

UGC MAJOR RESEARCH PROJECT

Project title

**GRAPHENE OXIDE BASED POLYVALENT METAL
OXIDE NANOCOMPOSITE: PREPARATION,
CHARACTERIZATION AND EFFICIENCY
EVALUATION ON ARSENIC AND FLUORIDE
REMOVAL FROM CONTAMINATED WATER**

**Sanction order no: MRP-MAJOR-CHEM-2013-24291,
F. No.: 43-198/2014(SR)**

Final report Submitted To

The Joint secretary
University grants commission

Submitted by
DR. UDAY CHAND GHOSH
Principal Investigator
ASSOCIATE PROFESSOR (Retired),

DR. SASIKUMAR PALANI
CO- Investigator
**ASSISTANT PROFESSOR,
DEPARTMENT OF CHEMISTRY, PRESIDENCY
UNIVERSITY, KOLKATA, WB**

**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG NEW
DELHI – 110 002.**

Final Report of the work done on the Major Research Project.

(Report to be submitted within 6 weeks after completion of each year)

1. Project report No. Final MRP-MAJOR-CHEM-2013-24291
2. UGC Reference No.F. F.No.43-198/2014(SR)
3. Period of report: from 06.04.2016 to 30.06.2017
4. Title of research project GRAPHENE OXIDE BASED POLYVALENT METAL OXIDE NANOCOMPOSITE: PREPARATION, CHARACTERIZATION AND EFFICIENCY EVALUATION ON ARSENIC AND FLUORIDE REMOVAL FROM CONTAMINATED WATER
5. (a) Name of the Principal Investigator Dr. UDAY CHAND GHOSH
(b) Name of the Co Investigator Dr. Sasikumar Palani
(c) Dept. Of Chemistry
(d) University/College-where work has progressed Presidency University, Kolkata
6. Effective date of starting of the project 06.04.2016
7. Grant approved and expenditure incurred during the period of the report:
 - a. Total amount approved Rs. 891200.00
 - b. Total expenditure Rs. 619961.00
- c. Report of the work done: (**Attached separately**)
 - i. Brief objective of the project
 - ✓ Aimed to develop smart material for the treatment of high arsenic (> 0.01 mg/L) and high fluoride (> 1.5 mg/L) contaminated groundwater.
 - ✓ To estimate the efficiency of the material, effect of solution pH, reaction kinetics for the rate of adsorption reaction and the reaction equilibrium for thermodynamics are to be studied.
 - ✓ To estimate the regeneration of arsenic/fluoride adsorbed material.
 - ✓ To estimate the filter design parameters of material packed fixed bed for removing arsenic and fluoride for efficiency judgment.

To assess the efficiency of developed material comparing with the existing materials
 - ii. Work done so far and results achieved and publications, if any, resulting from the work (Give details of the papers and names of the journals in which it has

been published or accepted for publication _____

(1) Maji, S.; Ghosh, A.; Gupta, K.; Ghosh, A.; Ghorai, U.; Santra, A.; Sasikumar, P.; Ghosh, U. C. Efficiency Evaluation of Arsenic(III) Adsorption of Novel Graphene Oxide@iron-Aluminium Oxide Composite for the Contaminated Water Purification. *Sep. Purif. Technol.* **2018**, *197*, 388–400. <https://doi.org/10.1016/j.seppur.2018.01.021>.

(2) Kanrar, S.; Debnath, S.; De, P.; Parashar, K.; Pillay, K.; Sasikumar, P.; Ghosh, U. C. Preparation, Characterization and Evaluation of Fluoride Adsorption Efficiency from Water of Iron-Aluminium Oxide-Graphene Oxide Composite Material. *Chem. Eng. J.* **2016**, *306*, 269–279. <https://doi.org/10.1016/j.cej.2016.07.037>.

- iii. Has the progress been according to original plan of work and towards achieving the objective. if not, state reasons: Yes, the report of the work is in accordance with our original proposal
- iv. Please indicate the difficulties, if any, experienced in implementing the project Even though we received our fund nearly sanctioned amount, we were unable to utilize them beyond project period as we received it very late
- v. If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the Commission on a separate sheet.

Project is completed as per our proposal


- vi. If the project has been completed, please enclose a summary of the findings of the study. One bound copy of the final report of work done may also be sent to University Grants Commission. **(Attached separately)**
- vii. Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as
- (a) Manpower trained -4
- (b) Publication of results - 2


SIGNATURE OF THE PRINCIPAL INVESTIGATOR

Dr. Uday Chandu Ghosh
Associate Professor (Retd.) (WBES)
Department of Chemistry & Biochemistry
Presidency University (Erstwhile
Presidency College)



REGISTRAR
Registrar
Presidency University
Kolkata
(Seal)


SIGNATURE OF THE CO-INVESTIGATOR

Dr. Sanjay Kumar Paul
Assistant Professor
Department of Chemistry
Presidency University, Kolkata-700 073

**UNIVERSITY GRANTS
COMMISSION BAHADUR SHAH
ZAFAR MARG NEW DELHI – 110 002**

**PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING
THE FINAL REPORT OF THE WORK DONE ON THE PROJECT**

1	Title of the Project	GRAPHENE OXIDE BASED POLYVALENT METAL OXIDE NANOCOMPOSITE: PREPARATION, CHARACTERIZATION AND EFFICIENCY EVALUATION ON ARSENIC AND FLUORIDE REMOVAL FROM CONTAMINATED WATER
2 (a)	NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR	Dr. UDAY CHAND GHOSH, Department of Chemistry, Presidency University, 86/1, College Street, Kolkata – 700073
2 (b)	NAME AND ADDRESS OF THE Co- INVESTIGATOR	Dr. Sasikumar Palani, Department of Chemistry, Presidency University, 86/1, College Street, Kolkata 700073
3	NAME AND ADDRESS OF THE INSTITUTION	Presidency University, 86/1, College Street, Kolkata 700073
4	UGC APPROVAL LETTER NO. AND DATE	F. No. 43-19812014 (SR) dated 30.11.2015 (MRP-MAJORCHEM-2013-24291) (General)
5	DATE OF IMPLEMENTATION	April 06, 2016, the Date of Fund entered into the University account (as per the University Rule.)
6	TENURE OF THE PROJECT	Two (2) years (July 01, 2015 to June 30, 2017)
7	TOTAL GRANT ALLOCATED	8,91,200.00
8	TOTAL GRANT RECEIVED	8,27,000.00
9	FINAL EXPENDITURE	6,19,961.00
10	TITLE OF THE PROJECT	GRAPHENE OXIDE BASED POLYVALENT METAL OXIDE NANOCOMPOSITE: PREPARATION, CHARACTERIZATION AND EFFICIENCY EVALUATION ON ARSENIC AND FLUORIDE REMOVAL FROM CONTAMINATED WATER
11	OBJECTIVES OF THE PROJECT	<p>✓ Aimed to develop smart material for the treatment of high arsenic (> 0.01 mg/L) and high fluoride (> 1.5 mg/L) contaminated groundwater.</p> <p>✓ To estimate the efficiency of the material, effect of solution pH, reaction kinetics for the rate of adsorption reaction and the reaction equilibrium for thermodynamics are to be studied.</p> <p>✓ To estimate the regeneration of arsenic/fluoride</p>

		adsorbed material. ✓ To estimate the filter design parameters of material packed fixed bed for removing arsenic and fluoride for efficiency judgment. ✓ To assess the efficiency of developed material comparing with the existing materials
12	WHETHER OBJECTIVES WERE ACHIEVED	Achieved and report attached separately
13	ACHIEVEMENTS FROM THE PROJECT	Attached separately
14	SUMMARY OF THE FINDINGS	Attached separately
15	CONTRIBUTION TO THE SOCIETY	The materials those have been developed for the detoxification of arsenic and fluoride contaminated water can be used for the filtering material preparation for public use
16	WHETHER ANY PH.D. ENROLLED/PRODUCED OUT OF THE PROJECT	NIL
17	NO. OF PUBLICATIONS OUT OF THE PROJECT	Two and attached (1) Maji, S.; Ghosh, A.; Gupta, K.; Ghosh, A.; Ghorai, U.; Santra, A.; Sasikumar, P.; Ghosh, U. C. Efficiency Evaluation of Arsenic(III) Adsorption of Novel Graphene Oxide/iron-Aluminium Oxide Composite for the Contaminated Water Purification. <i>Sep. Purif. Technol.</i> 2018, 197, 388-400. https://doi.org/10.1016/j.seppur.2018.01.021 . (2) Kanrar, S.; Debnath, S.; De, P.; Parashar, K.; Pillay, K.; Sasikumar, P.; Ghosh, U. C. Preparation, Characterization and Evaluation of Fluoride Adsorption Efficiency from Water of Iron-Aluminium Oxide-Graphene Oxide Composite Material. <i>Chem. Eng. J.</i> 2016, 306, 269-279. https://doi.org/10.1016/j.cej.2016.07.037 .



Dr. Uday S. Ghosh
 (PRINCIPAL INVESTIGATOR)
 Department of Chemistry
 Presidency University (Presidency
 Presidency College)



(REGISTRAR)
 Registrar
 Presidency University
 Kolkata



(CO-INVESTIGATOR)
 Dr. Anil Kumar Ghosh
 Associate Professor
 Department of Chemistry
 Presidency University, Kolkata-700 073

Final Report Assessment / Evaluation Certificate
(Two Members Expert Committee Not Belonging to the Institute of Principal Investigator)

It is certified that the final report of Major Research Project F. No. 43-198I2014 (SR) dated 30.11.2015 (MRP-MAJORCHEM-2013-24291) entitled "Graphene oxide based polyvalent metal oxide nanocomposite: preparation, characterization and efficiency evaluation on arsenic and fluoride removal from contaminated water" by Dr. UDAY CHAND GHOSH, PI, and Dr. Sasikumar Palani, Co-I, Department of Chemistry, Presidency University, 86/1, College Street, Kolkata – 700073

has been assessed by the committee consisting the following members for final submission of the report to the UGC, New Delhi under the scheme of Major Research Project.

Comments/Suggestions of the Expert Committee:-

The report is comprehensive and very satisfactory

Name & Signatures of Experts with Date:-

Name of Expert	University/College name	Signature with Date
1. Dr. Arnab Halder	Head, Presidency University, Kolkata	 Head 26/03/2021 Department of Chemistry Presidency University Kolkata-700073
2. Prof. Gandhi Kumar Kar	Presidency University, Kolkata	 26.3.2021  Dr. Gandhi Kumar Kar Professor Department of Chemistry Presidency University, K Kolkata-700073
3. Prof. Shyamal Kumar Chattopadhyay	IIST, Shibpur (External Member)	 26.03.21  Dr. S.K. Chattopadhyay Professor Department of Chemistry Indian Institute of Engineering Science and Technology Shibpur, Howrah - 711 103, West Bengal, INDIA
4. Prof. Abhishek Dey	IACS, Jadavpur (External Member)	  Dr. Abhishek Dey Professor School of Chemical Sciences Indian Association for the Cultivation of Science Jadavpur, Kolkata - 700 032

It is certified that the final report has been uploaded on UGC-MRP portal. It is also certified that final report, Executive summary of the report, Research documents, monograph academic papers provided under Major Research Project have been posted on the website of the University/College.

(Registrar)


 Registrar
 Presidency University
 Kolkata

Seal

**GRAPHENE OXIDE BASED POLYVALENT METAL OXIDE NANOCOMPOSITE:
PREPARATION, CHARACTERIZATION AND EFFICIENCY EVALUATION ON
ARSENIC AND FLUORIDE REMOVAL FROM CONTAMINATED WATER**

Objective of the Project:

- ✓ Aimed to develop smart material for the treatment of high arsenic (> 0.01 mg/L) and high fluoride (> 1.5 mg/L) contaminated groundwater.
- ✓ To estimate the efficiency of the material, effect of solution pH, reaction kinetics for the rate of adsorption reaction and the reaction equilibrium for thermodynamics are to be studied.
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- ✓ To estimate the filter design parameters of material packed fixed bed for removing arsenic and fluoride for efficiency judgment.
- ✓ To assess the efficiency of developed material comparing with the existing materials

Present Work

The preparation of GO-incorporated hydrous iron(III)-aluminium(III) mixed oxide (GIAMO) composite with extensive characterizations, and the results evaluated on arsenic and fluoride adsorption efficiency over the as-prepared material for removal from the aqueous solutions with modelling of data.

ACHIEVEMENTS FROM THE PROJECT:

Reagents

Arsenic(III) oxide (99.9% Aldrich, USA), Sodium fluoride used for the preparation of fluoride source in solution was analytical grade (purity: 99.95%, BDH, England) reagent. Sodium 2-(para-sulfophenyl azo)-1,8-dihydroxy-3,6-naphthalene disulfonate (SPADNS) and zirconyl oxychloride used for fluoride estimation were both guaranteed reagent (G.R., Merck) grade. Graphite flakes used for preparation of GO was procured from Sigma Aldrich. The chloride salts of aluminium and iron were purchased from Merck (India), and rest chemicals used were of reagent grade (Merck).

Arsenic (III) solution

The stock solution of arsenic(III) (100 mgL^{-1}) was prepared by dissolving 0.1320 g of arsenic(III) oxide in 10 mL of 4% (w/v) sodium hydroxide, acidified with 2.0 mL of concentrated

hydrochloric acid, and diluted to 100 mL with arsenic free deionized water. The solution of a required As(III) concentration for working was made by diluting the stock with 0.2% (v/v) hydrochloric acid. The stock solution was prepared freshly after every 3 days and frozen to prevent oxidation.

Arsenic(III) analysis

Arsenic(III) in samples was analyzed with UV–vis spectrophotometer (Hitachi model 3210) and atomic absorption spectrophotometer attached with hydride generator assembly (Analyst-100, Perkin Elmer) by the methods described in ‘Standard methods for the examination of water and wastewater analysis’. Here, the arsenic(III) in samples was determined by adding hydrochloric acid (32%, v/v), potassium iodide (10%, w/v), and sodium borohydride (3%, w/v). The arsine (AsH_3) gas evolved was absorbed in silver diethyl dithiocarbamate (SDDC) solution in chloroform solvent, which gives red to pink color. Absorbance value of the pink to red solution was analyzed at a wavelength 535 nm against the reagent blank. In atomic absorption spectrophotometer, arsine gas was directly placed on the flame and absorbance was measured against the hollow cathode lamp of wavelength 193.7 nm. The absorbance value was compared with the calibration curve for arsenic concentration.

Fluoride stock solution

The stock solution of fluoride (1000 mg L^{-1}) was prepared by dissolving 2.210 g of NaF in 1.0 L of doubly distilled water. The working solution of a required concentration was made by exact dilution procedure with 0.01 M NaCl solution (ionic strength, $I = 0.01 \text{ M}$). The fluoride solutions of initial concentration, $[\text{F}]_0$ used for the experiments were ranged between 5.0 and 35.0 mg L^{-1} at an $I = 0.01 \text{ M}$.

Fluoride analysis (APHA, AWWA and WPCF, Washington DC. 1996)

UV–vis spectrophotometer (model U-3210, Hitachi Japan) was used for the colorimetric analysis of fluoride

Preparation of hydrous iron(III)-aluminium(III) mixed oxide (HIAMO)

A measured volume solution of 1.0(M) AlCl_3 in 0.1(M) HCl and that of 1.0(M) FeCl_3 in 0.1(M) HCl were mixed together (1:1 v/v). Aqueous NH_3 (1:1, v/v) solution was added drop wise from a dropping funnel to the well stirred mixed metal ion solution to attain the pH at ~ 7.0 . Here, both iron(III) and aluminium(III) were hydrolyzed and precipitated to corresponding mixed hydroxide gel, which was filtered, washed and dried in air oven to convert it to hydrated oxide.

Synthesis of graphene oxide (GO)-incorporated iron-aluminium mixed oxide (GIAMO):

Graphene oxide (GO, prepared as per previously reported)-incorporated iron-aluminium mixed oxide were prepared in simple chemical preparation method. In simple manner GO of different mass amount (Table 1) was taken separately in Erlenmeyer flasks and sonicated at least for an hour in water phase for complete dispersion. The well dispersed GO suspension was mixed to 100 mL of FeCl_3 solution (1 N) + 100 mL of AlCl_3 solution (1 N) and sonicated again for an hour. Once the time of sonication over, 1:1 NH_3 solution was added drop wise into the well stirred mixture until the pH of the solution rose up to ~ 7.0 . Jelly like brown solid mass was kept as such with the mother liquid for 24 h and filtered, washed until chloride free which was dried at $60\text{--}65\text{ }^\circ\text{C}$ inside an oven. Finally, the composite was crushed and sieved out to a range of desired particle size ($140\text{--}290\text{ }\mu\text{m}$) and also to powder for carry out the experiments.

Table 1: Ingredients composition used for preparation of GIAMO composites.

Graphene oxide (g)	1(N) FeCl_3 (mL)	1(N) AlCl_3 (mL)	Material
0	100	100	IAMO
1	100	100	GIAMO-1
2	100	100	GIAMO-2
3	100	100	GIAMO-3
4	100	100	GIAMO-4
5	100	100	GIAMO-5
6	100	100	GIAMO-6

Effect of GO dose on arsenic and fluoride adsorption over GIAMO

The increase of GO amount incorporated from $0.3 \rightarrow 0.7 \rightarrow 1.0 \rightarrow 2.0 \rightarrow 3.0$ g per 0.2 g equivalent amount of Fe-Al mixed oxide, from an aqueous arsenic(III) solution ($C_i = 5.0\text{ mg L}^{-1}$) which was nearly 10 to 35% higher than pristine IAMO (60–65%). The arsenic(III) removal increase linearly with GO content in GIAMO, and significant maxima attained at GIAMO-1.

Similarly the fluoride adsorption amount (q_e , $\text{mg}\cdot\text{g}^{-1}$) increased with enhancing GO loading amount up to 3 g. per 0.2 fraction gram unit formula amount of the mixed oxide. This confirms the optimized GO dosage amount (3.0 g per 0.2 fraction gram formula amount of HIAMO) required for the composite matrix for maximum fluoride adsorption, i.e. GIAMO-3 is good for fluoride adsorption.

Therefore, the studies of the samples GIAMO-1 (for As) and GIAMO-3 (for F) sample only has been highlighted.

Arsenic adsorption from aqueous media using GIAMO-1

Among the as-prepared GIAMO samples, *three samples consisting 1.0, 2.0 and 3.0 g of GO show equally good (92–95%) arsenic(III) removal efficiency*, which is 30–35% higher than pristine iron-aluminium oxide (IAMO) from an aqueous solution ($5.0 \text{ mg As}^{\text{III}}\cdot\text{L}^{-1}$) at pH 7.0 (± 0.2) and 303 K. Thus, 1.0 g GO-inserted GIAMO (**GIAMO-1**) sample was characterized as microcrystalline (10–15 nm) with BET surface area about 1.45 times higher than IAMO and investigated for the arsenic(III) adsorption. Optimized pH for arsenic(III) adsorption is 6.0–8.0. The kinetic data agree more closely with pseudo-first order equation ($R^2 = 0.98\text{--}0.99$) than pseudo-second order equation ($R^2 = 0.92\text{--}0.93$). The equilibrium data describe the Langmuir isotherm ($R^2 = 0.97\text{--}0.98$) better than the Freundlich isotherm ($R^2 = 0.91\text{--}0.92$), showing the Langmuir monolayer capacity $42.2836 \text{ mg}\cdot\text{g}^{-1}$ at 293 K which drops to $24.9170 \text{ mg}\cdot\text{g}^{-1}$ at 313 K. High negative enthalpy change ($\Delta H^\circ \sim -224 \text{ kJ}\cdot\text{mol}^{-1}$) is responsible for the spontaneous reaction ($\Delta G^\circ = \text{negative}$) despite unfavorable entropy change ($\Delta S^\circ = -0.71 \text{ kJ}\cdot\text{mol}^{-1}$). The order of competitive effect of PO_4^{3-} , SO_4^{2-} and HCO_3^- on arsenic(III) removal efficiency is $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{HCO}_3^-$. However, the high $\text{HCO}_3^- (> 200 \text{ mg}\cdot\text{L}^{-1})$ enhances the arsenic(III) removal efficiency of this material. 2.0 M NaOH can regenerate arsenic adsorbed GIAMO-1 only up to 50–60%. 0.65 g. of composite per L of high arsenic ($A_{\text{Total}}: 0.115 \text{ mg L}^{-1}$) groundwater can upgrade to potable standard, encouraging possible safe use for high arsenic water treatment. Highly negative enthalpy change, poor regeneration, FTIR, XRD and CV analyses of arsenic-rich solid suggested that arsenic(III) is stabilized over the solid surface without oxidation by surface complex formation.

Fluoride adsorption from aqueous media using GIAMO-3

Similarly, among all composition of GIAMO, the compound GIAMO-3 i.e. 3g GO incorporated iron aluminum oxide showed highest fluoride adsorption capacity (q_e , $\text{mg}\cdot\text{g}^{-1}$) at pH ~ 7.0 and ambient temperature. The material showed an increase of q_e with pH up to ~ 5.5 , and then reduced. Kinetically, fluoride adsorption took place obeying the pseudo-second order model. The Langmuir adsorption isotherm described the equilibrium data best with monolayer

adsorption capacities 22.13, 22.90 and 27.75 mg g⁻¹ at 288, 308 and 318 K, respectively, indicating endothermic nature of adsorption process, which was also confirmed from the thermodynamic analysis of equilibrium data. Fluoride adsorption efficiency of GIAMO had been predicted by modelling a single stage batch adsorber design parameters.

Characterization of GIAMO

Fig. 1 shows the FTIR spectra of as-prepared GIAMO, HIAMO and GO, respectively. The absorption bands at 1733 and 1620 cm⁻¹ indicate the stretching vibration of the CO and the CC of oxidized graphite flakes, respectively. The bands at around 1397, 1223 and 1049 cm⁻¹ are assigned for carboxyl (COOH), epoxy CO and alkoxy CO stretching vibrations, respectively. The broad band around 3400 cm⁻¹ is assigned for the stretching vibration frequency of OH groups. The band positions assigned for the GO are similar as reported in literatures. The bands at around 976, 1384, 1484, 3549 and 3660 cm⁻¹ are the signature bands of the hydrous metal oxides, which are also present in the HIAMO. The signature bands of the metal oxide gradually faded up from the spectra 1–6, confirming the presence of GO and metal oxides in the composites.

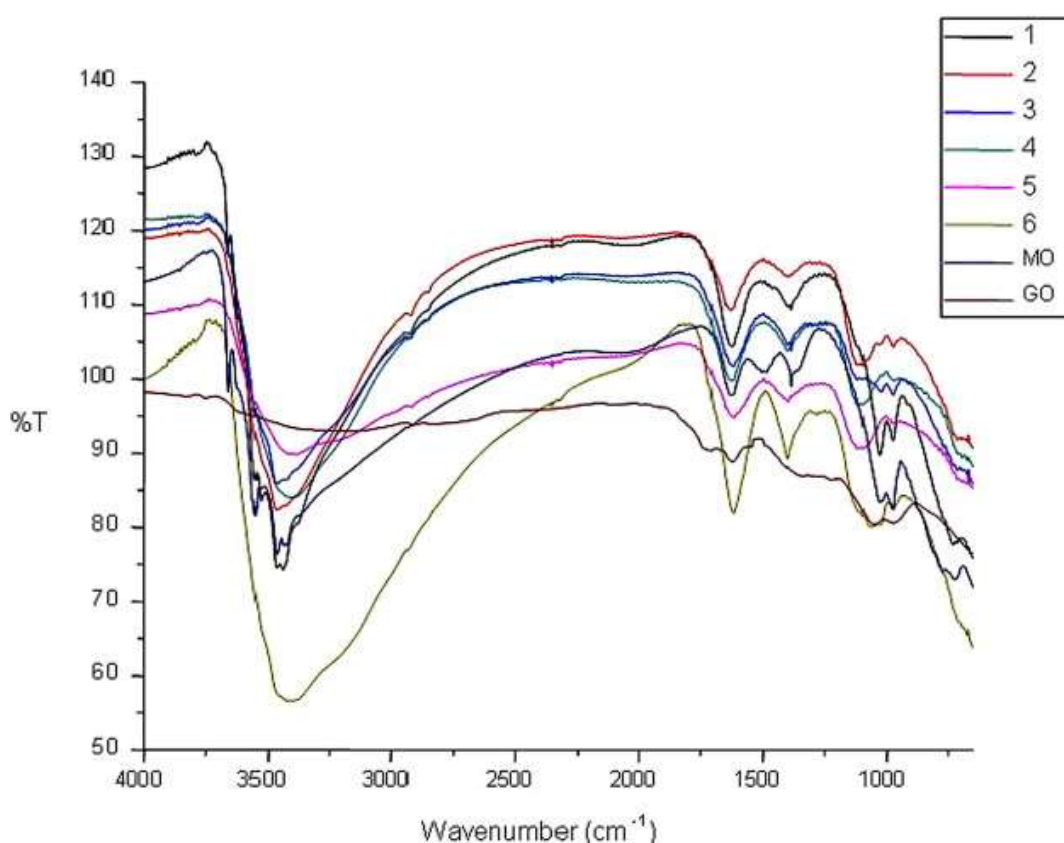


Fig. 1. Fourier Transform Infrared (FTIR) spectra of GIAMO samples comparing with graphene oxide (GO) and pure metal oxide (MO). 1, 2, 3, 4, 5 and 6 stand for one, two, three, four, five and six gram of GO incorporated in-situ into the matrix of 0.2 g formula unit mass amount of mixed oxide.

Fig. 2 shows the XRD patterns of (A) GO, (B) HIAMO, and (C) GIAMO for comparison. It is seen that the XRD pattern of GO (pattern-A) showed a diffraction peak with very high intensity at $2\theta = 10.63$ with a full width half maximum (FWHM) at ~ 0.82 and an unnoticeably poor peak at $2\theta = 36.12$. Moreover, the characteristic peaks of natural graphite at 2θ values 26.2, 44.8 and 55 were not found in pattern-A, indicating the GO used for the composite preparation with HIAMO is completely oxidized. The interlayer distance between the layer sheets was calculated to be 0.97 nm. The XRD pattern of HIAMO (pattern B) showed the representative peaks at $2\theta = 12.17, 27.23, 35.67, 39.67, 46.87$ and 56.25 indicating crystalline nature of the mixed oxide. The XRD pattern of the GIAMO (pattern-C) showed the presence of peaks at $2\theta = 27.23, 35.67, 39.67, 46.87$ and 56.25 indicating the signature of HIAMO in the GIAMO composite. However, intensity of the peak of GO ($2\theta = 10.63$) has been largely submerged but left the signature. Additional two peaks appeared clearly at 2θ value between 15 and 20 in pattern-C (GIAMO), which have been developed owing to the formation of some new phase via non-covalent interaction between HIAMO and GO in composite.

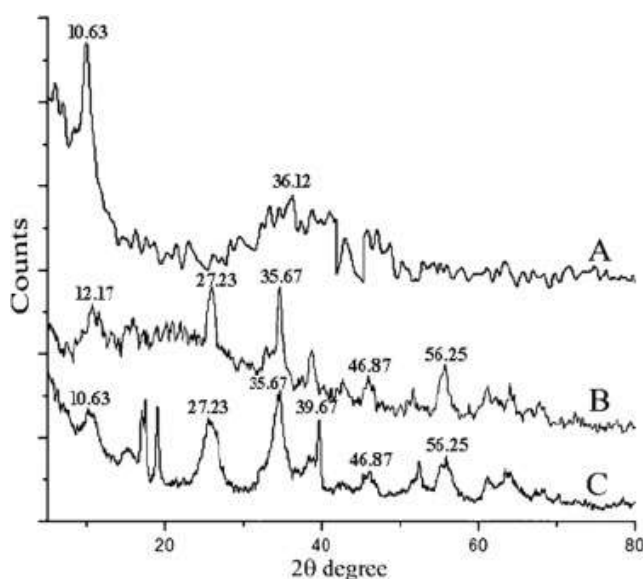


Fig. 2. Powder X-ray diffraction (XRD) patterns of (A) GO, (B) HIAMO and (C) GIAMO

Fig. 3 shows the images of transmission electronic microscopy (TEM) (image A: 40 nm and image B: 100 nm scales) including the selected area electron diffraction pattern (SAED) in inset of image-A, scanning electron microscopy (SEM) (image: C) and EDS spectrum (D) for the GIAMO material. The spindle like structures of the mixed oxide are irregularly dispersed and embedded into the matrix of the GO backbone. The surface of the GIAMO has appeared to be with irregular morphology and layers of CGM are observed with HIAMO particles incorporated

in between the layers. No separate layers of GO is observed in the SEM image, which supports that GO and HIAMO have well mixed with each other. The EDS spectrum of the adsorbent also confirms the presence of carbon, oxygen, iron and aluminium atoms in the adsorbent with percentage of the elements in the material.

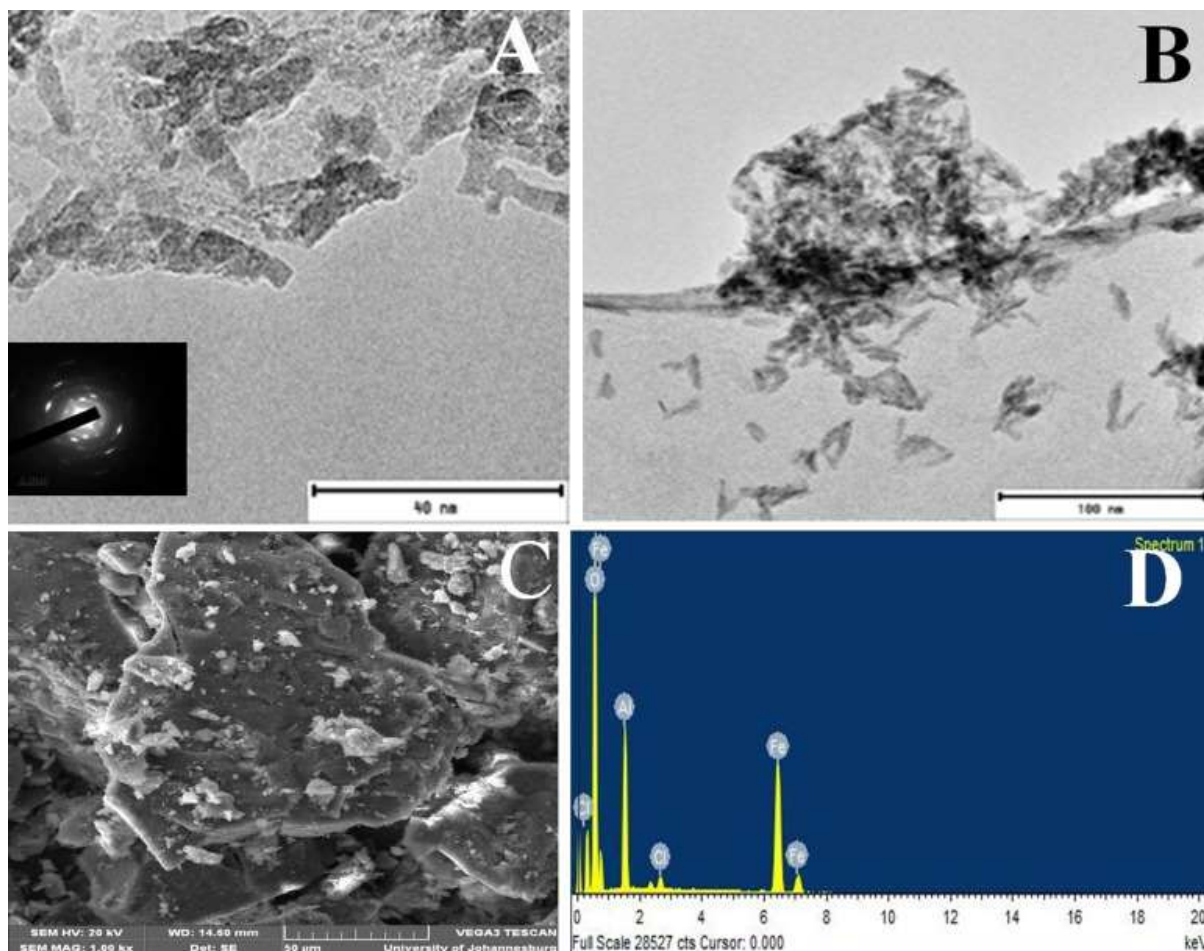


Fig. 3. Transmission electron microscopic images (A) 40 nm scale with SAED (inset), (B) 100 nm scale and (C) Scanning electron microscopic image with (D) EDAX spectra of GIAMO.

Fig. 4 shows the spectra of thermo gravimetric (TG) and differential thermal (DT) analyses of the as-prepared GIAMO. The TG spectrum recorded a rapid loss of mass up to a 450 °C temperature, which is 38% of the initially taken mass. Above that incinerated temperature, additional 4% mass loss was recorded. Thus, the total 42% mass disappearance leaving 58% residual mass of the initially taken amount is certainly owing to the combined loss of water from dehydroxylation of hydrous mixed oxide and GO of the composite. The DT spectrum recorded sharp two endothermic peaks at just below 100 °C and just before 300 °C, and two exothermic bands at around 250 °C and just below 450 °C. The endothermic DT peak appeared at just below 100 °C which is due to the loss of physically surface adhered water. Another endothermic DT

peak appeared at 300 °C which is due to elimination of water from the hydroxyl groups of hydrous metal oxide. Early exothermic DT band is probably for the thermal conversion of GO. The exothermic DT band (below 450 °C) appeared late has indicated the phase transition of the material.

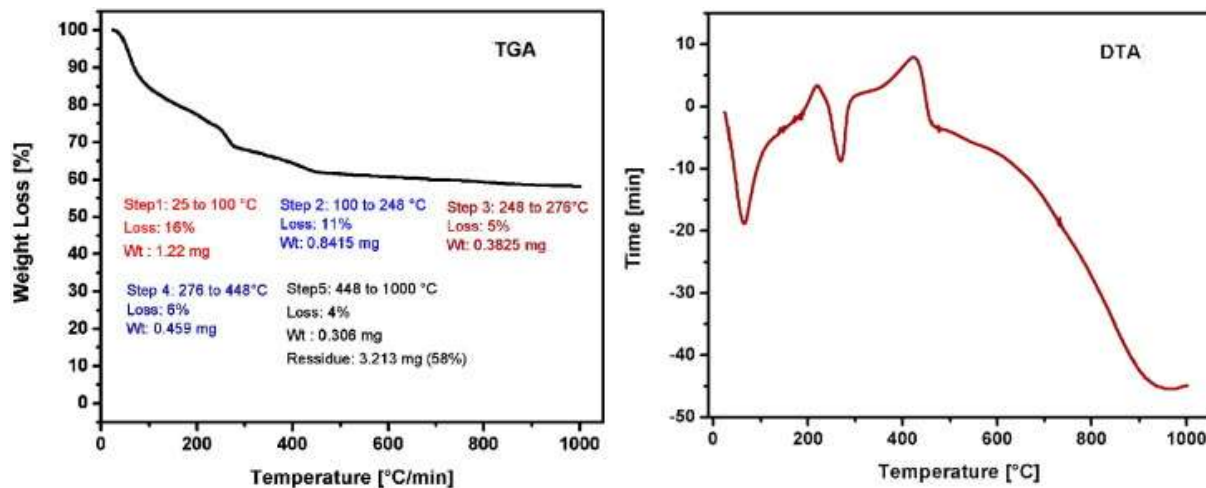


Fig. 4. Thermo gravimetric (TG) and differential thermal (DT) spectra of 3 g GO incorporated HIAGO composite material.

Zero-point surface charge pH (pH_{ZPC}) analysis

The zero-point surface charge pH (pH_{ZPC}) is an important parameter of adsorbent materials to be used in water purification since it can give an optimum pH condition for the applicability of the adsorbent in effective removal process. The pH_{ZPC} of the samples were estimated by the method of pH metric titration. Fig. 5 shows the pH_{ZPC} of GIAMO-1 and GIAMO-3. the pH_{ZPC} value of GIAMO-1 and GIAMO-3 have been estimated to be 6.58 and 5.73 respectively. At solution pH values lower than that required for attaining pH_{ZPC} , the sites become protonated and an excess positive charge develops on the surface. The contrary occurs at pH values higher than the pH_{ZPC} , where negative charge develops on the surface.

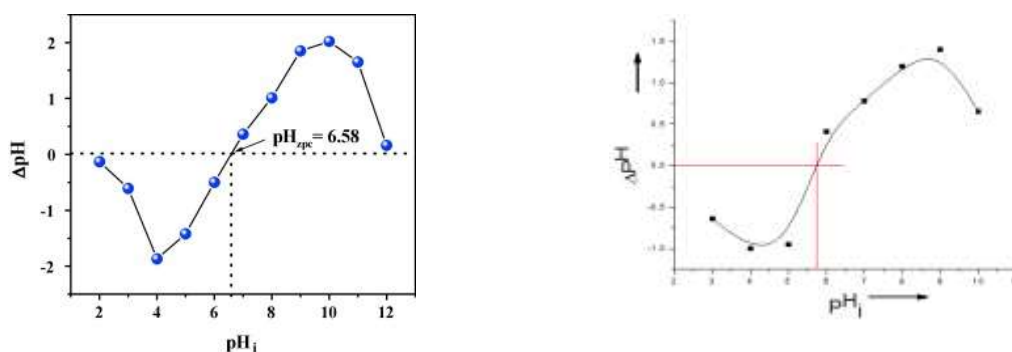


Fig. 5: ΔpH versus pH_I plots for pH_{ZPC} of GIAMO-1 (a) and GIAMO-3 (b)

Effect of pH

The arsenic adsorption amount (q_e) by GIAMO-1 was higher than those in pH_i range 3.0–5.0 but nearly same value in pH_i range 6.0–8.0. Again, the q_e amount reduced sharply when the pH_i of solution was increased to above 9.0.

Similarly fluoride adsorption by GIAMO-3 was higher at pH_i 6.0 and sharply reduced when increase the pH to above 7, imparts Columbic repulsion on fluoride of aqueous solution

Adsorption kinetics

The kinetics of an adsorption reaction is helpful to elucidate the reaction mechanism as well as the reaction rate informs the fastness of solute transfer from liquid to the solid surface giving idea about the lowest time of contact required for the designing of water filter

The kinetic data shown in Fig. 6 and 7, Table 1 and 2 were analyzed by the non-linear least square fit method using the most widely applied kinetic models such as pseudo-first order (PFO) (Eq. 1) and the pseudo-second order (PSO) (Eq. 2) equations.

$$q_t = q_e[1 - e^{-k_1 t}] \quad (1)$$

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

where k_1 (min^{-1}), k_2 ($\text{g mg}^{-1} \text{min}^{-1}$), q_t and q_e represents the pseudo-first order, the pseudo-second order rate constants, amount of fluoride adsorbed (mg g^{-1}) at any time t (min) and at equilibrium respectively.

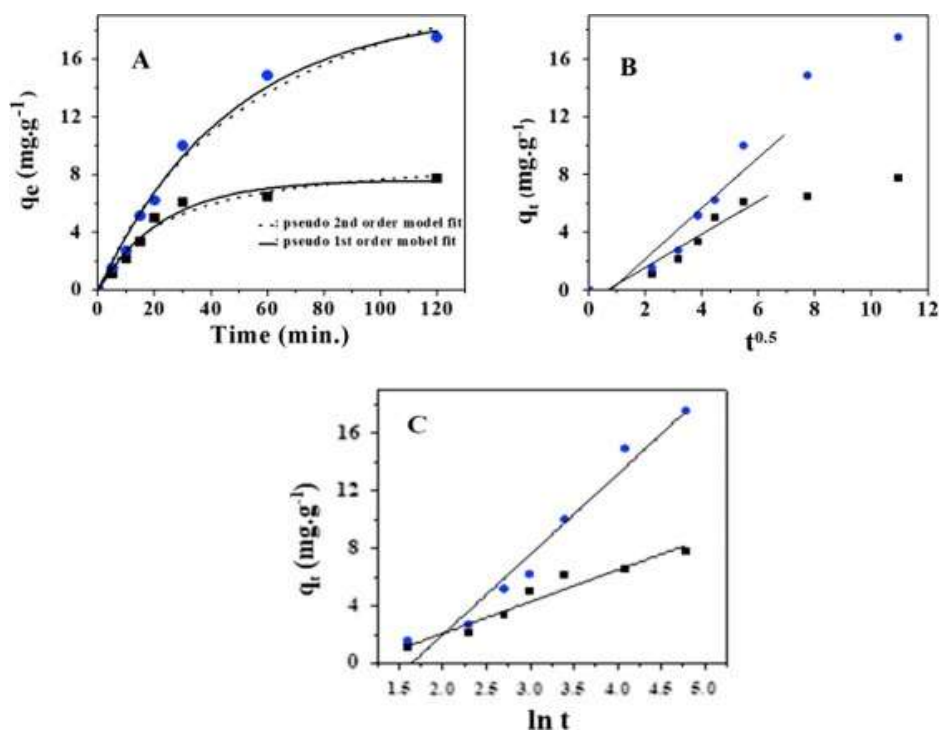


Fig. 6. The plots of (A) the q_t versus reaction time (t) including pseudo-first order (–) and pseudo-first order (...) model fits, (B) the q_t versus $t^{0.5}$ and (C) the q_t versus $\ln t$ on arsenic(III) adsorption reaction with GIAMO-1. = 10 mg·L⁻¹ and = 5 mg·L⁻¹.

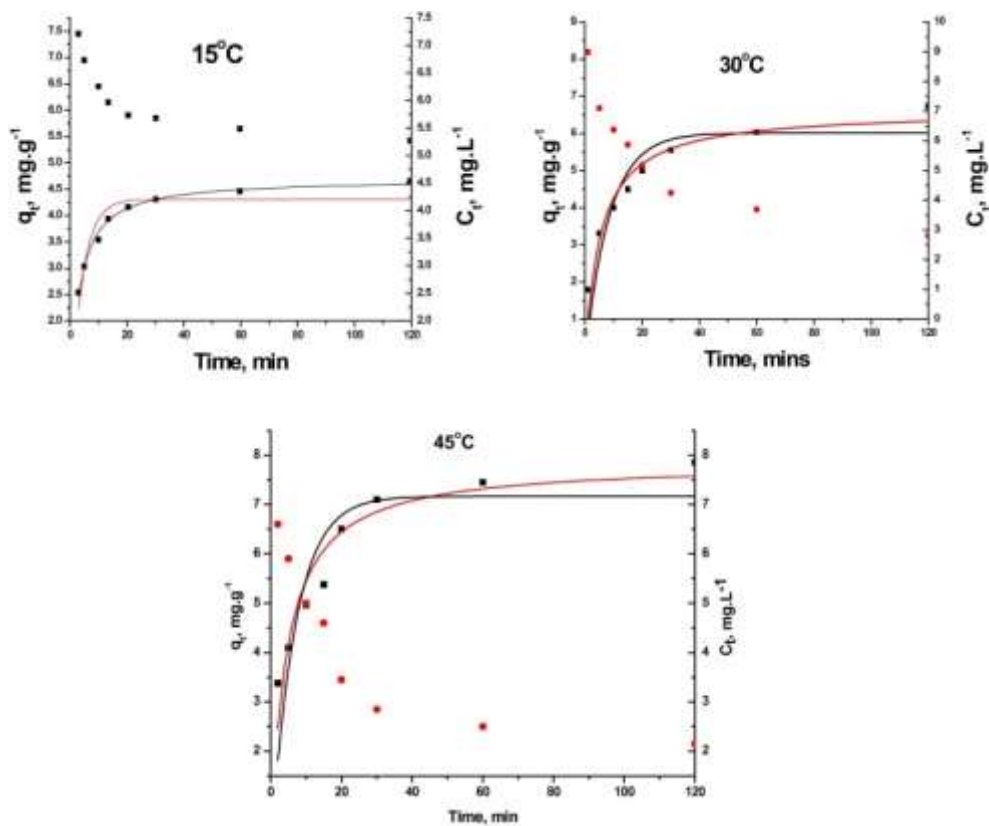


Fig. 7. Variation of time dependent fluoride adsorption capacity (q_t , mg g⁻¹) over GIAMO-3 against time of contact (min) at different temperatures with non-linear fits of data with pseudo first order (red) and pseudo-second order (black) kinetic model equations.

Table 1. The kinetic parameters estimated on the arsenic(III) adsorption by GIAMO-1 at pH ~ 7.0 and 303 K.

Models	Parameter	Concentration (mg·L ⁻¹)	
		5.0	10.0
Pseudo-first order (PFO)	R ²	0.9873	0.9874
	χ ²	0.2514	0.5082
	k ₁	0.0432	0.0216
	q _e	7.6251	19.4025
Pseudo-second order (PSO)	R ²	0.9258	0.9296
	χ ²	0.3396	0.8224
	k ₂	0.0044	27.4776
	q _e	9.5050	0.0006
Elovich	R ²	0.9289	0.9582
	χ ²	2.1095	7.7306
	a _e	0.7700	1.0810
	b _e	0.4550	0.1800
Intra-particle diffusion (IPD)	R ²	0.8891	0.8419
	χ ²	2.3986	8.2828
	k _i	1.1552	1.7602

Table 2. Kinetic parameters analyzed for the fluoride adsorption reaction with GIAMO-3 at different temperatures from an aqueous fluoride solution (fluoride concentration: 10 mg L⁻¹).

Parameters	15 °C		30 °C		40 °C	
	Pseudo-first order	Pseudo-second order	Pseudo-first order	Pseudo-second order	Pseudo-first order	Pseudo-second order
Rate constant	0.2427 ± 0.0329	0.0783 ± 0.0053	0.1172 ± 0.0281	± 0.0071	0.1468 ± 0.0377	0.0292 ± 0.0079
Q _e	4.3103 ± 0.1284	4.6964 ± 0.0499	6.0184 ± 0.4026	6.6202 ± 0.3269	7.1661 ± 0.4735	7.8504 ± 0.3926
R ²	0.88213	0.9906	0.8458	0.9424	0.7603	0.9068
χ ²	0.07485	0.0059	0.4541	0.1697	0.7481	0.2910

Inspection of the values (Table 1 and 2) of R² and χ² has indicated that the kinetic data of present reaction described the PFO model very well and better than the PSO model. That is the goodness of the kinetic data fit with PFO model is better than with PSO model for arsenic adsorption, whereas the PSO is better than PFO model for fluoride adsorption.

Adsorption equilibrium

Equilibrium of arsenic(III) and fluoride adsorption by GIAMO-1 and GIAMO-3 have been studied separately at 293, 303 and 313 K which can be capable to highlight the nature of adsorption. The adsorption data (q_e , mg g^{-1} and C_e , mg L^{-1}) obtained at equilibrium have been shown graphically in Fig. 8 and Fig. 9 and Table 3 and 4. These data have been analyzed by most common isotherm models such as Langmuir monolayer model equation (Eq. 3) and Freundlich multilayer model equation (Eq. 4) to know the maximum capacity of present material and the feasibility of this adsorption reaction under our experimental conditions.

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \quad (3)$$

$$q_e = K_F C_e^{1/n} \quad (4)$$

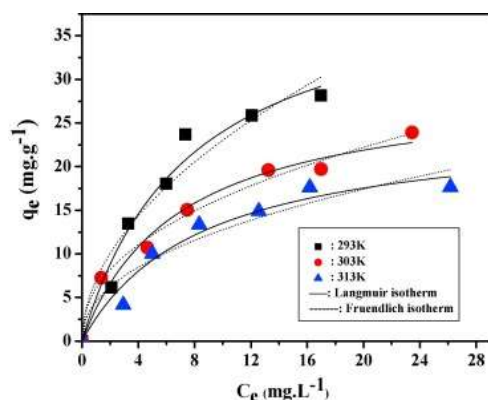


Fig.8: The plot on the variation of q_e versus C_e on the arsenic(III) adsorption by GIAMO-1 at $\text{pH} \sim 7.0$.

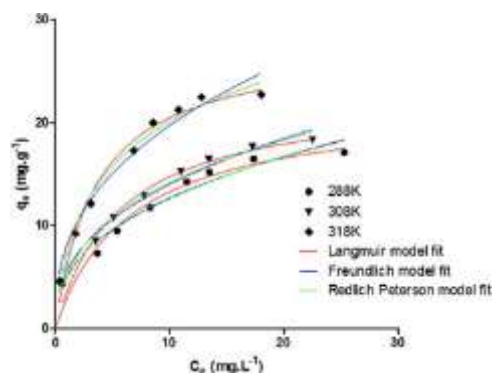


Fig. 9: Variation of fluoride adsorption capacity (q_e , mg g^{-1}) against the equilibrium solution fluoride concentration (C_e , mg L^{-1}) by GIAMO-3 at $\text{pH} \sim 7$

The experimental data were analyzed with nonlinear regression fit method of the mentioned models (Eqs. 3 and 4) (Fig. 8 and Fig. 9) on origin software. The isotherm parameters relating to each model equation have been estimated (Table 3 and 4). Comparison of the values of either the regression coefficient (R^2) or the statistical error (χ^2) reveals that the Langmuir model has explained the both arsenic and fluoride adsorption process much better than other models at the investigated temperatures. The better fit of the equilibrium data with the Langmuir isotherm model has suggested the monolayer surface coverage by the solute indicating the adsorption pockets of the material are energetically homogeneous and accessible equally by the solute.

Table 3. The isotherm parameters estimated on arsenic(III) adsorption by GIAMO-1 at pH ~ 7.0

Temperature (K)	Langmuir				Fruendlich			
	K_L	q_m	R^2	χ^2	K_F	n	R^2	χ^2
293	0.1315	42.2836	0.9741	3.8716	7.0240	1.9392	0.9207	7.6992
303	0.1453	29.4292	0.9785	0.9755	6.04629	2.3019	0.9196	1.7212
313	0.1190	24.9170	0.9785	1.9193	4.5531	2.2324	0.9095	4.1908

Table 4. The isotherm parameters estimated on fluoride adsorption by GIAMO-3 at pH ~ 7.0

Temperature (K)	Langmuir				Fruendlich			
	K_L	q_m	R^2	χ^2	K_F	n	R^2	χ^2
288	0.1520	22.03	0.9772	2.818	5.038	2.498	0.9642	5.310
308	0.1805	22.90	0.9814	1.774	5.579	2.502	0.9833	2.798
318	0.2813	27.75	0.9785	2.131	8.032	2.564	0.9714	9.234

Thermodynamics of adsorption reaction

Studies of the arsenic(III) adsorption reaction with increasing temperature (Table 5) showed that the adsorption capacity of GIAMO-1 lessened with the increase of temperature suggesting an exothermic process.

On other way the GIAMO-3 shows fluoride adsorption (Table 6) increases with increase of temperature suggesting an endothermic process occurs.

Table 5: The estimated Gibb's free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) on the arsenic(III) adsorption reaction with GIAMO-1 at pH ~ 7.0.

Temperature (K)	ΔG° (kJ·mol ⁻¹)	ΔH° (kJ·mol ⁻¹)	ΔS° (kJmol ⁻¹)
283	-22.97	-223.90	-0.71
293	-15.87		
303	-8.77		
313	-1.67		

Table 6: The estimated Gibb's free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) on the fluoride adsorption reaction with GIAMO-3 at pH ~ 7.0.

Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹)
288	-8.68	109.48	0.41
303	-9.18		
318	-9.8		

Desorption study: regeneration of the material achieved by treating the adsorbed materials with 0.1 N NaOH solution

Conclusion

In order to develop surface modified mixed metal oxide material aiming to apply for arsenic and fluoride rich groundwater treatment, graphene oxide (GO)-incorporated iron-aluminium oxide samples were prepared. Microcrystalline GO@iron-aluminium mixed oxide sample marked by GIAMO-1 and GIAMO-3 material has specific surface area higher than pristine iron-aluminium mixed oxide (HIAMO) sample and hence the higher adsorption capacity.

Note: The detailed study of characterization and other systematic studies are already published in following journals and attached the same here for your perusal^{1,2}

- (1) Maji, S.; Ghosh, A.; Gupta, K.; Ghosh, A.; Ghorai, U.; Santra, A.; Sasikumar, P.; Ghosh, U. C. Efficiency Evaluation of Arsenic(III) Adsorption of Novel Graphene Oxide@iron-Aluminium Oxide Composite for the Contaminated Water Purification. *Sep. Purif. Technol.* **2018**, *197*, 388–400. <https://doi.org/10.1016/j.seppur.2018.01.021>.
- (2) Kanrar, S.; Debnath, S.; De, P.; Parashar, K.; Pillay, K.; Sasikumar, P.; Ghosh, U. C. Preparation, Characterization and Evaluation of Fluoride Adsorption Efficiency from Water of Iron-Aluminium Oxide-Graphene Oxide Composite Material. *Chem. Eng. J.* **2016**, *306*, 269–279. <https://doi.org/10.1016/j.cej.2016.07.037>.