



Application of Hydrous Bismuth Oxide for Arsenic Removal from Aqueous Solutions

Manish Ranjan*†, Prabhat Kumar Singh* and Arun Lal Srivastav**

*Department of Civil Engineering, Indian Institute of Technology (BHU), Varanasi, India

**Chitkara University School of Engineering and Technology, Chitkara University, Himachal Pradesh, India

†Corresponding author: Manish Ranjan; manish040533@gmail.com

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 10-04-2020

Revised: 02-06-2020

Accepted: 04-06-2020

Key Words:

Arsenic removal
Metal pollution
Hydrous bismuth oxide
Langmuir isotherm
XRD; SEM

ABSTRACT

The present study is devoted to arsenic sorption on hydrous bismuth oxide (HBO) through batch and column studies. Advantage of the adsorbent includes arsenic removal in addition to the simultaneous removal of nitrate and fluoride from aqueous solution. Both the forms of arsenic tested by adsorbent in which affinity for arsenic (V) was found better than arsenic (III). Langmuir isotherm and pseudo-second-order kinetic models were found a fit with the experimental data. Calculation of adsorption energy and increased level of chloride in treated water indicated the possible role of physical adsorption and ion exchange phenomenon in arsenic(V) sorption. A fixed bed column study gave 615 mL of treated water [As (V) \leq 0.01mg/L] from 0.085 mg/L arsenic (V) spiked influent with a sorption potential of 13.1-19.6 μ g/g. XRD and EDS analyses confirmed the adsorption of arsenic (V) and the presence of chloride in the exhausted bed of adsorbent. The thermodynamic parameter has shown the endothermic and spontaneous process of adsorption.

INTRODUCTION

Groundwater is a major source of drinking water and its per capita availability is getting reduced over the last decades because of chemical contamination, hence its quality needs to be protected. Arsenic is one of the major groundwater contaminants widely found in the eastern regions of Indian sub-continent (Nath et al. 2008). Due to the adverse health effects including carcinogenic nature (Sarkar & Paul 2016), the maximum allowable concentration of arsenic in drinking water set by United States Environmental Protection Agency (USEPA) is 0.01 mg/L (Iesan et al. 2008). World Health Organization also recommended the maximum permissible limit of arsenic as 0.01 mg/L in drinking water (Vaclavikova et al. 2008). Hence, excess of arsenic in ground water used for drinking is toxic to humans and could be taken as serious threat for human health (Srivastav & Ranjan 2020). The removal of arsenic by adsorption process was studied in the present paper.

Arsenic is a semi-metal and commonly found in four oxidation states of +5, +3, 0, -3. Inorganic arsenic acids or arsenates (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-}) are found in the oxidation state of +5 and collectively referred as As(V), whereas arsenous acids or arsenites (H_3AsO_3 , H_2AsO_3^- , HASO_3^{2-} and AsO_3^{3-}) are found in the oxidation state of +3 and collectively referred as As(III) (Zhou et al. 2017). The

solubility of arsenic is greatly affected by pH of the solution (Mudhoo et al. 2011). Arsenic (V) predominates as H_3AsO_4 in aerobic waters (high redox potential) with lower pH (<2) whereas arsenic species H_2AsO_4^- and HASO_4^{2-} are found in pH range of 2-11 as shown in Fig. 1 (Khan et al. 2004). Similarly, arsenic (III) exists as H_3AsO_3 at low pH (<3) but gets easily replaced by H_2AsO_3^- as the pH increases beyond 9.2 and further at high pH (>12), only HASO_3^{2-} can be observed in water as shown in Fig. 1 (Mudhoo et al. 2011). Hence, pH is one of the prime factors for redox equilibrium (Fig. 1) between arsenic (V) and arsenic (III) thus, arsenic speciation and its mobility is greatly affected by pH as well as the redox potential (Doušova et al. 2003). But, oxygen present in air leads to an increase in the redox potential of the groundwater when it is exposed to the open atmosphere. Consequently, arsenic (III) immediately changes into arsenic (V) (Ngai et al. 2006). Hence, arsenic (V) is a dominant species over arsenic (III) in an oxidative environment (Sarkar & Paul 2016). The major component of arsenic (V) in aqueous environment are 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).

Adsorption process is one of the widely applied methods to remove arsenic from water due to its simplicity (Bhatnagar & Sillanpaa 2011). Many inorganic adsorbents are investigated for water treatment because organic

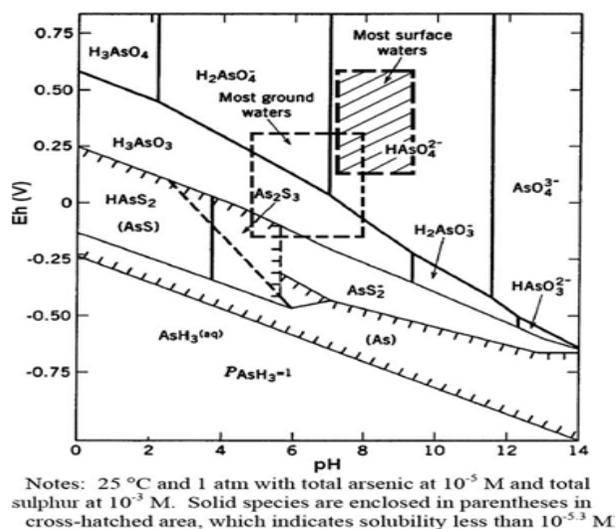


Fig. 1: Eh-pH diagram for arsenic (Mudhoo et al. 2011)

adsorbents reported to have fouling problems (Ustun et al. 2007). In the water, it is observed that metal oxide has a high affinity towards negatively contaminants (Yao et al. 2011). Several researchers have examined the application of hydrous metal oxide (HMO) as adsorbents for arsenic remediation from aqueous solutions. Hydrous metal oxides (HMOs) are amongst the largest group of studied inorganic materials because of having advantages like suitability for sorptive filtration and ease in regeneration and reuse. Among various metal oxides the oxide of titanium (Wagle & Shipley 2016), iron (Puente-Urbina & Montero-Campos 2017), activated alumina (Sinha et al. 2011), zinc (Li et al. 2011), aluminium (Park et al. 2012) and zirconium (Chaudhry et al. 2017) have been reported with good arsenic sorption capacity from water. Researchers have also used mixed oxides like Fe-Ti (Gupta & Ghosh 2009), Ce-Ti (Li et al. 2010), Fe-Zr (Ren et al. 2011), Fe-Cr (Basu & Ghosh 2011), Fe-Al (Basu et al. 2012), Fe-Cu (Zhang et al. 2013), Fe-Mn (Kong et al. 2014), Mn-Al (Wu et al. 2017), Zr-Ti (Anđelković et al. 2017), Fe-Ti-Mn composite oxide (Zhang et al. 2018), Fe/Al composite (Inchaurrondo et al. 2019) and Fe_3O_4 @ TiO_2 sheets nanocomposite (Deng et al. 2019) for the same.

A thorough literature review reveals that hydrous metal oxide has been used by many researchers for the removal of arsenic from water. Recently, hydrous bismuth oxide (HBO) is reported to have excellent and promising adsorptive properties of nitrate and fluoride sorption from aqueous solution. Initially, Fritsche (1993) found sorptive property of yellow bismuth hydroxide for nitrate removal. Further, Singh (1999) investigated the potentials of various bismuth compounds for nitrate removal from aqueous solution due to the ion exchange of nitrate with embedded chloride of

HBO. Hydrous Bismuth Oxide (HBO) is the precipitated product of bismuth trioxide in the presence of strong acid with a strong base. A ratio of 1:1 is used to make precipitate, which is designated as HBO1, similarly 1:2 and 1:3 named as HBO2 and HBO3 respectively. Excess of strong base results in polymerizations of HBO as reported by Ranjan et al. (2019). HBO2 and HBO3 are the final polymeric products of hydrous bismuth oxides which have excellent nitrate removal efficiency (82%) at the initial nitrate concentration of 62 mg NO_3^-/L (Singh et al. 2012). Further, Srivastav et al. (2014) reported a maximum sorption potential of 0.992 mg NO_3^-/g by HBO2 with 62 mg NO_3^-/L initial concentration in batch experiments. In another study, Singh et al. (2015) reported 0.974 mg NO_3^-/g nitrate sorption using HBO3 at neutral pH. Srivastav et al. (2013) observed that HBO1 has 0.196 mg F^-/g sorption potential at 20 mg F^-/L initial concentration. However, HBO2 could remove only 51% fluoride at 10 mg F^-/L of initial concentration with 100 g/L adsorbents Srivastav et al. (2015). To increase the anionic sorptive potential of HBO powders, Ranjan et al. (2015); (2019) prepared HBO2 adsorbent in the presence of varying concentrations of cations like Fe, Ca, Mg and Cu. This leads to increase the fluoride removal efficiency by 31% when HBO2 prepared in presence of 0.1M MgCl_2 with respect to unamended HBO2, whereas, HBO2 in presence of 0.07 M FeCl_3 found gainful to increase the nitrate sorption potential. Characterization of prepared materials has confirmed the presence of cationic ligands in the matrix of HBO2 material. Hence, the material exhibited high adsorption capacities towards nitrate (NO_3^-) and fluoride (F^-).

Based on the affinity exhibited by hydrous bismuth oxide towards major anionic contaminants (i.e., nitrate and fluoride) the possibility of arsenic removal from aqueous solution was tested and discussed in the present study. Adsorption behaviour of arsenic (V) and arsenic (III) by hydrous bismuth oxide (HBO1) was compared by keeping them under the same condition (Fig. 2).

Of both, arsenic (III) and arsenic (V) removals were examined by HBO1 under similar condition. But, removal efficiency for arsenic (V) was found to be 16.5% greater than arsenic (III). Lower adsorption of arsenic (III) can be better correlated to the uncharged (Fig. 2) form of arsenic species in environment relevant pH (Zhu et al. 2016). Hence, arsenic (V) removal using HBO1 was chosen for further experiments during the present study.

MATERIALS AND METHODS

Arsenic Solutions

4.1601 g of sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, E. Mark,

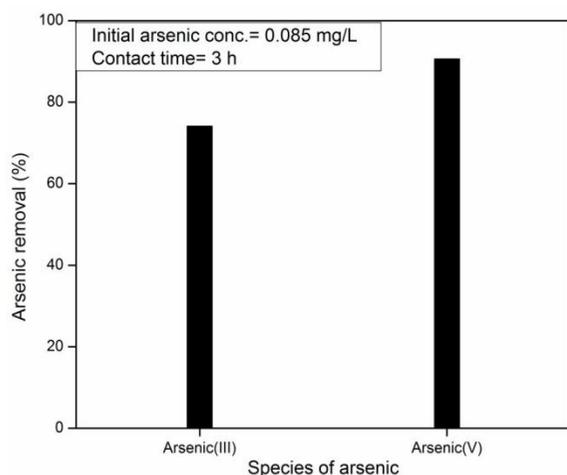


Fig. 2: Percentage removal of arsenic.

Germany) was dissolved in one litre of double distilled water in order to make 100 mg/L stock solution of arsenic (V). Further dilution methods were used for making the working solutions of arsenic.

Preparation of Hydrous Bismuth Oxide (HBO)

Hydrous Bismuth Oxide (HBO) was prepared by using bismuth trioxide powder of commercial AR grade. 0.1 M Bi_2O_3 was prepared by dissolving bismuth trioxide in 2N HCl solutions and precipitated hydrous bismuth oxide was obtained as per the method reported by Singh et al. (2012). Three forms of HBOs designated as HBO1, HBO2 and HBO3 were prepared using 0.1 M Bi_2O_3 solution in 2N HCl with successively increasing volumetric proportions of 2N NaOH in the ratio of 1:1, 1:2 and 1:3 respectively. The obtained precipitates were washed with distilled water till pH and chloride reduce to a minimum level. It is then kept in the oven drying at $103 \pm 2^\circ\text{C}$ for 24 h (Srivastav et al. 2015). HBO1 was visibly white in colour but yellow precipitate has been shown by HBO2 and HBO3. All three forms of Hydrous Bismuth Oxide (HBOs) was found better in the arsenate removal from water hence, HBO1 was selected for further study due to less cost of synthesis.

Measurement of Arsenic Concentration

Arsenator (Model No: Wag-WE10500 made by Wag-Tech, England) was used for determination of arsenic concentration in aqueous solutions.

The performance of adsorbent for arsenic removal was calculated by using equation (1):

$$\text{Arsenic removal (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

Where, C_0 and C_e are the initial and final concentrations of arsenic in mg/L.

Experiments with triplicate samples were carried out in at a controlled temperature of $25 \pm 2^\circ\text{C}$ and an average value is reported. Digital pH meter was used for the determination of pH. Sulphate, chloride and alkalinity (bicarbonate) were determined by titration method as given in Standard Method (Clesceri et al. 2005). Bismuth ion in treated water was determined by Atomic Absorption Spectrophotometer (Model AAS4141, ECIL, India).

Batch Experiment

A standard solution of 0.10 mg/L of arsenic (V) concentration was prepared from stock solution. Powder dosage of 6 g/L was taken with continuous stirring for 180 minutes. Finally, the powder was removed by using Whatman 42 filter paper and determination of pH, remaining arsenic, and chloride concentrations were carried out for filtrate. For kinetic studies, 100 mL of 0.05, 0.10, 0.15, 0.20 and 0.25 mg/L arsenic solution was taken for varying contact time from 60 to 360 minutes with 6 g/L adsorbent dosage at 298K. After 60 minutes of time interval, the filtrate was collected through Whatman 42 and pH, remaining arsenic and chloride was determined. Equilibrium studies were carried out on varying initial arsenate concentration from 0.05 to 0.25 mg/L. 100 mL of 0.05, 0.10, 0.15, 0.20 and 0.25 mg/L arsenic solution, with an initial neutral pH condition at temperatures of 298, 308 and 318 K were mixed with an adsorbent dose of 6 g/L with contact period of 180 minutes in agitating condition.

Column Experiment

The particle size of HBO1 powder is very fine and to use in column adsorption study, HBO1 powder and sand was mixed in the ratio of 1:4 (w/w). The sand was initially soaked in 0.1 N HCl for 24 h and then washed with sufficient distilled water. A glass column was filled up to the height of around 12 cm with the mixed media ($d_{10} = 0.18$, $C_u = D_{60}/D_{10} = 2.4$, $\text{pH} \sim 7.0$). A simulated solution of 0.085 mg/L arsenic (V) was taken for column study which resembles with the level of arsenate present in groundwater of our country. The arsenic contaminated water was passed with a flow rate of 1.23 mL/min, (EBC = 30.65 minutes). The samples of effluents were collected at a scheduled time interval and used for the determination of pH, chloride and arsenic concentration.

Characterization

To diagnose chemical species and structural arrangement of adsorbent (HBO1), the characterization was carried out using X-ray diffraction (XRD), Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The information about possible structural compound formed could be obtained from the X-ray diffraction pattern by X-ray

diffraction (Philips, Netherlands, 1710). Surface morphology and elemental analysis have been done by SEM and EDS (ZEISS EVO 18 Model-2045, Industrial Measurements and Medical Devices, Germany).

RESULTS AND DISCUSSION

Batch Experiment for Arsenic (V) Removal

The results of As (V) removal using hydrous bismuth oxide (HBO1) from aqueous solutions with 0.10 mg/L initial arsenic (V) concentration are given in Table 1.

Excellent removal efficiency (> 90%) of arsenic was observed using HBO1 powder is a significant finding of the present observations with 0.10 mg/L initial concentration in groundwater. The obtained pH water quality after treated water was in the range 8.3-8.5 indicating hydroxide ions were not eluted during As(V) adsorption. Hence hydroxide ions are not competing for anions for arsenic sorption on

HBO1. Chloride could be caustic agent for As(V) removal. Chloride seems to attach with the bismuth as loose bond and could be able to go for transitional exchange with As(V) under suitable condition, whereas hydroxide strongly bonded with bismuth and couldn't avail changes. Similar results were demonstrated by Ruixia et al. (2002) and Singh et al. (2012) with highlighting an elevated level of chloride in the effluent. Park et al. (2008) concluded the fluoride and nitrate sorption by cement paste column as the result of ion exchange mechanism.

Effect of Adsorbent Dosage

The effects of adsorbent dosage on As(V) removal and final pH were also studied and it ranges from 1 to 10 g/L with 180 minutes of contact time and 0.10 mg/L of initial As(V) concentration.

From Fig. 3a, it is observed that 6 g/L dosage was optimum for As(V) removal using HBO1 adsorbent.

Table 1: arsenic (V) sorption at different adsorbent dosage.

S No.	Dosage of HBO1 (g/L)	Water quality before treatment		Water quality after Treatment			Removal efficiency (%)	Chloride Exchange Ratio = Chloride eluted/ Arsenic sorbed
		pH	Cl ⁻ (mg/L)	pH	As(V) (mg/L)	Cl ⁻ (mg/L)		
1.	1	7.3	6.6	8.38	0.034	27	66	0.56
2.	2	7.2	6.6	8.40	0.023	22	77	0.56
3.	3	7.3	6.6	8.43	0.019	30	81	0.61
4.	4	7.4	6.6	8.40	0.012	31	88	0.59
5.	5	7.3	6.6	8.46	0.007	33	93	0.60
6.	6	7.4	6.6	8.52	0.006	37	94	0.62
7.	7	7.5	6.6	8.34	0.006	32	94	0.64
8.	8	7.3	6.6	8.46	0.006	31	94	0.62
9.	9	7.6	6.6	8.44	0.006	33	94	0.64
10.	10	7.5	6.6	8.47	0.006	28	94	0.62

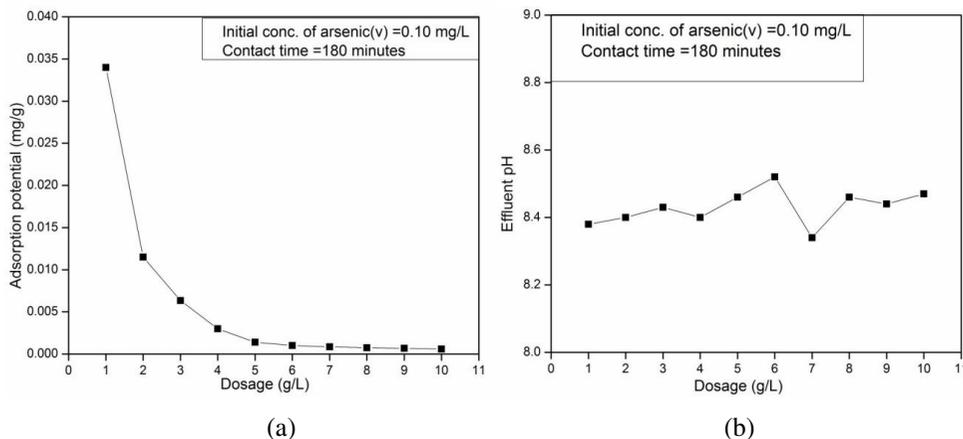


Fig. 3(a): Variation of adsorbent dosage on As(V) sorption. 3(b): Variation of adsorbent dosage on effluent pH.

Abundant numbers of adsorption sites are available at low dosages, but at higher dosages overlapping of active sites may reduce the effective surface area of adsorbent (Luther et al. 2012). Hence, further experiments were done by considering 6 g/L as optimum dosage for As(V) sorption.

Fig. 3b shows the treated water pH on As(V) removal with different dosages of HBO1 powder. It is observed that the solution pH did not get affected significantly due to As(V) removal by HBO1 in aqueous solution. Similar observations have been reported by Srivastav et al. (2014) and Singh et al. (2015) in his study for nitrate sorption by HBO2 adsorbent.

Effect of Contact Time

The variation of contact time on the adsorption of As(V) from the water was studied by taking five initial concentrations (0.05, 0.10, 0.15, 0.20 and 0.25 mg/L) of As(V) by hydrous bismuth oxide (HBO1). The contact time ranged from 60 to 360 minutes (Fig. 4a) and a time interval of 60 minutes was selected for samples collection.

Initially, 70-80 % of removal was reported in the initial contact time of 180 minutes and further, the rate of removal became slow or insignificant. During the initial stage, large numbers of active sites are available for adsorption but as the reaction progresses, the active sites are no longer available to occupy because of saturation (Swain et al. 2012). Hence, 180 minutes considered to be the optimum contact time for arsenic removal from aqueous solution for further studies. It was confirmed by Singh et al. (2015) with experimental data showing the maximum adsorption took place in the first 180 minutes of contact time.

Chloride Exchange Ratio (CER)

The effluents were found to have elevated levels of chloride with respect to the influent. Hence, HBO1 may contain some

amount of chloride sorbed in its material matrix, which could be exchanged with arsenic during sorption process. During equilibria study, apart from As(V) concentration, chloride level of treated water was also determined. Chloride Exchange Ratio (CER) may be defined as:

$$\text{CER} = \text{Chloride eluted (meq/g)} / \text{arsenic (V) taken up (meq/g)}$$

An analysis of total As(V) sorbed and chloride eluted in the water at a different dose of hydrous bismuth oxide (HBO1) was carried out. It is observed that CER of hydrous bismuth oxide (HBO1) is found in the range of 0.59 - 0.64. It indicates that possibly partial As(V) removal is through ion exchange mechanism with embedded chloride in HBO1 matrix. The nitrate removal experiment using yellow bismuth hydroxide and yellow hydrous bismuth oxide had been carried out by Fritsche (1993) and Singh et al. (2012) respectively. The authors emphasized the ion exchange mechanism responsible for nitrate sorption. No leaching of bismuth ion and increased concentration of chloride in treated water may be indicative of partial exchange of chloride with sorbed As(V) ions.

Effect of Competitive Anions

The presence of competitive ions bicarbonate (as alkalinity) and sulphate may hinder the adsorption of As(V) and because of this reason their effect has been also studied in the range from 1 to 5 meq/L (Fig. 4b) with 0.10mg/L initial As(V) concentration level.

It can be noted that As(V) removal efficiency of HBO1 decreased in order as given below:



The lower hydration energy of bicarbonate ion could be the reason for fast competing anions among bicarbonate ($\Delta G^\circ = 380$ KJ/mol) and sulphate ($\Delta G^\circ = -1,103$ KJ/mol).

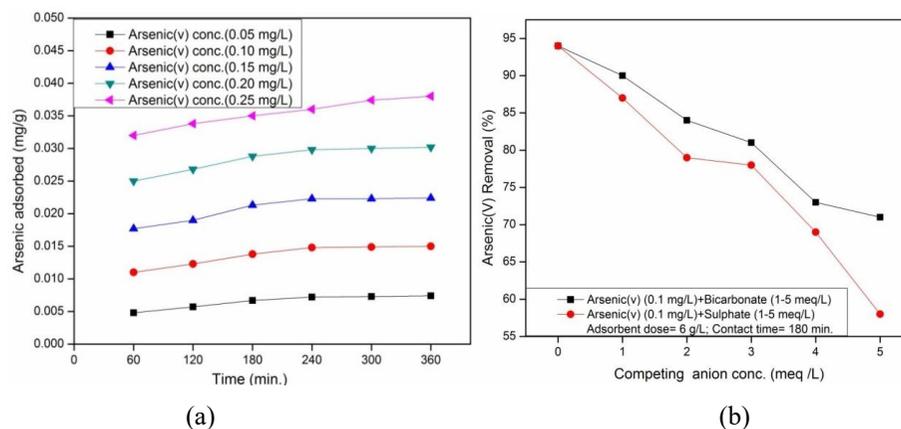


Fig. 4 (a): Effect of contact time on As(V) sorption. 4(b): Effect of competing anion on As(V) sorption.

Hydration energy with low value has more affinity towards adsorption in comparison to the ions which has high hydration energy (Gu et al. 2004, Song et al. 2012).

Column Experiments for As(V) Removal

The column study has also been done for enhancing the field applicability of HBO1 adsorbent in water treatment. A glass column (2cm diameter) was filled upto 12 cm depth with HBO1 powder mixed homogeneously with inert sand particles (1:4 ratio). As(V) solution was passed through the column with an influent concentration of 0.085 mg/L and 1.23 mL/min flow rate, which gave empty bed contact time (EBCT) as 30.65 minutes. Effluent samples were analysed for remaining As(V) concentration. The pH and breakthrough curve is shown in Fig. 5.

It is observed that the breakthrough of the column occurs around 500 minutes of duration after passing 615 mL of contaminated water, which gave a complete As(V) removal by consuming 13.1 µg/g of HBO1 adsorbent. The exhaustion point was found after 750 minutes after passing about 922 mL of contaminated water by consuming 19.6 µg/g adsorbent. Hence, fixed bed column study using HBO1 as adsorbent produces 615 mL of drinking water (As(V) ≤ 0.01mg/L) free from As(V) (0.085 mg/L) at inflow rate of 1.23 mL/min and pH 7.0 (±0.1), which indicates the applicability of HBO1 for arsenic removal from the aqueous solution. In a similar study, Fritsche (1993) conducted experiments using yellow bismuth hydroxide in column study for nitrate and other anions removal experiment and found 93 % of nitrate removal with 58.6 mg/L as influent nitrate concentration. Whereas in another study Singh et al. (2012) revealed the nitrate sorption through hydrous bismuth oxide (HBO2 and HBO3) in column study and reported the 5.31 mg/g and 6.2 mg/g of nitrate sorption capacity of adsorbent with 62 mg/L of nitrate as influent

using 5 g of wet precipitate of yellow hydrous bismuth oxide each.

Characterization

XRD analysis: Fig. 6 shows the XRD pattern of HBO1 which exhibits many peaks at 2 theta values of 24°, 26.2°, 29.57°, 30.24°, 32.72°, 47.1° and 57.2°. Crystalline nature of adsorbent was confirmed by the presence of sharp peaks (Ramli et al. 2007). Peaks corresponding to 2θ = 29.57, 30.24 and 32.72 are related with Bi₁₂O₁₇Cl₂ (File no-370702) as per the X-pert high score software (2009) which confirms the crystalline nature of HBO1. The observed composition of hydrous bismuth oxide (Bi₁₂O₁₇Cl₂) indicates the presence of chloride inside it and similar results were also observed by Srivastav et al. (2013).

SEM and EDS: The SEM image of HBO1 before and after As(V) adsorption was taken to know its surface characteristics with magnification: 50 K and 200 nm resolution (Fig. 7). The smooth surface and spherical nature of grains were found before adsorption but relatively high rough surface and angular grain were spotted after adsorption. The elemental analysis of the raw and exhausted adsorbent was also studied. The point of incidence of the spectrum and the resultant EDS spectrum for each test is attached and the elements found are shown in Fig. 7. Bismuth and chloride are the compositions of HBO1 before adsorption and but, after adsorption As(V) become an integral part of HBO1. This is probably due to the active chloride ion present in the matrix of adsorbent and with suitable condition its gets partially exchange with chloride and partially adsorbed in the rough surface of the adsorbent. Thus, appearance of As(V) in the exhausted adsorbent indicates that sorption of As(V) has possibly taken place on HBO1.

Kinetic studies: Kinetics studies have been conducted to evaluate the performance of a given adsorbent and mechanism

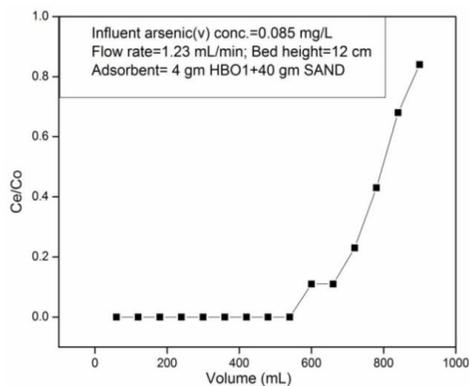


Fig. 5: As(V) sorption through column experiment.

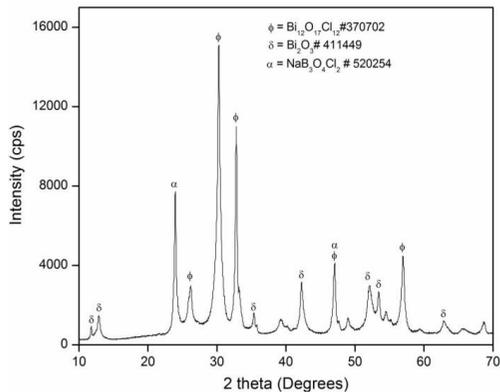


Fig. 6: XRD pattern of HBO1 powder.

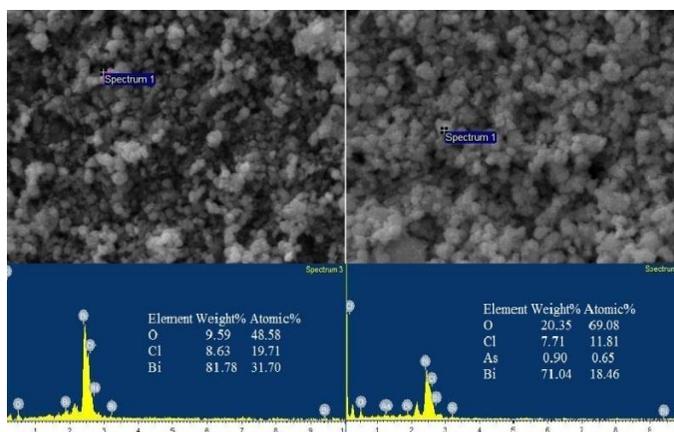


Fig. 7: SEM and EDS of HBO1 before and after adsorption.

of removal. In order to understand the sorption mechanism, three kinetic models have been applied with experimental results. Effect of five initial As(V) concentration (50, 100, 150, 200, 250 $\mu\text{g/L}$) and variation in contact time (60 minutes to 360 minutes) was observed. It was noticed that most of the arsenic removal took place within 180 min. and adsorption capacity increased from 4.8 to 36 $\mu\text{g/g}$. Pseudo-first-order, Pseudo-second-order and Weber-Morris kinetic models were applied to validate experimental data and derived kinetics parameters are given in Table 2.

Pseudo-first order: Lagergren (1898) presented a first-order rate equation to describe the kinetic process of liquid solid phase adsorption as mentioned in eq (2):

$$\log(q_e - qt) = \log q_e - \frac{K_1}{2.303t} \quad (2)$$

Where, q_e and q_t are adsorption capacity ($\mu\text{g/g}$) at equilibrium and at any time t ; K_1 = pseudo-first-order rate constant (time^{-1}). The linear interpolation of slope from the plots between $\log(q_e - q_t)$ versus t will give the adsorption rate constant (K_1). Fig. 8a presents the pseudo-first-order kinetic plot of As(V) sorption on HBO1 in aqueous solution. The plot of ' $\log(q_e - q_t)$ ' versus ' t ' was almost linear as it gave with rate constant ($K_1 \times 10^{-3}$) of 2.303, 4.606, 4.606, 4.606 and

2.303 min^{-1} . The value of K_1 showed the decreasing trend along with increasing initial As(V) concentration from 0.10 to 0.25 mg/L . A similar conclusion was drawn by Pirila et al. (2011) using hydrous titanium dioxide as adsorbent for arsenic removal. The rate constant during observations were found as 3.26×10^{-3} , 4.02×10^{-3} and 3.96×10^{-3} for arsenic sorption at 298K.

Pseudo-second order: The pseudo-second order adsorption kinetic model is given by Ho and McKay (1999) as given in eq. (3).

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where, q_e and q_t are adsorption capacity ($\mu\text{g/g}$) at equilibrium and at any time t ; K_2 = pseudo-second-order rate constant ($\text{g}/\mu\text{g}/\text{min}$). The linear interpolation of the graph between t/q_t versus t will give the values of q_e (1/slope) and adsorption rate constant K_2 (slope²/intercept). From Fig. 8b, the linear plot was observed which indicates the validity of pseudo-second-order kinetic model for all five initial As(V) concentrations. The values of pseudo-second-order rate constant ($K_2 \times 10^{-3}$) were calculated as 1.813, 1.892, 1.647, 1.841 and 2.527 within the specified concentration range. The reaction rate was faster for 250 $\mu\text{g/L}$ initial As(V) concentration, whereas

Table 2: The kinetic model parameters for the sorption of As(V) on HBO1.

Initial As(V) conc. ($\mu\text{g/L}$)	Pseudo-first order			Pseudo-second order			Weber-Morris model	
	$K_1 \times 10^{-3}$ (min^{-1})	q_e ($\mu\text{g/g}$)	R^2	$K_2 \times 10^{-3}$ ($\text{g}/\mu\text{g}/\text{min}$)	q_e ($\mu\text{g/g}$)	R^2	k_i ($\mu\text{g}/\text{g}/\text{min}^{0.5}$)	R^2
50	2.303	2.647	0.678	1.813	8.621	0.993	0.281	0.919
100	4.606	3.908	0.825	1.892	16.394	0.997	0.359	0.928
150	4.606	4.886	0.712	1.647	24.393	0.988	0.458	0.894
200	4.606	4.753	0.714	1.841	32.251	0.999	0.459	0.897
250	2.303	3.404	0.708	2.524	38.462	0.999	0.346	0.914

a slower reaction rate was observed at intermediate initial As(V) concentration (50, 100, 150, 200 µg/L). The lower values of K_2 indicate fast adsorption process (Ayoob et al. 2008). The correlation coefficients of pseudo-second-order kinetics were having a high degree of correlation than the pseudo-first-order. Hence, the kinetic study indicates pseudo-second-order reaction in the sorption process of As(V) by HBO1.

Weber-Morris model: The linear form of the intraparticle diffusion model given by Weber–Morris (Weber Jr et al. 1963) is as follows in eq. (4):

$$q = k_i \sqrt{t} \quad \dots(4)$$

Where, q = Arsenic adsorbed (µg/g); k_i = Rate constant; t = contact time (min). The values of intraparticle diffusion rate constants k_i could be determined from the slopes of the plots between \sqrt{t} ($\sqrt{\text{min}}$) and q (µg/g). From Fig. 8c, the plots show poor linearity ($R^2 = 0.894, 0.897$) at 150 and 200µg/L arsenic concentrations and high linearity ($R^2 = 0.919, 0.928$ and 0.914) at 50, 100 and 250µg/L arsenic concentrations. The intraparticle diffusion rate constants k_i were found to be 0.281, 0.359, 0.458, 0.459 and 0.346 mg/g /min^{0.5} for initial arsenic concentration of 50, 100, 150, 200 and 250 µg/L respectively. A linear representation of data elucidates the diffusion of the solute particle with the available pore site of adsorbent (Sujana & Mohanty 2010). Further non zero

intercepts represent the slow and complex diffusion process, which is not governed by a single mechanism (Gupta & Bhattacharyya 2011).

Adsorption isotherm models: Adsorption isotherm models have been incorporated to calculate the maximum adsorption capacity of the adsorbent. At the equilibrium stage, there is an apparent distribution of a solute between the solid and liquid phases (Manna & Ghosh 2007). Langmuir and Freundlich models are the most frequently used quantitative equations to describe present experimental adsorption data. Langmuir isotherm is based on the principle that each site on the surface of adsorbent is equally capable for adsorbing one molecule of adsorbate in a single monolayer thickness, whereas Freundlich isotherm could be applicable for heterogeneous surfaces of adsorbent with multilayer sorption (Milmile et al. 2011).

Langmuir isotherm: The Langmuir isotherms were chosen to determine the maximum adsorption capacity corresponding to the complete monolayer coverage on the hydrous bismuth oxide (HBO1). As given in eq. (5):

$$\frac{1}{q_e} = \frac{1}{q_0 b C_e} + \frac{1}{q_0} \quad \dots(5)$$

Where, C_e is the solute concentration at equilibrium (µg/L); q_e is the equilibrium arsenic uptake (µg/g); q_0 and bare Langmuir constants related to maximum monolayer capacity (µg/g) and energy of adsorption (L/µg). Value of q_0

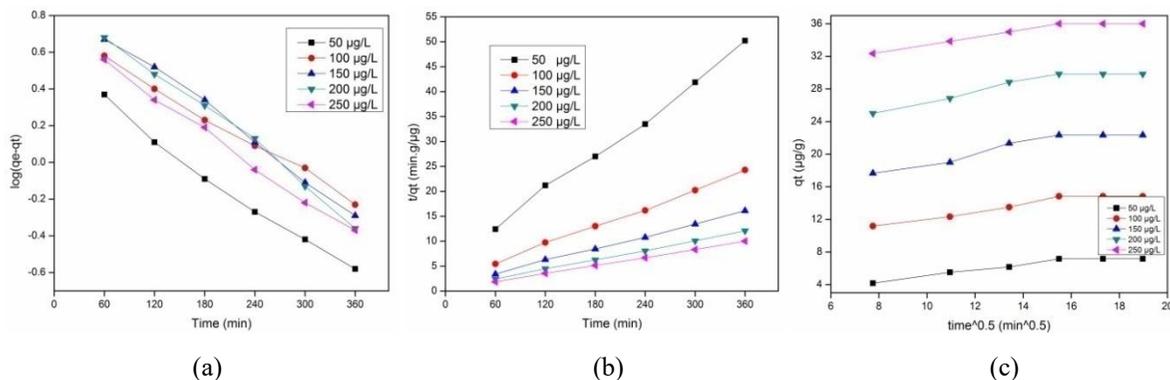


Fig. 8: Kinetic plot of As(V) on HBO1 (a) Pseudo-first order (b) Pseudo-second order (c) Weber–Morris kinetic.

Table 3: Isotherm parameters with thermodynamics for the sorption of Arsenic(v) on HBO1.

Temperature (K)	Langmuir parameters			Freundlich parameters			Dubinin–Radushkevich parameters			Thermodynamic parameters		
	q_0 (µg/g)	b (L/µg)	R^2	K_f	n	R^2	q_a (µg/g)	E (kJ/mole)	R^2	G° (kJ/mol)	H° (kJ/mol)	S° (J/mol)
298	83.33	0.011	0.96	1.14	0.97	0.94	4.073	5.42	0.96	-0.61	18.84	64.97
308	100	0.012	0.95	1.17	0.98	0.95	4.072	8.63	0.97	-0.95	-	-
318	125	0.019	0.97	1.24	0.99	0.96	4.067	6.20	0.96	-1.92	-	-

and b are calculated from the slope and intercept $1/C_e$ and $1/q_e$ (Fig. 9a) and is given in Table 3. q_0 was found to be 83.33, 100 and 125 $\mu\text{g/g}$ at 298K, 308K and 318K respectively. The Langmuir isotherm plot at different temperatures gives higher values of correlation coefficients (R^2). The highest value of ' q_0 ' was obtained as 125 $\mu\text{g/g}$ at the temperature of 318K (Table 4). A high value of q_0 at elevated temperature indicates the enhancement in arsenic sorption potential of HBO1 (Singh et al. 2015).

Freundlich isotherm: The expression of Freundlich equation is given below (eq. 6):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \dots(6)$$

Where, q_e = Equilibrium arsenic uptake ($\mu\text{g/g}$); C_e = Solute concentration at equilibrium ($\mu\text{g/L}$); K_f and n are the Freundlich constants corresponding to adsorption capacity and adsorption intensity, respectively. The value of " n " could be correlated with the favourable and unfavourable condition of adsorption. Hence " n " represents the bonding between adsorbate and adsorbent. Beneficial or favourable adsorption could be read if the value of n (>0) lies in between 1 and 10 (Ho & McKay 2011).

Fig. 9b shows the linearized plot of Freundlich isotherm for As (V) adsorption on HBO1. Regression coefficients (R^2) was found higher (>0.95) at all temperature. Based on the value of " n " adsorption seems to be 'beneficial' at elevated temperature of 318 K. Freundlich parameter, K_f is found as 1.14, 1.16 and 1.24 at 298K, 308K and 318K (Table 3). Increased value of K_f at higher temperature indicates the favourable condition of adsorption (Sharma et al. 2009). The adsorption patterns of HBO1 can be described well by the Langmuir isotherm as it has high correlation coefficient values than Freundlich with a maximum adsorption capacity of 125 $\mu\text{g/g}$ at a temperature of 318K. The suitability of

Langmuir isotherm leads to the conclusion that the homogeneous nature of sorption site dominated over the surface of adsorbent and single layer arsenic sorption took place over the surface of HBO1.

Dubinin-Radushkevich (D-R) isotherm: Dubinin-Radushkevich isotherm has also been included in the present study to make a clear understanding between adsorption and ion exchange. The equation of D-R isotherm is given below in eq. (7):

$$\ln q_e = \ln q_a - K^\circ \varepsilon^2 \quad \dots(7)$$

Where q_e =Arsenic adsorbed at equilibrium ($\mu\text{g/g}$), q_a = Theoretical adsorption capacity, K° = Adsorption energy constant.

E = Polanyi potential is given as follows in eq. (8) (Islam et al. 2010):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad \dots(8)$$

Where, R is the universal gas constant (kJ/mol K); T is the temperature(K). The high values of R^2 at 298K, 308K and 318K temperatures show a good correlation of data with D-R isotherm. The values of $K^\circ(\text{mol}^2/\text{J}^2)$ were calculated from Fig.8c and found as 0.017, 0.0067 and 0.013 $\text{mol}^2\text{kJ}^{-2}$ respectively at 298K, 308K and 318K.

The adsorption energy (E) was calculated using the following relation given in eq (9) (Sharma et al. 2009):

$$E = 1/\sqrt{(2K^\circ)} \quad \dots(9)$$

Process of adsorption can be easily classified into chemical, physical and ion exchange based on the adsorption energy (E). Physical adsorption will prevail if adsorption energy is below 8 kJ/mol , if it is between 8-16 kJ/mol ion exchange will take place, while if it is over 16 kJ/mol then

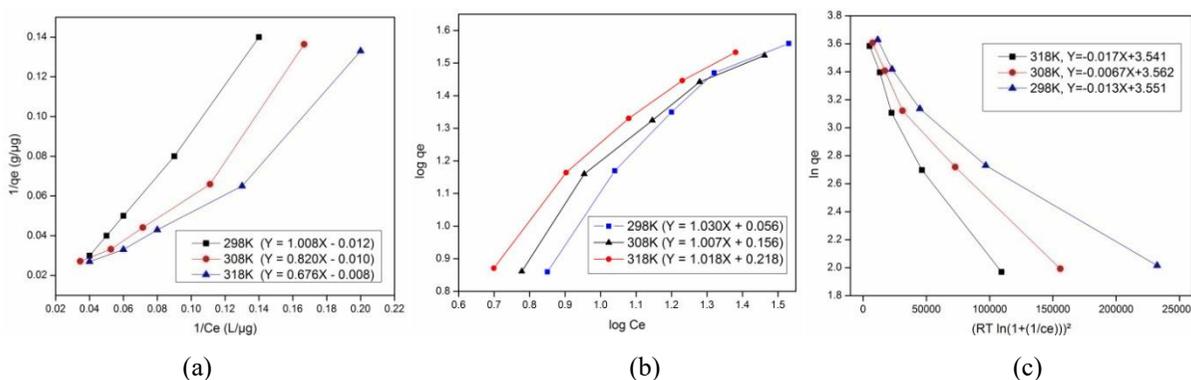


Fig. 9: Isotherm plot of As(V) sorption by HBO1 (a) Langmuir isotherm (b) Freundlich isotherm (c) DR isotherm.

Table 4: Arsenic(v) removal from water using hydrous metal oxides (HMOs)

Adsorbent	Optimum Temperature (°C)	Removal efficiency/potential (mg/g)	Optimum pH	Contact Time (h)	References
Granular titanium dioxide	25	41.4	7.3	2	Bang et al.(2005)
Manganese dioxide	-	53	4.3–3.9	2	Lenoble et al.(2004)
Hydrous stannic oxide	27	4.3	6.5–8.5	4	Manna and Ghosh (2007)
Hydrous ferric oxide	40	<100%	2-12	4	Jang and Dempsey (2008)
Cupric oxide	21-25	22.6	6-10	0.5	Martinson and Reddy (2009)
Magnetite (Fe ₃ O ₄)	20-30	0.485	8	1	Shipley et al.(2010)
Hydrous titanium dioxide	20-23	22.0–33.4	4-6	4	Pirila et al. (2011)
Hydrous zirconium oxide	25	3.6	7	4	Hang et al. (2011)
Iron oxide nano materials	25	671.1	6-9	1	Luther et al.(2012)
Hydrous cerium oxide	25	107	7	24	Li et al. (2012)
Zirconium oxide-coated marine	35	0.270	7	1.25	Khan et al. (2013)
Manganese oxide	25	71.2%	6	24	Hou et al. (2017)
Hydrous bismuth oxide	25	0.013-0.019	6.6-8.4	3	Present study

mechanism will be known as chemical adsorption (Inglezakis & Zorpas 2012). The values of E using Eq. (10) were found as 5.42, 8.63 and 6.20 kJ/mol respectively at the studied temperatures. Hence, the adsorption of arsenic on HBO1 is governed by physical adsorption process (Kanjilal et al. 2017). Srivastav et al. (2013) research supported the findings of adsorption energy highlighting the probability of physical adsorption.

Among all adsorption isotherm models, Langmuir isotherm as well as Freundlich fits well at all selected temperatures for arsenic sorption by HBO1. Based on the calculation of mean adsorption energy (E) from D–R isotherm, the mechanism of arsenic removal by HBO1 fall under the category of the physical adsorption process.

Many adsorbents have been tested for As(V) sorption from aqueous solution and listed in Table 4. The adsorption capacity of hydrous cerium oxide is reported as 107 mg/g (Li et al. 2012). While cupric oxide demonstrated the adsorption capacity of 22.6 mg/g (Martinson & Reddy 2009), hydrous titanium dioxide showed the capacity of 22.0–33.4 mg/g (Pirila et al. 2011). Iron oxide nanomaterial and zirconium oxide-coated marine came with an adsorption capacity of 671.1 mg/g (Luther et al. 2012) and 0.270 mg/g (Khan et al. 2013). In the present study, increasing value of arsenic sorption potentials was demonstrated by hydrous bismuth oxide (HBO1) with increasing temperature of 298 to 318 K and maximum of 19.6 mg/g adsorption capacity noted down at temperature of 318 K.

Thermodynamics Studies

Thermodynamic parameters like Gibbs free energy (G°),

enthalpy (H°) and entropy (S°) were determined for arsenic adsorption on HBO1 from eqs. (6) and (7) (Banerjee et al. 2014).

$$\ln M = \frac{\Delta S^{\circ}}{R} - \Delta H^{\circ}/RT \quad \dots(6)$$

$$\Delta G = -RT \ln M \quad \dots(7)$$

Where, R = Gas constant (8.314 J/mol K), T = Absolute temperature (Kelvin), M = Standard thermodynamic equilibrium constant (L/g).

Values of 'M' is obtained by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero q_e as the methods reported by Khan & Singh (1987). The intersection with the vertical axis gives the value of 'M'. Further, the value of ΔH° and ΔS° were calculated from the slope and intercept from the graph between $\ln M$ and $1/T$ (Liu and Liu 2008) as summarized in Table 4.

Spontaneous nature of the As(V) sorption by HBO1 is confirmed as the negative value of ΔG° was found at all temperatures. The more spontaneous behaviour of adsorption at higher temperature could be observed with a high value of ΔG° with increasing temperatures (Raji & Anirudhan 1998). The positive value of ΔH° suggests the endothermic nature of the sorption process (Tangkawanit et al. 2005). A positive value of ΔH° with magnitude 13.96 kJ/mol was also reported by Singh et al. (2015) during nitrate adsorption on hydrous bismuth oxide. No remarkable change in entropy (ΔS°) has been observed due to sorption of arsenic by HBO1. Similar results have been documented by Liu & Liu (2008) with a low value of entropy in sorption thermodynamics and further Chaudhry et al. (2017) verified with a value of 0.0144 kJ/mol/K as entropy change in his arsenic removal experiment using zirconium oxide-coated sand.

CONCLUSION

The present study elucidates hydrous bismuth oxide (HBO1) has augmented removal efficiency towards As(V) among arsenic species from aqueous solution. As(V) removal efficiency of 94 % and As(V) sorption potential of 13.1-19.6 mg/g has been found in batch and fixed-bed column study respectively. Elution of chloride can be better correlated with ion exchange phenomenon but adsorption energy calculation indicates that the process is governed by physical adsorption. Hence a mixed mechanism of ion exchange and physical adsorption can be concluded in As(V) sorption by HBO1. XRD analyses reveal the relevant peaks corresponds to $\text{Bi}_{12}\text{O}_{17}\text{Cl}_{12}$ (ID: 370702) indicating the presence of chloride inside it. Thus, results attribute that adsorbent shows a high efficiency of arsenic sorption and can be used as an efficient scavenger of arsenic from aqueous solution.

The affinity of hydrous bismuth oxide towards arsenic in addition to nitrate and fluoride (reported in the literature) makes it a unique adsorbent. Hence, hydrous bismuth oxide could be a better alternative for the simultaneous removal of all three major water toxins such as nitrate, fluoride and arsenic from aqueous solution. This aspect needs to be explored in future studies with close monitoring.

ACKNOWLEDGEMENTS

All the necessary facilities for this work have been provided by the Indian Institute of Technology (Banaras Hindu University), India. The author avails the opportunity to express sincere thanks to anonymous reviewers for their valuable comments and suggestion.

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