A comparative study on the batch performance of fluoride adsorption by activated silica gel and activated rice husk ash
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ABSTRACT
A comparative study was done for removal of fluoride by activated silica gel (ASiG) and activated rice husk ash (ARHA) through batch techniques. The fluoride removal performance of both adsorbents such as ASiG and ARHA was evaluated as a function of the initial concentration, adsorbent dose, contact time and pH. The adsorbent dose characterized as having high selectivity for fluoride and larger adsorption capacity. Characterization of ASiG and ARHA before and after fluoride adsorption was studied by SEM and FTIR study was done to get a better insight into the mechanism of adsorption. The rate of adsorption was rapid and followed pseudo-second-order kinetics for both adsorbents. The system followed the Langmuir isotherm model for both ASiG and ARHA with adsorption capacity 0.244 mg g⁻¹ and 0.402 mg g⁻¹ respectively.

Keywords: ASiG, ARHA, SEM, isotherm, kinetics.

1. Introduction
High concentrations of fluoride occurring naturally in ground water have caused widespread fluorosis (both dental and skeletal) throughout many parts of the world. The excessive fluoride intake leads to the loss of calcium from the tooth matrix aggravating cavity formation throughout life (Sujana and Anand, 2010). Severe chronic and cumulative over expose can cause the incurable crippling of skeletal fluorosis (UNICEF 2004). The dental or skeletal fluorosis is irreversible and no treatment exists (Sujana and Anand 2010). The removal of fluoride from water is one of the most important issues due to the effect on human health and environment (Ma et al., 2007). The optimum fluoride level in drinking water for general good health set by WHO (1993) is considered to be less than 1.5 mg/L. But many epidemiological studies have shown possible adverse effects of the longterm ingestion of fluoride, even in the places where people are consuming water with fluoride content of 1.5 mg/L (Sujana and Anand, 2010). Membrane filtration (Ndaiye et al., 2005), precipitation (Parthasarathy et al., 1986), nanofiltration (Simons et al., 1993), ion-exchange (Ruixia et al., 2002), electrocoagulation flotation (Hu et al., 2005) and adsorption (Mohapatro et al., 2004) have been used for fluoride removal. Among these methods, adsorption techniques is the most effective and widely used methods, because its universal has a low maintenance cost, and is applicable for the removal of fluoride even at low concentration (Chen et al., 2010). In recent years, to find out cost effective alternative for removing high fluoride content from waters many geomaterials have been tested (Wang and Reardon 2001; Mohapatro et al., 2004; Hiemstra et al., 2000; and Sujana et al., 2009). In the present study we tried to explore the fluoride removal efficiency of activated rice husk ash (ARHA) and its potentiality compare study with activated silica gel (ASiG).
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Nomenclature

\( C_{ae} \) equilibrium fluoride concentration on the adsorbent (mgL\(^{-1}\))
\( C_e \) equilibrium fluoride concentration in solution (mgL\(^{-1}\))
\( C_i \) Initial fluoride concentration (mgL\(^{-1}\))
\( C_t \) Equilibrium fluoride concentration at time \( t \)
\( D_a \) particle mean diameter (cm)
\( d \) density of the adsorbent (g/cm)
\( e \) porosity of the adsorbent
\( E_s \) mean free energy (kJ mol\(^{-1}\))
\( h \) initial adsorption rate (mgg\(^{-1}\)min\(^{-1}\))
\( K_f \) Freundlich constants relating multilayer adsorption capacity (mgg\(^{-1}\)) \( (Lg^{-1})^{1/n} \)
\( b \) Langmuir constant (Lmg\(^{-1}\))
\( R_L \) Dimensionless equilibrium parameter
\( K_T \) Tempkin constant related to equilibrium binding constant (Lmg\(^{-1}\))
\( B_1 \) Tempkin constant related to the heat of adsorption
\( k \) rate constant
\( K_{id} \) intraparticle diffusion rate constant (mg g\(^{-1}\)min\(^{-0.5}\))
\( K_1 \) pseudo-first-order rate constant (min\(^{-1}\))
\( K_2 \) pseudo-second-order rate constant (g mg\(^{-1}\)min\(^{-1}\))
\( m \) weight of adsorbent (g)
\( n \) Freundlich adsorption isotherm constant relating adsorption intensity
\( q_e \) equilibrium dye concentration on adsorbent (mgg\(^{-1}\))
\( Q_0 \) maximum adsorption capacity (mgg\(^{-1}\))
\( q_t \) amount of dye adsorbed at time \( t \) (mgg\(^{-1}\))
\( R \) universal gas constant (8.314 J mol\(^{-1}\)K\(^{-1}\))
\( R^2 \) correlation coefficient
\( \Delta S^0 \) entropy of reaction (J mol\(^{-1}\)K\(^{-1}\))
\( S_s \) outer surface of adsorbent per unit volume of particle free solution (cm\(^{-1}\))
\( T \) temperature (K)
\( t \) time
\( V \) volume of the solution (L)

Greek alphabets

\( K \) D–R isotherm constant (mmol\(^2\)J\(^{-2}\))
\( \varepsilon \) polanyi potential (J mmol\(^{-1}\)) = RT \ln(1 + 1/C_e)
\( \beta_L \) mass transfer coefficient (l/g)

2. Materials and methods

2.1 Materials

The black-gray rice husk ash was collected from the nearest rice mill. Then it washed with double distilled water and dried at 100\(^{0}\)C for 8 hours in an electric oven. After that it was crushed ground and sieved to obtain 250 µm size and stored it in a desicator with plastic
container for further use. Another adsorbent activated silica gel (ASiG) supplied by local authorized dealer (MERCK Pvt. Ltd.). In this study activated silica gel (ASiG) is a synthetic adsorbent, hence the characterizations of ASiG are not provided. The physical characteristics and composition of rice husk ash on dry basis are given in Table 1.

**Table 1:** Composition of Rice Husk ash on dry basis

| Physical properties/Chemical composition | Values            |
|------------------------------------------|-------------------|
| Average particle size                    | 150.47 µm         |
| Bulk density                             | 104.9 kg/m³       |
| Heating value                            | 9.86 MJ/kg        |
| BET surface area                         | 34.44 m²/g        |
| Average pore diameter by BET             | 42.603 Å          |
| pHZPC                                    | 6.0               |
| Silica(SiO₂)                             | 80-90%            |
| Alumina                                  | 1-2.5 %           |
| Ferric oxide                             | 0.5 %             |
| Titanium dioxide                         | Nil               |
| Calcium oxide                            | 1-2 %             |
| Magnesium oxide                          | 0.5-2.0 %         |
| Sodium                                   | 0.2-0.5 %         |
| Potash                                   | 0.2 %             |
| Loss on ignition                         | 10-20 %           |

2.2 Instrument

The SEM image of rice husk ash was taken by SEM analyzer (HITACHI, S-530, Scanning Electron Microscope and ELKO Engineering, B.U., BURDWAN). For FTIR spectroscopic studies (PERKIN-ELMER, FTIR, Model-RX1 Spectrometer, USA) spectrometer was used. The pH of the solutions at the beginning and end of the experiments were measured and the average values are reported. All the pH measurements were carried out by digital pH meter (Model no. Systronic-335). Analysis of fluoride was carried out by following SPANDS methods (APHA AWWA 1998 and Deshmukh et al., 2009) and Systronic UV-visible spectrophotometer ((Systronics, Vis double beam Spectro 1203) was used for colometric analysis.

2.3 Chemical used

Stock solution of fluoride was prepared by dissolving 0.221g sodium fluoride in 1L double distilled water. The measuring cylinder, volumetric flask and conical flask used were of PVC. The sodium fluoride used was of analytical grade (MERCK, Germany). The required concentration of fluoride solution was prepared by serial dilution of 1000 mg/L fluoride solution.

2.4 Batch equilibrium adsorption experiments

Data for sorption isotherm were generated by contacting 0.5g ARHA and 2.0g of ASiG with fluoride containing aqueous solution at pH 2.0. Samples of 100 ml fluoride solution at concentration range 1.5 to 15 mg/L were pipette into 100 ml plastic container and container were placed in a magnetic stirrer at fixed temperature 30°C. The shaking speed was set at 100 rpm. At the end of the experiment, samples were withdrawn from test container and filter
through 0.22 µm vacuum dried filter and residual fluoride concentration was measured by SPANDS method. The equilibrium sorption capacity was determined from the equation

\[ q_e = \frac{V(C_0 - C_e)}{m} \]  

(1)

2.5 Effect of equilibrium pH

Experiments were carried out by varying initial solution pH values within the range of 2-10, adjust with 0.1 (M) NaOH or 0.1 (M) HCl. Accordingly, adsorption was done by adding different amount of adsorbent.

3. Results and discussion

3.1 Effect of pH

The effect of pH on the adsorption of fluoride by using ASiG and ARHA is shown in the Table 2 and Figure 1. The results show that adsorption was maximum for both ASiG and ARHA at pH 2.0 and the removal was also not favour at pH above 2.0. This can be attributed to the distribution of fluoride and HF which are controlled by pH of the aqueous solution (Tor et al., 2009). As can be calculated from equation (1) (Calace et al., 2002). F⁻ ion is dominated species when pH of the solution is higher than pKₐ (3.16) of HF (Tor et al., 2009).

Table 2: Effect of pH on the adsorption of fluoride by ARHA and ASiG (initial fluoride concentration 5.0 mg/L; adsorbent 0.5g (ARHA) and 2.0 g (ASiG); contact time 60 minutes; volume of the solution 100 ml; agitation speed 250 rpm and temperature 303K)

| pH | % of removal ARHA | qₑ | pH | % of removal ASiG | qₑ |
|----|-------------------|----|----|-------------------|----|
| 2  | 62.29             | 0.613| 2  | 88.88             | 0.226|
| 4  | 57.56             | 0.595| 4  | 79.59             | 0.199|
| 6  | 58.48             | 0.584| 6  | 75.22             | 0.188|
| 8  | 55.94             | 0.575| 8  | 74.48             | 0.186|
| 10 | 55.76             | 0.557| 10 | 74.48             | 0.186|

Figure 1: Effect of pH on the adsorption of fluoride at an adsorbent dose 0.5 g/100ml; initial concentration 5.0 mg/L; contact time 60 minutes; temperature 303K

It is also seen in Table 2 when pH of the solution exceeded 2.0 there is steady decrease of adsorption. This may be explained by considering the pH ZPC for the activated rice husk ash(ARHA). The surface charge of the ARHA is assessed by the zero point charge (pH ZPC = 6.0). At pH < pH ZPC, the surface charge is positive, at pH = pH ZPC, the surface is neutral and at pH > pH ZPC, the surface charge is negative. As fluoride is negative charge, so it preferentially
attacks the adsorbent surface when the surface is positive in charge. At a pH, below pH \( \text{ZPC} \), more of the surface sites are positively changed and F will be adsorbed to a greater extent due to the attractive force between F- ions and positive change of rice husk ash. At pH 2.0, the specific adsorption of fluoride on ARHA and ASiG (Figure 1) is due to electrostatic interaction between positively charged adsorbent surface and negatively charged fluoride ions and can be modeled as follows (Cengeloglu et al., 2002; Tor, 2006).

\[
\begin{align*}
\Xi & \text{ MOH + H}^+ \leftrightarrow \text{MOH}_2^+ \quad (2) \\
\Xi & \text{ MOH}_2^+ + \text{F} \leftrightarrow \text{MF} + \text{H}_2\text{O} \quad (3) \\
\text{Overall reaction can be written as} \\
\Xi & \text{ MOH} + \text{H}^+ + \text{F}^- \leftrightarrow \text{MF} + \text{H}_2\text{O} \quad (4)
\end{align*}
\]

Where M represents the activated rice husk ash (ARHA) or activated silica gel (ASiG).

### 3.2 Effect of adsorbent dosage

The effect of the dosage of adsorbent on the adsorption of fluoride with initial concentration 5 mg/L was studied and the results shown in Figure 2. It can be seen that the percentage of removal increased with increasing dosage of adsorbent. The largest percentage removal was exhibited at 2.4g and 8.0g for ARHA and ASiG respectively. In Table 3, it can be seen that the adsorption loading of fluoride decreases with increasing dosage of adsorbent. The influence of dosage of adsorbent is mainly related to its surface area (Lv et al., 2006).

![Figure 2: Effect of adsorbent dose (g/100ml) on the adsorption of fluoride at pH 2.0; initial concentration 5.0 mg/L; contact time 60 minutes; temperature 303K](image)

![Table 3: Effect of adsorbent dosage (g/100ml) on the adsorption of fluoride by ARHA and ASiG (initial fluoride concentration 5.0 mg/L; pH 2.0; contact time 60 minutes; volume of the solution 100 ml; agitation speed 250 rpm and temperature 303K)](table)

| Adsorbent dosage (g/100ml) | % of removal | \( q_e \) | Adsorbent dosage (g/100ml) | % of removal | \( q_e \) |
|---------------------------|-------------|--------|---------------------------|-------------|--------|
| 0.2                       | 55.74       | 1.393  | 1.0                       | 53.91       | 0.265  |
| 0.5                       | 62.29       | 0.623  | 2.0                       | 88.88       | 0.222  |
| 0.8                       | 67.56       | 0.422  | 4.0                       | 94.31       | 0.118  |
| 1.2                       | 70.12       | 0.292  | 6.0                       | 93.6        | 0.078  |

*Note: ARHA = Activated Rice Husk Ash, ASiG = Activated Silica Gel*
3.3 Effect of contact time and adsorption kinetics

The removal of fluoride as a function of contact time is shown in Figure 3. It was observed that with fixed amount of adsorbent (both ARHA and ASiG) the removal of fluoride increased with time and then attained equilibrium after 100 min. After reaching maximum point of removal the adsorbent reached in saturated condition (see Figure 3). This experimental adsorption data was analyzed by application of the pseudo-first-order and pseudo-second-order kinetic models.

![Figure 3: Effect of contact time (minute) on the adsorption of fluoride at an adsorbent dose 2.4 g/100ml (ARHA) and 4.0 g/100ml (ASiG); pH 2.0; initial concentration 5.0 mg/L; temperature 303K](image)

**Table 4**: Effect of contact time (minute) on the adsorption of fluoride by ARHA and ASiG (initial fluoride concentration 5.0 mg/L; pH 2.0; adsorbent dose 2.4 g/100ml (ARHA) and 4.0 g/100ml (ASiG); volume of the solution 100 ml; agitation speed 250 rpm and temperature 303K)

| Contact time (min) | % of removal | q<sub>e</sub> | Contact time (min) | % of removal | q<sub>e</sub> |
|--------------------|--------------|--------------|--------------------|--------------|--------------|
| 20                 | 59.94        | 0.125        | 20                 | 51.54        | 0.064        |
| 40                 | 60.84        | 0.127        | 40                 | 61.20        | 0.076        |
| 60                 | 73.94        | 0.154        | 60                 | 94.31        | 0.117        |
| 80                 | 78.48        | 0.163        | 890                | 95.82        | 0.119        |
| 100                | 88.30        | 0.184        | 100                | 96.7         | 0.121        |
| 120                | 88.30        | 0.184        | 120                | 96.7         | 0.121        |

3.3.1 Pseudo first-order equation

The sorption kinetics may be described by a pseudo first-order equation. The linearized form of pseudo-first-order rate equation is given as (Lagrgen and Svenska, 1898).

\[ \log (q_e - q_t) = \log(q_e) - \left( \frac{K_1}{2.303} \right) t \]  

From the studied initial concentrations, the rate constant (K<sub>1</sub>) and theoretical equilibrium sorption capacities (q<sub>e</sub>), calculated from the slope and intercept of the linear plots of the
pseudo-first-order kinetic model are given in table 5. The coefficients of determination ($R^2$) for the linear plots are between 0.333 to 0.5672 (Table 5). In addition, $q_e$ (calculated) and $q_e$ (experimental) values are not in agreement with each other. Therefore, it could be suggested that the adsorption of fluoride by ARHA and ASiG was not a first-order reaction.

### 3.3.2 Pseudo second-order equation

The experimental data was also applied to the pseudo-second-order kinetic model (Ho et al., 1999) given as

$$\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (6)

For different concentration of fluoride, the fit of this model was controlled by each linear plot of $t/qt$ versus $t$ respectively. The constants can be calculated from slope and the intercept of the plots (Table 5). It can be seen from the results that $R^2$ values are higher those obtained from pseudo-first-order kinetic model. Additionally, theoretical and experimental $q_e$ values are in a good accordance with each other. Therefore, it is possible to suggest that the sorption of fluoride was carried by both of the adsorbents.

### Table 5: Kinetic parameters of adsorbents at different concentration of various adsorbent

| Adsorbents | Initial conc.(mg/l) | Pseudo-first-order | Pseudo-second-order | $q_{exp}$ |
|------------|---------------------|---------------------|---------------------|-----------|
|            | $K_1$ | $q_e$ | $R^2$ | $K_2$ | $q_e$ | $h$ | $R^2$ | $q_{exp}$ |
| ARHA       | 1.5  | 0.022 | 0.032 | 0.033 | 0.105 | 0.102 | 0.001 | 0.876 | 0.56 |
|            | 5.0  | 0.051 | 0.055 | 0.549 | 0.223 | 0.213 | 0.01  | 0.984 | 0.185 |
|            | 15.0 | 0.0154| 0.034 | 0.23  | 0.181 | 0.426 | 0.07  | 0.981 | 0.386 |
| ASiG       | 1.5  | 0.044 | 0.0027| 0.11  | 0.211 | 0.136 | 0.0043| 0.975 | 0.037 |
|            | 5.0  | 0.008 | 0.014 | 0.335 | 0.315 | 0.147 | 0.0068| 0.83  | 0.121 |
|            | 15.0 | 0.043 | 0.001 | 0.567 | 0.365 | 0.308 | 0.346 | 0.949 | 0.307 |

### Table 6: Mass transfer and intra-particle diffusion coefficients at different concentrations of various adsorbent

| Adsorbents | Initial conc. (mg/L) | Intra-particle diffusion | Surface mass transfer |
|------------|----------------------|--------------------------|-----------------------|
|            | $K_{id}$ | $I$ | $R^2$ | $\beta_{L}$ | $R^2$ |
| ARHA       | 1.5  | 0.007 | 0.022 | 0.790         | 8.99 $\times$ 10-3 | 0.7524 |
|            | 5.0  | 0.071 | 0.932 | 0.932         | 8.18          | 0.9345 |
|            | 15.0 | 0.216 | 0.912 | 0.912         | 2.27          | 0.8739 |
| ASiG       | 1.5  | 0.009 | 0.029 | 0.975         | 4.09          | 0.8299 |
|            | 5.0  | 0.009 | 0.024 | 0.830         | 1.42          | 0.9342 |
|            | 15.0 | 0.001 | 0.294 | 0.949         | 1.54          | 0.9468 |
3.3.3 Surface mass transfer coefficient

The external mass transfer diffusion model and intraparticle diffusion model can be applied to investigate the effects of the boundary layer and intraparticle diffusion on the fluoride removal process. The external mass transfer diffusion model, as an application of Fick’s laws, expresses the evolution of the concentration of the solute in the solution. The intra-particle mass transfer diffusion model has been extensively applied in adsorbate-adsorbent systems. In this work the model chosen refer to the theories developed by Weber and Morris (1963).
The initial rate of intraparticle diffusion is calculated by linearization of the curve \( q_t = K_{id} t^{0.5} \) (7)

Mass transfer analysis for the removal of fluoride was carried out using the kinetic model proposed by McKay et al., 1981, which describes the transfer of adsorbate in solution. The model is expressed:

\[
\ln \left( \frac{C_t}{C_0} - \frac{1}{1+mb} \right) = \ln \left( \frac{mb}{(1+mb)} \right) - \left( \frac{1+mb}{mb} \right) \beta_L S_S t
\]  
(8)

\[
S_S = \frac{6m}{D_a d (1-\varepsilon)}
\]  
(9)

The results are shown in Figure 6 and Figure 7. The plot of \( \ln \left( \frac{C_t}{C_0} - \frac{1}{1+mb} \right) \) versus \( t \) for fluoride gives a straight line and thus confirms the validity of the diffusion model for the F- removal on the adsorbents. The value of intraparticle diffusion and mass transfer coefficients were calculated from the slope of the straight line plot (Figure 6 and Figure 7) and were found in Table 6. From the Table 6, the values of \( k_{id} \) gradually increases due to increasing of initial F- concentrations and the \( \beta_L \) value decreases increasing with initial fluoride concentrations. This value indicates that the velocity of F- transport from the liquid phase to the surface of granular ceramic is sufficiently rapid to use for fluoride removal from water (Chen et al., 2010).

Figure 6: Surface mass transfer plots for adsorption of fluoride onto activated carbon from RHA at different concentrations
Figure 7: Surface mass transfer plots for adsorption of fluoride onto ASiG at different concentrations

Figure 6 and Figure 7 show the variation of the adsorption loading and dimensionless concentration $\ln\left(\frac{C_t}{C_0}\right) - \left(\frac{t}{\tau}\right)$ versus time (t). For all the concentration employed there is a monotonic inverse in the adsorption loading with time. It is interesting that at low initial concentration, fluoride ion is removed maximum from the solution. Thus, the overall adsorption process is not influenced by external mass transfer diffusion (Lv et al., 2006).

3.4 Effect of initial concentration of fluoride

The effect of varying the initial fluoride concentration on process of adsorption for the ASiG (4.0g) and ARHA (2.4g) was studied and is shown in Figure 8. It can be seen that in both the case the percentage of removal of fluoride increased with decreasing initial fluoride concentration. The minimum residual concentration of fluoride obtained is 0.585 mg/L and 0.147 mg/L with an initial concentration 5 mg/L for activated silica gel and activated rice husk ash respectively. When the initial concentration of fluoride is 1.5 mg/L, the adsorption loading of fluoride is the highest 0.149 mg/L for ARHA and 0.033 mg/L for ASiG (Table 7).

Figure 8: Effect of initial concentration (mg/L) on the adsorption of fluoride at an adsorbent dose 2.4 g/100ml (ARHA) and 4.0 g/100ml (ASiG); pH 2.0; contact time 100 minutes; temperature 303K
Table 7: Effect of initial concentration (mg/L) on the adsorption of fluoride by ARHA and ASiG (pH 2.0; adsorbent dose 2.4 g/100ml (ARHA) and 4.0 g/100ml (ASiG); contact time 100 minutes; volume of the solution 100 ml; agitation speed 250 rpm and temperature 303K)

| Initial concentration (mg/L) | % of removal | q<sub>e</sub> | Initial concentration (mg/L) | % of removal | q<sub>e</sub> |
|------------------------------|--------------|-------------|------------------------------|--------------|-------------|
| 1.5                          | 90.03        | 0.056       | 1.5                          | 97.8         | 0.037       |
| 3.0                          | 90.81        | 0.115       | 3.0                          | 97.1         | 0.073       |
| 5.0                          | 88.30        | 0.184       | 5.0                          | 96.7         | 0.121       |
| 7.0                          | 76.14        | 0.222       | 7.0                          | 88.4         | 0.155       |
| 10.0                         | 70.78        | 0.235       | 10.0                         | 86.2         | 0.215       |
| 15.0                         | 61.67        | 0.386       | 15.0                         | 81.8         | 0.307       |

3.5 Adsorption isotherms

Analysis of isotherm is very important for designing the sorption process. The experimental data were fitted with Langmuir, Freundlich Tempkin and Dubinin-Radishkevich isotherm. Langmuir sorption isotherm models the monolayer coverage of the sorption surfaces and assumes that sorption take places on a structurally homogeneous surface of the adsorbent (Tor et al., 2009).

**Langmuir**

This isotherm is given as (Langmuir, 1916):

\[ q_e = \frac{Q_0 b C_e}{1 + b C_e} \]  \hspace{1cm} (10)

The Langmuir parameters were obtained by fitting the experimental data to the linearized equation derived (Salim et al., 2009) from Eq. (10):

\[ \frac{1}{q_e} = \frac{1}{b Q_0} \frac{1}{C_e} + \frac{1}{Q_0} \]  \hspace{1cm} (11)

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, RL which is defined by Hall and Vermeylem (1966) as

\[ R_L = 1 / (1 + b C_0) \]  \hspace{1cm} (12)

The values of R_L indicate the type of isotherm to be irreversible (RL = 0), favorable (0 < R_L < 1), linear ( R_L = 1) or unfavorable ( R_L > 1) (Ouazene et al., 2010).

**Freundlich**

Freundlich equation is derived to model, the multilayer adsorption for the sorption on heterogeneous surfaces. The Freundlich model is formulated as (Freundlich 1906):

\[ q_e = K_f (C_e)^{1/n} \]  \hspace{1cm} (13)

The Freundlich parameters were obtained by fitting the experimental data to the linearized equation derived from Eq. (13)
\[ \log q_e = \log K_T + \frac{1}{n} \log C_e \]  \hspace{1cm} (14)

The above equation is linearized and a plot of \( \log q_e \) versus \( \log C_e \) will give a straight line of slope \( \frac{1}{n} \) and intercept \( K_T \).

**Tempkin**

The Tempkin isotherm (Wasewar et al., 2009) contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This isotherm assumes that (i) the heat of adsorption of all molecules in the layer decreases with coverage due to adsorbate-adsorbent interaction, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The Tempkin isotherm is represented by the following equation:

\[ q_e = \frac{R T \ln (K_T C_e)}{b} \]  \hspace{1cm} (15)

Equation (15) can be linearized as in equation (16).

\[ q_e = B_1 \ln K_T + B_1 \ln C_e \]  \hspace{1cm} (16)

Where, \( B_1 = \frac{R T}{b} \)

Regression of \( q_e \) versus \( \ln C_e \) enables the determination of isotherm constants \( K_T \) and \( B_1 \).

**Dubinin-Radushkevich**

The Dubinin–Radushkevich (D–R) isotherm is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential (Oguz, 2005), it is used usually investigate about the heterogeneity of the surface energies and has the following formulation:

\[ q_e = q_m \exp(-K \varepsilon^2) \]  \hspace{1cm} (17)

\( \varepsilon \) is equal to \( RT \ln(1 + (1/C_e)) \) (Kalavathy et al., 2010). The saturation limit \( q_m \) may represent the total specific microspores volume of the adsorbent (Erdem et al., 2004). The D-R constants \( q_m \) (mg/g) and \( K \) (mol\(^2\)/J\(^2\)) can be determined from the intercept and slope of the plot between \( \ln q_e \) versus \( \varepsilon^2 \). Figure 9 and 10 show the Langmuir, Freundlich, D-R and Tempkin the experimental data. The isotherm constants and \( R^2 \) values for each model are given in Table 8.

In this investigation, the Freundlich, the Langmuir, Tempkin and the Dubinin-Radishkevich (D-R) isotherm model were used to describe the equilibrium data. The Langmuir isotherm constants \( b \) and \( Q_0 \) were calculated from the slope and intercept of the plot between \( q_e \) and \( C_e \). The isotherm showed good fit to the experimental data with high correlation coefficients in case of ARHA over ASiG (Figure 9 and Figure 10). Freundlich constants \( K_f \) and \( 1/n \) were calculated from the intercept and slope of the straight line of the plot \( \log q_e \) versus \( \log C_e \). From Table 8, it is seen that the sorption capacity (\( K_f \)) higher in case of ASiG. The magnitude of \( n \) gives a measured of favorability of adsorption. The values of \( n \) between 1 and 10 (i.e. \( 1/n \) less than 1) represents a favorable sorption. For the present study the value of \( n \) also represented the same trend in both the adsorbent but \( 1/n \) value a little less in case of silica representing a beneficial sorption. In order to distinguish between physical and chemical bio-
sorption on the heterogeneous surfaces the equilibrium data were tested with the D-R isotherm model. In this study, Es values for both the adsorbent showed physisorption since its value less than 8 kJmol\(^{-1}\) (Table 8). The results from Tempkin equation (Table 8) indicated that both the adsorbent has high value of \(K_T\) that means the adsorption reactions are not proceed via ion exchange process (Ho,1995).

### Table 8: Isotherm parameters of various adsorbents

| Isotherm models | Adsorbents | ARHA | ASiG |
|-----------------|------------|------|------|
| Langmuir        |            |      |      |
| \(Q_0\)         |            | 0.402| 0.244|
| \(b\)           |            | 1.13 | 5.38 |
| \(R_L\)         |            | 0.066| 0.04 |
| \(R^2\)         |            | 0.983| 0.987|
| Freundlich      |            |      |      |
| \(K_F\)         |            | 0.177| 0.196|
| \(1/n\)         |            | 0.457| 0.425|
| \(R^2\)         |            | 0.914| 0.936|
| Tempkin         |            |      |      |
| \(K_T\)         |            | 13.96| 49.51|
| \(B_1\)         |            | 0.0789| 0.0542|
| \(R^2\)         |            | 0.938| 0.912|
| D-R             |            |      |      |
| \(q_m\)         |            | 0.284| 0.23 |
| \(\beta\)       |            | 0.04 | 0.013|
| \(E_s\)         |            | 3.535| 6.20 |
| \(R^2\)         |            | 0.956| 0.931|

### Figure 9: Comparison between the measured and modeled isotherm profiles for the adsorption of fluoride onto ARHA (Experimental condition: pH 2.0; adsorbent dose 2.4 g/100ml solution; contact time 120 min varying initial concentrations at 303K temperature)
Figure 10: Comparison between the measured and modeled isotherm profiles for the adsorption of fluoride onto ASiG (Experimental condition: pH 2.0; adsorbent dose 2.4 g/100ml solution; contact time 120 min varying initial concentrations at 303K temperature)

3.6 Instrumental analysis of adsorbent

3.6.1 Fourier Transform Infrared Analysis (FTIR)

The FTIR spectrum of RHA was recorded to obtain the information regarding the stretching and bending vibrations of the functional groups which are involved in the adsorption of the adsorbate molecules. The FTIR spectra of ARHA before adsorption of fluoride and after fluoride adsorption are shown in Figure 11 (a, b). The FTIR spectral analysis of ARHA shows distinct peaks at 3434, 2924, 2851, 1637, 1102 and 793 cm⁻¹. The broad and strong band at 3434 cm⁻¹ indicates the presence of –OH stretching. The –CH2 stretching vibration could be ascribed to the band that appeared at 2850 cm⁻¹. The strong peak at 1637 cm⁻¹ shows the presence of carbonate group. Absorption at 793 cm⁻¹ is due to carbon-halide stretching vibration. Hence, FTIR spectral analysis demonstrates the existence of functional groups like –CH2, -OH, -CO3 and –X on the surface of ARHA. After fluoride adsorption the intensity of hydroxyl carbonate and halide bands of the adsorbent are little than those of the adsorbent before adsorption of fluoride. Strong adsorption band of 3434 cm⁻¹ (indicative of –OH stretching vibrations) shifted to 3424 cm⁻¹ after fluoride adsorption. The results suggest that fluoride interact with –OH, -CO3 and carbonate functional group present in ARHA.

Figure 11: FTIR spectra of unloaded (b) and fluoride loaded (a) ARHA

3.6.2 SEM imaging
SEM analysis is another useful tool for the analysis of the surface morphology of an adsorbent. The porous and irregular surface structure of the adsorbent can be clearly observed in the SEM image shown in Figure (12-15). The SEM structure of ARHA before and after adsorption of fluoride showed little variation of surface structure. The heterogeneous pores and cavities provided a large exposed surface area for the adsorption of fluoride. The size of pores is clear indicative of the expected adsorption of fluoride onto the surface of the ARHA. The BET surface area, average pore diameter and average particle size of the adsorbent were 36.44 m$^2$/g, 42.603 Å and 150.47 µm respectively.

**Figure 12:** Photograph for ARHA before passing fluoride solution.(1000 magnification)

**Figure 13:** Photograph for ARHA before passing fluoride solution.(2000 magnification)
4. Conclusion

In this study the ability of ARHA and ASiG to remove fluoride from aqueous solution was investigated. The operational parameters such as pH, initial fluoride concentration, adsorbent dose and contact time were found to have an effect on the adsorption efficiency of ARHA and ASiG. The maximum adsorption of fluoride was found at pH 2.0 for both the adsorbent. According to Langmuir model the maximum adsorption capacity was found in case of ARHA and ASiG were 0.402 mg/g and 0.244 mg/g respectively. The equilibrium was attained at 100 minutes for both the adsorbents, but percentage of removal was 88.30 and 96.7 for ARHA and ASiG respectively. Further the adsorbent ARHA was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) techniques. The kinetic studies revealed that the adsorption process best fit the pseudo-second order kinetic model for both the adsorbents. Intraparticle diffusion was not the sole rate-controlling step. The study on equilibrium sorption revealed that Langmuir isotherm model give best fit to experimental data. The nature of adsorption of fluoride on ARHA and ASiG was physical adsorption as inferred from the Dubinin-Radishkevich (D-R) isotherm model. Therefore, the present study showed that both ARHA and silica gel could be used as an adsorbent for fluoride removal but ARHA showed little better performance over ASiG.

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