Introduction

In recent years, fluoride and fluorosis are globally common issues. Many developing countries have been facing problems with fluorosis. Due to natural and anthropogenic activities, the ground water becomes infected by fluorides [1,2]. Fluorine is one such pollutant that threatens living organisms especially humans [3]. Fluoride in drinking water has both merits and demerits to human health. Fluorides in trace amounts are essential for living beings for improvement of bone and dental enamel but higher concentration than 1.5 mg/L causes skeletal and dental fluorosis [4,5]. Industries such as glass and ceramic production, electroplating, brick and ironworks, semiconductor manufacturer and aluminum smelters produce fluoride contaminants that are discharged into water resources [6,7]. The effluents of these industries have higher fluoride concentration than natural waters, ranging from ten to thousands of mg/L [8]. According to the World Health Organization guidelines (WHO), the fluoride concentration in drinking water should not exceed 1.5 mg/L [9]. According to the Environmental Protection Agency (EPA) the maximum contaminant level of fluoride ions in drinking water is 4.0 ppm [10-12]. Excess fluoride is toxic but limited fluoride is necessary for calcification of dental enamel and bone formation. Excess intake of fluoride would lead to various diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility in women, male sterility, brain damage, Alzheimer’s syndrome, thyroid disorder and even death in severe cases [13,14]. About 40% of ingested fluoride is absorbed in the stomach as HF in aqueous solution. Prolonged and excessive intake of fluoride may result in serious health problems, fluorosis, which is characterized by mottling of teeth in mild cases and even the softening of bones and neurological damage in extreme cases [15]. It has been reported by several research groups that fluoride can interfere with DNA synthesis, carbohydrates, lipids, proteins, vitamins and mineral metabolism [16,17]. Besides, on short exposure, a high dose of fluoride affects kidney in both humans and animals [18]. Due to the toxic effects of fluoride on human health, tremendous research and development efforts are being put all over the developing countries for the removal of excess fluoride from drinking water. The removal of fluoride from aqueous solution is of prime concern. The methods for the removal of fluorides include chemical precipitation, ion exchange, membrane filtration, coagulation, electrochemical...
treatments, and adsorption using activated carbon, carbon nanotubes, activated alumina and other natural and synthetic materials [19-24]. Most of these methods have high operational and maintenance costs, low fluoride removal capacities, lack of selectivity for fluoride, low selectivity in presence of other competing ions, generation of large volumes of sludge and complicated procedures in the treatment process. The widely used adsorption methods are activated carbon (AC), activated alumina and other synthetic materials. These techniques cannot work effectively due to the short service life of adsorbent, blockage problem, more cost, and sensitivity to the pH of the solution [25]. However, the adsorption method has been reported as one of the most effective, economical and eco-friendly of the various defluoridation techniques [26-30].

The biosorption process using biomass waste is an eco-friendly and easy method. It is the promising alternative adsorbent over the conventional adsorbents in the adsorption process.

Table 1: The maximum Fluoride adsorption capacity of various raw adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity Q&lt;sub&gt;max&lt;/sub&gt;(mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrus limonium leaf</td>
<td>1.4</td>
<td>[37]</td>
</tr>
<tr>
<td>Sweet lemon peel</td>
<td>0.744</td>
<td>[38]</td>
</tr>
<tr>
<td>Citrus limetta peel</td>
<td>1.915</td>
<td>[39]</td>
</tr>
<tr>
<td>Ultrafine Tea powder</td>
<td>1.26</td>
<td>[40]</td>
</tr>
<tr>
<td>Sandalwood leaf powder</td>
<td>4.66</td>
<td>[41]</td>
</tr>
<tr>
<td>Banana peel</td>
<td>8.15</td>
<td>[42]</td>
</tr>
<tr>
<td>Neem leaf powder</td>
<td>4.70</td>
<td>[43]</td>
</tr>
<tr>
<td>Tamarind fruit shell</td>
<td>1.53</td>
<td>[44]</td>
</tr>
<tr>
<td>Pipal leaves</td>
<td>0.80</td>
<td>[45]</td>
</tr>
<tr>
<td>Chitosan</td>
<td>1.39</td>
<td>[46]</td>
</tr>
</tbody>
</table>

The improved selectivity and sorption capacities of low-cost adsorbents derived from waste bio-mass loaded with metal ions have drawn the attention of many researchers in this field. There is an increasing trend of using biomass-based fluoride adsorbents, very few studies show that raw biomass has the ability of the adsorption of fluorides. But raw biomass can show very low adsorption capacity as compared to the commercial anion exchangers. The adsorption capacities of fluoride by some raw biomass and various commercial adsorbents are shown in Table 1 and Table 2 respectively.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Modifying agent</th>
<th>Adsorption Capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seaweed(M - CSW)</td>
<td>Zr(IV) - CSW</td>
<td>18.05</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td>La(III) - CSW</td>
<td>11.02</td>
<td></td>
</tr>
<tr>
<td>Tea powder</td>
<td>UTP - Zr</td>
<td>12.43</td>
<td>[40]</td>
</tr>
<tr>
<td>Orange waste gel</td>
<td>Saponification</td>
<td>22.8</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td>loading Zr (IV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Azollafiliculoides</td>
<td>HCl</td>
<td>11.2</td>
<td>[50]</td>
</tr>
<tr>
<td>Orange waste</td>
<td>Conc. Sulphuric</td>
<td>13.49</td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td>acid, Zr(IV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porous corn starch</td>
<td>PS-Zr</td>
<td>25.41</td>
<td>[52]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Al(OH)₃, Coated</td>
<td>14.82</td>
<td>[53]</td>
</tr>
<tr>
<td>Rice straw</td>
<td>KMnO₄, Modified</td>
<td>15.77</td>
<td>[54]</td>
</tr>
<tr>
<td>Cotton cellulose</td>
<td>iron loaded</td>
<td>18.43</td>
<td>[55]</td>
</tr>
<tr>
<td>Orange waste</td>
<td>La-SOJR</td>
<td>20.33</td>
<td>[56]</td>
</tr>
<tr>
<td>Orange waste</td>
<td>Sc - SOJR</td>
<td>11.4</td>
<td>[56]</td>
</tr>
</tbody>
</table>

The low fluoride removal efficiency of raw biomass adsorbent compared to commercial adsorbents (as shown in Table 1 and Table 2) can be described due to the presence of negatively charged functional groups like amino, carboxyl, alcohols and ester on the surface of lignocellulosic materials of bio-mass, while positively charged functional group is limited[31-36].

Table 3: The maximum fluoride adsorption capacity of various agricultural waste adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Modifying agent</th>
<th>Adsorption Capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange waste</td>
<td>La – loaded HPG</td>
<td>28.57</td>
<td>[48]</td>
</tr>
<tr>
<td>Orange waste gel</td>
<td>La(III) - CSW</td>
<td>44.65</td>
<td>[47]</td>
</tr>
<tr>
<td>Amberlite 200 CT</td>
<td>Zr(IV) - CSW</td>
<td>25.46</td>
<td>[46]</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>Zr(IV) - CSW</td>
<td>39.9</td>
<td>[47]</td>
</tr>
<tr>
<td>Hardened alumina cement (ALC)</td>
<td></td>
<td>41.04</td>
<td>[47]</td>
</tr>
</tbody>
</table>

Due to the lack of anion binding sites on the polymeric backbone, raw biomass-based adsorbents are found to be less effective in the removal of fluoride. In addition, the polymeric organic compounds (cellulose, lignocellulose and lignin) can leach into the aqueous solution so raw biomass-based adsorbent retards the adsorption capacity of fluoride anion. Thus, in order to increase the adsorption capacity of raw biomass, it is modified depending on the nature of pollutants, which is depicted in Table 3. The adsorption capacity of modified metal loaded adsorbents is found to be excellent due to its high binding sites, selectivity towards fluoride, large surface area and chemical stability.
Mechanism of fluoride adsorption

Bio waste consists of cellulose, hemicellulose, pectin, lignin, and polyoses. Pectin contains carboxyl groups as well as its methyl ester groups. The methyl ester portion of pectin can be converted into a carboxyl group by saponification reaction using Ca(OH)$_2$ or NaOH. Thus, obtained saponified waste is further treated with rare earth metal ions. The carboxyl group and oxygen atom of the pyranose ring of pectic acid in the bio-waste form a stable five-membered chelate with the loaded metal ion. Due to hydroxyl ions as well as water molecules present in the coordination sphere of metal ions, it exhibits the ligand exchange mechanism with fluoride ions. Due to the steric hindrance of pectic acid, it is difficult to neutralize all the positive charges of the loaded metal ions with carboxyl groups. So, one or two positive charges of the loaded metal ion can be neutralized by carboxyl groups while other positive charges are neutralized by hydroxyl ions in the solution. The increase in the oxidation state of loaded metal ions increases the number of hydroxyl ions on the coordination spheres of the loaded metal ions that enhances the ligand exchange mechanism with fluoride ions. The equilibrium pH of the solution is found to be increased after the adsorption of fluoride indicating that hydroxyl ions are released during adsorption, which further supports the mechanism mentioned below [56].

Factors affecting adsorption

Effect of pH

The pH of an aqueous solution is an important parameter for the adsorption at a solution adsorbent interface. The adsorption of fluoride increases with increasing pH and it is in the pH range of 2-4, because of the presence of more protonated sites in the ion exchange with F$^-$, then decreased with further increase in pH. The low adsorption at low pH (pH<2) may be due to the formation of weakly ionizable hydrofluoric acid (pK$_a$ of HF = 3.2) or more than 95% of fluoride remains in the non-ionic form which is difficult to be adsorbed onto the anion exchange site of the adsorbent. The maximum fluoride adsorption was found to occur at pH 2-4. The decrease in fluoride adsorption at pH above 5 is due to the competition

![Figure 1: Adapted mechanism of saponification followed by metal ion loading](https://www.nepjol.info/index.php/JNCS)

![Figure 2: Adapted Mechanism on the adsorption and desorption of fluoride ion [56]](https://www.nepjol.info/index.php/JNCS)
of hydroxide ions for the adsorption sites because hydroxide ion concentration increases with the rise of pH of the solution [20,56,57].

**Effect of initial fluoride concentration and adsorbent dose**

The fluoride adsorption was found to be affected by both the adsorbent dose and the initial fluoride concentration. It was found that for a fixed fluoride concentration, the percentage of adsorption gradually increases with increasing adsorbent dose from 1.0mg/g to 5.0mg/g at 303 K. It might be due to the increased surface area and availability of more adsorption sites for fluoride adsorption. But for a constant dose, total available adsorption sites were limited so due to limited available adsorption sites, at higher concentrations of fluoride solution, there would be extreme competition among fluoride ions for the adsorption sites resulting in the decrease or constancy in adsorption [41]. Dehghani et al. [57] studied that fluoride adsorption increases with increasing adsorbent dose due to a greater extent of adsorption sites and more surface area.

**Effect of contact time and kinetic study**

The contact time of fluoride and adsorbent during adsorption is important in determining the kinetics of the process. The adsorption of fluoride depends on the contact time of the adsorbent and solution. Rapid uptake of fluoride and establishment of equilibrium in a short period of time denotes the efficiency of the adsorbents. In physical adsorption, most of the fluoride is adsorbed within a short interval of contact time. However, strong chemical bonding of the fluoride with adsorbents needs a longer contact time to reach equilibrium. In the beginning, the adsorption of fluoride increases rapidly with an increase in contact time then slows down and reaches equilibrium [57]. Khound et al. [41] studied the adsorption of fluoride with Sandalwood leaf powder (SLP) and the amount of adsorption increased with time up to 120 min. The rapid removal of fluoride at initial stages might be due to the vacant adsorption sites and it can adsorb more fluoride ions from the solution. The time-dependent adsorption data have been analyzed using three kinetic models, pseudo-first-order, pseudo-second-order and intraparticle diffusion model.

**Adsorption isotherms**

The adsorption isotherm determines how the fluoride molecules distribute between the liquid and solid phase during the adsorption process at an equilibrium state. Adsorption isotherm provides information about the effectiveness of the biomass for the removal of fluoride from contaminated water. The adsorption data were analyzed using Langmuir, Freundlich, Temkin, Redlich-Peterson and Sips isotherm [58]. Cai et al. [40] studied the Zr-loaded tea powder which is best fitted with the Langmuir isotherm model based on monolayer adsorption of adsorbate onto the adsorbent surface with the limited number of binding sites. Abu Bakar et al. [58] studied modified Palm Kernel Shell which is fitted with Freundlich, Redlich-Peterson and Sips isotherm.

**Thermodynamic study**

The thermodynamic feasibility and the spontaneity can be predicted by observing the effect of change of temperature upon the adsorption process and hence evaluating thermodynamic parameters; Gibb’s free energy of adsorption \( \Delta G^0 \), enthalpy of adsorption \( \Delta H^0 \) & entropy of adsorption \( \Delta S^0 \). An adsorption process is generally considered as physical if \( \Delta H^0 \) ˂ 84 KJ/mol and the chemical if \( \Delta H^0 \) lies between 84 – 420 KJ/mol [59]. With the rise in temperature, fluoride adsorption increases if adsorption is endothermic and decreases for the exothermic process.

**Effect of co-existing anions**

Various anions in the solution can interfere with fluoride removal in the adsorption process. The percentage of fluoride removal decreases in the presence of PO\(^{4-}\), SO\(^{2-}\), NO\(^{3-}\) and Cl\(^{-}\) anions. The uptake capacity depends on ionic radii. Ionic radii of fluoride, chloride and nitrate ions are 0.133, 0.181 and 0.179 nm which is quite similar. The ionic radii and surface charge densities of phosphate (0.238 nm) and sulphate (0.230 nm) anions are larger than of fluoride ions and interfere with the adsorption of fluoride at the active site. Sometimes, the addition of competitor anions in water causes an increase in pH. This increases in pH value results in the decrease of fluoride adsorption [57].

**Conclusion**

This review has attempted to cover a wide range of adsorbents and treatment techniques which have been used for the removal of fluoride from aqueous solution. The capacity of treatment techniques and

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https://www.nepjol.info/index.php/JNCS
their merits and limitations were highlighted. In addition to this, different types of adsorbent and their adsorption capacities were presented. It showed that chemically modified metal loaded biomass for the removal of pollutants has attracted the attention of more researchers. Chemically modified adsorbents enhance the adsorption capacity of fluoride due to a higher number of active binding sites, selective metal ion adsorption, rapid adsorption kinetics, improve structural stability and ion exchange capacity. These adsorbents were found to be efficient for fluoride removal, not only from the industries but also from the living organisms and the surrounding environment. The use of biomass adsorbents may contribute to the sustainability of the environment and water resources. Undoubtedly, biomass adsorbents provide a lot of promising benefits for commercial purposes in the future. More studies should be carried out for low-cost adsorption processes to enhance large scale use of biomass adsorbents. Low-cost adsorbents should be used to minimize cost and maximize heavy metal removal efficiency.

References
2. V. Sivasankar, S. Murugesh, S. Raj Kumar and A. Darchen, Cerium dispersed in carbon (CeDC) and its adsorption behaviour: A first example of tailored adsorbent for fluoride removal from drinking water, Chemical Engineering Journal, 2013, 214, 45-54.


