



Investigating simplified fixed bed design models for the adsorption of fluoride onto crushed burnt clay pot

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Abstract

The breakthrough curves of fluoride adsorption onto crushed burnt clay pot in mini column fixed bed depths of 15, 20, and 25 cm at a continuous flow rate of 2.5, 5, 10 and 15 ml/min were used to investigate the simplified fixed bed design models (BDST and EBRT). The influent fluoride concentration was 5 mg/L and the breakthrough point was taken at 30% of the influent concentration. Results indicate that the BDST curve had the form of straight line explaining more than 99.6% of the data and thus confirmed to obey the BDST model. For the same operating parameters of 50 cm bed depth and 36 cm/h flow rate, 350 L water could have been defluoridated using BDST model, however, in the case of the pilot experiment, 324 L were defluoridated from 5 to 1.5 mg/L fluoride. This was 8% higher only and hence was not significant. Similarly, when the bed depth data were analyzed, results indicate that at higher EBRT values, the adsorbent exhaustion rate were similar to the batch adsorption and thus the EBRT model could be used to optimize for the design of defluoridation unit. Therefore, the simplified fixed bed design models (BDST and EBRT) could be successfully applied to analyze the column performance and design a fluoride adsorption system based on crushed burnt clay pot as a sorbent media.

Keywords: Breakthrough Curve, BDST, EBRT, Crushed Burnt Clay Pot, Fluoride Adsorption.

1. Introduction

Fluoride when present in excess in drinking water is one of the few chemicals that may be of public concern. However, Fluoride intake to humans is necessary as long as it doesn't exceed the limits as it protects teeth decay. According to WHO, maximum allowable limit from water uptake to humans is 1.5 mg/L [1]. Reports by UNICEF [2] indicate that fluoride at elevated concentration is known to occur in a number of parts of the world and in such circumstances can have adverse impact on public health and wellbeing. Fluoride commonly occurs in the earth's crust making groundwater more susceptible to contamination [3]. Studies by WHO indicate that excessive exposure to fluoride can give rise to a number of adverse effects ranging from mild dental fluorosis to crippling skeletal fluorosis [4].

Defluoridation is a fluoride removal practice applied in areas where there is excess fluoride in drinking water and is an important practice to protect fluorosis at various levels. Recent studies indicate however, that the defluoridation device should be modest in investment, low maintenance cost, simple in design and operable at village level meeting acceptable water quality [5]. Among the various defluoridation methods, adsorption methods in packed bed are preferable due to easier operation, reasonable running and investment cost. Moreover the exhausted media could be replaced with virgin one at relatively longer period of time and no daily sludge encountered [6, 7]. Despite such advantages, there is no single method which meets the entire requirement and materials used as sorbent media may affect the water quality such as its pH, turbidity, hardness and bacteriological contaminants. Therefore care must be exercised when selecting the proper sorbent material for defluoridation practice [8].

Fluoride removal from water such as adsorption, membrane separation, and ion exchange techniques using commercial chemicals are expensive for developing countries. It is imperative therefore to search low cost defluoridation materials which can be used for communities in developing world. Certain studies [5], [8], [9], [10], [11], [12] revealed that fired clay chips and natural soils are among the large number of cost effective adsorbents which have been reported to

possess fluoride removal capacity. The chief advantage of using fired clays products and natural soils is that they are cheap and locally available.

Domestic clay column filters can be constructed by normally packing them using clay chips which can be obtained as waste of manufacturing brick, pottery or tile. The filter is based on up flow in order to allow settling of suspended solids within the filter bed. Certain studies in a number of countries, most notably in countries such as Sri Lanka showed that clay filters have been used with some success for defluoridation [13]. Though there is significant variability in the fluoride uptake capacity, they could be potential alternatives in developing countries.

It is widely known that adsorption processes provide a feasible technique for the removal of pollutants from water and wastewater [14] and is recognized as the most efficient, promising and widely used fundamental approach in water and wastewater treatment processes [15]. This is mainly hinges on its simplicity, economically viable, technically feasible and socially acceptable [16].

However, the principle of adsorption system design for defluoridation units requires a number of information. This could be obtained from series of batch, mini column and pilot plant studies. The latter is time consuming and expensive with regard to the amount of adsorbent and water usage. But, conducting a pilot scale column run is important to predict what would happen in a full scale column when various operating parameters are involved. These parameters include flow rate, feed and product concentration, bed height, particle size, type of adsorbent, pH, temperature and viscosity [17].

Numerous models have been developed for the design adsorption system, of which batch adsorption models are simple and useful to design batch adsorption units. However, their application for the design of continuous adsorption units is limited. Therefore, appropriate model which suits for continuous adsorption system is indeed needed to address the shortcoming arising from the batch adsorption models. The fixed bed mathematical model for a continuous flow in porous materials with one dimensional advection dispersion equation seems appropriate. This model assumes linear sorption isotherm of the solute onto the solid surface [18].

The model is helpful to predict the breakthrough curve in more accurate way. However, it needs to have the physical and kinetic parameters determined which could be obtained from batch adsorption studies or elsewhere from literatures. Moreover, the model requires the solution of a number of non-linear partial differential equation including physical and kinetic parameters which make tedious and time consuming to seek solutions as numerical method of solving is the only applicable option [19].

A simplified model to design a fixed bed adsorption column is therefore indeed needed. There are a number of simple design models available which are based upon general assumption. These include bed depth service time (BDST) model, empty bed residence time (EBRT) model and Thomas model. The applicability of simplified models is extensively studied for the removal of organic solutes by activated carbon and their applicability to model fluoride adsorption is now emerging. It has been indicated by Ghorai and Pant [20] that the bed depth service time (BDST) model was applied successfully for fluoride adsorption onto activated alumina.

The main design criterion in a fixed bed continuous flow adsorption system is to predict how long the adsorbent material would be able to sustain removing a specified amount of solute from solution before regeneration or replacement is needed. This period of time is known as the service time of the bed. The BDST model describes a relation between the service time of the column and the bed depth of packed column. Bohart and Adams [21] developed a relationship between the bed depth and the service time and have been applied successfully in a number of studies on fluoride adsorption onto activated Alumina [20], [7], [22]. However, its application for fluoride adsorption onto clay products has to be investigated.

Eritrea is among developing countries located in fluorosis endemic region sharing the East Africa rift valley. Hence, a study is required to exploit local and cheap fluoride adsorbent materials to remove excess fluoride from drinking water to protect fluorosis. Certain studies have already done to assess the fluoride level in water and according to those studies, the fluoride level reached about 4 mg/L [23], [24], [5] in some villages around Keren where fluorosis is salient. The fluoride level was in excess of the standard given by WHO [1] and the incidental of dental fluorosis was reported to be over 50% in children and about 20% among adults [23]. Alternative water sources are not easily available in such villages and hence treatment of fluoride contaminated water is the most reasonable approach. However, commercial defluoridation is not feasible for economic and technical reasons.

Therefore, developing countries such as Eritrea who are endemic to fluorosis should look for alternative local sorbent materials to be employed for defluoridation practices to minimize the cost of operation. Based on this, a study was carried out to assess and exploit local fluoride adsorbent materials and among them, crushed burnt clay pot was found a promising fluoride sorbent material. However, the prediction of the service time of those local materials remains difficult as their adsorption capacities varies and hence defy most of the models developed. The objective of this study was thus, to investigate the application of simplified fixed bed design models (bed depth service time, BDST, and empty bed residence time, EBRT) for the design of fluoride adsorption system onto crushed burnt clay pot and apply BDST model to predict the service time of an adsorption system at a given operating parameters.

2. Research methodology

2.1. Preparation and selection of crushed burnt clay pot particles

Keren town and its surrounding areas are well known for fired clay products in Eritrea. Fired clay pots were purchased from the market and then crushed down manually into grains. The grains were sun dried and graded using the US bureau of standards [25]. Particle size selection was made and particles ranging from 0.60-2.36 mm in diameter were selected for defluoridation by packing them in a mini column experiment in a fixed bed depth. The particle size selection was made to enhance the permeability and to decrease the turbidity and color of the water. The physical characteristics of the crushed burnt clay pot used in this study were published in another paper by the same author [5] and reference can be made if necessary. The photos presented in Fig. 1 shows the burnt clay pot which was used in the experiment.



Fig. 1: Burnt Clay Pot Before and after Crushing

2.2. Experimental setup of the mini column fixed bed continuous flow adsorption

Crushed burnt clay pot particles were washed with tap water until clear water was obtained. Fine particles which could block the adsorption sites and that might create clogging condition and interfere with the flow were removed before the experiment commenced. The media were then packed in a mini column fixed bed of 15, 20 and 15 cm height. The bed was supported and closed by cotton pad and rubber stopper respectively to prevent flow of adsorbent together with the effluent. Moreover, the bed was rinsed with distilled water and left overnight to ensure a closely packed arrangement of particles. Water containing 5 mg/L fluoride concentration was prepared by dissolving anhydrous sodium fluoride, NaF, in distilled water as explained in [5] and was pumped in a down flow mode by a peristaltic pump. The pump was used to control the flow rates at 2.5 ml/min, 5 ml/min, 10 ml/min and 15 ml/min for all the beds and maintained constant during each run. The experimental set up is presented in Fig. 2.

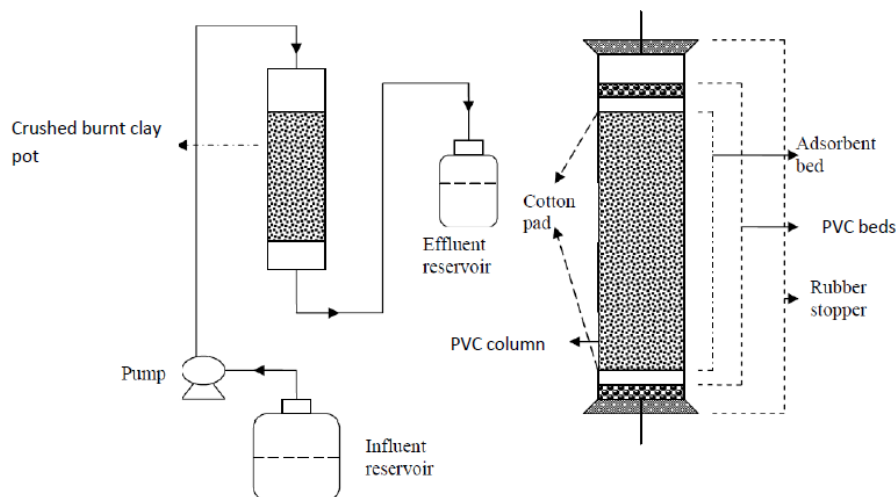


Fig. 2: Schematic Diagram for the Laboratory Scale Mini Column Experimental Apparatus

Samples were withdrawn at the outlet of the mini column at one hour interval using 100 ml measuring cylinder and the fluoride concentration was determined by the SPADNS method using Hanna HI 83099 model (COD & Multiparameter) as outlined by the American Public Health Association, American Water Works Association and Water Environment Federation [26]. A Breakthrough curve was generated at the desired breakthrough concentration at 30% of the initial fluoride concentration (5 mg/L) which was 1.5 mg/L and reproduced for bed depth analysis. The experiment was

carried out at room temperature (23 ± 1 °C) and the pH of the inflow was maintained at 7.10 ± 0.10 throughout the experiment. The results which were obtained in the breakthrough curves were then investigated if simplified fixed bed design models (BDST and EBRT) could be applied for the design of fluoride adsorption onto crushed burnt clay pot.

2.3. Bed depth service time (BDST) model

The BDST model is a model to predict how long the adsorbent material would be able to sustain removing a specified amount of solute from solution before actually regeneration or replacement is required. The model works based on a relation between the service time of the column and the depth of packed bed column. Bohart and Adams [21] developed a relationship between the bed depth, h_c , and the service time, T_b . However, Hutchins [27] has developed it to a linear relation between the bed depth (h_c) and the service time (T_b) of the form presented in equation (1).

$$T_b = \frac{N_o}{C_{ov}} h_c - \frac{1}{K C_o} \ln\left[\frac{C_o}{C_b} - 1\right] \quad (1)$$

Where: T_b = service time at breakthrough point (h)

N_o = the bed capacity (mg/cm^3)

h_c = packed-bed column depth (cm)

v = linear flow rate through the bed (cm/h)

C_o = initial influent fluoride concentration (mg/L)

C_b = effluent fluoride concentration at breakthrough (mg/L) and

K = adsorption rate constant (L/mg/h).

Equation (1) has the form of a straight line and hence the BDST curve could be expressed using the equation of a straight line of the form:

$$y = ax + b \quad (1.1)$$

Where: y = service time (T_b), x = bed depth (h_c), a = slope, and b = ordinate intercept.

In this case a and b are equivalent to:

$$a = \frac{N_o}{C_{ov}} \quad (1.2)$$

$$b = -\frac{1}{K C_o} \ln\left[\frac{C_o}{C_b} - 1\right] \quad (1.3)$$

The fixed bed depth data were analyzed and BDST parameters were determined from linear regression. The constants in Equation (1.1), the adsorptive capacity of the system (N_o) and the rate constant (K) was determined from the slope and intercept of a straight line of the plot of the service time against the bed depth from the experimental data. Then after the service time of different columns with different operating parameters were predicted by applying the BDST equation. Results of the service time obtained using the BDST model was compared with results obtained from a pilot study for the same operating parameters to cross check the validity of the model.

2.4. Empty bed residence time (EBRT)

Empty bed residence time (EBRT) as a design tool is used to determine the optimum adsorbent usage in the fixed bed adsorption column. The capital and operation costs of the adsorption system depend mainly on the EBRT and adsorbent exhaustion rate for a fixed liquid flow rate, feed concentration and adsorbent characteristics. The adsorbent exhaustion rate is the weight of adsorbent used in the column per volume of liquid treated at the breakthrough time. The adsorbent exhaustion rate before breakthrough time and EBRT model used data which were obtained from the BDST analysis as represented in equation (2) and (3). The adsorbent exhaustion rates were plotted against the EBRT values and hence the resulting curve was investigated to find out the optimum adsorbent usage.

$$\text{EBRT} = \frac{V}{Q_v} \quad (2)$$

$$R_a = \frac{M_a}{V_b} \quad (3)$$

Where : EBRT= Empty bed residence time

V =Bed volume

Q_v =Volumetric flow rate of water

R_a = Adsorbent Exhaustion Rate

M_a = Mass of Adsorbent used

V_b = Volume of Water Treated at Breakthrough point

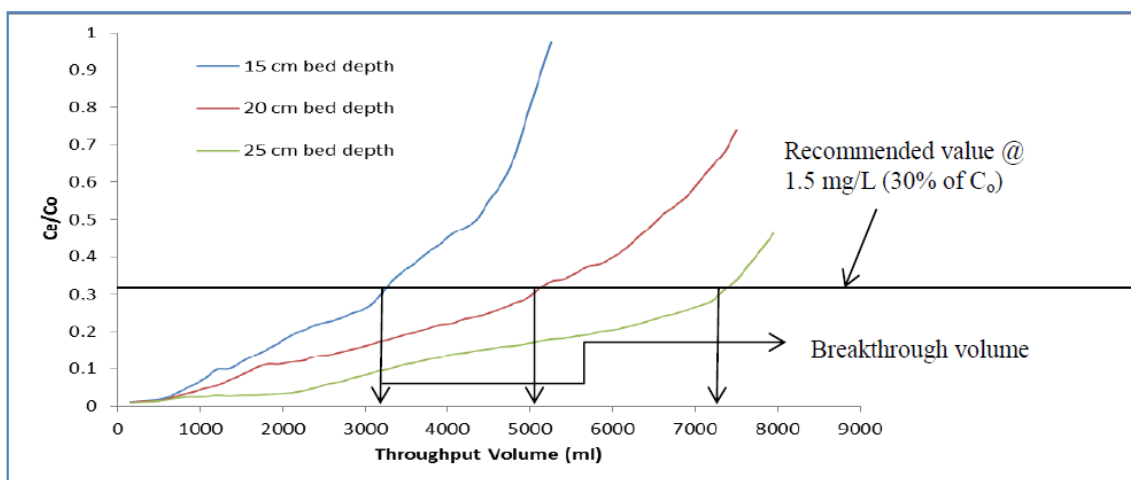
3. Results and discussions

3.1. Analysis of the breakthrough curves of mini-column continuous fluoride adsorption

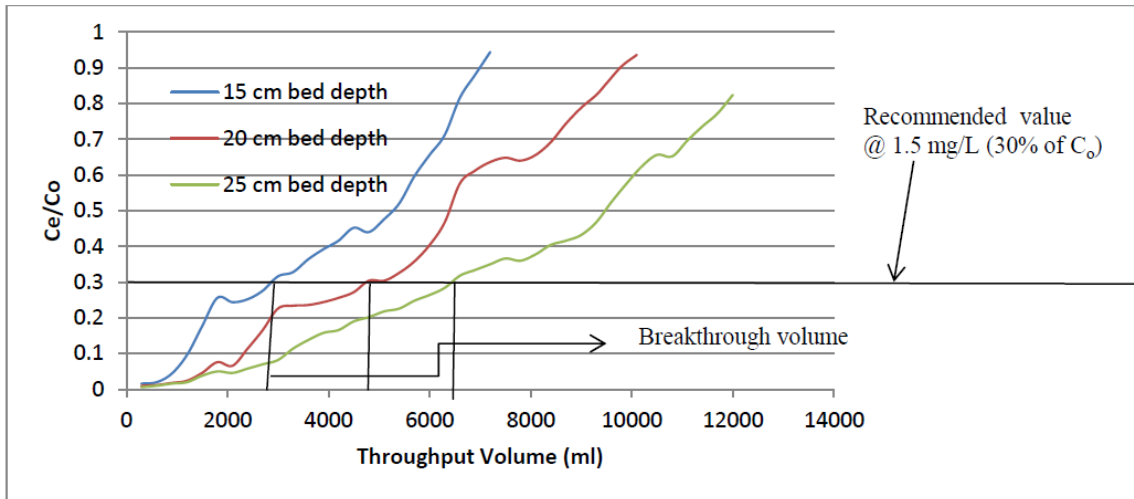
Crushed burnt clay pot was packed in a mini column in a fixed bed depth of 15, 20 and 25 cm and the experiment was run in a down flow mode as shown in Fig 3. The typical adsorption of fluoride onto crushed burnt clay pot media were studied by the same author elsewhere [5]. However, their breakthrough curves were reproduced here as presented in Figs. 4 to generate the fixed bed depth data for analysis of the BDST and EBRT models. The breakthrough curves indicated in a, b, c and d in Fig. 4 show the effect of bed depth and flow rate on the breakthrough curves of fluoride adsorption onto the crushed burnt clay pot at fixed bed depths of 15, 20, and 25 cm for a constant flow rate of 2.5, 5, 10 and 15 ml/min respectively. The detail characteristics of the breakthrough curves were discussed thoroughly in [5] and hence to avoid the duplication, only the curves are included here for analysis. The breakthrough was taken at 30% of the initial fluoride concentration ($C_e/C_o = 0.3$) as indicated by the horizontal line in a, b, c and d in Fig. 4 in which C_o and C_e are raw and treated water average fluoride concentration respectively. The horizontal line (recommended value by WHO at 1.5 mg/L fluoride level) crossing each curve in each figure indicates a point where the breakthrough occurred. The breakthrough volume and its corresponding breakthrough time was obtained by projecting the point of intersection vertically down for a given flow rate and the summary of the fixed bed depth data for analysis are presented in Table 1.



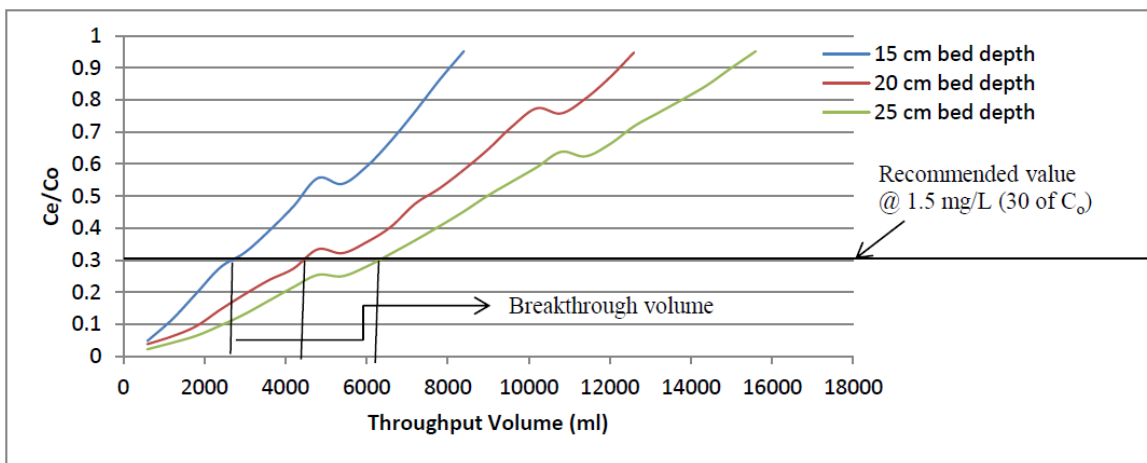
Fig. 3: Experimental Photo of the Mini Column Continuous Fluoride Adsorption onto Crushed Burnt Clay Pot



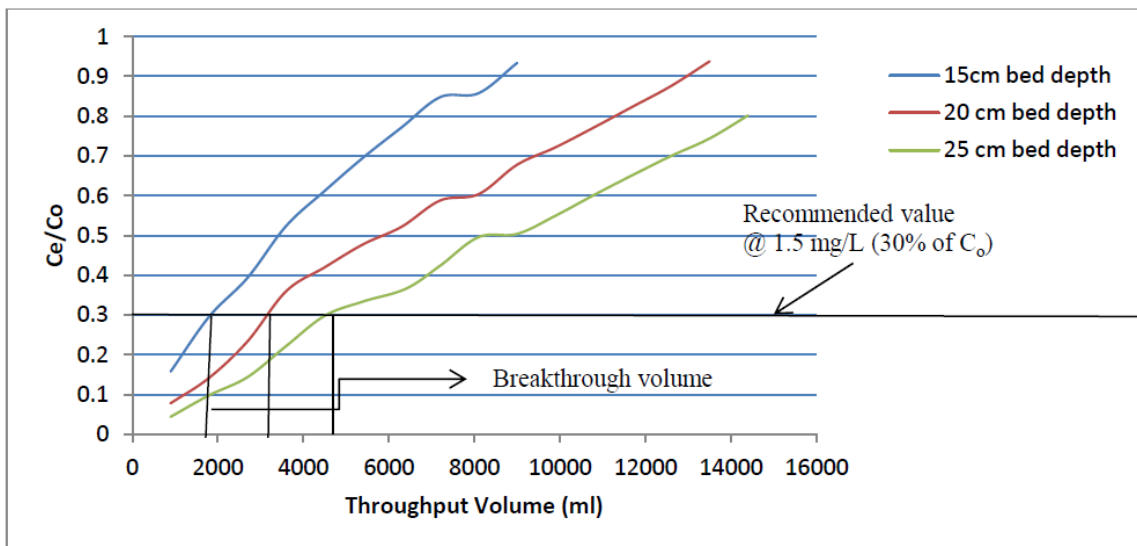
a) Effect Of Bed Depth on Breakthrough Volume at a Constant Flow Rate of 2.5 MI/Min ($C_o = 5$ Mg/L)



b) Effect Of Bed Depth on Breakthrough Volume at a Constant Flow Rate of 5 MI/Min ($C_o = 5 \text{ Mg/L}$)



c) Effect of Bed Depth on Breakthrough Volume at a Constant Flow Rate of 10 MI/Min ($C_o = 5 \text{ Mg/L}$)



d) Effect of Bed Depth on Breakthrough Volume at a Constant Flow Rate of 15 MI/Min ($C_o = 5 \text{ Mg/L}$)

Fig. 4: Breakthrough Curves of a Typical Adsorption of Fluoride Onto Crushed Burnt Clay Pot: Reproduced From [5]

3.2. Analysis of the bed depth service time (BDST) model

Table 1 shows the details of the variable bed depth at a fixed flow rate in a fixed bed column. BDST plots were constructed from the data using the breakthrough time (T_b) and the bed depth (h_c). The influent fluoride concentration

(Co) was 5 mg/L and 2.5, 5, 10 and 15 ml/min flow rates were used at 30% breakthrough for 15, 20 and 25 cm bed heights. Fig. 5 shows the BDST plots as obtained from the analysis of Table 1.

Table 1: Variable Bed Depth at A Fixed Flow Rate in A Fixed-Bed Column for the Removal of 5 Mg/L of Fluoride by Crushed Burnt Clay Pot (Internal Ø=2.3cm)

flow rate (ml/min)	bed depth (cm)	Bed volume (cm ³)	Adsorbent mass (g)	EBRT (min)	Vb (L)	Tb (h)	Adsorbent exhaustion rate (g/L)
2.5	15	62.35	60	24.94	3.20	21.33	18.75
	20	83.13	80	33.25	5.05	33.67	15.84
	25	103.91	100	41.56	7.30	48.67	13.70
5	15	62.35	60	12.47	2.93	9.75	20.48
	20	83.13	80	16.626	4.80	16	16.67
	25	103.91	100	20.782	6.40	21.167	15.65
10	15	62.35	60	6.235	2.605	4.33	23.03
	20	83.13	80	8.313	4.501	7.50	17.77
	25	103.91	100	10.091	6.15	10.25	16.26
15	15	62.35	60	4.157	1.80	2	33.33
	20	83.13	80	5.542	3.00	3.33	26.67
	25	103.91	100	6.927	4.50	5	22.22

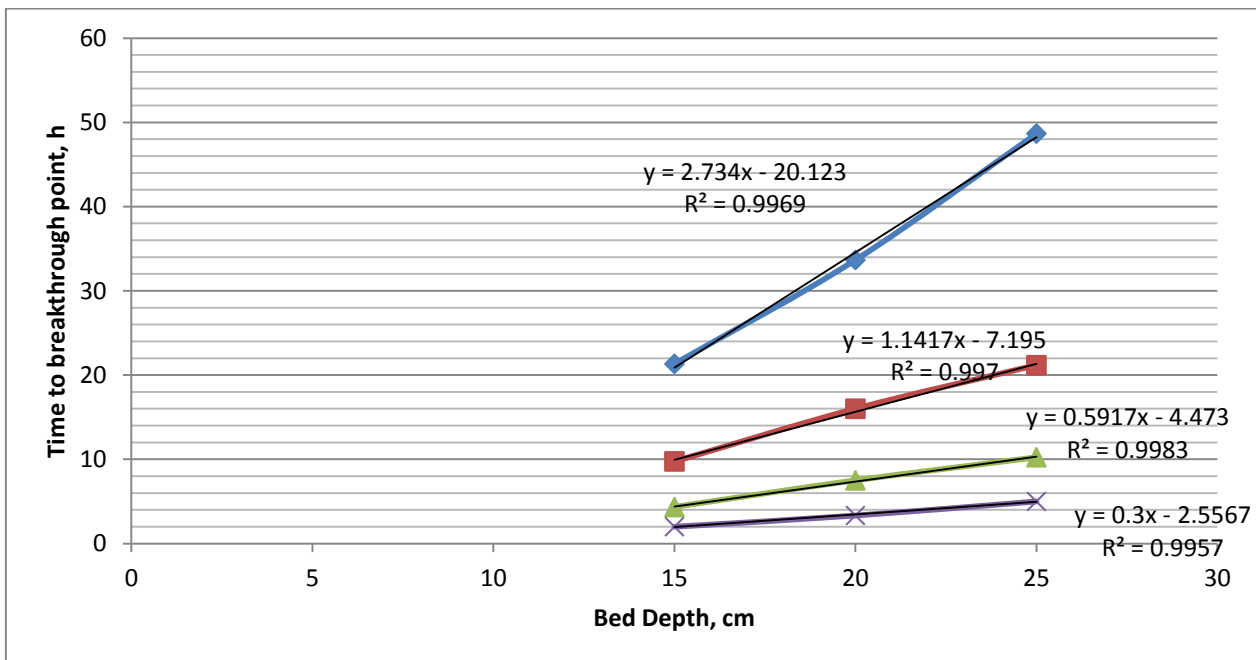


Fig. 5: BDST Plots At 30 % Breakthrough in A Fixed-Bed Column at Different Flow Rates: ◆-2.5; ■-5; ▲-10; X-15 ML/Min (Co = 5 Mg/L)

The analysis of the BDST plots show that when the time taken to breakthrough (service time) versus bed depth was drawn, the BDST curve obtained had the form of straight line. The BDST plots show that the fixed bed depth data were explained almost 99.6% (indicated by $R^2 \geq 0.996$) precisely in all four cases. Thus the BDST curves could be expressed using equation (1.1). This led to the conclusion that fluoride adsorption onto crushed burnt clay pots were in compliance with Hutchins equation [27] and thus equation (1) is applicable. Therefore, using equation (1.1) and solving the equations (1.2) and (1.3), the coefficients N_0 and K of equation (1) was determined for the four flow rates and are presented in Table 2. Therefore, the BDST model could be applied to predict the service time of a fluoride adsorption system onto crushed burnt clay pot.

Table 2: Constants of BDST Curve

Flow rate, Q_v (ml/min)	Linear flow rate, v (cm/h)	BDST constants	
		N_0 (mg/cm ³)	K (L/mg/ h * 10 ⁻³)
2.5	36	0.493	8.426
5	72	0.412	23.552
10	144.6	0.427	37.885
15	216.6	0.325	66.3

The constants of the BDST model (N_0 and K) indicated in table 2 was used in equation (1) to predict the service time of fluoride adsorption onto crushed burnt clay pot. The predicted service was also compared to result obtained from a pilot scale experiment for cross checking the validity of the BDST model to apply for scaling up of the adsorption system for larger applications.

3.3. Analysis of empty bed residence time (EBRT) model

From the BDST analysis, data used for the EBRT model was obtained. The breakthrough percentage was specified as before at 30% and hence the service time for the column before breakthrough was found from the min column experiment. From the typical analysis of Table 1, the adsorbent exhaustion rate was found by dividing mass of the adsorbent used by the volume of treated water at breakthrough, V_b . Thus the adsorbent exhaustion rate and the EBRT at various adsorbent bed heights were obtained as presented in Table 1. A plot of the adsorbent exhaustion rate versus EBRT was then constructed as shown in Fig 6. The figure indicated that the adsorbent exhaustion rate decreased with increasing EBRT. Besides, the figure shows that at lower flow rate, the operating line that was obtained in a batch adsorption system for the same medium shifted to the right indicating that it has got higher EBRT. Thus at higher EBRT values, the adsorption capacity of the medium in a continuous adsorption resembles of the batch adsorption system. This was mainly due to sufficient contact was given for fluoride adsorption to take place onto crushed burnt clay pot.

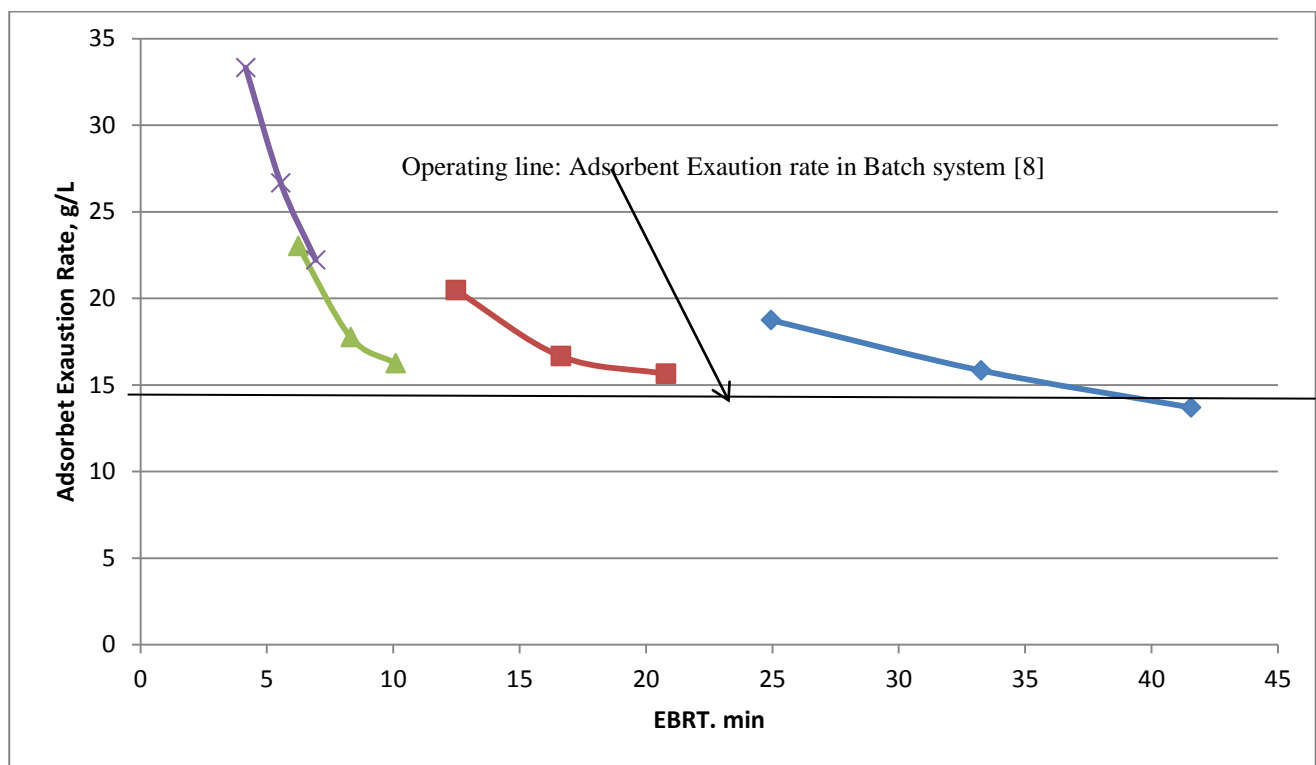


Fig. 6: Adsorbent Exhaustion Rate versus EBRT for ♦-2.5; ■-5; ▲-10, X-15 MI/Min

At lower flow rates, the curves tend to flatten and no significant reduction in adsorbent exhaustion rate was observed at contact time greater than 15 and 25 min for 5 and 2.5 ml/min flow rates respectively. The corresponding adsorbent exhaustion rate was 18.75 and 16.67 g/L. The figure further shows that the optimum adsorbent dose for the batch adsorption system was nearly 14 g/L [8] as indicated by the horizontal line. This was equivalent to the adsorbent exhaustion rate of 2.5 ml/min at a bed depth of 25cm which is indicated in Fig. 6 by the curve to the right. This indicated thus the same optimum dose of adsorbent in both batch and continuous adsorption was obtained and hence the EBRT model could be used to optimize an adsorption system based on crushed burnt clay pot as a sorbent media for fluoride uptake.

3.4. Prediction of service time for different operating parameters using the BDST model

Earlier, it was discussed that the BDST model could be applied to predict the service time of an adsorption system of fluoride onto crushed burnt clay pot. The BDST constants were determined (Table 2) and could be used in equation (1) to predict the service time. Table 3 presents the summary of the results of the predicted service time for different operating parameters for two possible scenarios. The other two scenarios were omitted intentionally as their breakthrough point were occurred earlier associated with high flow rates.

Table 3: Predicted Service Time of an Adsorption Column Based on Crushed Burnt Clay Pot at Different Operating Conditions for Two Different Scenarios Using the BDST Model.

hc (cm), v (cm/h), Co (mg/L)	Predicted bed service time (h)	Corresponding breakthrough volume, Vb (L)
Scenario 1: No=0.493 mg/cm ³ , K=8.426*10 ⁻³ L/mg/h and flow rate (Qv)=3 L/h (linear flow rate=36 cm/h)		
70, 36, 5	171.6	514
60, 36, 5	144.2	432
50, 36, 5	116.8	350
40, 36, 5	89.5	268
30, 36, 5	62.1	186
70, 36, 4	224.5	673
60, 36, 4	190.26	571
50, 36, 4	156	468
40, 36, 4	121.8	365
30, 36, 4	87.6	263
70, 36, 3	319.6	959
60, 36, 3	273.9	822
50, 36, 3	228	684
40, 36, 3	182.6	547
30, 36, 3	136.9	411
Scenario 2: No=0.412 mg/cm ³ , K=23.552*10 ⁻³ L/mg/h and flow rate (Qv)=6 L/h (linear flow rate=72 cm/h)		
70, 72, 5	72.9	437
60, 72, 5	61.4	368
50, 72, 5	50	300
40, 72, 5	38.6	231
30, 72, 5	27.1	162
70, 72, 4	94.7	568
60, 72, 4	80.4	482
50, 72, 4	66.1	396
40, 72, 4	51.8	310
30, 72, 4	37.5	224
70, 72, 3	133.5	801
60, 72, 3	114.4	686
50, 72, 3	95.4	572
40, 72, 3	76.3	457
30, 72, 3	57.2	343

The predicted service time in both scenarios was compared taking a reference operating parameters of the bed depth as 50 cm and initial fluoride concentration (F⁻) at 5 mg/L as indicated in bold in table 3. This reference values was selected because a pilot study was carried out at that operational conditions and thus making comparison would be easier in ideal condition. The results presented in Table 3 indicates that for a similar operating parameters of a fixed bed depth, when the linear flow rate increased from 36 to 72 cm/h for a bed of 50 cm and 5 mg/L F⁻, the service time could have been 50 h and the corresponding breakthrough volume could have been 300 L, which would be 50 L less than the value that could be obtained in a linear flow rate of 36 cm/h. This is mainly due to the fact that at higher flow rates, the adsorbent material has lower chances to interact with fluoride (lower contact time) resulting an early breakthrough point and hence the service time would have been reduced accordingly.

In addition to changing the flow rates, when the fluoride concentration in raw water was assumed at 3 mg/L, a service time of 228 h would have been obtained keeping the bed depth at 50 cm and linear flow rate at 36 cm/h resulting in a corresponding breakthrough volume of 684 L. In a similar condition, for a linear flow rate of 72cm/h, a service time of 95.4 h would have been obtained resulting in a corresponding breakthrough volume of 572 L and this is 112 L less than the value that could be obtained at 36 cm/h for the same parameters.

Similar trends would have been observed when the bed height was increased. For instance an increase in bed depth from 50 to 70cm, a service time of 171.6 h would have been obtained for a flow rate of 36 cm/h and 5 mg/L F⁻ resulting in a breakthrough volume of 514 L. In other words, an increase in bed depth by 40% (50 cm to 70 cm) would have been resulted in an increase in service time by 46.9% (Table 3).

Apparently, preliminary fluoride level study was carried out in some village in Keren, Eritrea where the burnt clay pot was purchased. The villages' water fluoride concentration ranged from 1.40-3.9 mg/L according to certain studies [5] and the average fluoride concentration was almost 3 mg/L. If the BDST model is to be applied for such cases to predict the service time of the bed that would be relevant for such villages (3 mg/L F⁻), a unit with a bed depth of 50 cm at a flow rate of 36cm/h could produce 684 L safe water before reaching the breakthrough point. This would serve the household for more than a month if 21 L water is the daily requirement for cooking and drinking for a family having 5-7 persons each consuming 3-4 L/day. For the same village and same situation, comparatively if the bed depth increased

by 40% (50 cm to 70cm) the service time would have increased by almost one-half and the household would get safe water (959 L) for at least 45 days which would offset the economic cost of the increased column length.

Result from the BDST model was compared to cross check the validity of the application of the BDST model with result from a pilot scale defluoridation experiment for the same material. The objective was to know what would happen ideally if a practical adsorption was to take place. According to the study [5], 324 L of water at breakthrough was treated in the pilot experiment; however, using BDST model for the same operating parameters, 350 L could have been treated. The increase was only 8% higher and thus was not significant. Practically, intra particle of the adsorbent and external resistance of the column itself could play a major role in the adsorption process along the column. Moreover, a number of factors like irreversibility of the sorption process at high sorbent solid phase loadings, dispersion and uneven flow pattern through the bed might have occurred and hence might affect the adsorption process thus increase the volume of water that could be treated when using the BDST model. It was also pointed out in [28], [7], [22] that similar remarks were made on fluoride removal in a fixed bed with Aluminum Oxide Hydroxide.

Besides, the average adsorption capacity and adsorbent exhaustion rate at breakthrough of the media in the pilot experiment was 0.27 mg/g and 13.10 g/L respectively [5]. However, when the BDST model was applied, the adsorption capacity and adsorbent exhaustion rate at breakthrough point were estimated to be 0.29 mg/g and 12.10 g/L respectively. But the increase was just nominal and the values were still tolerable. Thus when BDST model was applied to predict the service time, the change was not significant to what was observed in the pilot scale experiment. This indicate that the application of simplified fixed bed design models (BDST and EBRT) for fluoride adsorption onto crushed burnt clay pot could be successfully applied for further scale up for the design of larger scale defluoridation unit based on crushed burnt clay pot as a fluoride sorbent media.

4. Conclusion

Fluoride removals from water using commercial chemicals are not feasible for developing countries because of the cost involved. From recent studies, local low cost fluoride sorbent materials could be used for communities in developing world. Among the large number of cost effective local adsorbents, fired clay products and natural soils have promising fluoride removal capacity and hence can be packed in a column for continuous flow adsorption. Despite having variable adsorption capacities, their service time could be predicted using simplified fixed bed design models. The main design criterion in a fixed bed continuous flow adsorption system is to predict how long the adsorbent material would be able to sustain removing a specified amount of solute from solution before regeneration or replacement is needed.

A study was carried out to analyze the application of simplified fixed bed design models (BDST and EBRT) for fluoride adsorption onto crushed burnt clay pot. The breakthrough curves of fluoride adsorption onto crushed burnt clay pot in a mini column continuous adsorption were investigated and a fixed bed depth data were generated. Fixed bed depths of 15, 20, and 25 cm at a constant flow rate of 2.5, 5, 10 and 15 ml/min were employed for the analysis of simplified fixed bed design models (BDST and EBRT). The influent fluoride concentration was 5 mg/L and the breakthrough point was taken at 30% of the influent concentration (1.5 mg/L F⁻). Results indicate that the BDST curve obtained had the form of straight line and the data of the fixed bed depth were explained almost 99.6% ($R^2 \geq 0.996$) precisely in all cases and thus confirmed to obey the BDST model. The model parameters were evaluated and the model constants were determined to predict the service time of the media. The BDST model gave a good prediction for the service time for the change of system parameters, such as flow rate and bed depth when compared to the observed result from the pilot scale experiment. For the same operating parameters of 50 cm bed depth and 36cm/h flow rate, 350 L water would have been defluoridated when using the BDST model, however, in the case of the pilot experiment, 324 L were defluoridated from 5 to 1.5 mg/L F⁻. The predicted service time using the BDST model when compared to result from a pilot experiment was only 8% higher and thus this was not significant.

Similarly, when the bed depth data were analyzed for the application of EBRT model, results indicate that at higher EBRT values, the adsorbent exhaustion rate of the medium in a continuous adsorption was similar to the batch adsorption system. This indicated thus the same dose of adsorbent was used in both batch and continuous adsorption and hence the EBRT model could be used to optimize for the design of defluoridation unit based on crushed burnt clay pot as fluoride sorbent media. Therefore, the simplified fixed bed models (BDST and EBRT) could be successfully applied to analyze the column performance and design a fluoride adsorption system onto crushed burnt clay pot.

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