CHAPTER 4

Continuous Fixed-Bed Column Study and Adsorption Modeling to Evaluate Fluoride Removal Performance of Cerium(IV)-Incorporated Hydrous Iron(III) Oxide (CIHFO) Nanoaggregates from Groundwater

4.1. Introduction

Application of batch adsorption process to evaluate adsorption efficacy of any adsorbent have been traditionally followed for preliminary screening of the overall adsorption system associated with that particular adsorbent before utilisation of adsorbent in mass scale in costly operations. Batch process could yield fundamental information of proposed adsorbent regarding its effectiveness and also for removing specific contaminants and maximum uptake capacity of respective impurities. However, removal of fluoride by batch adsorption studies by many adsorbents have been reported in large (Bhatnagar *et al.*, 2011; Habuda-Stanić *et al.*, 2014; Sivarajasekar *et al.*, 2017; Vinati *et al.*, 2015) but the practical utility of an adsorbent in removing the fluoride from the water is mainly judge by column operation (Ghorai and Pant, 2004; Ghosh *et al.*, 2015; Rojas-mayorga *et al.*, 2015; Wang *et al.*, 2015). In the context of applicability, column operations are more competent mode of operation over batch adsorption process as these operations allows more efficient utilization of adsorbents. Generally, in column operations, adsorbent with certain bed height is in contact continuously by the fresh solution of desired initial experimental solute concentration so the given layer of adsorbent in a column remains practically constant in respect to the provided solute concentration. In such way, in column operation, maximum loading of the adsorbent at constant solute concentration ensured in contrast to continuously declining solute concentration in batch method thus lessening the effectiveness of the adsorbent. The column competence can be explicated well by means of breakthrough curves. A breakthrough curve can be obtained by plotting C_t/C_i (the ratio of column effluent concentration at any time, t (min) and initial effluent concentration) versus either volume treated or time of treatment. Breakthrough capacity, exhaustion capacity and degree of column utilization are the most important parameters of concern of the breakthrough curves. The breakthrough capacity (Q_b $mg.g^{-1}$) is the amount of the mass of adsorbate removed by the adsorbent at breakthrough concentration (C_b $mg.L^{-1}$) that is highest permissible limit of solute concentration. The degree of column utilization is defined as the mass adsorbed at breakthrough point divided by the mass adsorbed at complete saturation. The exhaustion capacity (Q_e $mg.g^{-1}$) is defined as the mass of the adsorbate removed by unit weight of the adsorbent at column exhaustion point. Evaluation of breakthrough curves characteristics (Patil *et al.*, 2012) will help to determine the usability of proposed adsorbent in cost effectively in industries as well as household areas. In this research work, the efficiency of CIHFO packed fixed-bed column for fluoride removal has been evaluated critically with varying filter designing parameters such as influent fluoride concentrations, height of fixed-beds and flow rate with kinetic modeling of the breakthrough data using Thomas model, bed height service time (BDST) model and statistical ANN and RSM models.

4.2. Column Design for Adsorption Experimental Set-up

Agglomerated nanoparticles (size: 841-1410 μm) of CIHFO was packed uniformly into three glass columns (height: ~ 59 cm, with internal diameter (id): 2.30 cm and with cross sectional area: 4.154 cm^2) over glass wool followed by glass beads and cotton to avoid void spaces, channels and cracks in fixed-beds and set up to the desired bed heights (**Scheme 4.1**). Before conducting experiment, each fixed- bed was washed five times with double distilled water (pH: 7.0-7.5). The effluent of each column was collected fraction wise (250 mL) for fluoride analysis. The fluoride enriched solution (pH: 7.5 ± 0.2, temperature: 30±2ºC) was allowed to flow down gravitationally through the fixed-bed columns.

Experimental set up for study the effect of fixed-bed height were conducted with column of heights: 6.0, 10.0 and 14.0 cm (bed volumes, BV (cm^3): 24.92, 41.54, 58.16 respectively), which were made by packing of 26.54, 35.8 and 44.6 g of CIHFO uniformly. The initial concentration of feed water sample (C_i) employed into fixed-beds was 5.0 $mg.L^{-1}$ with effluent discharge rate 1.0 (± 0.1) mL. min^{-1} (EBCT: 24.92, 41.54 and 58.16 min).

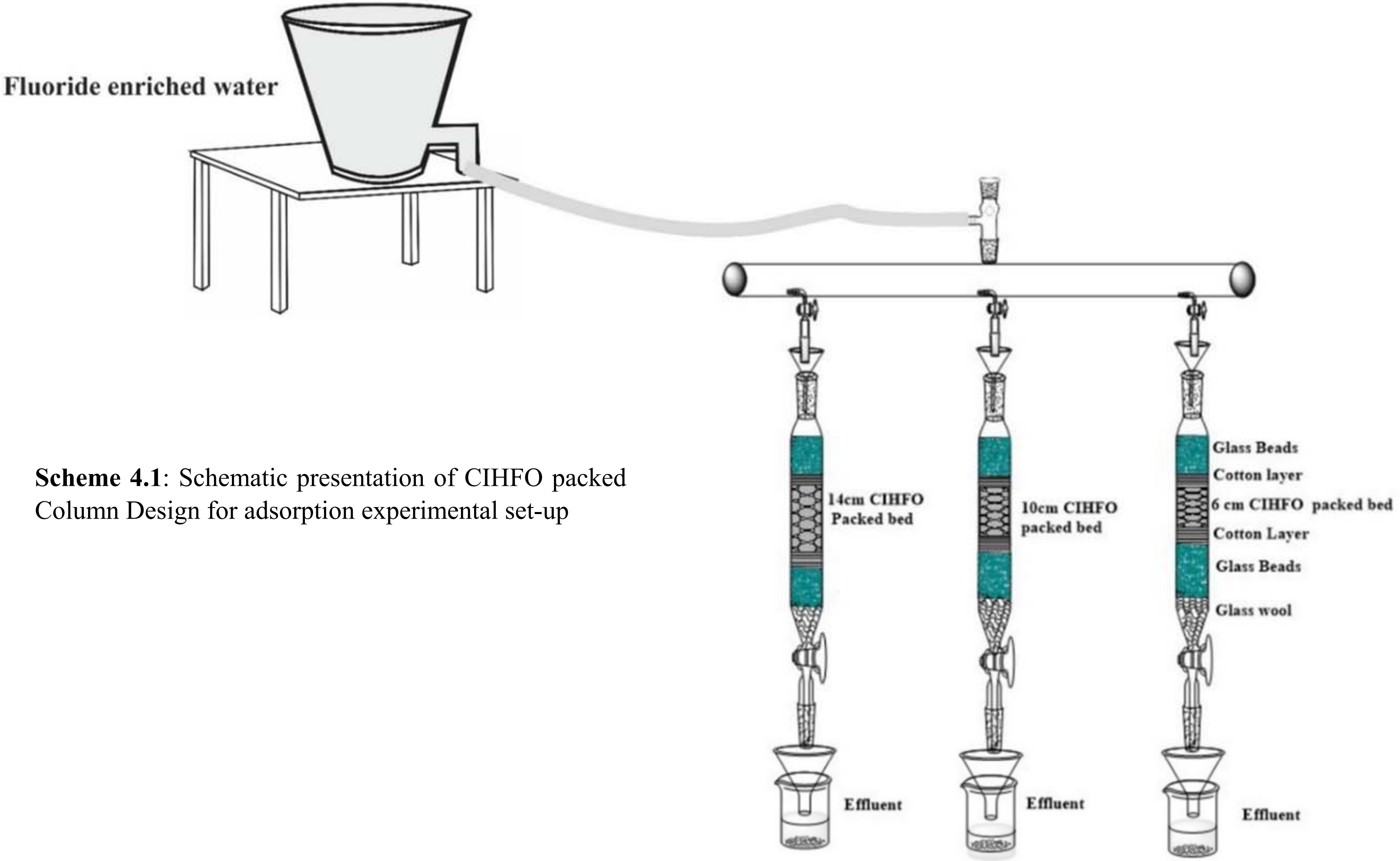
Experiments on the effect of discharge rates of effluent (1.0, 2.0 and 3.0 $mL.min^{-1}$) (EBCT: 41.54, 20.77 and 13.84 min) with C_i = 5.0 $mg.L^{-1}$ in feed water were conducted with three separate CIHFO fixed-beds of height 10.0 cm (BV: 41.54 cm^3). Experiments on the effect of fluoride concentration (C_i = 3.0, 5.0 and 9.0 $mg.L^{-1}$) in feed solution were conducted using three separate fixed-beds made by uniform packing 35.8 g CIHFO particles (bed height: 10.0 cm; BV:41.54 cm^3). The solution feeding rate was fixed with a rate of effluent discharge 1.0 (± 0.1) $mL.min^{-1}$ to move down through the fixed bed.

4.2.1. Water Sample Collection

A mass scale water needed for column feeding was collected from a tube-well (height: ~150ft) of college street area (Kolkata, India) was analysed for some parameters of water quality expressed in **table 4.1**.The analytical data of this water sample showed that the fluoride concentration was well below its maximum allowed level (0.64 $mg.L^{-1}$). Collected water sample spiked with definite volume of the standard fluoride solution to achieve the desired initial concentrations of fluoride (C_i = 3.0, 5.0 and 9.0 mg.L^{-1}) as required, which were used to evaluate performance efficacy of columns packed with CIHFO for fluoride removal.

Table 4.1: Some water quality parameters of the water sample before and after treatment through fixed bed of CIHFO packed column

Water Quality parameters	**Temp. (°C)**	**pH**	**Conductivity (µS)**	**Turbidity (NTU)**	**Salinity (mg.L^{-1})**	**Fluoride (mg.L^{-1})**	**Iron (mg.L^{-1})**	**TDS (mg.L^{-1})**	**Total Hardness (mg.L^{-1})**	**Calcium (mg.L^{-1})**	**Magnesium (mg.L^{-1})**
Before filtration	35	7.05	769	58	543	0.64	2.89	1024	89.67	55.98	33.69
After reaching breakthrough point **(bed height 10cm; flow rate 1mL.min^{-1}; initial fluoride conc. 5mg.L^{-1})**	31	7.5	654	78	349	1.58	2.05	1123	75.34	51.24	24.10

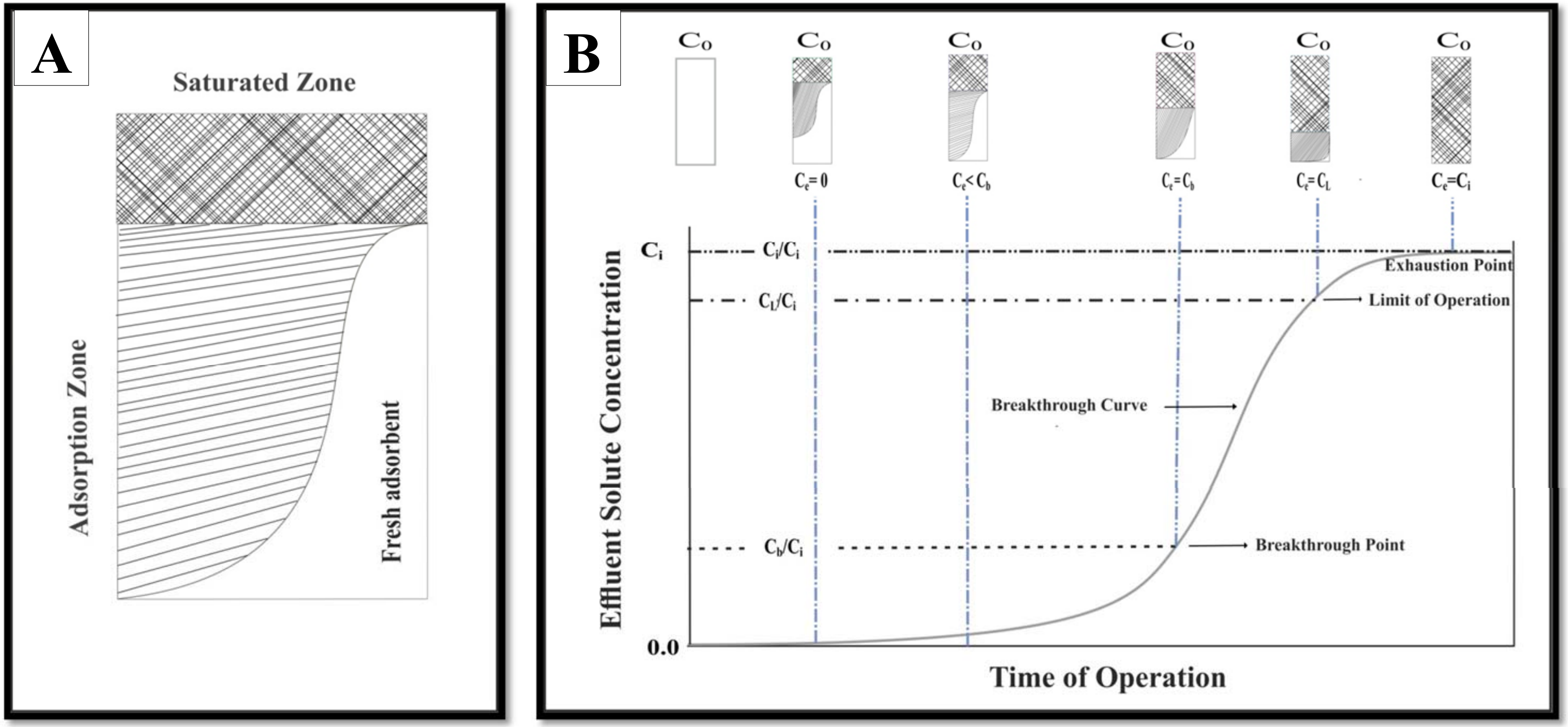


Scheme 4.1: Schematic presentation of CIHFO packed Column Design for adsorption experimental set-up

4.2.2. Column Adsorption Concept Under Transient Conditions

In this experimental procedure, the column operation was carried out with continuous flow of feed solution, and the column bed is stationary. It was observed that the effluent concentration of solute (fluoride) continuously changing consecutively from zero to that of feed concentration, with time. A plot could be created from the experimental data showing time verses C_t/C_i (the ratio of column effluent concentration at any time, t (min) and initial effluent concentration) a - S shaped curve can form and denoted to be as breakthrough curve (J. Thilagan *et al.*, 2015; Patil *et al.*, 2012). With continuation of experiment, the concentration of effluent change simultaneously with time, hence it can be assumed that the column was operating under unsteady state or transient conditions. The time when permissible solute concentration (1.5 $mg.L^{-1}$ for fluoride) appeared in the effluent, this point was accepted as breakthrough point time, and when the bed was almost exhausted with solute that time (value of $C_t/C_i \sim 0.95$) was cited as bed exhaust time.

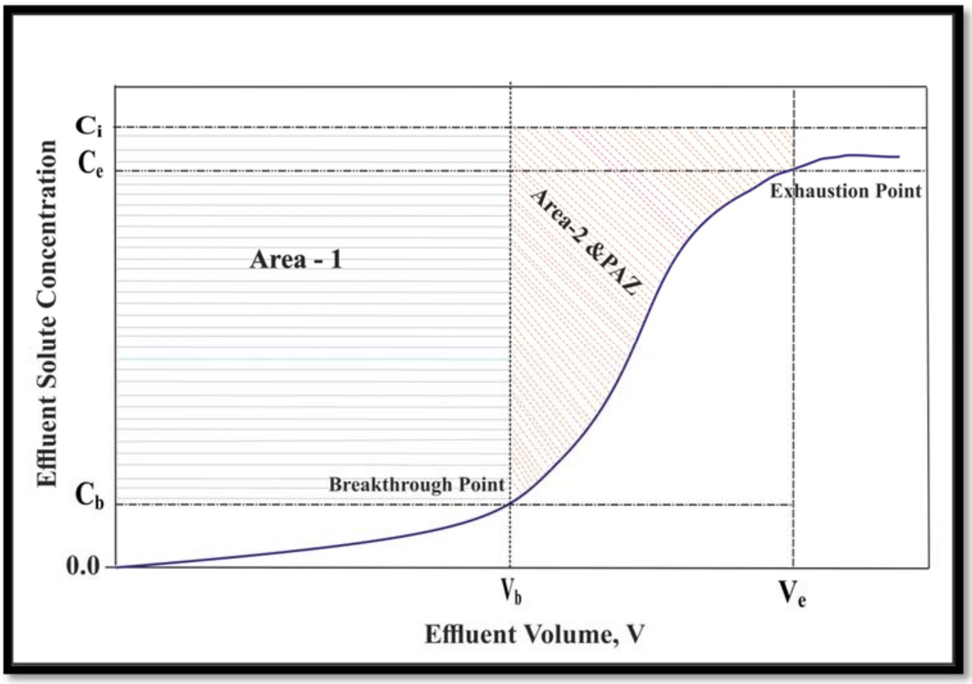
The relation between the nature of breakthrough curves and fixed bed adsorption column was nicely expressed by Michaels (J. Thilagan *et al.*, 2015; Patil *et al.*, 2012) who has proposed the concept of adsorption zone height, the most beneficial parameter for the fixed bed column designing. According to him, the adsorption zone height should be that part of the bed, where the solute concentration changes from a low value (breakthrough conc.) to a high value (bed exhaust conc.). He also enlightens about time span essential for the establishment of zone, and time required for the zone to move its own height down to the column. According to this concept, during the early stage of the experimental study, when influent passed through the inlet of the column, the upper few layers of the fresh adsorbent effectively adsorbed most solute because these upper layers were in contact with the solution at its maximum concentration level (initial concentration, C_i). The small amount of solute were able to escape from the first few layers of the adsorbent and then were removed from the solution in the lower strata of the bed and as a consequence no solute escape from the adsorbent. In the initial stage of operation (effluent concentration, $C=0$). The **primary adsorption zone** (PAZ – δ cm) is concentrated near the top of the column (**Scheme. 4.2**). With continuous flow of influent into the column, after a certain time, the top layers of the adsorbent become utmost saturated with the incoming solute and loss its effectiveness as an adsorbent. Hence, the PAZ now moves downward to access the fresher adsorbent in the column. Such wave like movement of this zone, along with continuous flow of initial concentration, exhibit a characteristic 'S' shape breakthrough curves with varying degree of steepness when the plot of C_t/C_i versus time or volume of effluent, for a constant flow rate generated, depicting that with increase in the ratio of C_t/C_i as zone moves through the column. As the PAZ moves downwards, more and more solute trends to escape in the effluent, as shown in **Scheme 4.2**. The plots of Experimental data generated from the breakthrough analysis were analyzed to determine the various types of column parameter. From breakthrough curve, the effectiveness of a column for removing of any contaminant in fixed bed column can also be illustrated.



Scheme 4.2: Schematic presentation of movement of primary adsorption zone during column operation and formation of Breakthrough curve during operation

4.2.3. Designing of Fixed Bed Absorber Packed with CIHFO

At breakthrough point and at exhaust point, the amount of a solute adsorbed over surfaces of the unit mass of adsorbent packed in fixed-bed column with CIHFO was estimated by calculating the area under the curve as schematically presented in **Scheme 4.3** by using the form of the following relations (Futalan *et al*., 2011; Ghosh *et al*., 2015) (Eq. 4.1 and 4.2) and expressed as Q_b (mg.g^{-1}) (area-1) and Q_e (mg.g^{-1}) (area-2 and PAZ) respectively.



Scheme 4.3: Schematic presentation of total adsorption capacity of the fixed bed column at breakthrough point and exhaustion point.

$$Q_b = \int_0^{V_b} \frac{C_i - C_t}{M}\, dv \qquad \textit{(Eq. 4.1)}$$

$$Q_e = \int_0^{V_e} \frac{C_i - C_t}{M}\, dv \qquad \textit{(Eq. 4.2)}$$

Where, Q_b and Q_e are breakthrough and exhaust point capacity respectively, C_i and C_t are initial feeding solution concentration and effluent concentration in certain time respectively. M denotes mass of adsorbent and V_b, volume of water passed until breakthrough reach whereas V_e is volume of water passed up to exhaust point.

The primary adsorption zone (PAZ) in the fixed bed column was enunciated by the breakthrough curve in which a part of bed over which there was a concentration reduction from C_e to C_b. It is assumed that this particular zone has a constant length or height, δ (cm), the total time t_e, required to form the PAZ of the column packed with CIHFO could be evaluated by the equation (***4.3)***.

$$t_e = \frac{V_e}{F_m} \qquad \textit{(Eq. 4.3)}$$

Here F_m is the mass rate flow to the column defined as the rate of movement of liquid mass through a unit area (Patil *et al.*, 2012). The time, t_δ associated for movement of the zone down its own length in the CIHFO packed column simple expressed by following equation.

$$t_\delta = \frac{(V_e - V_b)}{F_m} \qquad \textit{(Eq. 4.4)}$$

The red shaded portion represents the solute (fluoride) amount adsorbed by the CIHFO adsorbent in PAZ region from the breakthrough point to exhaustion point. If the height of the CIHFO packed column bed is D (cm), and if t_f is the time required for the formation of the adsorption zone, the height of adsorption zone is δ (cm) can be calculated from

$$\delta = D \times \frac{t_e}{t_e - t_f} \qquad \textit{(Eq. 4.5)}$$

The quantity of solute (fluoride) removed from the solution in PAZ from the breakpoint to saturation is U gram of solute. This is given by the red shaded area of Scheme 4.3 and expressed as (J. Thilagan et al., 2015; Patil et al., 2012)

$$\boldsymbol{U = \int_{V_b}^{V_e} (C_i - C)\, dV} \qquad \textit{(Eq. 4.6)}$$

If, all the adsorbent (CIHFO) of the PAZ region were already saturated with solute (fluoride), it would contain C_iV_a (total effluent accumulated during the appearance of the breakthrough curve is $V_a = V_e - V_b$) mass of solute (fluoride). Subsequently, at the breakthrough point, when the zone is still within the column, the fractional ability of the adsorbent in the zone still to adsorb solute (Ghosh *et al.*, 2015; J. Thilagan *et al.*, 2015; Patil *et al.*, 2012).

$$\boldsymbol{f = \frac{U}{C_i V_a}} \qquad \textit{(Eq. 4.7)}$$

When, f = 0, the adsorbent in this zone is effectively saturated, the time of formation of the zone at the top of the bed t_f should be substantially the same as the time t_δ required for the zone to travel a distance equal in the bed equal to its own height, δ (cm). Then again, if f =1, with the intention that the solid in the zone contains essentially no solute (fluoride), the zone-formation time surely very short, essentially zero. Such limiting conditions described by Eq.4.8 and total column saturation percentage also calculated by Eq.4.9 (Ghosh *et al.*, 2015; J. Thilagan *et al.*, 2015).

$$\boldsymbol{t_f = (1 - f)t_\delta} \qquad \textit{(Eq. 4.8)}$$

$$\%\ \boldsymbol{of\ saturation = [D - \delta(f)/D] \times 100} \qquad \textit{(Eq. 4.9)}$$

The breakthrough parameters as obtained for the present fixed bed column study, following above the relations (Eqs. 4.1- 4.9) are presented in **table 4.2.**

The residence time or EBCT is usually expressed as a relationship in between bed height of packed adsorbent in the column and linear discharge or flow rate of feeding solute (Ghosh *et al*., 2015).

$$\boldsymbol{EBCT = \frac{D}{\gamma}} \qquad \textit{(Eq. 4.10)}$$

Here γ, is denoted for the linear discharge rate through the fixed-bed in column ($cm^3.cm^{-2}min^{-1}$) of a bed height noted as D (cm).

Values of the Q_b ($mg.\ g^{-1}$) and Q_e ($mg.\ g^{-1}$) have been calculated by using the experimental data with the help of Eq.4.1 and Eq.4.2. An ascending pattern of values of both Q_b ($mg.\ g^{-1}$) and Q_e ($mg.\ g^{-1}$) found in association with increase of the bed height (Q_b = 492.38, 727.52 and 793.55 $mg.g^{-1}$ and Q_e = 56.51, 85.26 and 85.08 $mg.g^{-1}$ for bed height = 6.0, 10.0 and 14.0 cm, respectively) when input (C_i) feeding solution conc. was 5 $mg.L^{-1}$ and the rate of effluent discharge was 1.0 $mL.\ min^{-1}$. But, for other two parameters likely variation in rate of effluent discharge as well as change in initial feeding solute concentration, significant variation in pattern of obtained values of both Q_b ($mg.\ g^{-1}$) and Q_e ($mg.\ g^{-1}$) have been exhibited in **table 4.2**. It was observed that with increase of effluent discharge rate (rate of effluent discharge: 1.0, 2.0 and 3.0 $mL.\ min^{-1}$), both Q_b ($mg.\ g^{-1}$) and Q_e ($mg.\ g^{-1}$) value followed declining trend but with increase of initial solute concentration (C_i = 3.0, 5.0 and 9.0 $mg.L^{-1}$) values of Q_b ($mg.\ g^{-1}$) and Q_e ($mg.\ g^{-1}$) sharply increased.

For bed height and initial solute concentration variation, the length of primary adsorption zone **δ (cm)** increased sequentially whereas followed decreasing trend with the change of the rate of effluent discharge rate. It was firmly noticed that lesser time requirement is associated with the formation of PAZ with variation of column operating parameters like increase of bed height, rate of effluent discharge rate and initial solute concentration in input source. High percentage of column saturation and almost a stable range of the fractional adsorption capacity ensured that adsorption sites per unit of area have been properly utilised for adsorption process. Such condition was due to better surface coverage of CIHFO that enhanced primary adsorption sites and the higher percentage of column saturation. In this column study, Fractional fluoride adsorption capacity increased in each condition because of the greater fluoride loading per unit adsorption sites.

The EBCT values of the present fixed bed column study have been calculated from the obtained experimental data by using Eq.4.10 and it was found that values of EBCT increased with bed height (24.92, 41.54 and 58.16 min respectively for bed height 6.0, 10.0 and 14.0 cm) but decreased as the rate of effluent discharge increased (41.54, 20.77 and 13.84 min respectively for 1.0, 2.0 and 3 mL. min^{-1}). It can be presumed that under the defined operating conditions, when percolation of the input solution with solute through the fixed-bed happen, the process does not occur at a steady state. Hence it is too difficult to describe the dynamic behaviour of compound in a fixed-bed. The data of operational parameters obtained in these fixed bed column studies have been given an idea of the operating conditions required for breakthrough to occur and how much additional solution loaded per unit cross sectional area of the adsorbent would result in complete exhaustion of the capacity of the CIHFO adsorbent packed column. In approach of field application on large scale, these data can be useful for the designing domestic filter units using CIHFO as adsorbent for removal of fluoride in wide range of concentrations.

Table 4.2: Some important parameters of breakthrough curves analysis with variation of fixed-bed height, rate of effluent discharge and variation of initial fluoride concentration in feed water.

Parameter	**Bed height (cm)**			**Effluent rate (mL. min^{-1})**			**Input F^{-} concentration (mg.L^{-1})**		
	6.0	**10.0**	**14.0**	**1.0**	**2.0**	**3.0**	**3.00**	**5.00**	**9.00**
Q_b (mg.g^{-1})	492.38	727.52	793.55	727.52	659.07	545.00	590.78	727.52	1180.51
Q_e (mg.g^{-1})	56.51	85.26	85.08	85.26	73.74	63.14	82.40	85.26	156.42
V_b(mg)	141.29	202.51	218.60	202.51	181.56	142.85	370.12	202.51	149.35
V_e(mg)	235.49	279.32	257.84	279.32	214.28	181.81	402.59	279.32	214.28
V_a (mg)	94.2	76.81	39.24	76.81	32.72	38.96	32.47	76.81	64.93
F_m (× 10^3) (mg.cm^{-2}.min^{-1})	1.234	1.234	1.234	1.234	2.469	3.70	0.92	1.234	2.13
T_e (min.cm^2)	190.83	226.35	208.94	226.35	86.78	49.13	437.59	226.35	100.60
t_δ(min.cm^2)	76.33	62.24	31.79	62.24	13.25	10.52	35.29	62.24	30.48
f	0.018	0.025	0.031	0.025	0.037	0.027	0.023	0.025	0.032
t_f (min)	74.95	60.68	30.80	60.68	12.75	10.23	34.47	60.68	29.50
δ (cm)	9.88	13.66	16.42	13.66	11.72	12.62	10.85	13.66	14.14
% of saturation	97.0	96.5	96.36	96.5	95.66	96.59	97.5	96.5	95.47

4.3. Application of Cerium (IV) - Incorporated Hydrous Iron(III) Oxide (CIHFO) in Column Operation

4.3.1. Effect of Bed Height (adsorbent mass) on Breakthrough Curve

Dependence of bed height on breakthrough curve have been explored with input solute (fluoride) concentration 5 mg.L^{-1} through three separate CIHFO loaded columns (scheme 4.1) packed uniformly with 26.54, 35.8 and 44.6 g of the CIHFO up to the height of 6.0, 10.0 and 14.0 cm respectively. The influent rate maintained was 1.0 mL.min^{-1}. The breakthrough curve obtained is shown in Fig.4.1.

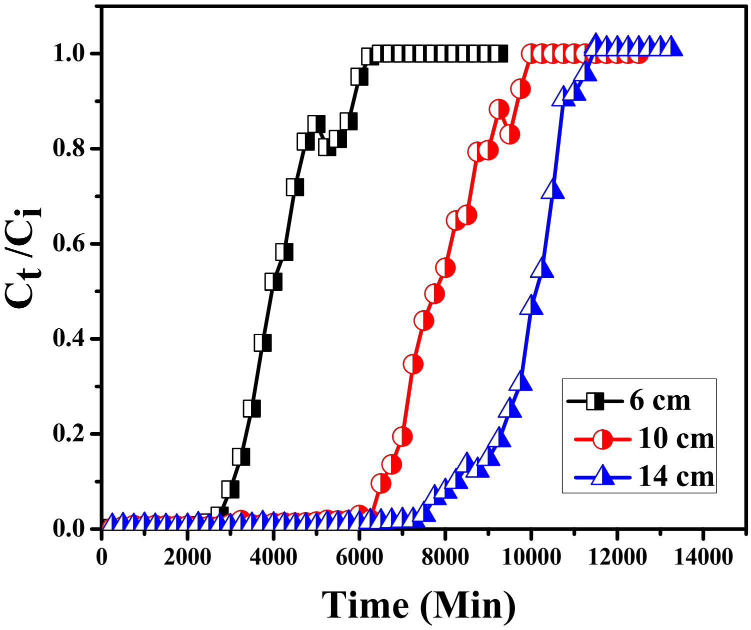


Fig. 4.1: Effect of bed height variation on breakthrough curve for fluoride adsorption by CIHFO at pH 7.0 (±0.2).

From pictorial presentation, it was found that the shape and the gradient of the curves were somewhat different with varying bed height. The breakthrough point (fluoride conc.1.5 mg.L^{-1}) achieved more rapidly in the columns with lower bed height. The higher uptake and gradual increase in slope of the breakthrough curves were observed at the initial stage of the curves. This gradual increase continued up to the breakthrough point of the curve after which the concentration of fluoride in effluent increased more quickly so as the slope of the curve. The columns with minimum bed height got saturated earlier than the higher ones.

The breakthrough volumes (V_b) for the columns with bed height 6.0, 10.0 and 14.0 cm were 3.6, 7.25, 10.0 L respectively at a fixed flow rate of 1 mL.min^{-1} corresponding to C_t /C_i ratio of 0.39, 0.346 and 0.306 respectively at breakthrough point. Breakthrough times have been taken for bed height of column 6.0, 10.0 and 14.0 cm sequentially were 3600, 7250 and 10,000 min. This was due to the increase in the empty bed contact time (EBCT) with increasing bed height (Ghosh *et al.*, 2015). The empty bed contact time for the column with bed height 6.0, 10.0 and 14.0 cm were 24.92, 41.54 and 58.16 min respectively. With increased EBCT, the diffusion process became more effective and the breakthrough volume (V_b) or breakthrough time (t_b) reached later. With increasing EBCT, the contact time between adsorbent and adsorbate increased and a higher amount of adsorbate got adsorbed to the bed and hence, the breakthrough volumes (V_b) increased with the increase of bed height or EBCT.

4.3.2. Effect of Flow Rate on Breakthrough Curve

Fig. 4.2 demonstrates the influence of influent flow rate on fluoride removal breakthrough curve at a fixed bed height (10 cm) of CIHFO column. It was observed that the breakthrough volume V_b (L) for the effluent rate (mL.min^{-1}) 1.0, 2.0 and 3.0 were 7.25, 6.5 and 5.5 L respectively corresponding to C_t/C_i ratio of 0.34, 0.29 and 0.36 at breakthrough point. Breakthrough times also taken for fixed bed with varying flow rate were 7250, 3250 and 1833 min respectively. The results showed that the decrease flow rate of influent from 3 to 1.0 mL.min^{-1} increased the breakthrough volume (V_b) or breakthrough time (t_b) which was due to the increase of EBCT (min). Lower the value of EBCT, less effective is the diffusion process resulting in lower adsorption uptake. Thus, the adsorbent needs much more time to bind to the solute effectively. The results also showed that the plateau of the breakthrough curve reached faster with increasing flow rate, which was due to the decrease of contact time between the solute in mobile phase and the surface of the stationary phase making quicker appearance of adsorption zone at the bottom of the column.

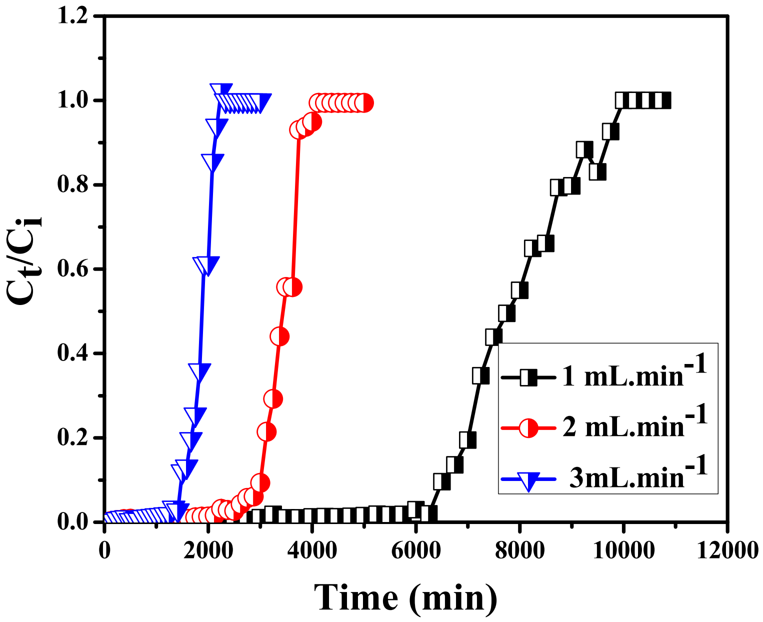


Fig. 4.2: Graphical presentation of effect of flow-rate on breakthrough curve for Fluoride adsorption by CIHFO at pH 7.0 (±0.2).

4.3.3. Effect of Concentration Variation on Breakthrough Curve

From the **Fig. 4.3** it was noticed that the breakthrough time decreased with increasing influent solute (fluoride) concentration. It was found that the breakthrough volume (V_b, L) for a fixed effluent flow rate 1.0 mL.min^{-1} corresponding to different input of fluoride concentrations 3.0, 5.0 and 9.0 mg.L^{-1} were 14.25, 7.25 and 5.75L respectively with corresponding C_t/C_i ratio value of 0.48, 0.306, 0.176. At lower influent fluoride concentrations, breakthrough was dispersed and appeared slowly. As influent concentration increased, sharper breakthrough was established. Such observations demonstrated that the change of concentration gradient effect vastly the saturation rate and breakthrough time.

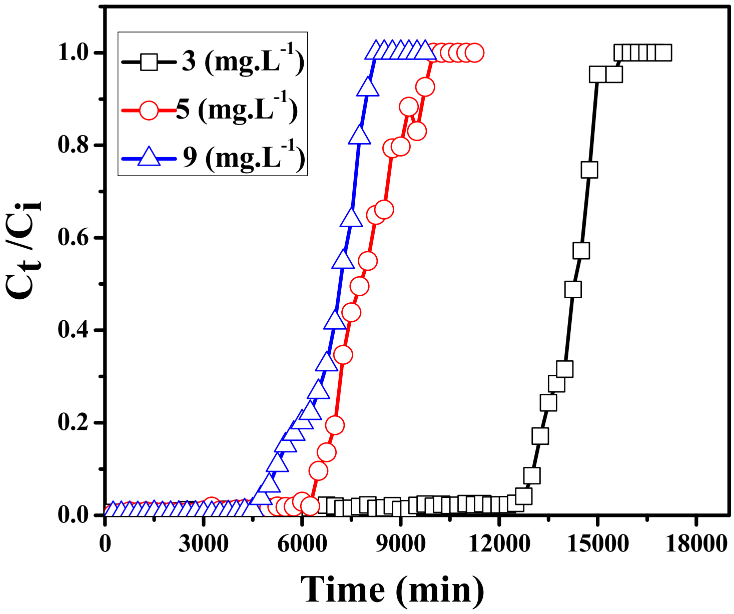


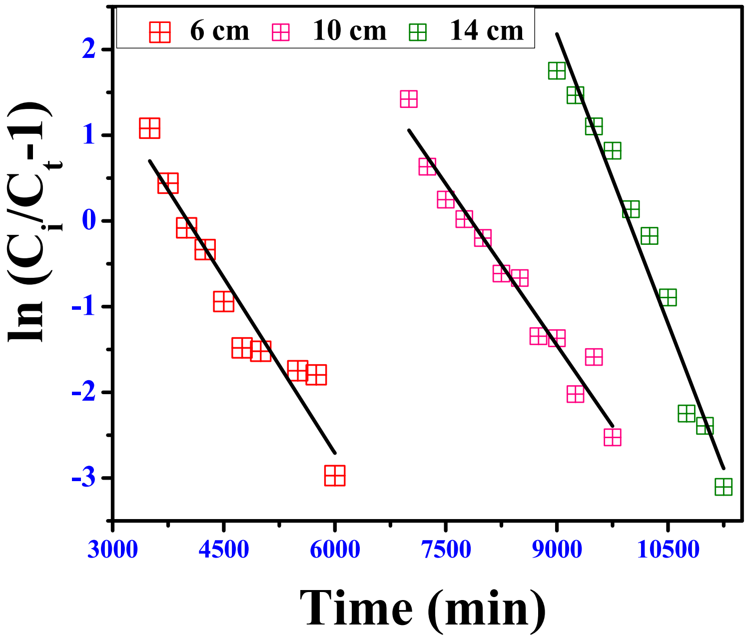
Fig. 4.3. Graphical presentation effect of initial concentration variation on breakthrough curve for Fluoride adsorption by CIHFO at pH 7.0 (±0.2)

This can be explained well by the fact that more adsorption sites are being saturated with increase in fluoride concentration. Hence, larger the influent concentration, the steeper the slope of the breakthrough curve but smaller the breakthrough time. These results demonstrated that diffusion process was concentration dependent. As the influent concentration increased, fluoride loading rate also increased, causing the driving force for mass transfer to increase, which resulted in certain decrease of adsorption zone length. Results showed that the increase of input solute concentration decreased the breakthrough volume (V_b) for attaining breakpoint despite EBCT values remaining the same, which was due to the appearance of more solute per unit area on the surface of the stationary phase. The breakthrough time (t_b, min), which was dependent on EBCT (min) should remain same for a fixed column bed height and effluent flow rate. As the rate of diffusion process was the same for a given EBCT and any solute loading in solution, the plateau in breakthrough curve should attain an identical position.

4.4. Fitting of Different Models on Breakthrough Curve

4.4.1. Thomas Kinetic Model

Dynamic behaviour of the fixed-bed column operation can be well elucidated by most widely accepted mathematical kinetics model developed by Thomas model (Thomas, 1944). The range of time (min) has been taken into consideration from the beginning to the end of breakthrough (Chen *et al.*, 2012). The relative constants and coefficients were obtained using linear regression analysis according to Eq. 2.33 and the obtained results were presented in Table 4.3 and expressed graphically in Fig.4.4. It was shown that the R^2 resulted from linear regression analysis have been ranged in between 0.90-0.96 ensuring good fitting of Thomas model with experimental data (Saha *et al.*, 2012). It has been observed that ascending trend of K_{Th} values associated with increase of the bed height and also with increase of the flow rate but declined gradually with increase of initial fluoride concentration. Higher Q_0 values have been obtained for both maximum bed height and lowest initial fluoride concentration. From this observation it can be assumed that fluoride adsorption over CIHFO packed fixed bed column highly influenced by the fluoride concentration gradient and amount of adsorbent medium. With higher flow rate both K_{Th} and Q_0 values followed descending trend that suggest lowest flow rate is preferable for column operation. Hence, lower fluoride concentration, lower flow rate and maximum bed height would produce better adsorption performance of CIHFO packed column for fluoride. Well-fitting of the Thomas model also favoured the fluoride adsorption over CIHFO indicating that the external and internal diffusions were not the limiting step (Chen *et al.*, 2012).



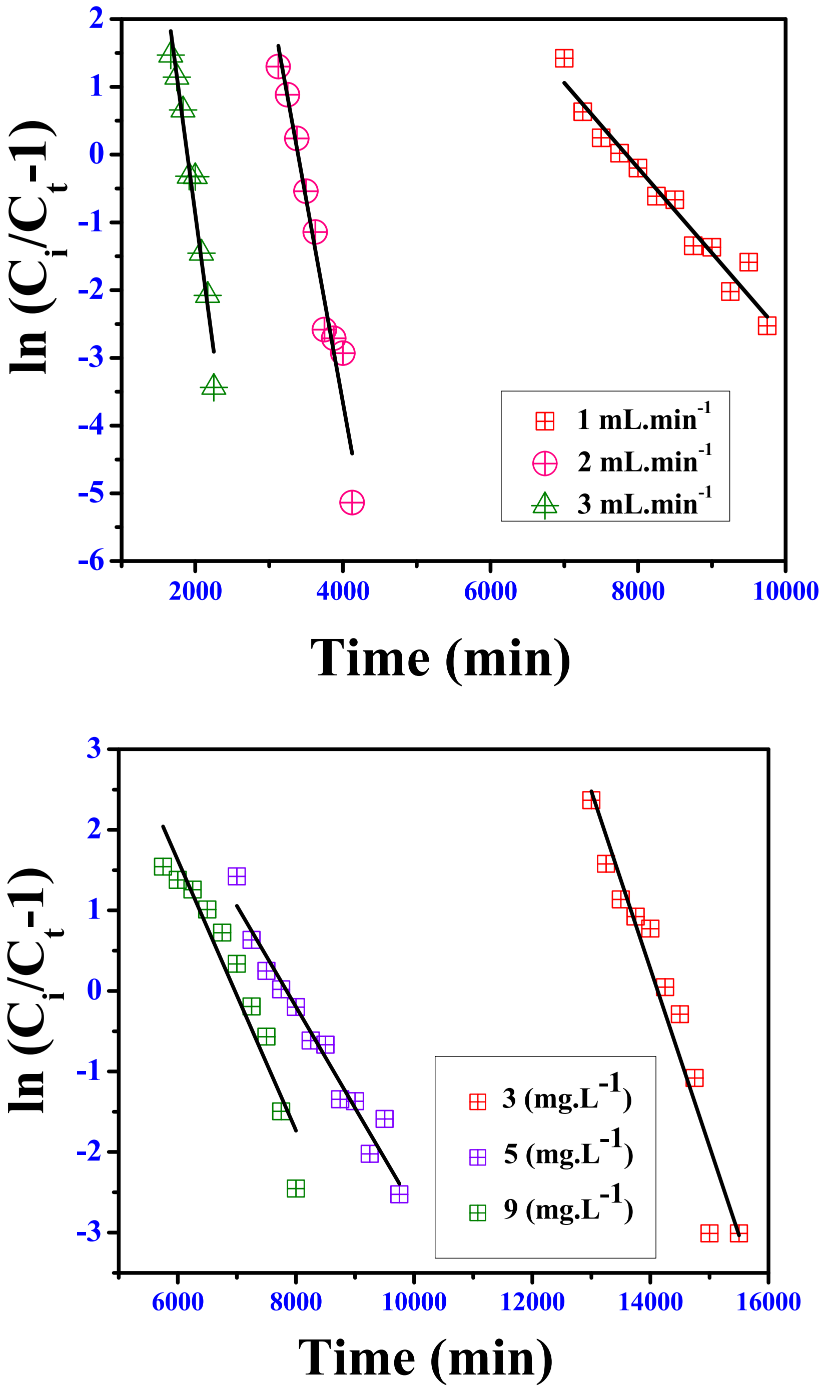


Fig. 4.4: Linear Thomas model fitting of breakthrough data obtained varying fixed bed-height, flow rate and initial fluoride concentration for evaluation of fluoride removal efficacy of CIHFO packed fixed-bed column operation in lab-bench scale from the spiked ground water.

Table 4.3: Thomas Kinetic Model Parameters Estimated for Fluoride Removal by CIHFO Packed Fixed-Bed Column

Parameters	**Bed Height (cm)**			**Flow Rate (mL. min^{-1})**			**Initial Fluoride Conc. (mg.L^{-1})**		
	6.0	**10.0**	**14.0**	**1.0**	**2.0**	**3.0**	**3.0**	**5.0**	**9 .0**
V_b(L)	3.750	7.250	9.750	7.250	6.50	5.55	14.0	7.250	5.75
V_e (L)	6.250	10.000	11.50	10.000	8.25	8.50	15.50	10.00	8.25
T_b (min)	3750	7250	9750	7250	3250	5550	14000	7250	5750
T_e (min)	6250	10000	11500	10000	4250	8500	15500	10000	8250
EBCT (min)	24.92	41.54	58.16	41.54	20.77	13.84	41.54	41.54	41.54
k_{Th} ($\times 10^{-3}$) (mL.min^{-1}mg^{-1})	1.36	1.25	2.25	1.25	6.02	8.11	2.20	1.25	1.68
Q_0 (mg.g^{-1})	5.47	9.84	22.44	9.84	20.4	15.34	31.13	9.84	11.69
R^2	0.92	0.95	0.96	0.95	0.95	0.95	0.92	0.95	0.90

4.4.2. Bed Depth Service Time (BDST) model

Initially, the BDST equation was derived originally from the Adams-Bohart model, afterward modified by Hutchins (Futalan *et al*., 2011). At present, it is widely accepted model applicable to understand the adsorption phenomenon involved in a fixed bed column operation system. It assumes that the rate of adsorption is explicated by the surface reaction between the adsorbate and the unused capacity of the adsorbent. This model does not consider the intra-particle mass transfer resistance and external film resistance where the adsorbate is directly adsorbed onto the surface of the adsorbent (Qaiser *et al*., 2009).The BDST equation shows a linear relationship between the bed height and breakthrough time, often called service time of the bed (Kumar and Chakraborty, 2009) and explained by the Eq.2.34-2.38. The BDST equation was applied on the column experimental data obtained from varying the bed height from 6.0 cm to 14.0 cm with effluent discharge rate of 1.0 mL.min^{-1} and initial concentration of 5.0 mg.L^{-1} that were kept constant. The dynamic bed capacity N_{BD} that is the adsorption capacity per unit volume of bed (mg.cm^{-3}) and adsorption rate constant, K_{BD} were computed to be 3847.5(mg.cm^{-3}), and 3.228×10^{-4} (L.mg^{-1}.min^{-1}), respectively. A larger value for K_{BD} implies that even at lower bed heights, breakthrough will occur at a later time whereas a smaller K_{BD} value needs a higher bed height to avoid breakthrough (Vijayaraghavan *et al*., 2004). The critical bed height, D_0 was determined to be 0.777 cm. This value is the minimum theoretical bed height of the CIHFO adsorbent that is sufficient such that the effluent concentration at $t = 0$ will not exceed the breakthrough concentration, C_b (mg.L^{-1}). High N_{BD} (3847.5mg. cm^{-3}) values suggested that CIHFO could be an efficient material for treatment of fluoride enriched groundwater, which is found to be similar to the results reported by few groups of researchers (Bhaumik *et al.*, 2013; Ghosh *et al.*, 2015).

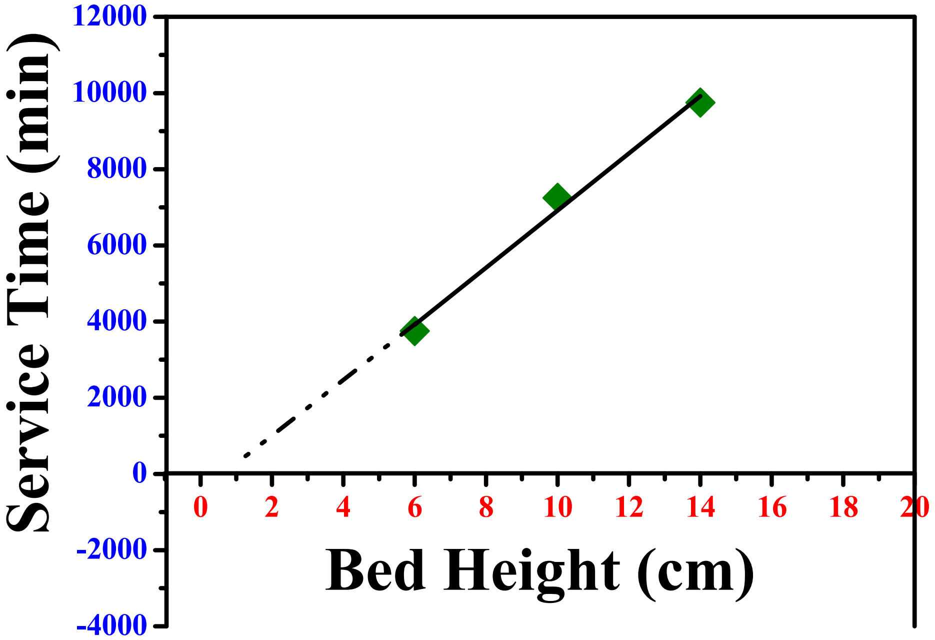


Fig. 4.5: The plot of Bed Depth Service Time (BDST) from the data obtained by CIHFO packed fixed-bed columns operations for treatment of fluoride enriched groundwater.

Table 4.4: The BDST Model Parameters Estimated For The Fluoride Removal by CIHFO Packed Fixed-Bed Column operation

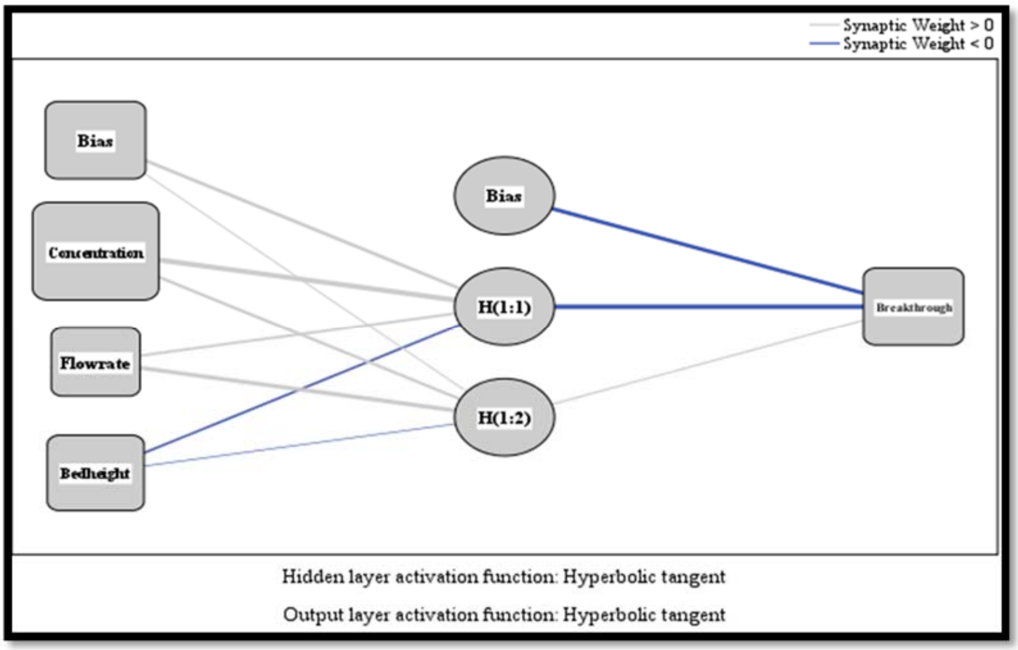
C_0 (mg.L^{-1})	C_b (mg.L^{-1})	D_0 (cm)	K_{BD} (L·mg^{-1}·min^{-1})	N_{BD} (mg·cm^{-3})
5.0	1.5	0.777	3.228×10^{-4}	3847.5

4.5. Modeling of the Adsorptive Removal of Fluoride by Artificial Neural Networking (ANN) Model: A statistical Approach

ANN is an advance mathematical or computational modeling procedure which is similar to that of biological neural networks applicable for the development of a nonlinear model using the neural networks toolbox made of input, hidden (consisting of weight and bias) and output layers located in the respective software environment (Ayodele *et al*., 2017). Applicability of ANN model has been successfully concerned for estimating and predicting adsorption characteristics that are genuinely considered as function of many variable parameters and also utilised for processing of information based on the connectionist approach. This model has the potentiality to mapping a set of input parameters into a set of output parameters by using existing data without knowing the intricate relationship among them. To identify patterns and extract trends in imprecise and complicated non–linear data, applicability of ANN is very authenticate (Giri *et al*., 2011). Considering adsorption as a complex non–linear process, neural network are found suitable for prediction of fluoride adsorption through fixed bed column operation. Neural network toolbox of SPSS–17 (SPSS Inc., Chicago, USA) mathematical software was used to evaluate fluoride removal efficiency of CIHFO under fixed bed column study. During the training, the ANN gave emphasis on to match the input and output values in order to minimize the difference between the predicted and the targeted values (Ayodele *et al*., 2017). Henceforth, the model responses were compared to the experimental data that has been used as a criterion in relation to the number of neurons in the hidden layer (Shi *et al*., 2017). The topology of ANN architecture of this study is illustrated in Fig.4.6.

A total of 223 experimental datasets, which were obtained from column adsorption experiments, were used to develop a three–layer feed–forward neural network model by applying hyperbolic tangent function under the normalized method for scale dependents. Out of these datasets, 71.2% were used to train the network and remaining were used for testing and validation of the ANN model. There were three neurons (viz; bed height, flow rate and initial fluoride concentration) in the input layer whereas one neuron, removal efficiency, in the output layer. The 4–3–1 ANN (including bias neuron) model is found to be working satisfactorily with an average relative error of 0.599 and sum square error of 3.915 during testing phase, indicating that the model is able to predict the fluoride adsorption efficiency with reasonable accuracy.

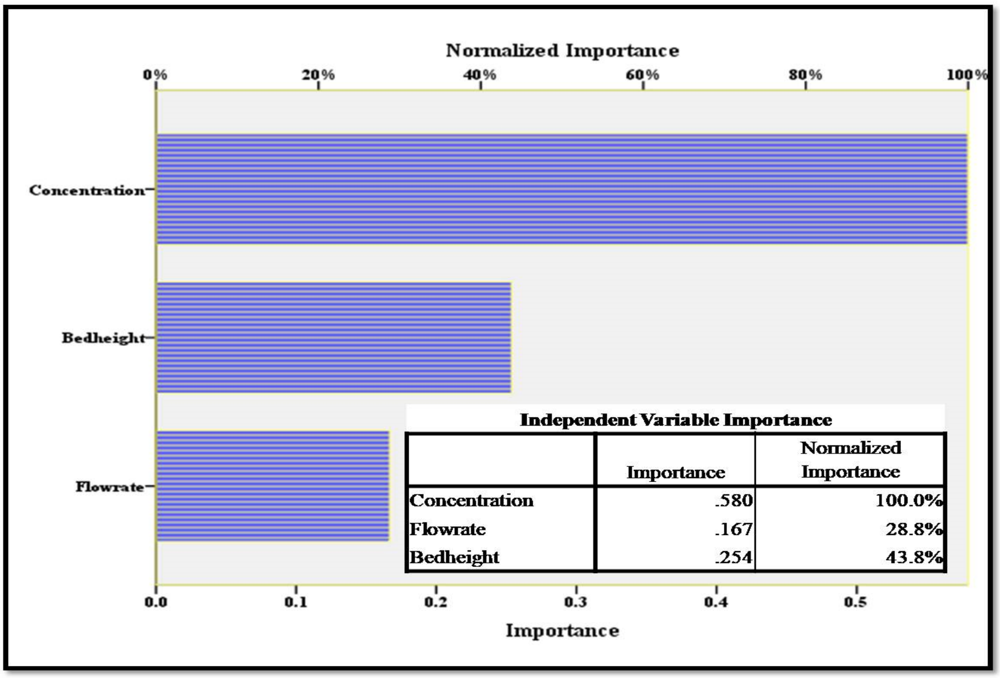
An importance analysis for the developed network was also performed to assess the relative effectiveness of the various operating (input) variables on the output variables (Roy *et al*., 2014, 2013). In the present scenario (Fig. 4.7), the degree of effectiveness of the input variables on the output variables was found to be in the order of initial concentration > bed height > flow rate for fluoride adsorption by CIHFO under fixed bed column operation. The influence percentages of these variables on the output were 100.0, 43.8 and 28.8%; respectively.



Hidden layer activation function: Hyperbolic tangent

Output layer activation function: Hyperbolic tangent

Fig.4.6: Neural Network architecture of fluoride adsorption by CIHFO



Independent Variable Importance

	Importance	Normalized Importance
Concentration	.580	100.0%
Flowrate	.167	28.8%
Bedheight	.254	43.8%

Fig. 4.7: Effect of various experimental (input) parameters on adsorption efficiency

4.6. Modeling of the Adsorptive Removal of Fluoride by Response Surface Methodology (RSM): A Fitting Process Model

4.6.1. Fitting of RSM Model

Response surface methodology (RSM) has been well acknowledged for developing, improving and optimizing the complex processes and to appraise the magnitude of various operational variables involved within the processes (Chowdhury and Saha, 2013; Roy *et al*., 2014). The most successful central composite design (CCD) in RSM was used for a set of three independent variables (initial fluoride concentration, flow rate, and bed height) to investigate their influence on the breakthrough time for removal of fluoride by continuous CIHFO packed fixed–bed column operation. The experimental conditions allied with these chosen independent variables with their units and notations are mentioned in **Table 4.5**.

Table 4.5: Independent variables and their levels employed in CCD

Variables	**Units**	**Notations**	**Level of Variables**	
			Low	**High**
Initial fluoride concentration	**(mg.L^{-1})**	A	3.83	8.85
Flow rate	**(mL.min^{-1})**	B	1	3
Bed Height	**(cm)**	C	6	14

"Design–Expert" software (version 7.0.3 Wiley. Ink) has been used for 2^3 full factorial CCD. As per this design, a total of 20 experiments in a duplicate have been employed to the CCD matrix as per **Table 4.6**. For validation of model, the actual responses have been fitted with existing linear, two factor interactions (2FI), cubic and quadratic model by CCD. On the basis of scores obtained from the sequential model sum of squares (**Table 4.7**), all these models have been evaluated and it has been observed that the quadratic model achieved the highest score.

The larger magnitude of F (590.41) and smaller value of p (< 0.0001) indicated the high significance of this model, and henceforth, the quadratic model has been considered and selected to continue the progress. Assessment of the adequacy and significance of this quadratic model can be further continued using the analysis of variance (ANOVA). The evidences be Fisher variation ratio (*F*–value), probability value (*p*–value), Lack of Fit, coefficient of determination *R*–squared (R_d^2), adjusted *R*–squared (R_{Adj}^2), predicted *R*–squared (R_{pred}^2) and adequate precision. Adequate precision is a signal to–noise ratio, which compares the range of the predicted values at the design points to the average prediction error. The ratios greater than 4 indicate adequate model discrimination. R_{Adj}^2 and R_{pred}^2 are measurements of the amount of variation around the mean and newly explained data, respectively. The *p*–value represents the degree of significance of each variable while *F*–value is a statistically valid measure of how well the factors describe the variation in the data about its mean (Abdollahi *et al*., 2012; Kumar and Phanikumar, 2013; Roy *et al*., 2014). The outcomes associated with the validation of quadratic model by ANOVA provide evidences such as high *F*–value (1166.04), very low *p*–value (< 0.0001), non–significant lack of fit (1.29), as well as high values for coefficient of *R*–squared (R_d^2 = 0.9988), adjusted *R*–squared (R_{Adj}^2 = 0.9980), predicted *R*–squared (R_{pred}^2= 0.9961) and the adequate precision (123.47).

Table 4.6: CCD for three used independent variables and the observed response (breakthrough time: min) for Fluoride adsorption

Standard order	**Run order**	**Factor 1**	**Factor 2**	**Factor 3**	**Response**
		A:Initial Fluoride concentration	**B:Flow rate**	**C:Bed Height**	**Breakthrough time**
		($mg.L^{-1}$)	**($mL.min^{-1}$)**	**(cm)**	**(min)**
4	1	5.13	1	6	2500
10	2	5.13	1	8	5000
14	3	5.13	1	10	7000
12	4	5.13	1	12	9000
20	5	5.13	1	14	11000
5	6	3.83	1	6	8250
2	7	3.83	1	8	11000
16	8	3.83	1	10	13750
19	9	3.83	1	12	16500
11	10	3.83	1	14	19000
17	11	8.85	1	6	2750
15	12	8.85	1	8	4250
18	13	8.85	1	10	5500
3	14	8.85	1	12	6750
8	15	8.85	1	14	8000
9	16	5.13	2	10	6250
13	17	3.83	2	10	12500
7	18	5.13	3	10	5250
1	19	3.83	3	10	10750
6	20	3.83	3	10	11000

Table 4.7: Sequential model sum of squares

Source	**Sum of squares**	***df***	**Mean square**	***F* value**	***p* value, Prob >*F***	
Mean vs Total	1548800000	1	19244865.7			
Linear vs Mean	272818887	3	983850.9	15.0187	< 0.0001	Suggested
2FI vs Linear	26330977.39	2	139876.3	2.61256	0.1086	Aliased
Quadratic vs 2FI	70114695.76	3	89980.5	590.408	< 0.0001	Aliased
Cubic vs Quadratic	358617.1838	4	32.4	8.16920	0.0090	Aliased
Residual	76822.67772	7	31.8			
Total	1918500000	20	1144315.5			

Moreover, Figure 4.8 shows the actual values versus predicted values of the Fluoride adsorption obtained from CIHFO packed fixed bed column operation that ensured an excellent agreement between the actual and predicted values. As observed, the validity (significance and adequacy) of the model was confirmed by the rational evidences. The empirical relationships relating the breakthrough time to the tested independent variables expressed in terms of unit less regression coefficient by the selected quadratic model is given by the following equation:

Breakthrough time = $3406.50 - 2999.47\,A - 332.70\,B + 3853.08\,C + 1126.28\,AB - 1329.17\,AC + 6078.87A^2 - 147.08\,B^2 - 190.48\,C^2$

Where A (initial fluoride concentration), B (flow rate) and C (bed height) are in coded factors.

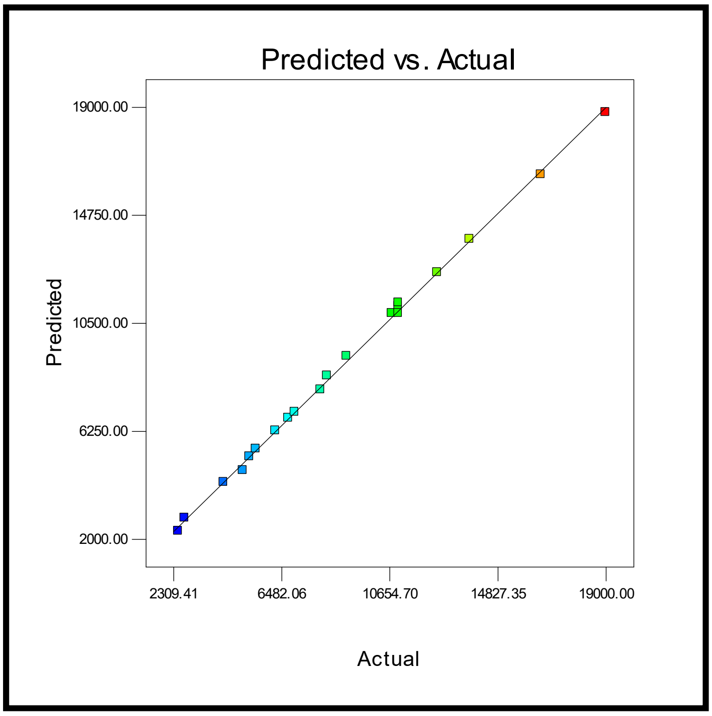


Fig. 4.8: Plot of actual response versus predicted response for CIHFO packed fixed bed column operation

Table 4.8 represented a regression analysis of the model equation. It has shown that the interaction effects of main variables as well as in-between of initial fluoride concentration and bed height were worth mentioning; whereas the square effects of flow rate and bed height acquired less attention. *p*–value greater than 0.1000 made the model term insignificant.

Table 4.8: Regression analysis of CCD

Model terms	Coefficient estimate	Standard error	*F* value	*p* value, Prob >*F*
Intercept	3406.50	213.88	1166.04	< 0.0001
A-Concentration	– 2999.48	247.01	147.46	< 0.0001
B-Flow rate	– 332.70	218.84	2.31	0.1566
C-Bed height	3853.08	73.94	2715.22	< 0.0001
AB	1126.28	256.10	19.34	0.0011
AC	– 1329.17	85.72	240.44	< 0.0001
A^2	6078.87	144.55	1768.64	< 0.0001
B^2	– 147.08	159.29	0.85	0.3756
C^2	– 190.48	122.80	2.41	0.1492

4.6.2. Interaction in-between the Independent Variables

4.6.2.1. Contour Plot

Fig.4.9 graphically explains the combined effect of initial fluoride concentration and flow rate on breakthrough time. In both cases, the breakthrough time has been shown declining pattern within the experimental range. Such performance can be elucidated in such a way that CIHFO adsorbent containing limited number of active binding sites has been saturated at a certain fluoride concentration (Roy *et al.*, 2014). When initial fluoride concentration is more, the active sites of adsorbent become more quickly saturated and hence breakthrough time is decreased. Similarly, at higher flow rates, the adsorption capacity was declined due to insufficient residence time of the solute in the column and diffusion of the solute into the pores of the adsorbent. Henceforth, leaving the fixed bed column before equilibrium has been reached with resultant earlier breakthrough time (Chowdhury *et al.*, 2013; Roy *et al.*, 2014, 2013b).

Fig.4.10 illustrates the interactive outcome of initial concentration and bed height on the breakthrough time. From the contour pattern it has been noticed that within the experimental range, the response function noted as the breakthrough time decreased with higher initial fluoride concentration but increased sequentially with rise of bed height. Such trend might be endorsed to the fact that enhancement of bed heights ensure availability of a large number of active binding sites of adsorbent for fluoride ions as a result, the fluoride ions gets enough time to contact with the adsorbent resulting in delayed breakthrough time. But higher fluoride concentration in turn exhaust the purifying CIHFO packed column bed more rapidly(Chowdhury *et al.*, 2013; Roy *et al.*, 2013b, 2014).

Whereas Fig**.4.11** shows the mutual intervention of flow rate and bed height upon the breakthrough time of CIHFO packed fixed bed column operation for fluoride adsorption. The interactive consequence of flow rate and bed height has a notable influence on the breakthrough time. It was observed from the contour pattern that the breakthrough time decreases with increasing flow rate at the same time as it increases with increasing bed height. Such breakthrough pattern can be explained in terms of short effective residence time of the fluoride in the CIHFO packed column bed as well as the availability of active binding sites of adsorbent, as already mentioned.

4.6.2.2. Perturbation Plot

The effects of independent variables like initial fluoride concentration (A) (mg.L^{-1}), flow rate variation (B) (mL.min^{-1}) and bed height (C) (cm) on the breakthrough time of CIHFO packed fixed bed column operation have been assessed. The individual effect of independent variables graphically presented in the perturbation plot. Generally, a perturbation plot does not exhibit the consequence of interactions and it is more likely to one factor–at–a–time experimentation. The perturbation plot for present fixed bed column operation as expressed in **Fig. 4.12** helps to judge against the outcome of all independent variables at a particular point in the design space. The response is plotted by changing only one factor over its range while holding the other factors constant. A steep slope or curvature resulted for a particular factor indicate the sensitivity of response of that factor mostly (Chattoraj *et al.*, 2014; Kumar and Phanikumar, 2013; Roy *et al.*, 2014). A relatively flat line shows insensitivity to change in that particular factor. The present result revealed that breakthrough time is more sensitive to initial fluoride concentration followed by bed height and flow rate variation.

4.6.3. Utilization of Desirability Functions for Optimization

The possible goals in the Design Expert software's are to maximize, minimize, target, in range and set to an exact value (factors only). In numerical optimization, the desired goal was preferred for each variable and response from menu (Chowdhury *et al.*, 2013; Kumar and Phanikumar, 2013; Roy *et* *al*., 2014). **Fig. 4.13** expressed as bar plot revealed the desirability values for optimization procedure in which the criterion was set as “maximum” for bed height, “minimum” for initial fluoride concentration, “in range” for flow rate. The purpose of the study was to analyse economically viable optimal conditions. The objective of this process was to find the maximum breakthrough time by utilizing the set of criteria. In this, the desirability value ranges from 0.987 to 1 for individual variables and 0.9871 for combination of all the variables. In the response surface changes, the best local maximum breakthrough time was found to be 18788.1 min when the independent variables retained at bed height 14cm, 3.0 (mg.L^{-1}) of initial fluoride concentrations and 1.0 mL.min^{-1} of flow rate at maximum desirability value of 0.987. Finally, for their validation, duplicate confirmatory column experiments were conducted using the optimal conditions. The experimental value, which coincides well with optimized result obtained from CCD, suggests that the CIHFO might be an effective and cost-effective adsorbent that can be effectively applicable for the treatment of bed height enriched drinking water.

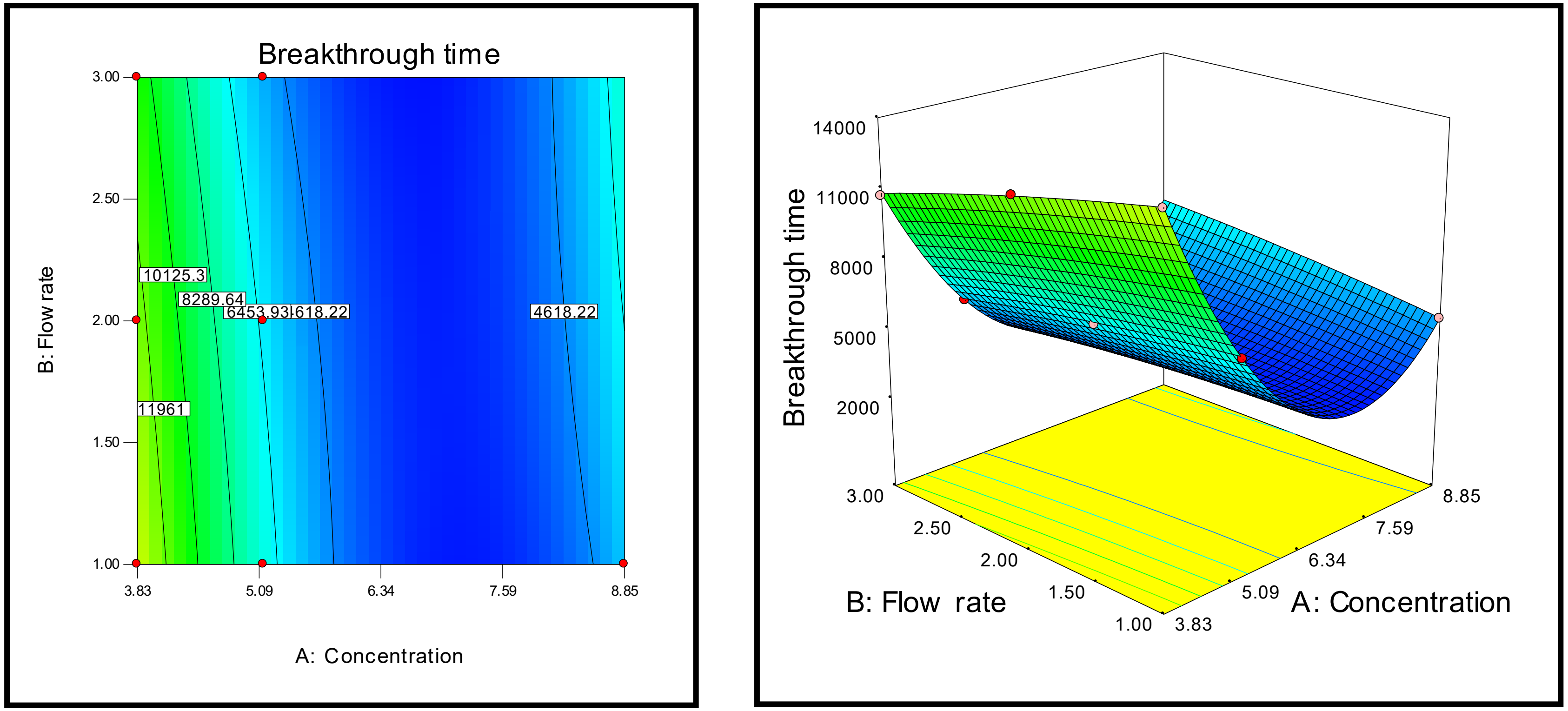


Fig. 4.9a: Two–dimensional contour plot

Fig. 4.9b: Three–dimensional response surface plot

Fig. 4.9: Plots showing the combined effect of initial fluoride concentration and flow rate on the breakthrough time for CIHFO packed fixed bed column operation (Bed Height 10 cm)

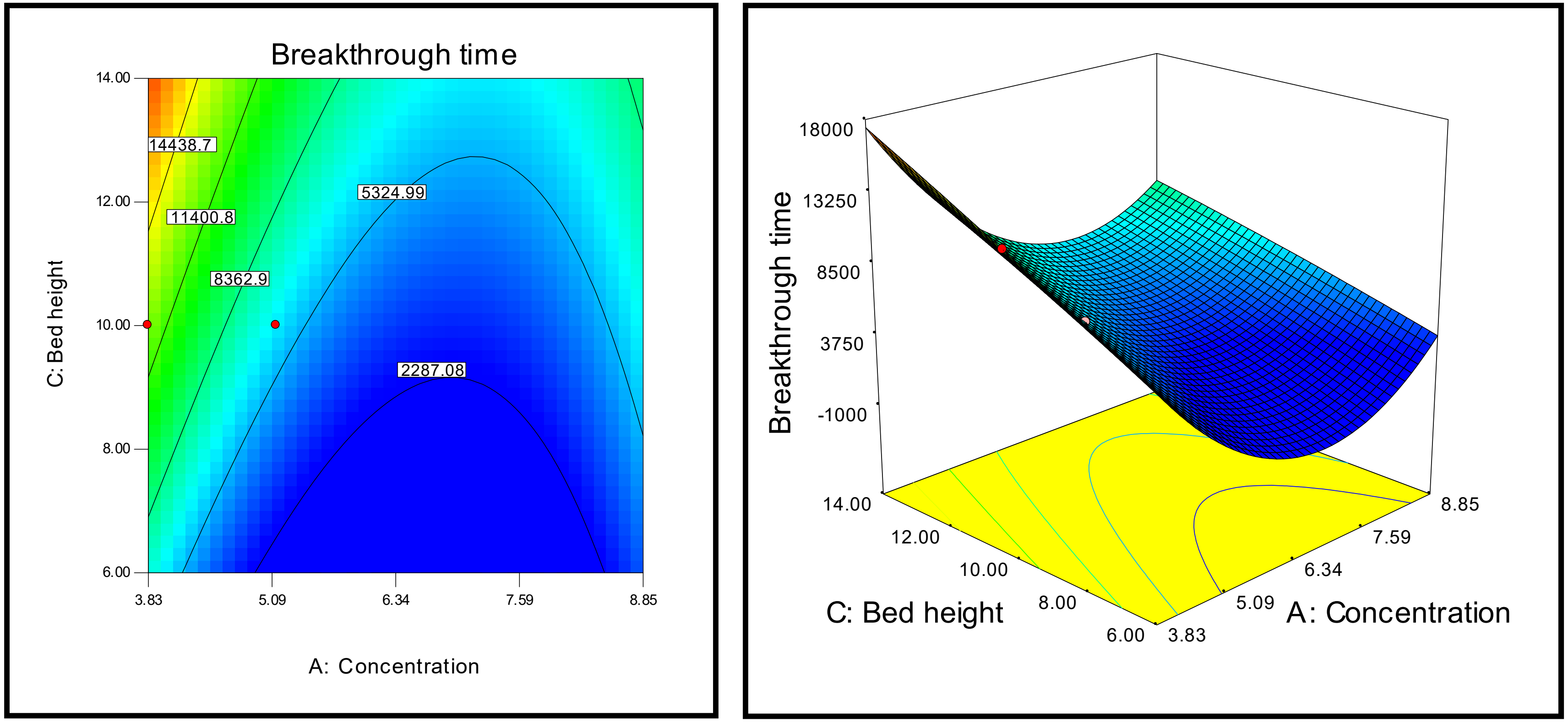


Fig. 4.10a: Two–dimensional contour plot

Fig. 4.10b: Three–dimensional response surface plot

Fig. 4.10: Plots showing the combined effect of initial fluoride concentration and Bed height variation on the breakthrough time for CIHFO packed fixed bed column operation (Flow rate 1.0 mL.min^{-1})

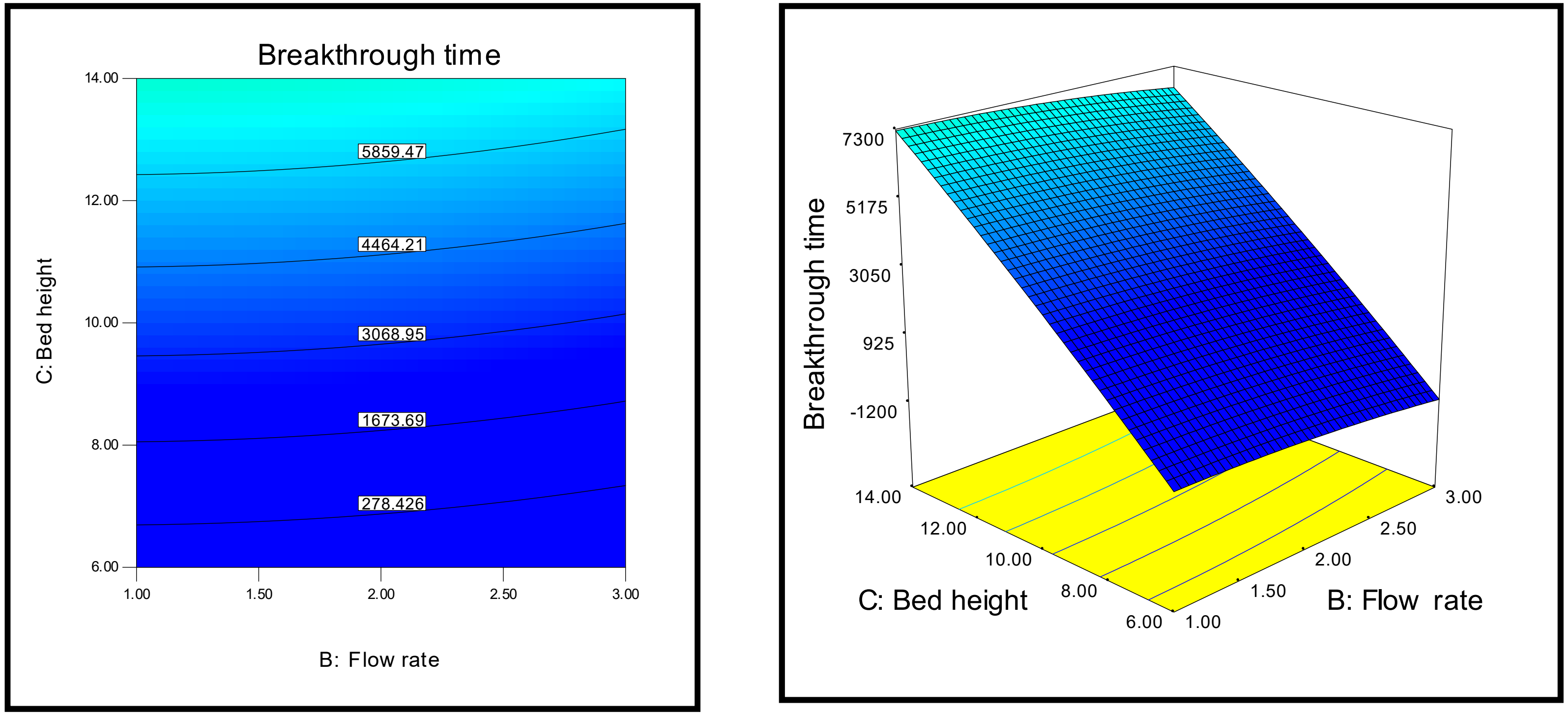


Fig. 4.11a: Two–dimensional contour plot

Fig. 4.11b: Three–dimensional response surface plot

Fig. 4.11: Plots showing the combined effect of Flow rate and Bed height variation on the breakthrough time for CIHFO packed fixed bed column operation (initial fluoride concentration 5.0 mg.L^{-1})

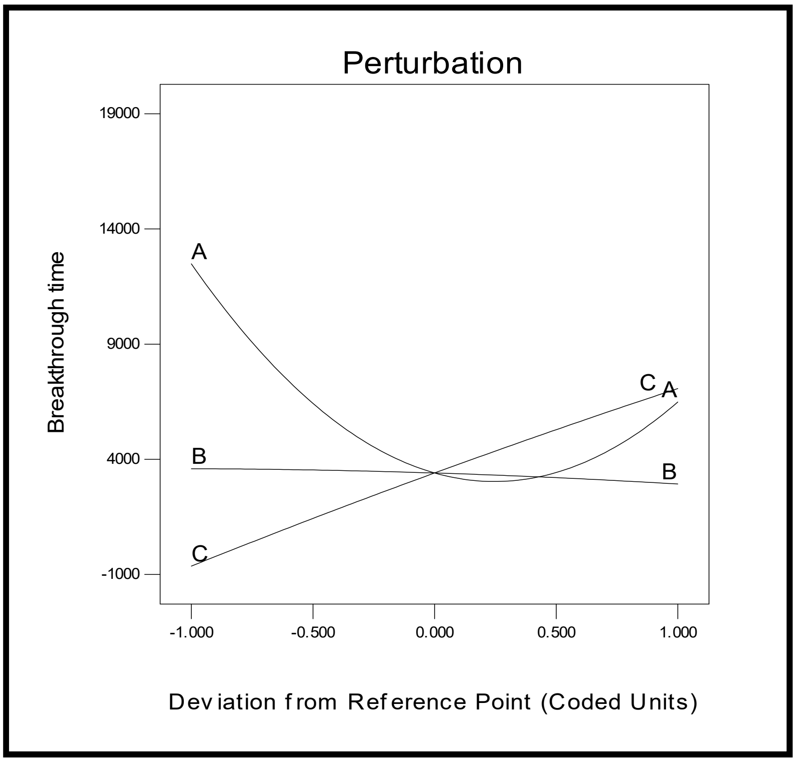


Fig. 4.12: Perturbation plot showing the effect of the tested variables on breakthrough time

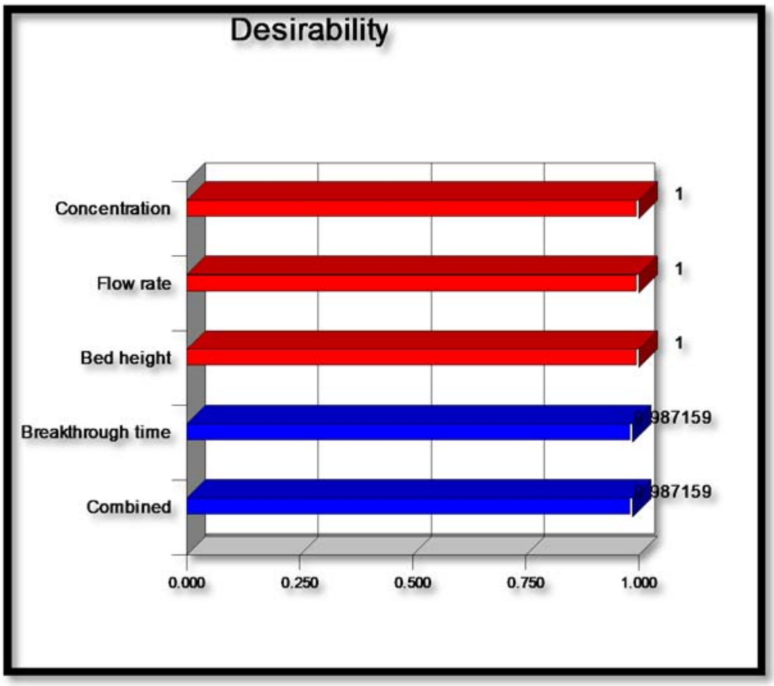


Fig. 4.13: Bar plot for optimization procedure

4.7. Performance Indicator

Performances of the fixed-bed columns are basically indicated by the number of bed volumes (BVs) treated before the breakthrough point. For a fixed bed mass, there is a direct relationship between the adsorption performance and the number of BVs treated before the breakthrough (Bhaumik *et al.*, 2013; Ghosh *et al.*, 2015). The latter can be calculated by the Eq.4.11.

$$\boldsymbol{BV} = \frac{\boldsymbol{Volume\ of\ water\ treated\ at\ breakthrough\ point\ (L)}}{\boldsymbol{Volume\ of\ adsorbent\ bed\ (L)}} \qquad \textit{\textbf{(Eq. 4.11)}}$$

Higher is the number of BV before the breakthrough point, the better will be the column performances. The adsorbents exhaustion rate (AER) also indicates the column performance efficiency. Value of the AER, which reflects the goodness of the bed performances, can be calculated by the Eq.4.12.

$$\boldsymbol{AER} = \frac{\boldsymbol{Mass\ of\ adsorbent\ (g)}}{\boldsymbol{Volume\ of\ water\ treated\ (L)}} \qquad \textit{\textbf{(Eq. 4.12)}}$$

Values of BV and AER calculated from the experimental data for the present case are shown in **Table-4.9**. It was observed that higher treated BV value has been increased with escalating fixed-bed height while processed BV number significantly has shown increasing trend with raise in the rate of effluent discharge and also with increase of initial fluoride concentration (C_i) in feed water. Again, the decrease of AER should indicate the enhancement of fixed-bed columns performances.

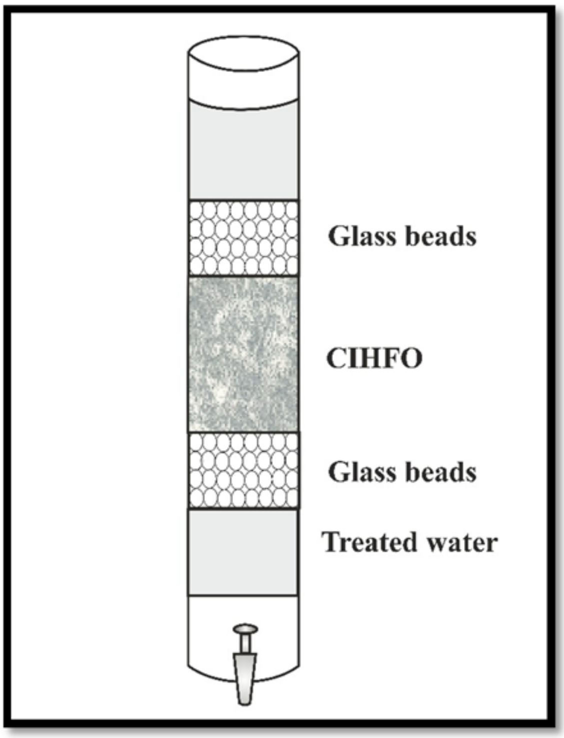
As the AER value (Table 4.9) reduced with increasing fixed-bed height, lowering of effluent discharge rate and reduction of C_i for the present system, it can be said that the CIHFO fixed-bed column displayed the well performance of fluoride removal.

Table 4.9: The Column performance indicators at Different Fixed Bed-Height, effluent discharge rate and initial fluoride concentration

Performance indicators									
Parameter	**Bed height (cm)**			**Effluent rate (mL. min^{-1})**			**Input F$^-$ concentration (mg.L^{-1})**		
Processed BV Number	**6.0**	**10.0**	**14.0**	**1.0**	**2.0**	**3.0**	**3.0**	**5.0**	**9.0**
	150.48	174.53	167.64	174.53	156.47	132.40	343.04	174.53	138.42
AER (×10^3) (mg.L^{-1})	7.07	4.93	4.57	4.9	5.50	6.50	2.51	4.9	6.22

4.8. Proposed Design of "Prototype" Filter Unit

Considering the results assembled by interpretation of designing parameters, Thomas kinetics model, BDST model, Artificial neural networking model and Central composite design (RSM) it was found that 'maximum' bed height, minimum fluoride concentration and moderate flow rate were favourable for CIHFO packed column operation for fluoride removal purpose. For fixed bed column adsorption study, the designing parameters, contour plot, perturbation Plot and desirability pattern are very useful tools for predicting the ultimate design of“Prototype” filter unit. These final outcomes have been considered for predicting the design of “Prototype” filter unit as single stage adsorber model. Designing of such filter unit is essential to extrapolate the experimental finding of fixed bed column operation to a large scale one which in turn could be applicable for designing a large scale water treatment setup. A schematic diagram of the Prototype” filter unit model is given below.



Scheme 4.4: Schematic diagram of proposed prototype filter unit

4.9. Conclusion

- ↔ Experimental studies on different parameters likely variation of bed height, flow rate and initial fluoride concentration involved in CIHFO packed fixed column operation revealed that the fluoride removal performances of CIHFO packed fixed-bed column was involved directly in proportional relation with the increment of both bed height and initial fluoride concentration but inversely proportional with increasing rate of effluent flow rate.

- ↔ R^2 values obtained from linear regression analysis of Thomas model have been ranged in between 0.90-0.96 satisfying good linear fitting of Thomas model with experimental data. Analysing the modeling data it can be said that lower fluoride concentration, lower flow rate and maximum bed height have great influence over better adsorption performance of CIHFO packed column for fluoride.

- ↔ High N_{BD} (3847.5 mg.cm^{-3}) resulted from the analysis of bed height variation breakthrough curves with BDST model suggested that CIHFO could be an efficient material for treatment of fluoride enriched groundwater. Column performance indicator also recommended that the CIHFO packed fixed-bed column could be considered as an effective medium for fluoride removal for higher fixed-bed height, slower rate of effluent discharge and lower initial fluoride concentration.

- ↔ For evaluation of CIHFO packed fixed bed column operation, ANN has been applied and as per the importance analysis of the developed ANN it was found that the initial fluoride concentration was acted as the key variable for the CIHFO packed fixed bed column operation followed by bed height and flow rate variation.

↔ Application of CCD to examine the interacting effects of different operating variables likely bed height (6.0-14.0 cm); flow rate (1.0–3.0 mL.min^{-1}) and initial fluoride concentration (3.0-9.0 mg.L^{-1}) upon breakthrough time for optimization fluoride adsorption over CIHFO packed fixed bed column operation. R^2 value of 0.999, model F–value of 1166.40 and its low p–value (< 0.0001) along with adequate precision (123.470) indicated the fitness of the response surface quadratic model developed in the present study.

↔ Desirability values optimized the operation criteria as "maximum" for bed height, "minimum" for initial fluoride concentration, "in range" for flow rate. The purpose of the study was to analyse economically viable optimal conditions. Henceforth, in this, the desirability value ranges from 0.987 to 1 for individual variables and 0.9871 for combination of all the variables. In the response surface changes, the best local maximum breakthrough time was found to be 18788.1 min when the independent variables kept at bed height 14cm, 3.0 (mg.L^{-1}) of initial fluoride concentration and 1.0 mL.min^{-1} of flow rate at maximum desirability value of 0.987.

↔ Overall, based on different modeling interpretations, an attempt has been made to design of "prototype" filter unit with an aim that it can be effectively utilise in domestic household for fluoride removal. It can be concluded in that way that the data presented in this experimental process can be further extrapolated for designing and establishing any efficient fluoride removal plan while treating the fluoride enriched groundwater.