Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.938251

55 (2015) 604–614
July

Taylor & Francis
Taylor & Francis Group

Synthesis of a novel adsorbent, hydrous bismuth oxide (HBO_2) for the removal of fluoride from aqueous solutions

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Received 23 November 2013; Accepted 20 April 2014

ABSTRACT

Hydrous bismuth oxides (HBOs) have been reported to have sorptive capacity to remove anions from water. We have synthesized three HBO adsorbents. The designations of all HBO media (HBO_1, HBO_2, and HBO_3) are based on the increasing concentrations of hydroxides. Present study has been devoted to explore the potential of HBO for the removal of fluoride from aqueous solutions. The removal of fluoride increased by increasing the temperature. The kinetics of removal of fluoride was governed by intraparticle diffusion. From the Dubinin–Radushkevich (D–R) isotherm model, the values of mean adsorption energy (E) were calculated and found below $8\,\mathrm{KJ\,mol^{-1}}$ which is an indication of physical adsorption of fluoride on HBO_2. Out of the competitive anions viz. bicarbonate, chloride, and sulfate, presence of chloride in solution has much effect on fluoride removal by HBO_2 adsorbent.

Keywords: Hydrous bismuth oxide (HBO_2); Fluoride removal; Kinetic studies; pH_{PZC}; Competitive anions

1. Introduction

Safe drinking water is essential to humans and other life forms. Access to safe drinking water has been improved over the last decades in almost every part of the world, but approximately one billion people still lack access to safe water and over 2.5 billion lack accesses to adequate sanitation. Sources of water (surface and groundwater) are available in plenty, however still scarcity of potable water is there among major problems in the world because of its contamination [1]. Quality maintenance of drinking and environmental water is very important in order to avoid toxic influences of contaminants on human beings and living creatures. For the conservation of water safety, the improvements and further developments of water treatment and analytical techniques have been needed [2]. To protect public health, environmental authorities have taken a more stringent attitude towards the presence of these toxic elements in drinking water. The World Health Organization has recommended maximum guideline value of fluoride in drinking water as $1.5\,\mathrm{mg\,l^{-1}}$ [3], while Bureau of Indian Standards has prescribed the desirable limit as 1.0 and $1.5\,\mathrm{mg\,l^{-1}}$ is in the absence of any alternative source of drinking water [4]. Presence of fluoride in drinking water can cause

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various types of fluorosis such as dental, skeletal, and crippling in human beings [5] and according to recent estimate, about 200 million people around the world are under the threat of fluorosis [6]. Major natural sources of fluoride in groundwater are the breakdown of rocks and soils or weathering and deposition of atmospheric particles. Fluoride contamination in ground water is a worldwide problem, and its concentration in drinking water at many places of the world exceeds the permissible values [7]. Dental and skeletal fluorosis is caused by very high concentration of fluoride intake [8,9]. The common techniques widely employed for the removal of fluoride from water are adsorption, ion exchange, precipitation, electro-dialysis, and reverse osmosis [5,10–12]. The unwanted chemical generation, disposal of wastes, higher maintenance costs, fouling, scaling, and degradation of membrane are the major disadvantages of membrane techniques as well as precipitation. Because of that, ion exchange and adsorption are widely accepted techniques which offer potential for the removal of fluoride better [5,10]. It is reported that adsorption is one of the most important methods for the removal of fluoride from water and number of adsorbents have been explored at global level for the removal of fluoride from water [7,13–15]. Bhatnagar et al. [16] and Loganathan et al. [17] have published comprehensive reviews on various types of adsorbents for removal of fluoride from aqueous solutions. During past few years, greater attention has been given for developing new and economically viable adsorbents for the removal of fluoride from aqueous solutions [18]. To overcome the existing problems of commonly used organic adsorbents and resins, and due to high removal efficiency of inorganic adsorbents, especially metal oxides (hydroxides) are being used by researchers across the world in water treatment systems [19]. Many inorganic adsorbents such as Mg-doped nano-ferrihydrite [5], titanium hydroxide-derived adsorbent [20], hydrous manganese oxide-coated alumina [21], granular ferric hydroxide [22], mesoporous alumina [23], $Fe_3O_4@Al(OH)_3$ magnetic nanoparticles [24], Al–Ce hybrid adsorbent [25], hydrous iron (III)–tin (III) bimetal oxide [26], and Fe–Al–Ce trimetal hydroxide [27] have been reported for the removal of fluoride from water.

Fristche [28] reported the removal of nitrate and other anions from water using yellow bismuth hydroxide precipitate. Singh and Ghosh [29] found the polymeric forms of hydrous bismuth oxide (HBO) to be more efficient in nitrate removal. Singh et al. [30] reported the preparation and properties of HBO powders for nitrate removal from aqueous solutions. HBOs were found to be efficient adsorbents for nitrate removal from water as well as its competitive anions such as bicarbonate and sulfate. In batch experiment mode HBO_2 and HBO_3 had very good sorption capacity to remove nitrate from water (HBO_2 ~66% and HBO_3 ~70%) at 14 mgN l^{-1} of initial nitrate concentration level [31]. Therefore, in present paper the possibility of fluoride removal is explored by HBO_2 which was found suitable for nitrate removal from water.

2. Experimental

2.1. Materials

All the chemicals used in the experiments were analytical reagent grade (AR) chemicals and obtained from Loba Chemie Pvt. Ltd, Mumbai, India. Bismuth trioxide (Bi_2O_3, MW = 466.0) powder of commercial AR grade was used without further purification to synthesize the HBO_2 powder. The method of synthesis adopted was similar as reported by Singh et al. [30]. At first 0.1 M Bi_2O_3 powder was dissolved in 2 N HCl and then 100 ml of 0.1 M Bi_2O_3 solution was mixed with 200 ml (ratio was 1:2) of volumetric proportions 2 N NaOH solution. The obtained precipitate was washed with distilled water to remove all unreacted impurities and dried at 100 ± 3˚C for 24 h to get in powder form. Because the volume of hydroxide was taken two times of bismuth solution, hence the powder was designated as HBO_2.

2.2. Determination of fluoride and pH

The concentration of fluoride in water was determined as per the electrode method given in Standard Methods [31]. Fluoride was measured by Ion Selective Electrode method using digital Ion/pH meter (HANNA HI 4222, Hanna Equipment (India) Pvt. Ltd, Navi Mumbai, India). A known volume (10–25 ml) of the sample was taken in a beaker and equal volume of TISAB (Total Ionic Strength Adjustment Buffer) solution was added to each sample and stirred with a magnetic stirrer for one minute. The electrode tip was immersed in the sample and reading was recorded directly when stable. pH of the samples was measured using digital Ion/pH meter (HANNA HI 4222) of Hanna Equipment (India) Pvt. Ltd, Navi Mumbai, India. The pre-calibration of instrument with known standards is required for sample analysis.

2.3. Fluoride adsorption experiments

Adsorption of fluoride onto HBO_2 was studied in batch experiment mode. A stock fluoride solution (100 mg l^{-1}) was made by using sodium fluoride for adsorption experiments. The required concentration of the fluoride solution was prepared by serial dilution of stock solution. A required adsorbent dosage was added to 100 ml fluoride solutions which were placed in a thermostat cum shaking assembly for 3 h of contact time. After that the solution was filtered by Whatman 42 filter paper and the filtrates were analyzed for fluoride and pH. All the experiments were carried out in triplicate and the average values are reported. The effect of pH, adsorbent dosages, time, and temperature were also observed.

3. Results and discussion

3.1. Characterization of HBO_2 adsorbent

The surface characteristics of HBO_2 were analyzed by using Fourier transform infrared spectrometry (FTIR) (Perkin Elmer spectrum RX1) and scanning electron microscopy (SEM). pH of point of the zero charge (pH_{PZC}) was determined by batch equilibrium method as described by Sharma et al. [32].

3.2. FTIR of HBO_2 adsorbent

Fig. 1 shows the FTIR spectrum of HBO_2 adsorbent.

The major absorption bands which indicate the presence of Bi–O bond were found at 464.1, 500.4, 671.7, and 767.8 cm^{-1}, respectively, and are indicative of presence of Bi–O bond [33]. The peaks which are found in between 3,300 and 3,600 cm^{-1} frequency range show the characteristics of OH group [34] and three peaks were found for OH groups such as 3,401.5, 3,504.3, and 3,596.3 cm^{-1} [35]. A single peak has been observed at 2,369.4 cm^{-1} and it may be due to the little carbonate impurity in the media. The absorption band from 2,360 to 2,370 cm^{-1} may also be due to the presence of carbonate [13].

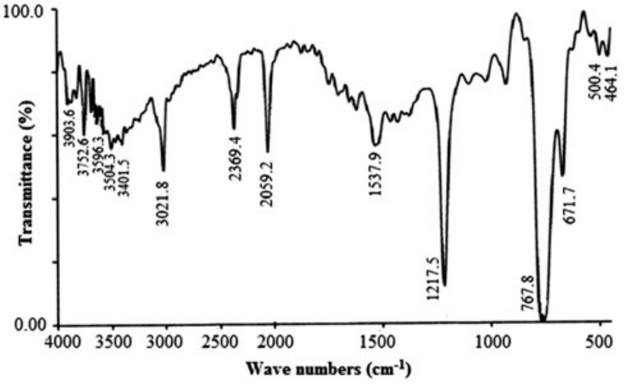

Fig. 1. FTIR spectra of HBO_2 adsorbent [33].

3.3. Surface morphology of HBO_2

The Surface morphology of HBO_2 adsorbent was observed by SEM image and it is given in Fig. 2.

It was observed that the surface of adsorbent is rough with presence of some pores on the surface of adsorbent. Presence of pores on the surface is a good characteristic for beneficial adsorption. The rough surface of adsorbents can retain greater number of adsorbate ions in comparison to the adsorbents having smooth surface. The kind of adsorbate may be negative or positive, for instance if the surface of adsorbent is positive it will attract anions like fluoride and if it is negative, it will attract cations. In present study, the rough surface of HBO_2, as observed by SEM analyses, will be helpful to adsorb a large number of adsorbate species.

3.4. Measurement of pH_{PZC}

Batch equilibrium method as used by Sharma et al. [32] was used to determine the pH_{PZC} of HBO_2. 0.20 g of adsorbent was immersed in 50 ml of 0.01 M NaCl solution with different pH values, and shaken for 48 h in capped bottles. 0.1 N NaOH and 0.1 N HCl solutions were used to adjust the initial pH values (4.0–12.0). Initial and final pH values were measured as pH_i and pH_f, respectively. pH_{PZC} was obtained after plotting the graph between pH_{final} vs. $pH_{initial}$ where intersection point of curves was obtained. The value of pH_{PZC} for HBO_2 is determined as 7.9.

The pH_{PZC} of HBO_2 was determined by adopting the method as reported by Sharma et al. [32].

3.5. Removal of fluoride by HBO_2

A removal of fluoride ~27.0 ± 1.0% at 10 mg l^{-1} of initial fluoride concentration was achieved in 3 h contact time. The pH of treated water was found to be around 7.3. From the initial results it appears that a less removal was achieved. The removal of fluoride by HBO_2 is found less but this material has been reported to be very efficient in nitrate removal by Singh et al. 2012 [30]. Fluoride removal by HBO_2 was studied via increasing the temperature and dosages, and some fruitful results were obtained as discussed below (Fig. 3).

3.6. Effect of adsorbent dosage

The fluoride removal (%) by HBO_2 increases from 13 to 51% (Fig. 4) with increasing adsorbent dosage 10–100 g l^{-1} in 3 h. At 10 mg l^{-1} fluoride level, the maximum fluoride removal by HBO_2 was about 51% with 100 g l^{-1} adsorbent dosage. Beyond 60 g l^{-1} of

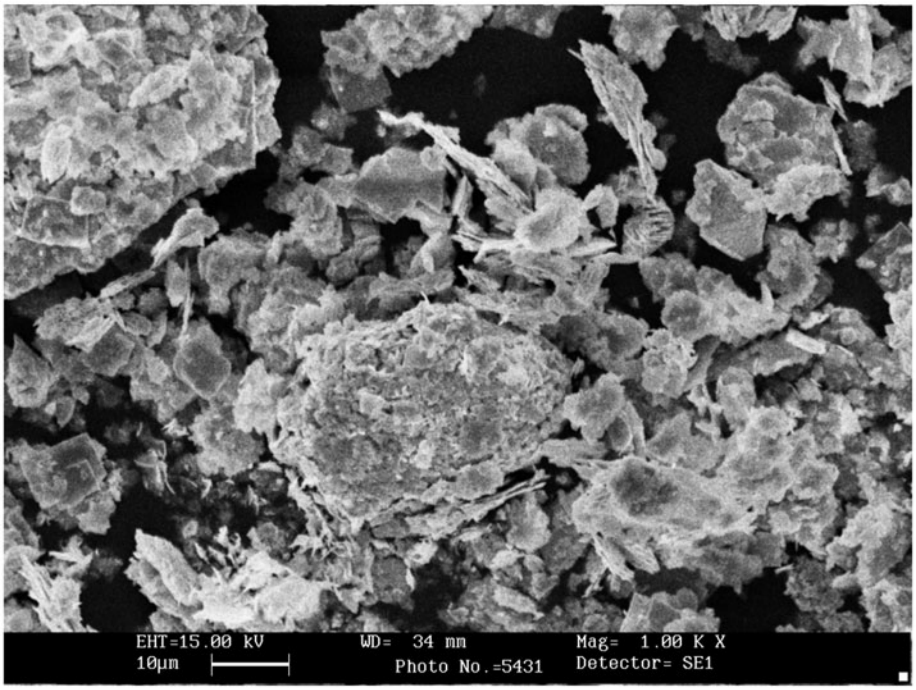

Fig. 2. SEM image of HBO_2 adsorbent [33].

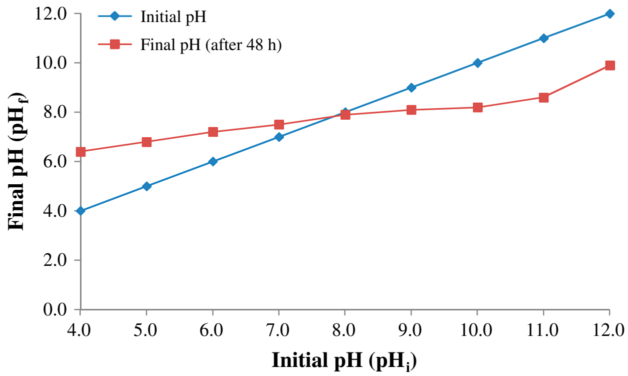

Fig. 3. pH_{PZC} determination plot for HBO_2 adsorbent.

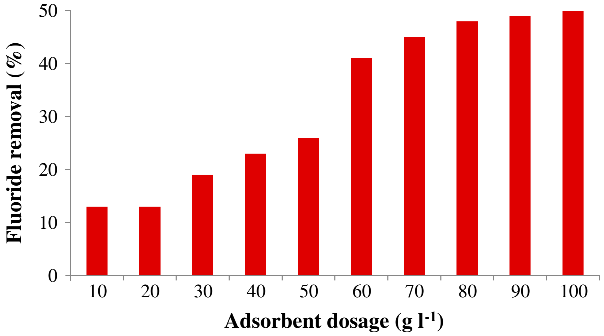

Fig. 4. Effect of adsorbent dosage on removal of fluoride by HBO_2.

adsorbent dosages no significant increase in fluoride removal was observed. The increase in fluoride removal with increasing adsorbent dosage could be attributed to the availability of more number of adsorption sites for adsorption and due to saturation of active adsorption sites, the removal might almost have stabilized [7,36].

3.7. Effect of pH

The effect of solution pH on fluoride removal was studied in the pH range of 4.0–12.0. As the pH of the fluoride solution increased, the adsorption of fluoride gradually decreased from 0.062 to 0.020 mg g^{-1}. However, the amount adsorbed per g of adsorbent (q_e) remained almost same up to pH 9.0, and after this, a significant reduction in fluoride adsorption was observed. The reduction of the amount of fluoride adsorbed in the alkaline pH range could be attributed to the competition of hydroxyl ions with fluoride for adsorption sites [10].

3.8. Effect of contact time and initial concentration

Fig. 5 shows the effect of initial concentrations (10–25 mg l^{-1}) and contact time (60–360 min) for fluoride removal by HBO_2.

Fig. 5 shows the time dependence of fluoride adsorption on HBO_2 at its various initial concentrations

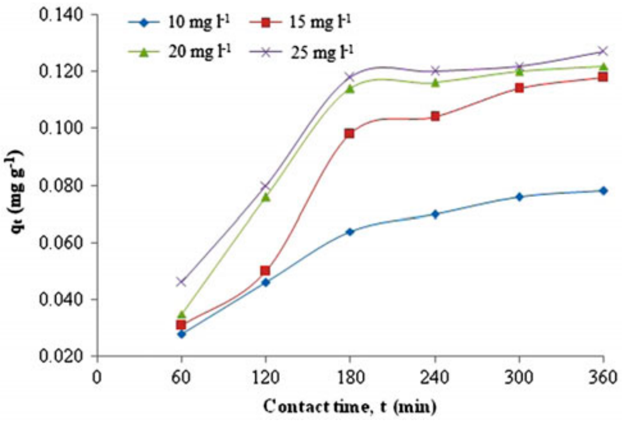

Fig. 5. Adsorption kinetic curves for the removal of fluoride by HBO_2.

viz. 10, 15, 20, and 25 mg l^{-1}, respectively. It has been observed that the amount of *F* adsorbed (mg g^{-1}) gets increased with increase in initial fluoride concentration and time; however, most of the adsorption takes place within 3 h. After the initial 3 h, the rate of adsorption was negligible and the residual fluoride concentration in solution reached around a constant value.

It is clear from Fig. 5 that loading capacity increased from 0.028 to 0.127 mg g^{-1} with increasing initial fluoride concentration from 10 to 25 mg l^{-1}. The equilibrium was attained within around 3 h for all four initial concentrations of fluoride.

Pseudo-first-order and pseudo-second-order adsorption kinetic models were used to study the kinetics of present experimental data. The pseudo-first-order adsorption kinetic model (Eq. (1)) is given as [37]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (1)$$

where q_e and q_t are the amounts of fluoride adsorbed (mg g^{-1}) at equilibrium and at any time *t* (min), respectively. The adsorption rate constant k_1 was determined from the slope of the linear plots of log (q_e–q_t) vs. *t* (Fig. 6).

The pseudo-second-order adsorption kinetic model (Eq. (2)) is given as [38]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (2)$$

The values of q_e (1/slope) and adsorption rate constant k_2 (slope^2/intercept) can be obtained by plotting t/q_t vs. *t* (Fig. 7).

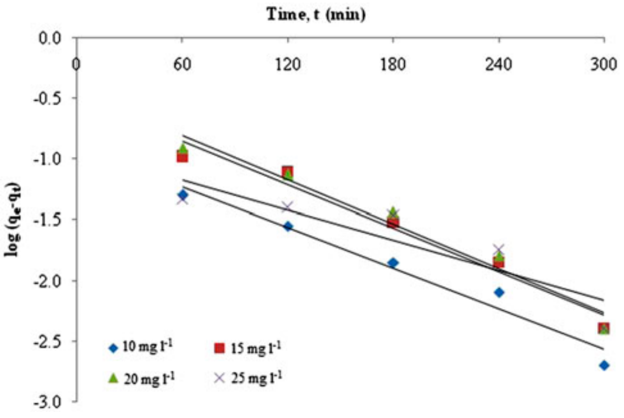

Fig. 6. Pseudo-first-order kinetic plot for fluoride adsorption on HBO_2.

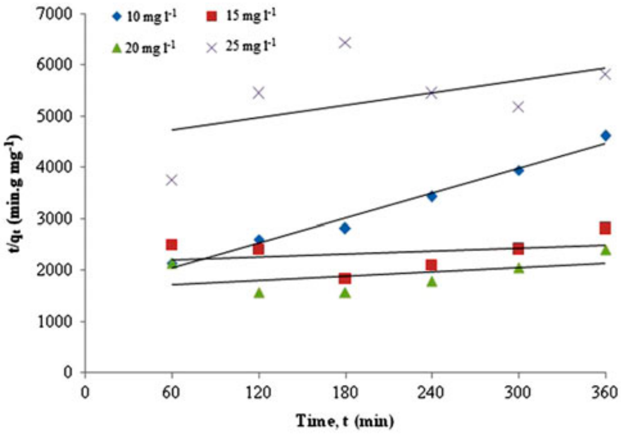

Fig. 7. Pseudo-second-order kinetic plot for fluoride adsorption on HBO_2.

Weber–Morris model (Eq. (3)) is used to know the possible contribution of intra particle diffusion on fluoride adsorption by HBO_2. The linear form of intra particle diffusion model given by Weber–Morris [39] is:

$$q_t = k_i t^{0.5} \qquad (3)$$

where k_i can be obtained from the slope of the plot of q_t vs. $t^{0.5}$.

The plots show good linearity ($R^2 = 0.953$, 0.944, 0.952 and 0.932). The values of intra particle diffusion rate constants k_i were calculated from the slopes of the plots from Fig. 8 and were found to be 0.004590, 0.010005, 0.011164, and 0.004461 mg g^{-1} $min^{0.5}$ for initial fluoride concentrations of 10, 15, 20, and 25 mg l^{-1}, respectively). In our findings the value of intercepts were −0.00385, −0.5023, −0.04811, and −0.02406.

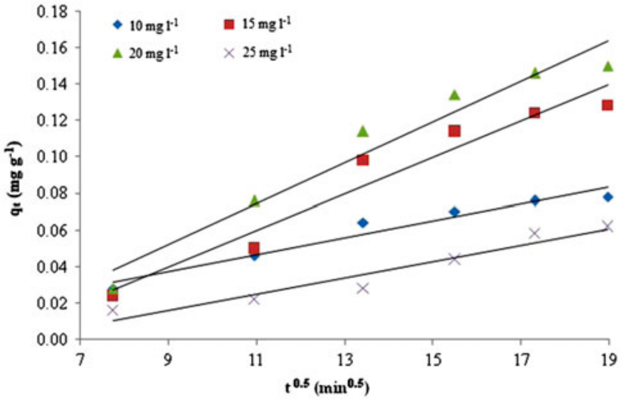

Fig. 8. Weber–Morris intraparticle diffusion plot for fluoride adsorption on HBO_2.

The adsorption kinetics constants and their correlation coefficients (R^2) obtained from the above models are given in Table 1.

Based on correlation coefficient (R^2) of linearized forms of kinetic models, the experimental data fitted the intraparticle diffusion model for all the initial concentrations of fluoride. However, pseudo-first-order kinetic model also shows good linearity except at 25 mg l^{-1} initial fluoride level than pseudo-second-order kinetic agreements. If the values of correlation coefficient (R^2) are in linear relation, it represents the control of sorption by intra particle diffusion and solute ions diffuse within the pores and capillaries of the adsorbent and provide available sites for adsorption [40]. Moreover, in intra particle diffusion plot, non-zero intercepts are taken as an indication of slow diffusion process and not being the sole governing factor [41]. Biswas et al. [13] referred such systems as "complex" in case of adsorption of fluoride by hydrated iron (III)–aluminum (III)–chromium (III) ternary mixed oxide and inferred that surface adsorption was responsible for removal along with diffusion. The increasing values of k_i with concentration indicate concentration diffusion [42,43]. Thus, as the values of k_i are increasing with increasing fluoride concentration up to 20 mg l^{-1}, the removal of fluoride by HBO^1 in this concentration range may be due to the concentration diffusion process.

3.9. Effect of temperature

The effect of temperature on fluoride removal by HBO_2 was investigated at different temperatures 293, 303, 313, and 323 K and has been given in Fig. 9.

The removal of fluoride by HBO_2 increased with increase in temperature. The removal increased from 39 to 84% at 10 mg l^{-1} (Fig. 9) concentration while temperature was increased from 293 to 323 K. The fluoride adsorption amount (q_e) (mg g^{-1}) on HBO_2 is found increasing with increase in temperature. The value of q_e increased from 0.078 to 0.316 mg g^{-1} while initial fluoride concentration was increased from 10 to 25 mg l^{-1} and temperature changes from 293 to 323 K. An increase in adsorption with rise in temperature may be due to activation of more sites on the surface of adsorbent with increase in temperature [44]. Mohapatra et al. [5] explained that increase in adsorption capacity (q_e) of fluoride with increasing temperature is due to control of the adsorption process by diffusion phenomenon. It is clear from the result that the removal of fluoride increased with increasing temperature and has indicated the endothermic nature of process for fluoride removal by HBO_2.

3.10. Isotherm studies for the removal of fluoride by HBO_2

Linearized forms of Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) equations were used to describe the fluoride adsorption on HBO_2 and the isotherm parameters of various isotherms are compiled in Table 2 as given below.

On the basis of correlation coefficient (R^2) values of all the three isotherms, none was found in very good linear relation. However, the R^2 values of D–R isotherm may be almost in linear relation except at 303 K temperature (Table 2).

Table 1
Kinetic parameters for fluoride adsorption on HBO_2

	Pseudo-first order			Pseudo-second order			Intraparticle diffusion	
C_i (mg l^{-1})	k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2	k_i (mg g^{-1} $min^{0.5}$)	R^2
10	0.01282	0.1262	0.962	0.0419	0.1236	0.980	0.004590	0.953
15	0.01373	0.3159	0.964	0.0004	1.1111	0.090	0.010005	0.944
20	0.01394	0.3575	0.963	0.0012	0.7179	0.223	0.011164	0.952
25	0.00948	0.1178	0.801	0.0036	0.2482	0.256	0.004461	0.932

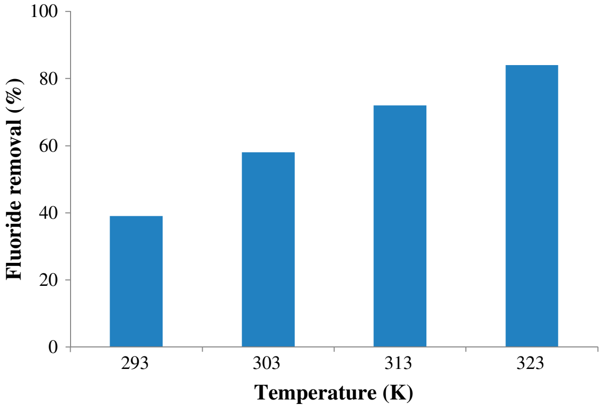

Fig. 9. Effect of temperature on removal of fluoride by HBO_2.

The mean adsorption energy (E) was calculated from the constant K of D–R isotherm using the relation given below [43]:

$$E = (2K)^{-1/2} \tag{4}$$

If the value of E is between 8 and 16 KJ mol^{-1}, the adsorption process follows chemical adsorption, while the value of E below 8 KJ mol^{-1} indicates the physical adsorption [7]. From the D–R isotherm the values of E were found to be 0.169, 0.180, 0.260, and 1.286 KJ mol^{-1}, respectively, for fluoride adsorption which is related to the physical adsorption and regeneration of adsorbent may be possible if physical adsorption is a prevailing phenomenon [45].

HBO has a definite potential to remove anions from aqueous solutions like nitrate, sulfate, and bicarbonate [30]. Singh et al. [30] reported preparation and properties of HBO_2 and HBO_3 adsorbents, which were found to be efficient for nitrate removal from aqueous solutions. As HBO_2 was found to be superior to remove nitrate from aqueous solutions, a scope of fluoride adsorption was also tested with the same adsorbent during present study. The value of mean adsorption energy (E) was calculated using D–R isotherm for fluoride adsorption on HBO_2 adsorbent and the value of E was found to be 0.169, 0.180, 0.260, and 1.286 KJ mol^{-1}, respectively at different temperatures, which is related to the physical adsorption [45]. Two possible reasons are already discussed to explain the increase in fluoride adsorption on HBO_2 along with increase in temperature: either due to activation of more number of sites on the surface of adsorbent with increase in temperature [44], or due to control of the adsorption process by diffusion phenomenon [5].

3.11. Adsorption capacities of different adsorbents for fluoride removal

Adsorption capacities (Langmuir's) of adsorbents vary with pH, initial concentrations of adsorbate,

Table 2
Isotherm parameters of Langmuir, Freundlich, and D–R equations for HBO_2

	Langmuir parameters		Freundlich parameters		D–R parameters	
Temp. (K)	q^0 (mg g^{-1})	b (l mg^{-1})	K_F (mg g^{-1})	n	q_m (mg g^{-1})	E (KJ mol^{-1})
293	0.32	0.06	0.036	1.96	0.1692	0.169
303	0.20	0.44	0.112	6.42	0.1799	0.180
313	0.34	0.29	0.106	2.70	0.2601	0.260
323	0.337	0.65	0.227	6.48	0.2858	0.286

Table 3
Langmuir adsorption capacities (mg g^{-1}) of adsorbents used in fluoride removal

Adsorbents	Langmuir adsorption capacity (mg g^{-1})	References
Calcite	0.39	[55]
Quartz	0.19	
Manganese dioxide-coated alumina	0.16–0.17	[56]
Synthetic hydroxyapatites	0.30–0.49	[57]
Bleaching powder	0.13	[58]
Activated alumina	1.1	[59]
TiO_2 adsorbent	0.69–0.85	[60]
Various low cost adsorbents	0.52–0.72	[61]
Hydrous bismuth oxide (HBO_2)	0.32–0.34	Present study

temperature, dosage etc. Recently, efforts are being made to develop efficient as well as economically viable adsorbents for the removal of contaminants from water. In this regards, several types of adsorbents including activated alumina [46], activated carbon [47], amorphous alumina [48], bleaching earth and clay [49], calcite [50], charcoal and zeolites [51], red mud [52] etc. have been reported (Table 3) for the removal of fluoride from aqueous solutions. Mostly, the adsorbents are not found suitable to bring down the fluoride level for drinking purpose [53,54].

It is clear from the reported work that the adsorbent was found efficient for the removal of nitrate from aqueous solutions. The regeneration of present adsorbent is possible, and the cost of treatment can be minimized. The Langmuir adsorption capacity (mg g^{-1}) of fluoride removal by HBO_2 adsorbent was found in 0.32–0.34 range along with rise in temperatures, which seems better than some adsorbents reported by various workers for quartz, manganese dioxide-coated alumina, and bleaching powder [55–58]. Therefore, during present study, the possibility of fluoride removal through the same adsorbent was also explored with an objective of developing single adsorbent for the removal of both the nitrate and fluoride from water for drinking purpose.

3.12. Effect of competing anions on removal of fluoride

Effect of presence of bicarbonate, sulfate, and chloride on fluoride removal by HBO_2 was observed with increasing anion concentrations from 1 to 5 meq l^{-1} of each of the ions (Fig. 10).

It is observed that the presence and increasing concentrations of all the three anions, viz bicarbonate, sulfate, and chloride reduce the fluoride removal potentials of HBO_2. For HBO_2, the effect of anions on fluoride removal is observed as:

Chloride > Sulfate > Bicarbonate.

It is a well-known fact that pH of any solution depends on the presence of bicarbonate, carbonate, or hydroxide species. Hence, it was inferred that increase in bicarbonate species competed with fluoride and the present adsorbent preferred bicarbonate over fluoride. It is reported that chloride and sulfate are outer-spherically sorbing anions [62], and these anions get readily adsorbed on the surface of HBO_2 than fluoride being an inner-spherically sorbing anion. Consequently, the removal of fluoride was found to decrease in the presence of bicarbonate. The hydration energy of chloride is lower (ΔG°, -363 KJ mol^{-1}) than sulfate (ΔG°, $-1{,}163$ KJ mol^{-1}). Perhaps due to this reason, chloride was adsorbed rapidly and was the strongest competing ion for fluoride adsorption by HBO_2. The anions have lower hydration energy and are adsorbed very fast with respect to the anions which have greater value of hydration energy [63,64].

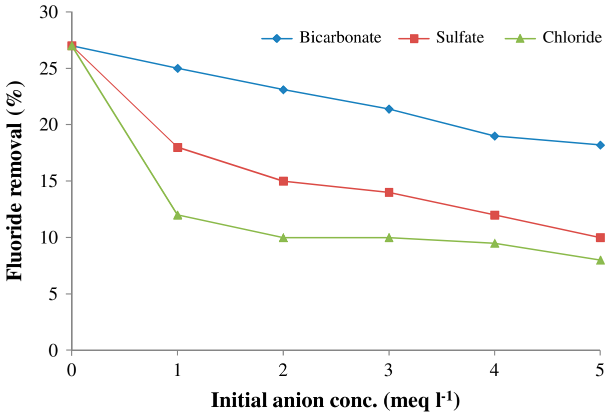

Fig. 10. Effect of competing anions on removal of fluoride by HBO_2.

4. Conclusion

HBO_2 has the potential to remove fluoride from water. The pH of treated water was recorded around 7.3 and this is under permissible range. This indicates that there is no hydroxyl ion replacement in water due to fluoride sorption on the adsorbent. Presence of OH group on the surface of present adsorbent was confirmed by FTIR analysis. Rough surfaces having some pores were also observed with the help of SEM image analysis. As the initial concentration and temperature of solution increases, the adsorption capacity of HBO_2 got increased. Up to pH 9.0, the removal of fluoride was almost at similar levels, after that it was found to decrease drastically. Hence, HBO_2 adsorbent can work over a wide range of pH for fluoride adsorption. After 3 h of contact time it was observed that the removal percentage was almost constant and attained almost an equilibrium condition. With the increase in adsorbent dosages fluoride removal was also increasing. As the temperature of solution increases the adsorption capacity and removal percentages were also increased (from 39 to 84%) and indicated the endothermic nature of fluoride removal process. Intra particle diffusion model was found in better linear relation than pseudo-first-order and pseudo-second-order kinetic models. While pseudo-first-order kinetic model fitted quite well for 10–20 mg l^{-1} initial fluoride concentration but reduced for 25 mg l^{-1} concentration level.

The value of pH_{PZC} of HBO_2 was found to be 7.9. The mean adsorption energy (*E*) calculated from D–R isotherm indicated that the physical adsorption was operative for fluoride removal and that can be regenerated. Detailed studies have further to be conducted prior to applying the synthesized material for treatment of drinking water at large scale.

Acknowledgment

The authors are thankful to Department of Science and Technology (DST), Government of India for providing financial support under WTI program.

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