Development of Appropriately Tailored Adsorbents for Effective Defluoridation of Water

SYNOPSIS
Submitted in partial fulfilment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

By
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ID No: 2012PHXF529H

Under the Supervision of
Prof. N. Rajesh

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1. Introduction

The contamination of groundwater due to fluoride is an important problem to be addressed. The challenges are manifold and it is imperative to develop effective methodologies for fluoride remediation. At low fluoride concentration levels, it helps in the normal mineralization of bones and formation of dental enamel. However, the excessive intake of fluoride would lead to skeletal and dental fluorosis. In addition to fluorosis, high fluoride concentration can also lead to adverse effects including cancer, digestive and nervous disorders, low hemoglobin levels, reduced immunity, urinary tract and respiratory problems. Based on the severe effects on human health by fluoride contaminated ground water, U.S. Environmental Protection Agency (USEPA) has recommended 4.0 mg L\(^{-1}\) as maximum contaminant level for fluoride in drinking water while WHO limits are within the range 1.0–1.5 mg L\(^{-1}\). This limit has been set as maximum 1.0 mg L\(^{-1}\) in Indian standards. Several techniques such as precipitation, coagulation, oxidation, solvent extraction, evaporation, distillation, reverse osmosis, ion exchange and electro dialysis are reported for fluoride removal. The risk of fluorosis due to fluoride contaminated ground water is prevalent in many countries of Asia, America, Africa and Europe. Hence, the contamination of groundwater due to fluoride is an important problem to be addressed. The challenges are manifold and it is imperative to develop effective methodologies for fluoride remediation. In India, fluoride was first observed in drinking water in the Nellore district of Andhra Pradesh in 1937. It has been observed that fluorosis is prevalent in Rajasthan, Madhya Pradesh, Andhra Pradesh, Telangana, Tamil Nadu, Gujarat, and Uttar Pradesh. Considering the gravity of the problem, and to surmount some of the inadequacies in the existing methods it is imperative to develop effective adsorbents with removal efficiency in the permissible limit (1.0–1.5 mg L\(^{-1}\)).

2. Objective of the Work

Solid phase extraction (SPE) involves the distribution of fluoride ions between the liquid and solid phase effectively by adsorption of fluoride on the surface. The impregnation of metal ions in the matrix would enhance the adsorption of fluoride ions from drinking water. The small size of fluoride, high electronegativity and behavior as a hard base makes it compatible with hard metal ions such as aluminium and zirconium. Taking
advantage of the fact that fluoride can complex effectively with these metal ions, biodegradable polymers and economically viable adsorbent materials (Cellulose biopolymer, Synthetic polystyrene divinyl benzene resin and graphene oxide) were explored for the effective detoxification of fluoride. Furthermore, the application of these sorbents for removal of fluoride ions from drinking water samples and taking it to the field application for real water samples were examined. The work presented in the following chapters deals with the development of the following:-

i. A novel Al and Zr impregnated cellulose adsorbent prepared using ultrasonication and microwave irradiation for the facile defluoridation of water.

ii. Aluminium hydroxide impregnated macroreticular aromatic polymeric resin as a sustainable option for defluoridation

iii. Graphene oxide–aluminium oxyhydroxide interaction and its application for the effective adsorption of fluoride

Various adsorption parameters such as pH, adsorbent dosage, isotherm studies, kinetics, thermodynamic parameters, aqueous phase volume, interfering ions and column studies were investigated in detail. The modified adsorbents were characterized thoroughly using BET surface area analysis, FT-IR spectroscopy, SEM, EDX, XRD and XPS studies. The concentration of metal ions (Al$^{3+}$ and Zr$^{4+}$) leached into the aqueous phase after adsorption (detectable if any) was checked using ICP-AES.

3. **Description of the Research Work**

The first chapter shows that a broad literature review which describes about cellulose, polymeric resins and graphene oxide materials modified with different metal and metal hydroxides for defluoridation. The materials and methods adopted for this research work described in the second chapter. The removal of excess fluoride from water requires the development of novel methods. In order to accomplish this, cellulose, polymeric resins and graphene oxide based adsorbents were tested for defluoridation. Adsorbents were prepared using microwave and ultrasonication methods.
The first method presented in the thesis (Chapter 3) deals with a novel microwave assisted preparation of Al-Zr impregnated cellulose biopolymer adsorbent and its application for defluoridation. The adsorbent prior and subsequent to the adsorption of fluoride was characterized comprehensively using Fourier transform infrared spectroscopy (FT-IR), Energy dispersive X-ray spectrometry (EDX) and X-ray diffraction (XRD) studies.

Figure 1. Schematic diagram of the interaction of fluoride with Al/ZrIC biopolymer adsorbent surface.
Microwave-assisted preparation of the adsorbent ensures efficient dielectric heating and under microwave (MW) irradiation there is rapid energy transfer from the cellulose hydroxyl groups to neighboring molecules.\textsuperscript{10} Further MW radiation also results in\textsuperscript{11} lowering of Gibbs energy of activation thereby promoting the effective interaction of the cationic Zr(OH)\textsuperscript{2+} and Al(OH)\textsuperscript{2+} hydroxides with the hydroxyl groups of cellulose. The mechanism of fluoride ion interaction with Al-Zr impregnated cellulose is shown in Figure 1. The metal ion interacts with the glycosidic linkage of cellulose in the form of a strong electrostatic attraction. The adsorption of fluoride is favored by the interaction of cationic aluminium and zirconium hydroxides through electrostatic, hydrogen bonding and complexation mechanism. The novel Al-Zr impregnated cellulose adsorbent exhibits an adsorption capacity of 5.76 mg g\textsuperscript{-1} and the experimental data showed a good fit to the Freundlich and Langmuir isotherm models. The spontaneity of adsorption and second order kinetic model describes the adsorption process. The adsorbent exhibits excellent adsorption up to 5 mg L\textsuperscript{-1} fluoride and shows good potential towards practical application.

The second method illustrates the utility of an ultrasound assisted methodology involving the impregnation of zirconium in a cellulose matrix and application for fluoride removal in aqueous solutions. The schematic representation of ultrasonic horn is depicted in Figure 2.

Figure 2. Schematic diagram of ultrasonic horn
The sonicator operates at a frequency $23 \pm 3$ kHz with a nominal output power of 500 W. The sonicator rod is made of stainless steel tip with 6 mm diameter. The adsorbent was prepared in methanol medium, the power dissipated using this solvent was found to be 8.2 W. The energy efficiency in methanol medium was found to be 2.92%. The net energy supplied for the preparation of the adsorbent through sonochemical method was found to be 0.5888 kJ g$^{-1}$.

![Figure 3. Schematic diagram depicting the interaction of fluoride ion with Zr impregnated cellulose biopolymer surface](image)
Ultrasonication ensures a green and quick alternative to the conventional time intensive method of preparation. During ultrasonication, the surface area increases due to cavitation effects onto the biopolymer surface. This could lead to cleaving of the hydrogen bond between the cellulose layers resulting in the disruption of the ordered packing of cellulose molecules. This enhances the interaction of the zirconium metal ion onto the surface of the cellulose biopolymer. Ultrasonication could also influence the degradation of cellulose which enhances the interaction between the zirconium ions to the glycosidic linkages present in the cellulose. A schematic representation of the mechanism is given in Figure 3. The mode of binding of the zirconium oxy chloride on cellulose could be visualized with a part of the molecule binding to the surface of cellulose containing primary and secondary hydroxyl group as well as the glycosidic linkages of the cellulose biopolymer. Since the adsorbent was prepared in methanol medium, it is probable that the alkoxy hydroxides can be hydrolyzed to the cationic zirconium hydroxide. The zirconium ion could interact with the cellulose primary hydroxyl group resulting in the formation of Zr-O bond. Fluoride from aqueous solution interacts with the cellulose hydroxyl groups and the cationic zirconium hydroxide. The adsorption of fluoride on the adsorbent was confirmed by FT-IR, XRD and EDAX analysis. The novel Zr impregnated cellulose adsorbent exhibits an adsorption capacity of 4.95 mg g\(^{-1}\) with the experimental data showing a good fit to Langmuir isotherm model. The second order kinetics describes the adsorption process very well. The study of thermodynamics indicates a spontaneous, exothermic adsorption process and a decreased randomness at the adsorbent-solution interface.

The fourth chapter of the thesis deals with potential application of aluminum hydroxide impregnated macroporous polymeric resin (Amberlite XAD 1180) as a sustainable option for defluoridation of water. The impregnation of aluminium hydroxide on to the residual vinyl groups (within the pores of the XAD1180 resin matrix) could be referred to as ‘alumylation’. The BET surface area of the Al(OH)\(_3\) incorporated polymeric resin adsorbent was found to be 373.73 m\(^2\)g\(^{-1}\). The mechanism of impregnation of aluminium hydroxide onto the macroporous polymeric resin matrix is shown in three steps (Figure 4).
Figure 4. Proposed mechanism for preparation of aluminum hydroxide impregnated macroporous polymeric resin adsorbent.
The mode of fluoride ion interaction onto the aluminium hydroxide impregnated macroporous polymeric resin adsorbent is shown in Figure 5. The schematic representation illustrates that in aqueous solution, Al (III) could exist as cationic hydroxides interact with fluoride through electrostatic interaction. Furthermore, the hydrogen bonding interaction between the metal hydroxyl groups (Al-OH) and F− would also enhance the interaction with the macroreticular resin matrix.

**Figure 5.** Schematic diagram depicting the interaction of fluoride with Aluminium hydroxide impregnated macroporous polymeric resin adsorbent

The adsorption of fluoride on the adsorbent was confirmed by FT-IR, PXRD and EDS analysis. Various characterization techniques supported the adsorption of fluoride through electrostatic, ion exchange and hydrogen bonding mechanism. The zero point charge of prepared adsorbent was found to be 5.01. The second order kinetics and the exothermic, spontaneous adsorption are other characteristic features associated with this method. The q_max obtained from the nonlinear Langmuir model was found to be 92.39 mg g⁻¹ and 36.61 mg g⁻¹ at pH 3.0 and 7.0 respectively. However, it was found to be 32.92 mg g⁻¹ for drinking water and a sample volume of 1500 mL on a laboratory scale column containing 5.0 mg L⁻¹ of fluoride could be brought down to less than 1.0 mg L⁻¹. This is attainable at the natural pH range prevalent in water and hence the method could pave way to develop a prototype and extend it to remediate fluoride in field applications. The adsorbent could be regenerated with sodium hydroxide.

Graphene oxide has emerged as an attractive member of carbon family in the same view of its high surface area and presence of various functional groups (hydroxyl, epoxy groups and carboxylic). The fifth chapter in the thesis deals with preparation of novel
aluminium oxy hydroxide [Al-O(OH)] modified graphene oxide by chemical precipitation method and its application for fluoride removal in real water samples. The presence of aluminium oxy hydroxide on the surface of graphene oxide was also confirmed by XRD analysis. Furthermore, XPS analysis reveals that a distinct Al 2p transition was observed at 74.7eV, characteristic of Al-O(OH) or pseudoboehmite. The zero-point charge of GO-Al-O(OH) adsorbent was found to be 7.54. The thermodynamically feasible adsorption is supported by the pseudo second order kinetics and a high Langmuir maximum adsorption capacity (51.42 mg g⁻¹) for GO-Al-O(OH) adsorbent. Ligand exchange and physical adsorption are mostly favored for the adsorption of fluoride and this was corroborated from the XPS studies (Figure 6). Batch studies reveals that the leached aluminum content in aqueous solution is very less (3.0-5.0 ppb) even at different initial fluoride concentrations in the pH range of 7.0-8.0 and is less than 200 ppb in pH 5.0 - 6.0 range. Furthermore, it is possible to treat 2.0 L of 5.0 mg L⁻¹ fluoride ion solution to bring the level within the permissible limits and the regeneration of the adsorbent was done using ammonium hydroxide. The regeneration of the adsorbent was done using ammonium hydroxide.

The summary of the methods are presented in the Table 1.

<table>
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<tr>
<th>Adsorbent</th>
<th>Suitable pH</th>
<th>Q_max (mg g⁻¹)</th>
<th>Isotherm</th>
<th>Kinetics</th>
</tr>
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<tr>
<td>Al-Zr-cellulose</td>
<td>4.5-5.5</td>
<td>5.76</td>
<td>Freundlich</td>
<td>Pseudo second order</td>
</tr>
<tr>
<td>Zr-Cellulose</td>
<td>4.5-5.5</td>
<td>4.95</td>
<td>Langmuir</td>
<td>Pseudo second order</td>
</tr>
<tr>
<td>Al(OH)₃-Resin</td>
<td>3.0-7.0</td>
<td>36.37</td>
<td>Freundlich and Langmuir</td>
<td>Pseudo second order</td>
</tr>
<tr>
<td>GO-Al-O-(OH)</td>
<td>6.5-8.0</td>
<td>51.42</td>
<td>Langmuir</td>
<td>Pseudo second order</td>
</tr>
</tbody>
</table>
Figure 6. Preparation of GO and GO-Al-O-(OH) adsorbent and the possible mechanism towards the fluoride ion adsorption
4. Field Application Study

The summary of the methods are presented in the Table 1. Graphene oxide-aluminium oxyhydroxide adsorbent has high adsorption capacity as compared to other modified adsorbents in the wide range of pH. Hence, the applicability of this material was tested in water samples collected from different places at Nalgonda district, Telangana. The fluoride spiked water can be treated with GO-Al-O(OH) adsorbent effectively either in a simple bucket system (Figure 7) or packed column prototype (Figure 8). The prototype model was developed and demonstrated successfully for the defluoridation of 50.0 L of water containing 5.0 mg L\(^{-1}\) F\(^-\) using 50.0 g of the adsorbent. The collected real water samples were analyzed before and after treatment with GO-Al-O (OH) adsorbent at Intertek Private Limited, Hyderabad (NABL Accredited Lab). The leaching of aluminium in the residual water is negligible and the prepared GO-Al-O(OH) adsorbent has good potential for defluoridation in real field water samples.

![Figure 7. A simple bucket system (A) with GO-Al-O-(OH) adsorbent (B) for defluoridation of water](image)
5. Summary and Conclusion
The removal of excess fluoride from water requires the development of improved and sustainable methods. In conclusion, the thesis presents a comprehensive overview of the chemistry of fluoride and efforts directed towards the development of novel adsorbents for defluoridation of water. The facile preparation of the adsorbent was accomplished by microwave and ultrasound assisted synthesis. The preparation, characterization, mechanistic aspects and application to defluoridation of water were discussed in detail. The summary of the results are presented in the Table 1. Among all other adsorbents, Graphene oxide-aluminium oxyhydroxide adsorbent has high adsorption capacity in the wide range of pH. Hence, the applicability of this material was demonstrated in real water samples.
6. References

2. Yadugiri, V. T. Curr. Sci. 2011, 100, 1475
8. Rajiv Gandhi National Drinking Water Mission (RGNDWM), Prevention and control of fluorosis in India, 1993

7. Proposed contents of the thesis

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LIST OF PUBLICATIONS

Publications relevant to thesis work


Contributions related to adsorption


Abstract presented in Conferences
