ABSTRACT
In the present study we did observed the defluoridation capacity of Treated Banana Peel from industrial waste water in a batch reactor. To find out the best operating conditions for maximum removal of fluoride we did varied various parameters and observed their effects on defluoridation capacity. The effects of time and initial concentration of fluoride on the % removal have been studied. Five kinetic models, the Elovich equation, pseudo second order and first order equations, were selected to follow adsorption process, and Pore diffusion. Pseudo second order equation could be used to describe adsorption of fluoride onto adsorbent. Kinetic parameters like correlation coefficients, rate constant, equilibrium adsorption capacities for each kinetic equation were determine and discussed. The best fitting of kinetic data to Elovich equation and pore diffusion model indicate that pore diffusion plays a vital role in controlling the rate of the reactions.

KEYWORDS: Fluoride, Bio adsorption, Treated Banana Peel, Industrial waste water.

INTRODUCTION
More than 25 nations of the world including India suffer from the contamination of fluoride in drinking water. Orissa is one of the states where 10 out of the 30 districts are suffering from fluoride contamination. Depending on the concentration and consumption of its total amount, fluoride ions in water have beneficial as well as detrimental effects.¹
One of the major environmental problems around the world is the fluoride related health hazards. Above a certain limit, fluoride affects every living organism viz. plants, humans, animals. Fluorine is also an essential element for humans and animals. For humans, however, the essentiality has not been demonstrated unequivocally, and no data indicating the minimum nutritional requirement are available although human health is adversely affected due to the presence of fluoride in excess amount. During these experiments the benefits of low fluoride dosing and the risk of high fluoride dosing have been studied.

**EXPERIMENTAL**

**Preparation of Bio adsorbent (banana peel) treated with hydrochloric acid**

From the local seller of banana from local market (Roorkee, Uttarakhand, India.) Banana peels were collected, after the collection of peel using tape water it is washed three times to remove the dust material. Bio adsorbent (banana peels) are initially dried in the sun light for two days than followed by hot air oven in the range of 80°C-100 °C for 36h. Then dried banana peels crushed in a jaw crusher and then sieved by 510 µm ASTM mesh. Screened material is treated with 0.1 M hydrochloric acid for 24 h. After treatment with acid, to make it neutral treated material is washed many (4 to 6) times. Washed material is then dehydrated in hot oven at 110°C for 24 h. The dried adsorbent is subsequently placed in seal pack container for use of experimental study.

The 100mg/L stock solutions of fluoride were prepared 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 room temperature (29±1) °C in round bottom flask in a horizontal incubator shaker. At the end of desired contact time, the round bottom flask was removed 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 waste water.

**Spectrophotometric methods**

In this method, a compound of a metal such as, iron, zirconium, thorium, lanthanum, aluminium, 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 more usually 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](image)

**Reaction of the complex with fluoride ions**

**Method for measurement of fluoride**

**Potentiometric Method:** Approved for national pollution discharge elimination system (NPDES) and safe drinking water act.
**TITLE:** SPADNS Method Analyze: Fluoride Instrumentation: UV spectrophotometer.

This method is used to determine the concentration of fluoride for industrial water, surface water, domestic waters and saline waters. In this method reagent are used SPADNS reagent, Zirconyl Chloride, HCl and Sodium Arsenate.

- **Stock solution** was prepared by dissolving 0.221 g of extra pure sodium fluoride in one Litre measuring flask and diluted to mark with distilled water.

- **SPDNS** solution was prepared by dissolving 0.958 g in 500 ml volumetric flask diluted up to the mark with distilled water. SPDNS (2-(parasulphonylazo)-1, 8-dihydroxyl-3, 6-naphthalene disulphonate).

- **Zirconyl acid reagent** was prepared by dissolving 0.133 g in 25 ml of millipore water in 500 ml volumetric flask and dilutes it, add 350 ml concentrated HCl and dilute up to the mark with millipore water.

- **Acid-zirconyl-SPDNS reagent** was prepared by mixing the equal volume of the acid zirconyl and SPADNS reagent.

- **Reference Solution** was prepared by adding the 10 ml of SPADNS solution to 100 ml of millipore water dilute 7 ml HCl to 10 ml with millipore water and add both the solution. Prepared solution can be used for 2 years.

  Sodium arsenate solution made by dissolving 5.0 g NaAsO₂ in millipore water in a one liter volumetric flask and dilute to the mark with millipore water

Recipe (formula) for SPADNS Solution

\[
\frac{Mg \ of \ Fluoride}{\text{Litre}} = \frac{A}{\text{Sample (mL)}} \times \frac{B}{C}
\]

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.

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

Where

- \(A_0\) represents zero sample absorbance
- \(A_x\) represents sample absorbance
- \(A_1\) represents reference absorbance
$A_0$ represents Absorbance at Zero Fluoride Concentration
$A_1$ represents Absorbance at Fluoride Concentration of 1 mg/L
$A_3$ represents Absorbance of sample prepared

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

**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.\(^7\) With respect to contact time Treated banana Peel reached saturation after 40, min respectively, which were fixed as their optimum contact times.

![Fig 1. Effect of contact time on adsorption of fluoride on Treated Banana 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.\(^8,9\) The SSE values were calculated by the equation,
\[
\text{SSE} = \sum \left( q_{e,\text{expt}} - q_{e,\text{cal}} \right)^2 / \left( q_{e,\text{expt}} \right)^2
\]

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, Bangham’s pore diffusion model, Weber and Morris intra-particle diffusion model, and Elovich equations have been discussed to identify the rate and kinetics of sorption of fluoride onto treated banana 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.\(^{[10, 11]}\) 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,

- \( q_e \) Amounts of fluoride adsorbed on adsorbent (mg g\(^{-1}\)) at equilibrium
- \( q_t \) Amounts of fluoride adsorbed on adsorbent (mg g\(^{-1}\)) at time \( t \) (min)
- \( k_1 \) Rate constant of pseudo first-order kinetics

Figure 2(a) shows the plots of linearized form of pseudo first-order kinetic model for the 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 \( q_{e,\text{cal.}} \) values were determined for each 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 Pseudo second order model was also described as pseudo-second order process using the following equation[12],

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \]

Where,

- \( q_e \) Amounts of fluoride adsorbed on adsorbent (mg g\(^{-1}\)) at equilibrium
- \( q_t \) Amounts of fluoride adsorbed on adsorbent (mg g\(^{-1}\)) at time \( t \) (min),
- \( k_2 \) Rate constant for the pseudo second-order kinetics

The plots of \( t/q_t \) versus \( t \) for the adsorbents are shown in Figure 2(b). The values of \( q_{e\text{cal.}} \) and \( k_2 \) were determined for each adsorbent from the slope and intercept of the corresponding plot and are compiled in Table 1.

The correlation co-efficient \( (R^2) \) values for pseudo second-order adsorption model have high values, i.e. 0.999 for all three bio-adsorbent Treated banana Peel. Comparatively in each case, 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 Treated banana Peel can be better described by pseudo second order model. Similar phenomenon has observed by others for the adsorption of fluoride on various adsorbents.[13-15]
Table 1: Table 1 consists of pseudo first order, pseudo second order, Weber and Morris, Bangham’s and Elovich models parameters and determine $q_{\text{ecal}}$ and experimental $q_{\text{expt}}$ values at 20 mg/l fluoride concentrations for all five kinetics models stated above.

### Pseudo first order

<table>
<thead>
<tr>
<th>Name of adsorbent</th>
<th>$k_1$ (min.$^{-1}$)</th>
<th>$q_{\text{expt}}$(mg/g)</th>
<th>$q_{\text{cal}}$(mg/g)</th>
<th>$R^2$</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated Banana Peel</td>
<td>0.3915</td>
<td>1.915</td>
<td>0.3221</td>
<td>0.9978</td>
<td>0.6832</td>
</tr>
</tbody>
</table>

### Pseudo second order

<table>
<thead>
<tr>
<th>Name of adsorbent</th>
<th>$k_2$ (min.$^{-1}$)</th>
<th>$q_{\text{expt}}$(mg/g)</th>
<th>$q_{\text{cal}}$(mg/g)</th>
<th>$R^2$</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated Banana Peel</td>
<td>0.67832</td>
<td>1.915</td>
<td>1.942</td>
<td>0.9999</td>
<td>0.00019</td>
</tr>
</tbody>
</table>

### Intra particle diffusion

<table>
<thead>
<tr>
<th>Name of adsorbent</th>
<th>$k_{\text{id}}$ (mg/g.min.$^{-0.5}$)</th>
<th>$q_{\text{expt}}$(mg/g)</th>
<th>$q_{\text{cal}}$(mg/g)</th>
<th>$R^2$</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated Banana Peel</td>
<td>0.027</td>
<td>1.915</td>
<td>1.7272</td>
<td>0.9366</td>
<td>0.0096</td>
</tr>
</tbody>
</table>

### Pore diffusion

<table>
<thead>
<tr>
<th>Name of adsorbent</th>
<th>$k_0$</th>
<th>$q_{\text{expt}}$(mg/g)</th>
<th>$q_{\text{cal}}$(mg/g)</th>
<th>$R^2$</th>
<th>$\alpha$</th>
<th>SSE</th>
</tr>
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<tbody>
<tr>
<td>Treated Banana 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>
</tr>
</tbody>
</table>

### Elovich equation

<table>
<thead>
<tr>
<th>Name of adsorbent</th>
<th>$\beta$</th>
<th>$q_{\text{expt}}$(mg/g)</th>
<th>$q_{\text{cal}}$(mg/g)</th>
<th>$R^2$</th>
<th>$\alpha$</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated Banana 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>
</tr>
</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.$^{[11]}$

$$q_t = k_{\text{ip}} t^{0.5} + C$$
Where, $C$ is the intercept, determined by the thickness of the boundary layer and $kip$ 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(a) for Treated banana 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.[16]

Though intra-particle diffusion renders straight lines with correlation co-efficient more than 0.98 for 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[17] and indicates some degree of boundary layer control which implies that intra-particle diffusion is not only rate controlling step.[18] The data were further used to learn about the slow step occurring in the present adsorption system using pore diffusion model.

![Fig 3a Intra particle diffusion plot Treated Banana peel](image_url)
**Bangham’s model**: Bangham model adsorption process is described by Bangham model equation.\[^{19}\]

\[
\log\log\left(\frac{C_i}{C_i-q_i,m}\right) = \log\left(\frac{K_0.m}{2.303.V}\right) + \alpha.\log(t)
\]

Where

- \(C_i\) = 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

\[
\log\log\left(\frac{C_i}{C_i-q_i,m}\right)
\]

To plot \(\log t\) against \(\log q_t\) (fig.4) for Treated Banana peel sorbent. The plot was found to be linear for adsorbent with correlation co-efficient indicating that kinetics confirmed Bangham’s equation and therefore the adsorption of fluoride onto treated banana peel was pore diffusion controlled. Similar trend was observed in the literature for the adsorption of fluoride onto waste carbon slurry.

![Figure 4: Pour diffusion plot of Treated Banana peel](image)

**Elovich Equation**

The Elovich equation\[^{19}\]

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

Where,

- \(\alpha\) = Initial sorption rate (mg/g min)
β 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.\textsuperscript{[20]} And this equation should apply at conditions where desorption rate can be ignored.\textsuperscript{[21]} 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 treated banana peel.

![Fig 5. Elovich Equation plots of Treated Banana peel.](image)

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 treated banana peel.

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

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.

REFERENCE


