Nat. Volatiles & Essent. Oils, 2021;08(2): 238-245

Elimination of Fluoride from Water Using Natural Adsorbent *Pistacia vera* (Pista Shell)

Ravi Kant[1,*], Kalpana Rawat[2], Keshav Kumar Saini[3]

[1] *Department of Chemistry, Government Post Graduate College, Noida-201301, India
[2] Lloyd Institute of Management and Technology, Plot No. 11, Knowledge Park-II, Greater Noida-201306, India
[3] Department of Chemistry, Dyal Singh College (University of Delhi), Lodhi Road, New Delhi-110003, India

***Corresponding Author:** Ravi Kant
*Department of Chemistry, Government Post Graduate College, Noida-201301, India

---

Abstract

The availability of clean water for human consumption is a universally acknowledged human right and an essential component of human flourishing. One of the quality characteristics which is of concern when it comes to water is fluoride. The World Health Organization (WHO) has set a limit of 1.5 mg / L for fluoride ion because of the harm it can do to living things' teeth and bones. The current research aims to examine the efficacy of the natural adsorbent *Pistacia vera* (Pista shell) in removing fluoride ions from water-based solutions or samples. The most efficient and thorough elimination of fluoride ions was the focus of the controlled trials. It was noted that the fluoride ion was most effectively removed up to 60% when the pH was neutral, specifically 7.0. Additionally, the significance of temperature in the removal of fluoride ions from water was established. The fluoride was successfully eliminated, according to EDAX. To find the greatest fit, we also looked at kinetic and isotherm models.

Keywords: Adsorption, Fluoride Removal, *Pistacia vera*, Adsorbent.

Introduction

Various concerns about fluoride's impact on public health have been recognized and finds its way into nearly all water sources, but at varying concentrations. Cosmetics, medications, chewing gum, toothpaste, mouthwash, and other oral hygiene products all include it. When present in trace amounts, it helps humans avoid dental issues, but when present in large quantities, it becomes toxic. Fluoride content of drinking water should be between 1 -1.5 mg/L, according to World Health Organization (WHO) recommendations. Several health problems, including dental and skeletal fluorosis, can arise from consuming more fluoride than the recommended quantity (1,2). It is a chronic condition that affects over 23 countries worldwide, inducing India. Estimated number of fluoride-related illnesses suffered by around 62 million individuals in India (3).

Adsorption, electro-filtration, reverse osmosis, coagulation/precipitation, ion exchange, dialysis, nano-filtration, ultra-filtration, and other techniques have been employed in various attempts to treat fluoride-containing drinking water (4-11). Adsorption is one of the surface-related technique for the excision of both inorganic as well as organic impurities. The adsorption strategy is one of the most adaptable defluorination techniques available due to its low cost, broad range of end uses, cultural and social acceptance, compliance with regulations, sustainability, and comparative ease of application. (12-16). Lots of materials/substances are available in nature and in living things might have special qualities that make them good adsorbents. Such class of materials is ideal for the large-scale adsorption since it is abundant in nature, cheap, and has a number of useful qualities (e.g., exchange ability, molecular sieve, etc.) (17-22). There have been a number of studies looking into ways to reduce fluoride levels in drinking water to the level set by the World Health Organization. Tembhurkar & Dongre (23) examined activated charcoal's potential to remove fluoride from water. When tested under optimized conditions, they reported that equilibrium was reached in 120 minutes and fluoride removal efficiency reached 94%. Similarly, Alagumuthu et al. (24) reported the efficacy of activated carbon derived from cynodondactylon in removing fluoride from water. They performed adsorption studies at neutral pH with particular variables such the initial adsorbate the concentration, duration of contact, dosage of adsorbent, temperature, and the effect of counter-anions. The adsorption reached equilibrium after 105 minutes, according to their observations. They highlighted the fact that the adsorption appears to match the predictions of the Langmuir and Redlich-Peterson isotherms models based on the experimental results. The thermodynamic data was used to determine endothermic adsorption. Turner et al. (25) used batch tests and surface-sensitive techniques to investigate the efficacy of broken limestone (99% pure calcite) in removing fluoride. Choi & Chen (26) investigated the efficacy of activated carbon, activated bauxite, and alumina activators are used as adsorbents to remove fluoride from various kinds of water. When fluoride levels are low, Fan et al. (27) studied the adsorption capacity and kinetics using various inexpensive adsorbents, including calcite, hydroxyapatite, fluorspar, quartz, and quartz activated. The possible natural adsorbents for the removal of fluoride were also examined by several additional research teams (28–34). The main goal of this study is to determine how well the natural adsorbent *Pistacia vera* (pista shells) removes the fluoride ions from the water samples or solutions.

Materials and Procedures

Standard fluoride solution preparation: Anhydrous sodium fluoride (NaF) is used to prepared stock solution for the whole experimental procedure. 221 milligrams of fluoride were dissolved in 1000 milliliters of distilled water to prepare a standard solution of 100 mg L-1 (100 ppm) final concentration. This stock solution was used to prepare further dilutions and aliquots.

Preparation of adsorbent from the *Pistacia Vera* shells: In present experiment shells of *Pistacia Vera* nuts are used as adsorbent. *Pistacia is a member of the family of Anacardiaceae, which also includes poison ivy, cashew nuts, mangos, and sumach. The sole species in this family that yields edible nuts big enough for commercial use is Pistacia vera L. Nut shells are gathered, cleaned of external contaminants using double-distilled water, and then dried.* This shell is very hard in nature, not easy to crush; hence the charcoal was prepared using this shell. Pista shell was burned, washed, dried in oven at 100ºC, then crushed using mortal pestle, and fine powder was prepared using mixer grinder. To obtain fine powder, using appropriate sieve of 60 BSS size was used.

Measurement of Fluoride: Progress of the adsorption was measured using Fluoride Ion Meter Panomex Model PX/IMC/321. This instrument is calibrated in the range of blank or 0.0 ppm to 100 PPM. To optimise the rate-affecting parameters, including pH, beginning concentration, the quantity of adsorbent, duration of contact, temperature, etc., a control experiment was conducted for 240–300 minutes.

3.0 Results and Discussion:

(a) Influence of pH: A crucial factor in adsorption is pH; based on the characteristics of the adsorbent's upper surface can vary or alter depending on the solution's pH value. pH was determined between 4.0 and 10.0, and the results are shown graphically in **figure 1**. It is observed that higher removal of fluoride of approx 52% is at neutral pH. While moving towards higher acidic or basic side the adsorption or the removal % decreases, it may be due to the interference of ionic strength of the solution. i.e. due to excess of H^+ ions or OH^- ions present in the solution.

(b) Effect of amount of adsorbent: This parameter is very important in case of adsorption for the removal of any pollutant. In this study, 50 mL of the fluoride solution (10 ppm) was taken, and the doses of adsorbent varied in the range of 0.25 gm. to 2.0 gm. to study the impact on the adsorption and graphically depicted in the

Figure 2. It was found that the percentage of the fluoride ions removed rises with increasing adsorbent quantity. This occurs because an increase in adsorbent quantity results in an increase in the adsorption site's surface area, which enhances the possibility for fluoride ions to attach to the adsorbent's surface.

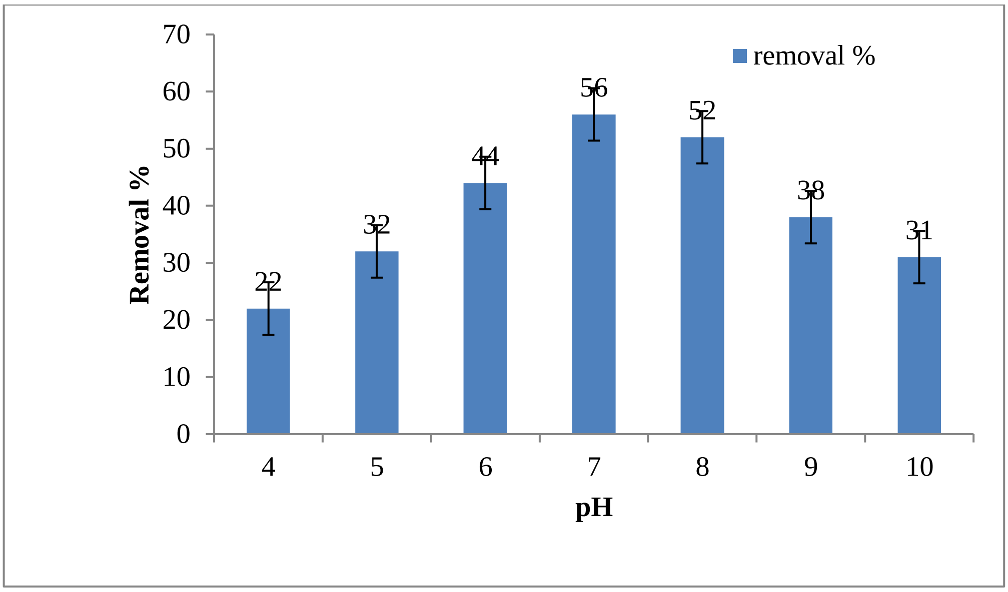

Fig. 1: Influence of pH

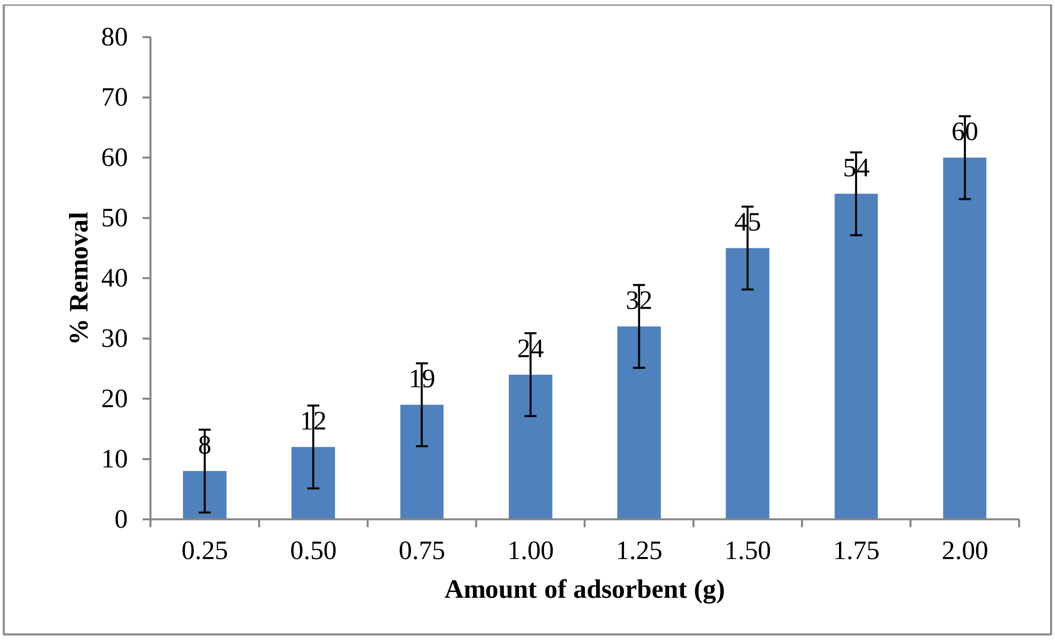

Figure 02: Effect of amount of adsorbent

(c) Effect of contact time: Adsorption is a time dependent phenomenon. Equilibrium time is one among important parameters for water treatment systems. A plot of % of removal of fluoride onto the adsorbent (Pista Shell) with respect to contact time of 0-240 min. was studied with a initial concentration on 10 ppm and different adsorbent dose of adsorbent (0.5, 1.0, 1.5 and 2.0 g) and represented in **figure 3**. It is observed that, at all adsorbent dose similar pattern of adsorption was observed. As we increase the adsorbent dose, the % of removal increases with respect to time. After attaining a peak at 180 min., the equilibrium phase is obtained. It is observed that at initial the adsorption was fast, it is due to more adsorption site was available at that moment.

(d) Influence of temperature: At pH 7.0, fluoride adsorption was also observed under appropriate conditions. concentration of 10 ppm, amount of adsorbent 0.10 g and at RT, 35, 45 and 55ºC **figure 4** indicates that the removal of fluoride *via* adsorption on pista shell increases as the temperature increase. In the beginning, the percentage of fluoride ions removal rises as the temperature rises, but at higher temperatures, % removal decreases, This can be explained by desorption, which may occur because van der Wall forces diminish at higher temperatures, resulting in less. Due to this phenomena desorption started.

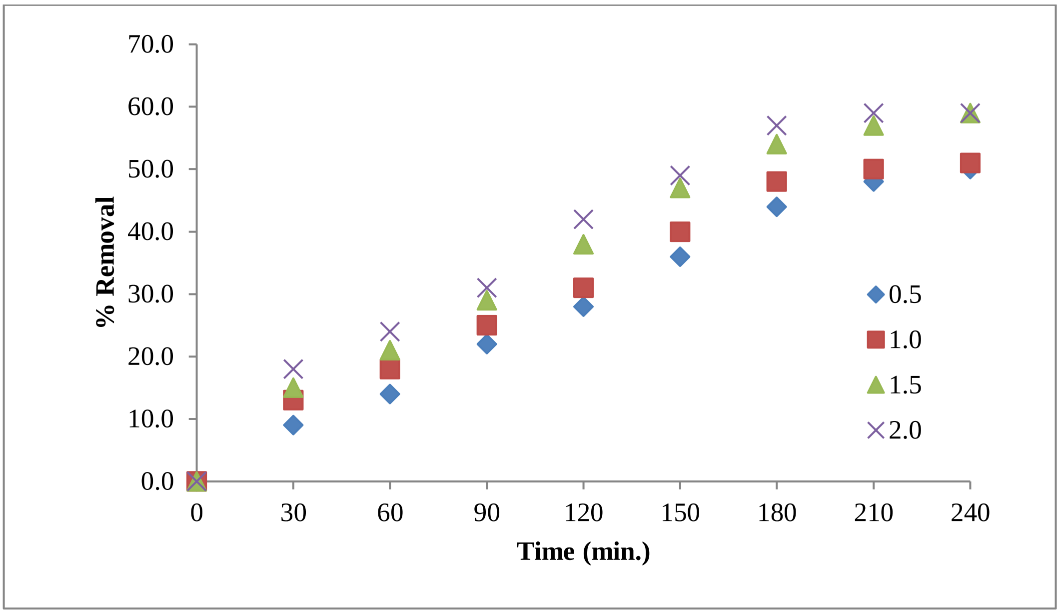

Figure 03: Effect of Contact time

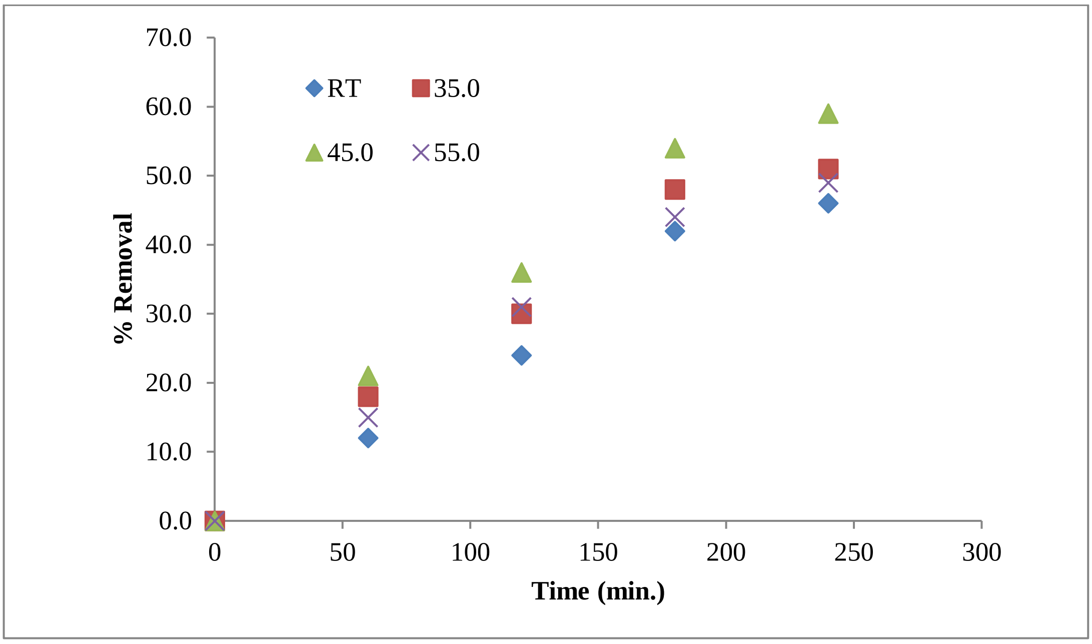

Figure 04: Effect of temperature

Adsorption Kinetics studies

Kinetics is a mathematical investigation of the chemical reaction rates and study of factors which affect the equilibrium. Furthermore, to the adsorption capacity, it speculates on the underlying mechanism that governs the process of adsorption.

Pseudo-first order: The following is an explanation of the linear form of the Lagergren pseudo-first order kinetic model:

$$\log(q_e - q_t) = \log q_e - k_1 \times t$$

where k_1 is the pseudo-first order kinetic model's rate constant (sec^{-1}) and q_e and q_t are the amounts ($mg\ g^{-1}$) of fluoride ions adsorbed at equilibrium and time t, respectively.

Pseudo-second order: The following is the expression for the pseudo-second order linear form:

$$\frac{t}{q_t} = \frac{k_2^{-1}}{q_e^2} + \frac{1}{q_e} \times t$$

where k_2 is a constant of pseudo-second order. A straight-line relationship appears when t/q_t is plotted versus t. From the slope and intercepts of this plot the value of q_e and k_2 can be determined.

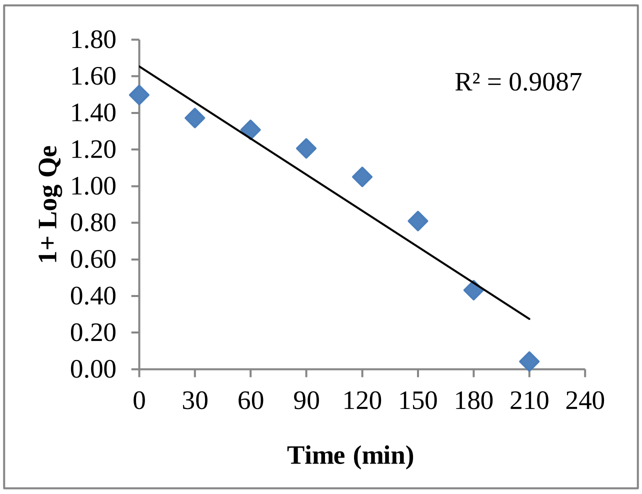

Fig. 05 a) First order kinetic plot

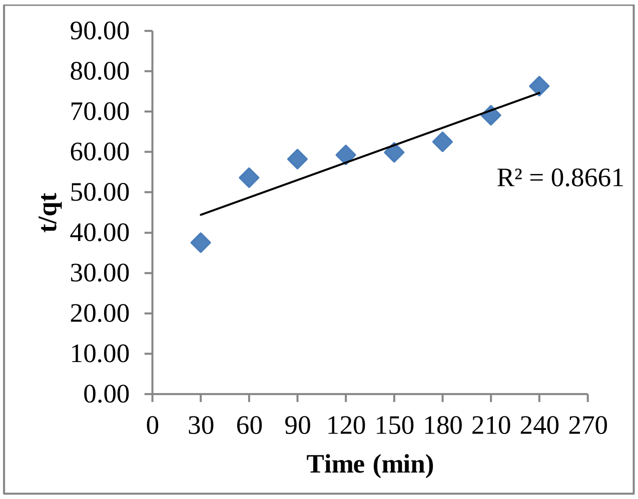

Fig. 05 b) Second Order Kinetic Plot

From above both first order and second order kinetic plots a correlation among adsorbent and adsorbate with respect to time, The linear regression correlations coefficient values (R^2) was utilized to determine the best-fit model. It is observed that the first order of kinetics (R^2 = 0.907) was followed by the adsorption of fluoride ions.

Adsorption Isotherm

The process of mass transfer between liquid and solid is known as adsorption is generally to refer to the interaction of liquid and solid phases. To explain the connection between the quantity of fluoride ions adsorbed and its concentration at equilibrium in the solutions, the Langmuir and Freundlich equations were studied as well. The equation for Langmuir isotherm shown below:

$$\frac{1}{q_e} = \frac{1}{q_m} \times K_L \times C_e + \frac{1}{q_m}$$

The Freundlich equation is relying on the adsorption at heterogeneous surface of the adsorbent and its straight line shown as below:

$$\log q_e = K_f + \frac{1}{n} \log C_e$$

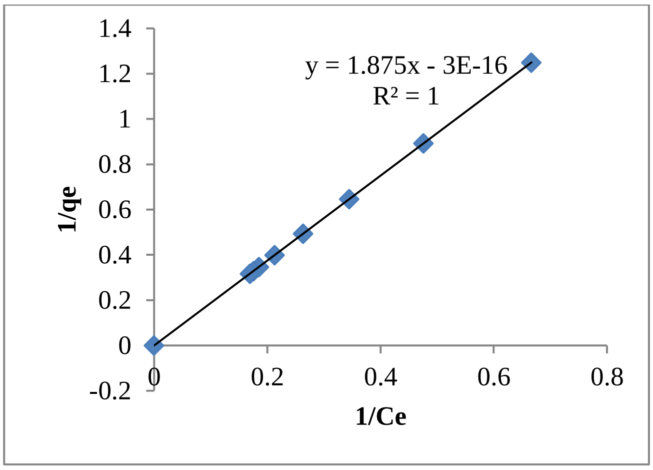

Fig.: 06 a) Langmuir isotherm plot

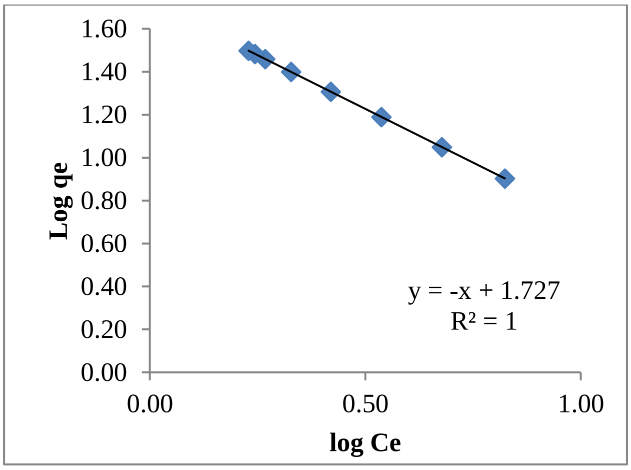

Fig. 06 b) Freundlich isotherm plot

R^2 values of the both isotherms suggest that, both models describe well adsorption of fluoride ions by Pista shell.

Characterization: SEM (scanning electron microscopy) and EDAX were utilized to characterize the carbon generated when *Pistacia vera* shells (untreated) burned and afterwards adsorption (treated) burned. The obtained image of SEM shows porous surface, which will be suitable for adsorption of fluoride ions **Figure 7**. EDAX image **Figure 8** of adsorbent shows the presence of fluoride ions in a minimal concentration, which conclude that fluoride is successfully adsorbed on adsorbent surface.

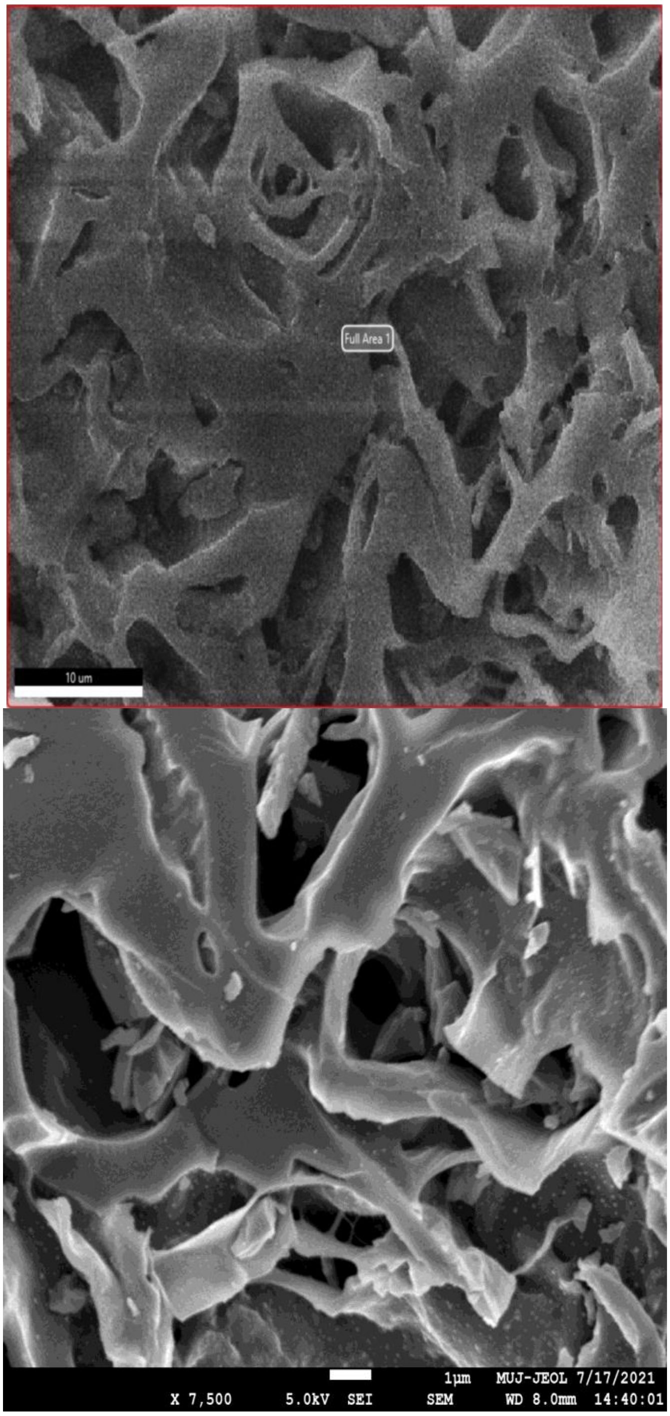

Figure 7 : SEM images of the adsorbent (untreated) prepared from *Pistacia vera* shells

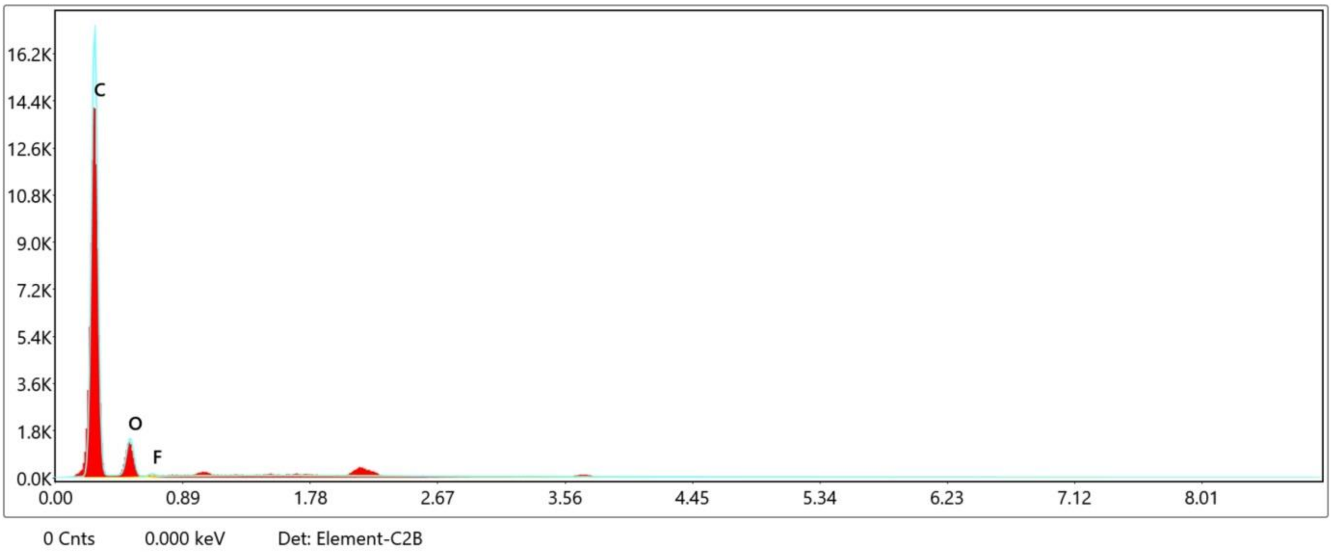

Figure 08: EDAX images of adsorbent (treated) prepared from *Pistacia vera* shells

Conclusion

The adsorption and removal of fluoride ion was examined on a low cost natural adsorbent *Pistacia Vera* shells. It was observed that maximum removal of F^{-} ions was attained at neutral pH with a removal of approx 60%. Equilibrium was obtained after the 180 min of interaction time. It was also observed that temperature is also play an important factor in the removal of fluoride ions from fluoride containing water. At elevated temperature the % of removal decreases. This study concludes that *Pistacia vera* shells will be a good candidate for the treatment of water containing higher fluoride content.

REFERENCES

1. S. Chidambaram, A. L. Ramnathan and S. Vasudevan, Water SA, 29 (3), 339 (2003).
2. R. C. Maheshwari, J. Hazard. Mater., 137, 456 (2006).
3. V. S. Chauhan, P. K. Dwivedi and L. Iyengar, J. Hazard. Mater. 139, 103 (2007).
4. S. S. Waghmare, and T. Arfin, Int. J. Innov. Sci. Eng. Technol, 2, 560 (2015).
5. S. Dubey, M. Agarwal, and A. B. Gupta, Environ. Poll., 77, 345 (2018).
6. M. Habuda-Stani, M. E. Ravan, and A. Flanagan, Mater., 7, 6317 (2014).
7. N. Kabay, O. Arar, S. Samatya, U. Yuksel, and M. Yuksel, J. Haz. Mater. 153, 107 (2008).
8. M. J. Haron, and W. M. Yunus, J. Environ. Sci. Health A. 36, 727 (2001).
9. S. A Figueiredo, R. A Boaventura, and J. M Loureiro, Sep. Purif. Technol., 20, 129 (2000).
10. K. M. Popat, P. S. Anand and B. D. Dasare, React. Polym. 23, 23 (1994).
11. C. S. Sundaram, N. Viswanathan and S. Meenakshi, J. Haz. Mater. 155, 206 (2008).
12. A. V. Jamode, V. S. Sapkal and V. S. Jamode, J. Ind. Institute Sci., 84, 163 (2004).
13. A. Bhatnagar, E. Kumar, and M. Sillanpää, Chem. Eng. J., 171, 811 (2011).
14. M. S. Onyango, and H. Matsuda, Adv. Fluorine Sci., 2, 1 (2006).
15. J. He, Y. Yang, Z. Wu, C. Xie, K. Zhang, L. Kong, and J. Liu, J. Environ. Chem. Eng., 8, 104516 (2020).
16. X. Fan, D. J. Parker, and M. D. Smith, Water Res., 37, 4929 (2003).
17. V. J. P. Poots, G. McKay, and J. J. Healy, Water Res., 10, 1061 (1976).
18. V. J. P. Poots, G. McKay, and J. J. Healy, Water Res., 10, 1067 (1976).
19. G. Blanchard, M. Maunaye, and G. Martin, Water Res., 18, 1501 (1984).
20. M. M. Nassar and Md. S. El-Geundi, J. Chem. Technol. Biotechnol., 50, 257 (1991).
21. A. K. Rai, R. Ameta and S. C. Ameta, J. Ind. Water Works Ass., LII, 130 (2020)
22. T. Sismanoglu, A. Ercag, S. Pura, and E. Ercag, J. Braz. Chem. Soc., 15, 669 (2004).
23. A. R. Tembhurkar, and S. Dongre, J. Environ. Sci. Eng., 48, 151 (2006).
24. G. Alagumuthu, V. Veeraputhiran, and R. Venkataraman, Archives Appl. Sci. Res., 2, 170 (2010).
25. B. D. Turner, P. Binning, and S. L. S. Stipp, Environ. Sci. Technol., 39, 9561 (2005).

26. W. W., Choi, and K. Y. Chen, J. Am. Water Works Ass., 71, 562 (1979).
27. X. Fan, D. J. Parker, and M. D. Smith, Water Res., 37, 4929 (2003).
28. R. Bhaumik and N K Mondal, Appl. Water Sci. DOI 10.1007/s13201-014-0211-9. (2014)
29. R. Bhaumik, N. K. Mondal, B. Das, P. Roy, K. C. Pal, C. Das, A. Banerjee, and J. K. Datta, E-Journal Chem. 9, 1457 (2012).
30. A. S. Jadhav, and M. V. Jadhav, Int. J. Recent Development Eng. Technol. 2, 41 (2014).
31. R. K. Bharalia and K. G. Bhattacharyya, Octa J. Environ. Res. 2, 22 (2014).
32. A. Sharma, S. L. Meena, S. Benjamin, D. Soni, R. Ameta and P. Tak, IJPAC 13, 193 (2018)
33. A. Mohammad and C. B. Majumder, Int. J. Res. Eng. Technol. 3, 776 (2014).
34. S. Mann and A. Mandal, Int. J. Eng. Res. Appl. ISSN : 2248-9622, 4, 116 (2014).