

MATERIALS AND METHODS

3.1 Material/Glassware

Borosilicate glasswares (Erlenmeyer flask, beaker, conical flasks, measuring cylinders, pipette, burette and volumetric flasks, glass columns), adsorption bottles, distilled water etc. have been used during the experiments.

3.2 Chemicals and Reagents

All the chemicals used in different experiments are analytical grade (AR) and obtained from Loba Chemie Pvt. Ltd., Mumbai, India. The major chemicals and reagents used during the experiments are bismuth trioxide (Bi_2O_3), hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium nitrate (NaNO_3), sodium fluoride (NaF), sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$), sulphamic acid ($\text{NH}_2\text{SO}_3\text{H}$), sodium borohydride (NaBH_4), sodium chloride (NaCl), silver nitrate (AgNO_3), Total Ionic Strength Adjustment Buffer (TISAB) for nitrate and fluoride, sodium bicarbonate (NaHCO_3), sodium sulfate (Na_2SO_4), barium chloride (BaCl_2), pH buffer solutions etc.

3.3 Instruments

The instruments used during the experiments include a digital Ion meter (HANNA HI 4222, Hanna Equipment's (India) Pvt. Ltd, Navi Mumbai, India) to determine the nitrate and fluoride concentrations in water and Wagtech Digital Arsenator (Model No: Wag-WE10500, Wagtech International, UK) for arsenic concentration measurements. An atomic absorption spectrophotometer (AAS4141,

Electronic Corporation of India Limited, Hyderabad, India) was also used to measure bismuth concentration in treated water. The pH measurement was carried out with the help of a digital pH meter (ITS 201, ISO-TECH system Pvt. limited, Varanasi, India). Other similar supporting instruments such as oven, magnetic stirrer, rotating orbital shaker etc. were used as available in the laboratory. Figure 3.1 and 3.2 show the digital pH meter and ion meter used when measuring nitrate and fluoride. Figure 3.3 and 3.4 show the arsenic measurement systems used during the experiments.



Figure 3.1: Ion meter for measuring pH



Figure 3.2: Ion meter for measuring nitrate and fluoride concentrations



Figure 3.3: Arsenator set up for measuring arsenic concentrations



Figure 3.4: Wagtech Digital Arsenator kit

3.4 Determination of pH, nitrate, fluoride, arsenic, and other parameters

All parameters were determined as per the Standard Methods, 21st edition (2005) (APHA, 2005). The nitrate and fluoride concentrations in water were measured by using Digital Ion-meter (HANNA HI 4222) of Hanna Equipments (India) Pvt. Ltd, Navi Mumbai, India with ion selective electrode (ISE) while the arsenic concentration was measured by Wagtech Digital Arsenator (Model No: Wag-WE10500, manufactured by Wagtech International, UK) according to the Standard Method (APHA, 2005).

Before determining the nitrate or fluoride concentration, the ion selective electrode was placed in 100 mg NO₃⁻/L or 100 mg F⁻/L for 1 h in order to charge the sensor module. All standard solutions were prepared in double distilled water. To prepare a standard nitrate solution of strength 0.1, 1, 10 and 100 mg NO₃⁻/L, sodium nitrate (NaNO₃) was taken for preparation and the instrument was calibrated. Similarly, 0.1, 1, 10 and 100 mg F⁻/L of standard fluoride (NaF) solution were prepared from sodium fluoride and instrument was calibrated. After calibration, the nitrate and fluoride concentrations of each sample were determined. A known volume (50 mL) of the sample was placed in a 100 mL volumetric flask, and 2 mL of Total Ionic Strength Adjustment Buffer (TISAB) solution was added to the sample and stirred with a magnetic stirrer for one minute. The electrode tip was immersed in the sample and the potential reading was recorded when it was stable. A Separate TISAB solution is required for each nitrate or fluoride determination. The pre calibration of instrument with known standards is required for sample analysis. For uniformity and consistency, all the readings were taken after a sample-ISE contact time of 2 min. Standard observations based on three triplicate samples were reported. The adsorption experiments were carried out in 100 mL Erlenmeyer flask.

All experiments were carried out at ambient temperature (25±2°C). Hanna ion meter (HANNA HI 4222) has the execution range of detection from 1×10⁻⁶ to 9.99×10¹⁰ concentration with a resolution of 0.1 conc./0.01 conc. The accuracy of instrument is ±0.5% (monovalent ions) at a temperature of 20°C. (User manual, Hanna Instruments)

In a typical laboratory analysis with an Arsenator, a flask is filled with 50 mL of sample solution, and a sachet of sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$) powder is poured into the solution. Next, a sodium borohydride (NaBH_4) tablet is dropped into the flask and a bung device loaded with filter slides is immediately pushed firmly into the mouth of the flask. The reaction is allowed to proceed to completion for 20 min. Afterwards the appropriate filter is removed from the bung device, its color is matched to the color chart, and if the visual measurement is less than 0.1 mg/L, the slide is inserted into the Arsenator and the result of arsenic concentration is recorded in $\mu\text{g/L}$. Otherwise, the solution is diluted accordingly and the above procedures is repeated again. The Wag tech digital arsenator (Wag-WE10500) used in this work provided a good linear calibration over the entire working range of 0–100 $\mu\text{g/L}$. The limit of detection of arsenator is around 2 $\mu\text{g/L}$ and its accuracy for the quality control standard of 50 $\mu\text{g/L}$ is around $\pm 10 \mu\text{g/L}$ or $\pm 20\%$ with 95% confidence (Safarzadeh-Amiri et al., 2011).

The determination of arsenic by Arsenator is based on the Gutzeit reaction, in which a sachet of sulfamic acid in arsenic solution (sample) is used to lower the pH of the solution and after the sulfamic acid has dissolved, a tablet of sodium borohydride (<10%) in 100 mL is inserted in conical flask containing 50 mL of arsenic solution with the lid closed. A reaction time of 20 min is reported in which arsine gas is evolved and trapped on a strip with a mercuric bromide coating on the lid. Thus, a change in the color of the strip on spectrophotometer indicates the concentration of arsenic in aqueous solution. Each time a blank (distilled water), a standard (0.01 mg/L using sodium arsenate), is used to calibrate the Arsenator before first use. Standard observations based on three triplicate samples are reported. The adsorption experiments are carried

out in 100 mL Erlenmeyer flask. All experiments, were performed at ambient temperature ($25\pm 2^\circ\text{C}$).

The pH of the samples was measured with a digital pH meter (ITS 201, ISO-TECH system Pvt. limited, Varanasi, India). The instrument was first calibrated with standard solution of pH 4.0, 7.0 and 9.2 using pH buffer solutions. The samples were then taken and pH was noted directly. Chloride in water was determined by Argentometric titration method using N/71 silver nitrate (AgNO_3) solution as the titrant and potassium chromate (KCrO_4) as indicator. The alkalinity (as mg CaCO_3/L) of water was determined by titrimetric method using N/50 HCl (titrant) with mixed indicators (Phenolphthalein and Methyl Orange).

The gravimetric method was used to determine the sulfate in the water samples. First, a 200 mL of water sample was taken and the pH was adjusted to 4.5-5.0 with HCl using a pH meter. Then 1 to 2 mL of HCl was added. It was then heated to boiling until solution volume reduced to 50 mL. Warm BaCl_2 solution is slowly added with stirring until the precipitation appears to be complete. The precipitate is digested at 80 to 90°C , preferably overnight, but not less than 2 h. The precipitate is washed with small portions of warm distilled water until washing liquids are chloride free. The filter and precipitate are placed in a weighed platinum/silica crucible and calcined at 800°C for 2 h. Then crucible is cooled in desiccators and weighed.

3.5 General experiment

3.5.1 Stock solutions for nitrate, fluoride, and arsenic

All chemicals used in this study were of analytical grade. NaNO_3 , NaF , and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (E. Mark, Germany) salts were used for the preparation of 1000 mg/L

stock solutions in deionized/distilled water (DI) with a pH of 6.94-7.1. All synthetic anion solutions for adsorption and analysis were prepared by suitable dilution of the stock solution in distilled water. Only glass reagent bottles were used for handling anions solution.

3.5.2 Batch adsorption experiment

A batch experiment was carried out to investigate the effect of adsorbent dose and contact time on the adsorption of nitrate, fluoride and arsenate as part of the study. Sodium nitrate, sodium fluoride and sodium arsenate (AR grade) were used to prepare all working solutions. Three hours of contact time were given at room temperature with solution in 100 mL Erlenmeyer flask. The contents were continuously stirred and finally filtered using filter paper. The remaining filtrates were then analyzed for different concentration of anions. First, the contact time and dosage were optimized and other parameters such as competitive anions were investigated. Observations based on three triplicate samples were averaged and reported.

3.5.2.1 Effect of adsorbent dosage

The effect of the adsorbent dosage on the removal of nitrate, fluoride, and As(V) were studied at initial concentration of 1.5 meq/L (≈ 95 mg/L) of nitrate, 0.25 meq/L (≈ 5 mg/L) of fluoride and 0.001 meq/L (≈ 0.08 mg/L) of As(V). The adsorbent dosage was varied from 10-150 g/L. After three- hour period, samples were filtered and pH, chloride, nitrate/fluoride/As(V) concentrations of all solutions were measured.

3.5.2.2 Effect of contact time

The time required to attain the state of equilibrium is termed as equilibrium time. In order to investigate the effect of contact time on nitrate, fluoride and As(V) removal, the duration up to 5 h was investigated in steps of 1 h.

3.5.3 Column adsorption experiment

For large scale field application, column operation is preferred because it provides an effective contact mode of the adsorbent with contaminated water. In order to investigate the behavior of adsorbents under dynamic condition, a fixed bed column operation is generally preferred (Ayoob and Gupta, 2006). Fixed bed column performance and construction is assessed using the breakthrough curve. The time and shape of the breakthrough curve are the essential parameters for determining the adsorption capacity of the column. The plot of dimensionless concentration C/C_0 versus the effluent volume at specific bed height and flow rate was used to obtain the breakthrough curve. The point at which the concentration (C) of nitrate, fluoride or arsenate in effluent reaches 10% of the influent concentration (C_0) was designated as the 'breakthrough time' and the corresponding volume as the 'breakthrough volume'. When the concentration (C) of nitrate, fluoride or arsenate in effluent reaches 90% of the influent concentration (C_0) in the breakthrough curve, this point has been referred to as the 'column exhaustion point' in the present study.

In order to provide sufficient porosity of the adsorbent medium, clean sand of slow sand filter specifications was mixed with hydrous bismuth oxide to be used in the column. The grain size distribution of mixed media is shown in Figure 3.5. Before the

addition of adsorbent material, a thin layer of sand was introduced in the bottom of column to prevent media loss. Figure 3.6 shows the experimental setup for the column adsorption experiment. Initially, a combination of 20 g HBO₁, 20 g clean sand and 20 g HBO₂ were used in the column study, but, it showed quick exhaustion of the adsorbents. Subsequently, the proportions were increased to get some observable values. In the column, nitrate exhaustion was occurring very quickly, but, fluoride and As(V) free water was obtainable in fair amounts, indicating the need to increase the proportion of HBO₂. Finally, through trial-and-error adjustments, the column with an internal diameter of 3 cm was filled with 50 g HBO₁, 150 g clean sand and 200 g HBO₂ to give a total media saturated height of 51 cm which resulted in complete removal of nitrate through the bed. This bed was used for observations in column study with mixed solution of nitrate, fluoride and As(V). The deionized /distill water was passed through the column until all of the free chloride was released.

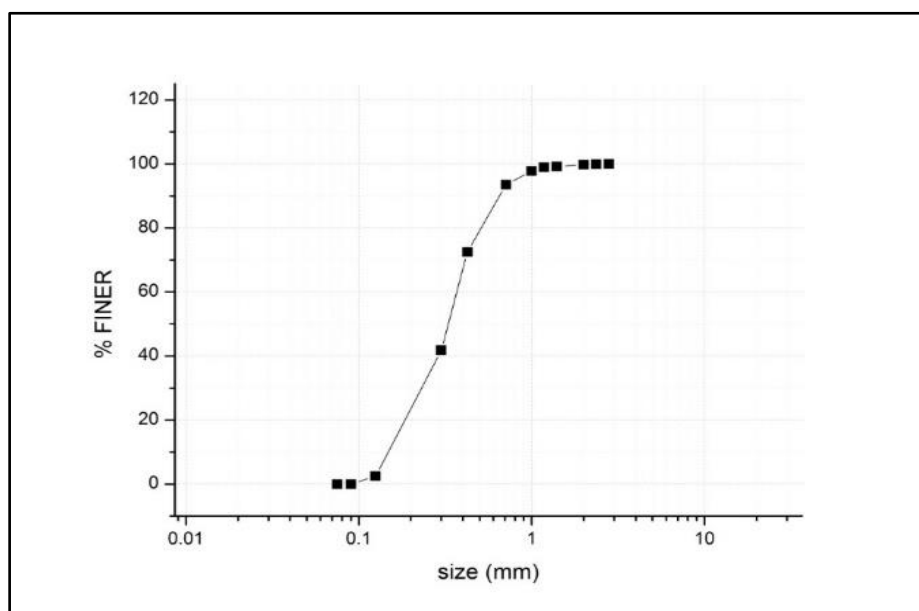


Figure 3.5: Grain size distribution of adsorbent

The influent through the column consisted of 1.5 meq/L (≈ 95 mg/L) NO_3^- , 0.25 meq/L (≈ 5 mg/L) F^- and 0.001 meq/L (≈ 0.08 mg/L) As(V) in mixed condition. A flow rate of 1.2–1.5 mL/min was maintained through the column. Samples were taken at regular interval of 30 minutes for water quality analyzes with regard to pH, residual nitrate, fluoride, As(V) and chloride concentrations.

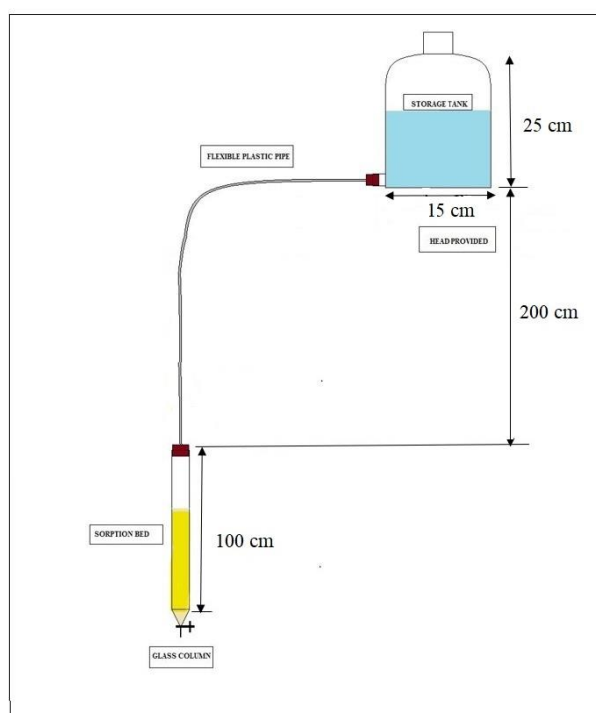


Figure 3.6: Experimental set up for Column experiment

3.5.4 Regeneration studies

In the present study, sodium hydroxide solution and sodium chloride solution with a uniform flow were used as regenerant. First, 500 mL of a 0.1 N NaOH solution is passed at a uniform flow rate of 1.2-1.5 mL/min (for around 6 h) through the adsorbing media, which is sufficient to detach most of the adsorbed contents on the bed. This is measured by the concentration of the contaminating ion in the regenerant

effluent. Once this is sufficiently low, 500 mL of 0.1 N NaCl solution is passed at the same uniform flow rate of approx. 1.2-1.5 mL/min (for 6 h) through the column. The effluent from the column is analyzed for residual chloride concentration. When the effluent from adsorption column reaches almost the same concentration as that of influent, it is understood that the adsorption column is fully regenerated. Finally, enough distilled water is passed through the column and the effluent is analyzed for its pH and chloride concentration. In the fully washed and regenerate column, the final pH is close to neutral (7.3-7.4) and there is almost no chloride in the effluent from the column bed.

3.6 Adsorption kinetics studies

Time-depended adsorption studies were performed in a batch system with the synthetic solution containing nitrate, fluoride and As(V) to find the maximum sorption capacity and rate constants. Three kinetic models: the first order kinetic model, second order kinetic model and Weber Morris kinetic model were examined. For the purpose, 100 mL of mixed solution in conical flask is added with 130 g/L of adsorbent and stirred continuously. Triplicate samples are filtered after 5, 10, 15, 20, 30, 45, 60, 75, 90, 120, 150, 180, 210, 240 minutes and analyzed for residual nitrate, fluoride, As(V) concentrations.

3.7 Adsorption isotherm studies

The parameters of the adsorption isotherm are measure of surface properties and the affinity for adsorbent at the fixed temperature. Langmuir, Freundlich and Dubinin-

Redushkevich (DR) isotherms are few frequently studied models to understand the adsorption processes.

Isotherm studies were performed by mixing of 130 g/L adsorbent with 100 mL mixed solution containing 70 to 95 mg/L nitrate, 3 to 5 mg/L fluoride and 0.08 to 0.10 mg/L As(V). All experiments were conducted with mixing at 250 rpm for 180 min contact time at constant temperature. For thermodynamic studies, experiments were carried at 298 K, 308 K and 318 K to achieve equilibrium.

3.8 Competing anions studies

For competing ions study, effects of bicarbonate and sulfate were examined. The concentration of these anions was varied from 1 to 5 meq/L (1 meq/L of sulfate = 48 mg/L of SO_4^{2-} and 1 meq/L of bicarbonate = 50 mg/L as CaCO_3) to simulate the real field conditions. After 3h, samples were filtered and analyzed for residual nitrate/fluoride/arsenic and pH.

3.9 Calculation of adsorption potential (mg/g) and percentage removals of nitrate, fluoride and arsenic

The mixed solution contained 1.5 meq NO_3^- /L (≈ 95 mg/L) of nitrate, 0.25 meq F⁻/L (≈ 5 mg/L) fluoride and 0.001 meq/L (≈ 0.08 mg/L) of As(V) in adsorption experiments. The number of ions adsorbed i.e, adsorption potential (q_e in mg/g) and removal efficiency (%) were calculated using the expression as (Eqs. 3.1, 3.2):

$$\text{Adsorption potential } (q_e) = \frac{C_o - C}{m} \quad (3.1)$$

$$\text{Adsorption efficiency } (\%) = \frac{C_o - C}{C_o} \times 100 \quad (3.2)$$

Where, C_0 and C are the initial concentration (mg/L) and residual/Final concentration (mg/L), m is the mass (g) of HBO per liter of solution.

3.10 Characterization of adsorbents

XRD, SEM, EDS and FTIR analyses were performed to characterize the adsorbent and understand the mechanism of adsorption. The pH_{PZC} value were determined by Fast alkalimetric titration method as used by Huang and Ostovic (1978), Srivastav et al. (2014).

XRD:

To understand the properties and dominant chemical species in HBOs, X-ray diffraction (XRD) analysis was performed. XRD patterns were obtained using an X-ray diffractometer (Philips1710, Netherland).

SEM:

Scanning electron microscopy plays an important role in understanding the interactions between HBO and targeted anions. The Scanning Electron Microscopy (SEM) Images were found by SEM and EDS (ZEISS EVO 18, Model-2045, Germany).

EDS:

Energy dispersive X-ray spectroscopy correlates with the elemental analysis of the adsorbent. The Images of energy dispersive X-ray spectroscopy (EDS) was found by SEM and EDS (ZEISS EVO 18, Model-2045, Germany).

FTIR:

FTIR provides quantitative evidence of the surface functionality of the adsorbent. FTIR spectrum was collected using FTIR spectrometer (Nicolet iS5, THERMO Electron Scientific Instruments LLC, USA).

pH_{PZC}:

The behavior of adsorbent can be predicted by its point of zero charge (pH_{PZC}) value. pH lower than the pzc value, the system is said "below the pzc.", the acidic water donates more protons than hydroxide groups below the pzc, and so the adsorbent surface gets positive charged (attracting anions). Therefore, it favors the sorption of target anions with vice versa (Mukhopadhyay et al., 2017).

The zero-charge pH of the adsorbent was determined using fast alkalimetric titration method (Huang and Ostovic, 1978; Agarwal et al., 2006; Sharma et al., 2009). For this purpose, 100 mL of NaCl solution with a strength of 0.01 and 0.001 N were prepared. 1.0 g of HBO_{12mix} powder was added, and stirred continuously for 12 h and titrated in presence of the powder with 0.1 N HCl and another with 0.1 N NaOH. The volume of acids or alkali consumed corresponding to each pH difference of 0.5 unit was recorded. The samples were allowed to settle and the solid materials were filtered off through Whatman 42 filter paper. The filtrates were titrated similarly. The net titration curve for each ionic strength was obtained by subtracting the titration curve of the filtrate samples from that of the portions with the powder. In the absence of specific chemical interaction between the individual electrolyte and the sorbent surface, the net titration curves usually meet at a point that is defined as pH_{PZC}.

3.11 Determination of bismuth concentration in treated water

The determination of bismuth was carried out using Atomic Absorption Spectrophotometer (Element AS AAS4141) (Electronic Corporation of India, Hyderabad, India). The Direct Air-Acetylene Flame Method (3111 B) was followed according to Standard Methods (APHA, 2005) for the determination of bismuth in aqueous solution.

3.12 Standard solutions for nitrate, fluoride, and arsenic

NaNO_3 , NaF , and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ salts (E. Mark, Germany) were used for preparations of 1000 mg/L stock solutions in deionized water (DI). In addition, a mix solution (containing all three water contaminants) with 1.5 meq/L (≈ 95 mg/L) of nitrate, 0.25 meq/L (≈ 5 mg/L) of fluoride and 0.001 meq/L (≈ 0.08 mg/L) was prepared. These concentration levels were selected based on the average and maximum values of contaminants reported in groundwater (Delorme et al., 2007; Devi et al., 2008; Bibi et al., 2015).

3.13 Selection of adsorbent

For simultaneous removal of nitrate, fluoride and arsenic from water, bismuth-based media being of recent origin was selected to be studied in detail. Hydrated bismuth oxides (HBOs) have been reported as a promising sorptive material for removing anionic contaminants such as nitrate and fluoride from groundwater (Srivastav et al., 2013, Singh et al., 2015). Therefore, in the present study, HBOs were studied to evaluate their sorption potentials for nitrate, fluoride, and arsenic from a mixed solution in coexisting condition. Both forms of arsenic, As (III) and As(V) were

tested and it was observed that removal efficiency of arsenate (As(V)) was higher than the arsenite (As(III)). Therefore, As(V) was chosen for further experiments.

3.14 Preparations of Hydrous Bismuth Oxide (HBO) media

The method of preparation for HBOs was followed as given by Fritsche (1993) and Singh (1999). AR grade Bismuth trioxide powder is the base material for all other HBOs preparation. A 0.1 N Bi_2O_3 solution in 2N HCl forms the starting point of all further preparations of hydrous bismuth oxides (HBOs). For this purpose, 4.66 g Bi_2O_3 is dissolved in 100 mL of 2 N HCl solution. Since, Bi_2O_3 is very sparingly soluble, the content is continuously mixed until it is completely dissolved.

Mixing this Bi_2O_3 solution (in 2N HCl) with 2N NaOH solution in different volumetric ratio give precipitates of differing colors and characteristics. The precipitate that is formed at a volumetric proportion of 1:1 of 0.1 M Bi_2O_3 (in 2 N HCl) with 2 N NaOH is designated as HBO₁, and is visibly colored white. Similarly, the precipitate obtained by mixing 0.1 M Bi_2O_3 in 2 N HCl with 2 N NaOH in a ratio of 1:2 (v/v) is expressed as HBO₂ and in a ratio of 1:3 (v/v) referred to as HBO₃. Both HBO₂ and HBO₃ are visibly yellow in colour. A reaction time of 1 h is given for precipitation and settling. Finally, excess hydroxide and chloride ions are removed from the precipitate by decanting and washing with double distilled water. Washed precipitates are dried in an oven at $103 \pm 2^\circ\text{C}$ for 24 h and stored in clean containers for later use. The specific gravity is an important characteristic of solid material. An average of three determinations for each powder gave the mean specific gravity of 5.8 ± 0.1 , 7.00 ± 0.08 , and 6.9 ± 0.1 for HBO₁, HBO₂ and HBO₃.