5 and Figure 8, respectively. Inspection of the data revealed that the agreement of isotherm data fitted well with the Freundlich isotherm for anion sorption. Sorption isotherm of nitrate tries to synchronize with fluoride and As (V) isotherm at higher temperatures, whereas As (V) adsorption data appear to follow the DR isotherm equation more closely than others. Increased temperature leads to an increase in the threshold energies of solute particles which results in more molecular collision at higher temperatures. Hence, the removal process was considered as endothermic nature of adsorption (Ayoob & Gupta 2008).

The DR isotherm model is used to evaluate whether the nature of adsorption is physical, ion-exchange or chemical in nature. The value of adsorption energy constant ( $K$ ) derived from the DR isotherm can be further used to differentiate the process governed by the physisorption, ion exchange or chemisorption by calculating adsorption energy. The expression for adsorption energy is given below (Equation (10)):

$$\text{Adsorption energy } (E) = 1/\sqrt{(2K)} \quad (10)$$

The values of mean free energy of sorption ( $E$ ) calculated for the present cases are shown in Table 5 with other evaluated parameters.



**Figure 7** | Kinetic plots for pseudo first order, pseudo second order and Weber–Morris models.

From the DR equation and according to the value of  $E$ , an adsorption process may be one of three types: (i) Physisorption if  $E \leq 8.0$  kJ mol/L; (ii) Ion-exchange if  $8.0 < E < 16.0$  kJ mol/L; and (iii) Chemisorption if  $E \leq 16.0$  kJ mol/L (Saha *et al.* 2016). It has been found that the  $E$  value (kJ/mol) is 7.8–14.22. These  $E$  values indicated that the anion sorption by HBO<sub>12mix</sub> is dominated by ion exchange phenomena followed by physical adsorption.

### Thermodynamics studies

Thermodynamic parameters in terms of changes in Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were

determined as per Equations (11) and (12):

$$\ln M = \frac{\Delta S^\circ}{R} - \Delta H^\circ / RT \quad (11)$$

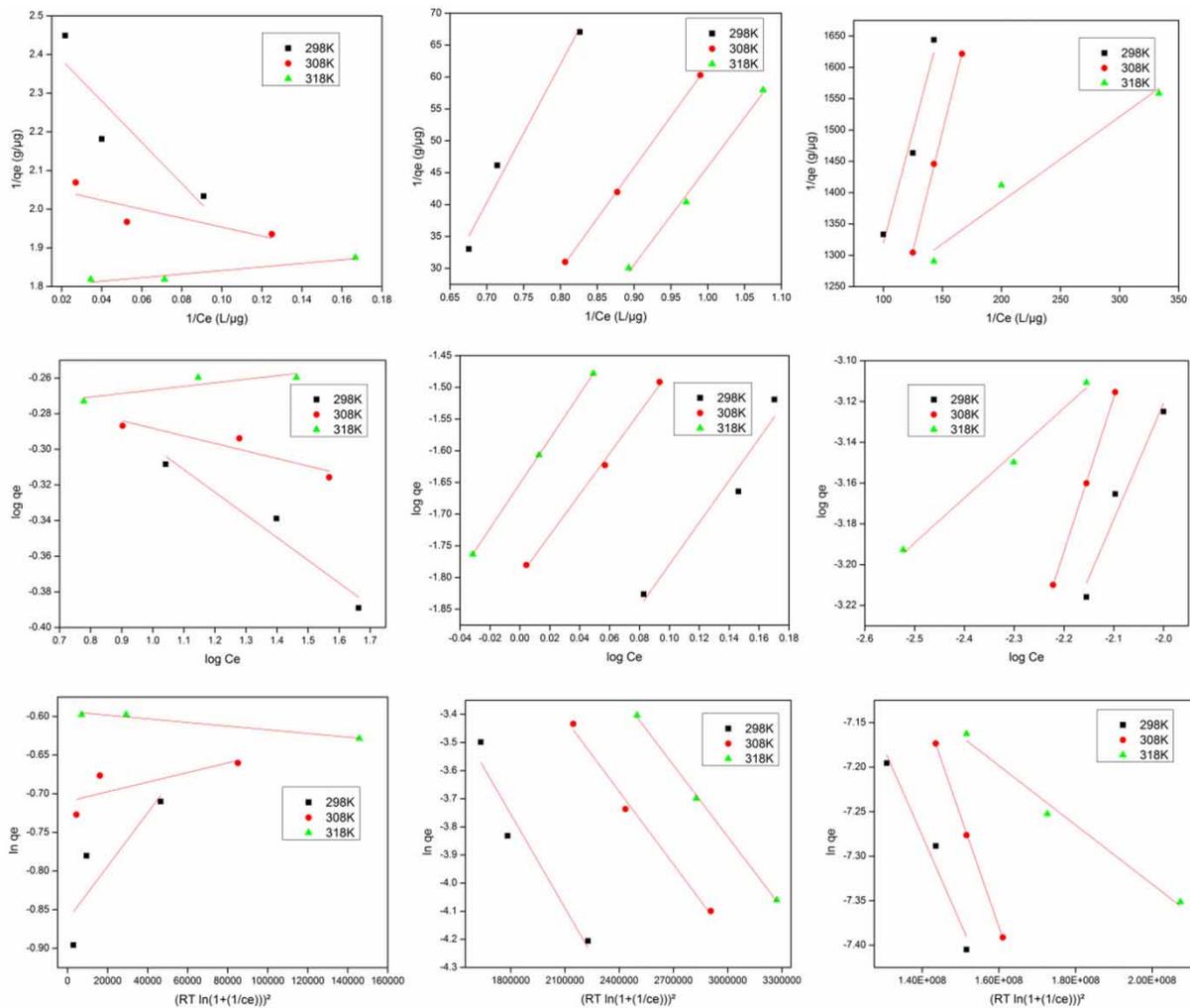
$$\Delta G^\circ = -RT \ln M \quad (12)$$

where  $R$  (8.314 J/mol K) is the gas constant,  $T$  is the absolute temperature (K), and  $M$  (L/g) is the standard thermodynamic equilibrium constant.

Values of ' $M$ ' are obtained by plotting  $\ln(q_e/C_e)$  versus  $q_e$  and extrapolating to zero  $q_e$  as per the methods suggested by Khan & Singh (1987) and Basu *et al.* (2010). The intersection with the vertical axis gives the value of ' $M$ '. Further, the value of  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the slope and

**Table 5** | Isotherm parameters of adsorption

Temperature (K)	Langmuir			Freundlich			Dubinin-Radushkevich			$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol)
	$q_0$ (mg/g)	$b$ (L/mg)	$R^2$	$K^?$	$n$	$R^2$	$q_m$ (mg/g)	$E$ (kJ/mol)	$R^2$			
Nitrate												
298	0.401	0.467	0.715	0.746	5.84	0.950	0.422	8.21	0.680	-56.98	29.79	68.61
308	0.483	1.78	0.825	0.954	4.00	0.874	0.492	9.56	0.750	-87.06		
318	0.557	3.87	0.926	1.100	3.49	0.786	0.552	16.50	0.977	-129.54		
Fluoride												
298	0.008	0.513	0.979	1.14	0.473	0.952	0.173	14.22	0.939	0.008	26.02	49.56
308	0.009	0.610	0.998	1.31	0.551	0.977	0.202	8.28	0.992	0.010		
318	0.010	0.701	0.995	1.52	0.605	0.996	0.274	7.80	0.995	0.009		
As (V)												
298	0.001	85.44	0.964	5.710	0.654	0.957	0.020	10.02	0.961	298	24.47	61.05
308	0.002	46.84	0.997	3.706	0.504	0.993	0.004	15.55	0.994	308		
318	0.001	24.09	0.970	1.659	0.379	0.991	0.001	17.12	0.987	318		



**Figure 8** | Linear isotherm plots for Langmuir, Freundlich and DR models.

intercept from the graph between  $\ln M$  and  $1/T$  (Liu & Liu 2008) as summarized in Table 5.

The values of  $\Delta G^\circ$  suggest that the spontaneous nature and higher temperature favors anion sorption. The positive value of  $\Delta H^\circ$  suggests that adsorption of anions over HBO is endothermic in nature. The magnitude of  $\Delta H^\circ$  if lies in between 2.1 and 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 (Banerjee *et al.* 2014). In this case the  $\Delta H^\circ$  value corresponds to the intermediate range between physical and chemical adsorption. Thus anion sorption onto HBO<sub>12mix</sub> is ion exchange in nature.

### Characterization of adsorbent

In order to characterize the materials for their physical and chemical combination properties, X-ray diffraction pattern, scanning electron microscopy, energy dispersive detector, FTIR spectroscopy analysis and pH<sub>pzc</sub> determinations were performed.

### X-ray diffraction

In order to understand the characteristics and dominant chemical species in HBO<sub>12mix</sub>, XRD analysis was performed. The presence of multiple peaks in XRD patterns indicates the broadly crystalline character of adsorbent

(Ramli *et al.* 2007). 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 (2009). 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>Cl<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.

A comparison for XRD peaks of HBO<sub>12mix</sub> before and after adsorption (Figure 9) indicated that new peaks appeared due to the adsorption of nitrate, fluoride and As (V) on the surface of the adsorbent. This could be attributed to the adsorption of nitrate, fluoride and As (V) on the surface of HBO<sub>12mix</sub> with polymeric character. Reductions in the chloride peak after adsorption could be the result of the ion exchange process with chloride ions with target anions. Similar results are attributed by Huang *et al.* (2015) in his studies. Hence, based on the above results, it can be inferred that the ion exchange between HBO<sub>12mix</sub> and anions present in solution was the main adsorption mechanism.

### pHpzc of HBO<sub>12mix</sub>

The behavior of adsorbent can be easily predicted by knowing its point of zero charge (pHpzc) value. The pH<sub>pzc</sub> represents a condition in which the surface hold equal electrical charge density of positive and negative ions because of the neutral condition when the pH is lower than the pzc

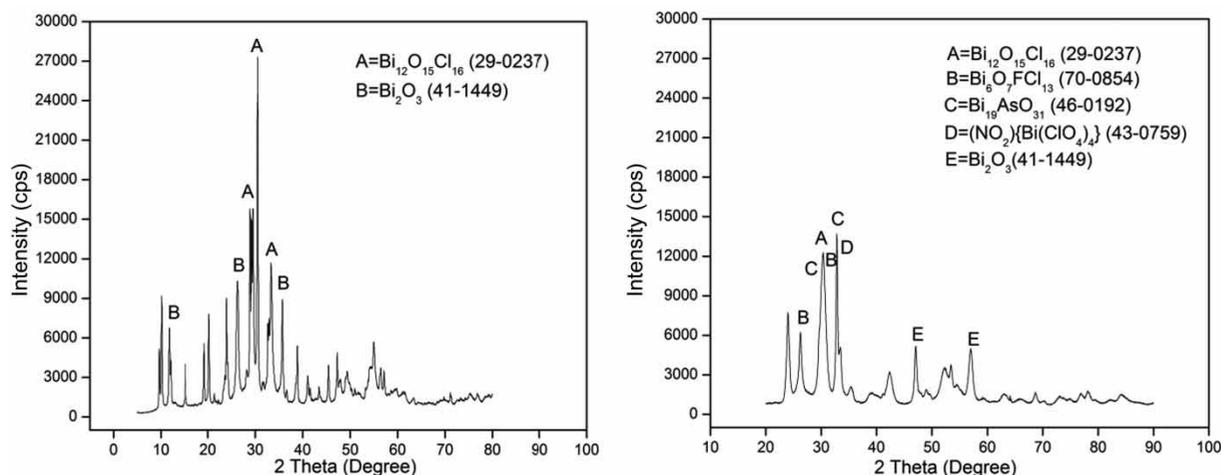


Figure 9 | XRD patterns of adsorbent before and after adsorption.

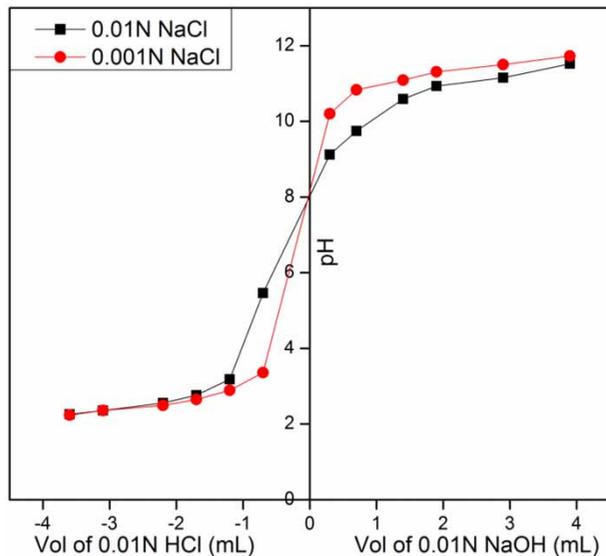


Figure 10 |  $pH_{PZC}$  of  $HBO_{12mix}$ .

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 favors the sorption of target anions. Conversely, above pzc the surface is negatively charged (attracting cations/repelling anions) and favors the sorption of positive anions (Mukhopadhyay *et al.* 2017).

To know the effect of pH on the sorption process, the point of zero charge ( $pH_{PZC}$ ) was measured. The pH of point of zero charge of adsorbent was determined using the fast alkalimetric titration method (Agarwal *et al.* 2006). The  $pH_{PZC}$  of  $HBO_{12mix}$  is found to be  $8.0 \pm 0.2$  (Figure 10)

where the net surface charge becomes zero as the surface of adsorbent becomes neutral attributing to equal density of negative and positive charge. Hence suitability and possibility of anionic uptake (nitrate, fluoride and As (V)) favors only with the condition of  $pH < pH_{PZC}$  ( $8.0 \pm 0.2$ ) due to columbic forces of attraction. Similarly, the force of repulsion will act as  $pH > pH_{PZC}$  ( $8.0 \pm 0.2$ ).

### SEM and EDS

SEM analysis has been carried out to determine the surface morphology of adsorbent. Figure 11 shows the irregular surface morphology of the adsorbent. The SEM spectrum indicates the granular and spongy formation which later becomes exhausted with a heterogeneous and rough surface, whereas the EDS spectrum analysis demonstrated that the adsorbent is composed of Bi and Cl and the presence of target anions were also confirmed by EDS after adsorption (Figure 12). Hence, the existence of nitrate, fluoride and arsenic on the surface of exhausted adsorbent in addition to bismuth and chloride were detected from EDS analysis which is also in agreement with our data findings in XRD analysis.

### FTIR

FTIR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. The FTIR spectrum of prepared adsorbent before and after adsorption is depicted in Figure 13. The distinctive absorptions bands corresponding to anions contaminants attached to the matrix of

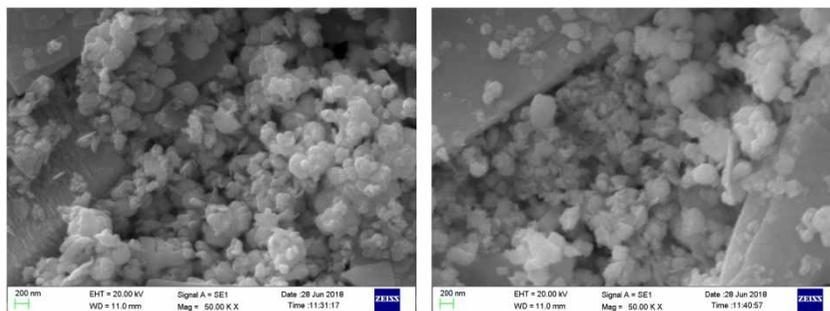


Figure 11 | SEM micrographs of the adsorbents before and after adsorption.

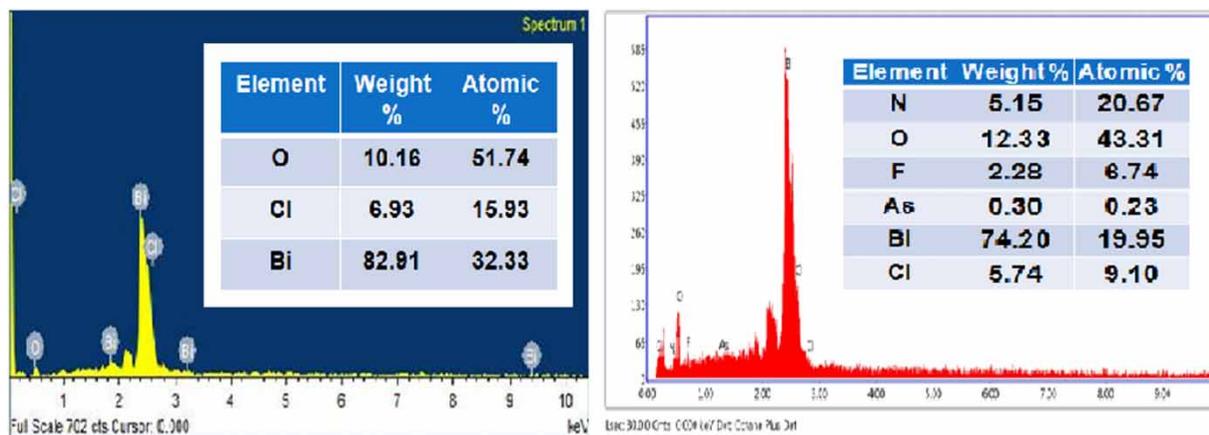


Figure 12 | EDS patterns of the adsorbents before and after adsorption.

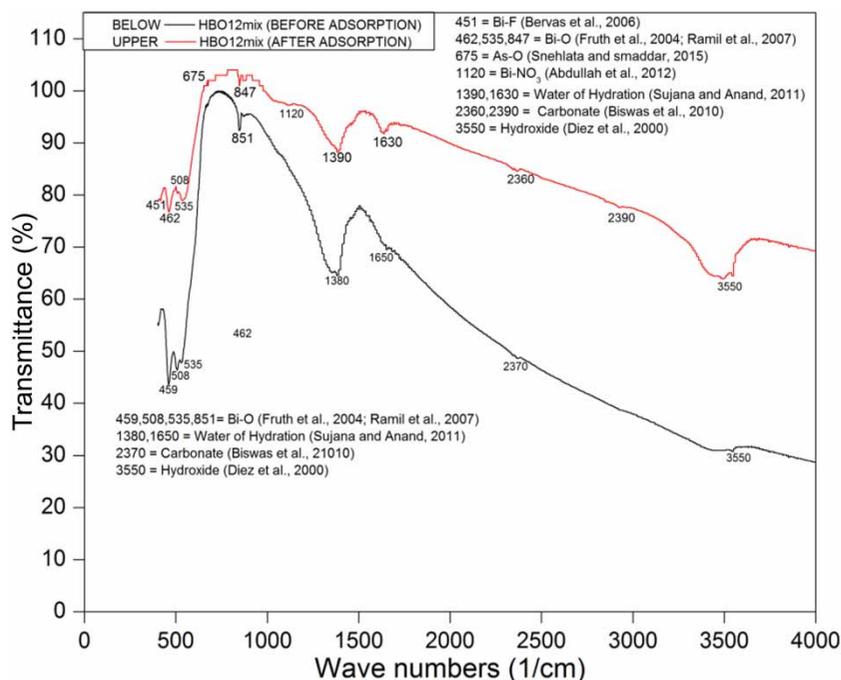


Figure 13 | FTIR patterns of the adsorbent before and after adsorption.

HBO<sub>12mix</sub> after adsorption. The broad absorption peaks of 530 and 846 is due to the Bi-O bond (Fruth *et al.* 2004; Ramli *et al.* 2007). Further, water molecules and hydroxide were spotted at peaks of 1,380, 1,620 (Sujana & Anand 2011) and 3,430 (Diez *et al.* 2000) respectively. In addition

to these, various new peaks were appeared at 441, 530, 675, 1,045, 1,274 and 1,310. Bervas *et al.* (2006) and Escudero *et al.* (2014) specified absorption bands corresponding to wave numbers 441 and 530 cm<sup>-1</sup> only as characteristics of the Bi-F bond. The sharp peak at 1,274 and 1,310 cm<sup>-1</sup>

could be due to the existence of  $\text{BiNO}_3$  (Abdullah *et al.* 2012a, 2012b). In addition, the frequency at  $675$  to  $1,045\text{ cm}^{-1}$  shows characteristics of the As-O bond (Pena *et al.* 2006; Snehata & Samadder 2015). The FTIR detected new peaks as a result of nitrate, fluoride and arsenic adsorption. The distinctive absorption bands corresponding to nitrate, fluoride and arsenate in addition to those of bismuth and hydroxyl ions indicate that the target anions have become an integral part of the adsorbents. FTIR analysis of the tested materials supports the results obtained through XRD and EDS analysis.

### Cost analysis

An attempt was made to compare conventional adsorbent based on the cost of preparation as the cost of synthesis of the adsorbent is the major factor for its selection in adsorption study. The overall cost of  $\text{HBO}_{12\text{mix}}$  should not be very high for its large scale preparation and application. The preparative cost of the reported sorptive material ( $\text{HBO}_{12\text{mix}}$ ) appears comparable with some of the adsorbents used in the adsorption process. The overall cost (US\$/kg) for the preparation of different adsorbents is given in Table 6.

The cost of adsorbent mainly depends on the scale of application, reuse potential, sorption potential and synthesis of adsorbent. The current study demonstrated the concurrent removal efficiency of nitrate, fluoride and As (V) for up to three cycles. The adsorbent will be economically viable as it can be regenerated/reactivated for many cycles after it has been exhausted. Regeneration of  $\text{HBO}_{12\text{mix}}$  adsorbents is quite possible for up to 3–4 cycles. Moreover,

**Table 6** | Cost analysis of different adsorbent

Adsorbent	Cost	Reference
Activated alumina	~2.3	Rubel (1983)
Activated carbon	~48.0	Gupta <i>et al.</i> (2018)
Amorphous alumina	~70.0	Rubel (1983)
Hydrous bismuth oxide (HBO1)	~59.0	Srivastav <i>et al.</i> (2013)
Hydrous bismuth oxide mix ( $\text{HBO}_{12\text{mix}}$ )	~64.0	Present study

most likely the cost will also get reduced when it will be synthesized on a large scale.

### Mechanism for the removal of nitrate, fluoride and arsenic

Electrostatic force and ion-exchange on the protonated surface of adsorbent could be responsible for nitrate, fluoride, and As (V) adsorption with chloride release (Ruixia *et al.* 2002). Hence, release of  $\text{Cl}^-$  from the hydrous bismuth oxide ( $\text{HBO}_{12\text{mix}}$ ) during the sorption process could lead to the conclusion that chloride ions adhere to the surface with weak interaction and was easily replaced at suitable conditions ( $\text{pH} < 8.0 \pm 0.2$ ). Ion exchange could be seen as a dominant sorption mechanism for concurrent removal of nitrate, fluoride and As (V). The risk of bismuth leaching in treated water was also taken into account during the present study and the results show that most bismuth ions were firmly fixed within the matrix of hydrous bismuth oxide ( $\text{HBO}_{12\text{mix}}$ ). Hence, adsorbent could be considered as a type of environment-friendly material for nitrate, fluoride, and As (V) pollutant removal from water.

### CONCLUSIONS

The performance of each hydrous bismuth oxide was evaluated for concurrent removal of nitrate, fluoride and As (V) removal from aqueous removal. The HBO1 was best for removal of fluoride and As (V) whereas HBO2 was best for removal of nitrate and As (V) at a higher dosage. Removal of all three with  $\text{HBO}_{12\text{mix}}$  were tested and it was found that the maximum removal was 52% for nitrate, 71% for fluoride and 92% for As (V), observed at a dosage of 130 g/L with a contact time of 3 h. The column adsorption experiment shows that approximately 750 mL of contaminant free drinking water could be directly availed by consumers whereas 1,180 mL (fluoride and arsenic free) and 3,512 mL (arsenic free) of drinking water could be used by households. The interaction between target anions and bismuth bounded chloride played a vital role by the ion exchange mechanism. XRD, SEM, EDS and FTIR results confirm the integration of target anions into

the matrix of HBO<sub>12mix</sub>. No secondary pollution was observed due to the elution of bismuth in treated water. Hence, HBO<sub>12mix</sub> can be considered as a potential adsorbent for the elimination of nitrate, fluoride and arsenic concurrently. This may be used as a potential sorbent for developing a point of use (POU) water treatment unit for the removal of nitrate, fluoride and arsenic existing in concurrent conditions.

## ACKNOWLEDGEMENTS

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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