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Preparation and properties of hydrous bismuth oxides for nitrate removal from aqueous solutions

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ABSTRACT

With an ultimate objective of developing an inorganic sorptive media for nitrate removal from water for drinking purpose, preparation and properties of hydrous bismuth oxides (HBOs) were studied. Three HBOs, designated as HBO_1, HBO_2 and HBO_3 were prepared using 0.1 M Bi_2O_3 solution in 2 N HCl and 2 N NaOH in 1:1, 1:2 and 1:3 volumetric proportions respectively. In column tests, with 1 meq l^{-1} (=14 mg N l^{-1}) nitrate in distilled water as influent solution, HBO_1, HBO_2 and HBO_3 were found to remove 0.6, 1.2 and 1.4 mg N g^{-1} (dry mass basis) at controlled flow rates of 1.20–1.45, 1.45–2.10 and 1.30–2.10 ml min^{-1} from the respective columns. Regeneration attempt of the used media by passing 0.1 N NaOH solution gave a nitrate recovery ratio (RR) of 0.9 for HBO_1 and HBO_2 and 0.5 for HBO_3. In the second cycle of nitrate laden water application, whereas HBO_2 and HBO_3 showed decreased nitrate removals, HBO_1 exhibited increased uptake. On dry mass basis HBO_1, HBO_2 and HBO_3 precipitates showed a nitrate removal of 1.1, 0.7, and 1.0 mg N g^{-1} respectively in the second cycle. Thus, in two cycles HBO_1, HBO_2 and HBO_3 precipitates were found to remove 1.7, 1.9 and 2.4 mg nitrate from solution per g (dry mass) respectively. The effluent pH remains fairly in the range of 7.0 to 8.9, indicating that OH^- ions are not released from HBOs in significant quantity due to nitrate sorption. The precipitates apparently held appreciable amount of chloride which may play important role in nitrate removal process.

Keywords: Adsorption; Inorganic sorptive media; Nitrate removal; Hydrous bismuth oxide; Regeneration and reuse

1. Introduction

Increasing nitrate concentration in ground and surface waters have been reported from many parts of the world including India. Ground water remains the major source of drinking water supply in suburban and rural areas and high nitrate levels may pose direct health threat to the public health. Consumption of water with high nitrate concentrations has been correlated with methemoglobinemia, stomach cancer, early onset of hypertension, increased infant mortality, central nervous system birth defects, non-Hodgkin's lymphoma, initiation of kidney diseases, oral cancer, cancer of colon, rectum and other gastrointestinal cancers, and Alzheimer's disease [1–8]. The current maximum allowable concentration for nitrate in drinking water ranges from 2.5 mg N l^{-1} in Norway to 23 mg N l^{-1} in Netherlands [9]. USA, Canada, Poland and India recommend a maximum

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allowable limit of 10 mg N l^{-1} (equivalent to 45 mg NO_3^-/l^{-1}). European Economic Community established the Maximum Contaminant Level (MCL) of 11.3 mg N l^{-1} (50 mg NO_3^- l^{-1}) and a recommended level of 5.65 mg N l^{-1} (25 mg NO_3^- l^{-1}) for nitrate [10,11]. As a result of recent evidence of presence of nitrite in some water supplies, the World Health Organization (WHO) has proposed a provisional guideline value for nitrite as 3 mg NO_2^- l^{-1} [12] and Health and Welfare Canada has taken 3.2 mg NO_2^- l^{-1} as maximum acceptable concentration (MAC) [13].

A number of reviews of methods available for nitrate removal from water for drinking purpose have been reported [14–16]. Several treatment processes including catalytic reduction [17,18], biological denitrification [19,20], chemically catalyzed microbial reduction [21], ion exchange [11,22–24], a combination of ion exchange and membrane bioreactor [25], reverse osmosis [26], elecrodialysis [27–29], bio-electrochemical reactors [30] and adsorption [31–33], have been reported to remove nitrate from water with varying degrees of efficiency, cost and ease of operation. Raw water quality parameters, such as presence of organic matter and sulphate concentrations have an impact on the ion exchange process, but their impact on heterotrophic denitrification is not expected to be significant. Thus, biological denitrification is applicable to surface waters, as the process can adjust better than ion exchange process to variation in water quality, such as natural organic matter (NOM), Total dissolved solids (TDS), suspended solids, nitrate and sulphate levels [15]. In ion exchange process, anion exchange resins, which are used in nitrate removal from water, are found to be more sensitive to fouling with organic materials [34]. Natural waters contain organic, inorganic and biological compounds in various ratios. Organic fouling results in production of low quality (high conductivity, low pH), low amounts of water and some serious problems such as early breakthrough and long washing periods after regeneration [34]. Thus, use of organic resin based ion exchange materials for drinking water treatment at small scale, where the unit may be used intermittently, and the feed water from natural sources may contain a host of microbial populations, poses a different challenge to protect the resin from degradation and ensure safe drinking water chemically as well as microbiologically. Use of inorganic sorptive media appears appropriate under such conditions. The adsorption properties of hydrous oxides, such as alumina, silica and ferric oxide have been known for many years and it has been established that adsorption presumably takes place through ion exchange [35]. Some of the hydrous metal oxides/inorganic materials have been used in drinking water treatment application. Hydrous titanium dioxide [36], iron–zirconium (Fe–Zr) binary oxide adsorbent [37], nanocrystalline TiO_2-based adsorbent [38], manganese oxide-coated-alumina for As (III) [39], graphene oxide/ferric hydroxide composites [40] and granular Fe–Ce oxide adsorbent [41] have been used for arsenic removal from water. In case of fluoride removal from water hydrous-manganese-oxide-coated alumina (HMOCA) [42] granular ferric hydroxide (GFH) [43], Titanium hydroxide-derived adsorbent [44] amorphous iron and aluminum mixed hydroxides [45] have been reported.

However, a review of literature concerning anion exchange properties of these hydrous metal oxides indicates that either nitrate ion has not been studied thoroughly or very few of reported materials have shown nitrate sorptive properties. Bhatnagar et al. [46] have compiled the various adsorbents for nitrate removal from water. Bhatnagar et al. [47] evaluated the feasibility of nano-alumina for nitrate removal from aqueous solutions. Fritsche [48] reported removal of nitrate and other anions from water by yellow bismuth hydroxide precipitate. Bismuth is one of the least toxic of heavy metals [49] and basic bismuth nitrates are used in many pharmaceutical or beautycare applications. Theoretically bismuth forms two hydroxides, bismuthous hydroxide, $Bi(OH)_3$ and bismuthyl hydroxide, BiOOH, both of which are white in color in their monomeric forms [50,51]. Hence in order to explore its possible use in drinking water treatment applications for nitrate removal, an in-depth study of formation and properties of yellow bismuth hydroxide appears essential. This paper discusses some of the theoretical basis of formation of hydrous bismuth oxides (HBOs), and experimental observations in relation to their nitrate sorptive (removal) properties.

2. Materials and methods

Bismuth trioxide (Bi_2O_3, MW 466.0) powder of analytical reagent (AR) grade was used as the starting material for all bismuth based preparations. A 0.1 M Bi_2O_3 solution in 2 N HCl served as the working solution for all further processing. Three HBOs were prepared by mixing the bismuth trioxide working solution and 2 N NaOH in 1:1, 1:2 and 1:3 volumetric proportions. After mixing the reagents, a reaction time of 1 h was allowed and then supernatants were decanted. The precipitates were washed thoroughly with sufficient distilled water to remove all unreacted chemicals. Finally the precipitates were filtered in small batches through Whatman 42 filter paper under vacuum to remove maximum amount of water. The precipitates so obtained were designated as HBO_1, HBO_2 and HBO_3 respectively.

All experiments were conducted at a nitrate contamination level of 1 meq l^{-1} (= 14 mg N l^{-1}, equivalent to 62 mg NO_3^- l^{-1}) in distilled water. Nitrate determinations in water were made using Micro-2 ion meter with nitrate selective electrode (ISE 311), manufactured by Toshniwal Process Instruments Pvt. Ltd., Ajmer (India). The pH of solutions was measured using digital pH meter (Model 335, Systronics, India). Alkalinity, chloride and sulfate concentrations in column effluent were measured as per Standard Methods [52]. X-ray diffraction (XRD) patterns were obtained using X-ray diffractometer (Philips 1710, the Netherlands).

Three parallel columns were run using 60 cm long, 2.50 cm internal diameter transparent cylindrical tubes, fitted with perforated glass at the base. In order to retain the fine precipitate particles without loss, 5 g of acid washed (0.1 N HCl, 24 h) sand (250 µm ≤ *d* ≤ 425 µm) was used in each column to provide uniform bed. HBO_1, HBO_2 and HBO_3 pastes of 5.0 g each were put in the respective columns and sufficient distilled water was passed through beds to clean the washable impurities before applying the desired feed solution in down flow mode under a constant static head of about 2 m. Effluents were collected continuously in 25 ml volumetric flasks and analyzed for nitrate, pH and chloride concentrations.

3. Results and discussion

3.1. Nitrate removal

Visibly HBO_1 is predominantly white in color, while HBO_2 and HBO_3 are broadly yellow. Based on purely theoretical considerations, hydrochloric acid solution of Bi_2O_3 may produce two forms of bismuth hydroxides, $Bi(OH)_3$ and BiOOH as follows, both of which are white in colour in their monomeric forms [50,51]:

(A)

$$Bi_2O_3(c) + 6HCI(aq) = 2BiCI_3(aq) + 3H_2O(I)$$

$$2BiCI_3(aq) + 6NaOH(aq) = 2Bi(OH)_3(c) + 6NaCI(aq)$$

$$Bi_2O_3(c) + 6HCI(aq) + 6NaOH(aq) = 2Bi(OH)_3(c) + 6NaCI + 3H_2O(I) \quad (1)$$

$$\Delta G_f{}^\circ = -118.55 - 31.37 - 99.23 - 138.55 - 91.78 - 56.68$$

(B)

$$Bi_2O_3(c) + 6HCI(aq) = 2BiCI_3(aq) + 3H_2O(I)$$

$$2BiCl_3(aq) + 6NaOH(aq) = 2BiOOH + 6NaCl(aq) + 2H_2O$$

$$Bi_2O_3(c) + 6HCI(aq) + 6NaOH(aq) = 2BiOOH(c) + 6NaCI + 5H_2O(I) \quad (2)$$

$$\Delta G_f{}^\circ = -118.55 - 31.37 - 99.23 - 88.4 - 91.78 - 56.68$$

where $\Delta G_f{}^\circ$ is the Gibb's free energy of formation (kcal mol^{-1}) under standard state conditions.

The Gibb's free energy change, ΔGr° for reactions as per Eqs. (1) and (2) are −95.67 and −108.73 kcal respectively. Hence both the reactions seem feasible, but bismuthyl hydroxide, BiOOH may be the eventual product of reactions, as

$$Bi(OH)_3(c) = BiOOH(c) + H_2O(I);\ \Delta Gr^\circ = -6.53\,kcal \quad (3)$$

It is interesting to note that formation of both the forms of bismuth hydroxide in their monomeric form requires an acid to hydroxide ratio of 1:1 only, as evident from Eqs. (1) and (2). HBO_1 has been prepared using an acid (solution of Bi_2O_3) to hydroxide ratio of 1:1 and thus its colour is in line with the theoretical prediction for monomeric $Bi(OH)_3$ or BiOOH. Theoretically a monomeric BiOOH compound should be colorless, as univalent $[Bi = 0]^+$ or $[Bi \rightarrow 0]^+$ radicals are colorless [50] and there is no indication that they ever go in covalent form [53]. However, HBO_2 and HBO_3 which are yellow in color and have been prepared in presence of extra hydroxide, appear to be "presumably" polymeric [54]. In case of hydrous ferric oxide precipitate formation also, it has been reported that polymerization is accelerated by a higher hydroxide ion concentration and elevated temperature [55,56]. The color of a substance is determined by its absorption spectrum and colorless ions have absorption bands in ultraviolet range. However, if through a perturbing influence, like formation of a bond with increasingly great covalent character, a single absorption band of an ion were increased in wave length, so as to pass through the visible spectrum, the color of the ion by transmitted light would go through the sequence of lemon yellow, yellow, orange, red, purple and so on. Thus, this sequence of color may be used as a measure of the amount of covalent character of compounds with colorless ions [57]. Thus, it appears that HBO_2 and HBO_3 which are yellow in color and are formed under the presence of excess hydroxide ions are polymeric forms of bismuthyl hydroxide, BiOOH, and possibly have developed some covalent character in its structure.

Fig. 1 shows the effluent quality from the three columns with respect to nitrate, pH and chloride concentrations. The weighed amount of the precipitate in each column was 5 g, but due to physico–chemical differences

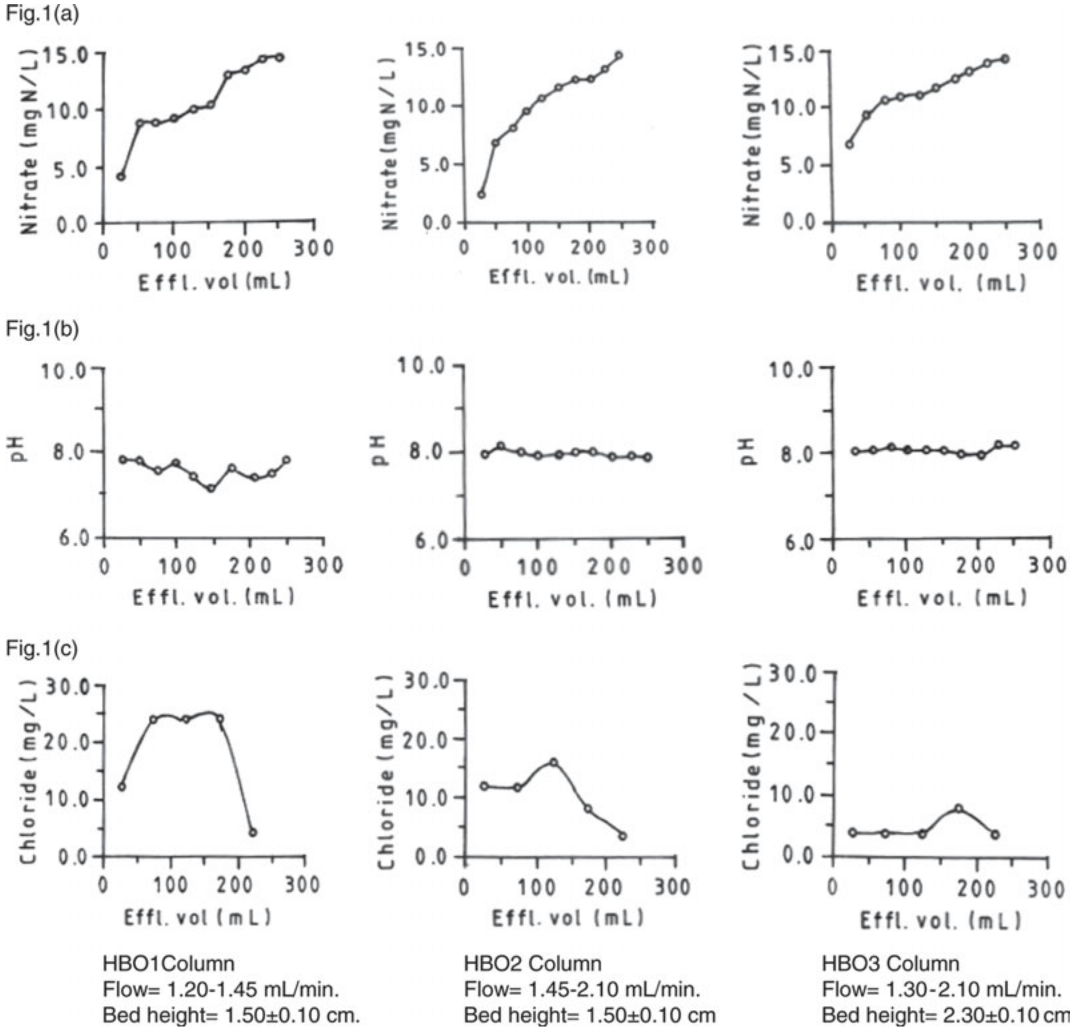


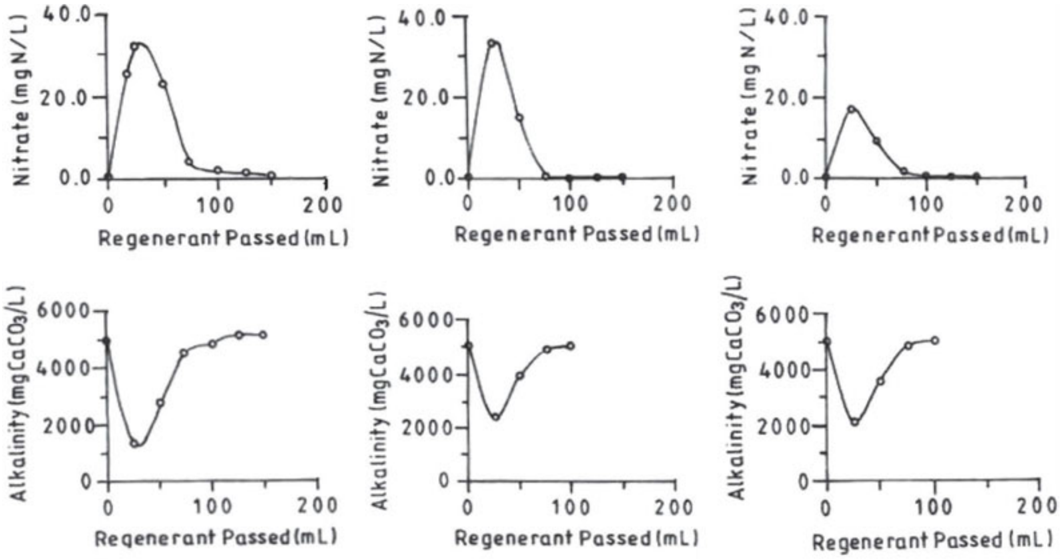
Fig. 1. Effluent quality from HBO columns with 5 g of wet precipitate.

of the materials formed, the bed heights in different columns were different and the free flow rates also varied.

Although even at controlled flow rates the depths of the precipitate in the columns were found inadequate with respect to nitrate removal, the trends indicated removal of nitrate by all the three hydrous bismuth oxide materials. In order to make quantitative evaluation, solid content of the precipitates were estimated. An average of three determinations for each precipitate gave a solid content of 38.38%, 15.82% and 17.60% for HBO_1, HBO_2 and HBO_3 respectively. On dry mass basis, each gram of HBO_1, HBO_2 and HBO_3 were found to remove 0.6, 1.2, and 1.4 mg N respectively at 1 meq l^{-1} influent nitrate level in the given run.

Fig. 1(b) shows the variation of pH with effluent volume. The effluent pH from HBO_1 varied between 7.0 and 7.8 and those from HBO_2 and HBO_3 between 7.8 and 8.2. The effluent pH from HBO_2 and HBO_3 seemed to be more stable than that from HBO_1 column. HBO_3 precipitate in above set of experiments corresponds to the yellow bismuth hydroxide used by Fritsche [48]. He passed 20 ml of 50 mg NO_3^- l^{-1} laden water from a bed of 10 g wet precipitate and on the basis of pH measurement of the eluate in a parallel separate column anticipated displacement of OH^- from the precipitate by NO_3^- being removed. Fritsche [48] however, did not report monitoring the effluent pH continuously. The pH of effluents in the range 7.8–8.2 indicates that OH^- is not released in any significant proportion due to nitrate uptake by the media.

Fritsche [48] also reported exchange of Cl^- for nitrate due to Cl^- impurity of the sorbent to minor extent. In order to examine such possibilities, chloride concentrations of samples of the effluents from the columns were also analyzed. Fig. 1(c) shows the results in this regard. Obviously, the effluents were found to have elevated levels of chloride with respect to the influent. Thus all the three HBO precipitates appear to contain varying degree of held chloride.



HBO1Column HBO2 Column HBO3 Column

Fig. 2. Characteristics of effluents during regeneration of precipitate in columns by 0.1 N NaOH.

Fritsche [48] showed elution of sorbed nitrate from the yellow bismuth hydroxide precipitate bed by 0.1 N NaOH solution. Following similar lines, an attempt was made to elute the sorbed nitrate for regeneration and reuse of the material in nitrate removal. Fig. 2 shows the results of a regeneration attempt of precipitates by 0.1 N NaOH solution in free down flow mode. Hydroxide alkalinity expressed in terms of mg $CaCO_3$ l^{-1} has been applied as a measure of regenerant consumption during the process. It is observed that the regenerant effluents show peak nitrate concentrations when the hydroxide consumption by the precipitates are maximum. An apparent correlation between nitrate elution from the bed and hydroxide ion consumption indicate that nitrate sorption takes place mostly at exchangeable sites in the materials.

For quantitative evaluation, defining 'recovery ratio (RR)' as the ratio of total nitrate eluted by the regenerant (meq) to the total nitrate sorbed in the precipitate before regeneration (meq), whereas HBO_1 and HBO_2 give RR of 0.9, it is 0.5 for HBO_3. Thus, HBO_1 and HBO_2 precipitates appear to elute most of the sorbed nitrate, but HBO_3 seem to retain almost 50% of it.

The regenerated columns were washed with sufficient distilled water before applying the nitrate solution for the second cycle. The flow rates and all other conditions were maintained similar to the first cycle. Fig. 3 shows the effluent qualities through columns in first and second cycles.

It is observed that all the three HBO precipitates started taking up nitrate from the influent solution once again. Interestingly, while for HBO_2 and HBO_3 the nitrate uptake potentials appeared to have decreased in the second cycle, it got increased for HBO_1. While passing 0.1 N NaOH solution through beds for regeneration, some further transformation in HBO_1 appears to have taken place to effectively increase nitrate uptake by this precipitate. On dry mass basis HBO_1, HBO_2 and HBO_3 showed a nitrate removal of 1.1, 0.7, and 1.0 mg N g^{-1} respectively in the second cycle. The pH of effluents ranged 7.0–8.2, 8.1–8.3 and 8.1–8.9 for the three respective columns. Whereas chloride releases from HBO_1 and HBO_2 appeared to have decreased, it increased for HBO_3 in the second cycle. This appears to indicate that HBO precipitates hold replaceable chloride under varying structural arrangements in the fabric and may have some correlation with the nitrate uptake by the material. This aspect needs further planned exploration.

3.2. Competing anions studies

Presence of alkalinity (bicarbonate) and sulfate interfere the removal of nitrate from water. Hence, the removal of alkalinity (bicarbonate) and sulfate has been studied by HBOs. Fig. 4 shows the removal of alkalinity (bicarbonate) by HBO_1, HBO_2 and HBO_3. It is clear that HBO_1 performed best (~77% removal) regarding alkalinity (bicarbonate) removal from water in the comparison of HBO_2 and HBO_3. Fig. 5 shows the removal of sulfate from water by similar media. HBO_2 and HBO_3 both are very much efficient in removing sulfate from water. HBO_2 removes 73% and HBO_3 removes 75% of sulfate. When these three contaminants were mixed in the concentration of 1 meq l^{-1} each (Nitrate = 14 mg NO_3^--N l^{-1}, alkalinity

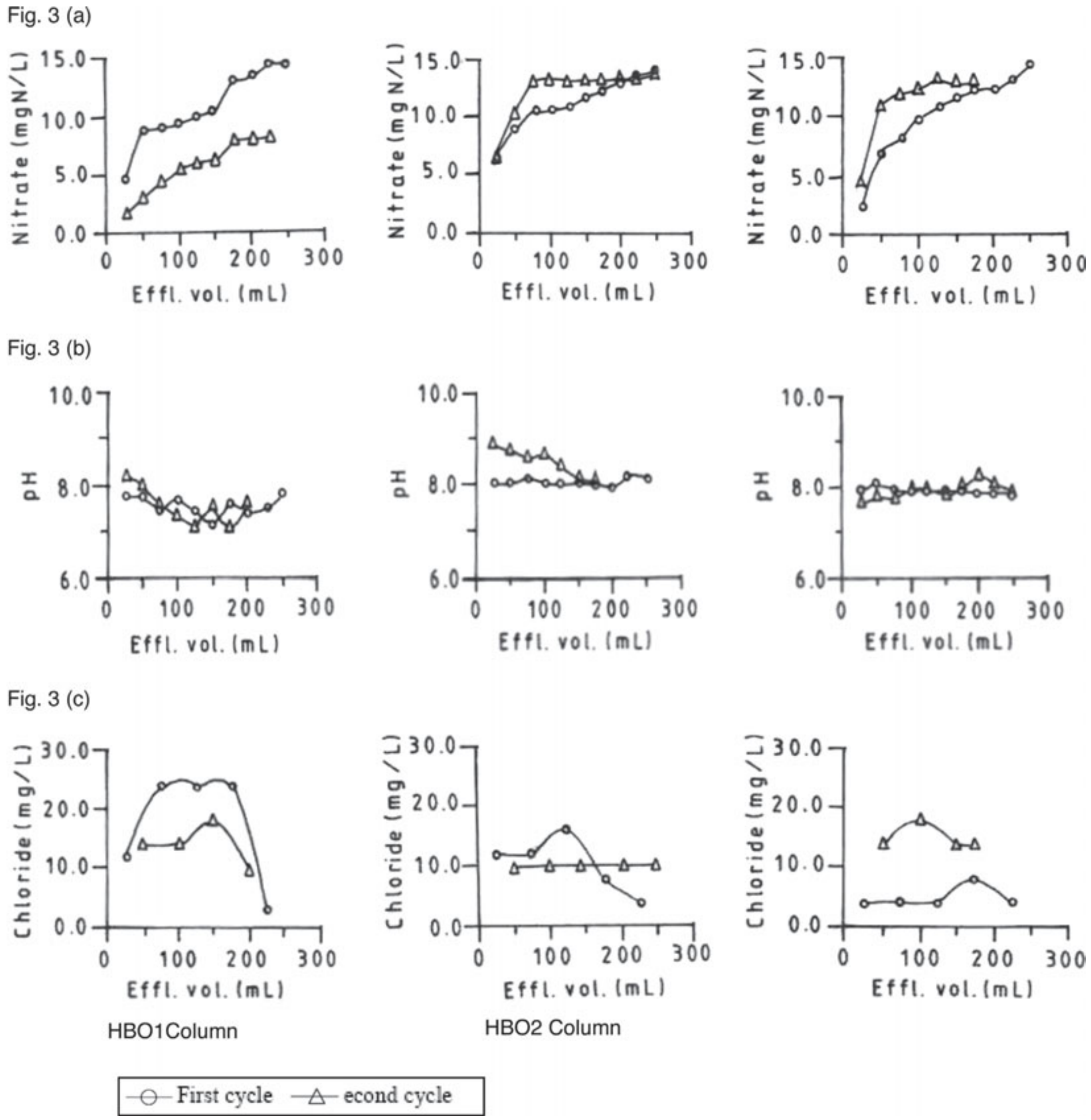


Fig. 3. Effluent qualities from HBO precipitate columns in two cycles.

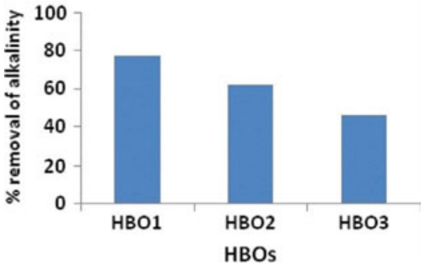


Fig. 4. Removal of alkalinity (bicarbonate) by HBOs.

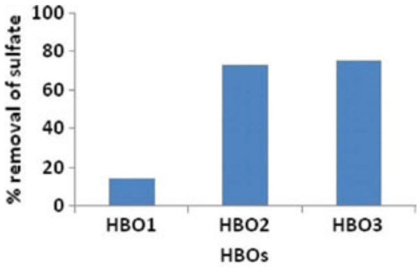


Fig. 5. Removal of sulfate by HBOs.

(bicarbonate) = 61 mg l^{-1}, sulfate = 48 mg l^{-1}) HBO_2 and HBO_3 still very good in the removal of nitrate. The removal percentage of alkalinity significantly decreases by HBO_1 from 77% to 22%. Sulfate has been removed almost same level by all HBO_1, HBO_2 and HBO_3 (Fig. 6).

3.3. X-ray diffraction

The X-ray diffraction (XRD) pattern of HBO_2 (Fig. 7) and HBO_3 (Fig. 8) show the presence of peaks which indicates these are crystalline in nature. The major

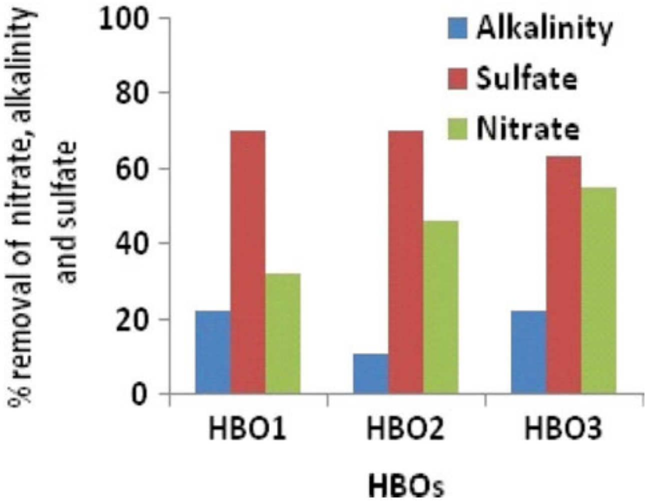


Fig. 6. Removal of nitrate, alkalinity (bicarbonate) and sulfate by HBOs when mixed 1 meq l^{-1} each.

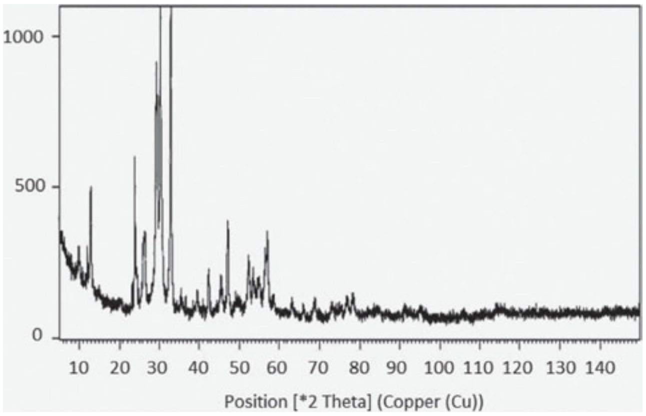


Fig. 7. X-ray diffraction pattern of HBO_2.

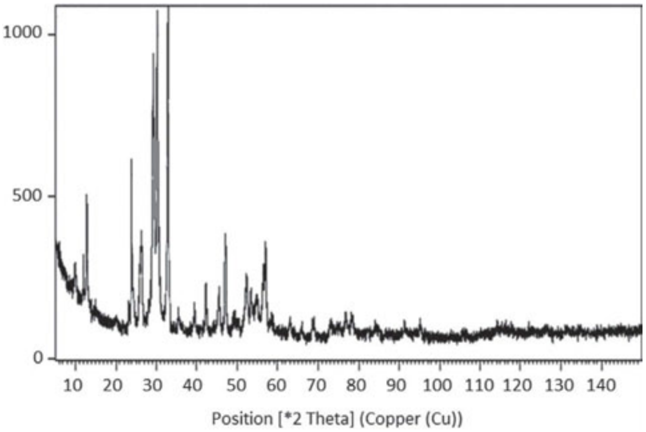


Fig. 8. X-ray diffraction pattern of HBO_3.

peaks appeared at 2θ = around 33° and 55° are shows the Bismuth oxide chloride [BiOCl] compound (as per the JCPDS File no. 03-1125) and the peaks around 30°, 32° and 56° are may be the characteristics of Bismuth hydroxide [Bi(OH)3] compound (as per the JCPDS File no. 01-0898).

3.4. Comparison of the relevant studies

Fritsche [48] performed the experiment on the removal of nitrate and other anions from water by yellow bismuth hydroxide' precipitate. In the present study, three forms of HBOs, designated as HBO_1, HBO_2 and HBO_3 were prepared using the method similar to that of Fritsche [48], but with increasing volumetric proportion of 1:1, 1:2 and 1:3 of 0.1 M Bi_2O_3 solution in 2 N HCl and 2 N sodium hydroxide solution respectively. Thus, the 'yellow bismuth hydroxide' as prepared by Fritsche [48] corresponded to HBO_3 in this study. HBO_1 has been prepared to get bismuth hydroxide, as per Eqs. (1)–(3). HBO_2 has been planned to get an intermediate product between HBO_1 and HBO_3 for comparative purposes.

- A continuous flow of 14 mg NO_3^--N l^{-1} (1 meq l^{-1}) solution has been passed. On dry mass basis, each gram of HBO_1, HBO_2 and HBO_3 were found to remove 0.6, 1.2, and 1.4 mg N respectively at 1 meq l^{-1} influent nitrate level and in earlier work it was passed 20 ml of 50 mg NO_3^- l^{-1} laden water from a bed of 10 g wet precipitate.
- Fritsche [48] said that OH^- ions were responsible for nitrate removal without continuous measurement of pH of effluent. The pH of effluents were measured continuously and found in the range of 7.0–8.9 indicates that OH^- is not released in any significant proportion due to nitrate uptake by the media. The precipitates are found to hold appreciable amounts of chloride which may play important role in nitrate removal process.
- Fritsche [48] showed elution of sorbed nitrate from the yellow bismuth hydroxide precipitate bed by 0.1 N NaOH solution. In present study the regeneration of precipitates by 0.1 N NaOH solution in free down flow mode was achieved.

During this study the regenerated column was used for the second cycle of nitrate solution. The flow rates and all other conditions were maintained similar to the first cycle. Interestingly, while for HBO_2 and HBO_3 the nitrate uptake potentials appeared to have decreased in the second cycle, it got increased for HBO_1, on dry mass basis HBO_1, HBO_2 and HBO_3 showed a nitrate removal of 1.1, 0.7, and 1.0 mg N g^{-1} respectively in the second cycle.

The pH of effluents ranged 7.0–8.2, 8.1–8.3 and 8.1–8.9 for the three respective columns. But Fritsche [48] did not mention the second cycle of column study.

4. Conclusions

Inorganic sorptive media are the preferred alternative for contaminants removal from ground and surface waters for drinking purpose, particularly in small scale applications. Hydrous bismuth oxides have shown high potential for the removal of nitrate from water. However, the conditions of preparation of the material affect the nitrate removal characteristics. Even though the theoretical considerations suggest the need of only 1:1 volumetric ratio of 2 N HCl solution of Bi_2O_3 and 2 N NaOH for formation of both known forms of bismuth hydroxides, $Bi(OH)_3$ as well as BiOOH, and the product should be white in color, presence of extra hydroxide are found to have significant affect on the physico–chemical properties of the product formed. In presence of excess hydroxide, polymerization of units appears to take place, which gives yellow colour to the materials formed. The sorbed nitrate can be eluted from the precipitates by passing sodium hydroxide solution and the precipitates may be reused for further nitrate removal. The pH of effluent remains fairly in the range from 7.0 to 8.9, indicating that OH^- ions are not being released in significant quantity due to nitrate sorption. The precipitates are found to hold appreciable amounts of chloride which may play important role in nitrate removal process. In presence of bicarbonate and sulfate both HBO_2 and HBO_3 were very good in the removal of nitrate from water.

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