Fabrication of Multi-functionalized Graphene Oxide Doped Alginate Hybrid Spheres for Enhanced Fluoride Adsorption

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Abstract
In this current study, aminated graphene oxide (AGO) doped on alginate (Alg) matrix offers AGO@Alg hybrid spheres was developed to investigate its potential for retention of fluoride from water. The sophisticated characterization methods likely TGA, SEM, XPS and FTIR studies of AGO@Alg hybrid spheres were attained to recognize its physicochemical properties like thermal stability, morphology, elemental binding energy and functional groups determination. The responsible parameters for fluoride adsorption on AGO@Alg hybrid spheres were optimized under a batch mode to achieve improve defluoridation capacity (DC). The developed AGO@Alg hybrid spheres follow the electrostatic interaction mechanism on fluoride removal. The adsorption isotherms (Langmuir, Temkin, Dubinin–Radushkevich (D–R) and Freundlich models), kinetics (reaction and diffusion based models) and thermodynamic parameters (ΔS°, ΔG° and ΔH°) were investigated at 303, 313 and 323 K. To minimize the cost-effectiveness of AGO@Alg hybrid spheres the reusability test was carried out. The suitability of AGO@Alg hybrid spheres was also analyzed for the fluoride contaminated field sample taken from fluoride prevalent village.

Keywords Graphene oxide · AGO · Alginate · AGO@Alg spheres · Defluoridation · Field aptness: Recyclability

1 Introduction
Fluoride is considered as crucial nutrient liable for the dental and bone mineralization in our body. But surplus fluoride in potable water leads to the irremediable disease in human is described as fluorosis [1]. Therefore the acceptable level of fluoride in drinkable water is fixed as 1.5 mg/L as recommended by WHO [2]. Hence, the safeguarding of fluoride is the finest remedy. The frequently explored removal methods like biological process, ion-exchange, adsorption, reverse osmosis and precipitation [3–7] are researched with the environmental researchers towards defluoridation wherein adsorption method is the finest method due to its simplicity, easy operation and economical one [8].
Recently several adsorbents material namely metal oxides, activated alumina, zeolite, polymeric material, activated carbon, clay materials, etc. [9–13], were reported towards fluoride removal and these materials have some limitations such as poor selectivity, low surface area and low adsorption capacity [14]. To overcome this difficulty, in this study carbon-based adsorbent material like graphene oxide based material was utilized towards fluoride removal. The mother of carbon-based material is graphene which consist of carbon atoms with single layers attached collectively by covalent bonds (sp2) [15]. The exfoliation of graphene could be attained with intercalation, thermal expansion, reduction, chemical modification and oxidation [16]. Among the numerous techniques, graphite oxidation with strong oxidizing agents to form graphene oxide (GO) which is non-conductive hydrophilic active carbon material has expected huge interest owing to its easy preparation method [17]. The introduction of the functional groups such as ketone, epoxide, carboxylic acid and alcohol with disruption of aromatic lattice builds GO to be hydrophilic in nature using modified Hummers method.
for the graphene oxidation [18]. In addition, GO has some unique advantages like physical, chemical and mechanical properties. However, GO possess poor selectivity and low adsorption capacity towards fluoride adsorption [19]. To enhance the adsorption property of GO material, amine functionalized GO based materials was developed towards fluoride removal.

Recently, amine functionalized GO based materials were utilized towards toxic ion removal and other potential applications. Currently, Hassandoost et al. developed Ce³⁺/Ce⁴⁺ modified Fe₃O₄ nanoparticles anchored onto GO for decontamination of oxytetracycline from water [20]. Firouzjaei et al. prepared GO based copper metal–organic framework (MOFs) nanocomposites for dye removal from water [21]. Wang et al. synthesized N-doped 3D graphene aerogel for catalytic degradation of antibiotic contaminants in water [22]. Zuo et al. fabricated MOFs–reduced GO nanomaterial for chromate removal from drinking water [23]. Ahsan et al. developed MOF/graphene oxide and MOF/CNT nanocomposites for Bisphenol A removal from aqueous medium [24]. Ploychompoo et al. prepared Zn-MOF-74/rGO/PAM composites for Bisphenol A removal from aqueous medium [25]. Saghi et al. fabricated zirconium [24]. Zuo et al. fabricated MOFs–reduced GO nanomaterial for chromate removal from drinking water [23]. Ahsan et al. developed MOF/graphene oxide and MOF/CNT nanocomposites for Bisphenol A removal from aqueous medium [24]. Ploychompoo et al. prepared Zn-MOF-74/rGO/PAM composites for effective fluoride adsorption from water [26]. Singh et al. synthesized novel defluoridation pencil and Al₂O₃/GO cellulose based 3D-hydrogel for effective fluoride adsorption from water [27, 28]. Hence, limited number of investigations was executed towards fluoride removal using GO supported hybrid materials. However, the powder form of amine functionalized GO materials has some limitations such as create pressure drop during filtration [29]. To prevail over these problems, biopolymer like alginate (Alg) encapsulated AGO material was developed towards fluoride removal.

Currently, enhanced usage of biopolymers and biomaterials for adsorption system has received more consideration owing to their abundance, eco-friendly, bio-functional, low cost and biocompatible nature [30, 31]. Alg is one of the biopolymer which has capable cross-linking talent with functional groups and explored for various pollutant removal from aquatic environment [32]. In addition, the structurally modified AGO favors to equivalently disperse into Alg poly-matrix which gives easily separable biohybrid spheres namely AGO@Alg hybrid spheres for enhanced fluoride removal.

Hence, the present investigation AGO@Alg hybrid spheres was prepared and practically employed towards adsorption of fluoride from aqueous medium. The fluoride adsorption onto AGO@Alg hybrid spheres, the liable parameters was investigated in batch mode to achieve the enhanced DC. The sophisticated characterization methods likely TGA, SEM, XPS and FTIR studies of AGO@Alg hybrid spheres and their fluoride adsorption were attained to recognize its physicochemical properties like thermal stability, morphology, elemental binding energy and functional groups determination. The nature, feasibility and order of the fluoride adsorption onto AGO@Alg spheres were explored by adsorption isotherms, thermodynamic parameters and adsorption kinetic models. The mechanism of fluoride adsorption on AGO@Alg spheres was also elucidated. To minimize the cost-effectiveness of AGO@Alg hybrid spheres the reusability test was carried out. The suitability of AGO@Alg hybrid spheres was also analyzed for the fluoride contaminated field sample taken from fluoride prevalent village.

2 Experimental Section

2.1 Materials

Sodium fluoride (NaF), potassium permanganate (KMnO₄), ethanol (CH₃CH₂OH), sodium chloride (NaCl), hydrogen peroxide (H₂O₂), sodium nitrate (NaNO₃), sodium alginate (Alg), calcium chloride (CaCl₂), ethylenediamine (EDA), graphite powder, sulphuric acid (H₂SO₄), potassium sulphate, sodium bicarbonate, N,N-dimethylformamide (DMF) were supplied from Merck, India.

2.2 Preparation of AGO@Alg Spheres

AGO was synthesized via modified Hummer’s system [33]. AGO was prepared using EDA using standard procedure [34]. To prepare AGO@Alg spheres, Alg (2 g) was completely dissolved in deionized water (100 mL). Then, 0.1 g of the developed AGO was slightly dispersed with deionized water. Further, the AGO solution was added into Alg solution. The mixture of solution was strongly stirring by using the stirrer for 2 h to attain the uniform AGO@Alg biocomposite solution. After that, AGO@Alg biocomposite solution was gradually dropped into 2% CaCl₂ (50 mL) solution to obtain an exploitable AGO@Alg hybrid spheres. The obtained AGO@Alg spheres were reserved in the mother liquor upto 24 h for strengthening purpose [35]. Lastly, AGO@Alg spheres were filtered and it was dried out in oven at 80 °C upto 2 h for defluoridation studies. The graphical figure of the synthesis of AGO@Alg hybrid spheres was portrayed in Fig. 1.

2.3 Fluoride Adsorptive Experiments

The prepared AGO@Alg spheres were poured with 50 mL of initial fluoride solution (10 mg/L) was taken into 250 mL iodine flask and it was shaken with thermo mechanical shaker with time period ranges from 10 to
60 min. Further, the equilibrium fluoride concentration was analyzed by fluoride ion selective electrode. The adsorbate pH concentration of 3 to 11 was modified with addition of 0.1 mol of HCl/NaOH. The adsorption kinetics and isotherms studies towards fluoride removal was conducted with taking different initial fluoride adsorbate solution of 8 to 14 mg/L with altered temperatures at 303, 313 and 323 K. The defluoridation capacity (DC) was measured by following Eq. (1),

\[ \text{Defluoridation capacity (DC)} = \frac{C_i - C_e}{m} \cdot V \times 1000 \frac{\text{mgF}^-}{\text{kg}^{-1}} \]

(1)

where \( C_i \) is the initial fluoride concentration (mg/L), \( C_e \) is the final fluoride concentration (mg/L), \( V \) is the volume of fluoride solution (L) and \( m \) is the amount of AGO@Alg spheres dosage(g).

### 2.4 Adsorbent Characterization

The presence of functional composition of AGO@Alg hybrid spheres were recognized with Fourier transform infrared (FTIR) [model: JASCO-460 plus], Thermogravimetric (TG) analysis (model: Universal V4.5A TA) was achieved to detect the thermal stability of GO, AGO and AGO@Alg spheres. The morphological image of AGO@Alg hybrid spheres with fluoride adsorption was scrutinized by scanning electron microscope (SEM) (Model: Vega3 Tescan). The binding state of the elements present in AGO@Alg spheres and fluoride adsorbed AGO@Alg spheres was studied by X-ray photoelectron spectroscopy (XPS) [PHI—VERSAPROBE III].

### 2.5 Analysis

The fluoride equilibrium concentration was found by Thermo Orion Benchtop multiparameter kit (model: VERSA STAR92) using fluoride ion selective electrode [36]. The solution pH from 3 to 11 was tuned by pH electrode with same instrument. The \( \text{pH}_{\text{pzc}} \) (pH at zero point charge) of AGO@Alg hybrid spheres was analyzed by pH drift system. The water quality responsible parameters (WQPs) viz., total hardness, dissolved oxygen, temporary hardness, chloride and total dissolved solids were evaluated by standard protocol.

### 2.6 Regeneration Studies

The investigation was made to assess the recyclable behavior of AGO@Alg hybrid spheres. Approximately 0.1 g of fluoride treated AGO@Alg spheres were decanted into 50 mL of 0.1 M NaOH eluent. Further, the blended solution was magnetically stirred in mechanical shaker for the period of optimal time. Afterwards, AGO@Alg hybrid spheres were detached by centrifugation and then the after equilibrium fluoride concentration was measured using fluoride electrode. Afterward AGO@Alg hybrid spheres were sluiced with HCl (0.01 M) and after dehydrated in hot air oven, further it was recycled for fluoride adsorption experiments. This route was reiterated for numerous periods and finally the fluoride removal efficiency of AGO@Alg hybrid spheres was measured as following equation,

\[ \text{Removal efficiency (\%)} = \frac{C_i - C_e}{C_i} \times 100 \]

(2)

### 2.7 Statistical Tools

The fitness of isotherm and kinetic models were verified by chi-square analysis (\( \chi^2 \)), correlation coefficient (r) and standard deviation (sd). Besides, all the experimental data towards defluoridation were determined using the Microcal Origin software (version 15).
3 Results and Discussion

3.1 Functional Groups Investigation

To aid the occurrence of chemical composition and chemical bond between–NH$_2$ and GO was studied by FTIR analysis. FTIR spectra of Alg, AGO, GO, AGO@Alg spheres and fluoride adsorbed AGO@Alg spheres were depicted in Fig. 2a and b. From the obtained results of FTIR, the sheet of GO have the carbonyl group (C=O) in the carboxylic acid was placed at end of edge corner (c.f. Fig. 2a). The adsorption stretching vibration peaks of C=O in the carboxylic acid was detected at 1725 and 1630 cm$^{-1}$ [37]. Besides, adsorption of stretching −OH was attribute to the monitored broad band at 3452 cm$^{-1}$ [38]. Besides, the stretching vibration mode of other groups like C–O was noticed at 1400 cm$^{-1}$ and C–H was detected at 2938 and 2852 cm$^{-1}$ [39]. Further, modification of amine groups (AGO); also the GO bands were detected at 1723 cm$^{-1}$. Though, the other bands at 1628 and 1400 cm$^{-1}$ roughly disappeared or subsided obviously and new band observed at 1580 cm$^{-1}$ was improved attribute to the adsorption of N–H stretching vibration in-plane and this was noticeably signify GO was efficiently functionalized with EDA [40] (c.f. Figure 2a and b). The comparative high intensity bands noted at 3300–3600 cm$^{-1}$ and it was destabilized, after functionalization of amine groups attribute to the N–H stretching vibration in –NH$_2$ groups [41]. For Alg FTIR spectra, the −OH and −COOH groups stretching vibration bands were noted at 1629 and 3396 cm$^{-1}$ respectively [42] (c.f. Fig. 2b). After Alg incorporation with AGO, the corresponding AGO and Alg peaks were reappeared in the AGO@Alg hybrid spheres which denote that Alg successfully incorporated with AGO (c.f. Fig. 2b). For AGO@Alg hybrid spheres, the corresponding intensity peaks of N–H, OH and −COOH were increased than AGO and Alg which signifies the good formation of AGO@Alg hybrid spheres [43]. In addition, the FTIR spectra of AGO@Alg hybrid spheres noted that no new peaks were observed compared to AGO and Alg, revealing that there was no chemical bond formed with addition of Alg. After defluoridation, the corresponding peaks were increased may due to more fluoride ion occupies the adsorbent surface which signifies that fluoride ion efficiently attract with AGO@Alg hybrid spheres (c.f. Fig. 2b). For fluoride adsorbed AGO@Alg hybrid spheres, the significant −NH$_2$ groups vibration intensity (3300–3600 cm$^{-1}$) was reduced compared to AGO@Alg hybrid spheres which may due to protonated −NH$_2$ groups attract fluoride through electrostatic interaction. In addition, the corresponding, the −OH groups stretching vibration bands at 1629 cm$^{-1}$ was diminished after fluoride adsorption which may due to protonated −OH groups in the form of −OH$_2^+$ is attract fluoride through electrostatic interaction mechanism.

3.2 Thermal Stability Investigation

TGA analysis results of AGO@Alg hybrid spheres, AGO and GO were depicted in Fig. 3. The minor weight loss arisen around 100 °C is due to loss of water. Then, the foremost weight loss noted in the region of 180 °C is
attributed to labile oxygen functional groups weight loss [44]. After, yet again, the thermal stability of GO was raises after functionalization of \(-\text{NH}_2\) groups [45]. The maximum decomposition of amine groups were noted at 358 °C for AGO was shown in Fig. 3. Moreover, the encapsulation of Alg with AGO, the primary decomposition temperature of AGO@Alg hybrid spheres started to reduce, because particles start to aggregate once they have exceeded the crucial level of loading. Therefore, these results recommend that the AGO improve the thermal stability of AGO@Alg hybrid spheres.

### 3.3 Surface Morphology Analysis

The surface morphological study of the prepared AGO@Alg hybrid spheres was assessed with SEM investigation (c.f. Fig. 4). Digital and dried picture of AGO@Alg hybrid spheres was portrayed in Fig. 4a and b. SEM micrographs of GO expose that the “sponge cake” shapes on account of stack structure of the GO sheets. After functionalized with amine, the AGO contain porous nature of randomly

![Fig. 3 TGA spectra of GO, AGO and AGO@Alg hybrid spheres](image)

![Fig. 4 Digital image of a AGO@Alg hybrid spheres, b dried AGO@Alg hybrid spheres, SEM micro-graphs of c AGO@Alg hybrid spheres at 10 µm and d fluoride adsorbed AGO@Alg hybrid spheres at 10 µm](image)
aggregated thin sheets forms and disordered framework because of amine groups are functionalized with GO sheet which demonstrated AGO was successfully synthesized. Further AGO encapsulated with Alg (AGO@Alg hybrid spheres), the surface was structurally modified due to Alg encapsulation with AGO (c.f. Fig. 4c). After fluoride adsorption, the morphology of AGO@Alg hybrid spheres was altered owing to fluoride ion occupies the pores of AGO@Alg hybrid spheres (c.f. Fig. 4d).

### 3.4 XPS Studies

XPS is a very helpful technique for investigate the composition of the functional groups present in the adsorbents. The occurrence of all the composition of functional groups in AGO@Alg spheres was explored semi-quantitatively using concluded the valance state and binding energies changes. The XPS wide scan spectra result of AGO@Alg spheres and fluoride adsorbed AGO@Alg spheres were depicted in Fig. 5 and Table S1 (supporting information). The attribute peaks of O1s, N1s, and C1s were experimentally noted at 533, 399, and 285 eV (c.f. Fig. 5a–c). This obviously exhibit that after functionalized amine with GO, the intensity peak of N 1 s was increased. This results demonstrated that after functionalized amine with GO the atomic percentage of the N in the adsorbents was improved from the GO of zero to AGO of 12.5% as well as the atomic ratio of N/C raises to 0.169 which clearly point out the amine functionalized route successfully makes N–H groups on GO surface [46]. This surveillance is finely reliable by FTIR spectra results. The

![XPS individual spectra of a C 1 s, b O 1 s and c N 1 s of AGO@Alg hybrid spheres](image-url)
Ascribe peaks of GO was attribute to the C1s spectrum typically noted at 284.8, 286.6, 287.1, and 287.6 eV which was attributed to GO was well fitted with corresponding peaks of sp² hybridized C atoms, C=OH, C–O (epoxy/ether) groups, and C=O (carbonyl/carboxyl), respectively. In addition, the extra constituent peak was noticed at 285.8 eV in C 1s spectrum of AGO which was attributed to C=N groups. Significantly, the intensity peaks of oxygen concentration was diminished were observed. In addition, the intensity peaks of C 1s was diminished were observed at 286.6 to 288.0 eV [47]. From Fig. 5c, the attributed spectrum of N 1s of NH₂-GO could be deconvoluted into two peaks with the binding energy of 398.7 and 399.8 eV were allocated to CO–NH (pyridinic) and C-NH₂ (primary amine) individually which demonstrates the ethylenediamine was reacted with oxygen group of graphene oxide.

Further, Alg encapsulation with AGO, the corresponding peaks such as C, N and O was reappeared in AGO@Alg hybrid spheres with slightly variation of intensity peaks which may due to Alg encapsulation with AGO [48]. Afterwards, for fluoride treated in AGO@Alg hybrid spheres, the corresponding peaks such as C, N and O was also reappeared in fluoride adsorbed AGO@Alg hybrid spheres with new peaks of fluoride which indicates fluoride adsorption was confirmed onto AGO@Alg hybrid spheres. After defluoridation, the intensity peaks were reduced owing to fluoride adsorption happened onto the AGO@Alg hybrid spheres.

3.5 Effect of Agitation Time

During the agitation time studies, the DCs of GO, AGO and AGO@Alg spheres was performed at varied adsorption time ranges from 10 to 60 min. The contact time results shows that the GO, AGO and AGO@Alg hybrid spheres have the superior DCs of 2450, 4001 and 4440 mgF⁻/kg at 50, 40 and 30 min respectively, while the GO and AGO developed in this investigation have smaller DC and attained the saturation point arrived at 50 and 40 min of contact time respectively (Fig. 6a). The developed AGO@Alg spheres possess improved DC than AGO and GO owing to the presence of alginate functional groups namely hydroxyl and carboxylic acid groups present in AGO@Alg spheres which are not present in AGO and GO. Since, it was assumed that AGO@Alg hybrid spheres utilized for residual fluoride adsorption studies by preferred 30 min of equilibrium time.

3.6 Effect of AGO@Alg Hybrid Spheres Dosage

In this dosage test, AGO@Alg dosage was used in the choice of 0.05–0.25 g. From the observed results, at initial stage the DCs of AGO@Alg hybrid spheres were enhanced from 0.05 to 0.1 g, achieve utmost at 0.1 g and after 0.1 g of AGO@Alg spheres was adsorption ability slowed down (Fig. 6b). However, AGO@Alg hybrid spheres dosage raises, the DCs was too enhanced upto 0.1 g of dosage and then get diminished. The high AGO@Alg hybrid spheres dosage ranges above 0.1 g, the binding sites of AGO@Alg spheres and the

![Fig. 6](image-url)
accessibility higher than initial fluoride solution thus DC was diminished. Therefore, 0.1 g of AGO@Alg spheres dosage was selected as optimized dosage for further defluoridation experiments.

3.7 Impact of Initial Fluoride Concentration

The initial fluoride concentrations were preferred as 2, 4, 6, 8, 10, 12 and 14 mg/L which subsequently separately soaked with 0.1 g of AGO@Alg spheres. The DC of AGO@Alg hybrid spheres were progressively improved as initial fluoride solution was greater and achieves equilibrium (Fig. 6c). At greater fluoride solution, the strong mass transfer was triumph over with transportable force at AGO@Alg hybrid spheres/fluoride surface consequently DC rises at 10 mg/L of fluoride concentration. Hence, the best initial fluoride solution was chosen as 10 mg/L for remaining fluoride removal studies.

3.8 Influence of Adsorbate pH

The acidic and basic condition of adsorbate solution not only modifies the surface possibilities of the AGO@Alg hybrid spheres adsorbent then similarly modifies the assembly of ions. From Fig. 6d the DC sloped with rises of adsorbate pH from 3 to 6, suggesting that pH 6 was the optimized state for fluoride adsorption onto AGO@Alg hybrid spheres. From Fig. 6d, the DC descended with raises of pH from 3 to 6, suggesting the pH 6 was the optimized condition for fluoride adsorption on AGO@Alg, the strong of mass transfer was electrostatic interaction is one of the defluoridation mechanism which find made by the attraction of positive charge of the AGO@Alg hybrid spheres with fluoride ion [49]. The pH of AGO@Alg hybrid spheres treated fluoride water is experimentally identified as neutral. Hence the synthesized AGO@Alg hybrid spheres may be utilized at various pH environments.

The observed result of pH_{ZPC} analysis demonstrates that at pH < pH_{ZPC} the AGO@Alg hybrid spheres surface entirely protonated (c.f. Fig. 6e). The protonated surface of AGO@Alg hybrid spheres was adsorbed by fluoride ion via electrostatic attraction. In disagreement, at pH > pH_{ZPC} the AGO@Alg hybrid spheres surface was fully occupied by OH_{−} ions instead of fluoride ion. Furthermore, the solution of pH medium was achieves pH 7 after defluoridation which state the suitability of AGO@Alg spheres at diverse pH environment.

3.9 Co-ions and Selectivity Studies

Mostly potable water comprises multiplicity of interfering anions; these interfering anions may influence the fluoride adsorption by AGO@Alg hybrid spheres. The obtained results of Fig. 6f noticeably signifies the somewhat influence of AGO@Alg hybrid spheres in the occurrence of other challengers ions viz., SO_{4}^{2−}, NO_{3}^{−}, HCO_{3}^{−}, HCrO_{4}^{−}, Cl− and PO_{4}^{3−} in aqueous medium. The declared challenger’s ions have the diverse undesirable effects. Unexpectedly, the DC was drastically fallen when the HCO_{3}^{−} ion was engaged onto the active sites of the AGO@Alg hybrid spheres. The first reason could be comparable ionic size of HCO_{3}^{−} with F− ion and the second reason is the binding force attraction of HCO_{3}^{−} with AGO@Alg hybrid spheres was stronger than SO_{4}^{2−}, NO_{3}^{−}, HCrO_{4}^{−}, Cl− and PO_{4}^{3−} [50]. In addition, SO_{4}^{2−}, PO_{4}^{3−}, HCrO_{4}^{−}, Cl− and NO_{3}^{−} too have the rivalry in existence on defluoridation.

Additionally, the selectivity studies of AGO@Alg hybrid spheres on defluoridation was examined and shown in Fig. 6g. The attained results of AGO@Alg hybrid spheres have the boosted DCs to fluoride than the other adsorbates (SO_{4}^{2−}, HCrO_{4}^{−}, HCO_{3}^{−} and Cl−). Therefore, the results indicate that the synthesized AGO@Alg hybrid spheres have tremendous selectivity nature for fluoride removal and it was practically applicable for fluoride removal studies.

3.10 Isotherms Studies

The isotherms models of adsorption studies namely Langmuir [51], Freundlich [52], Dubinin–Raduskevich (D–R) [53] and Temkin [54] were employed to decide the optimum data of AGO@Alg hybrid spheres towards fluoride removal was conducted by chosen of varied initial fluoride solutions viz., 8 to 14 mg/L and varied temperature viz., 303, 313 and 323 K. The n values of Freundlich isotherm > 1 and 0 < 1/n < 1 condition the relevant of Freundlich isotherm. The stronger interaction of AGO@Alg spheres onto fluoride adsorption was stated by Freundlich isotherm and its n value > 1 and 0 < 1/n < 1 state the suitability of Freundlich isotherm. The measured value of Q_{0} (mg/g) in Langmuir isotherm was receiving improved with raises of temperature through defluoridation process.

Additionally, the R_{L} value of Langmuir isotherm was obtained from 0 to 1 reveals the feasible nature of defluoridation by AGO@Alg hybrid spheres. The E values of D–R from 7 to 9 kJ/mol denotes fluoride adsorption was physisorption nature while the E values above 10 kJ/mol the signify fluoride adsorption was chemisorptions nature [55]. The K_{F} and B_{1} isotherm constants were attained from the linear plot of q_{e} vs ln C_{e} (Temkin plots) which was used to find the chemical adsorption of the fluoride onto the surface of AGO@Alg hybrid spheres. In addition the attained values of E above 9 kJ/mol denote the interaction of AGO@Alg hybrid spheres to fluoride adsorption was identified to be chemisorption nature. The attained isotherm result of AGO@Alg hybrid spheres towards fluoride adsorption was
declared that Langmuir (monolayer adsorption) isotherm more applicable model than Temkin, D–R and Freundlich isotherm model owing to lower values of sd and χ² with greater r value respectively (c.f. Table 1).

3.11 Thermodynamic Studies

Thermodynamic factors like standard enthalpy change (ΔH°), standard entropy change (ΔS°) and Gibbs free energy change (ΔG°) was determined by Khan and Singh strategy [56]. The values of ΔG° < 0 and ΔH° > 0 indicate spontaneous and endothermic in nature of fluoride adsorption. In this investigation, the obtained value of ΔG° < 0 indicates the fluoride adsorption of AGO@Alg hybrid spheres was spontaneity nature. During adsorption, the obtained experimental values of ΔH° is positive noticeably reveals that enthalpy is absorbed between AGO@Alg hybrid spheres and fluoride [57]. In addition, the enhancement of DCs (Q°) at monolayer coverage with raising temperature represents the endothermic nature of fluoride adsorption by AGO@Alg hybrid spheres (c.f. Table 1). Moreover, the attained ΔH° values below than 40 kJ/mol states the defluoridation by AGO@Alg hybrid spheres was chemical adsorption nature. Additionally, the obtained values of ΔS° was around zero which demonstrates randomness was occurred almost nil after fluoride adsorption due to no further driving force particle was arisen but they stick onto the AGO@Alg hybrid spheres surface.

3.12 Kinetics Studies

To identify the order of fluoride adsorption onto AGO@Alg spheres by the kinetic experimental data was concluded with facilitate of reaction-based models such as pseudo-first-order [58] and pseudo-second-order [59] and diffusion-based models such as particle [60] and intraparticle diffusion [61] model which experimental data are portrayed in Table S2. The vital parameters of kinetic models towards defluoridation by AGO@Alg hybrid spheres viz., k_{ad}, k, r, q_{e}, h and r were given in Table S2. Hence, it was noted from the attained parameters of pseudo-second-order that the values of q_{e} increasing with raises in temperature than pseudo-first-order denotes the promising of AGO@Alg hybrid spheres in the miscellaneous temperatures viz., 303, 313 and 323 K. Hence, the kinetics of pseudo-second-order model was attained the uppermost r values and smallest sd values which

Table 1 Adsorption isotherm and thermodynamic studies of AGO@Alg hybrid spheres for fluoride adsorption

| Isotherms & thermodynamic parameters | Values         | 303 K | 313 K | 323 K |
|-------------------------------------|---------------|-------|-------|-------|
| Freundlich                          |               |       |       |       |
| I/n                                 | 0.786         | 0.789 | 0.793 |
| n                                   | 8.093         | 8.097 | 8.103 |
| k_{F} (mg/L mg)^{1/n}                | 4.256         | 4.258 | 4.263 |
| r                                   | 0.980         | 0.983 | 0.987 |
| sd                                  | 0.359         | 0.361 | 0.364 |
| χ²                                  | 0.156         | 0.157 | 0.159 |
| Langmuir                            |               |       |       |       |
| Q° (mg/g)                            | 4.432         | 4.438 | 4.441 |
| b (L/g)                              | 1.023         | 1.027 | 1.033 |
| R_L                                 | 3.013         | 3.017 | 3.022 |
| r                                    | 0.988         | 0.991 | 0.994 |
| sd                                  | 0.975         | 0.979 | 0.983 |
| χ²                                  | 0.468         | 0.476 | 0.781 |
| Dubinin—Radushkevich                |               |       |       |       |
| k_{DR} (mol^{2}/L^{3})              | 6.62E-02      | 6.71E-02 | 6.76E-02 |
| X_{m} (mg/g)                         | 4.255         | 4.259 | 4.265 |
| E (kJ/mol)                           | 9.898         | 9.909 | 9.916 |
| r                                    | 0.953         | 0.956 | 0.959 |
| sd                                  | 0.968         | 0.972 | 0.975 |
| χ²                                  | 0.692         | 0.696 | 0.702 |
| Temkin                              |               |       |       |       |
| K_{T} (L/g)                          | 4.285         | 4.291 | 4.296 |
| B_{1}                                | 2.554         | 2.559 | 2.562 |
| r                                    | 0.974         | 0.979 | 0.981 |
| sd                                  | 0.625         | 0.635 | 0.656 |
| χ²                                  | 0.258         | 0.264 | 0.268 |
| Thermodynamic parameters            |               |       |       |       |
| ΔG° (kJ/mol)                         | -2.73         | -2.78 | -2.83 |
| ΔH° (kJ/mol)                         | 2.24          |       |       |
| ΔS° (J/mol/K)                        | 0.26          |       |       |
denotes pseudo-second-order model more pertinent models towards defluoridation by AGO@Alg hybrid spheres. Fluoride released within the interior pore area of AGO@Alg hybrid spheres through the fluoride adsorptions method. The rate of diffusion improved when fluoride ion come into within owing to diffusion rate was improved. The particle and intraparticle diffusion models of straight linear plots of AGO@Alg hybrid spheres to fluoride adsorption were plotted by ln (1−Ct/Ce) vs t and qt vs t0.5 respectively. It was chiefly completed that from the attained parameter values of intraparticle diffusion model such as higher r and lower sd values exhibits their prospective for defluoridation by AGO@Alg hybrid spheres.

3.13 Defluoridation Mechanism of AGO@Alg Spheres

The plausible mechanism of AGO@Alg spheres towards fluoride adsorption was mainly controlled by electrostatic attraction (c.f. Fig. 7). The prepared AGO@Alg hybrid spheres have the active functional groups like amine and hydroxyl groups. The aminated GO contains lot of active amine groups and Alg possess reactive functional groups like –OH groups. In general, the protonated groups have high tendency to interact with fluoride ion by the use of electrostatic attraction. At acidic pH condition, AGO@Alg hybrid spheres gets fully protonated and the protonated AGO@Alg hybrid spheres interact with fluoride ion by the electrostatic attraction mechanism [62].

Further the defluoridation mechanism was supported by the instrumentation techniques like FTIR, SEM, XPS and pHzpc analysis. The observed result of pHzpc analysis demonstrates that at pH < pHzpc, surface of the AGO@Alg hybrid have –NH2 and –OH groups on its surface and these groups were protonated at optimized pH circumstances (c.f. Fig. 6e). The protonated NH3+ and OH2+ groups adsorbs fluoride ion by way of the electrostatic attraction. In FTIR studies, for fluoride adsorbed AGO@Alg hybrid spheres, the significant –NH2 groups vibration intensity (3300–3600 cm−1) was reduced compared to AGO@Alg hybrid spheres which may due to protonated –NH2 groups (−NH3+) attract fluoride through electrostatic interaction. In addition, the corresponding, –OH groups stretching vibration bands at 1629 cm−1 was diminished after fluoride adsorption which may due to the protonated –OH groups in the form of −OH2+ attract fluoride through electrostatic interaction mechanism. Further fluoride adsorption mechanism was verified by XPS analysis, before fluoride adsorption C, N and O were present, after fluoride adsorption, the corresponding peaks such as C, N and O was also reappeared in fluoride adsorbed AGO@Alg hybrid spheres with new peaks of fluoride which indicates fluoride adsorption onto AGO@Alg hybrid spheres was confirmed. After defluoridation, the intensity peaks were reduced owing to fluoride adsorption happened onto the AGO@Alg hybrid spheres.

![Fig. 7 The defluoridation mechanism of AGO@Alg hybrid spheres](image-url)
3.14 Comparison Study

A comparative study of adsorption capacity of the numerous adsorbent materials for fluoride adsorption was shown in Table 2. From the results, the synthesized AGO@Alg hybrid spheres possess superior DC compared to many other adsorbents.

3.15 Field Water Analysis

To check the AGO@Alg hybrid spheres aptness at field conditions, the fluoride containing field sample was assembled from a village in Dindigul district, Tamilnadu. The fluoride concentration was found in the field water is 3.05 mg/L. The synthesized AGO@Alg hybrid spheres acquire the high affinity towards fluoride as their equilibrium concentration after the treatment was identified to be below WHO tolerance level (c.f. Table 3). However, the other water quality deciding parameters such as total hardness, dissolved oxygen, total dissolved solids, iron, PO$_4^{3-}$, NO$_3^-$, Cr(VI), electrical conductivity and chloride of the real water sample was too proscribed by AGO@Alg hybrid spheres confirms its field aptness.

3.16 Reusability Studies of AGO@Alg Spheres

To check the recyclability and cost effectiveness of AGO@Alg hybrid spheres was conducted by regeneration studies. Herein, NaOH (0.1 M) was utilized as eluent for adsorption–desorption cycle of AGO@Alg hybrid spheres [74]. Hence, 0.1 g of fluoride treated AGO@Alg spheres were entirely immersed into 0.1 mol of NaOH. The observed result indicates addition of NaOH in all the cycles, the fluoride removal efficiency was diminished gradually which is depicted in Fig. 8. The possible reason is OH$^-$ ion in NaOH exchange fluoride ion by ion-exchange due to this removal efficiency of AGO@Alg hybrid spheres was gradually diminished in each and every cycle. Moreover, practically removal efficiency of 80% was attained upto 6 cycles. Henceforth, the recyclability of AGO@Alg hybrid spheres was chosen upto 6 cycles.

4 Conclusions

This exploration focused on the development of AGO@Alg hybrid spheres for efficient and selective fluoride retention from water. A recyclable AGO@Alg hybrid spheres was
synthesized through a typical solvothermal process. The prepared AGO@Alg hybrid spheres exhibit the enhanced DC of 4440 mgF⁻/kg within 30 min of optimum time. The adsorbate pH was mostly changed the nature of AGO@Alg hybrid spheres surface which influence DC. The highest DC adsorbate pH was mostly changed the nature of AGO@Alg hybrid spheres (4440 mgF⁻/kg), which was detected at the solution pH ~ 6, and the process attains saturation within 30 min. The HCO₃⁻ ion present in ordinary water was noticeably influences during fluoride adsorption. The attribute of AGO@Alg hybrid spheres were investigated with various sophisticated instrumental techniques like XPS (binding energy), TGA (Thermal stability), FTIR (Functional groups analysis) and SEM (surface morphology) analysis. The kinetics studies of AGO@Alg spheres were achieved wherein pseudo-second-order and intraparticle diffusion models were well matched for fluoride adsorption. Moreover, the Langmuir adsorption isotherm of AGO@Alg hybrid spheres was apt for fluoride adsorption. The fluoride adsorption spontaneity and endothermic nature was stated by the thermodynamic studies. The fluoride adsorption mechanism of AGO@Alg spheres was typically retained by the electrostatic interaction. The recyclability of AGO@Alg hybrid spheres was reached upto 6 cycles. Besides, AGO@Alg spheres were applied with the field fluoride water sample and results show that the prepared AGO@Alg hybrid spheres reduces all the water quality parameters which indicates their suitability at field level. The above results revealed the successful preparation of simple, cheap and recyclable AGO@Alg spheres, which can be benefited for the defluoridation of water.

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