

Synthesis of adsorbents from natural and waste materials and its application in removal of fluoride from an aqueous solution and ground water

**SUMMARY OF
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SUMMARY

Water is the essence of life and a vital condition for life to exist and for economic progress to occur. Water resource quality has been dropping and degrading in recent decades. Drinking water is a valuable and usually spend that must be preserved and kept free of contaminants. Fluoride-bearing minerals are the fundamental source of fluoride ions in groundwater. These minerals are sellaite, fluorspar, topaz, williamite, fluorite, chabazite, etc. Through the dissolution of these minerals' fluoride ions contaminate groundwater. Instead of natural sources, some anthropogenic causes add fluoride effluents in water from industrial processes, particularly in fertilizer, cement, glass, steel, electroplating, and semiconductor, industries. Fluoride poisoning in drinking water caused by natural and anthropogenic activity has been identified as one of the key issues providing a serious hazard to human health globally. If fluoride ions consume in low amounts, it is a crucial chemical for humans in preventing cavities and helping the mineralization of tooth tissues. Excess fluoride intake can cause several fluorosis-related disorders, therefore removing excess fluoride from water is a global concern. Therefore, the treatment of fluoride-contaminated water is an urgent need for the community. Several methods have been applied for fluoride removal including the Nalgonda technique, nanofiltration, ultrafiltration, reverse osmosis, and electrodialysis. However, these techniques are highly expensive, complex operating systems. Among the various treatment strategies used for fluoride removal, adsorption is a well-studied and commonly utilized defluoridation process due to its simple design, easy operation, and low cost. Adsorbent-based removal is considered as inexpensive, easy in handling, and high efficiency. The adsorption process has been extensively researched and provides good results, particularly with mineral-based adsorbents as well as surface

modified adsorbents. Various studies have been carried out related to adsorbent synthesis from different types of raw materials and investigated their efficiency for fluoride removal from water. The raw materials for adsorbent synthesis are available in abundance and the preparation of adsorbent from these materials not only deals with the problem of waste management but also may be a way of treatment of fluoride contaminated water. In this study, natural and waste materials are utilized for the synthesis of adsorbents. Mentha plant ash, *Juncus effusus* plant biomass, pond clay soil, and carbon of waste cartridge were used for adsorbent preparation and their application for removal of fluoride from water.

The whole study was divided into four phases and the key outcomes of these phases are summarised here:

Phase 1: Characterization and application of sodium-aluminium modified adsorbent from Mentha plant ash for fluoride removal from water.

- In this phase, adsorbent was prepared from Mentha plant ash that produces after the burning of plant biomass during oil extraction.
- Mentha plant is a cash crop, the purpose of selecting this type of waste was their availability in large quantity and require to manage this.
- In this phase, Mentha plant ash-based adsorbent was synthesized by using sodium hydroxide and sodium aluminate solution. Firstly, Mentha ash was washed with 1.5M of the sulfuric acid solution then a combination of Mentha ash and sodium hydroxide prepared in the ratio of 1:1.3 and subsequently heated at 600 °C for 90 minutes in a muffle furnace. In the heated product, 50 mL sodium aluminate solution was added dropwise and stirred for 1 h. The obtained mixture was washed with distilled water several times to till the neutral level.

- The prepared adsorbent was characterized by SEM & EDS, XRD, FTIR, BET, Zetapotential, and pHzc.
- MPA particles have irregular and crystalline clustered shapes with 5 μm average in size. The shape of the Na-Al-MA particles was seen as irregular and in clustered form after the SEM analysis.
- FTIR spectrum revealed the presence of carboxylic (-COOH), C-H bending of the methyl group, asymmetric stretching of Al-O-Si, =C-H group due to the presence of alkane and hydroxyl group (-OH) in the adsorbent.
- XRD analysis observed that the synthesized material is semi-crystalline in nature and BET surface area is found to be 59 m^2/g and microporous in nature.
- The particle size of the adsorbent was found 0.6 μm (600 nm), and the value of zeta-potential of the material was found to be +35 mV. The value of pHzpc of adsorbent is found to be 7.2.
- The synthesized adsorbent was applied for the removal of fluoride and the adsorption process was optimized by different operating conditions (dose of adsorbent, fluoride concentration, pH, contact time and temperature), and adsorption process was evaluated using adsorption isotherm, kinetics and thermodynamics.
- Batch studies revealed that the maximum removal of fluoride by prepared Na-Al-MA material was found to be 86% at neutral pH and at laboratory temperature.
- It was found that Na-Al-MA removed ~58.9%, ~61.5%, ~57.6%, and ~62.5% fluoride from Chouhatta Handpump, School Handpump, Chitisapur Handpump, and Submersible Handpump, respectively.

- It was revealed that after comparing data of Langmuir, Freundlich, and Temkin isotherm, the Langmuir isotherm model and their adsorption data were found to be compatible.
- It was concluded after comparing pseudo-first-order kinetic and pseudo-second-order kinetic, the adsorption of fluoride on Na-Al-MA followed pseudo-second-order adsorption kinetic.
- The negative value of ΔG indicates that the adsorption of fluoride onto Na-Al-MA is a spontaneous process

Phase 2: Characterization and application of Lanthanum modified adsorbent from pond clay soil for fluoride removal from water

- This is the second phase in which pond clay soil was converted into an adsorbent by using lanthanum oxide.
- A 15 g fine powder of washed clay soil was taken in the clean beaker and added the 0.1 M solution of lanthanum oxide and the mixture was subjected to stirring on a magnetic stirrer for 2 h. The obtained mixture was calcinated in a muffle furnace at 500 °C for 1 h and then washed with distilled water several times.
- The synthesized adsorbent was characterized by SEM with EDS, FTIR, XRD, XPS, BET, pH_{zpc}, PSA and Zetapotential.
- SEM results confirmed the particles of the clay soil are clumped, irregular, and flaky structures, whereas modified clay has a comparatively large and clumped flaky shape and rough surface. EDS revealed the presence of La and F on the adsorbent surface. TEM analysis revealed the size of raw clay was in the range of 84 nm to 159 nm while LMC was measured 255 nm to 288 nm. XRD pattern confirmed that montmorillonite, illite, quartz, and kaolinite are present in clay soil. The BET surface area of LMC was measured to be 6.54 m²/g and the total

pore volume was found $0.0914 \text{ cm}^3/\text{g}$. The XPS peak of 845.5 eV confirmed the presence of Lanthanum on the surface of modified clay and 650 eV confirmed successful adsorption of fluoride on adsorbent. The Zeta potential of the LMC was +25.1 eV and its particle size was 600-1000 nm by PSA analysis. The pHzpc of the adsorbent was measured to be 6 which indicates its surface was positively charged.

- The prepared adsorbent was applied for the removal of fluoride from aqueous solution and groundwater by the adsorption process. This adsorbent was also tested in the column for a continuous adsorption process.
- The adsorption process was optimized by various operating parameters such as dose of adsorbents, pH of the solution, fluoride concentration, temperature, shaking time, and co-existing ions.
- Fluoride removal by the continuous process was carried out by two different bed depths of adsorbent (3 cm & 6 cm) and flow rate (5 mL/min & 10 mL/min).
- The removal of fluoride was conducted by adsorption, the maximum removal of fluoride was found to be 97%.
- Batch studies revealed that the maximum adsorption of fluoride by prepared LMC material was found to be 1.96 mg/g at neutral pH and room temperature.
- The presence of sulfate and bicarbonate ions in the aqueous solution showed negative results for fluoride adsorption.
- Data from the column study showed that, as the bed length increased from 3 cm to 6 cm, the saturation time increased from 390 min to 480 min, and the processed effluent increased from 2025 mL to 2400 mL with a flow rate of 5 mL/min. The saturation time for a flow rate of 10 mL/min increased from 180 min to 225 min

- The LMC test for groundwater treatment observed significant results, fluoride ions removed ~62.5%, ~64.1%, ~69.2%, and ~58.4% from Chouhatta handpump, school handpump, Chitisapur handpump, and submersible, respectively.
- Fluoride adsorption was followed best by Langmuir isotherm and the adsorption kinetics followed with pseudo-second-order kinetic. Fluoride adsorption on clay soil-based adsorbent was found exothermic process.
- Thomas model was best fitted for the fixed bed adsorption process. The adsorbent was found effective upto three cycles of regeneration.

Phase 3: Characterization and application of Zirconium activated carbon for fluoride removal from water

In this phase activated carbon was synthesized from the aquatic plant biomass (*Juncus effusus*). 150 mL solution of zirconium oxychloride (0.1M) was taken in a beaker and added 30 g of biomass powder and mixed it well. Oven-dried mixture was subjected to thermally activated in a muffle furnace at 500 °C for 90 min. The washed activated carbon was applied for the removal of fluoride from water.

- Activated carbon was successfully synthesized from *Juncus effusus* plant biomass and it was characterized by SEM, EDS, FTIR, XRD, pH_{zpc}, and Zeta potential.
- The results of microstructure analysis comprise a rough and irregular appearance under the SEM observation.
- EDS spectrum confirmed the presence of C and Zr in activated carbon and C, Zr, and F are present after fluoride adsorption. No significant peaks for synthesized Zr-AC were assigned to confirm crystalline nature.

- The zero-point charge of the adsorbent was measured to be 6.4 and this value indicates the slightly acidic nature of the adsorbent.
- Adsorption of fluoride was optimized under varying conditions (dose of activated, initial fluoride concentration, contact time, pH of the solution, and temperature).
- About 93% of fluoride ions were successfully removed by Zr-AC having the highest efficiency of 2.31 mg/g at 10 mg/L concentration, neutral pH, and 25 °C temperature.
- After the treatment of the groundwater samples, fluoride ions were significantly removed. Fluoride ions removed ~63%, ~65.3%, ~63.4%, and ~66.66% from Chaouhatta village handpump, school hand pump, Chitisapur handpump, and submersible pump water, respectively.
- Adsorption of fluoride on Zr-AC followed Freundlich isotherm, pseudo-second-order kinetic as well as exothermic thermodynamic system.

Phase 4: Characterization and application of iron modified activated carbon from waste cartridge for fluoride removal from water.

This phase covers surface modification of waste carbon from discarded cartridges of water filters. Waste carbon was modified with iron, 30 g of carbon, and 5 g of ferric chloride mixed well and calcinated at 450 °C for 1h. Washed and oven-dried carbon was utilized for the removal of fluoride from water.

- Physical and chemical characterizations were done by SEM with EDS, FTIR, XRD, XPS, Zeta potential, and pH_{Zpc}.
- SEM results show that modified carbon appeared as irregular shape and EDS spectrum confirmed the presence of iron on the adsorbent surface and fluoride on

its surface. XRD spectrum confirmed the crystalline and amorphous nature and XPS results revealed the presence of Fe and F on the surface of carbon at binding energy 863 eV and 650 eV. pH_{zpc} of the carbon was found to be 6.3 which indicates a positive charge on the carbon surface.

- Surface modified carbon was applied for the removal of fluoride from water by the adsorption process. It was also tested in a designed continuous flow system with different bed depths of carbon (3 cm and 6 cm) and flow rates (5 min/L and 10 min/L).
- Optimization of fluoride removal was conducted by different adsorption conditions such as dose of carbon, contact time, initial fluoride concentration, temperature, and pH of the solution.
- The maximum removal efficiency was achieved to be 93% with a dose 5 g/L, fluoride concentration 10 mg/L, pH of the aqueous medium neutral, and normal temperature.
- Column study revealed that, at a flow rate of 5 mL/min, the adsorbent gets saturated in 510 min while at a flow rate of 10 mL/min, it takes 240 min for 3 cm bed depth, in the case of 6 cm bed depth, 990 min and 490 min was taken at flow rate 5 mL/min and 10 mL/min, respectively.
- Adsorption results revealed that fluoride removal occurred ~60.7%, ~66.6%, ~65.3%, and ~70.8% from Chouhatta handpump, school handpump, Chitisapur handpump, and submersible water, respectively.
- Langmuir isotherm and pseudo-second-order kinetic fitted well for the adsorption of fluoride on SM*C and this adsorption process was found exothermic in nature.