Studies on Defluoridation of Water by Tea Ash: An Unconventional Biosorbent

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Abstract: Residual part of tea as a household waste was effectively used for removal of fluoride from aqueous medium. The variable operating parameters such as pH, initial fluoride concentration, sorbent particle size, agitation time and temperature. The defluoridation capacity increases with increasing adsorbent dose and contact time but decrease with initial concentration of fluoride solution. Moreover, acidic pH (6) showed the highest removal of fluoride. Further defluoridation follows second order kinetics and Langmuir and Freundlich adsorption isotherm. The surface and sorption characteristics were analyzed using FTIR and SEM techniques. For domestic and industrial applications, defluoridation with 100% achievement and subsequent regeneration of adsorbent was performed with a household water filter and fixed bed column respectively.

Keywords: Fluoride removal, Batch study, Tea residue, Isotherm study, Thermodynamic study

Introduction
Fluoride is one of the most potent groundwater pollutant. Excess intake (>1.5 mgL⁻¹) may cause fluorosis (dental, skeletal and non-skeletal) along with various neurological complication. Removal of fluoride from the ground water is challenging task among the scientists. Various technologies already developed to remove fluoride from drinking water by coagulation, membrane filtration, ion exchange, etc. But due to high cost for processing such technology is unfit for developing country. Therefore there is a great need for environmental friendly and low cost technology. One such low cost technology is adsorption and which is effective for removal of fluoride. Many low cost adsorbents such as Tamarind seed; Tamarind gel; Duck weed spirodela polyrrhiza were used for removal of fluoride.
Fluoride is known to be a natural contaminant for ground water resources globally\(^1\). The removal of fluoride from water is one of the most important issues due to its ill-effects on human health and environment\(^2\). According to World Health Organization\(^3\) the maximum permissible limit of fluoride concentration in drinking water is 1.5 mg L\(^{-1}\). There are lot of methods developed for removal of excess fluoride from drinking water, such as the use of ion exchange columns, coagulation, use of membranes and electrochemical methods, the high cost of these technologies makes them unpractical for developing countries\(^4\). Among these techniques, adsorption seems to be an effective, environmentally friendly economical one\(^5\). Over the last few years numbers of investigations have been conducted to test the low cost adsorbent for fluoride removal such as activated alumina\(^6\), titanium-rich bauxite\(^7\), manganese oxide-coated alumina\(^8\) and carbon nanotubes\(^9\). Moreover, plant materials like serpentine and Tamarind gel\(^10\), Tamarind seed\(^1\), Duck weed Spirodela Polyrrhiza\(^11\); \textit{Hydrilla Verticillata}, Royale Plants\(^12\) are also reported to accumulate fluoride and hence application as defluoridation agents has been suggested. The utilization of agricultural waste materials is increasingly becoming a vital concern because these wastes represent unused resources and in many cases present serious disposal problems.

Numerous waste biomass sources are available in different parts of the world, on which some experimental adsorption properties have been reported \textit{e.g.} rice husk\(^13\), rice husk ash\(^14\), egg shell\(^15\), peanut shells\(^16\), corn cobs\(^17\), saw dust\(^18\), coir dust\(^19\), dry tree leaves and barks\(^20\), tea and coffee waste\(^21-22\), rice and wheat bran\(^23-24\) and sea weeds\(^25\). From the literature review it is learnt that the biosorptive defluoridation study is limited and hence in the present work is performed with the tea residue. This work investigates the potential of tea waste from nearest shop for removal of fluoride ions from aqueous solutions. The optimum operating conditions drawn equilibrium data and sorption kinetics for fluoride removal using water washed tea waste were obtained. Batch studies were conducted to ascertain practical applicability. Using both laboratory aqueous solution and groundwater field samples, the study aims to devise a simple, cheap and viable defluoridation method that could be adopted easily by village communities and urban dwellers.

**Experimental**

The tea residue collected from nearest teashop in local market of Burdwan Municipality, Burdwan Municipality, West Bengal, India was used for the experiments. Soluble and coloured components were removed from tea by washing with boiling water. This was repeated until the water was virtually colourless. After thoroughly washing, the adsorbent was sun dried and it is burned in muffle furnace (Paragon, Model no. PTC-1) at 500 °C for 30 minutes and dried tea ash was sieved and stored in sealed polythene bags. The activated tea ash powder (AcTAP) material was subjected to various physicochemical parameters and used for sorption. The fraction 50 µm was used for all the experiments except for the effect of particle size tests.

**Instrument used for adsorbent characterization**

The surface area of the adsorbent was measured by a surface area analyzer (Quantasorb Model, Qs. 7). The porosity and density of the adsorbent were determined by mercury proximate and specific gravity bottles, respectively elemental analysis was carried out with Perkin Elmer 2400 CHN Elemental Analyzer. Adsorbent surface characterized by FTIR analysis (PERKINELMER, FTIR, Model-RX1 Spectrometer). The pH of the solution was
measured by using digital pH meter (model no. Systronic-335). Fluoride was measured by ion selective electrode (Thermo Orion 370 PerpHecT Ion Selective Benchtop Meter). Scanning electron microscope was done by (HITACHI, S-530, Scanning Electron Microscope and ELKO Engineering, B.U., BURDWAN).

**Determination of zero point charge**

The zero surface charge characteristics of the tea ash were determined by using the solid addition method\(^{26}\). 50 mL of 0.1 M KNO\(_3\) solution was transferred to series of 100 mL conical flasks. The initial pH (pH\(_i\)) of the solutions was roughly adjusted from 1.0 to 10.0 by adding either fixed strength of HNO\(_3\) (0.05) or 0.1N KOH. Then 1.5 g of AcTAP was added to each flask which was securely capped immediately. The flasks were then placed into a constant temperature water bath shaker and shaken for 24 h. The pH values of the supernatant liquid were noted after 24 h.

**Synthetic contaminated water preparation**

A synthetic solution of fluoride was prepared from analytical grade sodium fluoride (MERC, Bombay) and stored in polythene (TARSON made) bottle. The pH of the solution was adjusted to the required level, using HCl (0.1 N) and NaOH (0.1 N) solutions.

**Batch adsorption studies**

Adsorption experiments were carried out for the determination of pH, adsorbent dose variation, equilibrium time and kinetics, selection of an isotherm, effect of temperature and evaluation of thermodynamic parameters. The influence of pH (2.0-10.0), adsorbent concentration (0.2-2.4 g L\(^{-1}\)) and particle size (200-350 µm), contact time (40, 60, 120, 180, 240 and 300 min), initial fluoride concentration (1.5,5.0,7.0,10.0,15.0,35.0 and 50.0 mg L\(^{-1}\)) and temperature (303, 313, 323 and 333 K) were evaluated during the present study in a 250 mL Erlenmeyer flasks and 100 mL of fluoride solution of known concentration was added for constant shaking (at 300 rpm) during 1hr in a temperature controlled magnetic stirrer at 303 ± 1K and then the solids were separated through filtration. The solutions were collected for analysis and fluoride concentration in the solution was determined by using ion selective meter. Each experiment was conducted three times and average values are reported. Control experiments, performed without addition of adsorbent, confirmed that the sorption of fluoride on the walls of Erlenmeyer flasks was negligible. The amount of fluoride adsorbed per unit adsorbent (q\(_e\)) (mg g\(^{-1}\)) was calculated according to a mass balance on the fluoride concentration using Eq. (1):

\[
q_e = \frac{(C_i - C_f)V}{m}
\]

Where, V = Volume (L) of the equilibrated solution, m = Mass of the adsorbent (g), C\(_i\) = Initial concentration of metal ion (mg L\(^{-1}\)), C\(_f\) = Equilibrium concentration of Fe\(^{2+}\) (mg L\(^{-1}\)).

The percent removal (%) of dyes was calculated using the following equation:

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

**Results and Discussion**

**Characterization of adsorbent**

The physicochemical characteristics of tea ash are given in (Table 1). The surface characteristics make it suitable for sorptive defluoridation. The sorption is characterized under determination of zero point charge (pH\(_{ZPC}\)) of the adsorbent. Adsorption of cation is favored at pH>pH\(_{ZPC}\), while the adsorption of anion is favored at pH<pH\(_{ZPC}\) (Figure 1)\(^{26}\).
Figure 1. Zero Point charge of AcTAP

FTIR spectra of tea ash before and after F adsorption are shown in Figure 2a and b respectively. The band at 3427 cm\(^{-1}\) is due to O-H vibration of aliphatic alcohol and the two peaks at 2853 cm\(^{-1}\) and 2925 cm\(^{-1}\) indicate the presence alkane C-H stretching. A significant shift of the peak from 796 cm\(^{-1}\) to 875 cm\(^{-1}\) occurs probably due to the aromatic C-H bond get disturbed by fluoride. The band at 1097 cm\(^{-1}\) is due to stretching vibration of C-OH group of carboxylic acid. The band at 1097 cm\(^{-1}\) is also shifted to 1094 cm\(^{-1}\) after F adsorption. Scanning electron microscopy (SEM) observation (Figure 3a, 3b and 3c) shows rough surface of the adsorbent that provides large surface area for adsorption. Although adsorbent showed no change in its morphology after F adsorption. The micrograph (Figure 3c) very similar to Figure 3a indicated that the regeneration of fluoride from adsorbent surface has been occurred.

Figure 2a. IR Spectrum of AcTAP (before fluoride loaded)
Effect of pH

The effect of pH on the fluoride removal from aqueous solution by using AcTAP is shown in Figure 4. This result shows that removal of fluoride ion is most appreciable in the pH range 2.0-7.0 with a peak value at pH 6.0. This may be explained by considering pH_{ZPC} (Table 1) for the AcTAP because removal of fluoride by adsorption process is highly dependent on solution pH as it can alter the surface charge of the adsorbent\(^27\). Hence, in the

![Figure 2b. IR Spectrum of AcTAP (after fluoride loaded)](image)

![Figure 3a. Scanning electron microscopy of activated tea ash before passing fluoride solution. a) No cluster found.](image)

![Figure 3b. Scanning electron microscopy of activated tea ash after passing fluoride solution. b) Cluster found.](image)

![Figure 3c. Scanning electron microscopy of activated tea ash after regeneration of. c) After regeneration no cluster found](image)
present work, the highest removal capacity was performed at pH 6.0, since $pH_{ZPC} = 6.5$, the surface will be positively charged. Decrease in removal capacity was observed below and above pH 6.0 (Table 2), which may be attributed to unfavorable surface charges and competition for adsorption sites due to excess anions at alkaline conditions\textsuperscript{27}.

![Effect of pH on adsorption of fluoride ion onto adsorbent](image)

**Figure 4.** Effect of pH on removal of fluoride onto AcTAP (experimental conditions: Initial fluoride concentration: 5.0 mgL\textsuperscript{-1}, adsorbent dose: 0.8 g/L with particle size 100 µm, agitation speed: 300 rpm, Contact time: 60 minutes, Temperature: 303 K)

**Table 1.** The main physicochemical characteristics of adsorbent

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Tea-waste</th>
<th>Activated tea waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. surface area, m\textsuperscript{2} g\textsuperscript{-1}</td>
<td>477.69</td>
<td>494.31</td>
<td></td>
</tr>
<tr>
<td>ii. Particle size, µm</td>
<td>50-300</td>
<td>50-300</td>
<td></td>
</tr>
<tr>
<td>iii. Elemental analysis, %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>58.33</td>
<td>85.6</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>7.73</td>
<td>5.23</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.44</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>32.42</td>
<td>12.6</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.51</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>iv. Ash content, %</td>
<td>4.76</td>
<td>5.33</td>
<td></td>
</tr>
<tr>
<td>v. Moisture content, %</td>
<td>5.66</td>
<td>2.11</td>
<td></td>
</tr>
<tr>
<td>pH\textsubscript{ZPC}</td>
<td></td>
<td>6.5</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.** Effect of pH on adsorption of fluoride by AcTAP

<table>
<thead>
<tr>
<th>pH of the solution</th>
<th>$q_e$, mg g\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>5.45</td>
</tr>
<tr>
<td>4.0</td>
<td>5.52</td>
</tr>
<tr>
<td>6.0</td>
<td>5.59</td>
</tr>
<tr>
<td>7.0</td>
<td>4.69</td>
</tr>
<tr>
<td>8.0</td>
<td>3.27</td>
</tr>
<tr>
<td>10.0</td>
<td>3.22</td>
</tr>
</tbody>
</table>
Effect of particle size and adsorbent dose

Particle size is an important factor in adsorption because adsorption is a surface phenomenon and the extent of adsorption is expected to be proportional to the surface area available for adsorption. In the present work, the effect of adsorbent particle size was investigated by using the average particle size (50, 100, 150, 200, 250, and 300 µm) (Figure 5). Increase in particle size from 50 to 300 µm reduces the adsorption level from 89.6 to 77.8 percent. It may be due to the smaller particle size of adsorbent gives large surface area, increases the adsorption capacity. The effect of adsorbent dose on fluoride adsorption was studied at fixed initial concentration (5 mg L⁻¹) (Figure 6). The extent of percentage of adsorption increased with increase in the adsorbent dose while loading capacity (amount of fluoride adsorbed per g of the adsorbent) gradually decreased for decreasing the number of interaction site between the adsorbent and adsorbate. This is probably due to increase of adsorption sites. From the trend it appears that a maximum level (51.3 to 97.6 %) of fluoride adsorption occurs with increase in adsorbent dose from 0.2 to 2.4 g L⁻¹ and then the adsorption is not changed with the adsorbent dose due to establishment of equilibrium condition. Distribution coefficient (K_{DC}) usually calculated in this study to define the partitioning of an element in a system. Distribution coefficient reflects the binding capacity of the surface for adsorption. It is expressed by using the following equation.

$$K_{DC} = \frac{C_{eq}^\text{anion ads}}{C_{eq}^\text{anion diss}} C_p$$

In the present study the value of K_{DC} increased with increase of adsorbent dose at a constant pH (Figure 7) which indicates the heterogeneous nature of the adsorbent surface.

**Figure 5.** Effect of particle size on the adsorption of fluoride by AcTAP (experimental conditions: Initial fluoride concentration: 5.0 mg L⁻¹, pH: 6.0, adsorbent dose: 0.8 g/L, agitation speed: 300 rpm, Contact time: 60 minutes, Temperature: 303 K)
Figure 6. Effect of Adsorbent dose on the adsorption of fluoride by AcTAP (experimental conditions: Initial fluoride concentration: 5.0 mgL$^{-1}$, pH: 6.0, particle size: 50 µm, agitation speed: 300 rpm, Contact time: 60 minutes, Temperature: 303 K)

Figure 7. Plot of distribution coefficient vs. adsorbent dose (experimental conditions: Initial fluoride concentration: 5.0 mgL$^{-1}$, pH: 6.0, particle size: 50 µm, agitations speed: 300 rpm, Contact time: 60 minutes, Temperature: 303 K)

Effect of agitation speed

Studies on the effect of agitation speed were conducted by varying speeds from 100 to 400 rpm, at optimum pH of 6.0 with adsorbent dose of 2.4 g L$^{-1}$ and contact time of 60 min at 303 K (Figure 8). At a given time, fluoride removal increases with the increase in the speed of agitation. The reason for the increase is the diffusion of adsorbate towards the adsorbent surface$^{31}$ and also better contact between the adsorbent and adsorbate is possible$^{32}$. Similar findings for fluoride removal by using activated charcoal have been reported by other investigator$^{32}$. 
Figure 8. Effect of agitation speed on removal of fluoride onto AcTAP (experimental conditions: Initial fluoride concentration: 5.0 mgL\(^{-1}\), pH: 6.0, adsorbent dose: 2.4 g/L and particle size 50 µm, agitation speed: 300 rpm, Contact time: 60 minutes, Temperature: 303 K)

Effect of contact time and adsorption kinetic model

The adsorption rate of fluoride at different initial concentrations (5.0, 10.0 and 50.0 mg L\(^{-1}\)) was investigated by varying the time ranging from 40 to 300 min (Figure 9). Figure 10 also shows that with a fixed amount of AcTAP, the adsorption of fluoride increased with time and then attained equilibrium after 180 min at different initial concentrations indicating the independent nature of time to reach equilibrium conditions. Figure 9 also indicate initial adsorption is very rapid and slow approach to equilibrium. A similar finding has been reported for removal of fluoride onto lanthanum incorporated chitosan beads\(^{27,29}\).

Figure 9. Effect of contact time on removal of fluoride onto AcTAP at various concentrations (experimental conditions: pH: 6.0, adsorbent dose: 2.4 g/L and particle size 50 µm, agitation speed: 300 rpm, Temperature: 303 K)
In the present study, two main types of kinetic models viz. reaction-based models and diffusion based models were frequently used to determine various kinetic parameters of the adsorption system. The experimental data was analyzed by application of the sorption kinetics pseudo-first-order and pseudo-second-order kinetic models. A simple pseudo-first order kinetic model also known as Lagergren equation is presented as

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

(4)

Where, $q_e$ is equilibrium F$^-$ concentration on adsorbent (mg g$^{-1}$) and $q_t$ is amount of F$^-$ adsorbed at time $t$ (mg g$^{-1}$), $k_1$ is pseudo-first-order rate constant (min$^{-1}$). The rate constants were calculated from the linearized plots of log ($q_e$-$q_t$) vs. $t$. The pseudo-second-order model is commonly used as

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

(5)

$$h = k_2 q_e^2$$

(6)

Where, $k_2$ is pseudo-second-order rate constant (g mg$^{-1}$ min$^{-1}$) and $h$ = initial adsorption rate (mg g$^{-1}$ min$^{-1}$). The values of kinetic parameters and correlation coefficients of the adsorption kinetic models obtained from the linear plots of $t/q_t$ vs. $t$ are presented in Table 3. It is apparent from the values of correlation coefficients that the fitness of the pseudo-second-order model is better as compared to pseudo-first-order model. Additionally, comparing the experimental removal capacities ($q_{e,\text{exp}}$) and calculated values ($q_{e,\text{cal}}$) at different initial concentrations the experimental results obey the pseudo second-order model.

The adsorption capacities at different initial concentrations varying with contact time are shown in Figure 10. By pore diffusion or particle diffusion model, sorption of a liquid adsorbate on porous solid adsorbent can be determined. This model can be written as:

$$B = \frac{\pi^2 D}{t^2}$$

(7)

Where $B$ (pore diffusion coefficient) is determined as the slope of the plots of $B_t$ vs. $t$ (Figure not shown) at different initial fluoride concentrations by using equation:

$$B_t = -0.4997 - \ln \left(1 - \frac{q_t}{q_e}\right)$$

(8)

According to, intraparticle diffusion model is commonly used to characterize the sorption data and be expressed as:

$$q_t = K_t t^{0.5} + I$$

(9)

Table 3. Kinetics parameters for adsorption of fluoride by AcTAP at different initial concentrations

<table>
<thead>
<tr>
<th>Different initial conc., mg L$^{-1}$</th>
<th>$q_{e,\text{exp}}$, mg g$^{-1}$</th>
<th>$q_{e,\text{cal}}$, mg g$^{-1}$</th>
<th>$k_1$, min$^{-1}$</th>
<th>$R^2$</th>
<th>$q_{e,\text{cal}}$, mg g$^{-1}$</th>
<th>$k_2$, mg g$^{-1}$ min$^{-1}$</th>
<th>$h$, mg g$^{-1}$ min$^{-1}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>2.07</td>
<td>0.23</td>
<td>0.002</td>
<td>0.005</td>
<td>2.11</td>
<td>0.08</td>
<td>0.36</td>
<td>0.99</td>
</tr>
<tr>
<td>10.0</td>
<td>3.81</td>
<td>3.66</td>
<td>0.008</td>
<td>0.238</td>
<td>4.58</td>
<td>0.04</td>
<td>0.08</td>
<td>0.99</td>
</tr>
<tr>
<td>50.0</td>
<td>9.42</td>
<td>3.87</td>
<td>0.002</td>
<td>0.088</td>
<td>14.95</td>
<td>0.005</td>
<td>0.1</td>
<td>0.82</td>
</tr>
</tbody>
</table>
Figure 10. Effect of contact time on removal of fluoride onto AcTAP (experimental conditions: Initial fluoride concentration: 5.0 mgL\textsuperscript{-1}, pH: 6.0, adsorbent dose: 2.4 g/L and particle size 50 µm, agitation speed: 300 rpm, Temperature: 303 K)

Where, \( K_i \) is intraparticle diffusion coefficient and \( I \) intraparticle diffusion is model constant. Table 4 shows that the diffusion coefficient values decreased with increasing initial fluoride concentrations due to decreasing of available open sites to adsorption\textsuperscript{34} whereas intraparticle diffusion rate increased with this order. The values of correlation coefficients (\( R^2 \)) for particle diffusion model are closer to unity supporting that particle diffusion of fluoride adsorption is contributing more towards rate controlling step. However, in case of intraparticle diffusion model, plots did not pass through the origin (the intercept values are between 0.024 and 0.775) which indicates that the adsorption of fluoride on AcTAP is a complex process involving surface adsorption. Simultaneously, the increase in intercept values of intraparticle diffusion model with increasing initial concentrations indicates increasing of boundary layer effect.

Table 4. Pore diffusion and intraparticle rate parameters at different initial fluoride concentrations

<table>
<thead>
<tr>
<th>Concentration, mg L\textsuperscript{-1}</th>
<th>Pore diffusion coefficient</th>
<th>( R^2 )</th>
<th>Intraparticle diffusion coefficient</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>( 2.77 \times 10^{-4} )</td>
<td>0.95</td>
<td>0.024</td>
<td>0.94</td>
</tr>
<tr>
<td>10.0</td>
<td>( 2.28 \times 10^{-6} )</td>
<td>0.96</td>
<td>0.186</td>
<td>0.91</td>
</tr>
<tr>
<td>50.0</td>
<td>( 1.77 \times 10^{-8} )</td>
<td>0.98</td>
<td>0.775</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Effect of initial concentration

The adsorption of fluoride onto AcTAP was conducted by varying initial fluoride concentration using optimum adsorbent dose (2.4 g L\textsuperscript{-1}) with 50 µm particle size, pH 6.0, agitation speed 300 rpm at temperature 30 \textdegree C for a contact time of 180 min. The percentage removal of fluoride decreased with increase in initial fluoride concentration (Figure 11) and showed a little decrease at higher concentrations having a limited number of active sites. This is probably due to increase the ratio of ions/adsorbent and also saturated the higher energy sites, adsorption begins on lower energy sites, resulting decreases in the adsorption efficiency\textsuperscript{35} Figure 11 also shows the amount of adsorbed fluoride increased with increase in initial concentrations due to increasing concentration gradient acts as increasing driving force to overcome all mass transfer resistances of the fluoride between the aqueous and solid phase, leading to an increasing equilibrium sorption until sorbent saturation is achieved\textsuperscript{1}. 
Effect of temperature

It is well established that temperature is an additional factor greatly influence any adsorption process. The effect of solution temperature was investigated at 303, 313, 323 and 333 K. The results summarized in Figure 12, indicating the adsorption rate decreased with increase in temperature. This result indicates low temperature favours the removal of fluoride molecules by adsorption onto AcTAP as well as the adsorption process is exothermic in nature. The decreasing of removal may be due to at high temperature the thickness of the boundary layer decreases due to increased tendency of the molecules to escape from the adsorbent surface to the solution phase, which results in a decrease in the adsorption capacity as temperature is increased\textsuperscript{36}. Similar results were previously reported by\textsuperscript{37}.

Figure 11. Effect of initial concentrations on the removal of fluoride onto AcTAP (experimental conditions: pH: 6.0, adsorbent dose: 2.4 g/L and particle size 50 µm, agitation speed: 300 rpm, contact time: 180 minutes, Temperature: 303 K)

Figure 12. Effect of temperature on the removal of fluoride onto AcTAP (experimental conditions: Initial fluoride concentration: 5.0 mgL\textsuperscript{-1}, pH: 6.0, adsorbent dose: 2.4 g/L and particle size 50 µm, agitation speed: 300 rpm, contact time 180 min, Temperature: 303 K)
Adsorption isotherms

Analysis of data by adsorption isotherms is very important to design of a adsorbent and for calculating the adsorption efficiency of the adsorbent systems. In this study Langmuir, Freundlich, D-R and Tempkin adsorption isotherm models are analyzed and mathematical expressions of these models are given in Table 5.

Table 5. Mathematical equations of different isotherm models

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>Mathematical equations</th>
<th>Plots</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( \frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_{\text{max}}} ) (9)</td>
<td>1/q_e vs. 1/C_e</td>
<td>[43]</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( \log q_e = \log K_f + \frac{1}{n} \log C_e ) (10)</td>
<td>log q_e vs. log C_e</td>
<td>[27]</td>
</tr>
<tr>
<td>Dubinin-Radushkevich (D–R)</td>
<td>( \ln q_e = \ln q_{\text{m}} - \beta \varepsilon^2 ) (11)</td>
<td>ln q_e vs. \varepsilon^2</td>
<td>[43]</td>
</tr>
<tr>
<td>Tempkin</td>
<td>( q_e = B \ln A + B \ln C_e ) (12)</td>
<td>q_e vs. ln C_e</td>
<td>[26]</td>
</tr>
</tbody>
</table>

The linear equation of Langmuir model plotted 1/q_e vs 1/C_e gives a straight line (R^2 = 0.995 to 0.983) at different temperatures, indicating that Langmuir adsorption is followed by the adsorption very well data at all temperatures. The values of Langmuir constant (K_L) and maximum adsorption capacity (q_m) were calculated from the slope and intercept of the plots at different temperatures are reported in Table 6. With increasing temperature, the values of both K_L and q_m (adsorption capacity) are decreased indicating higher temperature induces lower adsorption capacity. The Freundlich adsorption isotherm is based on heterogeneity of the surface for the fluoride removal by adsorption. Freundlich constant is K_f and n is another constant informing the degree of heterogeneity of the surface sites. The values of K_f and 1/n have been evaluated from the graph by plotting log q_e vs. log C_e and complied in Table 6. The values of n between 1 and 10 represents a favorable adsorption and for the present study according to this model the value of n also presented the same trend of beneficial adsorption. The high correlation coefficients (R^2) and maximum adsorption capacity values at all temperatures indicate the adsorption data of fluoride ions onto AcTAP better fitted with the Langmuir equation and suggests the monolayer uniform adsorption. Figure 13 also supports this but in case of lower fluoride concentration adsorption process followed by both Langmuir and Freundlich isotherm models. The essential characteristics of this model can be expressed in terms of a dimensionless parameter, separation factor (R_L) which describes the type of adsorption and is calculated by

\[ R_L = \frac{1}{1 + K_L C_e} \]

The values of R_L were 0.17 to 0.28 at different temperatures representing highly favourable adsorption of fluoride ions onto AcTAP. The D-R isotherm is widely used to determine the physical or chemical adsorption phenomenon and related to heterogeneity of energies over the surface. The estimated value of Es from the constants (\( \beta \)) of D-R isotherm model using equation (\( Es = \frac{1}{\sqrt{\beta}} \)), where \( \beta = \text{D-R constant} \) ranging from 5.01 to 1.42 at different temperatures for present study were found in the range expected for physical adsorption. Table 6 also shows that the constant (A), maximum adsorption capacity (q_m) and correlation coefficient values lower at higher temperature. By plotting q_e vs. ln C_e, the Tempkin constants were calculated from the linear equation and these values with correlation coefficients at different temperatures are also reported in Table 6.
Table 6. Adsorption isotherm constants for adsorption of fluoride by AcTAP at different temperatures

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Langmuir isotherm</th>
<th>Freundlich</th>
<th>D-R</th>
<th>Tempkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_L$</td>
<td>$R_L$</td>
<td>$q_m$</td>
<td>$K_f$</td>
</tr>
<tr>
<td>303</td>
<td>0.97</td>
<td>0.17</td>
<td>8.55</td>
<td>0.999</td>
</tr>
<tr>
<td>313</td>
<td>0.61</td>
<td>0.24</td>
<td>7.81</td>
<td>0.993</td>
</tr>
<tr>
<td>323</td>
<td>0.55</td>
<td>0.27</td>
<td>7.15</td>
<td>0.948</td>
</tr>
<tr>
<td>333</td>
<td>0.28</td>
<td>0.41</td>
<td>7.03</td>
<td>0.912</td>
</tr>
</tbody>
</table>

Tempkin constant ($A$, Tempkin constant related to equilibrium binding constant (L mg$^{-1}$)) and $B$ is Tempkin constant related to the heat of adsorption. In comparing the experimental results with different isotherm models are plotted in Figure 13 which also indicates the better fitness of adsorption data to the Langmuir adsorption isotherm. This result suggests that the adsorbed fluoride ions did not compete each other and ions were adsorbed by forming a monolayer onto AcTAP. Table 7 summarizes the comparison of the maximum fluoride adsorption capacities of various sorbents including present study and shows that AcTAP has high adsorption capacity of fluoride than other reported adsorbents, reflecting a promising utility for AcTAP utilization in fluoride removal from contaminated water.

Figure 13. Comparison between the measured and modeled isotherm profiles for the removal of fluoride by using AcTAP on different initial concentration (mg L$^{-1}$): (experimental condition pH of the solution: 6.0, adsorbent dose: 2.4g/L, particle size: 50 mm, agitation speed: 300 rpm, contact time: 180 minutes, temperature: 303 K)

Table 7. Previously reported adsorption capacity of various types of waste biomass for fluoride

<table>
<thead>
<tr>
<th>Name of adsorbent</th>
<th>Adsorption capacity, mg g$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cynodon dactylon</td>
<td>4.75</td>
<td>[44]</td>
</tr>
<tr>
<td>Tamarind seed</td>
<td>6.09</td>
<td>[1]</td>
</tr>
<tr>
<td>Used Tea powder</td>
<td>0.05</td>
<td>[45]</td>
</tr>
<tr>
<td>Activated carbon from Acacia Arabica</td>
<td>2.06</td>
<td>[46]</td>
</tr>
<tr>
<td>AcTAP</td>
<td>8.55</td>
<td>Present study</td>
</tr>
</tbody>
</table>
Adsorption kinetics
In order to investigate the kinetic of process such as the mechanism of adsorption and potential rate controlling steps, basically the order of process has to be studied. From the Table 3, it is clear that the fluoride adsorption process is entirely followed pseudo-second order kinetics. Many publication were also studied the kinetic order of adsorption process onto solid support which could use as primary data to propose the possible adsorption mechanism, leading to understanding of adsorption nature of fluoride onto solid support 42.

Activation energy and thermodynamic study
The activation energy (E_a) for fluoride ions adsorption onto AcTAP was calculated by using Arrhenius equation:

\[ \ln k = \ln A - \frac{E_a}{RT} \]  \hspace{1cm} (13)

E_a value (E_a = 32.01 kJ mol^{-1}) calculated from the slope of a plot of ln k vs. 1/T (Figure 14). The magnitude of activation energy gives an idea about the type of adsorption. According to literature 38, this E_a value indicates that the fluoride ions adsorption process is physical adsorption in nature. This result corresponds well with those from D-R isotherm. Thermodynamic parameters associated with the adsorption process viz. Gibb’s free energy change (\( \Delta G^0 \)), enthalpy change (\( \Delta H^0 \)) and entropy change (\( \Delta S^0 \)) were calculated using the following equations:

\[ K_c = \frac{C_x}{C_s} \]  \hspace{1cm} (14)

\[ \Delta G^0 = RT \ln K_c \]  \hspace{1cm} (15)

\[ \log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \]  \hspace{1cm} (16)

The values of \( \Delta H^0 \) and \( \Delta S^0 \) obtained from the slope and intercept by plotting \( \ln K_c \) vs. 1/T (Figure 15) are shown in Table 8. The negative value of \( \Delta G^0 \) at all temperatures indicates the feasibility of the fluoride ions adsorption and the process is spontaneous in nature. Lower values of \( \Delta G^0 \) with increasing temperature supports adsorption easier at lower temperature. The negative value of \( \Delta H^0 \) suggests the exothermic nature of adsorption process and the negative value \( \Delta S^0 \) shows the process is enthalpy driven.

Figure 14. Arrhenius equation plot for removal of fluoride onto AcTAP
Figure 15. Thermodynamic plot log $K_d$ vs. $1/T$ for removal of fluoride onto AcTAP

Table 8. Activation energy and thermodynamic parameters for adsorption of fluoride by AcTAP

<table>
<thead>
<tr>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta G^0$ (kJ mol$^{-1}$)</th>
<th>$1/T$ (K)</th>
<th>$\Delta H^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^0$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.01</td>
<td>-10.19</td>
<td>303 K</td>
<td>-83.21</td>
<td>-0.241</td>
</tr>
<tr>
<td></td>
<td></td>
<td>313 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>323 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>333</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Desorption study

Desorption study helps to elucidate the adsorption and recycling of the spent adsorbent and the adsorbate. Different regeneration media like 25% NaOH and 1(N) HCl were used for desorption of fluoride. The desorption of adsorbed fluoride on AcTAP resulted about 91.68%.

Field data analysis

With a view to making use of the adsorbent in practical applicability of AcTAP for defluoridation in actual field conditions, the AcTAP was tested with fluoride contaminated groundwater collected from affected area of Birbhum district in West Bengal, India. The physicochemical characteristics of groundwater sample are shown in Table 9. The results show that the $F$ levels in the ground water samples collected from study area decreased to <1 mg L$^{-1}$, which is well below the limits of WHO drinking water standards. Comparing the fluoride removal by AcTAP from synthetic solution and field groundwater indicates that there is no significant difference suggesting AcTAP can be exploited for defluoridation in both household and community level and thus the use of AcTAP is a thoughtful and economic attempt for its valuable, necessitous and needy utilization for contaminated groundwater treatment process in affected areas.

Table 9. Physicochemical analysis of groundwater samples collected from study area (Nowpara)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Nowpara</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.7</td>
</tr>
<tr>
<td>Conductivity, mS cm$^{-1}$</td>
<td>3.0</td>
</tr>
<tr>
<td>Fluoride, mg L$^{-1}$ as (F$^-$)</td>
<td>10.0</td>
</tr>
<tr>
<td>Total hardness, mg L$^{-1}$ as Ca and Mg</td>
<td>40.0</td>
</tr>
<tr>
<td>Chloride, mg L$^{-1}$ as (Cl$^-$)</td>
<td>31.48</td>
</tr>
<tr>
<td>Sulphate, mg L$^{-1}$ as (SO$_4^{2-}$)</td>
<td>112.2</td>
</tr>
<tr>
<td>Phosphate, mg L$^{-1}$ as (PO$_4^{3-}$)</td>
<td>0.048</td>
</tr>
<tr>
<td>Ammonical nitrogen, mg L$^{-1}$</td>
<td>0.095</td>
</tr>
<tr>
<td>COD, mg L$^{-1}$</td>
<td>24.0</td>
</tr>
<tr>
<td>Iron, mg L$^{-1}$ as Fe$^{2+}$</td>
<td>0.153</td>
</tr>
</tbody>
</table>
Conclusion
A new medium, waste tea ash has been developed for fluoride removal in this study. Numerous advantages of the waste tea ash make the waste an excellent adsorbent for removal of fluoride from aqueous solution under acidic pH and further increases of pH showed less adsorption. The adsorption process nicely fitted with Langmuir adsorption isotherm indicating monolayer adsorption and adsorption of fluoride decreased with increase in temperature in the range of 303-333 K. Again the adsorption process was observed to follow a pseudo-second-order kinetic model and correlation coefficient values for particle diffusion model are closer to unity suggests that particle diffusion of fluoride adsorption is more towards the rate controlling step than intraparticle diffusion model. Moreover, distribution coefficient results indicate the heterogeneous nature of adsorption surface. Thermodynamic data indicates that reaction favors at lower temperature, exothermic in nature and enthalpy driven. It was also shown that tea ash has enough potential to remove fluoride (8.55 mg g⁻¹) from aqueous solution and subsequently 91.68 % fluoride can be regenerated from the adsorbent surface. Therefore, the activated tea ash is promising material for fluoride removal from aqueous solution as well as contaminated groundwater.

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References