International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 09 Issue: 07 | July 2022 www.irjet.net p-ISSN: 2395-0072

Tinospora cordifolia – AS BIOADSORBENT FOR REMOVAL OF FLUORIDE FROM WATER

Athul Haridas[1], Harshan K G[2]

[1]*M.Tech Scholar in Environmental Engineering, Department of Civil Engineering, M.Dasan Institute of Technology, Kozhikode, Kerala, India*

[2]*Associate Professor, Department of Mechanical Engineering, M.Dasan Institute of Technology, Kozhikode, Kerala, India*

Abstract — *An adsorption study in a batch and column was carried out by using Tinospora cordifolia as a bio-adsorbent for the removal of fluoride from water. In the batch study the adsorbent size, adsorbent dosage, initial fluoride concentration and the time of contact are considered. The adsorbent is dried using the sunlight and powdered using grinder and sieved through the 300 µm, 150 µm, 75 µm sieves to obtain the corresponding particle size. Here we applied the adsorbent dosage as 1 g/l, 2.5 g/l and 3 g/l and the initial fluoride concentration as 3 mg/l, 5 mg/l and 7 mg/l. The contact time considered are 5 minutes,10 minutes,15 minutes,30 minutes and 45 minutes. The batch study shows that 150 µm sized adsorbent removed fluoride efficiently with a adsorbent dosage of 2.5 g/l and initial fluoride concentration of 3 mg/l with contact time of 30 minutes. On the basis of this the column study was conducted with adsorbent size 150 µm and initial fluoride concentration 3 mg/l. A column with diameter 50 mm and height 60 cm are used. The experiment conducted by varying the adsorbent bed depth as 15 cm, 25 cm and 35 cm and also varying the flow rate as 14 ml/min and 22 ml/min. The first cycle completed with this three bed depth and find out the best column. The column with bed depth 15 cm and flow rate 14 ml/min shows 87.97% fluoride removal. Then the second cycle repeated with this same parameter and find the saturation point for the column, after the saturation of the column the adsorbent required regeneration, here we used Sodium Hydroxide (NaOH) solution for this. After completing the second cycle the column is washed with NaOH solution and repeat the experiment as third cycle. About 90% of regeneration is achieved near to the saturation point.*

Key Words: Adsorption, Fluoride, Bio-adsorbent, Regeneration, Removal

1. INTRODUCTION

The quality of water resources has been declining and deteriorating in recent years [8]. Fluoride is naturally found in many of the ground water sources. Consumption of water having excess fluoride over a prolonged period leads to a chronic ailment known as fluorosis. Fluorosis is a crippling disease affecting bones, teeth and soft tissues [5]. Fluoride enters into the human body through a variety of sources like water, food, air, medicine, and cosmetics. Among these, drinking water is the most common source which makes fluoride available to human beings. Fluoride is known to have both beneficial and detrimental effects on health, depending on the dose and duration of exposure. The desirable concentration of fluoride as F^- in drinking water is 1.0 mg/l. Low F^- content (< 0.60 mg/l) causes dental caries, whereas high (>1.20 mg/l) fluoride levels result in fluorosis. Hence, it is essential to have a safe limit of F^- concentration of between 0.60 and 1.20 mg/l in drinking water. The Bureau of Indian Standards (BIS) prescribed desirable limit as 1.0 mg/l and maximum permissible limit in the absence of alternate source as 1.5 mg/l. In India, about 62 million people are at risk of developing fluorosis from drinking high F^- water [6]. Low amount of fluoride is necessary in the prevention of tooth decay and the development of proper bone structure in humans and animals. It is considered to be a micro nutrient for humans since it prevents dental caries by decreasing the rate of demineralisation of the dental enamel or reverses the progression of existing decay by promoting the rate of remineralisation. High doses of fluoride lead to the development of dental and skeletal fluorosis, depending on the concentration of fluoride in drinking water [12].

Adsorption is the preferred technique for fluoride removal at community and household levels in rural areas because of its low cost and ease of operation, high efficiency, easy accessibility, environmental benignity, and needless of operational skill and electric power to run, and since adsorbents can in principle be reused and recycled making it ideal for use in less developed rural areas. It has the added advantage that it can be applied to a decentralized water supply system. The availability of different adsorbents in large amounts and low costs make them potential candidates for the fluoride removal in remote areas [16].

The main objectives of this study are to evaluate the performance of *Tinospora cordifolia* as a bio adsorbent for the fluoride removal of water, using batch study and column performance. In the batch study we are considering

the parameters like Adsorbent dosage, Initial concentration, Size of adsorbent and contact time. Similarly in column performance we are considering Initial concentration, Bed depth and Flow rate. And to check the possibility of regeneration study using NaOH as regenerant.

2. MATERIALS AND METHODOLOGY

2.1 Adsorbent Used

*Tin**o**spora cordifolia* commonly known as "Chittamrit" in Kerala state, India belongs to Menispermaceae family of kingdom Plantae used as adsorbent material for the study. It is a genetically diverse, large, deciduous climbing shrub mainly found at higher altitude. Some variety of active components derived from the plant like steroids, aliphatics, diterpenoid lactones, alkaloids, and glycosides are isolated from the different parts of the plant, like root, stem, leaves etc

2.2 Adsorbent Preparation

In this study we are using the plant stem for conducting the experiment. The stem of the plant is collected and it is washed with distilled water to remove the dust and other impurities. Then the stem is shredded into small size to ensure fast drying. The shredded stem is allowed to dry under sunlight till complete moisture is removed and then it is powdered with the help of grinder and sieved through 300 micron, 150 micron and 75 micron to obtain the respected particle size of adsorbent.

2.3 Preparation of Fluoride Solution

The required sample solution is made up by diluting the Fluoride standard solution traceable to SRM (Standard Reference Material) from NIST (National Institute of Standards and Technology) NaF in H_2O, Made in Germany, EMD Millipore Corporation.

2.4 Batch Study

To study the effect of various controlling parameters like adsorbent size, adsorbent dosage, initial fluoride concentration, and time of contact on the fluoride removal capacity of *Tinospora cordifolia.* The batch experiments were conducted using a total sample volume of 1000 ml for each adsorption run, and the samples were agitated in a reciprocating shaker. The adsorbent size used for the experiment are 300 micron, 150 micron and 75 micron. The adsorbent dosage is taken as 1 g/l, 2.5 g/l and 3 g/l. The initial fluoride concentration of 3 mg/l. 5 mg/l and 7 mg/l are considered. 5 min, 10 min, 15 min, 30 min and 45 min are considered as the contact time for this experiment.

2.5 Column Study

The column experiment for the removal of fluoride from the water by *Tinospora cordifolia* was performed using a 50 mm diameter and 60 cm length P.V.C pipe, and it is attached to a flow control valve for adjusting the flow through the column.

The adsorbent is sandwiched between the layers of glass beads to prevent the loss of adsorbent. The depth of adsorbent is considered as 15 cm, 25 cm, and 35 cm and considering the flow rate as 14 ml/min and 22 ml/min. The prepared fluoride solution is allowed to pass through the adsorbent in the column and the samples were collected in 5 min, 10 min, 15 min. 30 min and 45 min for each adsorption run.

(i) Breakthrough Study

In the adsorption the adsorbent gets completely saturated at some point due to the unavailability of adsorption site on adsorbent, and the adsorption starts decreasing. Thereafter the adsorbent become completely lifeless. To find this saturation point we continued second cycle with the best column selected from the cycle 1 column study.

2.6 Regeneration of Bio-Adsorbent

In the environmental and economic aspects, the regeneration of adsorbent is very important. After every adsorption run the chance for the adsorbent get exhausted is possibly very high, to avoid this we need to regenerate the adsorption capacity of the adsorbent. Here we are using 0.1 M NaOH solution for this purpose. After the saturation of the adsorbent the NaOH solution is passed through the adsorbent bed, and fluoride removal is checked again.

3. RESULTS AND DISCUSSION

3.1 Batch Study

In the Batch study we are mainly considering the parameters such as adsorbent size, adsorbent dosage, initial fluoride concentration and time of contact, the detailed result of this parameters are included in the following sections.

(i) Effect of Adsorbent Size

The study of the effect of adsorbent size on the fluoride removal efficiency was carried out by using 75 µm, 150 µm and 300 µm sized adsorbent.

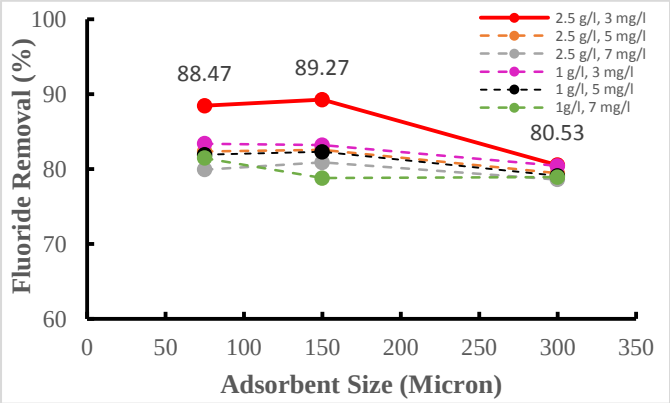

Fig -1: Effect of Adsorbent size on the removal efficiency of Fluoride.

A maximum of 89.27% removal is obtained for the 150 µm sized adsorbent and 88.47 % removal is obtained for 75µm sized adsorbent, but considering the 300 µm sized adsorbent the removal declines to 80.53%. Fig-1 shows the effect of adsorbent size on the fluoride removal capacity of the adsorbents.

(ii) Effect of Adsorbent Dosage

The study of the effect of adsorbent dosage on the fluoride removal efficiency was carried out with a dosage of 1 g/l, 2.5 g/l and 3 g/l. The study is done by keeping the adsorbent size as 150 µm and varying the initial fluoride concentration as 3 mg/l, 5 mg/l and 7 mg/l.

With initial fluoride concentration 3 mg/l and adsorbent dosage 2.5 g/l and 3 g/l shows a removal of 89.27% and 89.20% respectively, and 83.20% fluoride removal for 1 g/l adsorbent dosage. Similarly for 5 mg/l initial fluoride concentration 82.58% removal achieved for both 2.5 g/l and 3 g/l adsorbent dosage and 82.30% obtained for 1 g/l adsorbent dosage. In the case of 7 mg/l initial concentration, 80.89% and 80.87% fluoride removal achieved for 2.5 g/l and 3 g/l and 78.80% removal for 1 g/l adsorbent dosage. From this analysis it is clear that 2.5 g/l adsorbent dosage shows better removal than the other dosages considered.

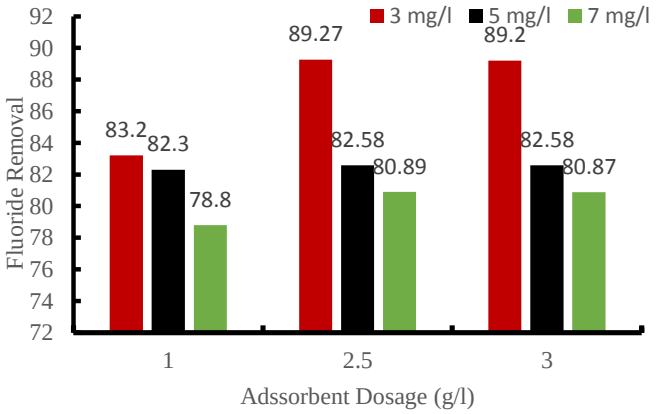

Fig -2: Effect of Adsorbent Dosage on the removal efficiency of Fluoride.

Fig-2 shows the effect of adsorbent dosage on the fluoride removal capacity of the adsorbents.

(iii) Effect of Initial Fluoride Concentration

The effect of initial concentration on the extent of removal of the fluoride was studied by varying the concentrations from 3 mg/l, 5 mg/l and 7 mg/l. While keeping the adsorbent size as 150 µm and adsorbent dosage as 2.5 g/l.

For this study two contact time are considered 15 minutes and 30 minutes, the initial concentration with 3 mg/l shows 89.27% fluoride in 30 minutes and 86.87% fluoride removal in 15 minutes. For 5 mg/l initial fluoride concentration shows 82.92% removal in 30 minutes and 82.58% in 15 minutes. And 80.89% and 82.04% fluoride removal for 7 mg/l initial fluoride concentration at 30 minutes and 15 minutes respectively.

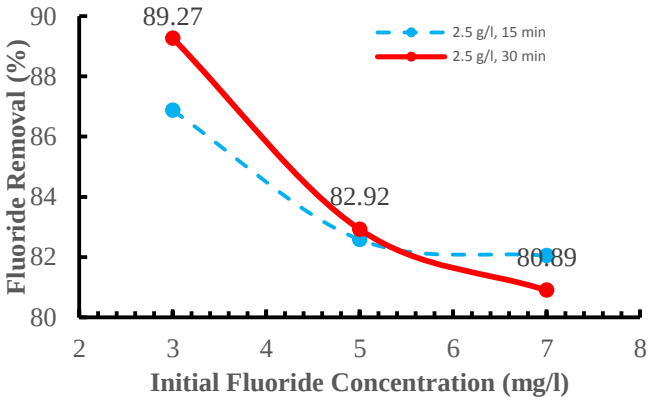

Fig -3: Effect of Initial Fluoride Concntration on the removal efficiency of Fluoride.

The results obtained were plotted as percentage removal of fluoride versus initial concentration of the fluoride ion in the solution as shown in Fig.3. We can see

that the percentage removal of the fluoride ion has decreased with an increase in initial concentration of the fluoride ion.

(iv) Effect of Contact Time

The study of the effect of contact time on the fluoride removal efficiency was carried out by varying it from 5 to 45 minutes, keeping the adsorbent size as 150 µm, adsorbent dosage as 2.5 g/l and with an initial concentration of 3 mg/l.

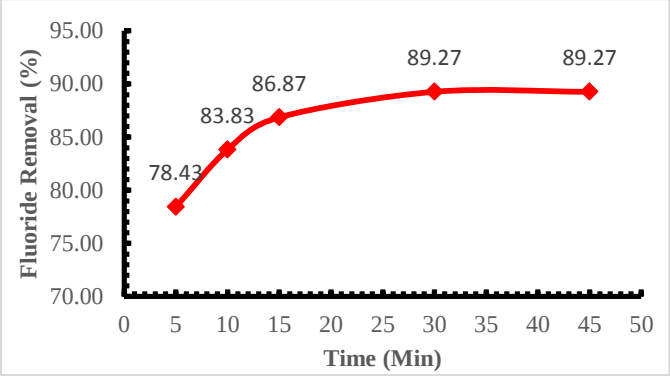

Fig -4: Effect of Time on Fluoride Removal

Fig.4 shows the effect of contact time on the fluoride removal capacity of the adsorbents. As contact time increases percent removal also increases initially and gradually attains almost an equilibrium condition in nearly 30 minutes. A maximum of 89.27% removal could be accomplished by the adsorbent *Tinospora cordifolia.*

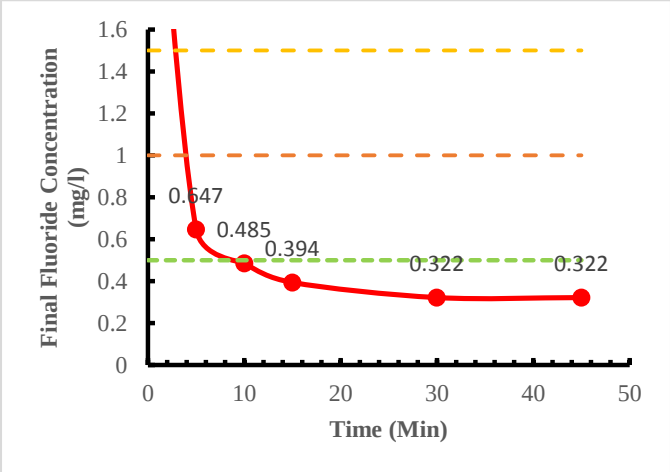

Fig -5: Final Fluoride Concentration verses Time (Batch Study)

The final fluoride concentration verses time graph is shown in the Fig.5, the gradual decrease in final fluoride level is observed after 30 minutes there is no further decrease observed. After showing the highest removal the adsorbent gets fully saturated and hence further increase in adsorption will not occur.

3.2 Column Study

From the batch study we noted that the adsorbent *Tinospora cordifolia* shows better performance with adsorbent size 150 µm and for an initial fluoride concentration of 3 mg/l for 30 minutes at an adsorbent dosage of 2.5 g/l. In the column study we are mainly considering the parameters such as depth of adsorbent bed and the flow rate.

(i) Effect of Adsorbent Bed Depth

For this set of experiment the bed depth is taken as 15 cm, 25 cm and 35 cm, we have passed the 3 mg/l fluoride solution through the column and collected the samples at an interval of 5 min, 10 min, 15 min, 30 min and 45 min with flow rate of 14 ml/min and 22 ml/min. A fluoride removal of 87.97% is obtained for 15 cm bed depth, 87.30 % and 85.97% of fluoride removal are achieved by column with adsorbent bed depth 25 cm and 35 cm respectively at the flow rate of 14 ml/min. From this analysis it is clear that for 14 ml/min flow rate, effect of adsorbent bed depth on fluoride removal is negligible, but in 22 ml/min flow rate the fluoride removal increases with increase in adsorbent bed depth. That is if flow rate increases the depth required are also more for more adsorbent sites.

(ii) Effect of Flow Rate

In the column study 14 ml/min and 22 ml/min discharge is considered. The 14 ml/min flow rate shows better removal in all adsorbent bed depth considered. The 22 ml/min shows less removal, this is due to the time of holding the fluoride solution in the adsorbent column is less in higher flow rate and which is higher in low flow rate. For 14 ml/min the final fluoride concentration at 5 minutes is 0.638 mg/l and it decreased to 0.361 mg/l in 45 minutes. In 22 ml/min flow rate final fluoride concentration observed as 0.652 mg/l at 5 minutes and decreased to 0.495 mg/l at 30 minutes. From this it is clear that if flow rate increases the adsorption decreases.

(iii) Effect of Time on Final Fluoride Concentration

The final fluoride concentration verses time graph is shown in Fig.6, for 5 minutes all bed depth and flow rate show almost same removal.

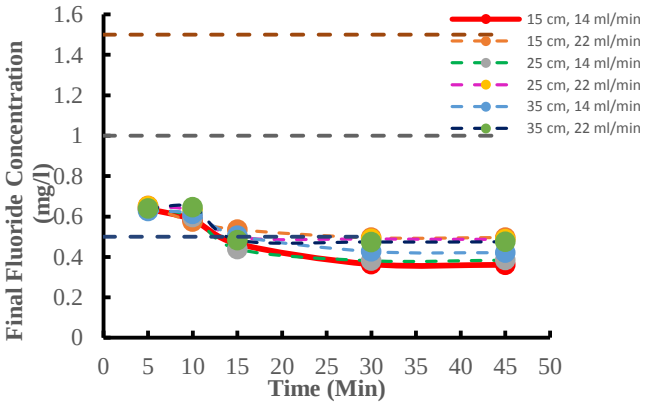

Fig -6: Final Fluoride Concentration verses Time (Column Study)

The best removal observed for the column with 15 cm bed depth and 14 ml/min flow rate for 5 minutes the final fluoride concentration is 0.683 mg/l and the minimum fluoride concentration observed at 45 minutes as 0.361 mg/l.

(iv) Break through Study

Breakthrough analysis shows, the fluoride removal increases gradually in the initial phase and after some point it become stable which means there is no increase in adsorption takes place.

A fluoride removal of 78.20% obtained at 5 minutes and increases gradually increased to 87.27% removal at 75 minutes. After 75 minutes there is no further increase in adsorption occurs, and at 105 minutes a small drop in fluoride removal occurs. The graph represents stable line from 75 minutes to 90 minutes and then it declines which means the removal efficiency decreases.

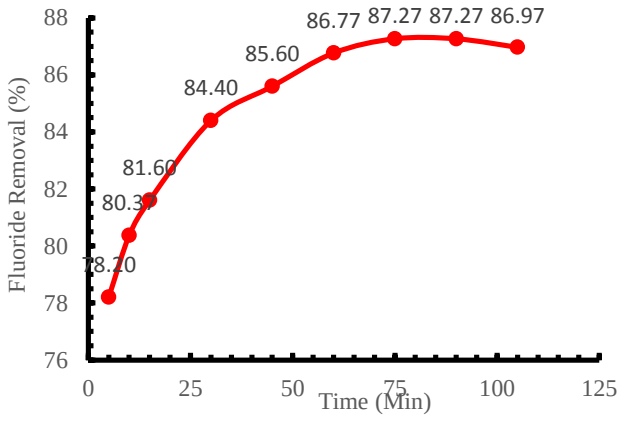

Fig -7: Breakthrough Curve.

The highest fluoride removal achieved at 75 minutes and at 105 minutes a small drop in fluoride occurs.

3.3 Regeneration Study

Before throwing the adsorbent after its saturation we need to check the possibility of regeneration. Sodium Hydroxide solution was used as regenerant.

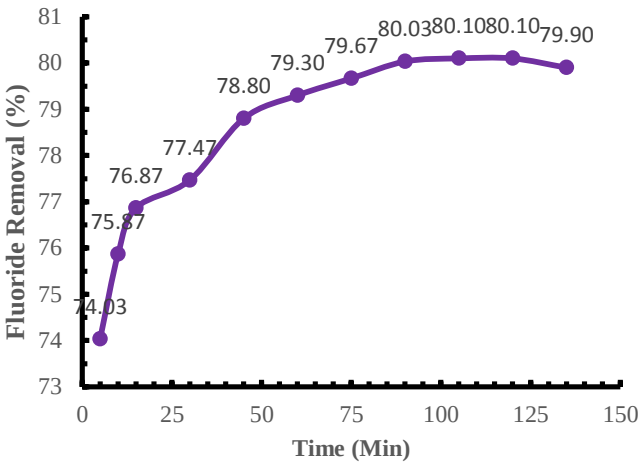

Fig -8: Effect of NaOH on Regeneration of Adsorbent.

After saturation of the adsorbent column in cycle 2 is washed with NaOH solution. Initially a fluoride removal of 74.03% occurs at 5 minutes and it gradually increases to 75.87% in 10 minutes, 76.87% in 15 minutes, 77.47% in 30 minutes, 78.80% in 45 minutes, 79.30% in 60 minutes, 79.67% in 75 minutes, 80.03% in 90 minutes and the highest removal of 80.10% in 105 minutes and 120 minutes, which shows that the regenerated adsorbent get saturated and no further increase in adsorption occurs. After 135 minutes the removal gets a slight decline to 79.90%.

This study shows that the regeneration of adsorbent is possible for the adsorbent used in this experiment. 90% regeneration of adsorbent is achieved near to the saturation point.

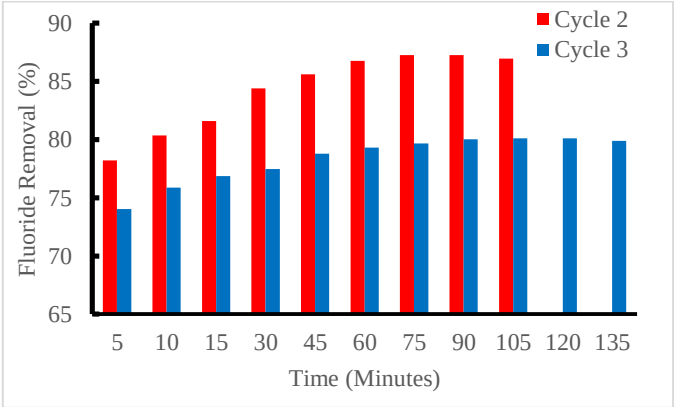

Fig -9: Comparison of adsorption cycle 2 and cycle 3.

The Fig-9 shows the comparison between cycle 2 and cycle 3. In cycle 2, a maximum of 87.27% fluoride removal occurs and in cycle 3 it declines to 80.10%.

4. CONCLUSIONS

The fluoride contamination in the water is very serious issue faced in many places in the world. The plant *Tinospora cordifolia* as a bio adsorbent used for the removal of fluoride from the water is a naturally occurring material with great availablity, it possesses some medicinal values and moreover with high fluoride removal efficiency.

In this study we conducted a batch study and a column study, in the batch study we are mainly considered four parameters namely Adsorbent size, adsorbent dosage, Initial fluoride concentration and time of contact. The adsorbent size used for this experiment are 75 µm, 150 µm, and 300 µm. The adsorbent dosage 1 g/l, 2.5g/l and 3 g/l. The initial fluoride concentration of 3 mg/l, 5 mg/l and 7 mg/l are chosen. The time varying from 5 minutes to 45 minutes as time of contact. After the batch experiments with this parameter, we obtained best fluoride removal for adsorbent size 150 µm and an initial concentration 3 mg/l with adsorbent dosage 2.5 g/l at 30 minutes time.

On the basis of the result obtained from the batch study we are conducted the column study using 150 µm sized adsorbent and with an initial fluoride concentration of 3 mg/l. In the column study we are mainly focusing on the adsorbent bed depth and flow rate through the column. For this study we are chosen three adsorbent bed depths 15 cm, 25 cm and 35 cm. And two flow rates 14 ml/min and 22 ml/min. As the first cycle of the column study has completed, we noticed that column of 15 cm bed depth with 14 ml/min flow rate shows 87.97% fluoride removal. After this we need to find out the saturation point of the column for breakthrough analysis of adsorbent. In the second cycle with bed depth 15 cm and flow rate 14ml/min, the experiment continues as similar to the first cycle the fluoride removal increases gradually to 87.27 % and after 75 minutes it become stable which means that the adsorbent gets saturated, no further increase in removal is possible using the same adsorbent bed.

As the column get saturated in the second cycle, before throwing it we need to try a regeneration study on it. Using NaOH solution the column is washed and continued the third cycle. The 74.03% fluoride removal in 5 minutes and gradually increases to 80.03% in 90 minutes and 80.10% 105 minutes, after 105 minutes no further increase in removal seen in the column. By comparing the cycle 2 and cycle 3 around 90% of regeneration achieved near to the saturation point.

From this sets of experiments, we can conclude that the plant *Tinospora cordifolia* can be used for adsorbent for removing fluoride from water, as it shows high removal efficiency and regeneration characteristics.

REFERENCES

[1] Anirban Chowdhury, Mrinal K. Adak, Arnab Mukherjee, Prasanta Dhak, Julekha Khatun, Debasis Dhak, (2019) A critical review on geochemical and geological aspects of fluoride belts, fluorosis and natural materials and other sources for alternatives to fluoride exposure, Journal of Hydrology, Volume 574, Pages 333-359, ISSN 0022-1694, https://doi.org/10.1016/j.jhydrol.2019.04.033.

[2] Ankita Dhillon, Sapna, B.L. Choudhary, Dinesh Kumar, Surendra Prasad, (2018) Excellent disinfection and fluoride removal using bifunctional nanocomposite, Chemical Engineering Journal, Volume 337, Pages 193-200, ISSN 1385-8947. https://doi.org/10.1016/j.cej.2017.12.030

[3] Chakraborty, Meena & Pandey, Madhurima & Pandey, Piyushkant. (2021). Fixed bed column performance of Tinospora cordifolia for defluoridation of water. Water Supply. 21. 10.2166/ws.2021.045.

[4] Cox, Charles Raymond & World Health Organization. (1964). Operation and control of water treatment processes / Charles R. Cox ; prepared in consultation with twenty-four specialists in various countries. World Health Organization.

[5] D. Eunice Jayashree, P. Senthil Kumar, P. Tsopbou Ngueagni, Dai-VietN. Vo, Kit Wayne Chew, (2020) Effective removal of excessive fluoride from aqueous environment using activated pods of Bauhinia variegata: Batch and dynamic analysis, Environmental Pollution, Volume 272, 2021, 115969, ISSN 0269-7491, https://doi.org/10.1016/j.envpol.2020.115969.

[6] Das, Malay & Attar, Salim. (2011). Comparative Study of Batch Adsorption of Fluoride Using Commercial and Natural Adsorbent. Research Journal of Chemical Sciences. 1. 68-75.

[7] E., Shaji & Bindu, & Viju, J. & Thambi, D.S. (2007). High fluoride in groundwater of Palghat District, Kerala. Current Science. 92. 240-245.

[8] Jayashree, D. & Pooja, G. & Ponnusamy, Senthil Kumar & Gurunathan, Prasannamedha. (2020). A review on fluoride: Treatment strategies and scope for further research. DESALINATION AND WATER TREATMENT. 200. 167-186. 10.5004/dwt.2020.26010.

[9] Jiabin Chen, Renjie Yang, Zhiyong Zhang, Deyi Wu, (2021) Removal of fluoride from water using aluminum hydroxide-loaded zeolite synthesized from coal fly ash, Journal of Hazardous Materials, Volume 421, 2022, 126817, ISSN 0304-3894, https://doi.org/10.1016/j.jhazmat.2021.126817.

[10] Junyong He, Ya Yang, Zijian Wu, Chao Xie, Kaisheng Zhang, Lingtao Kong, Jinhuai Liu, (2020) Review of fluoride removal from water environment by adsorption, Journal of Environmental Chemical Engineering, Volume 8, Issue 6, 104516, ISSN 2213-3437 https://doi.org/10.1016/j.jece.2020.104516.

[11] P. Senthil Kumar, S. Suganya, S. Srinivas, S. Priyadharshini, M. Karthika, R. Karishma Sri, V. Swetha, Mu. Naushad & Eric Lichtfouse , (2019) Treatment of fluoride-contaminated water. A review. Environ Chem Lett 17, 1707–1726. https://doi.org/10.1007/s10311-019-00906-9.

[12] Rajkamal Mohan, Robin K. Dutta, (2020) Continuous fixed-bed column assessment for defluoridation of water using HAp-coated-limestone, Journal of Environmental Chemical Engineering, Volume 8, Issue 4, 103840, ISSN 2213-3437, https://doi.org/10.1016/j.jece.2020.103840.

[13] Ramesh, ST & Gandhimathi, R. & P.V., Nidheesh & Taywade, Manoj. (2012). Batch and Column Operations for the Removal of Fluoride from Aqueous Solution Using Bottom Ash. Environmental Research, Engineering and Management. 2. 12-20. 10.5755/j01.erem.60.2.1396.

[14] Raveendra M. Hegde, Richelle M. Rego, Krishna Murthy Potla, Mahaveer D. Kurkuri, Madhuprasad Kigga, (2020) Bio-inspired materials for defluoridation of water: A review, Chemosphere, Volume 253, 126657.

[15] Shreyas J. Kashyap, Ravi Sankannavar, G.M. Madhu, (2021) Fluoride sources, toxicity and fluorosis management techniques – A brief review, Journal of Hazardous Materials Letters, Volume 2, 2021, 100033, ISSN 2666-9110.

[16] Tesfaye Akafu, Achalu Chimdi, Kefyalew Gomoro, (2019) "Removal of Fluoride from Drinking Water by Sorption Using Diatomite Modified with Aluminum Hydroxide", Journal of Analytical Methods in Chemistry, Article ID 4831926.

[17] Tolkou, A.K.; Manousi, N.; Zachariadis, G.A.; Katsoyiannis, I.A.; Deliyanni, E.A. (2021) Recently Developed Adsorbing Materials for Fluoride Removal from Water and Fluoride Analytical Determination Techniques: A Review. Sustainability 13, 7061. https://doi.org/10.3390/su13137061.

[18] Umma Salma Rashid, Achintya N. Bezbaruah, (2020) Citric acid modified granular activated carbon for enhanced defluoridation, Chemosphere, Volume 252, 126639, ISSN 0045-6535,