# 4.1 INTRODUCTION

Literature study indicated that most of the reports on fluoride adsorption are related to batch method and only a few literature have been reported in fixed bed column systems which are more relevant for large scale and real operating system of the fluoride contaminated water [Nur *et al.* (2014), Bhatnagar *et al.* (2011), Loganathan *et al*. (2013)]. The information collected from the batch experimentation is not sufficient to apply to the treatment plants (i.e. column operations). Thus, for the industrial application of fluoride removal by adsorption, column studies thought to be very useful. Furthermore, the regeneration and desorption studies were also conducted to reuse the adsorbent which makes it economical (reduces operational costs). This chapter concern with the adsorptive remediation of fluoride by rGO/ZrO$_2$ nanocomposite by fixed bed up flow continuous column method. Moreover, the effect of various operating conditions on the column performance was also evaluated along with regeneration study of the column.

## 4.2 MATERIAL AND METHOD

The column adsorption studies were performed in up-flow fixed-bed column made up of graduated borosilicate glass column (length 30cm and internal diameter 1 cm). The column was packed with required amount of rGO/ZrO$_2$ for the removal of fluoride from water. The column was operated at three different bed height i.e. 2.5, 5, 7.5 cm and flow rates 1.66, 3.32, and 4.98 mL/min. In addition to it the column experiments were also conducted at different fluoride concentrations (10. 15, and 25 mg/L). The effluent was collected from the upper end of the column at fixed time interval and the residual fluoride ion concentration was analyzed. The exhausted column was regenerated with the help of 10% NaOH solution by up-flow method. The regenerated column was used for the next cycle of adsorption-desorption and the efficiency of the column was tested up to three cycles.

## 4.3 RESULTS AND DISCUSSION

The column experiments were performed at laboratory scale to examine the potentiality of rGO/$ZrO_2$ for the fluoride removal. Various column parameters such as initial $F^-$ concentration, bed height, and flow rate were strongly influence the column performance and are discussed below. Different mathematical models i.e. Thomas, BDST, and Yoon–Nelson models were also applied to the experimental data to predict the breakthrough curves. In addition to it regeneration and reused studies of the exhausted column also carried out for the efficient utilization of the uptake capacity of the rGO/$ZrO_2$ adsorbent.

### 4.3.1 Effect of bed height

`The breakthrough curve at different bed heights i.e. 2.5, 5 and 7.5 cm was evaluated and are represented in Figure 4.1. The breakthrough performance at variable bed height was studied at the constant initial concentration of fluoride (25 mg/L) and flow rate (1.66 mL/min). The parameters were calculated from the breakthrough curves and are given in Table 4.1. The findings showed that with an increase in bed height the $V_{eff}$ i.e. treated volume of the water also increased. This statement can be accounted by the fact that as the bed height increases the axial dispersion in mass transfer decreases thus the diffusion of adsorbate onto the adsorbent will increase. Therefore, the adsorbate ion spent sufficient time in the column to get diffused into the adsorbent and large volume of water can be treated.

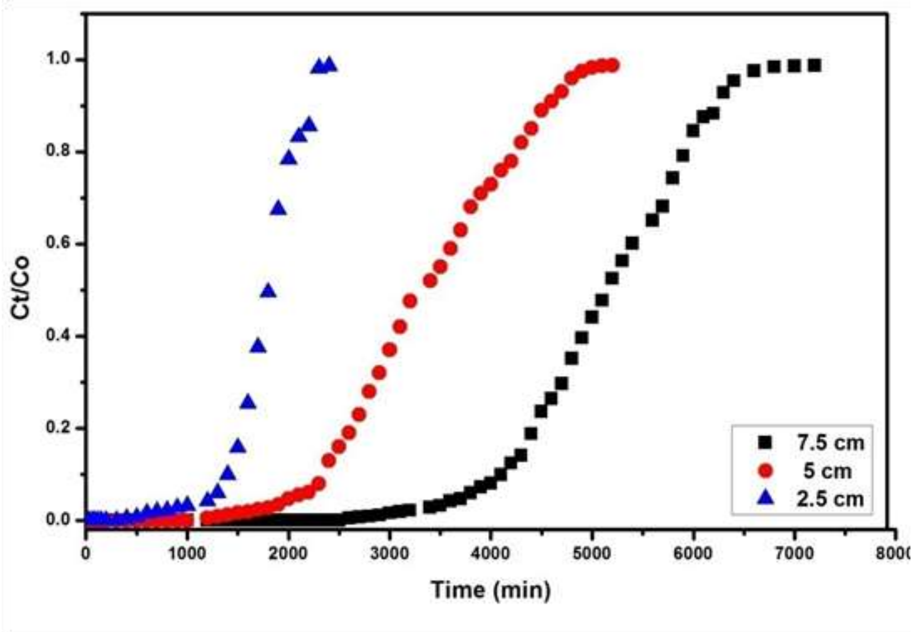


**Figure 4.1. Breakthrough curve for fluoride adsorption at different bed heights**

As a result the uptake capacity was also increased with the increase in bed height. Highest adsorption capacity i.e. 45.7 mg/g of rGO/$ZrO_2$ for fluoride was found at a maximum bed height of 7.5 cm. The uptake capacity also increased as the column bed become progressively longer because the longer bed have more adsorbent which contain the large number of binding active sites than that of column of smaller bed height. It was also revealed that with the increase in bed height the breakthrough and exhaustion time both increased. A similar behavior was also reported by Hasan et al. for the adsorptive remediation of selenium in a fixed-bed column by wheat [Hasan *et al.* (2009)]. The breakthrough time is the important factor of the fixed-bed column operations. Therefore it can be concluded that large volume of effluent can be treated by employing maximum bed height. Whereas, lower breakthrough time was obtained with smaller bed height as it gets saturate very early.

### 4.3.2 Effect of flow rate

In order to investigate the effect of flow rates on the adsorption of fluoride by rGO/$ZrO_2$, the experiments were conducted at constant fluoride concentration of 25 mg/L and bed height of 7.5 cm by varying the flow rates from 1.66 - 4.98 mL/min. The breakthrough curve thus obtained is represented in Figure 4.2.

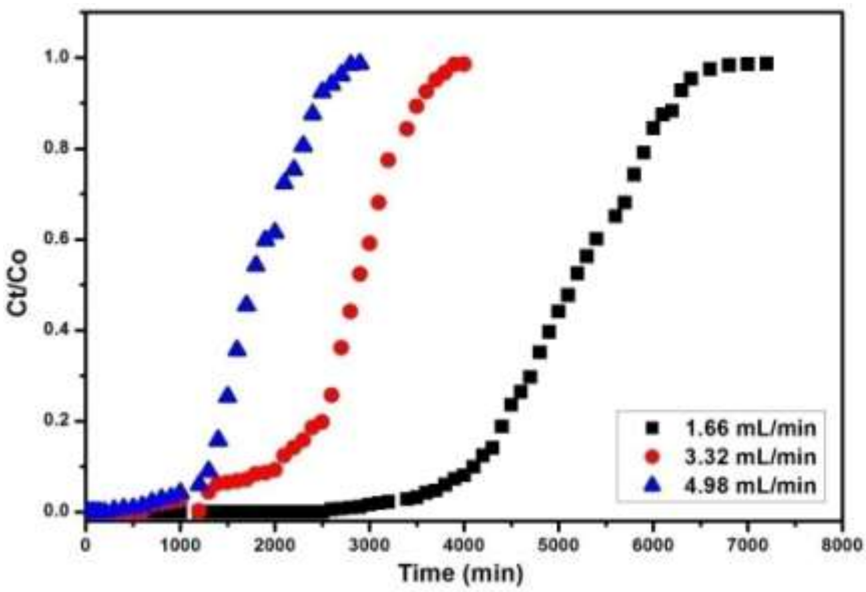


**Figure 4.2. Breakthrough curve for fluoride adsorption at different flow rates**

Different parameters i.e. treated volume, breakthrough times, exhaustion times and adsorption capacity of fluoride obtained from breakthrough curve are listed in Table 4.1**.** It was observed that breakthrough time, exhaustion time and uptake capacity all are showing decreasing trend with increases in flow rate except the treated volume which increased with increase in flow rate. When the flow rate is lower then the adsorbent stayed for longer duration in the column and hence; it got enough time to adsorb on the adsorbent. Whereas at higher flow rates resident time of the adsorbent become low, thus metal ions did not interact with the adsorbent for sufficient time to bind strongly [Ranjan *et al*. (2009)]. On the other hand, the uptake capacity of the adsorbent also reduced because the residence time of the adsorbate shortened at a higher flow rate so that solute left the column before the establishment of the equilibrium. The similar results are also reported by many researchers in the literature [Ahmad and Hameed (2010)]. Consequently, it can be concluded that the column operated at lower flow rate resulted in high uptake capacity because it leads to the greater residence time of the adsorbate in the column [Vijayaraghavan *et al.* (2004)]. This study also indicated that when column operated at a higher flow rate, it exhausted very early which thus adsorption capacity of the adsorbent utilized improperly.

### 4.3.3 Effect of fluoride concentration

The effect of low rate on the breakthrough curve investigated at three fluoride concentration (10, 15 and 25 mg/L) by keeping bed height (7.5 cm) and flow rate (1.66 mL/min) constant (Figure 4.3). The breakthrough time, exhaustion times, treated volume and adsorption capacity at different flow rate were determined and given in Table 4.1. It was found that both breakthrough as well as exhaustion time both, increased with increasing fluoride concentration. As can be seen in the Table 4.**1** that the treated volume of effluent lowered with increase in fluoride concentration hence; extended breakthrough obtained at lower fluoride concentration i.e. the large volume of water can be treated at low inlet adsorbate concentration. This fact can be explained as that at lower metal concentration the concentration gradient will also lower thus the transport of metal ions become slower due to decreased diffusion coefficient thus increased the breakthrough time. At the higher metal concentration breakthrough time and exhaustion time decreased due to rapid saturation of the adsorbent bed which leads to shorter breakthrough and exhaustion time. It was also found that the uptake capacity was increased with increased in fluoride concentration.

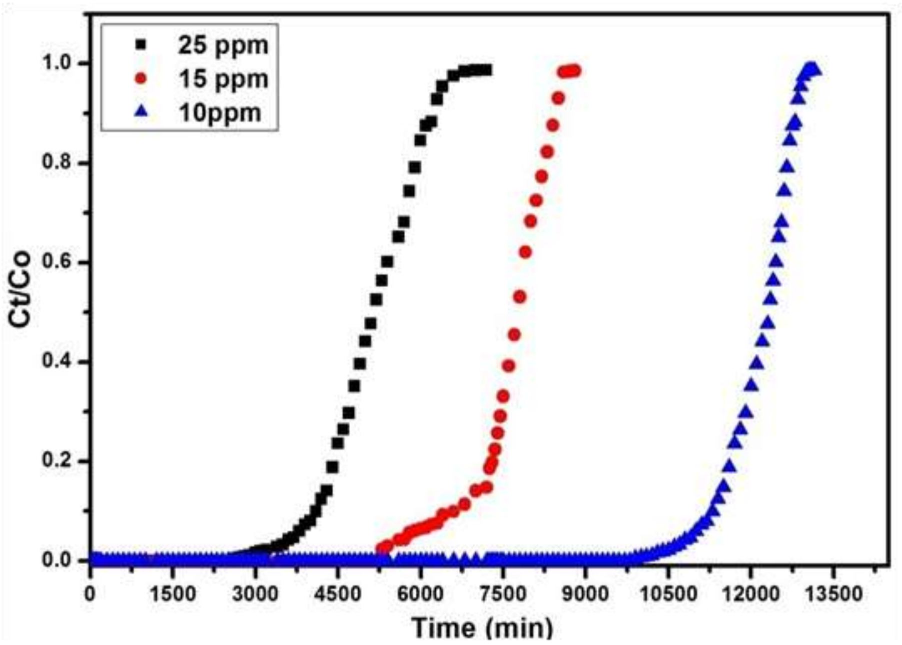


**Figure 4.3. Breakthrough curve for fluoride adsorption at different fluoride concentration**

The column showed superior adsorption performance at high adsorbate concentration because high concentration is the driving force for adsorption which arouse due to the concentration difference between the metal ion on the adsorbent and the metal ion in the solution which actually was higher at higher metal ion concentration [Aksu and Gönen (2004), Ranjan *et al.* (2009)]

**Table 4.1. Adsorption data for fixed-bed rGO/ZrO$_2$ column for fluoride adsorption at different process parameters.**

| Process parameters | Veff (mL) | $t_b$ (min) | $t_e$ (min) | q (mg/g) |
|---|---|---|---|---|
| **Bed height Z (cm) (conditions : Co= 25 mg/L, Q = 1 mL/min** | | | | |
| 2.5 | 3486 | 900 | 2100 | 31.1 |
| 5 | 8300 | 2500 | 5000 | 42.8 |
| 7.5 | 11952 | 3600 | 7200 | 44.7 |
| **Flow rate Q (mL/min) (conditions : Co= 25 mg/L, Z = 3 cm** | | | | |
| 1.66 | 11952 | 3600 | 7200 | 44.7 |
| 3.32 | 14276 | 1300 | 4300 | 32.2 |
| 4.98 | 14442 | 800 | 2900 | 15.5 |
| **Initial fluoride concentration (Z= 3 cm), Q = 1 mL/min)** | | | | |
| 10 | 15438 | 6400 | 9300 | 17.5 |
| 15 | 13612 | 5200 | 8200 | 43.1 |
| 25 | 11952 | 3600 | 7200 | 44.7 |

**4.3.4 Application of bed depth service time model (BDST)**

The graph of service time versus bed height at two different flow rates 1.66 mL/min and 3.32 mL/min at fluoride concentration of 25 mg/L corresponding to the BDST model is presented in Figure 4.4 The parameters related to BDST model (rate constant ($k_a$), sorption capacity ($N_0$), and critical bed depth ($Z_0$)) are given in Table 2. The validity of BDST model was confirmed by high values of correlation coefficient ($R^2$) thus this model established that the service time varies linearly with the bed height of the column for this adsorption system. It is clearly seen from the Table 4.2 that $k_a$ i.e. rate constant values which were determined from the intercept of the BDST plots and found to be 0.00017and 0.00019 L/mg/min for the corresponding flow rate of 1.66 mL/min and 3.32 mL/min respectively. The term $k_a$ can be explained as the rate of the transfer of a metal ion from the liquid phase to solid. Results depicted that the value of $k_a$ influenced by the flow rate i.e. it increased with increase in effluent flow rate. Consequently, it can be concluded that initially, the system kinetics follow external mass transfer. Thus, for the large $k_a$ value shorter bed is needed whereas, the longer bed is required for the respective small value of $k_a$ in order to avoid breakthrough. The value of adsorption capacity ($N_0$) was also calculated and is given in Table 4.2.

The values of $N_0$ was found to be 71500 mg/L and 69930 mg/L at the flow rate of 1.66 mL/min and 3.32 mg/L respectively. The column capacity reduces with increase in flow rate in all cases. On the whole, the rate constant value and the column capacity both advocated that this is a highly efficient adsorption system for the fluoride removal by rGO/$ZrO_2$. Table 4.2 also contains the values of critical bed depth ($Z_0$) which was calculated for the flow rates of 1.66 mL/min and 3.32 mL/min which was found to be 0.56 cm and 1.12 cm respectively. Result displayed the value of $Z_0$ which gets increased with increase in flow rates which is in support of the finding of the breakthrough studies at the different flow rate that efficiency of the column decreased at a higher flow rate of effluent [Hasan *et al*. (2010)]. Another advantage of the BDST model involves the prediction of the slope of unknown flow rates by utilizing the known slope of the given flow rate. Therefore it is possible to design a new fixed bed column for new flow rate without further experimentation by simple modification in equation 2.3.4.4. For this adsorption system BDST model was applied for the two flow rates rate i.e. 1.66 mL/min and 3.32 mL/min and the obtained parameters are given in Table 4.3.

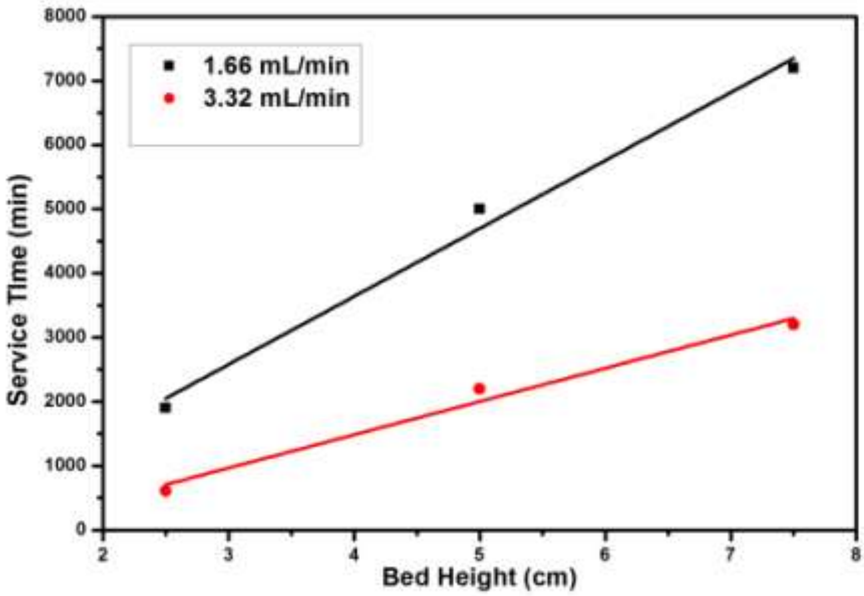


**Figure 4.4 Bed depth service time plot for fluoride adsorption onto rGO/$ZrO_2$ nanocomposite**

This modified equation of BDST was also applied to the new flow rate data so that we can compare the experimental and calculated values. Table showed that calculated and experimental values of slopes for the flow rate of 3.32 were in good harmony with each other. In addition, the intercept related to the slope was found to unchanged approximately as they supposed to remain constant with the variation of flow rates.

**Table 4.2. Bed depth service time (BDST) model parameters for the adsorption of fluoride.**

| Flow rate | $K_a$ (L/mg/min) | No (mg/L) | $Z_o$ (cm) |
|---|---|---|---|
| 1 mL/min | 0.00017 | 71550 | 0.56 |
| 3 mL/min | 0.00019 | 69903 | 1.12 |

**Table 4.3 Experimental and predicted BDST model equations for the adsorption of fluoride.**

| Flow rate | Analysis | Fitted Equation | $R^2$ |
|---|---|---|---|
| 1.66 mL/min | Experimental | Y=1060x-600 | 0.99 |
| 3.32 mL/min | Experimental | Y= 518x-586.6 | 0.98 |
| 3.32 mL/min | Predicted | Y=527x-586 | 0.99 |

### 4.3.5. Application of Thomas and Yoon–Nelson models

The equilibrium breakthrough data were also applied to the Thomas model at different fluoride concentration (10,15, and 25 mg/L) which can be represented as Figure 4.5 . The Results showed the plots was found to be highly linear at all mentioned fluoride concentration.

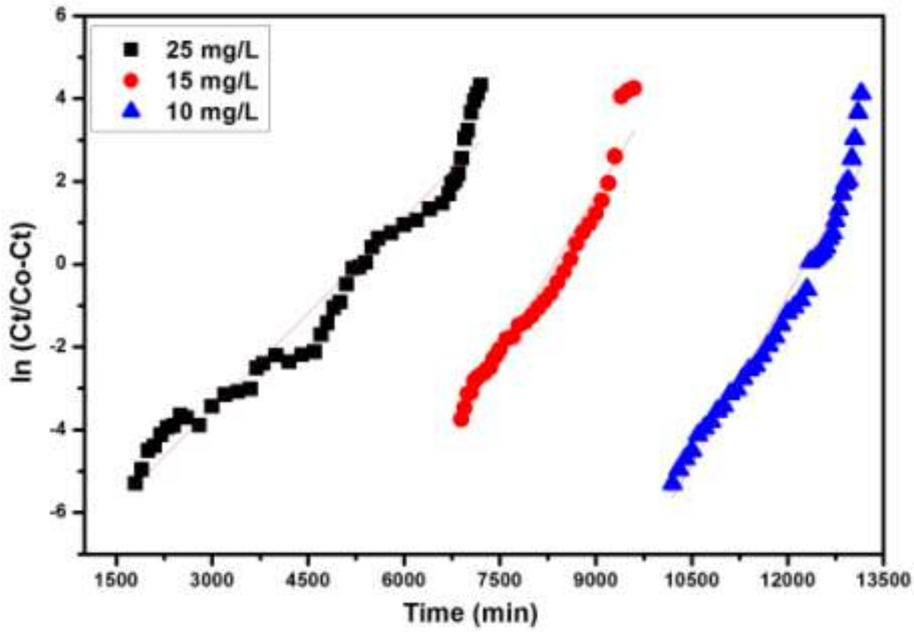


**Fig. 4.5. Adsorption curve according to Thomas model**

The Thomas parameters were calculated by slopes and intercepts of the linear plots of Thomas model which are given in Table 4.4**.** It was found that the uptake capacity predicted ($q_{Th}$) by the model was also increased with the increase in fluoride concentration as the experimental values of adsorption capacity. Further, the high value of regression coefficient ($R^2$) approved the validity of the Thomas model. Furthermore, the Yoon–Nelson model was also showed the good fit to the experimental data which was also supported by high values of $R^2$. Table 4.4 also contains the relevant parameters of this model. The value of Ʈ was determined at all fluoride concentrations from the plots which showed very close similarity with the experimental values. Thus, from the above discussion, the inference can be drawn that both the Thomas as well as Yoon-Nelson model well described the fluoride breakthrough model for column study.

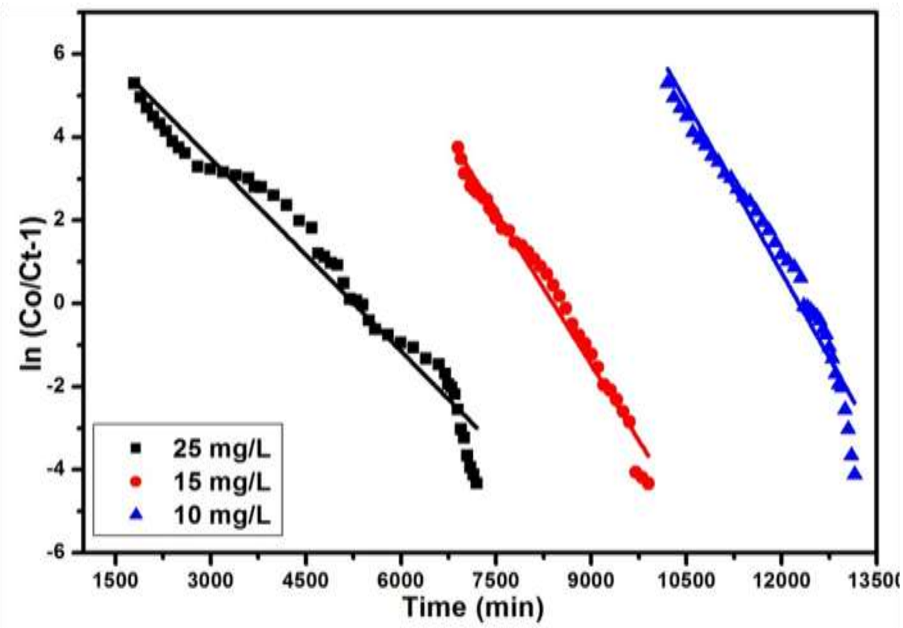


**Fig. 4.6. Adsorption model according to Yoon–Nelson model**

**Table 4.4. Parameters predicted from the Thomas and Yoon–Nelson models for the adsorption of fluoride at different fluoride concentrations.**

| | Thomas Model | | | Yoon Nelson Model | | | |
|---|---|---|---|---|---|---|---|
| **Fluoride conc. (mg/L)** | **$K_{th}$ (min$^{-1}$)** | **$q_{th}$ (mg/g)** | **$R^2$** | **$K_{YN}$ (L/min)** | **$\tau_{(exp)}$ (min)** | **$\tau_{(cal)}$ (min)** | **$R^2$** |
| 10 | 0.00025 | 17.2 | 0.96 | 0.0027 | 12350 | 12307 | 0.96 |
| 15 | 0.00016 | 42.7 | 0.96 | 0.0025 | 8600 | 8616 | 0.96 |
| 25 | 0.000056 | 45.6 | 0.99 | 0.0015 | 5400 | 5420 | 0.99 |

## 4.3.6 REGENERATION

The regeneration experiments of fluoride were done with 10% NaOH solution. The adsorbent was examined for the three adsorption-desorption cycle. For the three adsorption-desorption cycle, the breakthrough curves were plotted and are shown in Figure 4.6. Results showed that 10% NaOH provides about 97% elution efficiency which is shown in Table 4.5 along with other parameters. The breakthrough time reduces from 4200 to 1900 min from cycle I to III whereas, superb adsorption capacity was observed in all the three cycle with a slight reduction in adsorption capacity. The findings also revealed the good elution efficiencies (>95%) for this adsorption system for the three successive adsorption-desorption cycle. The elution time observed to be decreased from 270 min to 210 min with the successive progress of first elution cycle to the third. If the elution efficiencies found to be greater than >95% then ion exchange mechanism must involve in the adsorption process which is the another important conclusion of the regeneration study [Chen *et al.* (2013)]**.** Thus regeneration and reuse of the current adsorbent system provide the highly efficient way to treat fluoride containing water.

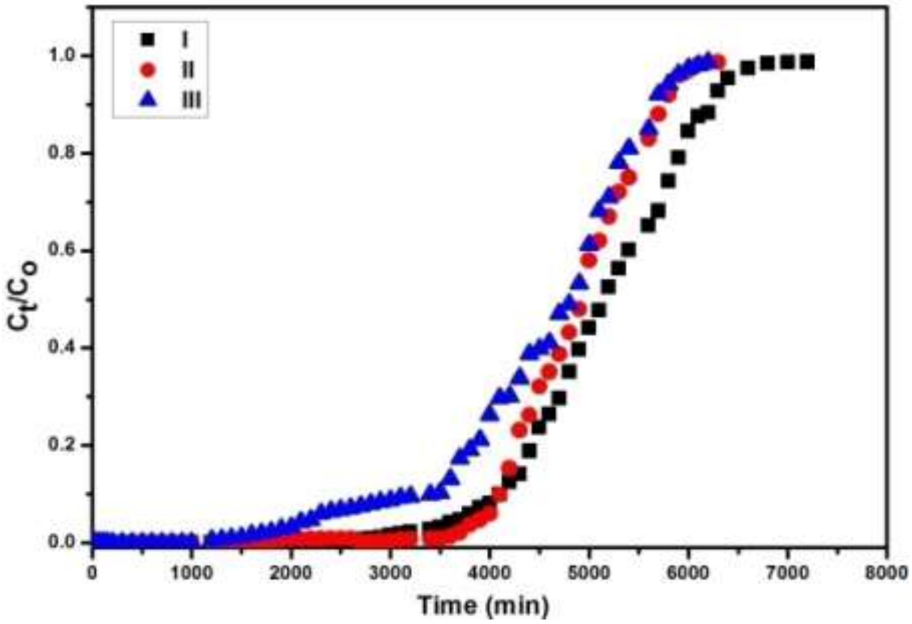


**Figure 4.7 Breakthrough curves for fluoride adsorption onto rGO/$ZrO_2$ during three adsorption-desorption cycles**

**Table 4.5. Adsorption process parameters for three sorption–desorption cycles of fluoride onto rGO/$ZrO_2$**

| Cycle | $V_{eff}$(mL) | $t_b$(min) | $t_e$(min) | q (mg/g) | Elution Time (min) | Elution Efficiency(%) |
|---|---|---|---|---|---|---|
| I | 11952 | 4200 | 7200 | 44.9 | 270 | 88.21 |
| II | 10790 | 2200 | 6600 | 43.7 | 220 | 94.83 |
| III | 9794 | 1900 | 5600 | 42.2 | 210 | 97.47 |

## 4.3.7 Adsorption column life factor

Since the adsorption performance shows as uniform reduction with the progress of cycle as a result the activity of the column can be determined as a function of the number of adsorption-desorption cycle. The life factor is the activity indicator of the adsorbent which can be predicted on the basis of important column parameter i.e. breakthrough time and column uptake capacity.

The life factor of the column was calculated and determined in terms of breakthrough time, using a linear regression equation [Hasan *et al.*(2009)]:

$$t_b = t_{b,i} + K_L n$$

Where $t_{b,i}$ represent the initial breakthrough time (min) and k stand for the corresponding life factor (min/cycle). The values of $t_{bi}$ and its corresponding life factor $k_L$ were calculated from the plot of $t_b$ and n (Figure 4.8), the relationships $t_b$ = 4533-300n was predicted. From these relationships, it was found that the column bed would be capable of avoiding the breakthrough time at t = 0 up to 15.11 cycle for $F^-$ removal.

Similarly, in order to calculate the life factor in terms of uptake capacity the following regression was used [Hasan *et al.* (2009)]:

$$q = q_i + K_L n$$

Where qi is the initial uptake capacity (mg/g), and $K_L$ represents the life factor (per cycle). The value of qi and $K_L$ were determined by the equation q=42.8-2n. From this equation, it was predicted that the column bed would be completely exhausted after 21.4 cycles. It was observed from above investigation that, the life factor calculated on the basis of breakthrough time was lesser as compare to predicted by the uptake capacity which implies that before becoming the uptake capacity zero, the breakthrough time became zero. Therefore, the number of cycle i.e. 15.11 predicted on the basis of breakthrough time would be valid for predicting the life factors.

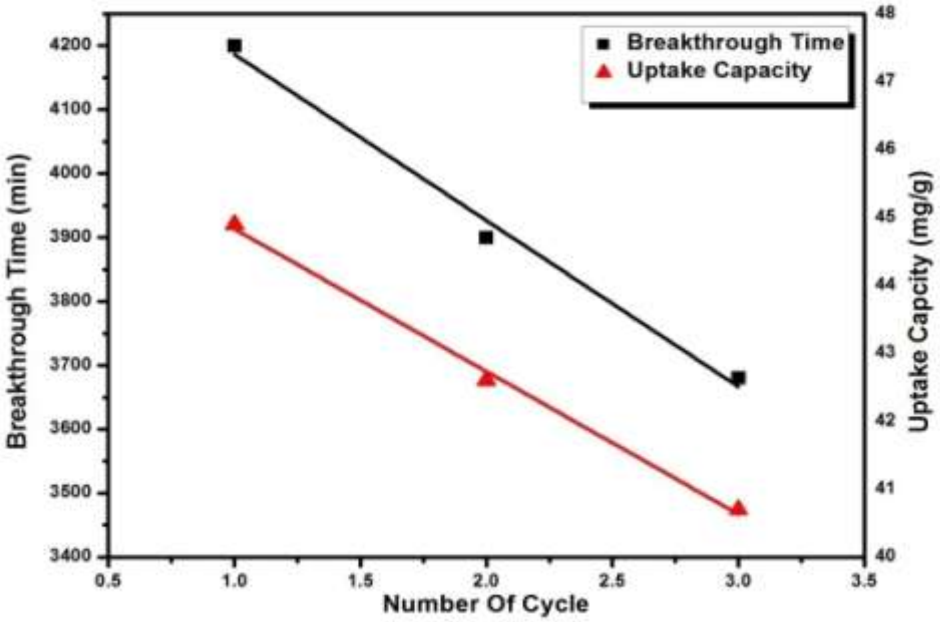


**Figure 4.8 Linear plot of breakthrough time and fluoride uptake and critical bed length with respect to the number of cycles**

## 4.4 CONCLUSION

The present adsorption system was found to be very efficient for fluoride removal from water in fixed bed column system. The different column parameters i.e. initial concentration of fluoride, flow rate of effluent and bed height of the adsorbent column strongly influence the adsorption performance of the rGO/$ZrO_2$. The uptake capacity of the adsorbent enhances with the increases in the bed height and the fluoride concentration while the adsorption performance decreased with the increase in flow rate. The maximum column performance was observed at flow rate of 1.66 mL/min, initial concentration of 25 mg/L, and bed height of 7.5 cm. The highest adsorption capacity was found to be 44.7 mg/g. The BDST model fitted well to the experimental data which provide the linear relationship between service time (t) and bed height (Z). This model was also used to predict and design column parameters of the flow rate of 3.32 mL/min from the known flow rate i.e. 1.66 mL/min. The Thomas and Yoon-Nelson model also used to describe this adsorption system. The regeneration studies were carried out with 10% NaOH solution to investigate the adsorption performance for the three adsorption-desorption cycles of the rGO/$ZrO_2$ for fluoride removal. The excellent uptake capacity was found for all the three cycles. The life factor studies indicated that the present adsorbent (rGO/$ZrO_2$) supposed to have sufficient bed capacity for up to 15.11 cycles to avoid breakthrough at time t = 0.