CHAPTER-5

SUMMARY AND CONCLUSIONS

5.1 Summary

The presence of high concentrations of nitrate, fluoride and arsenic in groundwater for drinking is a known problem in many parts of India and the world. Hydrous bismuth oxides (HBOs) have been shown to have sorptive properties for anionic contaminants. The present study focused on simultaneous removal of these contaminants from coexisting state by HBOs. Central Ground Water Board (CGWB) of India has reported many districts in the country where all the three contaminants are found in the groundwater sources.

Three HBOs, designated as HBO_1, HBO_2 and HBO_3 were examined for removal of nitrate, fluoride and arsenic, presence in drinking water. A 1:1 weight basis mixture of HBO_1 and HBO_2 powders was designated as HBO_{12mix} and that of HBO_1 and HBO_3 as (HBO_{13mix}). The main observations of the present study can be summarized as follows:

1. From the coexistence of nitrate, fluoride and arsenic together in an aqueous solution, both forms of arsenic: As(III) and As(III) are removed to a considerable extent by HBO_1 powder. At the initial concentrations tested, As(III) removal is around 75%, while As(III) removal by HBO_1 is > 90%. Due to higher preference for As(III), this form was examined in all further studies.
2. Initial concentrations of 95 mg/L (≈1.5 meq/L) of nitrate, 5 mg/L (≈0.25 meq/L) fluoride and 0.08 mg/L (≈0.001 meq/L) As(III) are considered to be

simultaneous present in groundwater, intended for drinking. Such levels correspond to the difficult groundwater conditions reported for these pollutants in India. According to Indian Standards (IS 10500: 2012) Specifications for drinking water, the desirable concentrations for the respective contaminants in treated water should be:

Nitrate Conc. (as NO_3^-) < 45 mg/L (Removal required > 52%)

Fluoride Conc. (as F^-) = 1.0-1.5 mg/L (Removal required > 70%)

Arsenic (V) Conc. (as As(V)) < 0.01 mg/L (Removal required > 88%)

3. From the coexisting solution composition with the above-mentioned concentration levels, the relative performance in terms of the percentage removal of these anionic contaminants by various forms of HBOs are found as follows:

HBO_1: As(III) > Fluoride > Nitrate

HBO_2: As(III) > Nitrate > Fluoride

HBO_3: As(III) > Nitrate > Fluoride.

Since HBO_2 and HBO_3 were observed on similar lines with almost equal efficiency, only HBO_2 was selected to be used in further studies for the purpose of nitrate removal and it was decided to investigate a combination of HBO_1 and HBO_2 for simultaneous removal of all the three contaminants.

4. A 1:1 weight-based mixture of HBO_1 and HBO_2 (designated as HBO_{12mix}) was tested to remove all three contaminants from the solution at the same time. In batch experiments, with a dosage of 130 g/L and a contact time of 3 h, the removal (in terms of concentration reduction) of the respective anions from a distilled water was

based on 95 mg/L (≈1.5 meq/L) of nitrate, 5 mg/L (≈0.25 meq/L) fluoride and 0.08 mg/L (≈0.001 meq/L) of As(III) were observed together as follows:

Nitrate: ≈ 52 %

Fluoride: ≈ 71%

Arsenic (V): ≈ 92%

5. The kinetic studies for nitrate, fluoride and As(III) removal by HBO12mix powder in the batch mode of experiments clearly showed pseudo first order kinetics.

6. The adsorption isotherm studies with HBO_{12mix} powder for all the three coexisting contaminants, show the most suitable models:

Nitrate : Freundlich Isotherm

Fluoride : Langmuir Isotherm

Arsenic (V): Dubinin-Redushkevich (D-R) Isotherm

7. The estimation of thermodynamic parameters give following results:

(a) The Gibb's free energy change ΔG^o was found to be negative, indicating that the sorptive removal of anions on HBO_{12mix} powder is spontaneous.

(b) The negative values of ΔG^o increase with increasing temperature, which suggests that the sorptive reactions are endothermic in nature.

(c) The enthalpy change (ΔH^o) varies in the range 24.47 -29.79 (kJ/mol). These values are closer to the (ΔH^o) range of 2.1–20.9 kJ/mol for physical adsorption, and far less than 80–200 kJ/mol for chemical adsorption (Basu et al., 2010;

Banerjee et al., 2014), physical adsorption appears to be the main mechanism in nitrate, fluoride and As(III) removal by HBO_{12mix} powder.

8. Among two major competative anions (HCO_3^- and SO_4^{2-}) commonly present in groundwater, the preference series for HBO_{12mix} powder:

   (a) For nitrate removal, Bicarbonate (HCO_3^-) > Sulfate (SO_4^2) > Nitrate (NO_3^-).

   (b) For fluoride and As(III) removal, Sulfate (SO_4^2) > Bicarbonate (HCO_3^-) > Fluoride (F^-)/ As(III).

At the same concentrations, bicarbonate affects the nitrate removal % more adversally than sulfate, but for fluoride and As(III), sulfate is more harmful than bicarbonate.

9. In characterization of HBO_{12mix} powder :

(a) Multiple peaks in XRD patterns indicate crystalline nature of the material.

(b) The composition of a possible chemical compound, such as $Bi_{12}O_{15}Cl_{16}$ indicated by X-pert high score software from XRD pattern analysis, suggests a polymeric structure of compounds formed in HBO_{12mix} with significant presence of embedded chloride.

(c) SEM images show a rough and granular surface of HBO_{12mix} powder, which indicates good surface adsorptive potentials of the material from aqueous solutions.

(d) EDS patterns and elemental analysis show a significant amount of chloride embedded in the material.

(e) FTIR spectrum analysis shows the presence of 'water of hydration' and 'hydroxide' in HBO_{12mix} powder.

10. After sorption of nitrate, fluoride and As(III) on HBO_{12mix}, characterization of used powder by:

(a) XRD pattern analysis and X-pert high score software, presence of chemical compositions such as $(NO_2)Bi(ClO_4)_4$, $Bi_6O_7FCl_{13}$ and $Bi_{19}AsO_{31}$ that indicate the attachment of nitrate, fluoride and arsenic on the material.

(b) EDS shows the presence of N, F and As in elemental analyses. In addition, the percentage of chloride decreases.

(c) FTIR analysis shows additional peaks near wave bands 1120, 675 and 451 indicating the presence of Bi-NO_3, As-O and Bi-F respectively.

These observations confirm adsorption of nitrate, fluoride and arsenic on the suface of HBO_{12mix}.

11. In fixed bed downflow mode of column experiments , using distilled water spiked with 95 mg/L (≈1.5 meq/L) of nitrate, 5 mg/L (≈0.25 meq/L) fluoride and 0.08 mg/L (≈0.001 meq/L) As(III) as influent, the effluent shows the removal of contaminants for a short period of time. The breakthrough of nitrate occurs first, followed by fluoride and finally after a long time for As(III). The pH of effluent remains in the range of 6.5-8.5, which suggests that the hydoxyl ion does not play a role in the process. An increased chloride chloride content in the effluent suggest an exchange of chloride from the material instead of adsorbed nitrate, fluoride and As(III).

12. Regeneration of the fixed bed column by passing 0.1N NaOH followed by 0.1N NaCl and washing with distilled water for reuse appeared feasible.
13. Use of the actual groundwater with 95 mg/L (≈1.5 meq/L) nitrate, 5 mg/L (≈0.25 meq/L) fluoride and 0.08 mg/L (≈0.001 meq/L) As(III) as influent in the column, the mixed powder in the bed showed a significant reduction in alkalinity and sulphate along with nitrate, fluoride and arsenic with appreciable increase in the chloride concentration in the effluent. This shows that the HBO_{12mix} powder has good potential to remove anionic species from groundwater including nitrate, fluoride and arsenic as contaminants of concern for drinking purposes.
14. The HBO_{12mix} powder shows impressive and promising potential for arsenic removal from contaminated groundwater. Alkalinity and sulfates are the major competing anions that significantly reduce the nitrate and fluoride removal potentials of the powder.
15. The chloride embedded in HBOs serves as an exchange anion for nitrate, fluoride and arsenic along with bicarbonate and sulfate removed from aqueous solution.

5.2 Conclusions

1. Hydrous Bismuth Oxides (HBOs) appear to have a significant sorptive potentials for removing nitrate, fluoride, and arsenic from contaminated ground.
2. In coexisting conditions, at the concentration most commonly found in groundwater, arsenic is the most preferred anionic contaminant followed by fluoride and nitrate for HBOs in terms of removal potentials.
3. Among the three forms of HBOs, designated as HBO_1, HBO_2 and HBO_3 examined during this study while HBO_1 shows preferential adsorption of As(III), followed by fluoride, HBO_2 and HBO_3 prefer As(III) followed by nitrate.

4. A mixture of HBO_1 and HBO_2 (designated as HBO_{12mix}) appears to be a potential material for the simultaneous removal of nitrate, fluoride and arsenic from groundwater under coexisting conditions.

5. While the pHpzc of HBO_1 is around 6.5, it is around 8.0-8.2, for HBO_{12mix}. The increased pH_{pzc} of HBO_{12mix} appears to make it more suitable for removing anionic contaminants from water in the normal pH range.

6. Chloride embedded in the polymeric structure of the material, appears to be the exchange anion in the sorptive removal of contaminants and competitive anionic species from water.

7. The release of Cl^- from the hydrous bismuth oxide (HBO_{12mix}) during the sorption process could lead to the conclusion that chloride ions adhere to the surface with weak interaction and could easily be replaced under suitable conditions (pH< 8.0 ±0.2).

8. Alkalinity followed by sulfate are the most important competitive anions for the removal of nitrate, fluoride and arsenic through such media.

9. Regeneration of sorptive material can be done using NaOH and NaCl solutions, followed by bed washing with water.

10. In order to reduce the contaminants level to drinking limits, a pretreatment of the water to reduce alkalinity and sulfate appears to be desirable and an increase in the HBO_2 content is essential.

11. HBO_{12mix} may be used as a potential sorbent for development of a point of use (POU) treatment unit to remove arsenic and fluoride that are simultaneously present in groundwater. The nitrate removal remains low.

5.3 Suggestions for future work:

Based on experiences gained in the course of present study, the following suggestions can be made for further studies in order to achieve the objectives of the present work:

1. As alkalinity appears to be most potential competitive anion. The alkalinity can be investigated in the aqueous environment to pretreat the water.

2. Embedded chloride are observed to be the exchange ion for adsorbed anionic contaminants, a detailed study of formation and existence of chloride within the structural matrix may be undertaken to understand the full scientific facts and behavior of HBOs in an aqueous environment.

3. A non-thermal method of dehydration the materials can be examined to harness the full sorption potentials of HBOs.

4. The optimization and sustainability of the spent adsorbents still needs to be researched and developed.

5. The effect of common groundwater ions such as calcium, manganese, iron and ammonium ions on the removal of specific contaminants by HBO_{12mix} must be further investigated.