

ADSORPTION BEHAVIOR OF EGGSHELL MODIFIED POLYALTHIA LONGIFOLIA LEAF BASED ALUMINA AS A NOVEL ADSORBENTS FOR FLUORIDE REMOVAL FROM DRINKING WATER

Sanghratna Waghmare¹, Dilip Lataye², Tanvir Arfin³, Nilesh Manwar⁴, Sadhana Rayalu⁵, Nitin Labhsetwar⁶

^{1, 3, 5, 6} Scientists, Environmental Materials Division, CSIR – NEERI, Nagpur, Maharashtra, India

² Asst. Professor, Civil Engineering Department, VNIT, Nagpur, Maharashtra, India

⁴ Project Fellow, Environmental Materials Division, CSIR – NEERI, Nagpur, Maharashtra, India

ABSTRACT

The present study reveals about the fluoride removal from drinking water by means of adsorption through the Egg shell modified Polyalthia longifolia leaf based alumina (PBA+ES) technique. Various method were employed to characterize the adsorption mechanism such as X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). The fluoride removal capacity of PBA+ES adsorbents were investigated in batch studies, column and domestic defluoridation performance for drinking water. The Results of the experiment concluded that the batch adsorption studies show high efficiency for removal of fluoride. The pseudo-first-order, pseudo-second-order and intra particle diffusion kinetic models were applied to verify the experimental data. The pseudo-second-order equation and the equilibrium data was attained by Langmuir equation. The maximum adsorption capacity of PBA+ES was 20.62 mg/g. The five sorption-desorption cycles exhibited for regeneration where the results of the thermodynamic study reveals about the nature of the adsorption process to be spontaneous and endothermic. For on-field and domestic application, the adsorbent performance was studied in a fixed bed column and household water filter. It is also noticed that PBA+ES is efficient, easy, captive method used for the fluoride removal from the contaminated water. The present study suggest about the simple, effective, suitable method for fluoride removal from contaminated water.

Keyword: - Adsorbent; Kinetics; Thermodynamic; Eggshell; Leaf base alumina

1. INTRODUCTION

Water is the basic need of life on earth. Water will get contaminated by natural resources and industrial effluents. Fluoride is one of the contaminant element available in water and focused worldwide due to its serious health hazard effects on human being and animals like dental fluorosis, skeletal and non-skeletal fluorosis when found exceeding limits of 1.5 mg/L as per WHO[1]. On the contrary, it will helps to prevent teeth decay when found within permissible limit of 1.0 - 1.5 mg/L. Indian standards for drinking water recommend an acceptable fluoride concentration of 1.0 mg/L and an allowable fluoride concentration of 1.5mg/L in potable waters (BIS 10500, 1991) [2].

The excess fluoride will be removed by defluoridation methods. The defluoridation method may be broadly divided into five categories such as adsorption [3], ion-exchange [4], coagulation-precipitation [5], membrane filtration [6] and electro dialysis [7]. Each defluoridation method has some unique advantages and disadvantages. These above techniques are out of order. Therefore, adsorption is an efficient and economically viable technology for the removal of fluoride.

The botanical name of False Ashoka is *Polyalthia longifolia*. It is a lofty evergreen tree and found in tropical parts of India. *Polyalthia longifolia* has several applications such as removal of chromium using leaves [8], removal of Cd (II) using seed [9] etc.

Eggshell has a cellulosic structure and it contains of amino acids group. It is assumed to be a noble biosorbent [10]. The external face of the eggshell is fully coated by mucin protein that contains a soluble cork for the holes in the skin.

The objective of this study was to explore the possibility of utilizing eggshell powder with leaf alumina as a new low-cost adsorbent for application of removal of fluorine from drinking water. The outcome of particular parameters such as pH, adsorbent dose, contact time, initial concentration of fluoride and temperature were studied. The Langmuir and Freundlich isotherm models were used to describe the adsorption data. The kinetics of the adsorption process was also examined. The thermodynamics parameters were also calculated from adsorption process. The adsorption fluoride uptake capacity was also studied in a fixed bed column as well as in a household domestic defluoridation unit.

2. MATERIALS AND METHODS

2.1 MATERIALS

Raw eggshells were gathered from the market as a fresh one. It was immediately washed with water and dried completely. Then, the eggshell was immersed in 5% H_2SO_4 for 1 h and finally it was stripped thoroughly. The stripped eggshell was washed with deionized water and dried at room temperature. The eggshells were now grounded to powder form for the experimentation.

2.2 REAGENTS

Aluminum sulphate and all other chemicals used in this study were analytical grade obtained from E-Merck India Ltd., Mumbai, India. Total ionic strength adjustor buffer (TISAB III) solution was purchased E-Merck India Ltd., Mumbai, India. A stock solution of fluoride was prepared by dissolving NaF in RO (reverse osmosis)-deionized water and working solution was obtained by appropriate dilutions of the stock solution.

2.3 SYNTHESIS OF PBA+ES ADSORBENTS

PBA+ES adsorbent were synthesized in the following form with the help of sufficient amount of chemical in appropriate apparatus. 5.56 g of aluminium sulfate (reagent grade) was dissolved in 25 mL of distilled water. Ashoka leaf powder (1.5 g) and eggshell powder (1.5 g) were added in aluminium sulfate solution. The mixture was now stirred on horizontal shaker ((Model no. CIS -24, Remi Instruments, Mumbai, India) for 4 hours. After shaking whole mixture was transferred in the evaporating dish and dried at 110°C in the muffle furnace for 3 hr followed by calcination at 450°C for 6 hr. Calcined material was then grounded in a mortar pestle and washed with distilled water in 1:20 (material: distilled water) ratio by shaking on horizontal shaker for 24 h followed by 1 h more washing. Finally material was dried at 70°C in oven for 4 h.

2.4. PHYSICAL CHARACTERIZATION MEASUREMENTS

Fourier Transform Inferred (FTIR) spectra of the ES-LA adsorbent in KBr pellets were recorded on Bruker, Model Vertex 70 spectrometer under ambient conditions in the wave number ranging from 600 to 4000 cm^{-1} . The X-ray diffraction (XRD) analysis of the ES-LA adsorbent material was carried out by the XRD technique with the help of Phillips PW-1830. Cu $\text{K}\alpha$ radiation was used at the scanning range of $2\theta = 10- 80^\circ$ with a speed of 0.5 s/step and a

scan step of 0.02° at room temperature. Scanning electron microscopy (SEM) images of LA@ES were performed using Jeol, JXA-840 A.

2.5. BATCH ADSORPTION STUDIES

Stock solution (100 mg L^{-1}) was prepared by dissolving 0.221g anhydrous sodium fluoride to 1 L of deionized water. The solution was diluted later on the desired concentration for practical implication. In the plastic bottle, the known weight of adsorbent was added to 100 mL of the desired fluoride. It was then stirred in magnetic stirrer and kept at room temperature for fixed interval of time. The material was now filtered and through fluoride ion selective electrode (Orion star - A214), the fluoride concentration in the residual solution was pit to analyze. Before the determination, total ionic strength adjusting buffer (TISAB) was added to the filtered solution for maintaining the ionic strength, pH, and disregarding the interference effect of complexing ions. For investigating the effect of contact time, adsorbent dose, initial concentration, pH and coexisting ions etc. procedure were carried out.

3. RESULT AND DISCUSSION

3.1 ADSORBENT CHRACTERIZATION

3.1.1. FOURIER TRANSFORMED INFRARED SPECTROSCOPY (FT-IR)

Figure 1 shows the FTIR spectra of PBA+ES recorded before and after adsorption for clearing the concept of the nature of fluoride adsorption on samples. The FTIR spectra for before and after fluoride treated surface of adsorption gives the idea about the molecular group and small alteration in the surrounding area of the surface group like -OH groups, F^- , in the absorption bands in between the range of 3300 cm^{-1} to 3600 cm^{-1} showing the characteristics features of OH group [11]. For noticing the stretching and bending vibration of adsorbed water, the band at 3616 cm^{-1} and the peak at 1690 cm^{-1} were assigned. The peak at 1121 cm^{-1} was observed due to the bending vibration of hydroxyl group of metal oxides (Al-OH) [12]. In Fig.1 (b) clearly shows that after fluoride adsorption, the band at 3616 cm^{-1} was shifted to 3615 cm^{-1} . The band at 3616 cm^{-1} was assigned for the stretching vibration of both the hydroxyl group on adsorbent such as metal oxides and adsorbed water. There is a gradual decline in the intensity of transmittance in after fluoride treated adsorbents at 3616 cm^{-1} indicating the exchange of -OH from its surface [13]. It is observed that after the fluoride adsorption, the peak was not disappearing but the shape of the peak was changed. The intensity of -OH bands at $3650\text{-}3615 \text{ cm}^{-1}$ was reduced showing displacement to the high frequency in the fluoride treated adsorbent occurring due to the fluoride adsorption or exchange. It was showed that the intensity of peaks at 1650 cm^{-1} and 1150 cm^{-1} decreases referring, the disappearance of surface hydroxyl groups on the adsorbent. The results stated that hydroxyl group on the surface in highly involved in defluoridation of water. The bands ranging between 400 and 800 cm^{-1} can be attributed for the stretching band of metal oxides. The stretching peaks at band 3394 , 1020 and 650 cm^{-1} corresponding to H-O-H , Al-O and Al-F-Al bond was noticed. Al-F-Al bond stretching matches with the analysis done for various amorphous tri-fluoride complexes [14]. A band attributed at 2377 , 2377 and 1396 cm^{-1} was because of the presence of a carbonate [15,16]. This data gives a confirmation that along with adsorption, the ion exchange mechanism is comparatively responsible for fluoride removal.

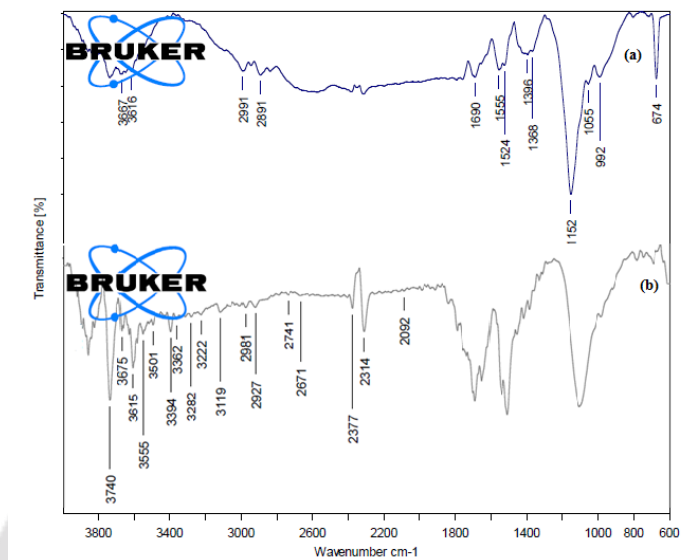


Fig -1: FTIR of (a) before adsorption and (b) after adsorption

3.1.2. X-RAY DIFFRACTION

The XRD patterns of the PBA+ES adsorbent before and after adsorption of fluoride are depicted in **Figure 2**. The XRD study reveals that the structure of adsorbent showed significant changes after the fluoride was adsorbed. The PBA+ES are mainly amorphous. It is known that amorphous materials have good adsorbent properties due to their high specific surface area and availability of the most active sites on their surfaces [17]. After the adsorption, the peak intensity was slightly high which suggests that the uptake of fluoride ions by the adsorbent is partly by chemical adsorption and shows the formation of aluminum fluoride complexes.

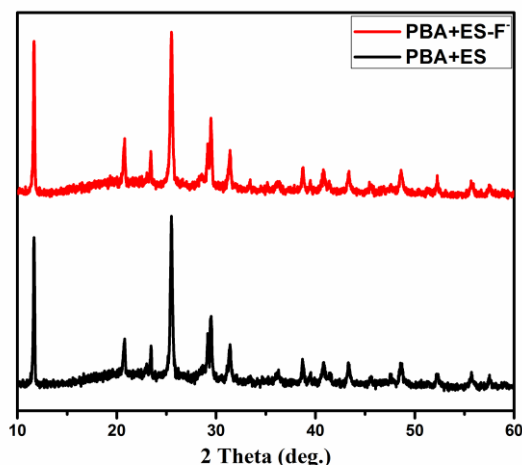


Fig -2: XRD of (a) before adsorption and (b) after adsorption

3.1.3. SCANNING ELECTRON MICROSCOPY (SEM)

SEM was responsible for the characterization of surface morphology [18, 19]. It provide ample direction for various aspects such as preparation of well-ordered precipitates, composite pore structure, micro/macro porosity, homogeneity, thickness, surface texture and crack-free [20]. The **Figure 3** (a) shows the SEM image of PBA+ES as such where the sample is heterogeneous in nature with dense structure possessing no visible cracks. It is also shows about the two types of product carried out such as large micro plates and small nanoparticles where the surface of a large micro plate was coarse with an irregular sharp edge. The calcium and alumina are found in coarse and fine particle sizes adhere on carbon particles. The particles have the thick wall as opened where wider porosity is organized with pores of different shape and size. The **Figure 3** (b) shows the SEM image after fluoride adsorption resembling that glowing metallic spots were absent revealing that the fluoride is adsorbed on PBA+ES. The spots were made of dense and loose aggregated small particles and it formed the pores with the nonlinear channel which was not totally interconnected with each other. The particle was not condensed in a regular form, but it showed a heterogeneous structure made of different size.

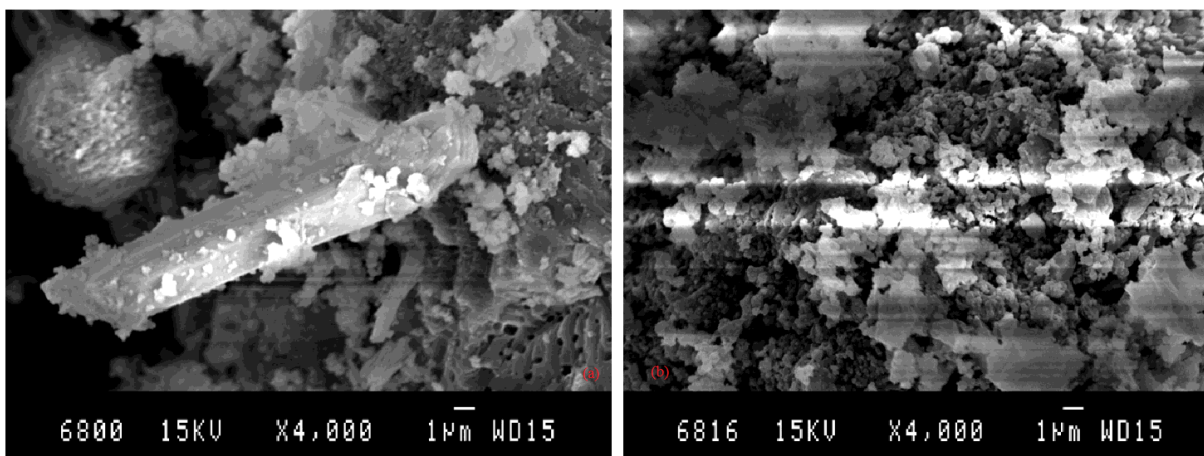


Fig -3: SEM of (a) before adsorption and (b) after adsorption

3.2. BATCH ADSORPTION STUDY

3.2.1. EFFECT OF ADSORBENT DOSE

Figure 4. shows the effect of the dosage on the percentage of fluoride removal and adsorption capacity studied at the contact time of 24 hrs. The results states that with an increase in dosage from 0.02 to 0.1 g/100 ml, the percentage of fluoride removal also tends to increasing. It is also deliberately found that with an increase in dose, the reaction sites present is also increased [21]. But at 0.2 mg/100 ml of adsorbents, possess only a slight alteration in the fluoride removal. It finally concludes by suggesting that adsorption reaction reaches to the dynamics equilibrium.

The high amount of adsorption capacity at a specific low adsorbent dose reveals the fact that there is an excess availability of the active adsorption sites of the adsorbent surface. It also exacerbates that the decrease in the adsorption capacity with increases in the adsorbent dose leads to the excessive presence of adsorbents for the adsorption process after the equilibrium is attained for fluoride adsorption. Satish *et al.* [22] observed about the same pattern of adsorption during study related to kinetics and thermodynamics of water defluoridation by using biosorbents. It was noticed that two lines intersect with each other at 0.04 g/100ml point. Therefore, the point 0.04 g/100 ml of the adsorbent was selected as optimum dose for further experiment to be carried out.

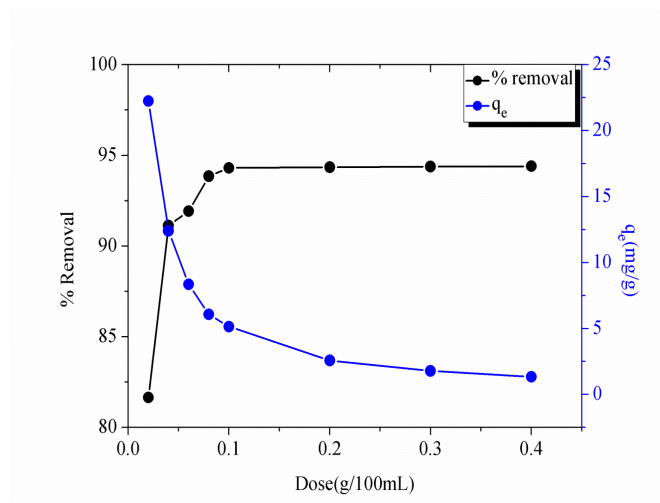


Fig -4: Effect of adsorbent dose on the removal of fluoride ion, temp 30 °C, pH 6.7 ± 0.3 , 150 rpm, and contact time 24 h

3.2.2. EFFECT OF INITIAL FLUORIDE CONCENTRATION

The effect of initial fluoride concentration on the adsorption capacity of adsorbent were studied with the help of varied amount of initial fluoride concentration ranging from 2.54 to 51.8 mg/L with the pH of 7 and temperature of 30 °C in **Figure 5**. It is observed that the adsorption capacity increases with an increasing in initial concentration that tends to possess the utility of less accessed and energetic active sites which is due to the properties of increased diffusivity and captivities activity of fluoride on the increased concentration. It was due to the resistance capacity with the pore diffusion that the adsorption sites lying on the interior surface enough to be accessed [23]. Lv *et al.* [24] found the same results for fluoride adsorption when they treated water with high fluoride concentration by MgAl- CO_3 layered double hydroxides. The percentage of removal decreases with increase in initial fluoride concentration due to saturation of adsorption sites on the surface. The experimental data revealed that the fluoride removal was more than 85% from water if its concentration is upto 10 mg/l.

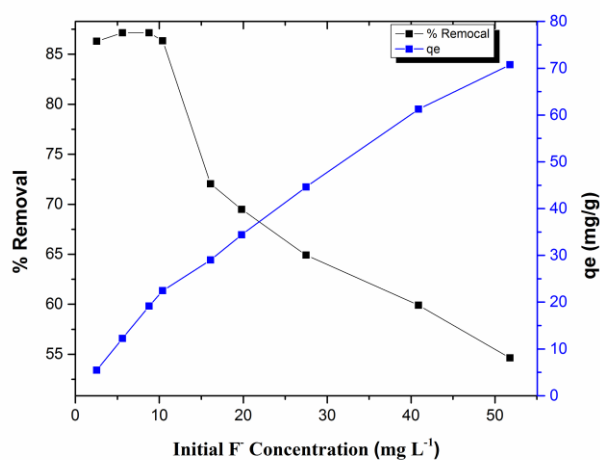


Fig -5: Effect of initial concentration on the removal of fluoride ion at dose of 0.04g/100ml, temp 30 °C, pH 6.7 ± 0.3 , 150 rpm, and contact time 24 h

3.2.3. EFFECT OF pH

The pH of the solution is an important factor affecting the adsorption process for fluoride at the solid-water interface. Therefore, effects of pH solution were carried out in the range of 3.0 to 11.89, which was carried out at the adsorbent dose of 0.04 g/100 ml, temperature of 30 °C and contact time of 24 hr.

The result of the experiment conducted is shown in **Figure 6**. It was noticed that when the pH was increased from 3 to 7, the efficiency of removal of fluoride for adsorbents also tends to increase, which could established a conjecture that the surface was protonated in acidic medium. Hence, it was concluded that in acidic medium, the maximum fluoride removal was attained due to the ubiquitous increase of the attractive forces connecting between positive charge of surface and negative charge of fluoride ions [25] and at the pH of 7, the percentage of fluoride removal was found to be more than 80.00% and adsorption capacity of 19.5 mg/g.

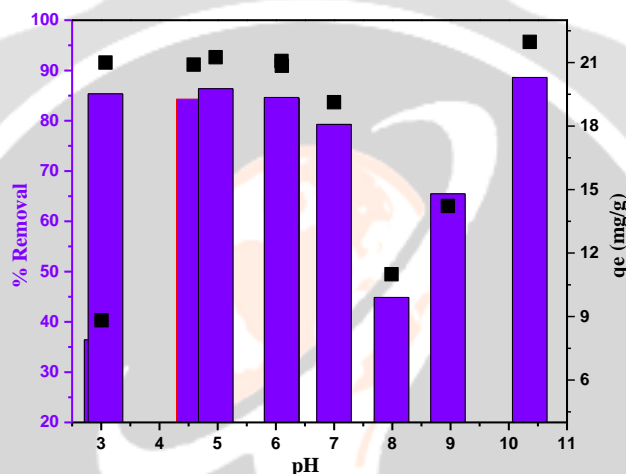


Fig -6: Effect of pH on the removal of fluoride ion at adsorbent dose of 0.04 g/100 ml, temp 30 °C, 150 rpm, and contact time 24 h

3.2.4. EFFECT OF CO-EXISTING IONS

The drinking water contaminated by fluoride contain some other anions which capable enough to compete with the sorption of fluoride. The adsorption study were performed in the presence of salt solution of 0 to 600 mg/l amount in NaCl, NaNO₃, NaHCO₃, Na₂CO₃ and Na₂SO₄ separately at an initial fluoride concentration of 10 mg/l. **Figure 7** shows the effect of such co-existing ions on fluoride removal. From the results, it is quite evidential that chloride ion shows significant influence on the fluoride removal. The above ions do not show any effect at concentration of 600 mg/l for the fluoride removals expect the one that is ions, HCO₃⁻ ions. The ions such as NO₃⁻, CO₃²⁻, SO₄²⁻, and Cl⁻ ion do not shown any influence on the defluoridation process. He *et al.* [26] suggested for the same results for fluoride adsorption when treating the water with optimized Zr-based nanoparticle-embedded PSF blend hollow fiber membrane.

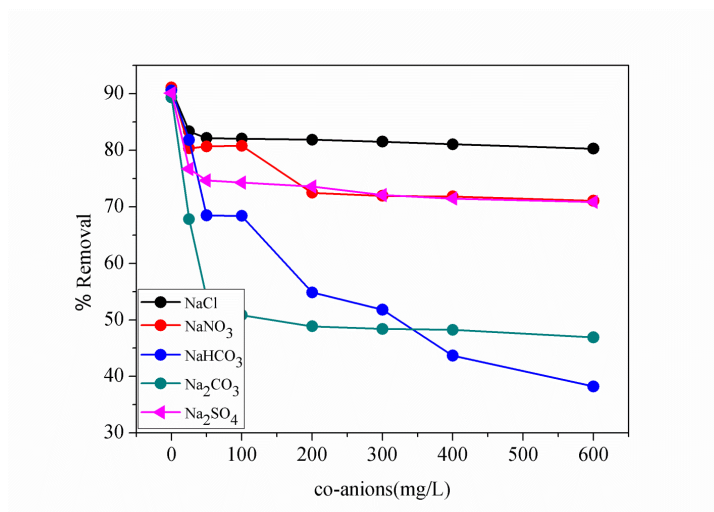


Fig -7: Effect of co-existing ions on the removal of fluoride ion at adsorbent dose of 0.04 g/100 ml, temp 30 °C, 1 pH 6.7 ± 0.3 , 50 rpm, and contact time 24 h

3.3. ADSORPTION EQUILIBRIUM

One of the basic parameter for designing of batch adsorption system is an adsorption capacity. The equilibrium adsorption study of PBA+ES was carried out at neutral pH for the temperature of $30 \pm 1^\circ\text{C}$. For the assigning total exhaustion of the adsorbent, the initial fluoride concentration was performed for different range.

The linear isotherm equations for Langmuir and Freundlich are shown in equations (1) and (2) respectively [27, 28].

$$\frac{1}{q_e} = \frac{1}{(q_{\max} K_L) C_e} + \frac{1}{q_{\max}} \quad (1)$$

where q_e = the amount of fluoride adsorbed capacity (mg/g); q_{\max} = the maximum amount of adsorbent that can be adsorbed per unit mass adsorbent (mg/g); C_e = equilibrium concentration of F^- (mg/L); K_L = Langmuir isotherm constant (L/mg).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

where C_e (mg/L) and q_e (mg/g) are the equilibrium concentration of F^- in the solution and the amount of F^- adsorbed at equilibrium respectively; K_F is the empirical Freundlich constant (mg/g) and $1/n$ is Freundlich exponent.

The Langmuir and Freundlich isotherm plots concluded from the adsorption of fluoride by PBA+ES are shown in **Figures 8 and 9**. The isotherm parameter of both the model was compared and presented in **Table 1**. Among both the model Freundlich isotherm was suitable for the adsorption capacity, which is shown through the value of high correlation coefficient (R^2). Freundlich adsorption isotherm indicated surface heterogeneity of adsorbent. The surface functionalization of the sorbents was responsible for enhancing the number of active sorption sites for fluoride sorption. The predicted q_{\max} , the maximum adsorption capacity, value of PBA+ES is 20.62 mg g^{-1} investigation into fluoride removal. The complete evidence is also presented by Jin *et al.* [29] in support of the isotherm modeling. The value of dimensionless separation factor (r) for initial fluoride concentration of 10 mg/l was found to be $0.18 < 1$ indicated that the fluoride adsorption was favorable.

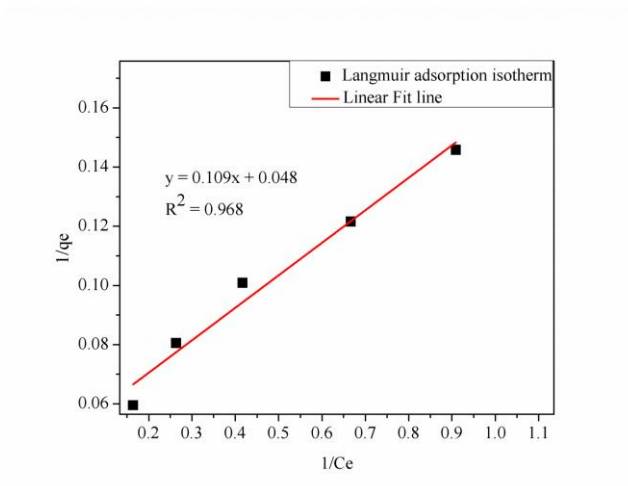


Fig -8: Linear model of Langmuir isotherm for the removal of fluoride at dose of 0.04g/100ml, pH 7, temp 30 °C, contact time 24h and initial concentration of 10 mg/l

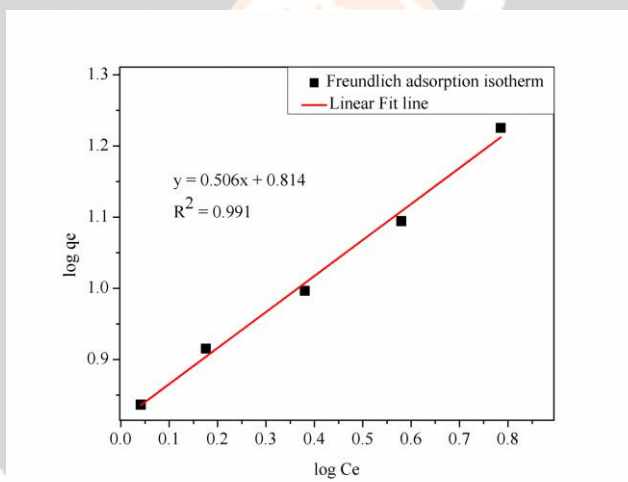


Fig -9: Linear model of Freundlich isotherm for the removal of fluoride at dose of 0.04g/100ml, pH 7, temp 30 °C, contact time 24h and varied initial concentration of adsorbate

Table -1: Comparison of different adsorption isotherm model parameters of fluoride adsorption on PBA+ES

Isotherm models	Model parameters	Estimated parameters
Langmuir	q_{\max} (mg g ⁻¹)	20.620
	K (L mg ⁻¹)	0.440
	correlation coefficient (R^2)	0.968
Freundlich	K_F (mg g ⁻¹) (mg l ⁻¹) ^{-1/n}	2.259
	1/ n	0.506
	correlation coefficient (R^2)	0.991

3.4. KINETIC STUDIES

Adsorption kinetics are deals with the rate at which sorption occurs. The rate is defined as the change of a given quantity over a specific period of time. The rate of fluoride adsorption on PBA was determined by studying the adsorption kinetics at different initial concentrations of 5.2, 9.3, 15.6 mg L⁻¹ at optimum dose. From **Figure 10**, it was observed that fluoride uptake was very rapid in the first 15 min and then the rate slowed down as the equilibrium was approached. The results obtained from the experiments were used to determine the rate-limiting step.

Kinetic models are used to examine the rate of the adsorption process and potential rate-controlling step. The potential rate of PBA+ES for fluoride removal following three different kinetic models: pseudo-first-order, pseudo-second-order and intra-particle diffusion was examined in this study.

For more frequently used rate equation for assigning the adsorption process is Pseudo-first-order kinetic model [30]. The linear form of pseudo-first-order model is given by Eq. (3)

$$\log(q_e - q_t) = \log q_e - \frac{K_{ads}}{2.303} t \quad (3)$$

where q_e (mg g⁻¹) and q_t (mg g⁻¹) are the amounts adsorbed at equilibrium and time t respectively, and K_{ads} (min⁻¹) is the pseudo-first-order rate constant.

The pseudo second order kinetic order equation [31] is expressed by Eq. (4)

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (4)$$

Where $h = Kq_e^2$

where K is pseudo second order rate constant (g mg⁻¹ min) and q_e is equilibrium adsorption capacity (mg g⁻¹).

Weber-Morris intra-particle diffusion model is used to determine the adsorption state limiting step and the linear form of Intra-particle diffusion model is given by Eq. (5). The equation form of the intra particle diffusion model as given by Weber-Morris [32]:

$$q_t = K_p t^{1/2} + C \quad (5)$$

where K_p and C are intra-particle diffusion rate constant (mg/g/min^{1/2}) and constant (mg/g) respectively. The value of C gives the information about the thickness of boundary layer.

The linear plots of first-order, second-order and intra-particle diffusion kinetic models are presented in **Figure 11, 12 and 13** respectively and the summary of the parameters estimated in the kinetic data models are represented in **Table 2**. It is inferred that the value of correlation coefficient (R^2) is higher for the pseudo-second order model as compared to the pseudo-first order model, which suggest that the present system follows the pseudo-second order kinetic. The adsorption rate constant (K_{ad}) was found to be 0.43471, 0.43107 and 0.37559 min⁻¹ for initial fluoride concentration of 5.2, 9.3 and 15.6 mg l⁻¹ respectively.

The plot for intra-particle diffusion shows that initially curved portion reflects film or boundary layer diffusion effect and the subsequent linear portion is attributed to the intra-particle diffusion effect. The K_p values were obtained from the slope of the linear portion of the curves and were found to be 0.89345, 1.81119 and 1.79139 mg g⁻¹ min^{-1/2} at an initial fluoride concentration of 5.2, 9.3 and 15.6 mg l⁻¹ respectively. The linear portion of the curves does not pass through the origin indicating that the fluoride adsorption mechanism of PBA+ES was rather complex one and both intra-particle diffusion and surface diffusion are involved in the rate-limiting step [34].

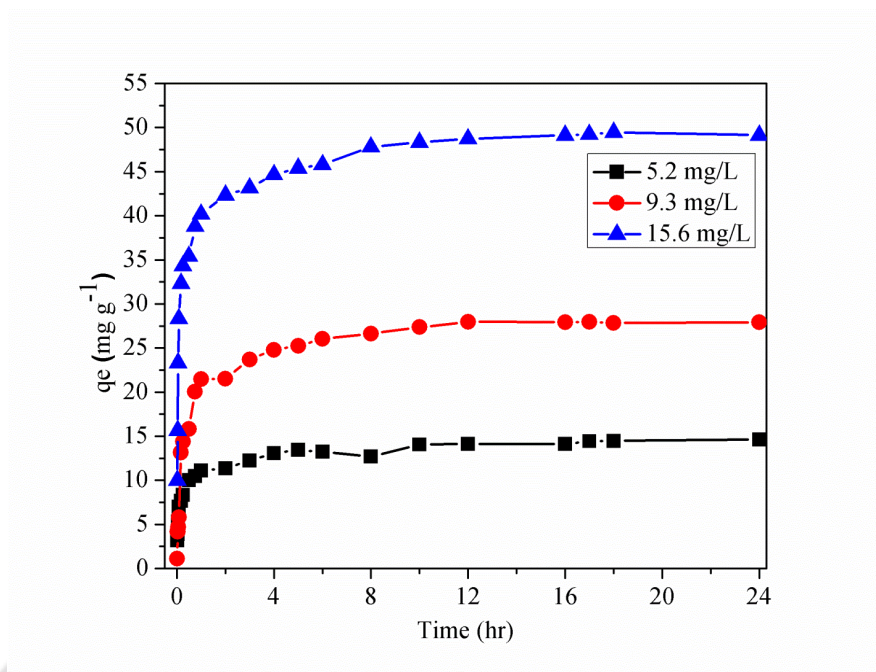


Fig -10: Effect of time on fluoride adsorption using PBA+ES

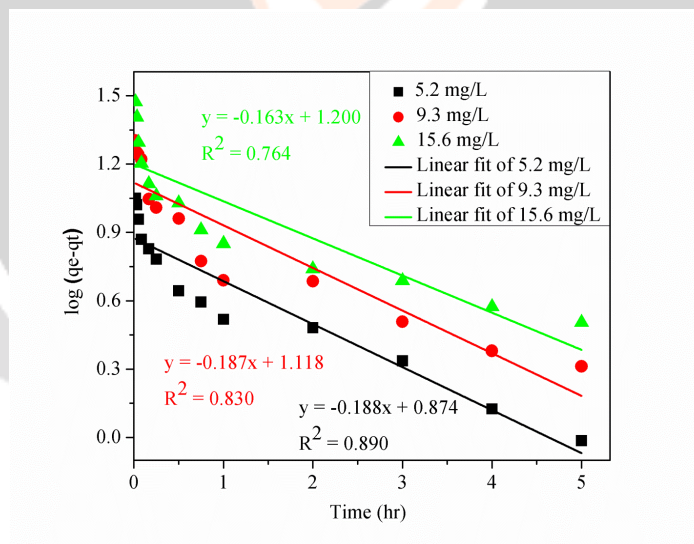


Fig -11: Linear model of first-order rate equation for the removal of fluoride at dose of 0.04g/100ml, pH 7, temp 30 °C, and initial concentration 10 mg/l

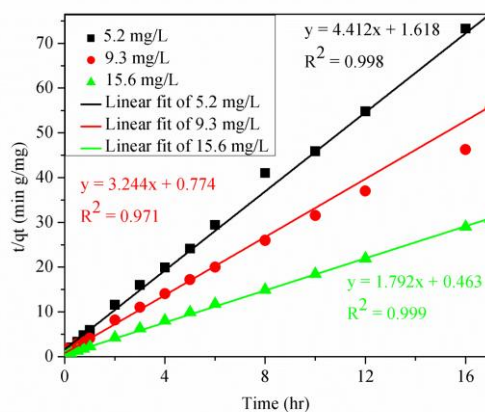


Fig -12: Linear model of second-order rate equation for the removal of fluoride at dose of 0.04g/100ml, pH 7, temp 30 °C, initial concentration 10 mg/l.

Table -2: Kinetic and statistical parameters of the three kinetic models

Co (mg l ⁻¹)	Lagergren Parameters			Pseudo Second Order Parameters				Particle Diffusion Model	
	q _e (mg g ⁻¹)	K _{ad} (min ⁻¹)	R ²	q _e (mg g ⁻¹)	K (g mg ⁻¹ min ⁻¹)	h (mg g ⁻¹ min ⁻¹)	R ²	K _p (mg g ⁻¹ min ^{-1/2})	R ²
5.2 (~5)	2.399	0.43471	0.890	0.227	12.0293	0.6179	0.998	0.89345	0.834
9.3 (~10)	3.061	0.43107	0.830	0.308	13.5871	1.2097	0.971	1.8119	0.825
15.6 (~15)	3.321	0.37559	0.764	0.558	6.9373	2.1597	0.999	1.79139	0.871

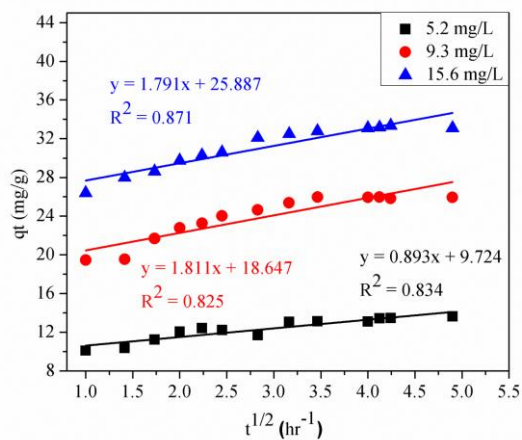


Fig -13: Linear model of intra particle diffusion for the removal of fluoride at dose of 0.004g/100ml, pH 7, temp 30 °C, initial concentration 10 mg/l

3.5. THERMODYNAMIC STUDY

In order to see the effect of temperature on adsorption of fluoride by PBA+ES, thermodynamic parameters associated with the adsorption process, viz. standard free energy change (ΔG°) (kJ mole^{-1}), standard enthalpy change (ΔH°) (kJ mole^{-1}) and standard entropy change (ΔS°) ($\text{J mol}^{-1} \text{K}^{-1}$) were calculated using following equations (6, 7 and 8) [35]

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

$$\Delta G^\circ = -RT \ln K_C \quad (7)$$

$$\ln K_C = \ln \frac{q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

where K_C = sorption equilibrium constant; R = Universal gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$); T = Temperature in Kelvin; q_e = amount of F^- adsorbed (mg/g) and C_e = Equilibrium concentration of F^- .

The adsorption process is greatly influenced by the effect of temperature examined at three various ranges of temperature i.e. 293, 303 and 323 K under the optimum condition and the thermodynamics parameter such as standard free energy change, standard enthalpy change and standard entropy were observed in **Figure 14** [36] and calculated value is listed in **Table 3**. The value of ΔG° obtained is negative which resembles the sorption process is spontaneous and feasible one. The standard free energy change (ΔG°) of the adsorption process decreases (-3.7490 to -1.9577) with increased in temperature that shows that the process is spontaneous and adsorption process decreased at high temperature. The values of ΔH° is positive which states that it is an endothermic process. It is commonly noticed that the magnitude of the ΔH° lies in the varied range of 0.00745 to 0.00491 kJ/mol for physical adsorption [37]. The spontaneous increase in the solid/liquid interface during the adsorption of fluoride is evidential by the positive value of ΔS° [38]. The overall facts prove that the highest degree of adsorption of fluoride is occurrence on the PBA+ES, which is mainly due to adsorbed water molecules discarded by the adsorbate species (F^-) that attains more translational entropy.

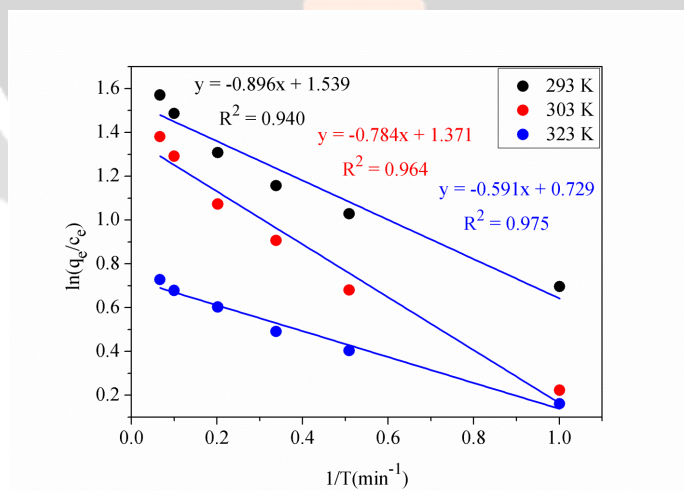


Fig -14: Effect of co-existing ions on the removal of fluoride ion at adsorbent dose of 0.04 g/100 ml, temp 30 °C, 1 pH 6.7 ± 0.3 , 150 rpm, and contact time 24 h

Table -3: Thermodynamic parameters for fluoride adsorption onto PBA+ES

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol.K)	K_c
293	-3.7490	0.0074	12.7952	1.0015
303	-3.4537	0.0065	11.3984	1.0014
323	-1.9577	0.0049	6.0609	1.0070

3.6 FIELD STUDY

To determine the practical usability of PBA+ES adsorbent for treatment of drinking water. The ground water by nearby village (Bhandara) having fluoride contamination was used for testing in batch study. The 0.4 g/L dose of adsorbent was added to field sample and then sample was shaken for 24 hours at room temperature at 150 rpm. The parameters of field sample before and after treatment were given in **Table 4**. The fluoride content of field sample was getting reduced after treatment within permissible limit along with the reduction of other parameters also. It was observed from the result that the sorbent, PBA+ES were effectively applicable for removing the fluoride from field water.

3.7 COMPARISON WITH OTHER ADSORBENTS

The maximum fluoride adsorption capacity of PBA+ES in the present study is compared with other adsorbents those reported earlier in the literature and represented in **Table 5**. However direct comparison of PBA+ES with reported adsorbents is difficult. According to the studies of the comparison table it has been cleared that PBA+ES is providing better adsorption capacities than other adsorbents.

3.8 COST COMPARISON OF PBA+ES WITH OTHER ADSORBENTS

The cost of adsorbent is a key factor for determining its techno-economic viability for defluoridation of water. The cost of adsorbent depends upon various factors like cost involved in synthesis of adsorbents, adsorption capacity, recycles and regeneration efficiency and proper fruitful disposal. The most of researcher were tried low cost materials for defluoridation by adsorption technique in developing countries like India. In this study, fluoride uptake by dead leaves powder of polyanthial longifolia acacia were enhanced by eggshell powder (Waste from poultry) and readily available commercial alum (Aluminium sulphate). The cost of PBA+ES composite adsorbent was work out to be Rs. 50.77/kg (0.76 \$/kg) which includes cost of raw materials and process cost. **Table 6** summarized the cost comparison of PBA+ES with other adsorbents used for defluoridation of water.

Table -4: Physico-chemical parameters of defluoridated drinking water from field by PBA+ES

Parameters	Before treatment	After treatment	Permissible Limit (BIS)
pH	7.4	6.9	6.5-8.5
Turbidity (NTU)	< 1.0	< 1.0	5.0
TDS (mg/L)	109	98	500
Conductivity ($\mu\text{S}/\text{cm}$)	120	96	-
Total hardness (mg/L)	330	285	300
Alkalinity (mg/L)	215	197	200
Fluoride (mg/L)	5.4	0.50	1.0
Chloride (mg/L)	235	193	250
Sulphate (mg/L)	21	18.5	200
Nitrate (mg/L)	5.6	4.7	45
Aluminium (mg/L)	< 0.002	<0.01	0.03
Calcium (mg/L)	67	42.5	75

Table -5: The comparison of maximum fluoride adsorption capacities of various adsorbents

Adsorbent	q_{max} (mg/g)	References
Pecan nut shells modified with a calcium solution extracted from egg shells (CMPNS)	0.81-2.51	[39]
Eggshell powder	1.09	[40]
Calcium chloride modified zeolite	1.766	[41]
Al-impregnated activated carbon	1.1	[42]
Alum-Bentonite	5.7	[43]
Aluminium oxide infused diatomaceous earth	13.141	[44]
Synthetic hydrous aluminum oxide (HAO)	14.79	[45]
Aluminium hydroxide coated rice husk ash	15.08	[46]
Al/Fe oxides loaded tea waste	18.52	[47]
Aluminum chloride and Calcium chloride treated powdered corn cob	15.12 mg/g and 18.9 mg/g	[48]
Alumina-chitosan composite	10.417	[49]
Alumina impregnated alginate beads	17.0	[50]
Calcium chloride impregnated wood charcoal	19.05	[51]
PBA+ES	20.62	Present study

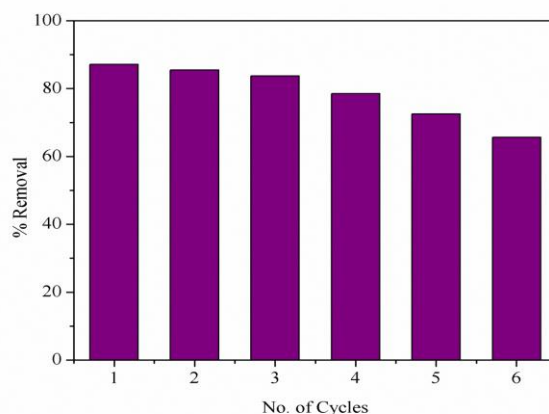
Table -6: Cost Comparison of PBA+ES with Other Adsorbents for Fluoride Removal

Adsorbent	Cost (US \$/Kg)	References
Activated Alumina	~2.3	[52]
Amorphous Alumina	~70.0	[53]
Activated Carbon	~25.0	[53]
Clay (Bentonite)	~1.0	[54]
Eggshell composite	~2.2	[55]
Bleaching powder	~1.0	[56]
Acid spent bleaching earth	~2.10	[54]
PBA+ES	0.76	Present Study

3.9 REGENERATION AND REUSE

To investigate the reusability of the adsorbents, six consecutive reusability adsorption cycle experiments were conducted for initial fluoride concentration of 10 mg/l, adsorbent dosage of 0.04g/100 ml and contact time of 24 hrs. The resulting adsorption capacity of adsorbents in reusability study is shown in **Figure 15**. The reusability experiment was carried out by repeating the adsorption experiment on used and oven dried sample under the similar condition used for the first cycle. It was observed that the used adsorbent still have significant fluoride uptake capacity. After five cycles, the removal rates gently decreased to 65.65%. This observation suggests that the adsorbent is suitable for fluoride removal in multiple cycles.

Reuse study shows that up to 3rd cycle material have fluoride removal efficiency more than 85% after that decreases to 65.65% in 6th cycle due to its weight loss 15.70% in repetition. This indicates that the adsorbent does not exhaust its fluoride uptake capacity in third cycles and oven drying of the used sample results in significant fluoride adsorption in subsequent cycles. After complete saturation, the exhausted adsorbent was subjected to regeneration using different regeneration media like HCl, NaOH, alum and combination of them [57,58]. It was observed that multiple treatments with an alum solution appears to be the promising regeneration media and a maximum of 95% regeneration was achieved with alum. The fluoride uptake capacity of regenerated PBA+ES reduces from 85% to 79% in first time and subsequently declines slowly.

**Fig -15:** Reusability of PBA for removal of fluoride

4.0 COLUMN STUDY

Column studies were conducted for PBA+ES only because of high adsorption capacity obtained in batch study with 10 mg/l of aqueous solution as well as to check the stability of adsorbent in continuous up-flow mode for on-field application. A stainless steel column of height 16.6 cm and internal diameter of 1 cm is used and filled with 11.57 g of PBA+ES adsorbent. The breakthrough curves of PBA+ES presented in **Figure 16**. The breakthrough point was considered when the fluoride concentration in the treated water exceeds 1.5 mg/L and 1mg/L as per WHO and Indian standards, which would be permissible limit for drinking water. The breakthrough time was estimated 1055 min and 876 min for respectively, for WHO and IS-15000 specification. Their corresponding breakthrough volume is 2.64 liters and 2.19 liters respectively. The specific safe water yield is 228 mg F/kg and 189.20 mg F/kg as well as breakthrough capacity is 2.28 mg/g and 1.89 mg/g respectively as per WHO and BIS limits. The volume of water treated at saturation point was 18.0 liters and exhaust point capacity was found to be 15.56 mg/g, which was more than half of the maximum Langmuir adsorption capacity of 20.62 mg/g in batch. The fluoride uptake capacity of PBA+ES in column is 1.89 mg/g and found on higher side as compared with capacity of fresh activated alumina (1.2 mg/g) [59]. Again Lounici *et. al* [60] has observed that the breakthrough and saturation capacity of activated alumina in a column were 1.75 and 2.2 mg/g in optimum conditions.

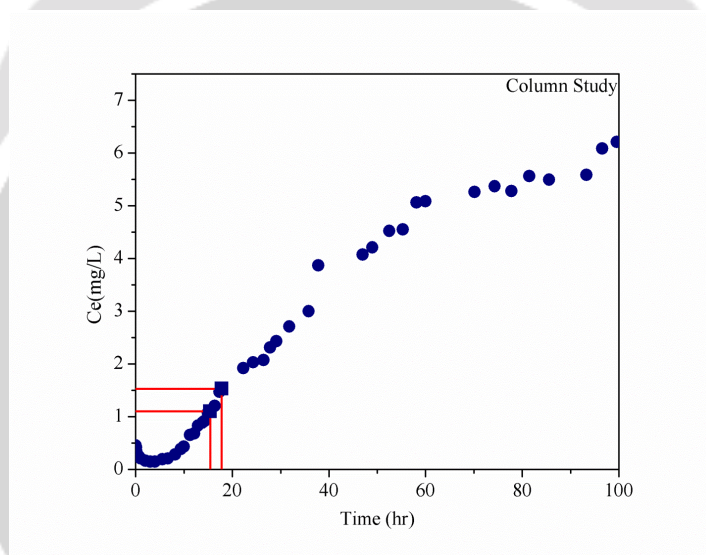


Fig -16: Column study of PBA+ES (column height=16.6 cm; column Diameter=1 cm; Bed height= 13.4; weight of material=11.57gm; Flow Rate= 2.5ml/min)

4.1 DOMESTIC DEFLUORIDATION UNIT

A simple domestic defluoridation unit has developed by using a commercially available gravity feed two stages two chamber stainless steel ceramic candle filter (Capacity of 16 liters) used mainly for water purification as shown in **Figures 17 (a) and 17 (b)**. A ceramic candle is fitted to bottom of upper chamber and a tap is fitted in bottom chamber with a suitable arrangement to withdraw pure water filtered through ceramic candle. The 25 g of adsorbent is filled in hollow portion of ceramic candle and plugged with cotton to remove any suspended particles and allow sufficient contact time for the adsorbent to remove fluoride from water. The tap water spiked with 10 mg/l of fluoride as feed water and was filled in upper container and allowed to flow through ceramic candle encapsulated with adsorbent slowly with its own rate. The flow rate of ceramic candle with adsorbent was observed to be 0.67 L/hr. and produced 6.7 liters of drinking water in 10 hours.

The quantity of adsorbent, number of candles and size of containers has to be optimized to produce more quantity of fluoride treated water (~20L) for one family of four members. The details of adsorbent needed to purify 20 L of water are explained as below;

Daily personal water demand (D) = 5 L/person/day

Number of users (P) = 4 persons

Daily volume of water required for one family = $P \times D = 20 \text{ L/day}$

Water required for one family per month (30 days) = $20 \times 30 = 600 \text{ L}$

Adsorbent required for treating 6.7 litre of fluoride contaminated water = 25 g

Adsorbent required to treat 600 L of fluoride contaminated water = $(25 \times 600) / 6.7 = 2239 \text{ g}$

Cost of adsorbent to treat 600 L of fluoride contaminated water = $\text{Rs.} 51 \times 2.239 = \text{Rs.} 114/\text{Month}$.



Fig -17: (a) DDU spare parts and (b) Assembled DDU

The aggregate water required for one family is evaluated to be around 600 L every month. The expense of treatment of 600 L of fluoride defiled water as required for one family is Rs. 114 every month. Hence PBA+ES adsorbent based defluoridation is found economical and techno viable. The cost of treatment of fluoride water with PBA+ES is roughly Rs. 1.00 per 5 L. A filter fitted with three candles encapsulated with adsorbent of 25g in each thus would produce 20.1 L (say 20 L) of safe drinking water with fluoride content less than 1.0 mg/l (Acceptable limit) as per BIS 10500: 2012 [61] in 10 hours. Lower feed concentration resulted into higher amount of fluoride treated drinking water and vice-versa. Therefore, it is recommended that PBA+ES more efficient and cheaper composite adsorbent for defluoridation of drinking water.

4.2 DISPOSALS OF EXHAUSTED ADSORBENT

The de-sorption of fluoride ions may carry out by using various chemicals like H_2SO_4 , HCl , HNO_3 , NaOH , EDTA etc. before use as filler. The fluoride ions will separate effectively by treating spent adsorbent by alkaline/acid regenerants and by using alum or lime additives. The solidification/stabilization of sludge into concrete cubes, bricks and blocks for housing will carry out by cement or lime [62-66]. Further the safe disposal of exhaust adsorbent may carry out by seal them into safe container and then this container may be land filled into a safe pit.

4.3 CONCLUSION

It has been found that fluoride contaminations in drinking water basically due to human activities posing a large risk loading to various diseases in humans. The creating nations like India relies on upon ground water as characteristic assets for the drinking water and also most piece of the universe are irrationally relied on upon it [67-77]. The current paper is mostly about the application of PBA+ES adsorbent in the removal of fluoride from drinking water that has consumed by human being on large scale. The FTIR studies show the active participation of the surface sites of the sorbent in the adsorbent interaction. The optimum pH range of fluoride removal was noticed to be 3.0 to 7.0, referring the application of fluoride removal adsorbent in natural water. The study also states that the pseudo-second-order kinetics model and Langmuir isotherm was captive models for adsorption kinetics and isotherms. The anions show negligible effect on the adsorption of fluoride except the HCO_3^{2-} which was clear from the study of effects of co-existing anions. The thermodynamic study formulated towards the spontaneous and endothermic nature of adsorption process. The household and column performance with PBA+ES in has been studied successfully. All such results of the research carried out amplifies that adsorbent PBA+ES was potential enough material to be used in the technological field for the removal of fluoride from drinking water.

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BIOGRAPHIES

	Sanghratna S. Waghmare is working as a senior scientist at Environmental Materials Division, National Environmental Engineering Research Institute (CSIR-NEERI), Nagpur. He has experience in condition assessment of RCC buildings and bridges using NDT and PDT techniques also engaged in development of building materials from wastes, design and development of instant houses and polymer composites from sisal fibers. Currently, he has been involved in defluoridation and carbon dioxide sequestration.
	Dilip H. Lataye is currently working as an Associate Professor in Department of Civil Engineering at Visvesvaraya National Institute of Technology, Nagpur. Dr. Lataye has been actively engaged in research related to various fields of defluoridation, water and wastewater treatment, air pollution control and hazardous waste management. He has published more than 15 scientific peers reviewed journal papers.
	Tanvir Arfin is currently working as a Scientist at Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), India. Dr. Arfin has been actively engaged in research related to various fields of electrochemistry, defluoridation, platinum group materials, polymer science, membrane, hybrid materials, graphite oxides and biomass energy. He has published more than 38 scientific peers reviewed journal papers and 10 book chapters.
	Nilesh R. Manwar is working as a Project Assistant at Environmental Materials Division, National Environmental Engineering Research Institute (CSIR-NEERI), Nagpur. He has experience in defluoridation by adsorption, photo catalysis, electrochemistry, materials development and characterization. He has published 5 papers in SCI journals.
	Sadhana Rayalu is currently working as a Senior Principle Scientist and Head at Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), India. Dr. Rayalu has been actively engaged in research related to various fields of defluoridation, CO ₂ sequestration, photocatalysis, photoelectrocatalysis, photofuel, photo voltaic, photothermal and biomimetic process. She has published more than 150 scientific peers reviewed journal papers and 14 patents.
	Nitin Labhsetwar is currently working as a Senior Principle Scientist at Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), India. Dr. Labhsetwar has been actively engaged in research related to various fields of defluoridation, CO ₂ sequestration, photocatalysis, photoelectrocatalysis, photofuel, photo voltaic, photothermal and biomimetic process. She has published more than 105 scientific peers reviewed journal papers.