CHAPTER-4

RESULTS AND DISCUSSION

With an ultimate objective to develop inorganic sorptive media for simultaneous removal of nitrate, fluoride and arsenic from water for drinking, the present study focused on the use of hydrous bismuth oxides (HBOs) for the purpose.

4.1 HBOs as possible sorbent for arsenic removal from aqueous solutions

Available literature on the subject suggests that hydrous bismuth oxides (HBOs) have been found to have affinity towards nitrate and fluoride from water in normal pH range; but they have not been tested for arsenic sorption. Analogically, HBOs may be expected to have affinity for arsenic also. Accordingly, the objective of this part of the study was to check the feasibility of using HBOs in arsenic removal and its preference towards arsenite (As(III)) or arsenate (As(V)) in the pH range of potable water. Hence both forms of arsenic were tested for their removal possibilities using $HBO_{1,}$ HBO_2 and HBO_3 powders with 3 h contact time. All the three forms of HBOs gave very good arsenic removal. Considering HBO_1 as the first option, the result of arsenic removal using HBO_1 is given in Table 4.1.

Table 4.1: Arsenic removal efficiencies of Hydrous Bismuth Oxides (HBO_1)

Arsenic Species	**Initial conc. (mg/L)**	**Final conc. (mg/L)**	**Sorptive potential (%)**
Arsenate (As(V))	0.085	0.008	91
Arsenite (As(III))	0.085	0.022	74

(Initial conditions: pH = 7.34, Dosage = 6 g/L, Contact time = 3 h)

It is thus observed that although both forms of arsenic are removed by sorption, the removal efficiency for As(V) is higher than As(III) in the given contact time. In general As(III) is found in ground waters with reducing environment and it gets converted to As(V) in oxidising conditions. pH is one of the prime factors for arsenic speciation and its mobility (Doušova et al., 2003). Oxygen present in air leads to increase the redox potential of the groundwater when it is exposed to the open atmosphere. Consequently, Arsenite (As(III)) changes into Arsenate (As(V)) (Ngai et al., 2006). Hence, Arsenate (As(V)) is dominant spices over Arsenite (As(III)) in an oxidative environment (Sarkar and Paul, 2016). The major components of Arsenate (As(V)) in aqueous environment are also anionic species ($H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}) and mostly found in the pH range of 6-8 as reported by Ngai (2002). Groundwater obtained from oxidizing environment will thus be favored by the proposed adsorbent with higher efficiency. Hence, As(V) was chosen for testing in further experiments.

4.2 Simultaneous removal of nitrate, fluoride and As(V) by HBOs from the mixed solution in batch adsorption experiment

A mixed solution having 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 was prepared. These contaminant levels were selected for two reasons: first, these are the levels of contamination reported in groundwater sources in India, and second, individually, all of these three selected contaminants can be removed to safe drinking water concentration levels using HBO powders. The minimum removal required to make the water safe for drinking at the selected level of contamination is 53% for nitrate, 70% for fluoride and 88% for As(V). To examine this feasibility, different HBOs were tested individually for nitrate, fluoride and As(V) removal from a mixed solution. Different dosage of dry powders of HBO adsorbents were taken in conical flask with 100 mL of contaminated water and left for 3 h contact time. After filtering through Whatman 42 filter paper, the samples were analyzed for the pH, nitrate, fluoride and As(V). Figure 4.1 gives the graphical presentation and Table 4.2 summarizes the results obtained in batch experiments for nitrate, fluoride and As(V) removal from mixed solution using individual HBOs: HBO_1, HBO_2 and HBO_3 powders. It is noted that with individual powders, the highest level (of 61%) of removal for nitrate is obtained by HBO_3 (very closely followed by HBO_2, to the extent of 60% of initial concentration), 68% for fluoride by HBO_1 and 91% for As(V) by HBO_1, HBO_2 as well as HBO_3. These observed percentage removals are higher than required to bring the treated water safe for drinking with respect to these contaminants.

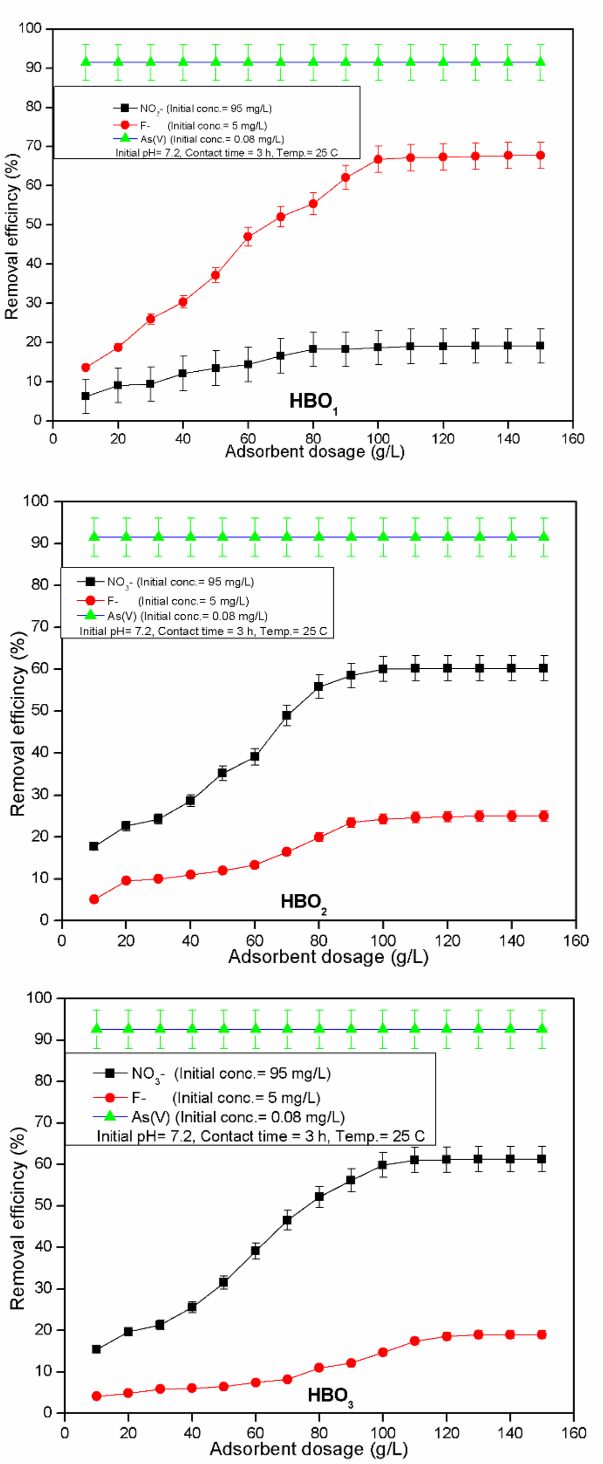


Figure 4.1: Effect of adsorbent dosages on simultaneous removal of contaminants from mixed solution

4.2.1. Effect of single adsorbents dosage

The effect of adsorbent dosage on simultaneous removal of nitrate, fluoride and As(V) from the mixed solution by HBO_1, HBO_2 and HBO_3 was studied. It was observed (Figure 4.1) that the removals of contaminants increase with increasing dosage and stabilize around 100 g/L. At this dosage, the removals of contaminants from the mixed solution environment are found as summarized in Table 4.2.

Table 4.2: Effect of adsorbent dosage on simultaneous removal of contaminants from mixed solution

Adsorbents	**Removal (%)**		
	Nitrate **(C_o= 95 mg/L)**	**Fluoride** **(C_o= 5 mg/L)**	**Arsenic(V)** **(C_o=0.08 mg/L)**
HBO_1	19	68	91
HBO_2	60	22	91
HBO_3	61	20	91

(Initial conditions: pH = 7.34, Dosage = 100 g/L, Contact time = 3 h)

It is observed that all the three forms of HBOs (HBO_1, HBO_2 and HBO_3) performed excellently well for As(V) with greater than 91% removal from the mixed solution.

Thus, based on the results reported in literature and the present study, the potentials of different forms of HBOs i.e., HBO_1, HBO_2 and HBO_3 with respect to three selected groundwater contaminants may be summarized as follows in Table 4.3.

Table 4.3: Sorptive potentials of HBOs for nitrate, fluoride and As(V) from water

Media	**Earlier results reported**		**Present study**
Hydrous bismuth oxides	**Affinity towards nitrate**	**Affinity towards Fluoride**	**Affinity towards Arsenate (As(V))**
HBO_1	Low (Singh, 2000)	High (Srivastav et al., 2013)	High
HBO_2	High (Singh, 2000; Srivastav et al., 2014)	Low (Srivastav et al., 2015)	High
HBO_3	High (Singh, 2000; Singh et al., 2015)	Low (Srivastav et al., 2013)	High

The method of preparation of hydrous bismuth oxide has significant effect on the physicochemical properties of the adsorbents (Singh and Ghosh 2000). HBO_1 has been prepared using an acid (solution of Bi_2O_3) to alkali ratio of 1:1, and as a final product, HBO_1 is white which is in line with the theoretical prediction for monomeric BiOOH. But successively, further addition of hydroxide in ratio 1:2 and 1:3 (v/v) leads to the formation of HBO_2 and HBO_3 which are assumed to be polymeric forms of BiOOH and yellow in colour.

Based on theoretical considerations, the reaction leads to the formation of two possible forms of precipitates, i.e., bismuthous hydroxides [$Bi(OH)_3$] and bismuthyl hydroxide [BiOOH] (Pourbaix, 1996), as given in Eqs. 4.1, 4.2.

$$Bi_2O_3(c) + 6HCl(aq) + 6NaOH(aq) \rightarrow 2Bi(OH)_3(c) + 6NaCl + 3H_2O(I) \quad (4.1)$$

$$\Delta G_f\,°(Kcal) = 118.55 + (6\times31.37) + (6\times 99.23) + [2\times(-138.55)] + [6\times(-91.78)] + [3\times(-56.68)] = -95.67$$

$$Bi_2O_3(c) + 6HCl(aq) + 6NaOH(aq) \rightarrow 2BiOOH(c) + 6NaCl + 5H_2O(I) \quad (4.2)$$

$$\Delta G_f\,°(Kcal) = 118.55 + (6\times31.37) + (6\times99.23) + [2\times(-88.4)] + [6\times(-91.78)] + [5\times(-56\ 68)] = -108.73$$

Both the reaction seems to be feasible, but $Bi(OH)_3$ could be an intermediate product as given in Eq. 4.3 (Singh et al., 2012).

$$Bi(OH)_3(c) \rightarrow BiOOH(c) + H_2O(l) \tag{4.3}$$

$$\Delta G_f\,°(Kcal) = 138.55 + (-88.4) + (-56.68) = -6.53\ Kcal$$

Where $\Delta G_f°$, is the Gibb's free energy of formation (Kcal/mole) under standard state conditions.

Bismuthyl hydroxides are sometimes written as BiO(OH) but could be bismuth oxide (Bi_2O_3) with variable water content (Briand and Burford, 1999). Initially, the hydrous bismuth oxide (HBO_1) is formed from univalent $[Bi = O]^+$ or $[Bi–O]^+$ radicals which is white in appearance and there is no indication that they ever go in covalent form (Sidwick, 1950). HBO_2 and HBO_3 which are yellow in colour and formed under the presence of excess hydroxide ions are possibly polymeric forms (Hollemann and Wiberg, 1960) of bismuthyl hydroxide (BiOOH) and might have developed some covalent character (Pauling, 1960). This may partially explain as to why hydroxyl ions in HBO_2 and HBO_3 have not been found exchangeable despite anions being sorbed. However, free chlorides sorbed in the polymeric structure of the hydroxide may facilitate partial exchange of anionic contaminants from the solution.

The yellow hydrous bismuth oxides (HBO_2/HBO_3) are found to have potentials for nitrate and As(V) sorption, whereas the monomeric hydrous bismuth oxide (HBO_1) shows higher uptake of fluoride and As(V).

Hence, from the above Table 4.3, it appears that a mixed media of (HBO_1 + HBO_2) or (HBO_1 + HBO_3) may have good potentials for simultaneous removal for all the three contaminants: nitrate, fluoride and As(V) from water. Hence experiments were conducted to check the potentials of the mixed powder, i.e. HBO_1 + HBO_2, designated as HBO_{12mix} and HBO_1 + HBO_3, designated as HBO_{13mix}.

4.2.2. Effect of mixed powder dosage

Equal proportions of HBO_1 and HBO_2 were thoroughly mixed and designated as HBO_{12mix}. Similarly equal proportions of HBO_1 and HBO_3 mixed together were designated as HBO_{13mix}. Dosage was varied from 10 to 150 g/L for 3 h contact time with continuous stirring at 250 rpm. After the contact time, filtered water samples were analyzed for residual nitrate, fluoride and As(V) concentrations. pH and chloride of the resultant solutions were also monitored and recorded. Results are presented in Table 4.4 and Figure 4.2(a).

Table 4.4: Simultaneous removal of nitrate, fluoride and As(V) from mixed solution using HBO_{12mix} powder

Dosage HBO_{12mix} (g/L)	**pH**		**Nitrate (C_o = 95 mg/L)**			**Fluoride (C_o = 5 mg/L)**			**As(V) (C_o = 0.08 mg/L)**		
	Initial pH	**Final pH**	**Final conc. (mg/L)**	**Removal (%)**	**Sorption potential (mg/g)**	**Final conc. (mg/L)**	**Removal (%)**	**Sorption potential (mg/g)**	**Final conc. (mg/L)**	**Removal (%)**	**Sorption potential (mg/g)**
05+05	7.34	7.91	84.3	11	1.07	3.8	22	0.12	0.019	81	0.00810
10+10	7.34	7.87	78.8	17	0.81	3.7	29	0.07	0.008	92	0.00460
15+15	7.34	7.86	72.8	23	0.74	3.5	31	0.05	0.008	92	0.00810
20+20	7.34	7.98	70.6	26	0.61	3.5	32	0.04	0.008	92	0.00460
25+25	7.34	8.13	66.7	30	0.57	3.4	33	0.03	0.008	92	0.00310
30+30	7.34	7.97	65.5	33	0.53	3.2	37	0.03	0.008	92	0.00230
35+35	7.34	8.11	62.3	38	0.51	2.9	44	0.03	0.008	92	0.00180
40+40	7.34	8.23	58.6	43	0.51	2.3	54	0.03	0.008	92	0.00150
45+45	7.34	7.85	54.9	45	0.48	2.0	61	0.03	0.008	92	0.00130
50+50	7.34	7.91	51.8	49	0.46	1.7	68	0.03	0.008	92	0.00120
55+55	7.34	7.80	48.3	52	0.45	1.5	70	0.03	0.008	92	0.00080
60+60	7.34	8.12	45.9	52	0.41	1.5	70	0.03	0.008	92	0.00076
65+65	7.34	8.21	45.6	52	0.38	1.4	71	0.03	0.008	92	0.00070
70+70	7.34	8.19	45.6	52	0.35	1.4	71	0.03	0.008	92	0.00065
75+75	7.34	7.97	45.6	52	0.35	1.4	71	0.03	0.008	92	0.00061

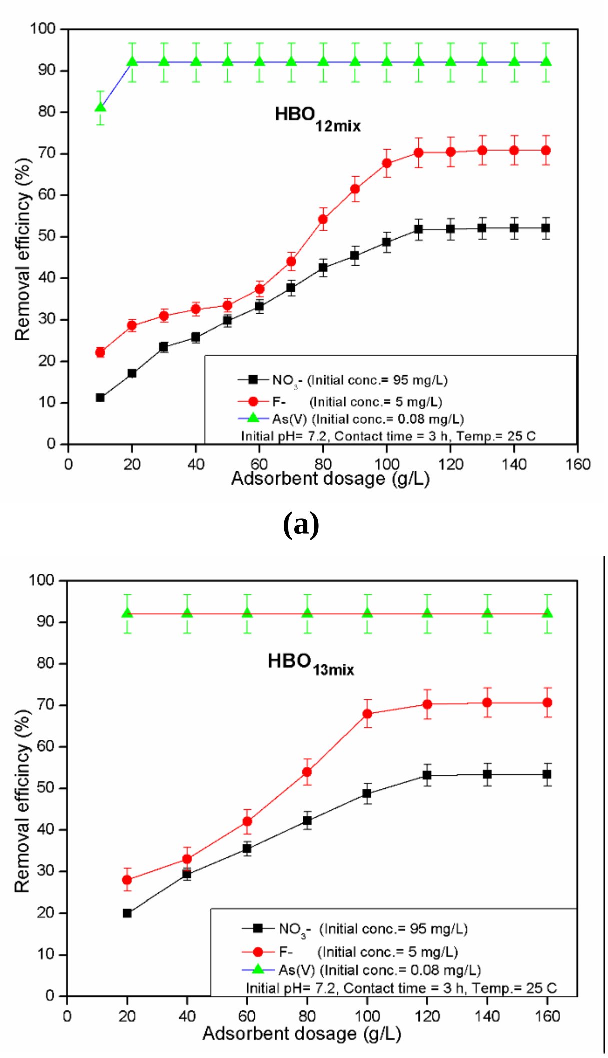
It is observed that for As(V), both HBO_{12mix} and HBO_{13mix} seem equally efficient beyond a powder dosage of 20 g/L and the removal is around 92%. The pH of treated water slightly increases and varied between 7.85 to 8.23. The nitrate concentration decreased from 95 mg NO_3^-/L to 45.6 mg NO_3^-/L (52% removal), whereas fluoride concentration reduced from 5 mg/L to 1.48 mg/ L (~71% removal) and As(V) reduced from 0.08 mg/L to 0.008 mg/L (92% removal) at a dosage of 130 g/L. The sorption potential showed a decreasing trend with increasing dosage of sorbents and varied from 1.07 mg/g to 0.35 mg/g for nitrate, 0.12 mg/g to 0.03 mg/g for fluoride and 0.008 mg/g to 0.0006 mg/g for As(V). A dosage of 130 g/L of adsorbents is found optimum. The marginal increment in pH may possibly be there due to interaction and effect of hydroxide in the matrix of HBO_{12mix} powder which is under permissible limit of drinking water.

A similar experiment was conducted using HBO_{13mix}. The removal of nitrate, fluoride and As(V) from the mixed solution was observed as shown in Table 4.5.

Table 4.5: Simultaneous removal of nitrate, fluoride and As(V) from mixed solution using HBO_{13mix} powder

Dosage HBO_{13mix} (g/L)	**pH**		**Nitrate (C_o = 95 mg/L)**			**Fluoride (C_o = 5 mg/L)**			**As(V) (C_o = 0.08 mg/L)**		
	Initial pH	**Final pH**	**Final conc. (mg/L)**	**Removal (%)**	**Sorption potential (mg/g)**	**Final conc. mg/L)**	**Removal (%)**	**Sorption potential (mg/g)**	**Final conc. (mg/L)**	**Removal (%)**	**Sorption potential (mg/g)**
10+10	7.34	8.14	76.3	20	0.96	3.94	28	0.071	0.008	92	0.00460
20+20	7.34	8.07	67.4	29	0.70	3.67	33	0.043	0.008	92	0.00230
30+30	7.34	7.98	61.6	35	0.56	2.96	38	0.036	0.008	92	0.00153
40+40	7.34	8.36	55.1	42	0.50	2.12	57	0.036	0.008	92	0.00115
50+50	7.34	8.21	48.9	49	0.47	1.65	70	0.030	0.008	92	0.00092
60+60	7.34	7.89	44.7	53	0.42	1.54	70	0.030	0.008	92	0.00077
70+70	7.34	7.94	44.5	53	0.36	1.50	71	0.026	0.008	92	0.00066
80+80	7.34	8.07	44.5	53	0.32	1.50	71	0.023	0.008	92	0.00058

With increasing dosage, the contaminants removal increased and a maximum of ~ 53%, 71%, and 92% removal for nitrate, fluoride and As(V) respectively was observed by HBO_{13mix} at a dosage of 120 g/L (Table 4.5 and Figure 4.2(b)). The sorption potential decreased from 0.96 to 0.32 mg/g for nitrate, 0.07 to 0.02 mg/g for fluoride and 0.0046 to 0.00058 mg/g for As(V). Based on these observations, as the gain in terms of percentage removal of contaminants is not very significant using HBO_{13mix}, we decided to work with HBO_{12mix} for all further experiments.



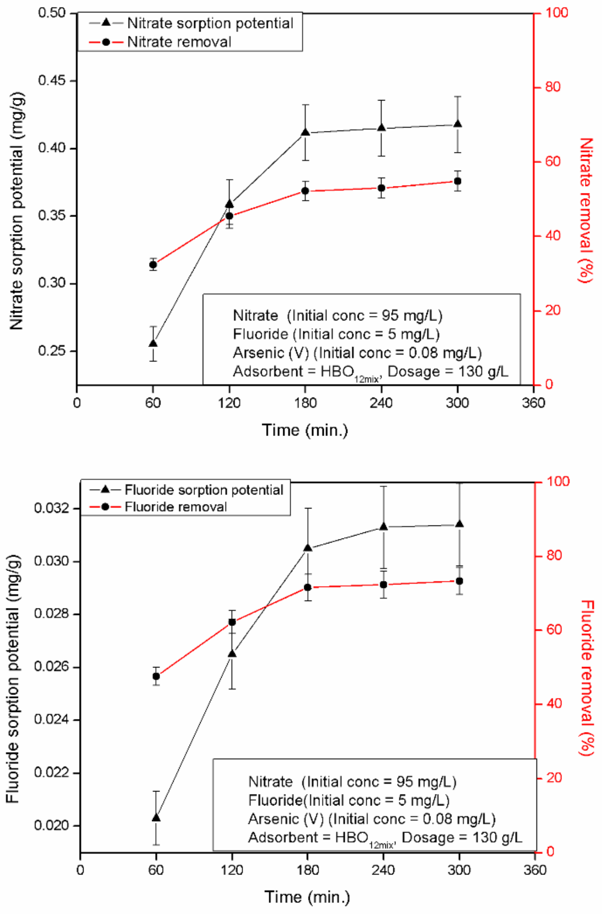
(a)

(b)

Figure 4.2: Effect of mixed powder (a) HBO_{12mix} and (b) HBO_{13mix} on simultaneous removal of nitrate, fluoride and As(V) from mixed solution

4.2.3. Effect of contact time

The effect of contact time was studied up to a period of 300 min (5 h) using HBO_{12mix} powder as adsorbent. The observations revealed that the nitrate removal efficiency increases from 32% at 60 min contact time to 46% and 54% at 120 and 180 min and still shows increasing trend with higher contact time. During 3 h contact period, the nitrate adsorption potential increases from 0.26 mg/g to 0.41 mg/g. Similarly for fluoride, removal efficiency increased from 48% to 62% and 73% in first 3 h and sorption potential increased from 0.20 mg/g to 0.31 mg/g. As(V) removal efficiency increased from 51% to 80% and 92% with 0.0003 mg/g, 0.0005 mg/g and 0.0006 mg/g sorption potentials at 60, 120 and 180 min contact time respectively (Figure 4.3).



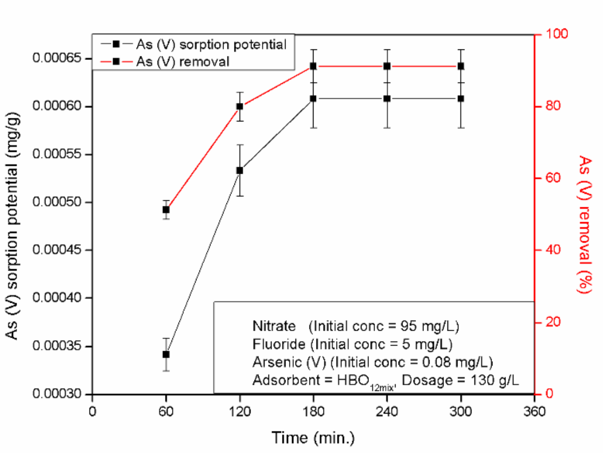


Figure 4.3: Effect of contact time on contaminants removal and sorption potentials of HBO_{12mix} powder from mixed solution

4.2.4 Preference of adsorption

In order to study the preferential nature of the powder for the studied contaminants, a mixed synthetic solution containing 1 meq/L (≈62 mg/L) of nitrate, 1 meq/L (≈19 mg/L) of fluoride and 1 meq/L (≈74 mg/L) of As(V) in distilled water was prepared and used in batch mode of application with a dosage of 130 g/L and 3 h contact time. The results of this set of experiments are shown in Table 4.6.

Table 4.6: Preferential sorptive characteristics of HBO_{12mix}

Composition of mixed solution	Initial Conc. (mg/L)	Final Conc. (mg/L)	Removal Efficiency (%)	Sorption Potential (mg/g)
Nitrate	62 (≈1 meq/L)	52.0	19.23	0.077
Fluoride	19 (≈1 meq/L)	03.1	83.52	0.122
As(V)	75 (≈1 meq/L)	00.1	99.80	0.576

(Initial conditions: Dosage = 130 g/L, Contact Time = 3 h)

Based on the results obtained, the order of preference and sorptive potentials of HBO_{12mix} powder for the given contaminants at 1 meq/L concentration level is found as:

As(V)> Fluoride > Nitrate

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

To simulate the real field condition, it is important to assess the properties of adsorbent in the presence of competitive anions. Sulfate and bicarbonate are the most common ions present in the groundwater. Hence, the effect of sulfate and bicarbonate ion presence were studied on sorption potential of HBO_{12mix} with dosage of 130 g/L and contact time of 3 h. A concentration range of 1-5 meq/L of sulfate and bicarbonate were tested. It is observed that bicarbonate ions affect more adversely on nitrate removal than sulfate, and sulfate ions affect removal of fluoride and As(V) more adversely than bicarbonate in simultaneous removal of the three targeted anionic contaminants. The results of the analyses are shown in Figure 4.4.

4.2.5.1 Effect of bicarbonate

It is observed that the removal of contaminant ions decreased in presence of bicarbonate and sulfate in the solution. At an initial pH of 7.34, dosage 130 g/L of HBO_{12mix} and 3 h contact time, the nitrate removal successively decreased from 54% with no bicarbonate to 12% at 5 meq/L (250 mg/L as $CaCO_3$) of bicarbonate in the solution. Similarly, fluoride removal decreased from 73% to 37% and As(V) removal decreased from 91% to 61% under similar conditions of increasing levels of bicarbonate (0 to 5 meq/L). As anion, bicarbonate itself got sorbed by 73%, reducing the concentration to 27% of initial only. The final pH of solution increased to 8. The effect of pH on defloridation was studied by Goswami and Purkait (2012). It indicates that HBO_{12mix} is potentially useful for sorption of nitrate, fluoride and As(V) below an alkalinity of around 3 meq/L (150 mg/L as $CaCO_3$).

4.2.5.2 Effect of sulfate

In presence of sulfate, the removal of nitrate decreased from 55% with no sulfate to 27% with 5 meq/L (≈240 mg/L SO_4^{2-}) of sulfate in the solution. Similarly, fluoride removal decreased from 73% with no sulfate presence to 28% at 5 meq/L (≈240 mg/L SO_4^{2-}) of sulfate and As(V) removal decreased from 92% with no sulfate to 51% at 5 meq/L (≈240 mg/L SO_4^{2-}) of sulfate. A 33% reduction in sulfate concentration was observed. While the initial pH of solution was 7.34, the final pH slightly increased to 8.

It is also observed that for nitrate removal, bicarbonate is more detrimental than sulfate on equal concentrations. During adsorption, multivalent nature of sulfate anions has been preferred over monovalent anions (Mohapatra et al., 2012). Hence, HBO_{12mix} is found potentially useful for sorption of nitrate, fluoride and As(V) below sulphate concentration of 2 meq/L (≈96 mg/L of SO_4^{2-} ≈ 142 mg/L of Na_2SO_4).

Thus, for nitrate removal, the preference series of anions appear as:

Bicarbonate >Sulfate.

Whereas for fluoride and As(V) removal, affinity followed the following order:

Sulfate > Bicarbonate.

From the characteristics of curves showing the decreasing trend of percentage removal, it is observed that the presence of competitive anions affects more severely on nitrate removal followed by fluoride and As(V). The decrease in fluoride and As(V) removal is much sharper once the concentrations of bicarbonate exceeds about 3 meq/L, i.e. about 150 mg/L of bicarbonate as $CaCO_3$ and sulfate exceeds about 2 meq/L i.e. 142 mg/L of sodium sulfate.

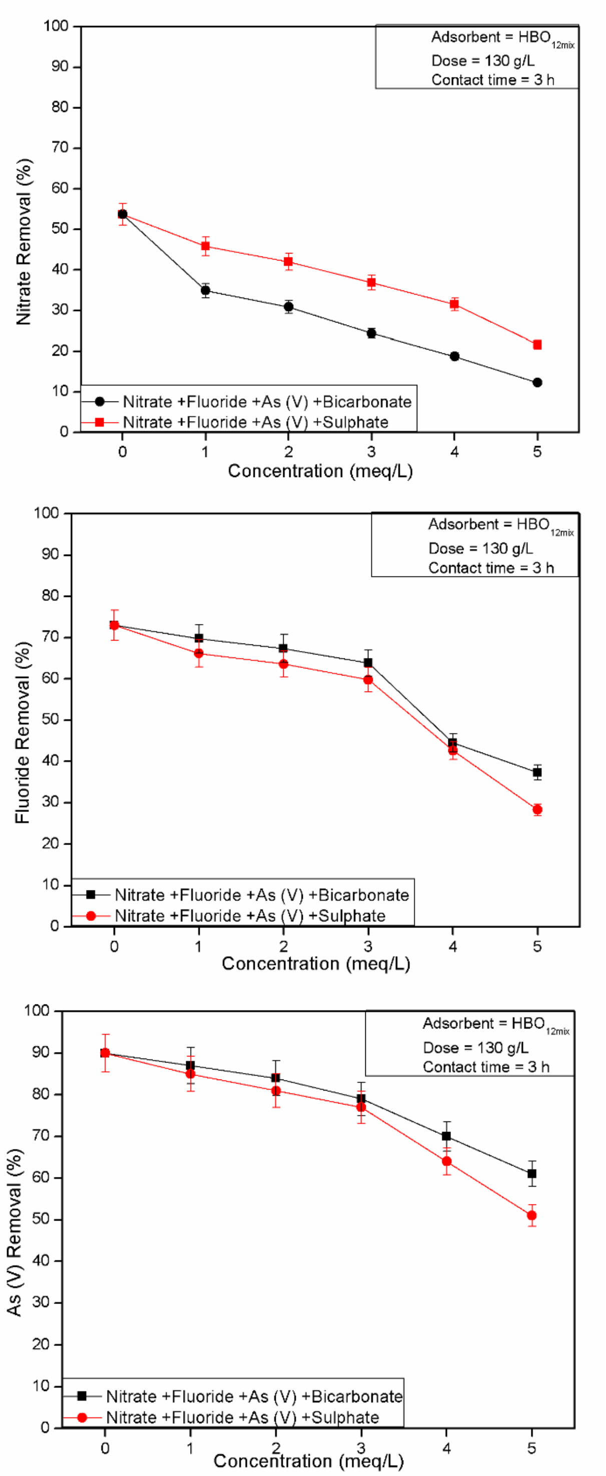


Figure 4.4: Effect of bicarbonate and sulfate ions on simultaneous removal of nitrate, fluoride and As(V) from mixed solution

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 3 meq/L (150 mg/L as $CaCO_3$) and Sulphate concentration of 2 meq/L (142 mg/L of Na_2SO_4).

4.3. Adsorption kinetics studies

Kinetics plays a significant role to evaluate the performance of a given adsorbent and to understand the adsorption mechanism. Adsorption is time-dependent process and it is very important to know the rate of adsorption for design and evaluation of the adsorbent in removing the pollutants in water/wastewater (Zawani et al., 2009). Several mathematical models have been developed to describe adsorption and diffusion processes. When adsorption is observed taking place, thermodynamic and kinetic aspects should be studied to know more details about its performance and mechanism. Except for adsorption capacity, kinetic performance of a given adsorbent has a great significance for the pilot application. From the kinetic analyses, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established. Generally speaking, adsorption kinetics is the base to determine the performance of fixed-bed or any other flow-through systems (Qiu et al., 2009). A rapid uptake of pollutant and establishment of equilibrium in a short period signifies the efficiency of adsorbent for its use in water treatment.

Contact time is an important factor for the development of surface charges at the surface of solid solution interface. The uptake of adsorbate is fast in initial stages of contact period and become slow near equilibrium. Large numbers of surface sites are available for adsorption at the initial stage and after sometimes, the remaining surface sites are difficult to occupy because of repulsive forces between the solute molecules of the solid and bulk phase (Khan et al., 2009).

Pseudo-first-order, Pseudo-second-order and Weber-Morris intra-particle diffusion models have widely been used to test adsorption kinetic data.

4.3.1 First order kinetic model

Lagergren (1898) presented a pseudo first-order rate equation (Eq. 4.6) to describe the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity. It is widely used to describe the adsorption of pollutants from wastewater (Tan et al., 2008; Sujana and Mohanty, 2010; Swain et al., 2012). It can be presented as follows:

$$dq_t/dt = K_1(q_e - q_t) \tag{4.4}$$

Integrating Eq.(4.4) with the boundary conditions of $q_t=0$ at $t=0$ and $q_t=q_t$ at time=t, yields (Ho, 2004):

$$\ln(q_e/q_e - q_t) = K_1 t \tag{4.5}$$

This can be rearranged to:

$$\log(q_e - q_t) = \log q_e - (K_1/2.303)t \qquad (4.6)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium in mg/g and q_t is the amount of solute adsorbed per unit weight of adsorbent at any time t in mg/g. K_1 (min^{-1}) is the pseudo-first-order rate constant for the kinetic model. The value of adsorption rate constant K_1 and q_e can be determined from the slope and intercept of the linear plots of log ($q_e - q_t$) versus t.

4.3.2 Second order kinetic model

The pseudo-second order adsorption kinetic model is based on the sorption capacity and by taking the assumption of dissociation anions in the solution and free sites available on the adsorbent surface. The expression (Eq. 4.7) of the pseudo-second order adsorption kinetic model is given as (Ho and McKay, 1999):

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (4.7)$$

The values of q_e (1/slope) and adsorption rate constant K_2 ($slope^2$/intercept) can be obtained by plotting t/q_t versus t.

The pseudo-second order kinetics suggests that the number of adsorption sites on the adsorbent surface and the number of adsorbate ions in the liquid phase together determine the rate of adsorption. The formation of chemical bond between adsorbate and adsorbing site is the rate-limiting step (Chaudhry et al., 2016).

4.3.3 Weber-Morris (WM) kinetic model

The kinetic data were also analyzed by the Weber-Morris (WM) kinetic model. The rate equation (Eq. 4.8) with linear form of intra particle diffusion model is given by Weber–Morris (1963) as:

$$q_t = K_3\sqrt{t} + c \qquad (4.8)$$

Where K_3 and c were calculated from slope and intercept of the plot of q_t versus $t^{0.5}$. Hence, intra particle diffusion rate constant is defined as gradient of the plot of sorption density versus square root of time. If the correlation coefficient approach to unity, which suggests the intra particle diffusion plays a major role in adsorption process. A straight line represents the control of sorption by intra particle diffusion and solute ions diffuse within the pores & capillaries of the adsorbent, which provides available sites for adsorption (Sujana and Mohanty, 2010).

Besides, the adsorption at the outer surface of the adsorbent, the adsorbate molecules may also diffuse into interior of the porous adsorbent (Mahramanlioglu et al., 2002). Adsorption diffusion models are always constructed on the basis of three consecutive steps (Lazaridis and Asouhidou, 2003):

(1) Diffusion across the liquid film surrounding the adsorbent particles, i.e., external diffusion or film diffusion or surface diffusion;

(2) Diffusion in the liquid contained in the pores and/or along the pore walls, which is so called internal diffusion or intra-particle diffusion or pore diffusion; and

(3) Adsorption and desorption between the adsorbate and active sites, i.e., mass action which involves transportation of ions from liquid phase to solid boundary of adsorbent.

However, adsorption reaction models originating from chemical reaction kinetics are based on the whole process of adsorption without considering these steps mentioned above.

Three adsorption kinetic models (Pseudo first order, Pseudo second order, Weber-Morris models) were applied with the experimental results based on three initial concentrations to understand the anions sorption on adsorbent in present study.

In order to understand the nature of kinetics of nitrate, fluoride and arsenic sorption at an adsorbent dosage of 130 g/L of HBO_{12mix} powder from solution, the kinetics was studied for time durations ranging from 5 min to 240 min at three selected concentrations, closer to the values commonly reported from different places in India.

Kinetic parameters were determined at each concentration assuming pseudo-first order, pseudo second order and Weber-Morris models (Table 4.7). In order to use the three concentration levels studied for comparative purposes, a trend analysis for variation of kinetic parameters was done (Table 4.8) to decipher the direction of shift in these parameters with changing concentrations of contaminants.

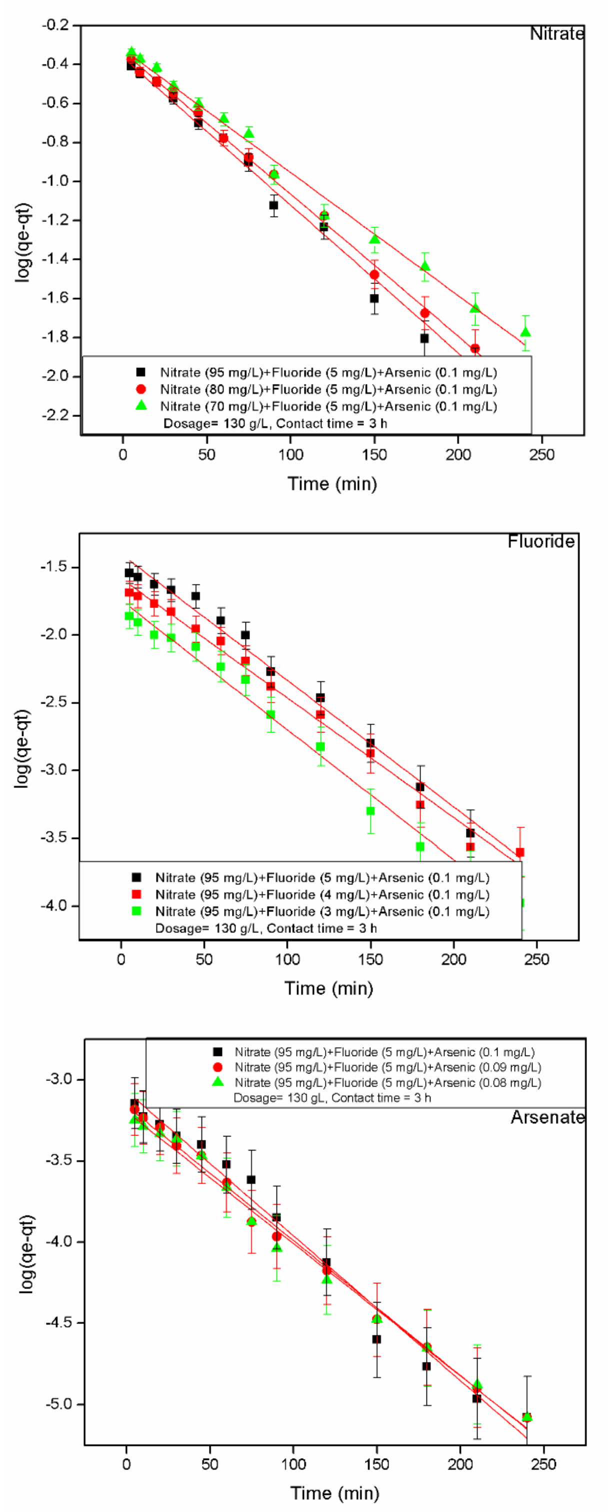


Figure 4.5: Linearized kinetic plots of pseudo first order model for nitrate, fluoride and As(V) sorption from mixed solution

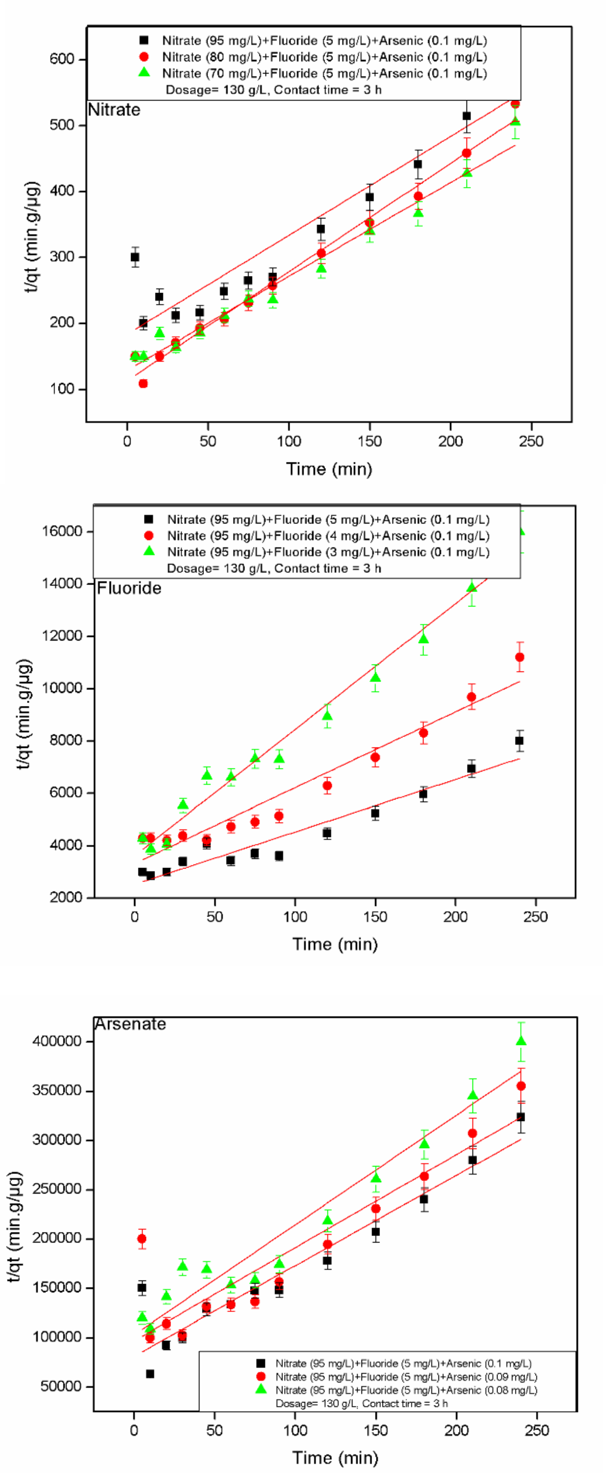


Figure 4.6: Linearized kinetic plots of pseudo second order model for nitrate, fluoride and As(V) sorption from mixed solution

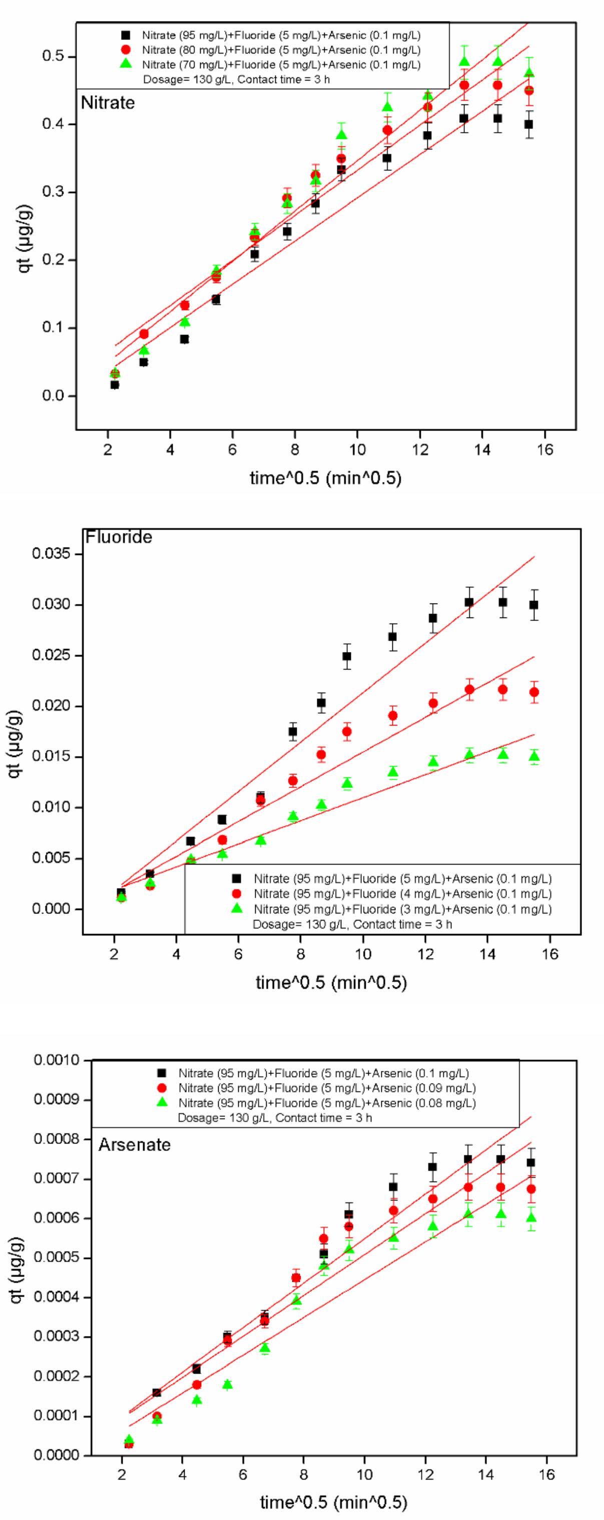


Figure 4.7: Linearized kinetic plots of Weber-Morris model for nitrate, fluoride and As(V) sorption from mixed solution

Table 4.7: Kinetic parameters for adsorption of nitrate, fluoride and As(V) on HBO_{12mix} powder

Initial conc. (mg/L)	Pseudo-first order model			Pseudo-second order model			Weber-Morris model		
	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/mg/min)	q_t (mg/g)	R^2	K_3 (mg/g/√min)	c	R^2
Nitrate									
70.0	0.013	0.510	0.989	0.015	0.784	0.977	0.037	0.024	0.953
80.0	0.016	0.463	0.995	0.013	0.743	0.754	0.033	0.027	0.954
95.0	0.018	0.458	0.987	0.012	0.667	0.882	0.031	0.030	0.941
Fluoride									
3.0	0.020	0.017	0.966	0.103	0.043	0.981	0.001	0.001	0.985
4.0	0.018	0.024	0.993	0.115	0.049	0.899	0.001	0.002	0.943
5.1	0.018	0.037	0.975	0.169	0.050	0.930	0.002	0.003	0.942
As(V)									
0.08	0.023	0.0006	0.985	0.012	0.0008	0.946	0.033	0.020	0.917
0.09	0.022	0.0007	0.992	0.013	0.0006	0.752	0.033	0.013	0.913
0.10	0.020	0.0008	0.964	0.024	0.0005	0.882	0.040	0.006	0.946

Linear plots of kinetic data and parameter of pseudo first order, pseudo second order and Weber-Morris models are shown in Figure 4.5-4.7. The values of various kinetic coefficients have been summarized in Table 4.7. 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. Based on relatively higher correlation coefficient the sorption of targeted contaminants on HBO_{12mix} may be said as being governed by pseudo first order kinetics for nitrate, fluoride and arsenic.

Highest regression coefficient (R^2) value of pseudo first order kinetic model was found as 0.989, 0.995, 0.987 for initial nitrate concentration of 70, 80, 95 mg/L. The regression coefficient of nitrate in mix solution increases with concentration except at 95 mg/L. The rate constant (K_1) determined by pseudo first order reaction for nitrate appears to be increasing with increasing concentrations. Similar trend has been suggested by Teimouri et al. (2016) while doing nitrate removal by nano ZrO_2 nanocomposite from the aqueous solution. Maximum rate constant (K_1) was found as 0.018 min^{-1} at 95 mg/L of nitrate concentration in mix solution. K_1 for fluoride and As(V) is observed to be decreasing with increasing concentrations due to quenching of binding sites and only few active sites are available for further interaction. Similar observations were made by Srivastav et al., (2013) and Yoon et al., (2016). K_1 for As(V) is higher, followed by fluoride and nitrate. Maximum nitrate adsorption capacity q_e was found as 0.510 mg/g in mix solution. Nitrate adsorption capacity q_e (mg/g) shows decreasing trend with increasing concentrations for nitrate, similar to observations recorded by Naushad et al., (2014). For fluoride and arsenic, increasing trends were noticed with increasing concentrations, as noted by Kumar et al., (2009) also. The trend shows that HBO_{12mix} powder gives higher adsorption capacity on lower nitrate concentrations and follows the pseudo first order kinetics to give maximum nitrate adsorption potential. Further, the maximum adsorption capacity of fluoride and arsenic on HBO_{12mix} is based on pseudo first order kinetics which shows increasing trend with increasing concentrations.

From Table 4.7, it is observed that nitrate removal process is governed by the pseudo-first order kinetics at all the nitrate concentrations studied (70, 80 and 95 mg/L), as the coefficient of correlation (R^2) values are highest in comparison to others. Assuming pseudo-first order kinetics, the adsorption capacities (q_t) of the adsorbent for nitrate are found to be decreasing from 0.510 to 0.458 mg/g with initial concentrations of nitrate increasing from 70 to 95 mg/L.

Highest regression coefficient (R^2) value of pseudo first order kinetic model was found as 0.966, 0.993, 0.975 for initial fluoride concentration of 3, 4, 5.1 mg/L. Maximum rate constant (K_1) was recorded as 0.020 min^{-1} at 3 mg/L of fluoride concentration in mix solution. Faster sorption process has been reflected by lower value of rate constant K_1 (Ayoob et al., 2008). Maximum fluoride adsorption capacity q_e (mg/g) increases with increasing concentration (Mukhopadhyay et al., 2017) but for nitrate, it decreases with increasing concentration (Bhaumik et al., 2015). Maximum fluoride adsorption capacity (q_e) was recorded as 0.037 mg/g. The analysis of available data revealed that HBO_{12mix} adsorbent shows maximum fluoride adsorption capacity following pseudo first order kinetics which have increasing trend with increasing concentration. Hence, for fluoride, pseudo-first order kinetic model is found to be give the best fit at initial concentrations 4 mg/L and 5.1 mg/L as their R^2 values are greater

(0.993 and 0.975 respectively) than the R^2 values of pseudo-second order kinetic model (0.899 and 0.930 respectively). However, at 3 mg/L fluoride concentration, R^2 value of pseudo-second order kinetic model is observed slightly higher than pseudo-first order model. Generally, R^2 values of pseudo-first order kinetic model are more close to 1.0 as compared to pseudo-second order kinetic model. Therefore, it appears that majority of the fluoride adsorption process is governed by the pseudo-first order kinetic model and based on regression coefficient. The adsorption capacities (q_e) are found to be increasing from 0.017 to 0.024 and 0.037 mg/g with increasing initial concentrations of fluoride of 3.0, 4.0 and 5.1 mg/L, respectively.

For As(V) removal by HBO_{12mix} also, pseudo-first order kinetic model is found to fit better than pseudo-second order. Highest regression coefficient (R^2) value of pseudo-first order kinetic model was found as 0.985, 0.992, 0.964 for initial arsenic concentration of 0.08, 0.09, 0.10 mg/L. The plot of pseudo-first order kinetic model shows the good linearity of data with HBO_{12mix}. The maximum rate constant (K_1) found in the case of arsenic sorption on HBO_{12mix} decreases with increase in arsenic concentration in the mix solution. Similar trend was notices for fluoride sorption (Bhaumik et al., 2015). Maximum rate constant (K_1) was estimated as 0.023 min^{-1} at 0.08 mg/L initial arsenic concentration in mix solution. Following pseudo first order kinetics, q_t values are found increasing from 0.0006 mg/g to 0.0008 mg/g with increasing initial concentrations in the studied range.

Such 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 Weber-Morris model, a linear correlation is taken as an indication of role of intra-particle diffusion during sorption of solute ions which presumably diffuse within the pores and capillaries of the adsorbents and available sites (Sujana and Mohanty, 2010). Further, the values of intercept in Weber- Morris linear plot is also used as an indicator to define the process of adsorption to be complex or governed by only one factor. The straight line and non-zero intercept plot from Weber-Morris model suggest that the process is "complex" and not driven by sole process of adsorption rather more than two mechanisms limiting the rate of sorption with slow intra-particle diffusion (Ayoob et al., 2008; Sen Gupta and Bhattacharyya, 2011). In our study, the values of intercept in Weber-Morris Model plots for nitrate and As(V) are found greater than zero, indicating the process of their adsorption to be complex and with slow intra particle diffusion. Unlike this, in case of fluoride, the intercept values are close to zero, indicating simple and fast rate of intra particle diffusion. Also, the regression coefficient of process lies in between of 0.913 to 0.985 with linear correlation suggesting that the rate controlling steps are not governed by single process and intra particle diffusion plays significant role in anions sorption by HBO_{12mix} in which solute particles diffuse within the pores of adsorbent and provides the active sites for adsorption and hence control the sorption process (Sujana et al., 2009). Thus, application of WM model to the kinetics of anions sorption by HBO_{12mix} indicates the surface diffusion at the beginning and thereafter pore diffusion governs the process of removal which is attributed to very slow diffusion of sorbate form the surface side to inner pores of adsorbent (Bhatnagar et al., 2010).

Table 4.8 presents the summary of trend analysis for kinetic parameters of nitrate, fluoride and As(V) on the HBO_{12mix} powder adsorbent.

Table 4.8: Trend analysis for kinetic parameters of nitrate, fluoride and arsenic sorption from the solution on HBO_{12mix} powder

Assumed order of kinetics	Physical significance of parameter	Observational trend of determined parameter		
		Nitrate	**Fluoride**	**As(V)**
Pseudo-first order model				
R^2	Correlation coefficient	First increases with concentration then decreases. 0.989-0.995-0.987	First increases with concentration then decreases. 0.966-0.993-0.975	First increases with concentration then decreases. 0.985-0.992-0.964
K_1 (min^{-1})	Rate coefficient	Increases with increasing concentration 0.013-0.018	Decreases with increasing concentration 0.020-0.018	Decreases with increasing concentration 0.023-0.020
q_e (mg/g)	Maximum adsorption capacity	Decreases with increasing concentration 0.510-0.458	Increases with increasing concentration 0.017-0.037	Increases with increasing concentration 0.006-0.008
Pseudo-second order model				
R^2	Correlation coefficient	First decreases then increases again with increasing concentration. 0.977-0.754-0.882	First decreases then increases again with increasing concentration. 0.981-0.899-0.930	First decreases then increases again with increasing concentration. 0.946-0.752-0.882
K_2 (g/mg/min)	Rate coefficient	Decreases with increasing concentration 0.015-0.012	Increases with increasing concentration 0.103-0.169	Increases with increasing concentration 0.012-0.024
q_e (mg/g)	Maximum adsorption capacity	Decreases with increasing concentration 0.784-0.667	Increases with increasing concentration 0.043-0.050	Decreases with increasing concentration 0.0008-0.0005
Weber-Morris model				
R^2	Correlation coefficient	Decreases with increasing concentration 0.953-0.941	Decreases with increasing concentration 0.985-0.942	First decreases then increases again with increasing concentration. 0.917-0.913-0.946
K_3 (mg/g/√min)	Rate coefficient	Decreases with increasing concentration 0.037-0.031	Increases with increasing concentration 0.001-0.002	Increases with increasing concentration 0.033-0.040

4.4 Adsorption isotherm studies

Adsorption isotherms are the fundamental requirements for the design of adsorption systems (Zawani et al., 2009). Isotherms express the specific relationship between the amount of solute adsorbed onto adsorbent surface in given experimental conditions and the equilibrium concentration of adsorbate in the liquid phase (Asgari et al., 2012). One of the most important characteristics of an adsorbent is the quantity of adsorbate it can accumulate which is normally obtained from the adsorption isotherms. The adsorption isotherms are constant-temperature equilibrium relationship between the quantity of adsorbate per unit of adsorbent (q_e) and its equilibrium solution concentration (C_e). Several equations or models, such as the Langmuir, Freundlich, Dubinin-Radushkevich (D-R) isotherm equations are available that describe the relationship between quantity of adsorbate and equilibrium concentration (Gupta and Suhas, 2009). The Langmuir, Freundlich and D–R isotherm equations are most commonly used in sorption studies (Ayoob and Gupta, 2006).

4.4.1 Langmuir isotherm model

The Langmuir isotherm is a theoretical isotherm developed in 1916 (Coulson and Richardson, 1991). This model is based on a few assumptions:

- All sites are identical and energically equivalent,
- Thermodynamically this implies that each site can hold one adsorbate molecule, adsorption cannot proceed beyond monolayer;
- The ability of a molecule to be adsorbed at a given site is independent of the occupation of neighboring sites, which mean, there will be no interactions between adjacent molecules on the surface and immobile adsorption, i.e., trans-migration of the adsorbate in the plane of the surface is precluded.

For adsorption of solute from a liquid, the Langmuir isotherm is expressed as Eq. (4.9):

$$\frac{1}{q_e} = \frac{1}{q_\circ b C_e} + 1/q_\circ \qquad (4.9)$$

Where, q_o is the maximum adsorption amount (mg/g) of adsorbate at complete monolayer coverage, q_e is the amount adsorbed per unit mass (mg/g) of adsorbent at equilibrium, C_e is the concentration at equilibrium (mg/L) and b (L/mg) is the constant related to binding energy of adsorption (Sairam et al., 2008). In the Langmuir equation, q_o (mg/g) and b are constant and can be determined from the slope and intercept.

The Langmuir adsorption equation takes the best-known theoretical treatments of non-linear sorption and suggests that adsorption take place on a homogeneous surface by monolayer sorption without interaction between adsorbent molecules. Besides, the model assumes uniform energies of adsorption onto the surface (Behnamfard and Salarirad, 2009; El-Nemr, 2009).

The Langmuir isotherms were chosen to determine the maximum adsorption capacity corresponding to the complete monolayer coverage on HBO_{12mix}.

4.4.2 Freundlich isotherm model

Freundlich isotherm equation can be applied to non-ideal adsorption on heterogeneous surfaces as well as multilayer sorption with interaction between adsorbed molecules (Milmile et al., 2011). Basically, Freundlich isotherm equation (Eq. 4.10) is given as:

$$q_e = K_f \, C_e 1/n \qquad (4.10)$$

This in linearised form (Eq. 4.11) may be written as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (4.11)$$

Where q_e is the maximum adsorption amount of adsorbate at equilibrium (mg/g), C_e is the equilibrium concentration of solution (mg/L) and, n is the Freundlich constant, which indicates the degree of favorability of adsorption and capacity of the adsorbent/adsorbate system. Moreover, K_f is isotherm constant related to adsorption capacity. Value of 1/n ranging from 0-1 indicates the bond between adsorbate and adsorbent with heterogeneous nature of the surface becomes more heterogeneous when its value closes to zero (Sujana and Mohanty, 2010). Hence, positive value of n ranging from 1 to 10 inferred to beneficial and favorable adsorption. The K_f and 1/n can be determined from the linear slope plot of q_e Vs $\log C_e$.

4.4.3 Dubinin-Redushkevich (DR) isotherm model

Langmuir and Freundlich adsorption isotherm constants do not provide any idea about the adsorption mechanisms (Islam et al., 2010). Dubinin-Redushkevich isotherm model is used to estimate the specious free energy of adsorption. In order to understand the adsorption type, whether physical or chemical, equilibrium data are tested with Dubinin-Radushkevich isotherm (Islam et al., 2010).

The Dubinin-Radushkevich (D-R) isotherm model considers that adsorbent size is comparable to the micropore size and the adsorption equilibrium relation for a given adsorbate-adsorbent combination can be expressed independently of temperature. The linearised form of D-R equation (Eq. 4.12) is expresses as:

$$\ln q_e = \ln q_a - K\varepsilon^2 \qquad (4.12)$$

Where q_e is the maximum adsorption amount of adsorbate at equilibrium adsorbed per unit mass of adsorbent (mg/g); q_a is the theoretical adsorption capacity; *K* is the constant related to adsorption energy; ε is Polanyi potential, given by:

$$\varepsilon = RT\ln(1 + \frac{1}{C_e}) \qquad (4.13)$$

Where R is universal gas constant (8.314 KJ/mol K), T is the temperature in Kelvin (K), C_e is the equilibrium concentration of anion (mg/L). The slope and intercept of the Inq_e vs ε^2 gives the constant value of *K* and q_a.

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

The value of adsorption energy constant (*K*) derived from D-R isotherm can be further used to differentiate the process govern by the physio-sorption, ion exchange or chemisorption by calculation of mean adsorption free energy. *E* gives the mean adsorption free energy (kJ/mol) per molecule of sorbate at the moment of its transfer to the solid surface from the bulk solution. The expression (Eq. 4.14) for mean adsorption energy is given below:

$$\text{Mean adsorption free energy } (E) = 1/\sqrt{2K} \qquad (4.14)$$

The values of mean adsorption energy (*E*) calculated for the present cases are shown in Table 4.8 with other evaluated parameters.

In order to perform the isotherm study, using the mix solution of nitrate, fluoride and As(V), the sorption experiments were carried out at three temperatures: 298 K, 308 K and 318 K and isotherm parameters were evaluated, keeping adsorbent dosage of 130 g/L and 3 h contact time. The linearized plots for Langmuir, Freundlich and DR model isotherms for nitrate, fluoride and As(V) have been shown in Figure 4.8-4.10 and the derived values of coefficients have been summarized in Table 4.9 & 4.10.

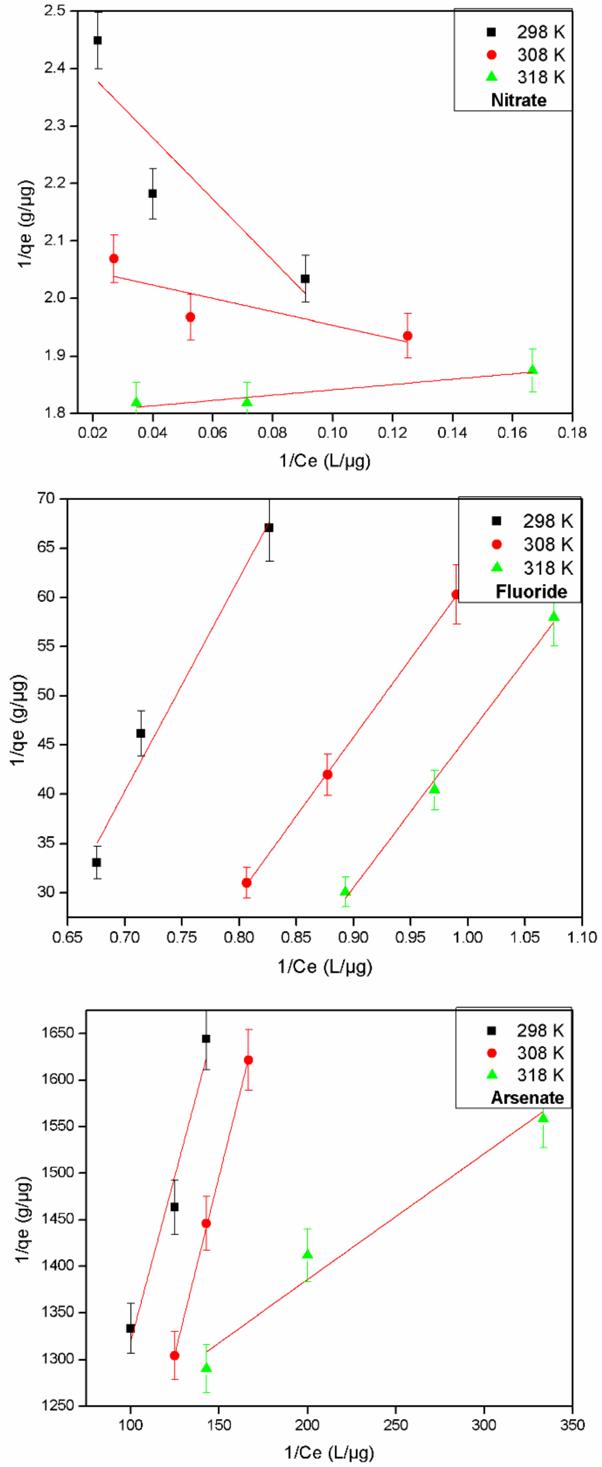


Figure 4.8: Langmuir isotherm linearized plots for nitrate, fluoride and As(V) sorption on HBO$_{12mix}$

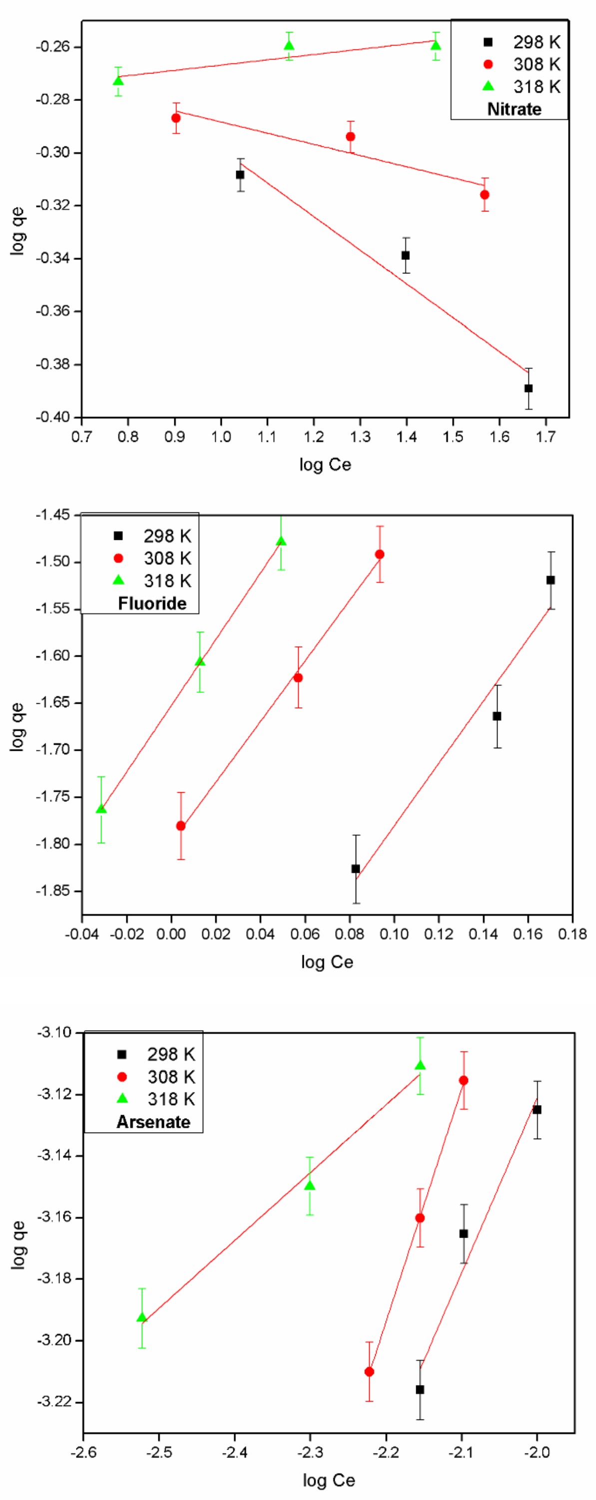


Figure 4.9: Freundlich isotherm linearized plots for nitrate, fluoride and As(V) sorption on HBO$_{12mix}$

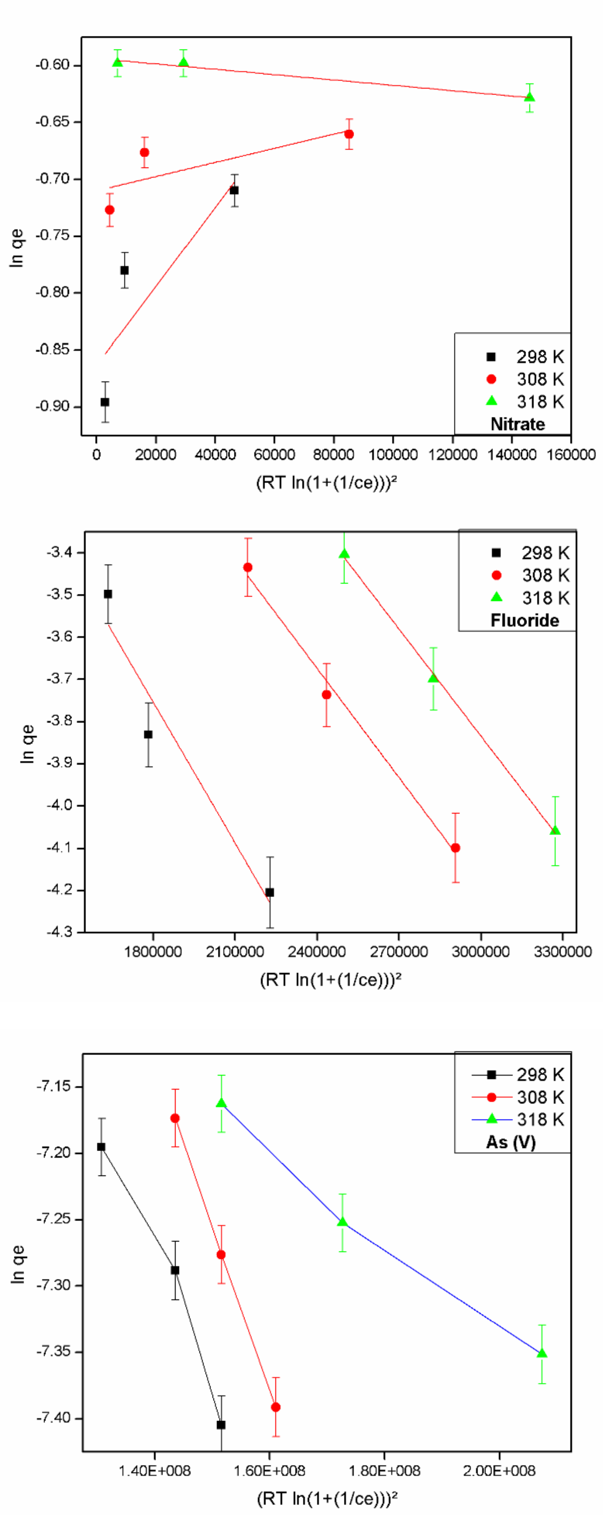


Figure 4.10: DR model isotherm linearized plots for nitrate, fluoride and As(V) sorption on HBO_{12mix}

Table 4.9: Initial and final parameters of adsorption isotherm on HBO_{12mix} powder

Temperature (K)	Nitrate			Fluoride			Arsenate		
	Co (mg/L)	Ce (mg/L)	q_e (mg/g)	Co (mg/L)	Ce (mg/L)	q_e (mg/g)	Co (mg/L)	Ce (mg/L)	q_e (mg/g)
298	95	46	0.715	5.1	1.48	0.030	0.10	0.010	0.00075
	80	25	0.825	4.0	1.40	0.021	0.09	0.008	0.00068
	70	11	0.926	3.0	1.21	0.014	0.08	0.007	0.00060
308	95	37	0.483	5.1	1.24	0.032	0.10	0.007	0.00076
	80	19	0.508	4.0	1.14	0.023	0.09	0.006	0.00069
	70	8	0.516	3.0	1.01	0.016	0.08	0.004	0.00061
318	95	29	0.550	5.1	1.12	0.033	0.10	0.005	0.00075
	80	14	0.551	4.0	1.03	0.024	0.09	0.003	0.00070
	70	6	0.553	3.0	0.93	0.017	0.08	0.002	0.00064

Table 4.10: Isotherm parameters for adsorption of nitrate, fluoride and As(V) on HBO$_{12mix}$ powder

Temperature (K)	**Langmuir Isotherm**			**Freundlich Isotherm**			**Dubinin-Radushkevich Isotherm**		
	qo (mg/g)	**b (L/mg)**	**R^2**	**K_f**	**n**	**R^2**	**q_a (mg/g)**	***E* (kJ/mol)**	**R^2**
Nitrate									
298	0.401	0.47	0.715	0.746	3.49	0.950	0.422	8.21	0.680
308	0.483	1.78	0.825	0.954	4.00	0.874	0.492	9.56	0.750
318	0.557	3.87	0.926	1.100	5.84	0.786	0.552	16.50	0.977
Fluoride									
298	0.008	0.513	0.979	1.14	0.473	0.952	0.173	14.22	0.939
308	0.009	0.610	0.998	1.31	0.551	0.977	0.202	8.28	0.992
318	0.010	0.701	0.995	1.52	0.605	0.996	0.274	7.80	0.995
As(V)									
298	0.001	85.44	0.964	5.710	0.654	0.957	0.020	10.02	0.961
308	0.002	46.84	0.997	3.706	0.504	0.993	0.004	15.55	0.994
318	0.001	24.09	0.970	1.659	0.379	0.991	0.001	17.12	0.987

The Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were used in equilibria study for the removal of nitrate, fluoride and As(V) from water. Analyses using the regression coefficient (R^2) indicate that the sorption of nitrate follows Freundlich isotherm, where as for fluoride, it is Langmuir and for As(V), D-R model fits the best.

The correlation coefficients (R^2) are found as 0.950, 0.874 and 0.786 at the selected temperatures 298, 308 and 318 K respectively for nitrate sorption in mix solution. The high correlation coefficient (R^2) values for the plots among mixed solution reaffirming the domination of nitrate sorption with Freundlich adsorption isotherm. From Table 4.10, it can be seen that at 298 K temperature, according to the values of R^2, the adsorption of nitrate is found to be fit with the assumptions of Freundlich isotherm. However, as the temperature of the water increases to 318 K, the nitrate adsorption process appears shifting towards Langmuir isotherm. Thus, it appears that the adsorption of nitrate at normal temperature takes place with heterogeneous layer formation as per Freundlich isotherm assumptions and subsequently on increased temperatures; it changes to mono layer formation. Also, the increasing values of K_f of Freundlich isotherm with temperature is an indication of favourable adsorption of nitrate on higher temperatures (Walker and Weatherley, 2001; Singh et al., 2015). Moreover, the values of “n” from the Freundlich isotherm are found 3.49 at 298 K and it increases with temperature to 5.84 at 318 K. Higher values of Freundlich constant (n) demonstrate that the anions sorption by HBO_{12mix} is more favorable at higher temperatures. As noted by Milmile et al. (2011), if the values of ‘n’ are in between 1-10, the adsorption process is said to be beneficial. Thus, adsorption of nitrate on HBO_{12mix} powder is indicated to be beneficial. Similar trend has been suggested by

Mehrabi et al. (2015) while doing nitrate adsorption experiment from water using composite of activated carbon and Fe_2O_3 nanoparticles.

The correlation coefficients (R^2) are found as 0.979, 0.998 and 0.995 at the selected temperatures 298, 308 and 318 K respectively for fluoride sorption in mix solution. The high correlation coefficient (R^2) values for the plots indicated good agreement of fluoride sorption data with Langmuir adsorption isotherm. However, on increasing temperature to 318 K, the values of correlation coefficients are almost same for both Langmuir as well as Freundlich isotherms. This indicates that possibly the adsorption process shifted from a homogeneous layer formation to heterogeneous layer formation with temperature increase. Value of Langmuir adsorption capacities (q_o) for fluoride on HBO_{12mix} powder is derived as 0.008 mg/g at 298 K temperature. The maximum Langmuir adsorption capacity (q_o) was estimated to be 0.01 mg/g at 318 K. The increasing value of q_o with temperature indicates that higher temperature helps the fluoride sorption capacity of HBO_{12mix}. The maximum Langmuir adsorption capacity can vary in relation to temperature due to many factors, such as chemical structure of the anions and adsorbent, molecular size and nature of the adsorbent (Piccin et al., 2011). Further, the values of binding energy (b) are increasing from 0.513 L/mg to 0.701 L/mg with increasing temperatures. An increasing trend of binding energy indicates endothermic adsorption process as reported by Srivastav et al. (2013) and Mukhopadhyay et al. (2017).

The correlation coefficients (R^2) are found as 0.961, 0.994 and 0.987 at the selected temperatures 298, 308 and 318 K respectively for arsenic sorption in mix solution. The correlation coefficients (R^2) values obtained for three selected temperatures were suggesting arsenic sorption fits well with D–R isotherm plot. Relative data based on regression coefficient suggesting the similar behavior of fluoride and As(V) in all isotherm models. From D–R Model also, the theoretical adsorption capacity (q_a) appears increasing with increasing temperature for nitrate and fluoride, but, decreasing for As(V). The values of q_a are obtained as 0.02, 0.004 and 0.001 mg/g respectively for arsenic sorption at 298, 308 and 318 K which shows the dwindling trend of q_a with higher temperatures were also observed by (Chaudhry et al., 2016). Whereas increasing trend of q_a was spotted for nitrate and fluoride at elevated temperatures (Singh et al., 2015). Maximum arsenic sorption capacity q_a was recorded as 0.02 mg/g. The study also indicates that the arsenic gives the higher adsorption capacity at lower temperatures whereas fluoride and nitrate adsorption capacity give the higher adsorption capacity at higher temperatures in working environment.

Comparing the values of Correlation coefficient (R^2) between Langmuir Isotherm and Freundlich Isotherm indicates that while at lower temperature (298 K), Freundlich isotherm fits well and with increasing temperatures of 308 and 318 K for nitrate sorption, the coefficient of correlation decreases, the same seems increasing for Langmuir isotherm. Thus, it appears that possibly the nitrate follows heterogeneous site sorption at lower temperatures, but subsequently turns towards mono layer formation as per Langmuir isotherm. Further, it can be seen that at 298 K temperature, based on R^2 values, the process appears to be taking place in accordance with Langmuir isotherm (monolayer formation) for fluoride sorption. On increasing the temperatures up to 318 K, R^2 value of Freundlich isotherm is found significantly greater than Langmuir isotherm. This indicates that the process is possibly changing from homogeneous mono layer formation to heterogeneous layer formation on increasing temperature. Thus, adsorption of fluoride and As(V) on HBO_{12mix} appears favourable at lower temperatures and following Langmuir and DR isotherm respectively whereas nitrate sorption on HBO_{12mix} follows Freundlich isotherm at lower temperatures.

In order to understand the adsorption process in terms of physio-sorption or chemisorption, D-R isotherm is applied with the experimental data of adsorptions of nitrate, fluoride and As(V). Langmuir and Freundlich isotherms are not able to give any idea about it (Fan et al., 2003). The R^2 values for D-R isotherm for nitrate, fluoride as well As(V) adsorption on HBO_{12mix} are found very high (> 0.939-0.995) at all selected temperatures, except adsorption of nitrate at 298 K and 308 K (where R^2 is 0.68 and 0.75 respectively).

Based on estimation of D-R isotherm parameter, the values of mean adsorption energy (*E*) for nitrate adsorption are found to range from 8.21-16.50 kJ/mol and increasing with temperature. The values of mean adsorption energy (E) < 8 kJ/mol indicates towards a physisorption process, 8-16 kJ/mol as ion exchange and $E > 16$ kJ/mol as chemisorption (Milmile et al., 2011; Swain et al., 2012). Hence, nitrate adsorption on HBO_{12mix} can be possibly said as an ion exchange process turning to chemisorption process on increasing the temperature. For fluoride adsorption, the value of *E* ranges 14.22-7.80 kJ/mol and decreases with increasing temperature. This indicates that fluoride adsorption on HBO_{12mix} powder is normally ion exchange at 298 K and tends to become physiosorption with increasing temperatures. For As(V), the values of *E* are in the range of 10.02 to 17.12 kJ/mol and increasing with temperature. This indicates that the sorptive removal of As(V) on HBO_{12mix} powder is ion exchange moving towards chemisorptions at higher temperatures. Hence, from the D–R equation and according to the *E* values (7.80-17.12 kJ/mol) indicated that sorption of anions by HBO_{12mix} is the largely through ion exchange phenomena followed physio-sorption and chemi-sorption to minor extent. Better regeneration could be availed in sorption process if the prevailing phenomenon accounted as physical adsorption. Table 4.11 presents a summary of variability of various isotherm parameters.

Table 4.11: Trend analysis for isotherm parameters of nitrate, fluoride and arsenic sorption from the solution on HBO_{12mix} powder

Isotherm Parameter	**Physical Meaning**	**Observations**		
		Nitrate	**Fluoride**	**Arsenate**
Langmuir Isotherm				
R^2	Correlation coefficient	Increases with temperature. 0.715-0.926	Increases with temperature. 0.979-0.995	Increases and then decreases Maximum 0.997 at 308 K
q_o (mg/g)	Adsorption capacity parameter	Increases with temperature. 0.414 at 298 K, 0.557 at 318 K	Increases with temperature. 0.008-0.010	Increases and then decreases Maximum 0.002 at 308 K
b (L/mg)	Constant ‘b’, which reflect binding energy of adsorption	Increases with temperature. 0.47-3.87	Increases with temperature. 0.513-0.701	Decreases with temperature. 85.44-24.09
Freundlich Isotherm				
R^2	Correlation coefficient	Decreases with temperature. 0.950-0.786	Increases with temperature. 0.952-0.996	Increases and then decreases. Maximum 0.993 at 308 K
K_f	K_f values is related to adsorption capacity of the sorbent. Increasing value of K_f indicates that adsorption is favorable at higher temperature	Increases with temperature. 0.746-1.100	Increases with temperature. 1.14-1.52	Decreases with temperature 5.710-1.659
n	The value of Freundlich Constant ‘n’ between 1-10 indicates beneficial and favorable adsorption	Increases with temperature. 3.49-5.84 Beneficial and favourable.	Increases with temperature. 0.473-0.605. Non beneficial and unfavourable at these temperatures.	Decreases with temperature. 0.654-0.379. Non beneficial and unfavourable at these temperatures.
Dubinin-Radushkevich Isotherm				
R^2	Correlation coefficient	Increases with temperature. 0.680-0.977	Increases with temperature. 0.939-0.995	Increases and then decreases Maximum 0.994 at 308 K
q_a (mg/g)	The theoretical adsorption capacity.	Increases with temperature. 0.442-0.552	Increases with temperature. 0.172-0.274	Decreases with temperature 0.020-0.001
E (kJ/mol)	(i) Physio sorption if $E \leq 8.0$ kJ/ mol (ii) Ion-exchange if $8.0 < E < 16.0$ kJ mol and (iii) Chemi sorption if $E \geq 16.0$ kJ/mol	Increases with temperature. 8.21-16.50 Physio sorption changing to ion exchange with increasing temperature.	Decreases with temperature 14.22-7.80. Ion exchange to Physiosorption.	Increases with temperature. 10.02-17.12 Ion exchange to chemisorption with increasing temperature.

Over all from D-R isotherm studies, the sorptive removal of selected contaminants is found as summarised in Table 4.12.

Table 4.12: Effect of temperature on nitrate, fluoride and As(V) sorption process on HBO_{12mix} based on mean adsorption energy (*E*) of D-R isotherm studies

Contaminant Anion	**Adsorptive removal process at 298 K and trend on increasing temperatures**
Nitrate	Ion exchange process tending to chemisorption process with increasing temperature.
Fluoride	Ion exchange process tending to become physiosorption with increasing temperatures.
As(V)	Ion exchange tending towards chemisorptions with increasing temperatures.

Another important observation from the isotherm study data analyses is with respect to the maximum adsorption capacity of $HBO_{12\ mix}$ powder for nitrate, fluoride and As(V). Table 4.13 summarises observations derived from various analyse in this regard.

Table 4.13: Trend analysis of maximum adsorption capacity (q_o) of HBO_{12mix} for nitrate, fluoride and As(V) from aqueous solutions

Maximum adsorption capacity (mg/g)	**Trend analysis for q_o with increasing concentration and increasing temperatures**		
	Nitrate	**Fluoride**	**Arsenate**
q_e as obtained following pseudo first order kinetics.	Decreases with increasing concentration 0.510-0.458 (mg/g)	Increases with increasing concentration 0.017-0.037 (mg/g)	Increases with increasing concentration 0.006-0.008 (mg/g)
q_e as obtained from pseudo second order kinetics.	Decreases with increasing concentration 0.784-0.667 (mg/g)	Increases with increasing concentration 0.043-0.050 (mg/g)	Decreases with increasing concentration 0.008-0.005 (mg/g)
q_o as obtained from Langmuir isotherm	Increases with temperature 0.414 (mg/g) at 298K 0.557 (mg/g) at 318K	Increases with temperature 0.008-0.010 (mg/g)	Increases and then decreases Max. 0.002 (mg/g) at 308 K
q_a as obtained from Dubinin-Radushkevich isotherm model.	Increases with temperature 0.442-0.552 (mg/g)	Increases with temperature 0.172-0.274 (mg/g)	Decreases with temperature 0.020-0.001 (mg/g)

Thus, maximum adsorption capacity (q_o) of HBO_{12mix} powder for nitrate is found as 0.784 mg/g following pseudo second order kinetics and it has decreasing trend with increasing concentration of nitrate in solution.

For fluoride, the maximum adsorption capacity (q_o) is estimated as 0.274 mg/g based on D-R model assumptions and it has increasing trend with increasing temperature.

For As(V), the maximum adsorption capacity (q_o) is estimated as 0.02 mg/g based on D-R model and it has decreasing trend with temperature.

4.5 Thermodynamic studies

Adsorption thermodynamics were determined using the thermodynamic equilibrium coefficients obtained at different temperatures and concentrations in order to verify possible adsorption mechanisms (Crini and Badot, 2008). Further, Thermodynamic studies are done to evaluate the nature and feasibility of adsorption process. Change in gibbs free energy($\Delta G°$), change in enthalpy ($\Delta H°$) and change in entropy ($\Delta S°$) are important parameters in such conditions of application. These thermodynamic parameters help us to predict the nature of adsorption process whether the process is spontaneous or not (Akar et al., 2011). Enthalpy (H) is the heat absorbed or released by chemical reaction or external heat transfer in the given system, whereas entropy (S) describes the disorder and randomness of molecules.

Gibbs free energy equation (Eqs. 4.15, 4.16) can be express as:

$$\Delta G° = -RT\ln P \qquad (4.15)$$

$$\ln P = \frac{\Delta S°}{R} - \Delta H°/RT \qquad (4.16)$$

Where R (8.314 J/mol K) is the gas constant, T is the absolute temperature (K), and P (L/gm) is the standard thermodynamic equilibrium constant. Values of 'P' is obtained by plotting In(q_e/C_e) versus q_e and extrapolating q_e to zero. The intersection with the vertical axis gives the value of 'P' (Khan and Singh, 1987; Basu et al., 2010). Further the value of change in enthalpy (ΔH^o) and change in entropy (ΔS^o) are calculated from using van't Hoff's plot, according to equation (4.13). The slope and intercept of graph between ln P and 1/T (Liu and Liu, 2008) based on equation (4.14) gives the value of ΔH^o and ΔS^o. Thermodynamic studies was done with mixed solution of nitrate conc. as 1.5 meq (C_o= 95 mg/L), fluoride conc. as 0.25 meq (C_o= 5 mg/L) and As(V) as 0.001 meq (C_o= 0.08 mg/L) using HBO_{12mix} as sorbent (Dosage: 130 g/L, Contact time: 3 h) at three temperatures: 298 K, 308 K and 318 K. Results of analyses are summarized below in Table 4.14.

It is observed that the values of ΔG^o for nitrate, fluoride and As(V) sorption are found negative at all temperatures, indicating the spontaneous nature of the sorption onto HBO_{12mix} surface (Akar et al., 2011). The increase in ΔG^o values with the increase in temperature implies that higher temperature favors this anionic sorption with spontaneous nature of the adsorption reaction. A similar result was reported by Uzun and Güzel (2004). The positive value of ΔH^o suggests that adsorption of anions over HBO_{12mix} is endothermic in nature. According to Basu et al. (2010) and Banerjee et al. (2014), the magnitude of adsorption enthalpy (ΔH^o) values in the range from 2.1–20.9 kJ/mol suggests the adsorption process to be physical and 80–200 kJ/mol to be chemical adsorption process. In the present case, ΔH^o value lies above 20.9 kJ/mole, but less than 80 kJ/mol, thus indicating a mixed mode of physico-chemical adsorption. Affinity of the adsorbent for anions is represented by positive value of change in entropy (ΔS^o) indicates irregular increase in randomness (Bayramoglu et al., 2009) and hence, the anions sorption process is spontaneous. This was due to the increase of randomness with increase in number of species at the solid-liquid interface when the anions distributed on to the solid surface of the adsorbent releasing chloride molecules in working pH.

Table 4.14: Thermodynamic parameters for simultaneous removal of nitrate, fluoride and As(V) by HBO_{12mix} powder

Temp. (K)	Gibbs free energy change ΔG° (kJ/mol)	Change in enthalpy ΔH° (kJ/mol)	Change in entropy ΔS° (J/mol/K)
Nitrate			
298	-56.98	29.79	68.61
308	-87.06		
318	-129.54		
Fluoride			
298	-39.64	26.02	49.56
308	-53.77		
318	-63.45		
As(V)			
298	-41.63	24.47	61.05
308	-59.51		
318	-61.79		

4.6 Simultaneous removal of nitrate, fluoride and As(V) by HBO_{12mix} from mixed solution in column adsorption experiment

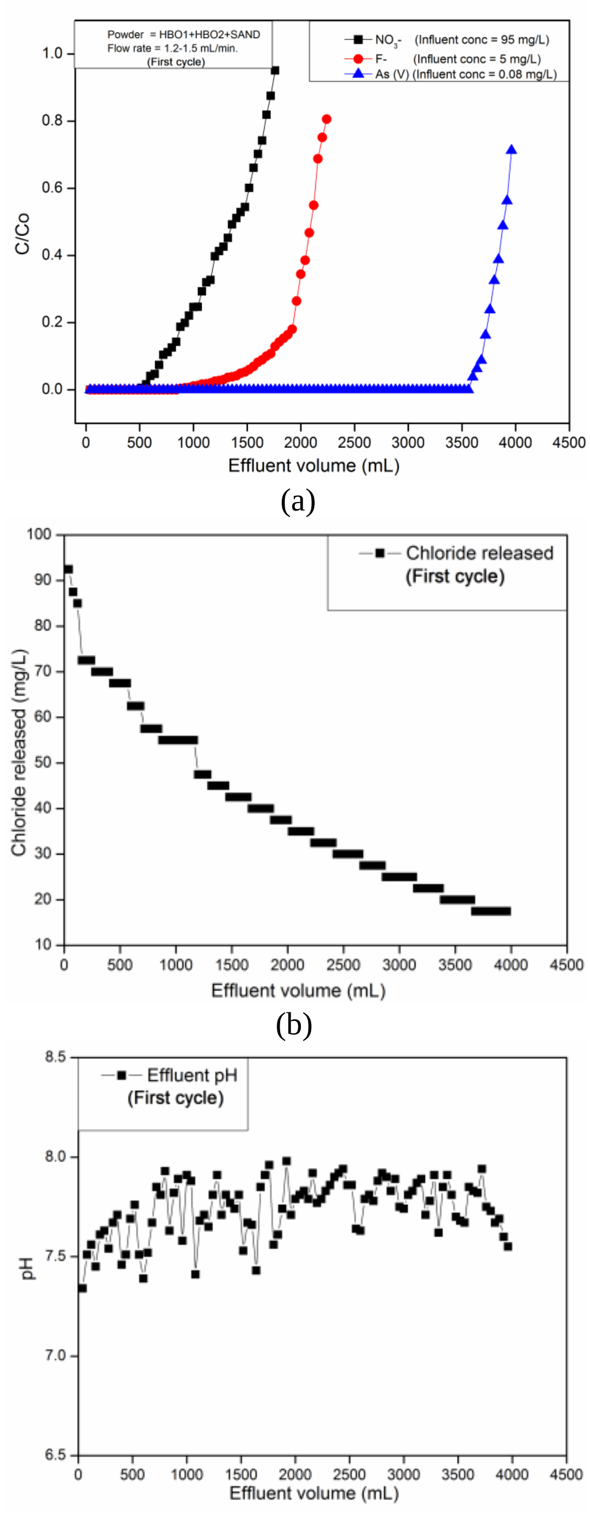
A fixed bed column study was carried out to consider the possible application of hydrous bismuth oxide in water purification system. Particle sizes of hydrous bismuth oxide powder are very fine in nature. In order to use them in column adsorption study, it was decided to prepare a porous bed using clean fine sand and HBO powders in suitable proportions. The sand to be used was initially cleaned by keeping it in 0.1 N HCl for 24 h and then washed it with sufficient distilled water. As HBO_1 has been observed to perform relatively better for fluoride and As(V), but removal of nitrate by HBO_2 is comparatively low, 50 g of HBO_1 was mixed with 150 g of clean sand and 200 g of HBO_2 was added into it. The whole mass was manually mixed to be used in the column. The mixed media (D_{10}= 0.18, C_u= D_{60}/D_{10} = 2.4) was used in a glass column (Internal diameter = 3 cm) to fill upto a height of around 51 cm (Total bed volume = 360.6 cm^3). The column was thoroughly rinsed by passing distilled water till the effluent reaches pH~7.0 and chloride in the effluent reduces to minimum. Subsequently, a synthetic solution consisting 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) (closely corresponding to contaminated groundwater with such anions in many parts of the country) was allowed to pass through the column. The flow rate approximated to ~1.2-1.5 mL/min or (~0.14 cm/min - 0.21 cm/min) giving an empty bed contact time (EBCT) of 240-300 min (≈ 4.25 h). Effluents were collected every 30 min and analyzed for pH, remaining nitrate, fluoride, As(V) and chloride.

4.6.1 First cycle of contaminants removal

Figure 4.11 summarizes the results of this set of experiments. 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 column gives 520 mL of nitrate, fluoride and As(V) free water (Figure 4.11(a)). Subsequently, it gives 840 mL of fluoride and As(V) free and 3560 mL of As(V) free waters. The breakthrough (C/C_o=0.1) for these anions occurs at around 720, 1000 and

3680 mL cumulative volume respectively. 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. The breakthrough pattern remains nitrate being first, followed by fluoride and As(V).

The exhaustion point (C/C_o= 0.90) for nitrate occurs around 1760 mL, followed by fluoride at 2240 mL and As(V) at 3960 mL. The variation of pH is in the range 7.34-7.98 (Figure 4.11(b)). The slight increase in pH may be due to interaction and effect of hydroxide in the matrix of the HBO_{12mix} with anions adsorbed. Final effluent being less than 8 indicates that as such no hydroxide ions are directly exchanged and released into the solution from adsorbents in lieu of the anions sorbed. Monitoring of chloride ions in the effluent, as presented in Figure 4.11(c) indicates that there is an increased level of chloride in the solution which shows diminishing trend with increasing volume. A partial exchange of chloride ions entrapped into the HBO_{12mix} with sorbed nitrate, fluoride and As(V) appears to be a possibility, which needs detailed evaluation.



(a)

(b)

(c)

Figure 4.11: 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

As defined by Singh (1999), Chloride Exchange Ratio (CER) may be taken as:

CER = Total increased chloride (meq) released into the solution/ Total anions (meq) sorbed from the solution

On segmental basis, the anions sorbed and chloride released from HBO_{12mix} powder used in the column in first cycle are found as given in Table 4.15.

Table 4.15: Relation between anions sorbed and chloride released from HBO_{12mix} in first cycle of column experiment

Effluent volume (mL)	Nitrate removed (meq)	Fluoride removed (meq)	As(V) removed (meq)	Anions sorbed (meq)	Chloride released (meq)	CER
0-520 mL	0.720	0.120	0.000400	0.840	0.608	0.723
520-840 mL	0.049	0.090	0.000036	0.139	0.101	0.726
840-1760 mL	0.743	0.115	0.000092	0.857	0.607	0.708
1760-2240 mL	0	0.281	0.0000424	0.281	0.201	0.715

From Table 4.15, it is observed that the CER values range between 0.70 and 0.72. Ruixia et al. (2002) also found similar result with ratio of the anion bound to Cl^- released and reported CER ratio of approximately 1 for adsorption of Fluoride, Phosphate by new type ion exchange fiber. Ion exchange between adsorbent and nitrate anion could be understood by the reaction as shown in Eq. 4.17.

$$[HBO_2]_nCl + NO_3^- \rightarrow [HBO]_nNO_3^- + Cl^- \qquad (4.17)$$

Electrostatic force and ion-exchange on the protonated surface of adsorbent could be responsible for targeted anions sorption with chloride release as shown in Eq. 4.17. Hence, release of Cl^- from the hydrous bismuth oxide (HBO_{12mix}) during the sorption process may indicate that chloride ions attached to the surface and matrix of particles with weak interaction are getting released by exchange for the anions adsorbed. Thus, ion exchange can partially be the sorption mechanism for removal of nitrate, fluoride and As(V) from mix solution.

4.7 Regeneration and reuse of HBO_{12mix}

4.7.1 First regeneration of HBO_{12mix} bed

Regeneration of the bed of HBO_{12mix} and sand was attempted to evaluate its reuse potentials in successive cycles. As chloride ion has been indicated to be the exchange anion, it was decided to regenerate the adsorbent bed with 0.1 N NaOH followed by 0.1 N NaCl solution.

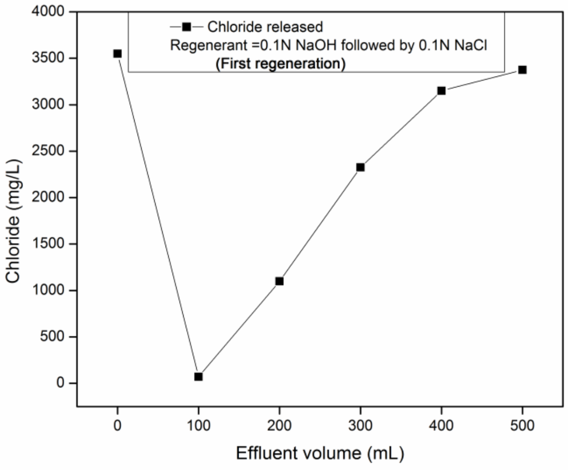


Figure 4.12: Chloride uptake by HBO_{12mix} adsorbent during first regeneration

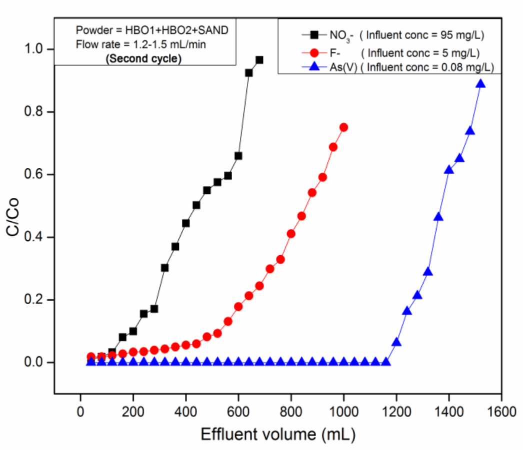
When 0.1 N NaCl solution is passed through the regenerated bed of HBO_{12mix} and sand, it is observed that the bed adsorbs a significant amount of chloride, as shown in Figure 4.12. After regeneration and charging the bed with sodium chloride solution, the column was thoroughly rinsed by passing distilled water to obtain neutral pH and almost zero background chloride concentration in the effluents.

4.7.2 Second cycle of contaminants removal

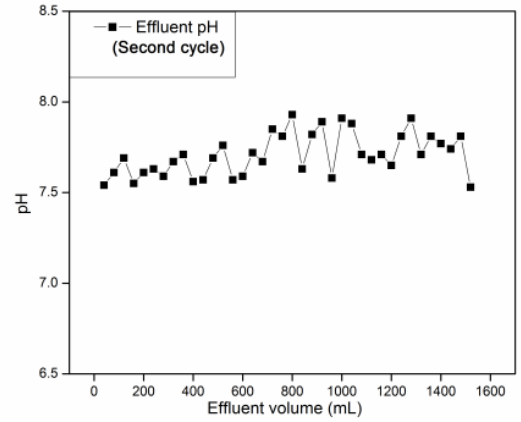
The regenerated column was again run using a mixed solution of nitrate (1.5 meq/L≈95 mg/L), fluoride (0.25 meq/L ≈5 mg/L) and As(V) (0.001 meq/L≈0.08 mg/L) as influent. The flow was maintained at 1.2-1.5 mL/min. Effluents were collected at an interval of 30 min and samples were analyzed for pH, nitrate, fluoride, As(V) and chloride concentrations. The results of analyses are found, as shown in Figure 4.13(a), (b), (c).

It is observed that the concentrations of nitrate, fluoride and As(V) in the effluent exceed their respective permissible limits just after treating around 200, 520 and 1200 mL of solution in the second cycle. The breakthrough ($C/C_o=0.1$) for these anions occurs at around 200, 520 and 1200 mL cumulative volume respectively (Figure 4.13(a)). Concentrations of these anions exceed their respective permissible limits for drinking after treating around 480, 780 and 1240 mL of nitrate, fluoride and As(V) in second cycle. The breakthrough pattern remains nitrate being first followed by fluoride and As(V).

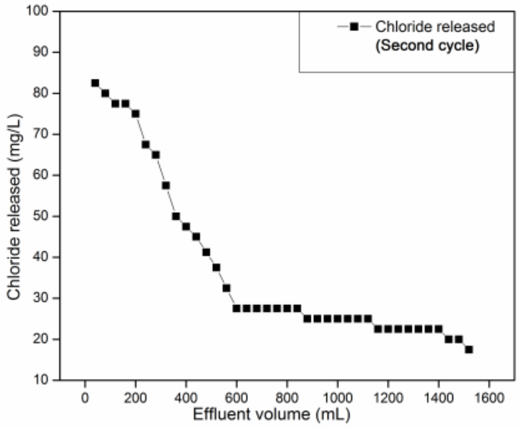
The pH of the effluent remains in 7.5-8.0 range (Figure 4.13 (b)), which is admissible for potable water. It also indicates that there is no release of hydroxide as ion exchange in lieu of the sorbed anions. The monitoring of chloride in the effluent indicates that there is increased level of chloride in it, which slowly decreases with increasing volume of effluent (Figure 4.13 (c)).



(a)



(b)



(c)

Figure 4.13: Removal of nitrate, fluoride and As(V) by HBO$_{12mix}$ 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

On the segment basis, the mass of anions sorbed and chloride released from HBO_{12mix} powder in second cycle of column operation, are summarized as given in Table 4.16.

Table 4.16: Relation between anions sorbed and chloride released from HBO_{12mix} in second cycle of column experiment

Effluent volume (mL)	Nitrate removed (meq)	Fluoride removed (meq)	As(V) removed (meq)	Anions sorbed (meq)	Chloride released (meq)	CER
0-600 mL	0.672	0.17	0.000065	0.842	0.513	0.609
600-1000 mL	0	0.162	0.000032	0.162	0.098	0.604

It is observed that the CER for sorption of nitrate, fluoride and As(V) on HBO_{12mix} bed in the second cycle is found around 0.6, indicating that ion exchange with chloride may be a major mechanism involved in the process of anions removal from the solution.

4.7.3 Second regeneration of the HBO_{12mix} bed

Once the $HBO_{12\,mix}$ bed mixed with sand was found exhausted, 500 mL solution of 0.1N NaOH was passed through the bed followed by passing equal volume of 0.1N NaCl. The monitoring of residual chloride concentration in the effluent reflected adsorption of chloride into the HBO_{12mix} bed, as shown in Figure 4.14. Subsequently the bed was washed with passing sufficient distilled water till near neutral pH and almost zero back ground chloride concentration in the effluent.

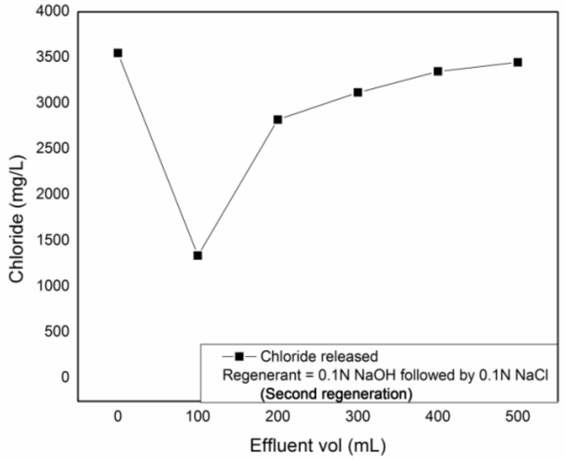


Figure 4.14: Chloride uptake by HBO_{12mix} adsorbent during second regeneration

4.7.4 Third cycle of contaminants removal

After the second regeneration the column, the third cycle of contaminants removal from the solution was performed. The flow was maintained at 1.2-1.5 ml/min. Effluents were collected at regular interval of 30 min and analyzed for pH, nitrate, fluoride, As(V) and chloride concentrations. The results of this set of experiments are shown in Figure 4.15(a), (b), (c).

It is observed that although the regenerated bed starts up taking anions again in the third cycle, the break through occurs quite quickly and permissible limits for nitrate, fluoride and arsenic for drinking water exceeds just after passing around 380, 580 and 1000 mL of influent synthetic solution (Figure 4.15(a)). The breakthrough ($C/C_o=0.1$) of anions occurs in the same sequence of nitrate followed by fluoride and arsenic with cumulative effluent volume of 120, 380 and 1000 mL respectively. The breakthrough pattern remains nitrate being first followed by fluoride and As(V).

The pH of effluent is observed in the range 7.8-8.0, which is acceptable for potable waters (Figure 4.15(b)). The monitoring of chloride ions in the effluent indicates exchange of chloride with sorbed anions from the synthetic influent solution, as summarized in Table 4.17 & Figure 4.15(c).

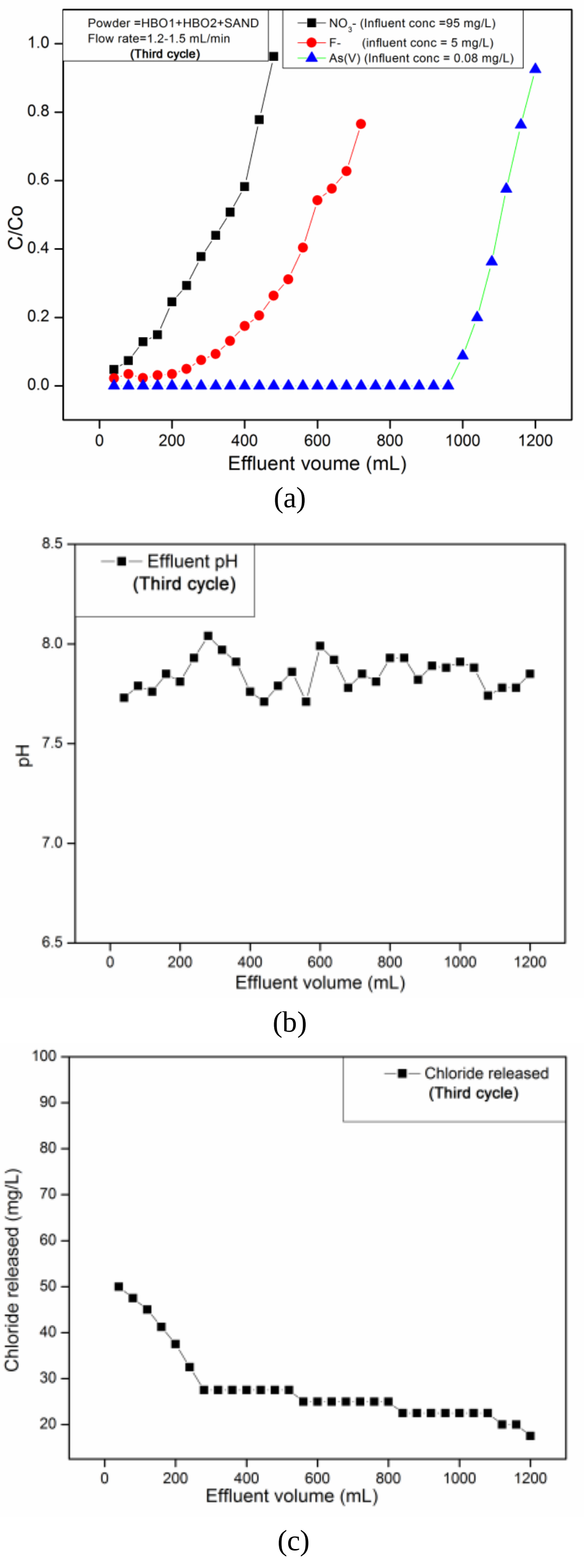


Figure 4.15: Removal of nitrate, fluoride and As(V) by HBO_{12mix} adsorbent in column mode of operation in third cycle; (a) Breakthrough curves for nitrate, fluoride and As(V); (b) Variation of pH with increasing volume of effluent; (c) Changing concentrations of chloride in effluent

Table 4.17: Relation between anions sorbed and chloride released from HBO$_{12mix}$ in third cycle of column experiment

Effluent volume (mL)	Nitrate removed (meq)	Fluoride removed (meq)	As(V) removed (meq)	Anions sorbed (meq)	Chloride released (meq)	CER
0-480 mL	0.499	0.116	0.00048	0.615	0.304	0.494
480-720 mL	0	0.120	0.00024	0.120	0.060	0.500

It is found that the CER for anionic contaminants removal by HBO$_{12mix}$ powder in the third cycle is around 0.5, which incidentally is lower than those observed in second cycle (CER~0.6).

For a relative view, Figure 4.16 presents the breakthrough curves of HBO$_{12\ mix}$ powder in all the three cycles of operations.

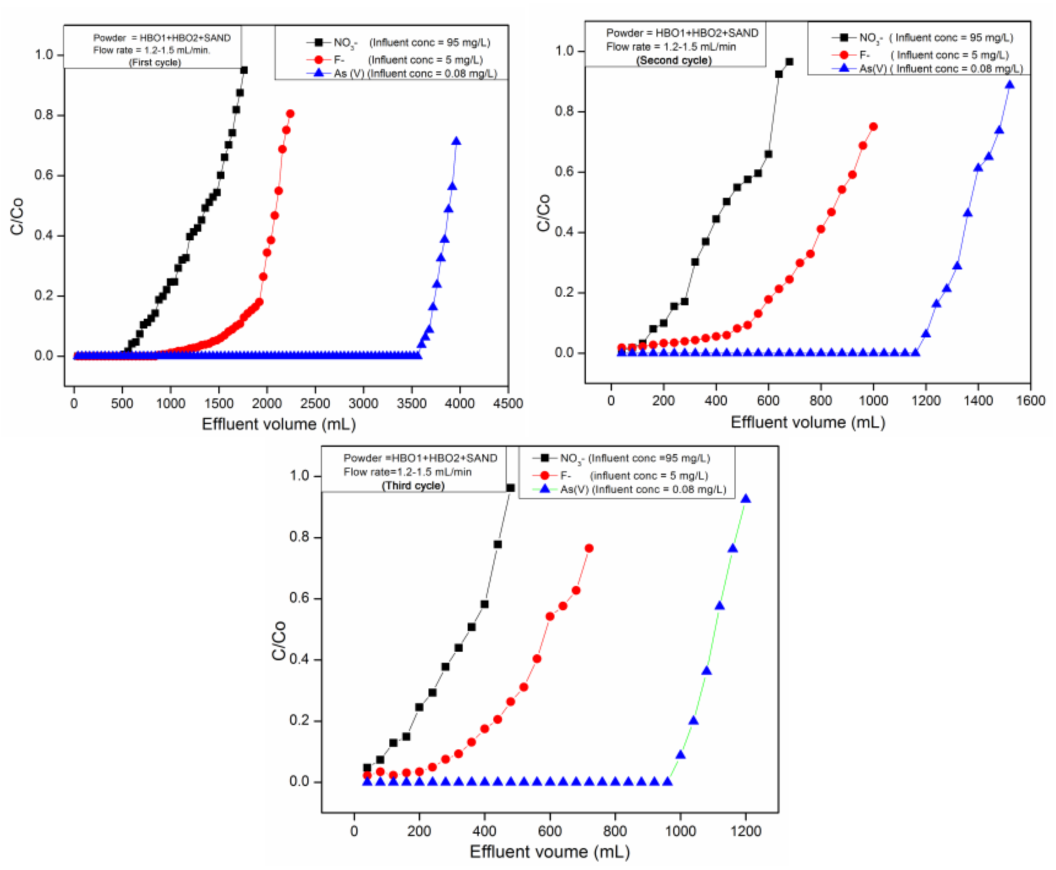


Figure 4.16: Breakthrough curves for nitrate, fluoride and As(V) through HBO$_{12mix}$ powder in down flow mode of operation in three cycles

It is observed that the HBO_{12mix} has good potentials of removal for As(V) followed by fluoride and nitrate. Nitrate ions are the least favored contaminant for this adsorbent. The HBO_{12mix} in the current set of experiments have a composition of HBO1: HBO2:: 1:4. Although nitrate removal and regeneration of the powder are reflected, there appears a very small nitrate sorptive potential of the media in current form. For fluoride the sorptive removal, regeneration and reuse are better than nitrate. As(V) appears the most preferred species amongst the three anionic contaminants tested.

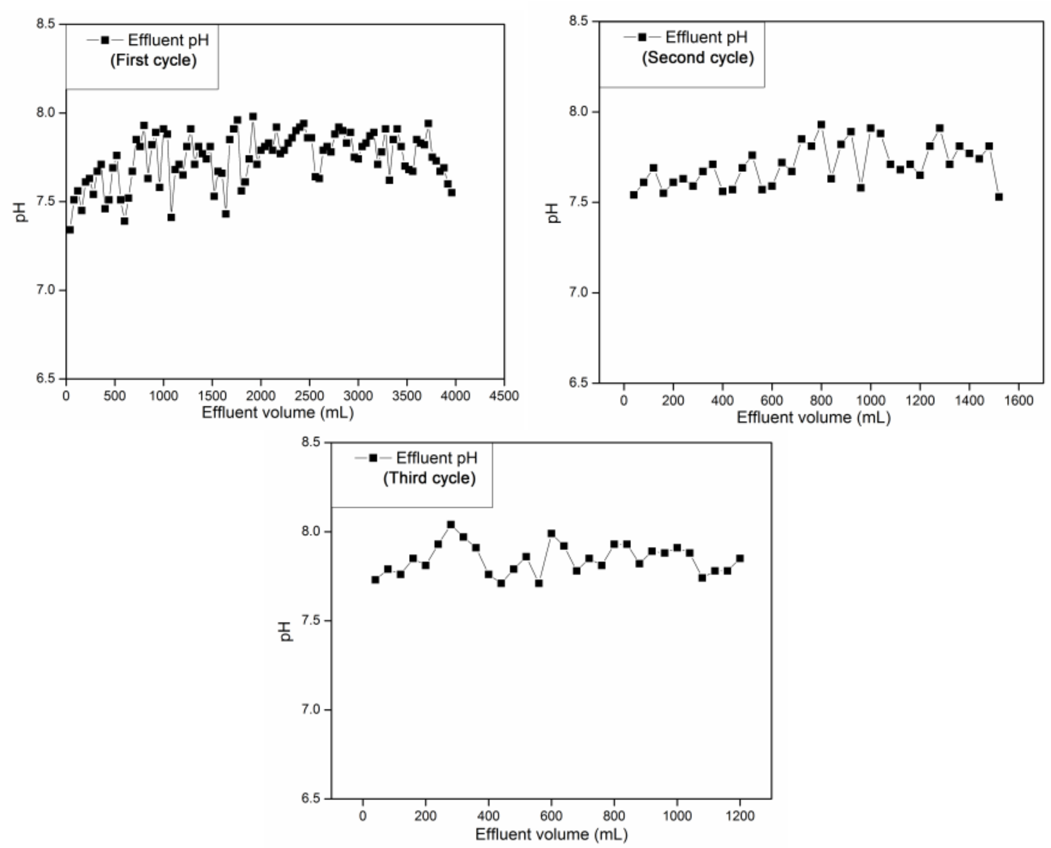


Figure 4.17: Variation of effluent pH through HBO_{12mix} powder in column mode of operation in three cycles

Figure 4.17 shows the variation of pH of the effluent in first, second and third cycles. Generally, the effluent pH remains in 6.8-8.0 range. There are two indications from this observation: (i) HBO_{12mix} powder treated water is potable from pH considerations, and (ii) hydroxyl ions are not the exchange anion in lieu of the sorbed contaminant, otherwise pH should have been around 10 or higher. Additionally, it is observed that while pH values are many times below 7.5 in first cycle, in the second cycle, it is always above 7.5 and in third cycle, it is higher than around 7.8. Thus, there appears an increasing trend in effluent pH after every cycle of regeneration of bed and reuse.

Overall results indicate that the removal potentials of HBO_{12mix} powder for nitrate, fluoride and As(V) decreases after each cycle of use. It was estimated that during regeneration, around 60% of sorbed anions were desorbed and the regenerated media could be used up to 3 cycles for such contaminants removal.

Exchange of chloride ion from the adsorption media has been reported by several investigators. Fritsche (1993) reported simultaneous removal of nitrate and others anions by yellow bismuth hydroxide and predicted that OH^- is the caustic agent responsible for nitrate sorption through ion exchange mechanism. Ruixia et al. (2002) observed removal of fluoride, phosphate and arsenate from synthetic waste waters using ion exchange fiber and reported chloride exchange as dominant mechanism. Park et al. (2008) conducted a series of experiments for simultaneous removal of fluoride, phosphate and nitrate using cement paste in the column and observed ion exchange with sulfate from the used medium.

4.8 Testing of experimental results by mathematical empirical models

Theoretical models were applied in fixed bed column system to model the adsorption under different operating conditions. With the help of a few semi empirical models such as Bohart-Adams model (Bohart and Adams, 1920), Thomas model (Thomas, 1944) and Yoon-Nelson model (Yoon and Nelson, 1984) breakthrough performance of adsorbent has been assessed with initial conc. 95 mg/L nitrate (≈1.5 meq/L), 5 mg/L fluoride (≈0.25 meq/L) and 0.08 mg/L As(V) (≈0.001 meq/L).

4.8.1 Bohart-Adams model:

Bohart Adams model proposed an equation for design of carbon adsorption column. The model assumes that the adsorption rate is proportional to both the residual capacity of activated carbon and concentration of sorbing species. Model is used to describe the initial part breakthrough curve. Bohart and Adams model has been widely used in the following form (Eq. 4.18) (Trgo et al., 2011):

$$\ln\left(\frac{C}{C_o} - 1\right) = K_{ba}(C_o t - \frac{q_{ba}\,H}{v}) \qquad (4.18)$$

Where C_o= Influent solute concentration (mg/L); C = Effluent solute concentration (mg/L); H = Hight of column, K_{ba} = Rate constant [mL/(min mg)]; q_{ba} = Maximum solid-phase concentration of solute (mg/g); v = Linear flow velocity of feed to bed (mL/cm^2); t = Service time of column under the above conditions (h).

4.8.2 Thomas model:

The model is applicable for the system of constant flow with no axial dispersion and its behavior matches with Langmuir isotherm. The linearized equation can be written as (Yan et al., 2001) in Eq. 4.19:

$$\ln\left(\frac{C}{C_o} - 1\right) = \frac{K_{th}}{Q(C_o V - q_{th}\,m)} \qquad (4.19)$$

Where C = Effluent solute concentration (mg/L); C_o = Influent solute concentration (mg/L); K_{th} =Thomas rate constant [mL/(min mg)]; q_{th} = Maximum solid-phase concentration of solute (mg/g); m = Mass of the adsorbent (g); V = Throughout volume (mL); and Q = Volumetric flow rate (mL/min).

4.8.3 Yoon Nelson model:

Yoon Nelson model is relatively a simple model for single component system. The expression could be written as Eq. 4.20 (Pantić et al., 2019):

$$\ln\left(\frac{C}{C_o - C}\right) = K_{yn}(t - r) \qquad (4.20)$$

Where C = Effluent solute concentration (mg/L); C_o = Influent solute concentration (mg/L); K_{yn} =Yoon Nelson rate constant (1/h); r = Time (t) when C/ C_o = 0.5.

Bohart Adams model, Thomas model and Yoon Nelson model have been used for mathematical description of experimental results. The experiment was performed with a depth of 51 cm and at controlled flow rate of 1.2~1.3 mL/min. The model parameters have been summarized in Table 4.18.

Table 4.18: Parameters of different mathematical models used on column study data

Models	**Linear dependences**	**Model parameters**			
			Nitrate	**Fluoride**	**As (V)**
Bohart Adams model	$\ln\left(\frac{C}{Co} - 1\right)$ vs t	K_{ba}	0.06	0.02	1.10
		q_{ba}	4.27	1.96	0.002
Thomas model	$\ln\left(\frac{C}{C_o} - 1\right)$ vs V	K_{th}	0.04	0.07	2.30
		q_{th}	3.40	0.97	0.005
Yoon Nelson model	$\ln\left(\frac{C}{Co - C}\right)$ vs t	K_{yn}	0.04	1.07	1.30
		r	2.00	6.00	8.00

The calculated value of Adam Bohart rate constant (K_{ba}) and adsorption capacity (q_{ba}) for nitrate was very close to the results obtained from Pantic et al. (2019). Similarly, Thomas model and Yoon Nelson model parameters are close to the values reported by Yan et al. (2011) and Trgo et al. (2010) respectively.

4.9 Performance of HBO_{12mix} powder in real groundwater of IIT (BHU) Varanasi spiked with nitrate, fluoride and As(V) contaminants

With a view to study the behavior of HBO_{12mix} powder in removing nitrate, fluoride and As(V) from actual groundwater under contaminated conditions, batch and column studies were conducted using IIT (BHU) campus groundwater. The natural groundwater available was added with 95 mg/L nitrate (≈1.5 meq/L), 5 mg/L fluoride (≈0.25 meq/L) and 0.08 mg/L As(V) (≈0.001 meq/L).

4.9.1 Batch experiments

Batch experiments were conducted using an adsorbent dosage of 130 g/L for a contact time of 3 h. The results of analyses for the initial and final solutions are presented in Table 4.19.

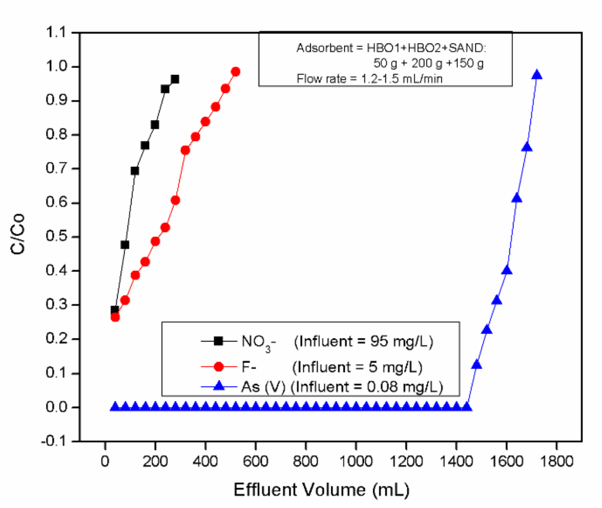
Table 4.19: Characteristics of initial and final solutions in batch experiments with groundwater spiked contaminants

Characteristic parameter	Initial conc.	Final conc.	Observed changes
pH	7.4	7.9	Slight Increase
Chloride (mg/L)	16	32.5	>50% Increase
Alkalinity (as mg/L $CaCO_3$)	305	80	≈73% Decrease
Sulphate (mg/L)	18	12	≈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

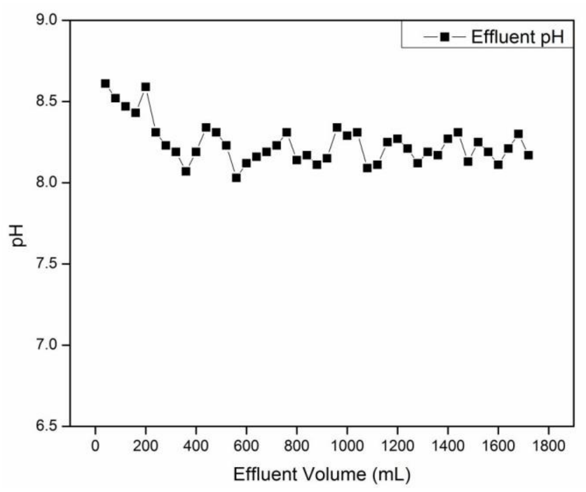
From Table 4.19 it is observed that all anions of the groundwater, except chloride get decreased by HBO_{12mix} powder. Among the added contaminants, removal (in terms of %) is highest for As(V) followed by fluoride and then nitrate. As it can be seen, alkalinity appears to be the major competing anion, followed by sulphate. In contrast, chloride concentration is found to be increased by more than 50 %. There appears a slight increase in pH also, although still within permissible limits for drinking. Hence, it can be concluded that HBO_{12mix} powder media removes all the three anionic contaminants of concern to a significant degree from groundwater conditions also having alkalinity, sulphate, chloride and other constituents. While alkalinity and sulphate are reduced in treated water with respect to initial values but chloride increases. It indicates that where as alkalinity and sulphates are also the competitive anions, the media is capable of simultaneous removal of nitrate, fluoride and As(V) if the concentrations are within 60 mg NO_3^-/L, 5 mg/L and 0.08 mg/L respectively.

4.9.2 Column experiments

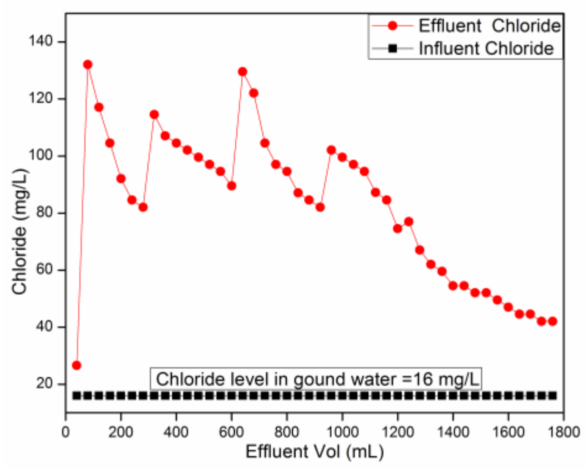
Column filled with a uniform medium of HBO_{12mix} powder and sand was used for down flow mode experiments. Existing groundwater of IIT (BHU) was added with around 95 mg/L (≈1.5 meq/L) nitrate, 5 mg/L (≈0.25 meq/L) fluoride and 0.08 mg/L (≈0.001 meq/L) of As(V) to be used as influent. Adsorbent was used by taking 50 g of HBO_1 with 150 g of clean sand and 200 g of HBO_2 was added into it. A flow rate of 1.2-1.5 mL/min was maintained and effluent samples were collected at regular interval of 30 minutes. The effluent characteristics were analyzed for pH, nitrate, fluoride, As(V), alkalinity, sulphate, chloride concentrations. Figure 4.18 summarizes the results of this set of experiments.


Adsorbent = HBO1+HBO2+SAND:
50 g + 200 g +150 g
Flow rate = 1.2-1.5 mL/min
C/Co
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
NO$_3$- (Influent = 95 mg/L)
F- (Influent = 5 mg/L)
As (V) (Influent = 0.08 mg/L)
0
200
400
600
800
1000
1200
1400
1600
1800
Effluent Volume (mL)

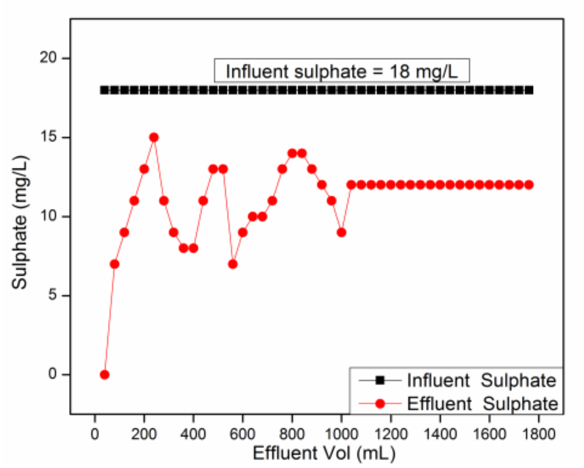
(a)


Effluent pH
pH
9.0
8.5
8.0
7.5
7.0
6.5
0
200
400
600
800
1000
1200
1400
1600
1800
Effluent Volume (mL)

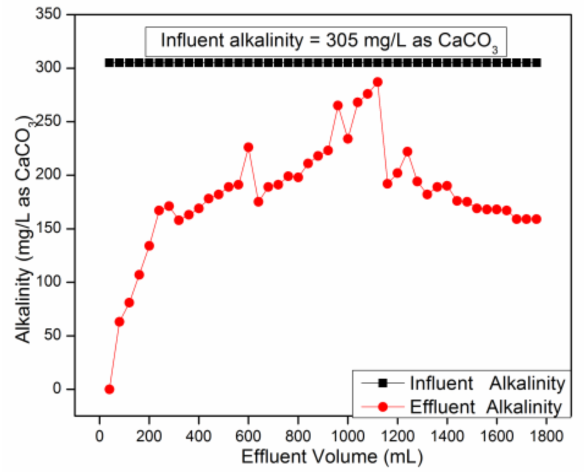
(b)


Effluent Chloride
Influent Chloride
Chloride (mg/L)
140
120
100
80
60
40
20
Chloride level in gound water =16 mg/L
0
200
400
600
800
1000
1200
1400
1600
1800
Effluent Vol (mL)

(c)



(d)



(e)

Figure 4.18: Characteristics of effluents from column using sand with HBO$_{12mix}$ in the bed and groundwater 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) Concentration of alkalinity in the effluent

The monitoring of chloride ions in the presence of anionic species bicarbonates, sulphates indicate exchange of chloride with sorbed anions from the synthetic influent solution, as summarized in Table 4.20.

Table 4.20: Relation between anions sorbed and chloride released from HBO_{12mix} in groundwater column experiment

Effluent volume (mL)	Nitrate removed (meq)	Fluoride removed (meq)	As(V) removed (meq)	Anions sorbed (meq)	Chloride released (meq)	CER
0-280 mL	0.303	0.0320	0.000298	0.33500	0.15	0.45

It is observed that in actual groundwater, where there is presence of anionic species such as bicarbonates, sulphates etc., the removal of nitrate and fluoride is considerably reduced, but the sorptive removal of As(V) still continues. The characteristics of breakthrough for nitrate and fluoride indicate that although the material remove small portion of these contaminants, the depth of column does not appear to be sufficient for complete removal (Figure 4.18(a)). The variation of pH shows that initially the effluent starts with higher values above 8.5, but gradually stabilizes between 8.5 and 8.0 (Figure 4.18(b)). This remains in pH range admissible for potable waters. There is a significant increase in chloride concentration in the effluent with respect to the initial level in the influent (Figure 4.18(c)). Both sulphate and alkalinity are reduced substantially with respect to the initial levels. Thus, it appears that the presence of higher concentrations of alkalinity and sulphate become competing and detrimental to the sorptive removal of nitrate and fluoride by HBO_{12mix} powder (Figure 4.18(d);(e)).

A sample computation of total anions sorbed and total chloride released in the effluent as the part of flow (between 0 mL to 280 mL volume of influent) during the column run gave the chloride exchange ratio of 0.45. The elevated level of chloride in the effluent and reduction in bicarbonate (measured as alkalinity) and sulfate concentrations in themselves point towards chloride exchange by HBO_{12mix} powder.

Between 0 mL to 280 mL volume of influent, average chloride value is around 85 mg/L, which is the resultant concentration after all interaction between the powder and total ions present around. A comparatively lower CER value may possibly be due to higher physio-sorption and/ or complex formation of anions and HBO_{12mix} particles. Therefore, some pretreatment of water for alkalinity and sulfate reduction appears necessary for effective use of this HBO_{12mix} for selected contaminants removal from groundwater.

4.10 Bismuth in $HBO_{12\ mix}$ treated water

Four samples of HBO_{12mix} were prepared for this experiment. 10 g of HBO_{12mix} was kept in 100 mL of distilled water for 24 h with continuous stirring. After 24 h, the samples were filtered by Whatman 42 and filtrate were analyzed for Bismuth concentration using Atomic Adsorption Spectrophotometer (AAS). The two standards solutions of bismuth were made by serial dilution: 0.1 and 0.4 mg/L. The corresponding concentrations observed through AAS were found as 0.143 and 0.467 mg/L respectively. This indicates that the results obtained from AAS analyses are reasonably acceptable. The concentration of bismuth in all the four replicates of HBO_{12mix} treated water was found 'zero', indicating there is no leaching of metallic bismuth in HBO_{12mix} treated water. These results are summarized in Table 4.21.

Table 4.21: Determination of bismuth in $HBO_{12\ mix}$ treated water

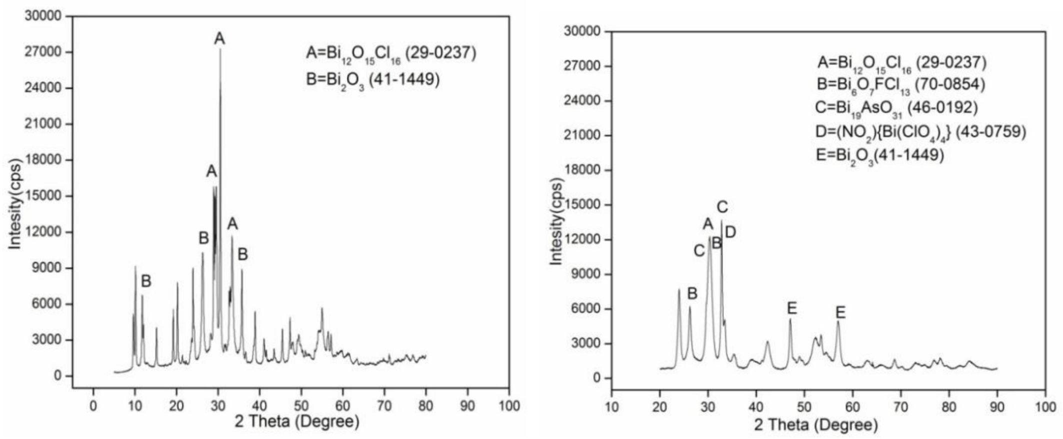
Sample	**Conc. (mg/L)**
Standard (0.1 mg/L)	0.143
Standard (0.4 mg/L)	0.467
HBO_{12mix}	0
HBO_{12mix}	0
HBO_{12mix}	0
HBO_{12mix}	0

4.11 Characterization of adsorbent

In order to characterize the materials for their physical and chemical combination properties, X-ray diffraction (XRD) pattern, Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS), Fourier-transform infrared (FTIR) spectroscopy analysis and pHpzc determinations were performed. Result of various characterization results are mentioned below.

4.11.1 X-Ray Diffraction (XRD) of HBO_{12mix}

In general, phase identification using X-ray diffraction relies mainly on the positions of the peaks in a diffraction profile and to some extent on the relative intensities of these peaks. The shapes of the peaks, however, contain additional and often valuable information. Presences of multiple peaks in XRD patterns indicate the broadly crystalline character of adsorbent (Ramli et al., 2007). The shape, particularly the width of the peak is a measure of the amplitude of thermal oscillations of the atoms at their regular lattice sites. It can also be a measure of vacancy and impurity element concentrations and even plastic deformation, any factor which results in a distribution of d-spacings. Crystallite size can also cause peak broadening. The well-known Scherrer equation explains peak broadening in terms of incident beam divergence which makes it possible to satisfy the Bragg condition for non-adjacent diffraction planes. Once instrument effects have been excluded, the crystallite size is easily calculated as a function of peak width (specified as the full width at half maximum peak intensity (FWHM)), peak position and wavelength. Warren and Averbach's method takes not only the peak width into account but also the shape of the peak. This method is based on a Fourier deconvolution of the measured peaks and the instrument broadening to obtain the true diffraction profile. The characteristic peaks are analysed with the X-pert high score software. The XRD pattern for HBO_{12mix} powder has been found, as shown in Figure 4.19(a). Presence of sharp peaks indicates the crystalline structure of the adsorbent.



(a) (b)

Figure 4.19: XRD patterns of HBO_{12mix} (a) in original form (b) after adsorption of nitrate, fluoride and arsenic onto the material

Using X-pert high score software, the 2θ values for major peaks (marked A) correspond to 29.11°, 30.56° and 33.43° and the chemical composition is identified as $Bi_{12}O_{15}Cl_{16}$ (29-0237). Additional peaks (marked B) at 2θ= 25.94° and 35.46°correspond to Bi_2O_3 (41-1449). XRD of spent HBO_{12mix} (after adsorption) material after adsorption of nitrate, fluoride and As(V) is found, as shown in Figure 4.19(b). It can be seen that the intensity of peaks have reduced. Peaks corresponding to 2θ = 23.92°, 30.56°, 33.43°correspond to $Bi_{12}O_{15}Cl_{16}$ (29-0237), and 2θ = 25.94°, 35.46° indicate presence of Bi_2O_3 (41-1449). However, there are additional peaks at 2θ = 33.42°, which indicate $(NO_2)Bi(ClO_4)_4$ (43-0759), 2θ = 23.92°, 30.16° indicating $Bi_6O_7FCl_{13}$ (70-0854), and 2θ =29.94°, 32.84° corresponding to $Bi_{19}AsO_{31}$ (46-0192).

The chemical compositions of possible compound (Table 4.22) clearly indicate the attachment of nitrate, fluoride and arsenic species on the adsorbent material.

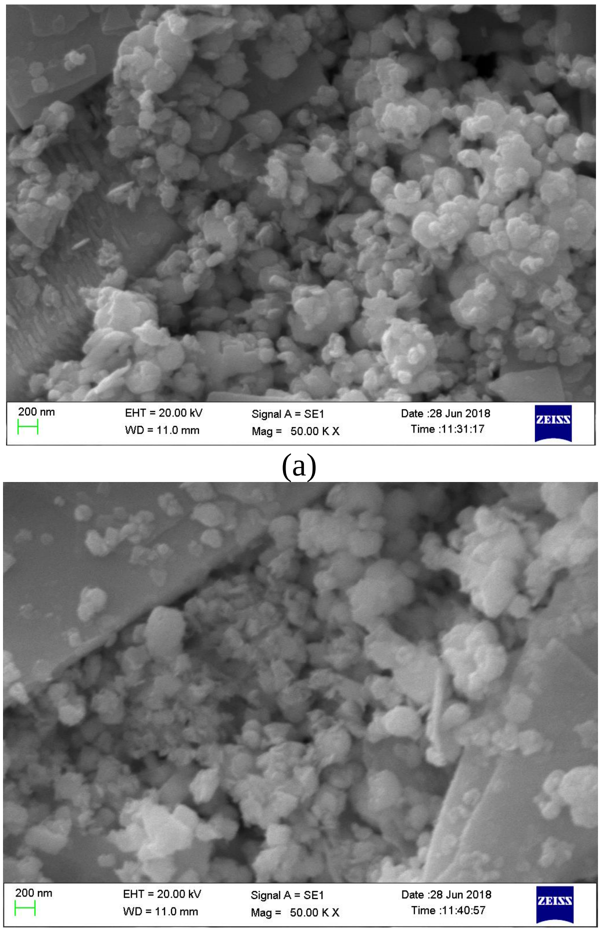
Table 4.22: XRD patterns of (a) Original HBO_{12mix} and (b) Spent HBO_{12mix}

HBO_{12mix}	Broad possible chemical compound	Designated as	2θ peak value	X-pert high score File no.
Original HBO_{12mix} (Before adsorption)	$Bi_{12}O_{15}Cl_{16}$	A	29.11°, 30.56°, 33.43°	29-0237
	Bi_2O_3	B	25.94°, 35.46°	41-1449
Spent HBO_{12mix} (After adsorption)	$Bi_{12}O_{15}Cl_{16}$	A	29.11°, 30.56°, 33.43°	29-0237
	Bi_2O_3	B	25.94°, 35.46°	41-1449
	$(NO_2)Bi(ClO_4)_4$	D	33.42°	43-0759
	$Bi_6O_7FCl_{13}$	B	23.92°, 30.16°	70-0854
	$Bi_{19}AsO_{31}$	C	29.94°, 32.84°	46-0192

Huang et al. (2015) also suggested ion exchange of arsenic and fluoride with chloride by MgAl layered double hydroxides, which showed shifting of XRD peaks in the interlayer spacing of adsorbent.

4.11.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) analysis has been done to know the surface morphology of adsorbent. Figure 4.20 shows the micrograph of HBO_{12mix} in (a) original (before adsorption) and (b) spent forms (after adsorption). The SEM analyses show granular irregular surface morphology of the adsorbent. A comparative view of tehse images at different magnification factors reveals that surface of spent adsorbent (after adsorption) become rough and spongy with comparison to raw/original adsorbent.



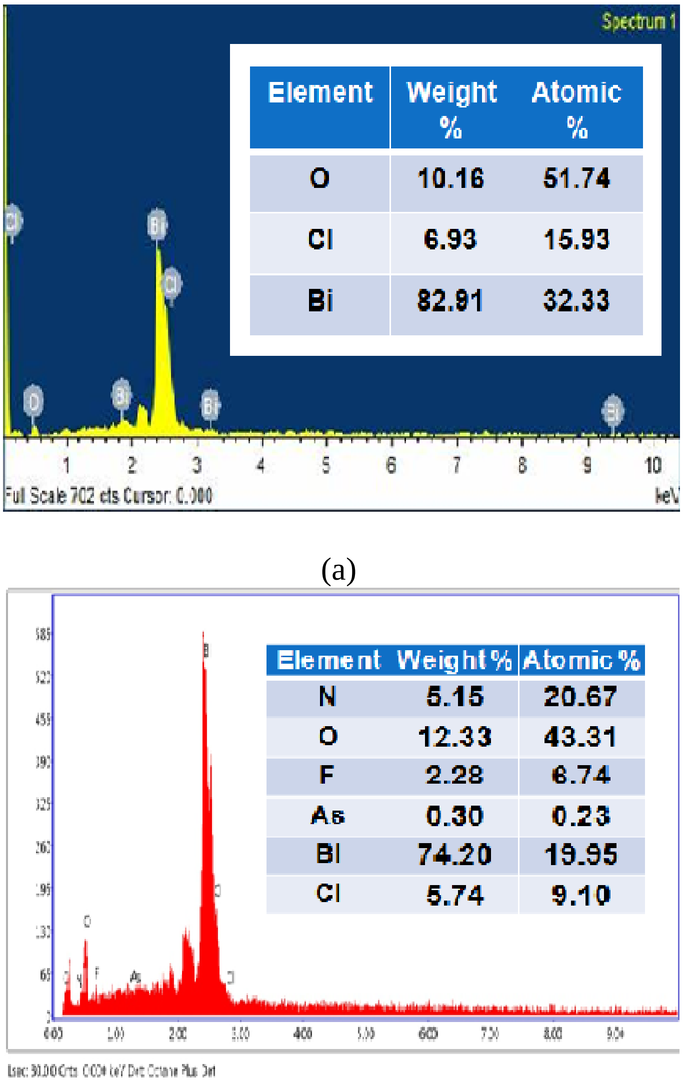
(a)

(b)

Figure 4.20: SEM micrographs of HBO_{12mix} (a) in original form and (b) after adsorption of nitrate, fluoride and arsenic from solution

4.11.3 Energy-dispersive X-ray spectroscopy (EDS)

Energy-dispersive X-ray spectroscopy (EDS) spectrum analysis reflects the broad elemental analysis of the material. The EDS obtained for HBO_{12mix} is shown in Figure 4.21. From EDS analysis (Figure 4.21(a)), it is observed that original form of HBO_{12mix} is broadly composed of BiO and Cl. After the adsorption of nitrate, fluoride and As(V) from the solution, the EDS of spent material (after adsorption) shows peaks corresponding to N, F and As, confirming the adsorption of anionic contaminants on the material (Figure 4.21(b)). The percentage of Cl^- appears to have decreased in spent material (after adsorption) with respect to original one. Furthermore, it can be inferred that presence of N, F and As on the surface of HBO_{12mix} becomes the integral part of media. Hence, existence of nitrate, fluoride and As(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.



Element	Weight %	Atomic %
O	10.16	51.74
Cl	6.93	15.93
Bi	82.91	32.33

(a)

Element	Weight %	Atomic %
N	5.15	20.67
O	12.33	43.31
F	2.28	6.74
As	0.30	0.23
Bi	74.20	19.95
Cl	5.74	9.10

(b)

Figure 4.21: EDS patterns of HBO_{12mix} (a) in original form and (b) after adsorption of nitrate, fluoride and arsenic from solution

4.11.4 Fourier Transform Infrared spectroscopy (FTIR)

In FTIR, infrared radiation is passed through the sample in which partial radiation is absorbed and some of it is transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample which corresponds to the frequencies of vibrations between the bonds of the atoms making up the material. Thus, no two materials could have same infrared spectrum. With the algorithms based on modern software, FTIR is an excellent tool for quantitative analysis. Spectra were measured on a Bio-Rad FTS-60 spectrometer and collected in the mid infrared region (4000– 400 cm^{-1}) after 256 scans at 2 cm^{-1} resolutions. Samples were prepared using the standard KBr (Merck) pellets method.

FTIR spectra of HBO$_{12mix}$ and spent material after adsorption of selected anionic contaminants are shown in Figure 4.22. Major functional groups responsible for adsorption are presented in the Table 4.23.

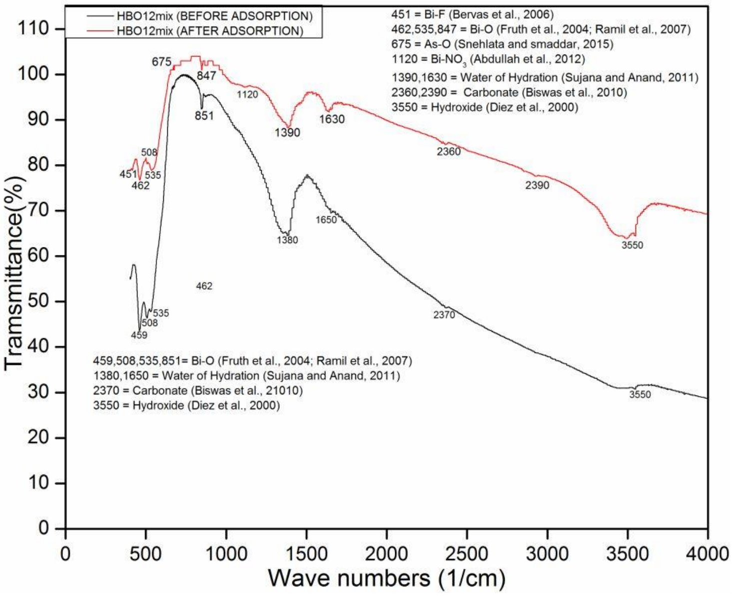


Figure 4.22: FTIR Spectra patterns of HBO$_{12\ mix}$ (a) in original form and (b) after adsorption of nitrate, fluoride and arsenic from solution

Table 4.23: FTIR Spectroscopic analyses of HBO$_{12mix}$ before (original form) and after adsorption

WAVE BAND OBSERVED for HBO$_{12mix}$		ASSIGNMENT	WAVE BAND (STANDARD)	REFERENCE
HBO$_{12mix}$ before adsorption	HBO$_{12mix}$ after adsorption			
535 851	508 847	Bi-O	200 cm^{-1} to 800 cm^{-1} 400 cm^{-1} to 600 cm^{-1}	Fruth et al., 2004 Ramli et al., 2007
1380 1650	1390 1630	Water of hydration	1300 cm^{-1} to 1650 cm^{-1}	Sujana and Anand, 2011
-	1120	Bi-NO$_3$	1200 cm^{-1} to 1350 cm^{-1}	Abdullah et al., 2011
-	451	Bi-F	400 cm^{-1} to 1000 cm^{-1}	Bervas et al., 2006
-	675	As-O	615 cm^{-1} to 764 cm^{-1}	Lata and Smaddar, 2015

Before adsorption, the original HBO$_{12mix}$ powder shows peaks near wave bands 535 and 851 cm^{-1} which are likely due to Bi-O bond (Fruth et al., 2004; Ramil et al., 2007). Other broad absorption peaks around 1380 and 1650 cm^{-1} are possibly due to water of hydration (Sujana and Anand, 2011). After adsorption of nitrate, fluoride and arsenic on the material, there seems some displacement of the absorption peaks. Thus, the wave band for Bi-O is observed at of 508 and 847 cm^{-1} and that for water of hydration shift to 1390 and 1630cm^{-1}. In addition to these shifts, there are additional peaks near wave bands 1120, 451 and 675 cm$^{-1.}$ which indicate presence of Bi-NO$_3$ (Abdullah et al., 2011), Bi-F (Bervas et al., 2006) and As-O (Sneh Lata and Smaddar, 2015) respectively. Thus, FTIR spectra analysis further confirms adsorption of nitrate, fluoride and arsenic anion species on HBO$_{12mix}$ material. 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. FTIR analysis of tested materials supports the results obtained through XRD and EDS analysis.

4.11.5 pH at point of zero charge (pHpzc)

The point of zero charge (pzc), in physical chemistry, is a concept relating to the phenomenon of adsorption and it describes the condition when the electrical charge density on a surface is zero. It is usually determined in relation to an electrolyte's pH, and the pzc value is assigned to a given substrate or colloidal particle. For example, the pzc of solid FeOOH is 9. The value of pH is used to describe pzc only for systems in which H^+/OH^- are the potential-determining ions (which is the common case). When 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 is positively charged (attracting anions). Conversely, above pzc the surface is negatively charged (attracting cations/repelling anions). At pzc, the colloidal system exhibits zero zeta potential (i.e., the particles remain stationary in an electric field). To know the effect of pH on the sorption process, point of zero charge (pH_{PZC}) was measured. The pH of point of zero charge of adsorbent was determined using fast alkalimetric titration method (Huang and Ostovic, 1978; Agarwal et al., 2006; Sharma et al., 2009). For the purpose, 100 mL of NaCl solution having strength of 0.1, 0.01 and 0.001 N were prepared. 1.0 g of HBO_{12mix} powder was added and stirred continuously for 12 h and titrated in presence of the powder with 0.1 N HCl and another one with 0.1 N NaOH. Volume of acids or alkali consumed corresponding to each pH difference of 0.5 unit was recorded. The samples were allowed to settle and the solid materials were filtered out through Whatman 42 filter paper. The filtrates were titrated similarly. The net titration curve for each ionic strength was obtained by subtracting titration curve of the filtrate samples from that of the portions with the powder. In the absence of specific chemical interaction between the single electrolyte and the surface of sorbent, the net titration curves, usually meet at a point that is defined as pH_{PZC}. 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. A range, rather than a specific pH value indicate a possible interaction between the media and the chloride solution used as electrolyte. Thus, for HBO_{12mix} pH_{PZC} being 8.0-8.2 indicates that at this pH the net surface charge becomes zero and the surface of adsorbent becomes neutral with equal density of negative and positive charge. Hence suitability and possibility of anionic uptake (nitrate, fluoride and arsenic) favours only with the solution for which $pH< pH_{PZC}$ due to columbic forces of attraction. Force of repulsion will act as $pH> pH_{PZC}$. The observations on pHpzc for HBOs by different researchers may be summarized, as given in Table 4.24.

Table 4.24: pHpzc of different forms of HBOs

S.N.	Type of HBO	pH_{pzc}	Reference
1	HBO_1	6.6	Srivastav et al., 2013
2	HBO_2	9.7-10.1	Singh, 1999
3	HBO_3	7.5	Singh et al., 2015
4	HBO_{12mix}	8.0-8.2	This study

4.12 Prospect and challenges of using HBO as an adsorbent for groundwater treatment in POU system

Various forms of hydrous bismuth oxides (HBOs) have been found to show anionic contaminants removal potentials from water. While HBO_1 is observed to be very strong adsorbent for As(V) and fluoride, HBO_2 and HBO_3 have almost equal level of nitrate sorptive properties. Hence HBO_{12mix} has been examined and found to be a good material for simultaneous removal of all the three contaminants of common concern. Bicarbonate and sulfate which are common anions present in ground water are competitive anions which adversely affect the performance of HBO_{12mix}. For their application in POU treatment system and efficient use, suitable pretreatment of ground water for bicarbonate and sulfate reduction may be required to keep the sorptive media useful for contaminants removal only. At present, there is no POU available for nitrate, fluoride or arsenic removal in Indian market. Hence, the present work is a way forward in this direction.

4.13 Cost analysis of HBO_{12mix}

An attempt was made to estimate the cost of production of HBO_{12mix} adsorbent and compare it with some of the other materials used for adsorption. Although the cost figures are from different horizons of time, the overall cost (US$/kg) for the preparation of some adsorbents is given in Table 4.25. For HBO_{12mix}, the cost of production works out to be about US $ 64/kg, which appears lower than that of amorphous alumina. The cost is likely to reduce once the material is prepared on larger scale and other steps of cost optimization are applied. The adsorbent may be economically viable as it has regeneration and reuse potentials. Once the material is finalized and the quantity for a family size POU treatment unit is fixed, the process of operation and regeneration may be studied and operation and maintenance (O/M) cost may be estimated. The current study focussed on identification of potential material for simultaneous removal of nitrate, fluoride and As(V) from the mixed solution and the material was used for up to three cycles of application after regeneration.

Table 4.25: Cost of production of some adsorbents

Adsorbent	Cost (US $/kg)	Reference
Activated alumina	~2.3	Rubel J. F., 1983
Amorphous alumina	~70.0	Rubel J. F., 1983
Hydrous bismuth oxide (HBO1)	~59.0	Srivastav et al., 2013
Activated carbon	~48.0	Gupta et al., 2018
Hydrous bismuth oxide mix (HBO_{12mix})	~64.0	Present study