FLUORIDE REMOVAL FROM GROUNDWATER BY ADSORPTION TECHNOLOGY

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Summary

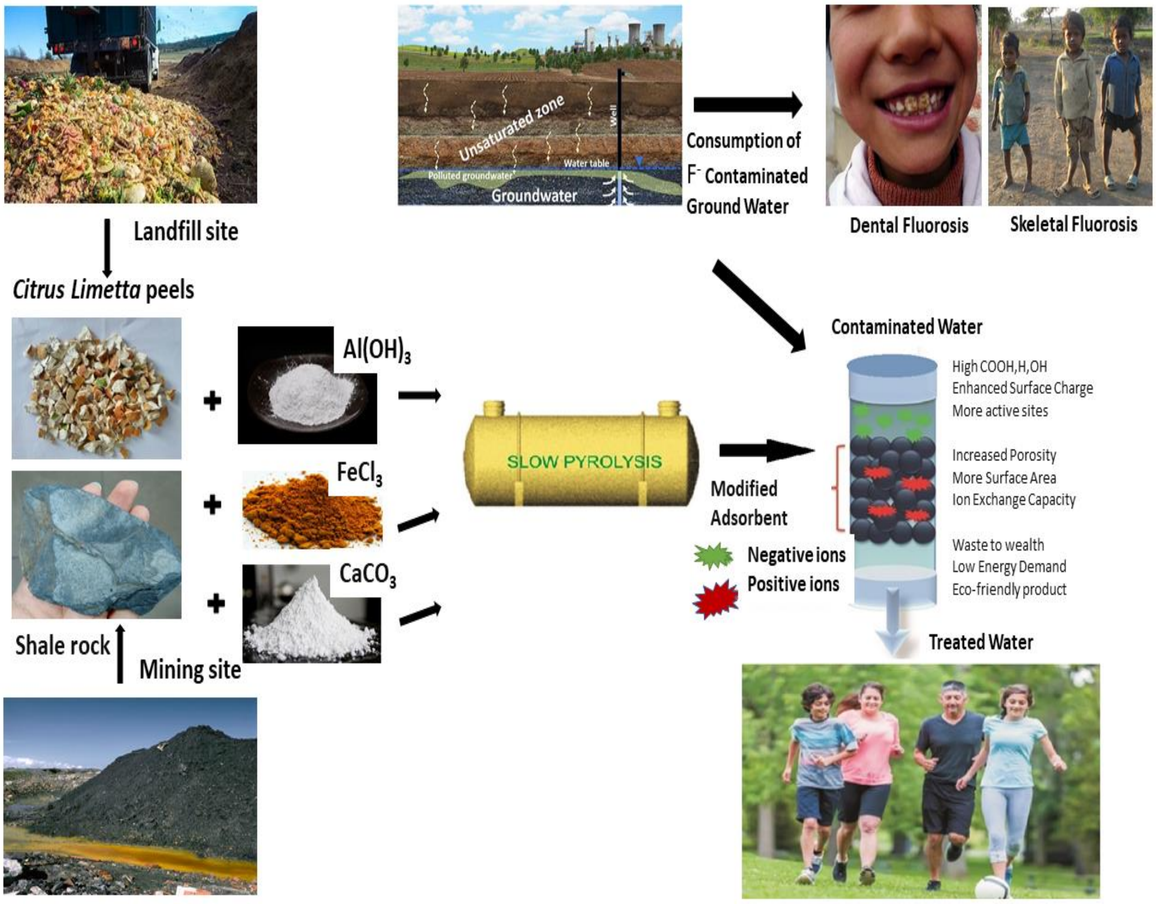
Introduction

One of the most important renewable natural resources is groundwater. The world's population currently extracts groundwater which is essential to the hydrological cycle at a rate two hundred times faster than that of oil each year (Costantini et al., 2023). Over 0.5 billion people from 106 countries are impacted by groundwater problems connected to arsenic contamination, out of the over 2.5 billion people that depend on groundwater globally for a clean drinking water supply (Shaji et al., 2021). As per World Health Organisation research (2011) groundwater of many sources around the world is unsafe for drinking purpose, due to high fluoride concentrations and other potentially harmful components (Xiao et al., 2022a). Contents of fluoride are among the main contaminants in groundwater and reports of high fluoride concentrations in various countries, including South America, Africa, Argentina, China, India, Brazil, Mexico, Nigeria, Iran, Pakistan, Kenya, and Sri Lanka (Shaji et al., 2024). Fluoride-bearing minerals in rocks and soil, such as fluorite (CaF_2), cryolite (Na_3AlF_6), fluocerite (CeF_3), villianmite (NaF), sellaite (MgF_2), fluorapatite (Ca5(PO4)3F), etc., weather and subsequently leach these minerals, resulting in fluoride contamination in groundwater (Brindha and Elango, 2019; Malago et al., 2017; Schlesinger et al., 2020). Over 21,000 and 18,000 tonnes of fluoride are added to the water by the ceramic and fertiliser sectors, respectively, while over 3500 tonnes are added by non-ferrous and metal foundries and over 40,000 tonnes are released by the steel industry (Rashid et al., 2020). There are several traditional techniques for defluoridation, including membrane filtration, adsorption, coagulation, electro-dialysis, ion exchange, and precipitation (Singh et al., 2018).

Objectives

1. Screening of biowaste/geomaterials as most effective adsorbent.
2. Characterization of screened adsorbents.
3. To study the effects of chemical modification on efficiency of selected adsorbent.
4. Optimization of defluoridation process for sustainable management of Fluoride in groundwater.

Preparation



Result and Discussion

Objective 1: Screening of biowaste/geomaterials as most effective adsorbent

It is crucial to screen several adsorbents for their removal efficiency towards fluoride under controlled settings before selecting an adsorbent for treating the pollutants present in groundwater and for batch experiments. Selecting potential biowaste or geomaterials use to be as effective adsorbents requires evaluating a material's removal capacity under various conditions. Peels from Oranges (*Citrus sinensis*), Bananas (*Musa*), Pomegranates (*Punica granatum*), Sweet Lime (*Citrus limetta*), and mine debris like Shale, Sandstone were selected for screening (Islam et al 2023; Pathak et al 2016).

The peels of bananas, sweet limes, pomegranates, oranges, and mining debris such as sandstone and shale were used to make the adsorbents for the preliminary study. The peels and rocks were washed, dried, ground, and sieved. To prepare the adsorbents, the powdered peels were heated for one hour at 350°C and shale at 800°C. In order to determine the removal efficiency of the following adsorbents, a small batch experiment with a constant minimum dose of 5 mg/L and 50 mg/L, at pH of 7, a fluoride concentration of 10 ppm, a contact period of 3 hours, at room temperature was conducted as the primary analysis of wet waste and geological material.

The adsorbent prepared showed the removal efficiency of 60%, 54%, 43% and 35% in case of sweet lime, orange peel, banana peels and pomegranate peel. The results showed that adsorbent removal efficiency of raw shale was 20 % whereas sandstone showed removal of only 5% thus sweet lime peels and shale were screened for further study.

Objective 2: Characterization of screened adsorbent

The material was characterized using a variety of instruments in order to see how the surface and chemical composition contribute to the adsorbent's ability to absorb fluoride. Instruments such as the scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDX, model no. JSM 6490-LV, JEOL, Japan), Fourier transform infrared spectrophotometer (FTIR, model no. NICOLETTM 6700, Thermo Scientific, USA), and X-ray diffraction (XRD, model no. PW 3040/60, PAN analytical, Netherlands) were used to characterize the adsorbents screened in the preceding chapter.

Characterization of sweet lime

- **Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray (EDX) analysis**

The results reflected that the adsorbent made from fruit peels have a rough, uneven surface with some fibers, lengthy flakes to spherical one. The heterogeneous surfaces with sporadic holes, pores, and cavities of various sizes and shapes as well as volatiles and the non-volatile from fresh biomass (peels) that remained and transformed into biochar. EDX analysis evaluated the elemental composition, the results showed a high percentage of carbon in addition to other elements like oxygen, hydrogen, and potassium in the biochar.

- **Fourier transforms infrared spectroscopy (FTIR)**

Biochar made from sweet lime peel indicated that the O–H (hydroxyl group) and N–H (amines), amine deformation (-NH and -NH_2), –OH bending, and C=O stretching. Additionally, C-O stretching.

- **X-ray diffraction (XRD)**

Wide peaks at 24° confirmed the presence of activated carbon atoms formed during carbonization. The presence of diffracted, blunt peaks determines amorphous nature of the adsorbent.

Characterization of Shale

- **Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray (EDX) analysis**

SEM images of the minerals and carbonaceous structure in coal samples show irregular particle size and shape distributions. The surface morphology revealed a non-uniform topography with minerals embedded in a carbon matrix. The EDX result showed that a considerable quantity of elements including traces of Sulphur(S), Oxygen (O), Carbon (C), Iron (Fe), Aluminium (Al), and Silicon (Si) in shale.

- **Fourier transforms infrared spectroscopy (FTIR)**

The sharp, medium-intensity peaks can be attributed to aliphatic and alicyclic CH_3, CH_2, and CH groups, aliphatic alcohols, ether groups (O–H, C–O–C), and the SO_4^{2-} group. In primary and secondary thiols, the stretching vibration bands of S–S and C–S bonds were found along with Si-O-Fe, SiO and Si-O-Al.

- **X-ray diffraction (XRD)**

The majority of the clay minerals in the shale, such as illite and kaolinite aid in the fluoride adsorption process. Quartz (SiO_2), kaolinite ($Al_2O_3\ 2SiO_2{\cdot}2H_2O$), hematite ($Fe_2O_3$), calcite ($CaCO_3$), and illite ($KH_3O$) (Al, Mg, Fe) 2(Si, $Al)_4O_{10}[(OH)_2{\cdot}(H_2O)]$ are the assemblages identified qualitatively using XRD spectra in the coal.

Objective 3: To study the effects of chemical modification on efficiency of selected adsorbent.

To examine the effect of chemicals modification on the adsorbent surface and their altered chemical composition to assist the adsorption of fluoride on prepared substance.

Chemical modification of Sweet lime peel with Al $(OH)_3$

In present investigation, aluminium hydroxide-sweet lime bio-sorbent ($Al(OH)_3$-SL, 1:3) was applied for defluoridation of groundwater. The chemically modified bio-sorbent was subjected to pyrolysis individually and in combination at 350° C for 1 hr

- **BET analysis and point of zero charge (pH_{ZPC})**

The particle size was tested after obtaining a homogenized sample of the chemically treated biochar. BET analysis reported surface area of 162 m^2/g, total pore volume of 2.35 cc/gm, average pore diameter of 56 Å suggesting mesoporous structure with greater surface area thus more active sites for binding fluoride.

The lines are intersecting at pH 6, represents pH_{zpc} of the adsorbent. The result showed slightly negative pH_{zpc} i.e. 6 suggesting dominating acid groups like phenolic and carboxylic groups.

- **Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray (EDX) analysis**

Results revealed that the chemically modified adsorbents AlOH-SL-A and AlOH-SL-B were having rough and irregular sphere. Micrographs expressed that the adsorbents are amorphous in nature with some macro and micro pores, presuming them to help in interchange or attachment of anions and cations. The results depicted that weight percentage of carbon and oxygen was increased from 28% to 45% and 40% to 48% proving increased carbonization in adsorbent AlOH-SL-B.

- **Fourier transforms infrared spectroscopy (FTIR)**

The absorption peak found between 400-900 cm^{-1} can be due to Al–O stretching. The FTIR results also showed the shift in peak from 1618.6 cm^{-1} in AlOH-SL-A to 1647.4 cm^{-1} in AlOH-SL-B reflecting ketones and carbonyl groups. Absorption peak at 1071.1 cm^{-1} and 1086.6 cm^{-1} may be due to silicates (Si–O group).

- **X-ray diffraction (XRD)**

Wide peaks at 24˚ confirmed the presence of activated carbon atoms formed during carbonization. The presence of diffracted, blunt peaks determines amorphous nature of the adsorbent. The structure of the carbonated biochar was concluded to be amorphous. For bio-sorbent AlOH-SL-B, 2ϴ values of 22.26, 28.02, 38.16, 48.65, 64.99 were assigned to 110, 120, 040, 131 and 250 hkl values according to the database in JCPDS file (005-0355) representing aluminum hydroxide

Chemical modification of Shale with $FeCl_3$

The chemically modified adsorbent $FeCl_3$-S (1:3 w:w)was subjected to pyrolysis in combination at 800°C for 1 hr. Composite were prepared by pyrolysis processes

- **Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray (EDX) analysis**

In the present study, adsorbents were initially porous and loosely packed but subsequent to fluoride exposure, they appeared compact, smooth and expanded volume suggesting that interlayer spacing was occupied by fluoride ions. In this study, the elements observed after modification of shale, were O, Fe, Cl, Si, Ca, K and Si. The result suggested that element O, C, Fe, Cl were mixed with shale during modification via heat treatment.

- **Fourier transforms infrared spectroscopy (FTIR)**

The most dominating peaks was at 3423 cm^{-1} which could be attributed to iron oxide – bonds in prepared adsorbent. After being loaded with fluoride, peak at 1020-1026 cm^{-1} showed C–F (strong), and the peaks in the range of 1634-1650 cm^{-1} were recognized to be due to H-O-H bonding, OH, –H (strong and sharp).

- **X-ray diffraction (XRD)**

The result shows that the presence of sharp and intense peaks proving crystalline structure. Additionally, 2θ angle around 20.88, 26.66, 50.167 were attributed to Quartz refers to 010, 011, 112, whereas 33.184 and 36.66 4 refers to (002, 021) pyrite mineral. The peaks at 35.639 (220) 39.48 (400) are reported to be due to iron oxide treatment to the adsorbent.

Chemical modification of Shale with $CaCO_3$

The chemically modified adsorbent $CaCO_3$-S (1:3) was subjected to pyrolysis in combination at 800°C for 1 hr. Composite $CaCO_3$-S were prepared by pyrolysis processes.

- **Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray (EDX) analysis**

The adsorbent exhibited a porous and loosely packed configuration, but following treatment, the fluoride loaded adsorbent underwent a transformation into a more compact, smooth, and voluminous form indicative of an enlargement in interlayer spacing which may be attributed to the presence of fluoride ions on the surface of adsorbent. the modification of shale for fluoride removal and identified elements such as Oxygen (O), Carbon (C), Silicon (Si), Calcium (Ca) in the modified shale, suggesting their incorporation via heat treatment.

- **Fourier transforms infrared spectroscopy (FTIR)**

The $CaCO_3$ presence was confirmed by the peaks at 2513 cm^{-1} and 878 cm^{-1} corroborating the functional groups –C–H and –C =. Spectral peaks falling within the 1020-470 cm^{-1} range were indicative of Si-O-Si bonding and C-F sharp bond owing to presence of fluoride after loading and organic compounds in shale sample.

- **X-ray diffraction (XRD)**

Shale predominantly includes quartz, clay, feldspar, calcite, pyrite, and dolomite. In the present study, distinct and sharp peaks at 2θ angles at 26.8 and 50.3 attribute to quartz and have a crystallographic plane whereas peaks at 29.5 and 39.5 represent calcite minerals whereas 21.06 stands for quartz. The calcium carbonate peaks are at 29.5 suggesting the treatment of calcium carbonate.

Objective 4: Optimization of defluoridation process for sustainable management of Fluoride in groundwater

Batch adsorption study of F^- removal using Sweet lime peel modified with Al $(OH)_3$

The optimisation of the bio-adsorbent made from modification of sweet lime peel waste when treated with $Al(OH)_3$ at 350 °C for 1 hr was done and the experiment was conducted using different adsorbent doses (1-8 gL^{-1}), fluoride concentration (2 to 10 ppm) and contact time (3 hours)

- **Effect of bio-sorbent dose on fluoride removal efficacy of bio-sorbent**

In order to examine the effect of dose on the removal capacity of bio-sorbent AlOH-SL-A and AlOH-SL-B, experiments were carried out with range of doses varying between 1 to 8 gL^{-1} at constant pH (7), fluoride concentration (2 ppm), contact time (3 hours) and room temperature. The results also revealed that fluoride removal with adsorbent AlOH-SL-A increased from 34 % to 70 % whereas removal potential of adsorbent AlOH-SL-B increased from 66 % to 86 % at 1 gL^{-1} and 5 gL^{-1} respectively. The possible decrease in the efficiency after the saturation point (5 gL^{-1}) might be due to mass aggregation which reduces the available sites and disturbs diffusion path.

- **Effect of contact time on fluoride removal efficacy**

The results also showed that the process of defluoridation started at 5 minutes and was maximum for the first 15 Minutes therefore the process slowed down and reached saturation point within 30 Minutes.

- **Effect of pH on fluoride removal efficacy**

The defluoridation efficiency of the biosorbent largely dependent upon the ionic strength of the aqueous solution. The initial adsorption capacity of fluoride increased from 86% to 94% with increase in pH from 3 to pH 6 of the working solution. There was no significant increase around pH 7 but as soon as the basic ions increased, the removal capacity was decreased significantly

Modelling of Adsorption isotherm and Kinetics

For adsorption study, 5 mgL^{-1} of bioadsorbent was added to varying fluoride concentration (2, 4, 6, 8, 10 ppm) with varying time interval (1-30 minutes). The results reflected that the adsorbent followed Langmuir isotherm (R^2 =0.975) more closely than Freundlich isotherm (R^2 = 0.948) which implies monolayer adsorption of fluoride over a homogenous carbonated sorbent.

The results concluded that AlOH-SL-B followed pseudo-second order kinetics more accurately than pseudo first order reflecting chemisorption of fluoride over the surface of bio-sorbent

Batch adsorption study of F^- removal using shale modified with $CaCO_3$

- **Effect of adsorbent dose on fluoride removal efficacy of adsorbent**

The effect of dose on the removal capacity of adsorbent ($CaCO_3$-S) was carried out with range of dose varying 10, 25, 50, 75, 100, 125 and 150 mgL^{-1} at constant pH with fluoride concentration of 2 ppm and contact time of 3 hours at room temperature. The present study showed that defluoridation was maximum at 50 mgL^{-1} and the adsorption decreased as the dose was increased.

- **Effect of contact time on fluoride removal efficacy**

The results obtained showed that the maximum removal of 75% was observed at 2 ppm concentration of fluoride with adsorbent dose of 50 mgL^{-1} whereas the adsorption potential decreased (64%, 57%, 50%, 47%) with increase in fluoride concentration (4, 6, 8, 10 ppm), respectively.

- **Effect of pH on fluoride removal efficacy**

The most effective contact time between fluoride working solution and chemically modified shale was reported to be 80 minutes. After the saturation was achieved, the increase in time duration from 80 minutes to 180 minutes, the adsorption of the fluoride decreases primarily due to saturation of active sites on $CaCO_3$-S.

Modelling of Adsorption isotherm and Kinetics

The results prove that Freundlich isotherm with R^2 =0.98 was more fit than Langmuir isotherm R^2 =0.96 proving multilayer adsorption of fluoride on the homogenous structure of chemically modified adsorbent ($CaCO_3$-S) and results concluded that $CaCO_3$-S followed psuedo second order kinetics more accurately reflecting chemisorption of fluoride over the surface of adsorbent with $R^2= 0.91$

Batch adsorption study of F^- removal using Shale modified with $FeCl_3$

- **Effect of adsorbent dose on fluoride removal efficacy of adsorbent**

The result also showed that fluoride removal efficiency increased from 20% to 50% with increase in adsorbent dose from 10–100 mgL^{-1}. The increment in adsorption efficiency can be explained to increased number of active sites indicating dose serve as a boon until saturation was achieved.

- **Effect of contact time on fluoride removal efficacy**

At varying time interval, the adsorption during first hour was observed to be maximum. With increase in time from 60 to 180 minutes, the removal percentage decreased from 50 % to 32% suggesting exhaustion of active sites in the initial reaction time.

- **Effect of pH on fluoride removal efficacy**

The results further depicted that the increase in pH from 2 to 10, the efficiency of adsorbent removal was decreased from 50% to 10%. At neutral pH, the removal efficiency was found to be 38%, thus this adsorbent is efficient in fluoride management for drinking water.

Modelling of Adsorption isotherm and Kinetics

For adsorption study, 100 mgL^{-1} of adsorbent was added to varying fluoride concentration (2, 4, 6, 8, 10 ppm) with varying time interval (1-180 Minutes).

The results proved that the adsorbent followed Freundlich isotherm (R^2 =

0.9299) more closely than Langmuir isotherm ($R^2 = 0.8508$) which implies multilayer adsorption of fluoride over a homogenous carbonated sorbent. The results concluded that adsorbent $FeCl_3$-S followed pseudo-second order kinetics more accurately reflecting chemisorption of fluoride over the surface of adsorbent.

The access to safe and clean water is a fundamental right of every human. However, the increment in contamination and subsequent scarcity of freshwater induced by climate change is posing serious threat to the survival of living organisms. Therefore, treating the contaminates is the only way to enhance the availability of the freshwater. The present study reflected that exploiting waste is an economical and sustainable solution for fluoride management in groundwater. The experimental evidence confirmed through FTIR and XRD that the chemically modified waste of citrus and shale can serve as the promising material towards groundwater treatment. Furthermore, adsorption isotherm and adsorption kinetics authenticated that adsorbent removed fluoride through chemisorption and multilayer adsorption. Therefore, utilizing waste materials can serve as the promising and suitable candidates for water purification. Further, adsorption through locally available waste can be the multi-beneficial approach towards waste management, water treatment and climate change mitigation.