REMOVAL OF FLUORIDE USING SWEET LEMON PEEL IN BATCH REACTOR: KINETICS AND EQUILIBRIUM STUDIES

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ABSTRACT

World Health Organization (WHO) sets the range of fluoride in ground water as 1 and 1.5 mg/L for India. The excess concentration of fluoride creates a problem of health. It affects the human and animal life. Fluoride creates a problem of skeletal as well as dental fluorosis. Small amount of fluoride is needed for dental protection. Its concentration less or more than the standard limits creates health problems. Therefore it is necessary to maintain the permissible range of fluoride in drinking water and hence the study of methods available is needed. This revived paper focuses over the different adsorbents with various parameters along the feasibility and fluoride removal efficiency.


INTRODUCTION

Fluoride (F⁻) contamination in groundwater recognized has been one of the serious problems worldwide.[¹] Fluoride is classified as one of the contaminants of water for human consumption by the World Health Organization (WHO), in addition to nitrate and arsenic, which causes large scale health problems.[²] Large fluoride concentrations in the groundwater occur in major parts of the globe.[³⁻¹²] Fluoride is widely distributed in the geological environment[¹³] and generally released into the groundwater by slow dissolution of fluorine-containing rocks.[¹⁴] Many minerals, e.g., fluorite, biotite, topaz, and their corresponding host rocks such as basalt, syenite, granite, and shale, contain fluoride that can be released into the groundwater.[¹⁵⁻¹⁷] The major source of human intake of fluoride is groundwater. Besides the
natural geological sources for fluoride enrichment in groundwater, various industries are also contributing to fluoride pollution to a great extent.\[18\] The industrial wastewater containing industries which discharge high fluoride concentrations include ceramic and glass production, electroplating, coal fired power stations, semiconductor manufacturing, brick and iron works, beryllium extraction plants and aluminium smelters.\[19\] It is found that more than 200 million people worldwide rely on drinking water with fluoride concentrations that exceed the WHO guideline of 1.5 mg/L.\[20\] Depending on the concentration and the duration of continuous intake, the impact of fluoride in drinking water can be estimated to mankind. Small amounts in ingested water are usually considered to have a beneficial effect on the rate of occurrence of dental caries, particularly among children.\[21\] Drinking water has a fluoride in small useful concentration range in relation to human health. On the contrary, excess intake of fluoride leads to many diseases such as arthritis, brittle bones, osteoporosis, cancer, infertility, Alzheimer syndrome, brain damage, and thyroid disorder.\[22, 23\] Fluorosis is a common problem of high fluoride ingestion manifested by mottling of embrittlement and teething mild cases of neurological and bones damage in severe cases.\[24\] The other effects include interference with DNA synthesis, problems in carbohydrates, lipids, proteins and metabolism, vitamin, minerals, gastro intestinal irritation, nervous system related problems, kidney and brain malfunctioning, effects thyroid activity etc.\[26-28\] In the view of toxic effects of fluoride on human health, there is an urgent need to find out an effective and physically strong technology for the removal of excess fluoride from drinking water and industrial waste water.

**EXPERIMENTAL**

The sweet lemon peel was used as the low cost natural bio-sorbent. These were sourced from local fruit stall in old market, Roorkee, India. The sweet lemon peels were dried, crushed and washed thoroughly with distilled water to remove adhering dirt. They were air dried in an oven at 100-120 °C for 24 hours after which drying material is crushed in jaw crusher and screened in 50μm mesh ASTM.

The prepared stock solution was 100mg/l fluoride, by dissolving 0.221g of anhydrous sodium fluoride (NaF) in one litre of millipore water. The test solution of 20mg/l fluoride concentration was prepared from stock solution. The selected concentration is the normal fluoride concentration in industrial waste water. All the experiments were carried out in 250 ml round bottom flasks, with 50 ml test solution at (29±1) °C in round bottom flask in
horizontal incubator shaker. At the end of desired contact time, the round bottom flask was separated from the shaker. Subsequently, samples were filtered using whatman no. 42 filter paper and filtrate was analysed for residual fluoride concentration by SPADNS method, described in the standard method of examination of industrial waste water and water.\(^{[28]}\)

**Spectrophotometric methods**

In this technique, a compound of a metal such as aluminium, iron, thorium, zirconium, lanthanum or cerium reacts with an indicator dye to build a complex of small dissociation constant. This complex reacts with fluoride to give a new complex. Because of the transformation in the configuration of the complex, the surface assimilation spectrum also shifts relative to the spectrum for the fluoride-free reagent solutions. This alteration can be observed by using a spectrophotometer. One of the essential dyes employed is trisodium 2-(parasulfophenylazo)-1, 8-dihydroxy-3, and 6- naphthalene disulfonate, generally recognized as SPADNS. Erichrome Cyanine R is one most commonly used dye. The dye reacts with metal ions to give a coloured complex. In the SPADNS method, zirconium reacts with SPADNS to build a red coloured complex. Fluoride discolours the red colour of the complex and therefore the alteration in absorbance can be calculated using a spectrophotometer.

![Formation of the SPADNS – ZrOCl2 complex](image1)

**Formation of the SPADNS – ZrOCl2 complex**

![Reaction of the complex with fluoride ions](image2)

**Reaction of the complex with fluoride ions**
Recipe for SPADNS Solution
\[
\frac{Mg \text{ of Fluoride}}{Litre} = \frac{A}{Sample \ (mL)} \times \frac{B}{C}
\]

Where
A represents Fluoride obtained by Curve (mg)
B represents diluted sample final volume (mL)
C represents diluted sample volume worn for development of color.

\[
\frac{Mg \text{ of Fluoride}}{Litre} = \frac{A_0 - A_{\infty}}{A_0 - A_1}
\]

Where
A₀ represents Absorbance at Zero Fluoride Concentration
A₁ represents Absorbance at Fluoride Concentration of 1 mg/L
Aₙ represents Absorbance of sample prepared

RESULTS AND DISCUSSIONS
Effect of contact time: A plot between time \( t \) (min) and amount of fluoride adsorbed with time \( q_t \) (mg g⁻¹) is plotted as shown in Figure 1. With increase in agitation time, fluoride removal also increases initially, but then gradually approaches a more or less constant value, denoting the attainment of equilibrium. Similar trend was also observed by other researchers during adsorption of fluoride onto protonated chitosan beads.²⁹ With respect to contact time sweet lemon peel reached equilibrium after 40 min which was fixed as their optimum contact times.

![Fig 1.Effect of contact time on adsorption of fluorite on sweet lemon peel](image)

Fitness of the kinetic models: The best-fit among the kinetic models was assessed by the
squared sum of errors (SSE) values. It is assumed that the model which gives the lowest SSE values is the best model for the particular system.\textsuperscript{30,31} The SSE values were calculated using the equation,

$$
SSE = \sum \left( \frac{(q_{e,\text{expt}} - q_{e,\text{cal}})^2}{(q_{e,\text{expt}})^2} \right)
$$

Where \( q_{e,\text{expt}} \) and \( q_{e,\text{cal}} \) denotes the experimental sorption capacity of fluoride (mg/g) at equilibrium time and the corresponding value that were obtained from the kinetic models. SSE values and various kinetic parameters for all the kinetic models were calculated and are summarized in Table 1.

**Adsorption Kinetics:** Five simplified kinetic models namely pseudo second-order, pseudo first-order, Weber and Morris intra-particle diffusion model, Elovich equations and Bingham’s pore diffusion model have been discussed to identify the rate and kinetics of sorption of fluoride onto Sweet lemon peel.

**Pseudo first order model:** The Lagergren’s rate equation is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase.\textsuperscript{32,33} The linear form of pseudo first-order rate expression of Lagergren is given as

$$
\log(q_e - q_t) = \log(q_e) - k_1 t/2.303
$$

Where, \( q_e \) and \( q_t \) are the amounts of fluoride adsorbed on adsorbent (mg g\(^{-1}\)) at equilibrium and at time \( t \) (min), respectively, and \( k_1 \) is the rate constant of pseudo first-order kinetics. Figure 2(a) shows the plots of linearized form of pseudo first-order kinetic model for the three sorbents. The plots were found linear with good correlation coefficients (>0.9)
indicating the applicability of pseudo first-order model in the present study. The pseudo first-order rate constant \( k_1 \) and \( q_{e(cal.)} \) values were determined for adsorbent from the slope and the intercept of corresponding plot (Figure 2(a)) and are listed in Table 1.

**Pseudo second order model**

The adsorption kinetics was also described as pseudo-second order process using the following equation:\[^{[34]}\]

\[
t/ q_t = 1/k_2 \cdot q_e^2 + \left(1/q_e\right) \cdot t
\]

Where, \( q_e \) and \( q_t \) have the same meaning as mentioned previously and \( k_2 \) is the rate constant for the pseudo second-order kinetics. The plots of \( t/q_t \) versus \( t \) for the three adsorbents are shown in Figure 2(b). The values of \( q_{e(cal.)} \) and \( k_2 \) were determined for each adsorbent from the slope and intercept of the corresponding plot and are compiled in Table 1.

![Graph](image)

The correlation co-efficient \( (R^2) \) values for pseudo second-order adsorption model have high values, i.e. 0.999 for the bio-adsorbent Sweet lemon peel. The \( R^2 \) value is higher than that of pseudo first-order model. The lower SSE values for pseudo second order model also indicate that the adsorption kinetics of fluoride onto Sweet lemon peel can be better described by pseudo second order model. Similar phenomenon has observed by others for the adsorption of fluoride on many adsorbents.\[^{[35-37]}\]
Table1: Table1 consists of pseudo first order, pseudo second order, Weber and Morris, Bangham’s and Elovich models parameters and calculated q<sub>ecal</sub> and experimental q<sub>expt</sub> values at 20 mg/l fluoride concentrations for all five kinetics models stated above.

<table>
<thead>
<tr>
<th>Name of adsorbent</th>
<th>k&lt;sub&gt;1&lt;/sub&gt; (min.&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>q&lt;sub&gt;e(expt)&lt;/sub&gt;(mg/g)</th>
<th>q&lt;sub&gt;e(cal)&lt;/sub&gt;(mg/g)</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>SSE</th>
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<tr>
<td>Sweet lemon peel</td>
<td>0.3915</td>
<td>1.915</td>
<td>0.3221</td>
<td>0.9978</td>
<td>0.6832</td>
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<table>
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<th>Name of adsorbent</th>
<th>k&lt;sub&gt;2&lt;/sub&gt; (min.&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>q&lt;sub&gt;e(expt)&lt;/sub&gt;(mg/g)</th>
<th>q&lt;sub&gt;e(cal)&lt;/sub&gt;(mg/g)</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>SSE</th>
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<tr>
<td>Sweet lemon peel</td>
<td>0.67832</td>
<td>1.915</td>
<td>1.942</td>
<td>0.9999</td>
<td>0.00019</td>
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<tr>
<th>Name of adsorbent</th>
<th>k&lt;sub&gt;id&lt;/sub&gt; (mg/g.min.&lt;sup&gt;-0.5&lt;/sup&gt;)</th>
<th>q&lt;sub&gt;e(expt)&lt;/sub&gt;(mg/g)</th>
<th>q&lt;sub&gt;e(cal)&lt;/sub&gt;(mg/g)</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>SSE</th>
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<td>Sweet lemon peel</td>
<td>0.027</td>
<td>1.915</td>
<td>1.7272</td>
<td>0.9366</td>
<td>0.0096</td>
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<table>
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<tr>
<th>Name of adsorbent</th>
<th>k&lt;sub&gt;0&lt;/sub&gt;</th>
<th>q&lt;sub&gt;e(expt)&lt;/sub&gt;(mg/g)</th>
<th>q&lt;sub&gt;e(cal)&lt;/sub&gt;(mg/g)</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>α</th>
<th>SSE</th>
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<tr>
<td>Sweet lemon peel</td>
<td>11.595</td>
<td>1.915</td>
<td>1.806</td>
<td>0.851</td>
<td>0.002</td>
<td>0.00324</td>
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</table>

<table>
<thead>
<tr>
<th>Name of adsorbent</th>
<th>β</th>
<th>q&lt;sub&gt;e(expt)&lt;/sub&gt;(mg/g)</th>
<th>q&lt;sub&gt;e(cal)&lt;/sub&gt;(mg/g)</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>α</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweet lemon peel</td>
<td>15.873</td>
<td>1.915</td>
<td>0.4708</td>
<td>0.9671</td>
<td>0.0693</td>
<td>0.5687</td>
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</tbody>
</table>

Intra particle diffusion

Rate of sorption is frequently used to analyse nature of the ‘rate-controlling step’ and the use of the intra-particle diffusion model has been greatly explored in this regard which is represented by the following Weber and Morris equation.<sup>[33]</sup>

\[ q_t = k_{ip} t^{0.5} + C \]

Where, C is the intercept, determined by the thickness of the boundary layer and \( k_{ip} \) is the intra-particle diffusion rate constant. According to this model, if adsorption of a solute is controlled by the intra-particle diffusion process, a plot of \( q_t \) versus \( t^{1/2} \) gives a straight line. Weber and Morris plots of \( q_t \) versus \( t^{0.5} \) are shown in Figures 3 for, sweet lemon peel. It
is evident from the plots that there are two separate stages; first linear portion (Stage I) and second curved path followed by a plateau (Stage II). In Stage I, nearly 50% of fluoride was rapidly taken up by bio-adsorbents within 5 min. This is attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surfaces. In Stage II, very slow diffusion of adsorbate from surface site into the inner pores is observed. Thus initial portion of fluoride adsorption by carbon adsorbents may be governed by the initial intra-particle transport of fluoride controlled by surface diffusion process and later part is controlled by pore diffusion. Similar dual nature with initial linear and then plateau were found in the literature.\(^{[38]}\)

Though intra-particle diffusion renders straight lines with correlation co-efficient more than 0.98 for all the sorbents, the intercept of the line fails to pass through the origin in each case. This can be explained by difference in the rate of mass transfer in the initial and final stages of adsorption\(^{[39]}\) and indicates some degree of boundary layer control which implies that intra-particle diffusion is not only rate controlling step.\(^{[32]}\) The data were further used to learn about the slow step occurring in the present adsorption system using pore diffusion model.

![Fig 3: Intra particle diffusion plot Sweet lemon peel](image)

**Bangham’s model:** Bangham model adsorption process is described by Bangham model equation.\(^{[40]}\)

\[
\log \log \left( \frac{C_i}{C_i - q_m} \right) = \log \left( \frac{K_o m}{2.303 V} \right) + \alpha \log(t)
\]

Where
Ci = the initial concentration of the adsorbate in a solution (mg/l)
V = volume of solution in (ml)
m = mass of the adsorbent (g/l)
q_t = The amount of adsorbate retained at time t (mg/g)
K_0 = constant

To plot \( \log \log \left( \frac{C_i}{C_i - q_t \cdot m} \right) \) versus log t (fig.4) for sweet lemon peel. The plot was found to be linear for adsorbent with correlation coefficient indicating that kinetics confirmed Bangham’s equation and therefore the adsorption of fluoride onto sweet lemon peel, was pore diffusion controlled. Similar trend was found in the literature for the adsorption of fluoride onto waste carbon slurry.

![Figure 4. Pour diffusion plot of sweet lemon peel](image)

**Elovich Equation**

The Elovich equation \(^{[41]}\)

\[
q_t = \frac{\ln(\alpha \beta)}{\beta} + \frac{\ln(t)}{\beta}
\]

Where,

\( \alpha \) = Initial sorption rate (mg/g min)
\( \beta \) is related to extent of surface coverage and activation energy for chemisorptions

When \( q_t \) versus \( \ln(t) \) (figure 5) is plotted on a sheet of graph the result follows Elovich equation. Confirmation to this equation alone might be taken as evidence that the rate determining step is diffusion in nature. \(^{[42]}\) And this equation should apply at conditions where
desorption rate can be ignored.\cite{43} The kinetic curve of sorption demonstrated good fitting with the model ($R^2>0.9$) which may indicate the diffusion rate-limiting is more prominent in fluoride sorption by sweet lemon peel.

![Figure 5. Elovich Equation plots of sweet lemon peel](image)

Comparative data of different bio adsorbents

Table 2 Comparative analysis of bio adsorbents defluoridation efficiencies.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Initial Fluoride Conc. (mg/l)</th>
<th>pH</th>
<th>% Removal</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sawdust raw</td>
<td>5</td>
<td>6.0</td>
<td>49.8</td>
<td>K.Y.Ashish et.al</td>
</tr>
<tr>
<td>Wheat straw raw</td>
<td>5</td>
<td>6.0</td>
<td>60.2</td>
<td>K.Y.Ashish et.al</td>
</tr>
<tr>
<td>Activated bagasse carbon</td>
<td>5</td>
<td>6.0</td>
<td>56.4</td>
<td>K.Y.Ashish et.al</td>
</tr>
<tr>
<td>Neempeepal</td>
<td>5</td>
<td>2.0</td>
<td>84.9</td>
<td>A.R.Tembalkar</td>
</tr>
<tr>
<td>Available activated Carbon</td>
<td>5</td>
<td>4.0</td>
<td>57.6</td>
<td>K.Y.Ashish et.al</td>
</tr>
<tr>
<td>Sweet lemon peel</td>
<td>20</td>
<td>4.0</td>
<td>59.6</td>
<td>Current</td>
</tr>
</tbody>
</table>

CONCLUSION

By fitting of the kinetic data, the dynamics of sorption could be better described by Pseudo-second order model indicating a Chemisorptive rate limiting for the adsorbents like sweet lemon peel.

Though the plots of intra-particle diffusion render straight line with good correlation coefficient, the tail passes through origin in each case.

This suggests that the process is ‘complex’ with more than one mechanism limiting the rate of sorption. The good fitting of the kinetics data to Elovich and Bangham’s equation indicate that pore diffusion plays a vital role in controlling the rate of reaction.

REFERENCES