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To cite this article: Hatem A. Gzar *et al* 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1184** 012005

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# Concrete particles for fluoride removal using continued fixed-bed and fluidized-bed systems

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**Abstract.** In the present study, fluoride ions removal from aqueous solution was studied by adsorption using a new low cost adsorbent which is concrete particles in continuous systems. The continuous systems included fixed and fluidized bed reactor. several operating conditions were used for both of fixed and fluidized column; flow rate (6,9 and 12) l/h, bed depth (6,12,20) cm inlet fluoride concentration (10,15 and 20) mg/l. Thomas and Yoon–Nelson models were used in this study using the data of breakthrough curves for the optimal conditions (bed height of 20 cm, influent flow rate of 6 l/h and inlet fluoride concentration of 10 mg/l). Adsorption capacity of the concrete particles was found to be 0.818 mg/g and 0.73 mg/g for fluidized and fixed bed respectively for the optimum conditions. The adsorption test using concrete particles adsorbent revealed the good performance of removing fluoride from aqueous solution.

**Keywords:** Concrete particles, Adsorption, Fluidized and Fixed-bed column, Fluoride removal, water treatment.

## 1. Introduction

Fluoride contamination is common in many countries around the world. Environmentally, there are two different routes responsible for fluoride contamination; anthropogenic sources and natural sources [1]. The first source can be resulted from several industrial activities, while the natural source of fluoride in water comes from the rocks that containing fluoride through which the water has infiltrated [2]. Fluoride can be useful or harmful and the allowable limit of fluoride is between (1mg/l-1.5mg/l) as establish by the World Health Organization (WHO) [3]. Fluoride can cause acute health problems when the concentration exceeds 1.5 mg/l such as dental and skeletal fluorosis, non-skeletal fluorosis. Furthermore, excess fluoride consumption for long time causes serious diseases like cancer, alzheimer, kidney damage, etc. For more than 30 nations over the world, the fluorosis was widespread among 200 million groups of people [4]. Several methods have been used to eliminate the fluoride ions in aqueous solution, the main weaknesses of many of these methods are the maintenance and operational high costs, small removal capacity, unwanted effects on water quality, complexity of the treatment procedures and production of big amount of sludge [5].

Among the techniques that used to treat fluoride in water the adsorption has been broadly used and showed good results and it is found to be more attractive technique to remove fluoride in term of low cost



and simple in design and operation [6]. A lots of materials from low cost type were used as an adsorbent. Generally, the low-cost substance that can be used as adsorbents are available in local places and need the least processing before using [7]. It has been evaluated such materials to remove fluoride from water, like light weight concrete [8] and cement paste [9] alumina cement granules [10], and they was showed good result to treat excess concentrations of fluoride. On the other side, the big amounts of demolished concrete generated from deteriorated and obsolete structures produces acute ecological and environmental problem. Concrete is a building material that produced from mixing of different materials like cement, sand, aggregate and water. The major advantage of using concrete waste material as an adsorbent for fluoride removal over the other chemical treatment techniques is that it does not create any chemical sludge. In the present study, concrete particles from local demolished buildings has been used as low cost adsorbent to remove excess concentrations of fluoride ions from water.

Continuous fixed bed system was used in the current study. Two important goals could be achieved simultaneously by using concrete particles as an adsorbent, recycle concrete waste and reduce the excess fluoride concentrations in water or wastewater, thus reducing the percentage of contaminants around us.

## 2. Materials and methods

### 2.1 Materials

*2.1.1 Collection and Preparation of the Adsorbent.* The adsorbent was made from concrete blocks from demolished buildings. The blocks were collected from two different local places they were cleaned, crashed with hand hammer to get small portions and grinded many times by mill agate mortar then sieved to obtain particles sizes between (0.6-0.075) mm. These particles have been washed with tap water several times then rinsed with distilled water. The product was dried in the oven for two days under 105°C then the adsorbent have been kept in plastic container to use in the experiments.

*2.1.2 Fluoride Solution.* The used chemicals were of analytical grade, and deionized water was used for solution preparation. Fluoride stock solution was prepared by dissolving 0.22 g of NaF in 1000 ml of deionized water and appropriate dilution from the stock solution was done to make fluoride solutions with a specific concentration for the experiments. The pH of the mixture was adjusted by using 0.1N HCL and/or 0.1N NaOH solution. The pH was measured with pH meter (Type EZDO model 6011, China). Before the experiments, all the polypropylene ware used for experimentation, dilution and storage were cleaned with detergent, thoroughly rinsed with tap water and finally rinsed with distilled water before use.

### 2.2. Methods

*2.2.1. Continuous system experiment.* The continuous system consists of two glass columns with 50 mm internal diameter and height of 1000 mm and 500 mm for fluidized and fixed columns respectively. Also, there is plastic distributors at the top and bottom for both of fixed and fluidized bed column to support the concrete particles and to remove the presence of particles in the effluent. A selected bed depth from concrete particles was laid in the two columns. The solution of fluoride ions was made in the feed basin of 50 L capacity using distilled water with a known concentration. The solution was adjusted using 0.1N NaOH or HCl. The solution was pumped to the adsorption columns through the flow meters with desired flow rate. It has been designated two points for samples taken.

Ones from the bottom of fixed bed and the other from the top of the fluidized bed column. Samples were taken from time to time and the concentration was accounted using spectrophotometer method.

The experiments have been done at 30°C. The breakthrough curves were formed from the drawing of discharge concentration ( $C_e/C_0$ ) versus time.

*2.2.2. Breakthrough curves models.* The column breakthrough curves were formed from the drawing of discharge concentration ( $C_e/C_0$ ) versus time (t), where  $C_0$  is the initial concentration (mg/l),  $C_e$  is the concentration of fluoride at equilibrium (mg/l). Two analytical equations were depended which are

Thomas and Yoon-Nelson models to explain the S-shaped curve of breakthrough after established the best conditions. The linear equation of Thomas model can be written as [11]:

$$\ln\left(\frac{C_0}{C_e} - 1\right) = \frac{K_{th}q_0m}{Q} - K_{Th}C_0t \quad (1)$$

$K_{th}$  is the constant of Thomas model (L/min.mg),  $q_0$  is the adsorption capacity of the bed (mg/g) and  $t$  is the time of total flow (min),  $m$  is the amount of adsorbent in the column (g),  $C_0$  is the inlet of fluoride concentration (mg/l),  $C_t$  is fluoride discharge concentration (mg/l) and  $Q$  is the flow rate (ml/min). The linear drawing of  $\ln\left(\frac{C_0}{C_t} - 1\right)$  against  $t$  can be provided the values of  $K_{Th}$  and  $q_0$  [12].

The linear equation of Yoon Nelson model as below [13]:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = K_{YN}t - \tau K_{YN} \quad (2)$$

Where:  $\tau$  (min) is the time necessary for 50% adsorbate breakthrough which determined from the intercept of linear draw of  $\ln\left(\frac{C_t}{C_0 - C_t}\right)$  against  $t$ , while the slope represents the rate constant  $K_{YN}$  ( $\text{min}^{-1}$ ) [14]. The experimental conditions for the continuous system are illustrated in table 1.

**Table 1.** Experimental conditions for the continuous system.

Adsorbent	Concrete particles material
Adsorbate	F <sup>-</sup>
Bed Depth (cm)	6, 12, 20
Flow rate (l/h)	6, 9, 12
Initial Concentration (mg/l)	10,15,20
Temperature, °C	30
Particle size (mm)	0.075 - 0.6
pH	6.00

### 3. Results and discussion

#### 3.1. Continuous system

The fixed and fluidized bed column experiment of has been obtained at 30°C and pH6. The effect of the pH value of the solution has been studied previous in batch system [15]. The breakthrough curves for both columns at different flow rates (6, 9, 12 l/h) are shown in figures 1 and 2.

It can be seen that the breakthrough curve slope for the fixed and fluidized beds increased with the increasing of the flow rate of the fluid. This result can explained by decreasing in contact time between the fluoride ions and concrete particles in the bed for the greater velocity which mean there was not enough time to achieve the equilibrium. These results are also consistent with that found by [16].

It has been used three different bed depths of concrete adsorbent (6, 12 and 20) cm. The results for both columns are illustrated in figures 3 and 4. It can notice that when the bed depth is smaller, the concentration of effluent fluoride increased rapidly comparing with bigger depth. As well as the bigger bed needs more time to be saturated since there is more surface area from the adsorbent that offering additional numbers of binding sites for fluoride ions to be adsorbed. These conclusions are same with [17].

The effects of different concentrations of fluoride ions are presented in figures 5 and 6. The results showed that the adsorption rate decreased when the initial concentration decreased and the breakthrough time was longer when fluoride concentration was low. This behaviour can be ascribed to diffusion rate that controlling by the concentration gradient. The increasing in fluoride concentration make the

breakthrough time and exhaustion time smaller as the binding sites will be exhausted fast. These results are similar to that obtained by [18].

It can be noticed that the effectiveness of fluidized bed column is slightly better than fixed bed column and the breakthrough time in the fluidized bed is longer than the fixed bed for the same operation conditions. This behaviour can be explained by several reasons such as the large surface area of the particle, the high mass transfer rate, the rapid mixing process in fluidized column and the occurrence of dead zone.

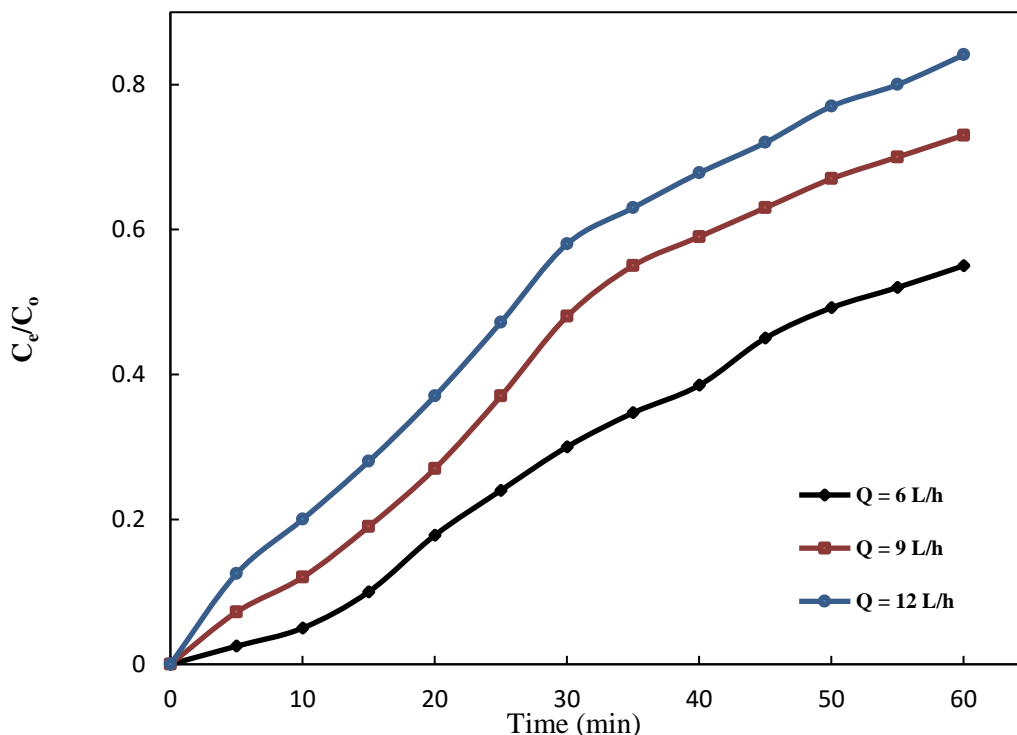
### 3.1. Modelling of continuous system

After setting the best removal conditions ( $L=20$  cm,  $Q=6$  l/h,  $C_0=10$  mg/l), Thomas and Yoon-Nelson models have been used to predict the breakthrough curves for both column fixed and fluidized bed.

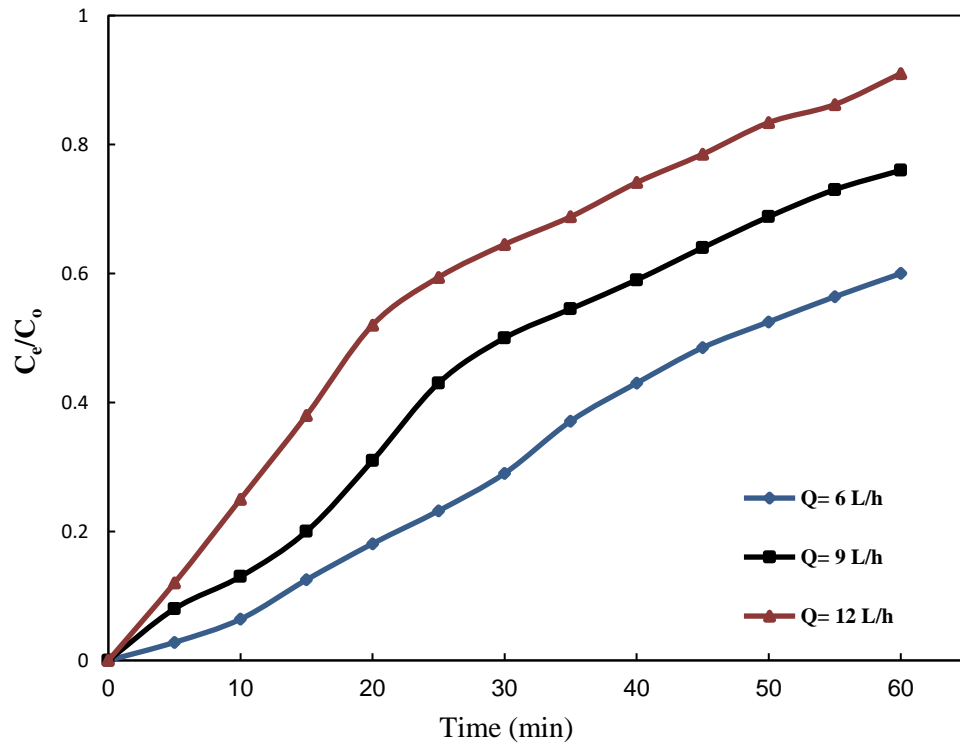
The two models showed a good match with the experimental data as illustrated in figures 7, 8, 9 and 10. In fixed bed column, Yoon and Nelson model ( $R^2=0.9812$ ) gives a better-fitting compared to Thomas model ( $R^2=0.975$ ). In fluidized bed, Thomas model with  $R^2=0.9724$  gives a little better fitting compared to Yoon-Nelson model with  $R^2=0.9718$ . This result may imply that the internal and external diffusions were not the only limiting step.

The values of  $R^2$  for both models are revealing the ability of using both models to expect the performance of adsorption for fluoride ions onto concrete particles in fixed and fluidized bed column. These results are the same as with [13] [19].

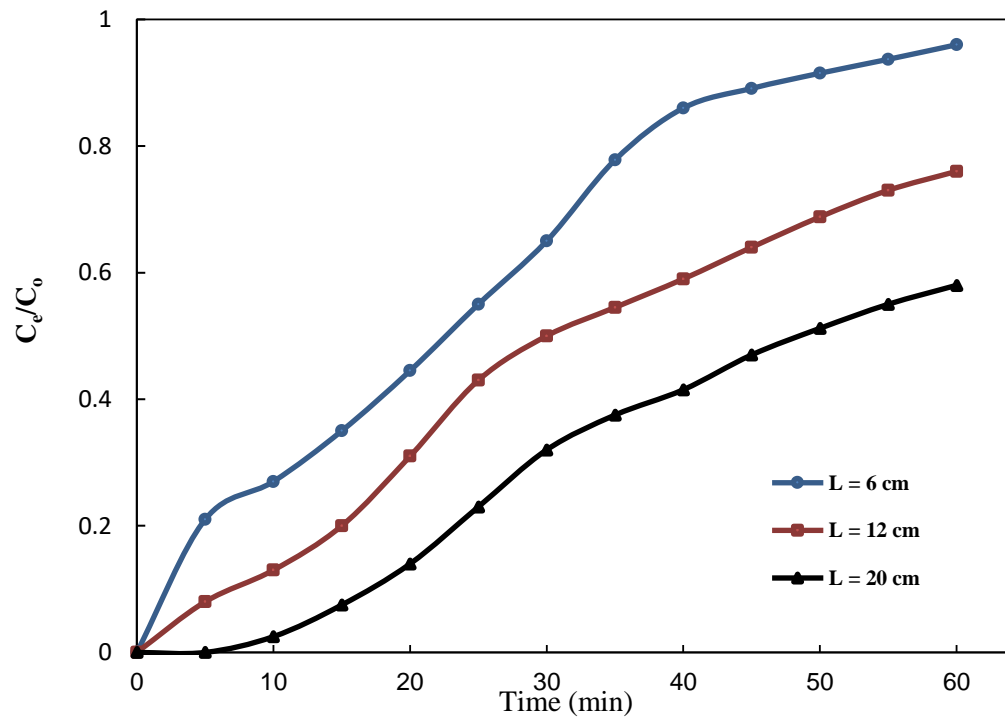
Adsorption capacity of the concrete particles was found to be 0.818 mg/g and 0.73 mg/g for fluidized and fixed bed respectively for the optimum conditions.



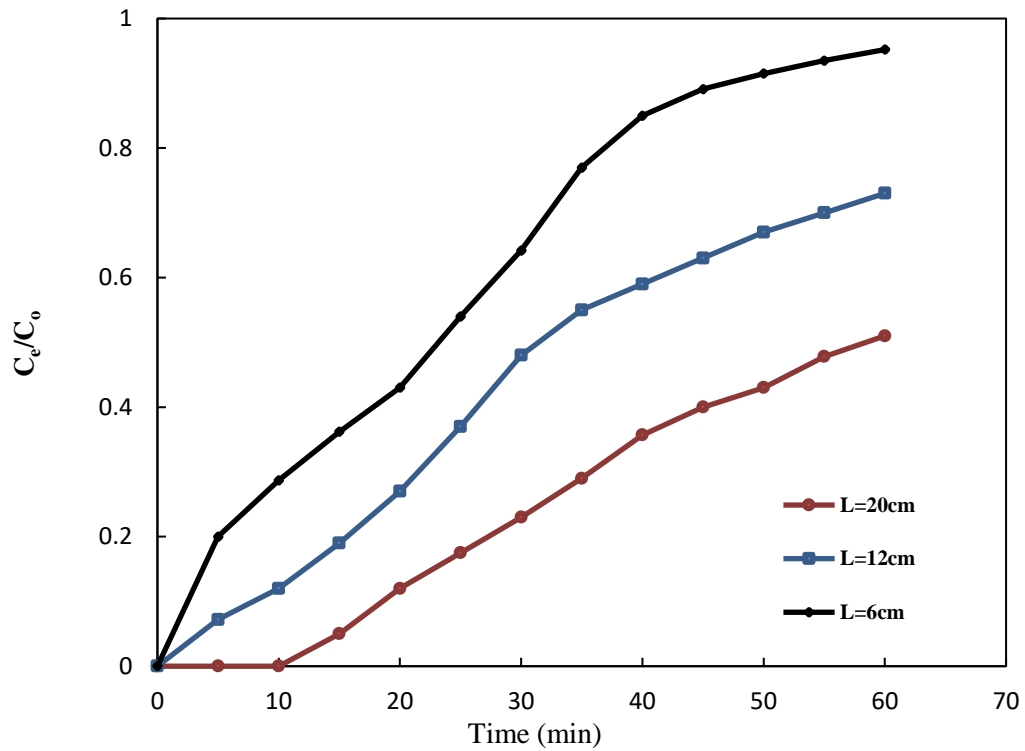
**Figure 1.** Breakthrough curves of fixed bed column for fluoride ions adsorption onto concrete particles at different flow rates at 30°C (pH 6,  $C_0=15$  mg/l, and  $L=12$  cm).



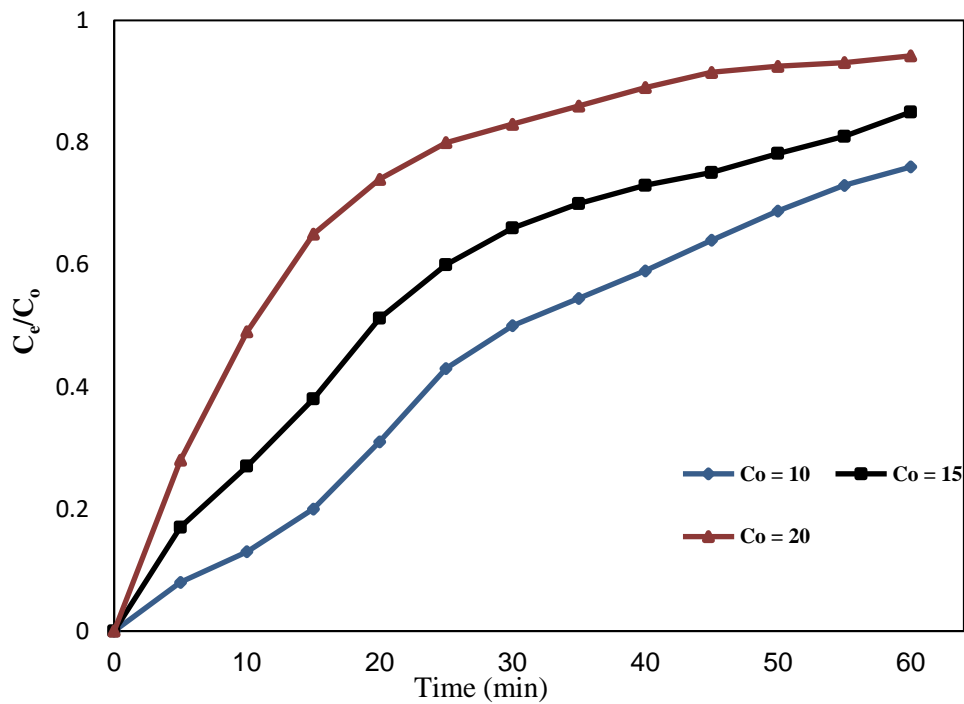
**Figure 2.** Breakthrough curves of fluidized bed column for fluoride ions adsorption onto concrete particles at different flow rates at 30°C (pH 6, C<sub>0</sub>=15 mg/l, and L=12 cm).



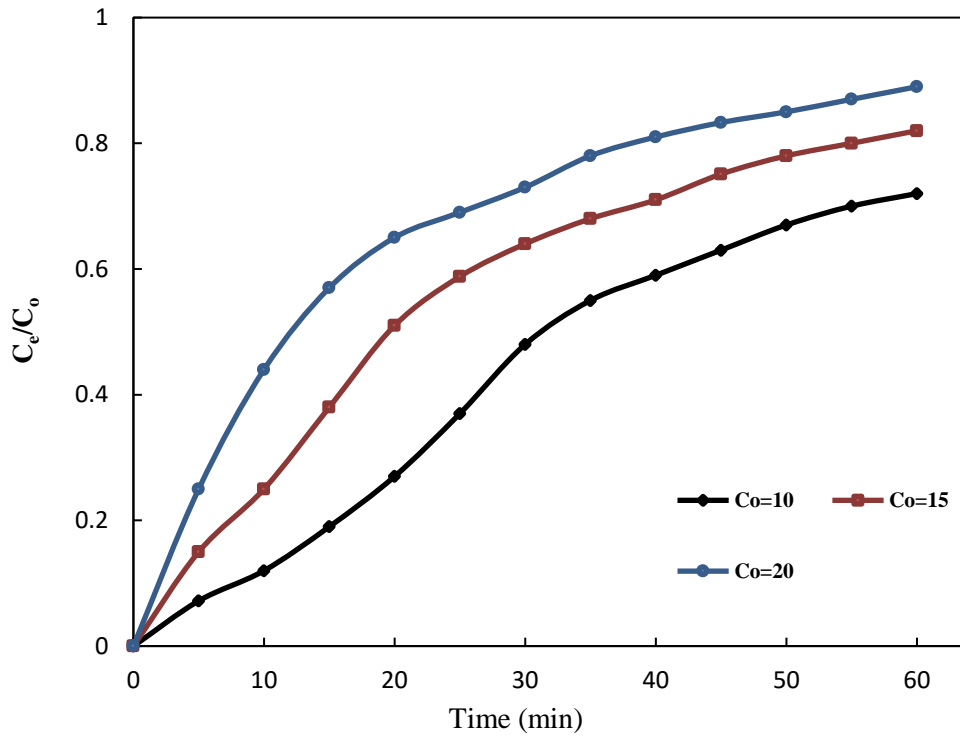
**Figure 3.** Breakthrough curves of fixed bed column of fluoride ions adsorption onto concrete particles for different bed depths at 30°C (pH 6, C<sub>0</sub>=15 mg/L, and Q=9L/h).



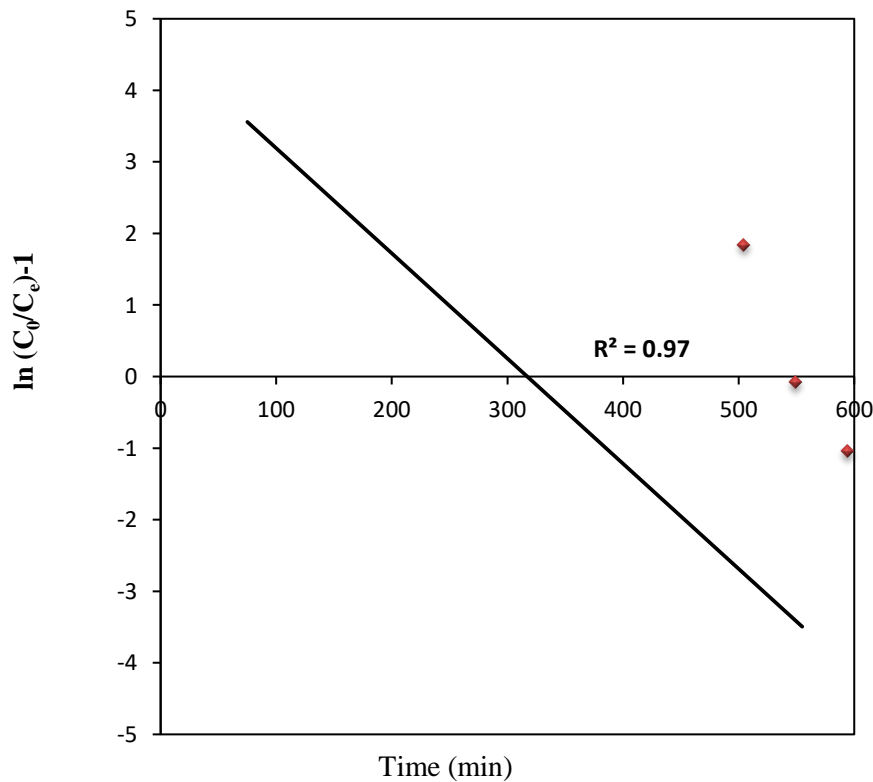
**Figure 4.** Breakthrough curves of fluidized bed column of fluoride ions adsorption onto concrete particles for different bed depths at 30°C (pH 6,  $C_0=15$  mg/L, and  $Q=9\text{L/h}$ ).



**Figure 5.** Breakthrough curves of fixed bed column for fluoride ions adsorption onto concrete particles at different initial concentrations at 30°C (pH6,  $Q= 9$  mg/l,  $L=12\text{cm}$ ).

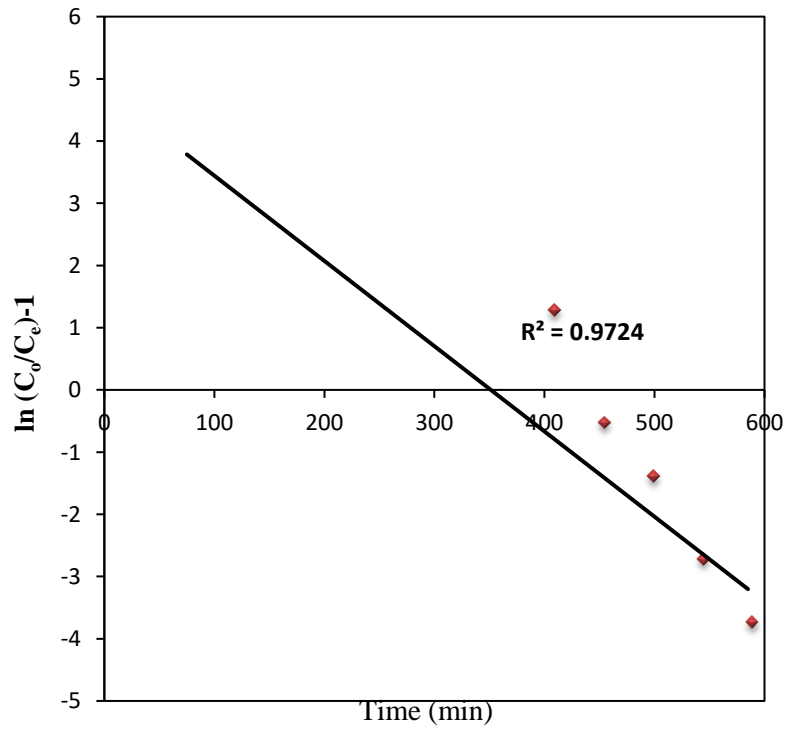


**Figure 6.** Breakthrough curves of fluidized bed column for fluoride ions adsorption onto concrete particles at different initial concentrations at 30°C (pH6, Q= 9 mg/l, L=12cm).

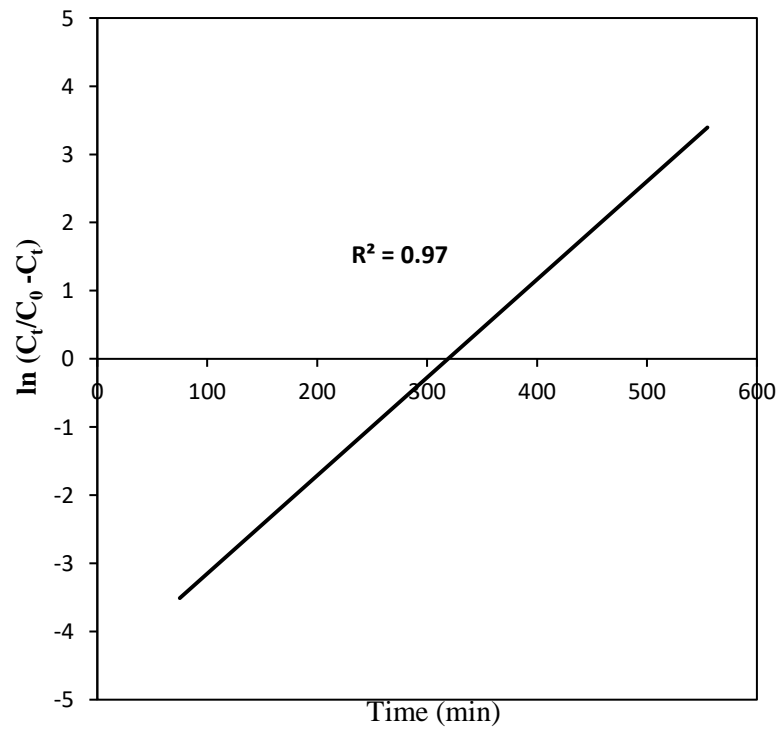


**Figure 7.** Thomas kinetic model plot of fluoride adsorption on concrete particles materials in the fixed bed.

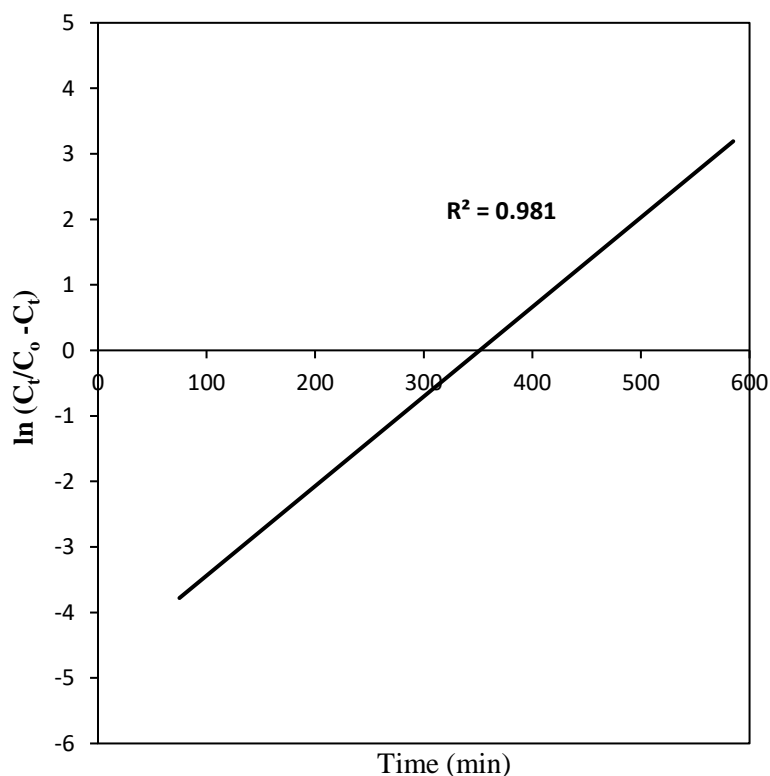




**Figure 8.** Thomas kinetic model plot of fluoride adsorption on concrete particles materials in the fluidized bed.



**Figure 9.** Yoon and Nelson model plot of fluoride adsorption on concrete particles materials in the fluidized bed.



**Figure 10.** Yoon and Nelson model plot of fluoride adsorption on concrete particles materials in the fixed bed.

#### 4. Conclusion

The current study shows that the ability of concrete adsorbent to remove fluoride ions in water. The performance of concrete particles in continuous mode and the breakthrough time were influenced by variation in bed depth, flow rate along with initial fluoride concentration. The column adsorption was enhanced by the decreased in flow rate and increase in bed depth. The experimental data for the optimum conditions successfully applied to the mathematical models of Thomas and Yoon-Nelson which were fitted well with these models.

#### 5. References

- [1] Samatya S, Yuksel U, Yuksel M and Kabay N 2007 Removal of Fluoride from Water by Metal Ions ( $Al^{3+}$ ,  $La^{3+}$  and  $ZrO$ ) Loaded Natural Zeolite *Sep. Sci. Technol.* **42** 2033–2047
- [2] Singh K, Lataye D H and Wasewar K L 2016 Removal of Fluoride from Aqueous Solution by using Bael (Aegle Marmelos) Shell Activated Carbon: Kinetic, Equilibrium and Thermodynamic study *Fluor. Chem*
- [3] Das N, Pattanaik P and Das R 2005 Defluoridation of drinking water using activated titanium rich bauxite *J. Colloid and Interface Sci.* **292** 1–10
- [4] Mukherjee S and Halder G 2018 A review on the sorptive elimination of fluoride from contaminated wastewater *J. Environ. Chem. Eng.* **6** 1257–1270
- [5] Yadav A K, Kaushik C P, Haritash A K, Kansal A and Rani N 2006 Defluoridation of groundwater using brick powder as an adsorbent *J. Hazard. Mater.* **128** 289–293
- [6] Bhatnagar A, Kumar E and Sillanpää M 2011 Fluoride removal from water by adsorption-A review *Chem. Eng. J.*, **171** 811–840
- [7] De Gisi S, Lofrano G, Grassi M and Notarnicola M 2016 Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review *Sustain. Mater. Technol.* **9** 10–40

- [8] Oguz E 2007 Equilibrium isotherms and kinetics studies for the sorption of fluoride on light weight concrete materials *Colloids Surfaces A Physicochem. Eng. Asp.* **295** 258–263
- [9] Kang W, Kim E and Park J 2007 Fluoride removal capacity of cement paste *Des.* **202** 38–44
- [10] Ayooob S and Gupta A K 2009 Performance evaluation of alumina cement granules in removing fluoride from natural and synthetic waters *Chem. Eng. J.* **150** 485–491
- [11] Liua J, Hub C and Huang Q 2019 Adsorption of Cu 2+ , Pb 2+ , and Cd 2+ onto oiltea shell from water *Bioresour. Technol.* **271** 487–491
- [12] Han R, Wang Y, Zou W, Wang Y and Shi J 2007 Comparison of linear and nonlinear analysis in estimating the Thomas model parameters for methylene blue adsorption onto natural zeolite in fixed-bed column *J. Hazard. Mater.* **145** 331–335
- [13] Talat M, Mohan S, Dixit V, Singh D K, Hasan S H and Srivastava O N 2018 Effective removal of fluoride from water by coconut husk activated carbon in fixed bed column: experimental and breakthrough curves analysis *Groundw. Sustain. Dev.* **7** 48-55
- [14] Kundu S and Gupta A K 2007 As(III) removal from aqueous medium in fixed bed using iron oxide-coated cement (IOCC): Experimental and modeling studies,” *Chem. Eng. J.* **129** 123–131
- [15] Almaliky E A and Gzar H A 2020 Geomaterials as cost effective sorbent to remove fluoride from water *Key Eng. Mater.* **870** 107–121
- [16] Ye Y, Yang J, Jiang W, Kang J, Hu Y and Hao H 2018 Fluoride removal from water using a magnesia-pullulan composite in a continuous fixed-bed column *J. Environ. Manage.* **206** 929–937
- [17] Kamble S P, Deshpande G, Barve P P, Rayalu S, Labhsetwar N K, Malyshev A and Kulkarni B D 2010 Adsorption of fluoride from aqueous solution by alumina of alkoxide nature : Batch and continuous operation *DES* **264** 15–23
- [18] Rojas-Mayorga C K, Bonilla-Petriciolet A, Sánchez-Ruiz F J, Moreno-Pérez J, Reynel-Ávila H E, Aguayo-Villarreal I A and Mendoza-Castillo D I 2015 Breakthrough curve modeling of liquid-phase adsorption of fluoride ions on aluminum-doped bone char using micro-columns: effectiveness of data fitting approaches *Journal of Molecular Liquids* **208** 114-121
- [19] de Franco M A E, de Carvalho C B, Bonetto M M, de Pelegrini Soares R and Féris L A 2018 Diclofenac removal from water by adsorption using activated carbon in batch mode and fixed-bed column: isotherms, thermodynamic study and breakthrough curves modeling *Journal of Cleaner Production* **181** 145-154