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# Fluoride Adsorption By Chlorine Doped Polyaniline In Continuous Column Mode Operation

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**Abstract**

This study focuses on optimisation of pH for fluoride uptake by adsorbent polymer polyaniline doped with chloride and synthesised on surface of jute fiber (PANI-Cl-Jute) in continuous column mode operation. At reactor bed depth of 1.5 m, flowrate of 1.2 mL/min and initial fluoride concentration of 5 mg/L, the breakthrough time at pH 1, 2, 4 and 6 were 11, 7, 5 and 1 hour respectively suggesting favourable adsorption at acidic pH. On characterized with Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Measurements (EDAX), F- uptake by PANI-Cl-jute was confirmed. Total amount of ions adsorbed at different bed depth of 1.5, 2 and 3 m yields and F- uptake of 11.87, 15.85 and 26.53 mg respectively thus amounting an average uptake of 0.07 mg F-/g PANI-Cl-jute against a higher uptake of 12.99 mg/g in batch mode studies. The formation of mass transfer zone in continuous mode unlike adsorption equilibrium in batch mode is the main reason for lower uptake in continuous column mode operation. However a throughput volume of 620 mL was able to achieve under the study condition with F- below the permissible limit suggesting the effective adsorption of F- by PANI-Cl-jute.

**Keywords**: Polyaniline, fluoride, adsorption, BDST, throughput volume

## Introduction

Fluoride is an essential element for our health and permissible its limit in drinking water as per WHO is 1.5 mg/L [1]. Excess fluoride in drinking water has harmful effects on human causing spotting and decolouration of teeth or skeletal fluorosis [2]. Various techniques of defuoridation include precipitation-coagulation [3], membrane separation process, ion exchange, electrodialysis, chemical precipitation [4], ion-exchange [5], reverse osmosis [6], nano-filtration [7], and adsorption [8]. Among these methods, adsorption is widely used method for the effective removal of Fluoride for its cost effective, no sludge regeneration, flexibility and simplicity of design and operation. In the last decades, several adsorbent have been employed like activated alumina, synthetic resin, red mud, tea leaves, rice husk, chitosan, etc and lately functional group based adsorbent has been used for its effective removal of fluoride. Amines are reported to get protonated with H+ in acidic medium and have strong affinity to bind highly electronegative fluoride ion [9,10,11]. To further increase the adsorption of fluoride, chloride doped amine based polymer will be synthesized on surface of jute fibre (PANI-Cl jute) as supporting materials employed for defluoridization. The doped chloride are postulated to be replaced by fluoride ions. Adsorption studies are generally carried out in batch mode operation but preferred continuous column mode operation in practical situation. This study emphasises on investigation of fluoride uptake in continuous mode. Optimisation of doped chloride amount, pH, different bed depth of the reactor are considered for this study.

## Materials and Methods

### Chemicals and Reagents

The adsorbent PANI-Cl-jute was prepared as per our previous studies [12]. All chemicals and reagents used are purchased from Merck (AR Grade) and used as received. Only, aniline for the preparation of polymer was distilled using KOH yielding only 65-70% volume and remaining discarded as impurities. All the samples were prepared using double distilled water and Fluoride stock solution of 100 mg/L were prepared daily. Further lower concentration for experiments were prepared by series dilution of the stock solution.

### Experimental Methodology

Fixed bed column for the adsorption study was set up using a PVC reactor of 4 cm diameter with various outlets at bed depths of 1.5, 2 & 3 m from the top. The column is fed with known quantity of PANI-Cl-jute and is well supported at bottom with cotton and PVC cover to prevent wash out and leakage. The reactors were fed with desire concentration of F- solution using peristaltic pump (Model: Miclins PP 60 Ex, India)controlling the required flow rate. Acidic and basic pH of solution is maintained by addition of HCl and NaOH of varied strength and maintained the added acid/base volume to be less than 1% of the total solution. At varied time, the effluents were collected from the various outlets for analysis of $F^-$. All experiments were conducted till the concentration of effluent becomes 95% of the initial $F^-$ concentration which is called the exhaustion. Fluorides concentrations were estimated using Ion selectivity electrode (Cole Parmer, USA) using TISAB buffer. Collection of effluents and estimation were all done in plastice ware avoiding glass ware to minimize the adsorption of fluoride in glass.

## Results and Discussion

### Characterization

The SEM images of PANI-Cl-jute before and after $F^-$ adsorption are shown in Fig.1 and 2 respectively where smooth and even surface disappears after $F^-$ adsorption. The EDX spectra of PANI-Cl-jute before adsorption (Fig. 3) contains no $F^-$ peak whereas the emerged after adsorption (Fig. 4).

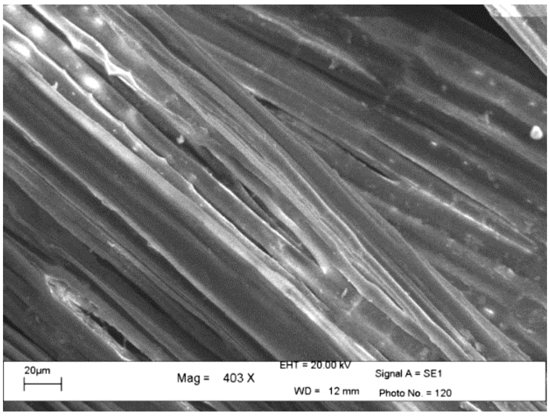


**Fig. 1:** SEM image of PANI-jute-Cl before $F^-$ adsorption

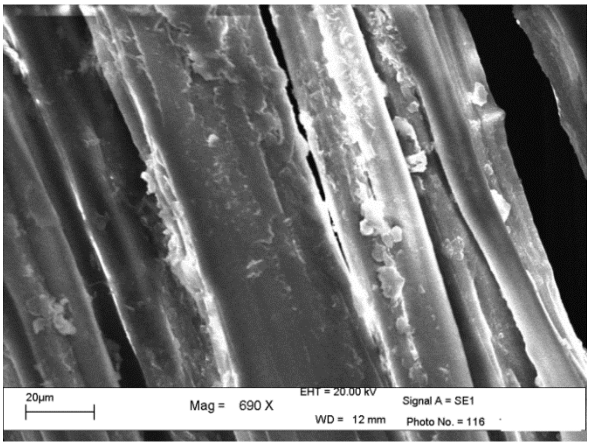


**Fig. 2:** SEM image of PANI-jute-Cl after $F^-$ adsorption

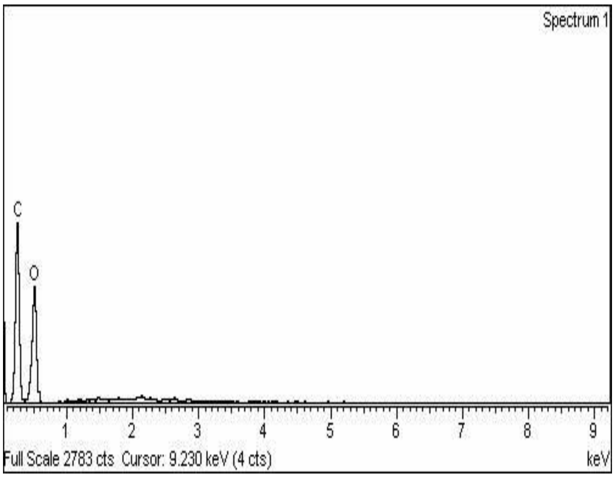


**Fig. 3:** EDAX image of PANI-jute-Cl before $F^-$ adsorption

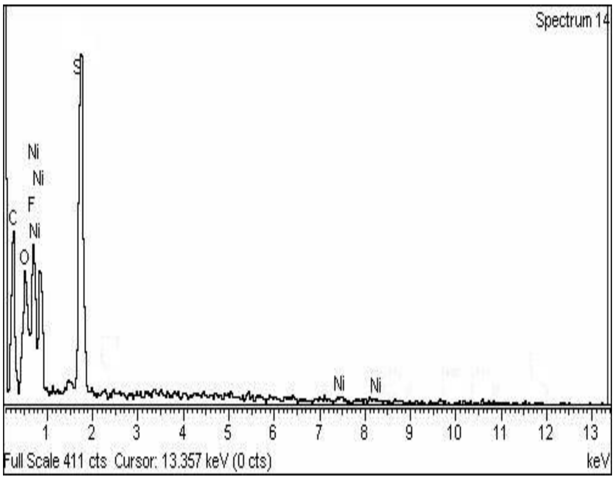


**Fig. 4:** EDAX image of PANI-jute-Cl after $F^-$ adsorption

**Chloride Doping**

During the synthesis of the adsorbent, the polymer polyaniline was doped by chloride introducing various chloride of 0.5, 1, 1.5 and 2 M. The obtained adsorbents PANI-Cl-jute were employed in column reactor with 1.5 m depth reactor, initial $F^-$ 5 mg/L and 1.2 mL/min flow rate. The result obtained is plotted in Fig. 5, obtaining a S-curve. From the figure, it can be seen that PANI-Cl-jute with 0.5 M and 1 M doped chloride started leaking at the beginning of the experiment itself at $C/C_o$ of 0.04 and 0.03 respectively. At chloride amount of 1.5 and 2 M, a throughput volume of 1150 and 1100 mL were achieved respectively. The optimum chloride doping was thus attained at 1.5 M chloride. With increased in chloride, more ion exchange with fluoride results higher uptake. However with higher doped chloride amount, excess chloride are leaked into the solution due to saturated doping of chloride on chain of PANI-Cl-jute. Thus all further works were carried out with PANI-Cl-Jute doped with 1.5 M.

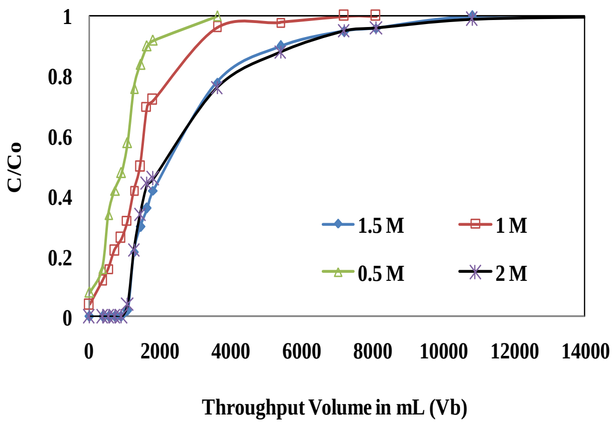


**Fig. 5:** Breakthrough curve for fluoride adsorption at various chloride doped PANI-Cl-jute

**Optimisation of pH**

In order to optimise the pH of the adsorption, experiments were conducted by maintaining influent pH from 1-6, bed depth of the reactor as 1.5 m, flowrate 1.2 mL/min and initial concentration of $F^-$ as 5 mg/L.. The results obtained is represented at Fig. 6. From influent pH 3 - 4, the effluent leaks $F^-$ at the beginning itself. pH 2 experiment makes breakthrough at 7.5 hours whereas that of acidic pH 1 have a breakthrough time of 12 hours. The finding clearly indicated that the optimum pH is acidic pH 1 for the adsorption of F- by PANI-Cl-jute. At acidic pH, the protonated amines of PANI-Cl-jute electro statically attract the anionic F- and adsorbs more fluoride ions.

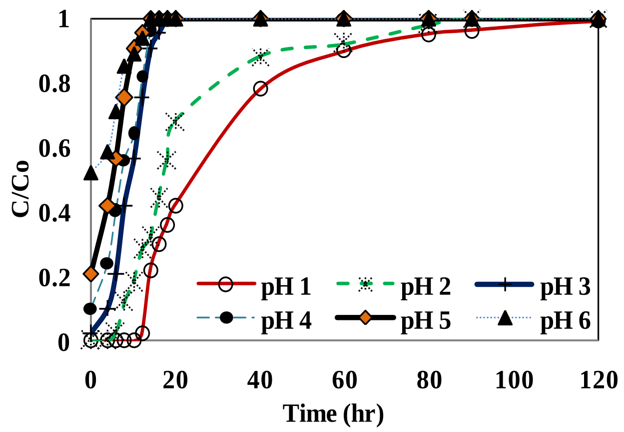


**Fig. 6:** Breakthrough curve at different pH for fluoride adsorption

**Effect of bed depth**

Effect on bed depth was studied at varied bed depth of 1.5 m, 2 m and 3.5 m which were filled with PANI-Cl-jute of 165g, 220 g and 330 g respectively. The experiment was conducted at flow rate of 1.2 mL/min and initial F- concentration of 5 mg/L. The breakthrough curve of the column reactor is shown in Fig. 7. The evaluated parameters for the continuous column experiment for F- adsorption by PANI-Cl-jute are shown in Table 1. The obtained curce is called S-curve or Breakthrough Curve. The area above the breakthrough curve denotes the total amount of $F^-$ ions adsorbed (mg).

With the increase in bed depth from 1.5 - 3 m, both the breakthrough time (considered at 5% effluent) and exhaust time (considered at 95% effluent) increased from 8.6 - 17.5 h and 88 - 200 h respectively. Subsequently, the corresponding throughput volume and exhaust volume were also increased from 0.62 L to 1.26 L and 6.33 L to 14.4 L respectively. Thus amount of $F^-$ ions adsorbed ($M_R$) were 11.87, 15.85 and 26.53 mg$F^-$ for bed depth of 1.5, 2 and 3 m respectively. As bed depth increase, the amount of active sites of adsorbent increase and adsorb higher $F^-$, thus treating more volume. Also, increasing the bed depth should lead to decrease in axial dispersion and encourage higher F- diffusion on PANI-jute. Similar cases are observed in almost all fixed bed studies [13, 14]. However despite more contact time between adsorbate and adsorbent with increase in bed depth, the qe value are almost same with 0.7-0.8 mg/g without much significant change.

This finding was compared with batch adsorption studies by conducting experiment with $F^-$ 10 mg/L contacting with 1 g/L PANI-Cl-jute. The amount of ions adsorbed, $q_e$ was observed to be 12.99 mg/g which is higher than that of continuous results with 0.7 mg/g. Very insignificant or miniumum adsorption of $F^-$ occurs beyond the Mass Transfer Zone in continuous column process and this may be due to strict chemical adsorption of $F^-$ on PANI-jute with minimum or insignificant physical diffusion. However equilibrium is achieved in batch process unlike the concept of mass transfer zone in column process resulting higher uptake. In practical application of fixed bed column either for water or waste water treatment, the fixed bed will be employed till the effluent is within permissible limit or breakthrough time. The running of fix bed after the occurrence of the breakthrough till the exhaust point is not necessary as ions will start leaking above the permissible limit. The purpose of running till the exhausting point is for study purpose to understand the column profiles and gain the inside mechanism.

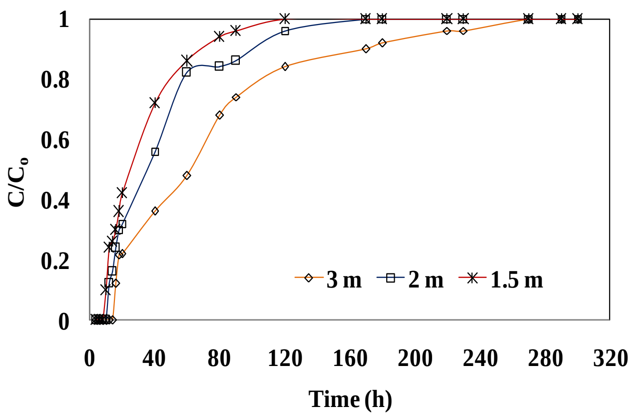


**Fig. 7:** Breakthrough curve at different bed depth of the reactor

**Comparison of performance between synthetic and actual fluoride contaminated ground water**

A comparative study between the synthetic fluoride contaminated ground water and actual ground water was carried out to evaluate the practical feasibility of employing PANI-Cl-jute. The actual ground water $F^-$ contamination was observed to be 3 mg/L, therefore synthetic $F^-$ contaminated water with 3 mg/L was also prepared. The S-curve for both the experiments are illustrated in Fig. 8. The actual ground water sample yields a breakthrough time of 6.5 hour against 9.5 hour for synthetic $F^-$ contaminated water yielding a respective throughput volume of 468 mL and 684 mL. Better efficiency of PANI-Cl-jute is obtained for synthetic since the presence of other co-ions in actual ground water probably hindered the adsorption process. Again, the S-curve of actual ground water is more steeper than that of synthetic water can be explained by the fact that adsorption is immediate in ground water and got exhausted sooner than the synthetic. The absence of co-ions in synthetic allows more $F^-$ ions to adsorb probably through diffusion also leading to flatter curve and finally achieve the exhaust at 150 hours of adsorption.

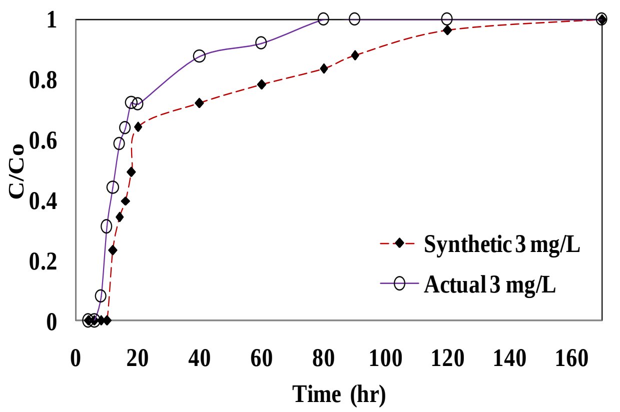


**Fig. 8**: Comaprision between adsorption from synthetic F- contaminated water and actual ground water

**Thomas Model Breakthrough**

The Thomas model is another widely used model and describes the breakthrough of the fixed bed column with no axial dispersion. Maximum adsorption capacity can be calculated from this model [15]. The linear mathematical expression is shown in Equation (1):

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{K_{Th} q_{Th} m}{Q} - K_{Th} C_o t \qquad \text{------------(1)}$$

Where A and B are the constant, t is the time (h), $K_{Th}$ is the Thomas rate constant (L/h/mg), $q_{Th}$ is the maximum solid phase concentration of the solute (mg/g), m is the amount of adsorbent (g), Q is the flow rate (L/min), $C_o$ and $C_t$ are the initial fluoride concentration & concentration at time t respectively (mg/L). The data of column with flowrate of 1.2 mL/min and $C_o$ 5 mg/L was fed on Thomas model equation and a plot of Service Time Vs Ln[$C_o$/C)-1] is obtained and illustrated at Fig.9. The correlation coefficients $R^2$ for the column at various depth were all above 0.95 and obeyed the Thomas model. Theoretical $q_{TH}$ value were evaluated and compared with experimental value ($q_e$) (Table 2). The error (%) for depth of 1.5 m and 2 m yields 33% and 16%

**Table 1:** Parameters of F- adsorption at continuous bed at different bed depth of reactors**.**

| Depth (m) | Breakthrough time ($T_b$) | Exhaust time ($T_e$) | Breakthrough volume ($V_b$) (L) | Exhaust Volume ($V_e$) | Mass of adsorbent , | Total amount of F- uptake (mg) | Total amount of F- uptake per unit gram of adsorbent ($q_e$) |
|---|---|---|---|---|---|---|---|

| | | | | (L) | m (gm) | | |
|---|---|---|---|---|---|---|---|
| 1.5 | 8.6 | 88 | 0.619 | 6.33 | 165 | 11.865 | 0.072 |
| 2 | 11.7 | 112 | 0.842 | 8.06 | 220 | 15.852 | 0.072 |
| 3 | 17.5 | 200 | 1.260 | 14.40 | 330 | 26.531 | 0.080 |

respectively whereas for the 3 m depth, the predicted values completely match with experimental value. This finding indicates the partial applicability of Thomas equation for $F^-$ adsorption on PANI-jute-Cl and its probably due to its equation derived from second order reversible reaction kinetics which is generally controlled by interphase mass transfer and not limited to chemical reaction kinetics[15].

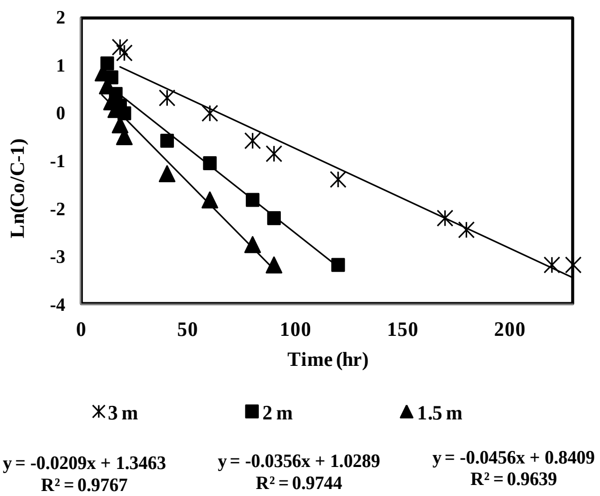


**Fig. 9:** Plot of linear Thomas model equation.

**Table 2:** Parameters of fitting Thomas Model for adsorption of $F^-$ on PANI-jute

| | Q:1.2 mL/min, Co:5mg/L | | |
|---|---|---|---|
| Bed Depth (m) | 1.5 | 2 | 3 |
| $R^2$ | 0.96 | 0.97 | 0.97 |
| $K_{TH}$ ($mL.min^{-1}g^{-1}$) | 0.009 | 0.007 | 0.004 |
| $q_{TH}$ (mg/g) | 0.04 | 0.05 | 0.07 |
| $q_e$, (mg/g) | 0.06 | 0.06 | 0.07 |

**Conclusion**

The study of fluoride adsorption by chloride doped polyaniline polymer, PANI-Cl-jute was investigated for the F- uptake at various conditions. The chloride concentration of 1.5 M was observed to be the optimum for doping with maximum $F^-$ uptake with throughput volume of 1150 mL. Optimum pH was observed at acidic pH 1 with maximum breakthrough time of 12 hours. At various bed depth of 1.5, 2 and 3 m, amount of $F^-$ ions adsorbed ($M_R$) were 11.87, 15.85 and 26.53 $mgF^-$ respectively with average uptake of 0.7-0.8

mg/g. The adsorbent PANI-Cl-jute proved to be an effective adsorbent for the defluioridization from ground water.

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