

## Chapter 2

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# Experimental

## 2. Experimental

### 2.1 Materials

#### 2.1.1 Limestone

The crude limestone sample, obtained as a gift from Bokajan Cement Factory, Bokajan, Assam, India was crushed and different particle size fractions were used for the experiments. Powder limestone of size  $\leq 170 \mu\text{m}$  also was obtained from Bokajan Cement Factory.

#### 2.1.2 Chemicals

Analytical grade sodium fluoride, sodium chloride, sodium bromide, sodium sulphate and potassium nitrate were obtained from Merck, Mumbai and were used without further purification. Analytical grade and technical grade PA were obtained from Merck, Mumbai and Bharat Trading, Guwahati, were used in laboratory experiment and in field trial, respectively.

#### 2.1.3 Water

Doubly distilled water was used for the preparation of stock solution of fluoride for laboratory batch experiments. Some experiments were carried out using groundwater amended with fluoride in view of practical field application. The groundwater used during the experiments was drawn from a shallow tube well of depth of approximately 14 m. Some relevant chemical parameters of the groundwater are mentioned in Table 2.1. The experiments described in the section, *2.4.5.2 Methods of fluoride removal from groundwater model unit*, on field trial were carried out with groundwater collected from the field sources of field trial sites.

##### *2.1.3.1 Preparation of synthetic feed water*

Synthetic fluoride stock solution of 1000 mg/L was prepared by dissolving calculated amount of sodium fluoride in distilled water or groundwater in a volumetric flask. Pre-acidified fluoride containing water of different initial concentrations was prepared by adding appropriate quantity of 85% (W/V) PA and fluoride stock solution in a volumetric flask and then making up the volume with distilled water or groundwater.

**Table 2.1.** Relevant parameters of groundwater used in laboratory experiments.

Parameter	Concentration in mg/L except pH
pH	7.47
Sodium, Na <sup>+</sup>	60.6
Potassium, K <sup>+</sup>	1.07
Calcium, Ca <sup>2+</sup>	2.50
Magnesium, Mg <sup>2+</sup>	2.4
Mercury, Hg <sup>2+</sup>	<0.001
Fluoride, F <sup>-</sup>	0.20
Chloride, Cl <sup>-</sup>	5.4
Sulphate, SO <sub>4</sub> <sup>2-</sup>	6.3
Phosphate, PO <sub>4</sub> <sup>3-</sup>	0.70
Total Hardness as CaCO <sub>3</sub>	80
Total Alkalinity as CaCO <sub>3</sub>	86

## 2.2 Analytical measurements

Fluoride concentration was measured on an Orion Multiparameter Kit (model: Orion 4-Star pH.ISE Laboratorytop) using an ion selective electrode (ISE) for fluoride. Total ionic strength adjustment buffer-III (TISAB-III) solution was added to sample solutions in the ratio of 1:10. The calibration of the ion meter was done at 0.1, 1.0 and 10 mg/L fluoride solution. Chloride concentration was determined using an ISE for chloride (model: Orion 4-Star pH.ISE Laboratorytop). The pH of the solutions was measured using a multiparameter kit (model 5 Star pH.ISE.Cond.DO Laboratorytop, Orion, USA) with temperature compensation. The calibration of pH was done with standard buffer solutions of pH 4.00, 7.00 and pH 10.00.

The metal ions in water before and after treatment were determined by using atomic absorption spectrophotometer (AAS, model Analyst 200, Thermo iCE 3000 series, USA). The presence of calcium, sodium and potassium ion concentrations was analyzed by a flame photometer (Systronic, Flame Photometer 128). The other ions *viz.*, sulphate, nitrate and phosphate concentrations were determined by UV-Visible

spectroscopic measurements on a Shimadzu UV-2550 UV-Visible spectrophotometer. The surface micrographs of unused and used limestone were studied by using a scanning electron microscope (SEM, model JSM-6390LV, Jeol, Japan) with Energy dispersive X-ray spectra (EDX) at an accelerating voltage of 15.0 kV. The surface of the sample was platinum coated before SEM analysis. The XRD data were recorded on a Rigaku Miniflex X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda= 0.154$  nm) at 30 kV and 15 mA using a scanning rate of 0.05°/s in 2 $\theta$  ranges from 10° to 70°. The Fourier transform infrared (FTIR) spectra were recorded on an IR spectrophotometer (model Impact 410 FTIR spectrophotometer, Nicolet, Japan). Particle size distribution was done on a nanotracs wave particle size and zeta potential analyzer (Model MN401).

### **2.3 Statistical Analysis**

One way analysis of variance (one-way ANOVA)<sup>284</sup> was performed to examine the real variations amongst the results of treatments under different conditions by calculating the least significant difference (LSD) amongst the data of fluoride removal with initial fluoride concentration ( $[F^-]_0$ ), initial phosphoric acid concentration ( $[PA]_0$ ) and flow rates. The statistical analyses were carried out using SPSS 16.

### **2.4 Methods**

#### **2.4.1 Methods of fluoride removal by limestone powder in presence of PA**

##### **2.4.1.1 Batch study**

For the fluoride sorption experiments, fluoride stock solution was prepared by dissolving known amount of NaF in a 2 L volumetric flask and the volume was made up to 2 L by double distilled water. Pre-acidified fluoride containing water was prepared by mixing known volume of fluoride stock solution and calculated volume of 85% W/V PA in a 2 L volumetric flask and then the volume was made up to 2 L. The pre-acidified water (100 mL) was added to a 250 mL Erlenmeyer flasks containing known amount of limestone powder ( $\leq 170$   $\mu$ m). The mixtures were agitated in the thermostated shaker at a speed of 200 rpm at fixed temperature maintained within 298 $\pm$ 1 K. For equilibrium experiments, the samples were taken out after different intervals of time and filtered through Whatman 42 filter paper. The remaining fluoride concentration and the pH of the filtrate were measured. The experiments on kinetics of fluoride sorption experiments were conducted at different  $[F^-]_0$  with fixed  $[PA]_0$  and adsorbent dose. Adsorption isotherms were

evaluated by conducting the batch experiments in absence or in presence of PA with different  $[F^-]_0$  and  $[PA]_0$  at fixed dose of adsorbent and contact time. The batch adsorption studies were carried out at five different temperatures, viz., 298, 303, 308, 313 and 318 K for evaluating the thermodynamic parameters of fluoride sorption. The experiments were repeated at least thrice in order to check reproducibility.

The amounts of fluoride adsorbed by limestone in mg/g at time  $t$  ( $q_t$ ) and at equilibrium ( $q_e$ ) were calculated by using Eqs. (2.1) and (2.2), respectively<sup>285</sup>.

$$q_t = (C_0 - C_t)V/m \quad (2.1)$$

$$q_e = (C_0 - C_e)V/m \quad (2.2)$$

where,  $C_0$ ,  $C_t$  and  $C_e$  are the initial fluoride concentrations (mg/L), fluoride concentration at time 't' and equilibrium fluoride concentration, respectively.  $V$  is the volume of the solution (L) and  $m$  is the mass of adsorbent taken (g).

#### **2.4.1.2 Effects of process parameters**

Fluoride removal was explained from the evidence of FTIR and XRD analysis. Fresh limestone and fluoride loaded limestone were characterised through FTIR and XRD spectra.

The effect of adsorbent dose on fluoride removal from aqueous solution was studied by carrying out the batch experiment in presence of 0.10 M  $[PA]_0$ , at fixed  $[F^-]_0$  of 5 mg/L for contact time of 3 h.

To see the effect of contact time on fluoride sorption, the batch experiment was conducted for different contact time at a fixed condition of other operational parameters.

Fluoride removal by limestone powder in presence of PA was studied by varying  $[PA]_0$  from 0.01 to 0.10 M to compare the fluoride removal performance of limestone powder in absence of PA.

#### **2.4.1.3 Adsorption kinetics**

The kinetics of fluoride removal by limestone powder in presence of PA was investigated through pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich kinetic models. The batch experiments were carried out using fixed adsorbent dose of 0.5 g/100 mL at different  $[F^-]_0$  range of 3-15 mg/L and each samples were collected after

different treatment time and filtered through Whatman 42 filter paper and the suspension was used for measurement of residual  $[F^-]$  and pH. The experiment was maintained at a fixed temperature of  $298 \pm 1$  K.

#### 2.4.1.3.1 Pseudo-first-order equation

The pseudo-first-order equation is expressed by the following equation<sup>286</sup>:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (2.3)$$

where,  $q_e$  and  $q_t$  are the fluoride adsorption capacities of sorbent at equilibrium and at time  $t$ , respectively, and  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo-first-order rate constant. The pseudo-first-order rate constant,  $k_1$ , can be calculated from the slope of the plots of  $\ln(q_e - q_t)$  vs. time 't'.

#### 2.4.1.3.2 Pseudo-second-order equation

The pseudo-second-order kinetic rate equation is expressed as follows<sup>286</sup>:

$$t/q_t = (1/k_2)(1/q_e^2) + (t/q_e) \quad (2.4)$$

where,  $q_e$  and  $q_t$  are the fluoride adsorption capacities of sorbent at equilibrium and at time  $t$ , respectively, and  $k_2$  is the second order rate constant ( $\text{g/mg min}$ ). The pseudo-second-order rate constant,  $k_2$ , and adsorption capacity at equilibrium ( $q_e$ ) were calculated from the slope and the intercept of the plot of  $t/q_t$  vs.  $t$ .

#### 2.4.1.3.3 Intra-particle diffusion model

The intra-particle diffusion model has been used to evaluate the rate determining step as well as whether the sorption takes place at outer surface or in the internal pores and voids within the matrix of the adsorbent<sup>286</sup>. Weber and Morris<sup>287</sup> describe the intra-particle diffusion model where the amount of fluoride adsorbed by limestone in  $\text{mg/g}$  at time  $t$ ,  $q_t$  is expressed as Eq. (2.5)<sup>287</sup>:

$$q_t = k_i t^{1/2} + C \quad (2.5)$$

where,  $k_i$  ( $\text{mg/g min}^{1/2}$ ) is the intra-particle diffusion rate constant. The values of  $k_i$  can be evaluated from the plot of  $q_t$  vs.  $t^{1/2}$ .

#### 2.4.1.3.4 Elovich model

The Elovich rate equation is one of the most useful kinetic models for describing chemisorption of adsorbate onto a solid surface<sup>288</sup>. The simplified form of this model is represented by Eq. (2.6)

$$q_t = (1/B) \ln(AB) + (1/B) \ln(t) \quad (2.6)$$

where, A ( $\text{mg/g min}^{-1}$ ) is the sorption constant of the fluoride ions and B ( $\text{g/mg}$ ) is the desorption constant of the fluoride ions. The values of A and 1/B can be evaluated from the slope and intercept of the plots of  $q_t$  vs.  $\ln(t)$ .

#### 2.4.1.4 Adsorption isotherms

For adsorption isotherm study on fluoride removal by limestone powder in absence and in the presence of PA, the batch experiments were conducted at different  $[F^-]_0$  of 3-15 mg/L for fixed adsorbent dose of 0.5 g/100 mL at  $298 \pm 1$  K. The sample were withdrawn after 3 h and used for measurement of residual  $[F^-]$  followed by filtration. Adsorption isotherms were studied using Freundlich, Langmuir, Dubinin-Radushkevich (D-R) and Temkin isotherm models.

##### 2.4.1.4.1 Freundlich isotherm

Freundlich isotherm predicts that the sorption takes place on heterogeneous surface. The linear forms of Freundlich isotherm can be represented by Eq. (2.7)<sup>289</sup>:

$$\ln(q_e) = \ln(K_F) + 1/n \ln(C_e) \quad (2.7)$$

where,  $q_e$ ,  $C_e$ ,  $K_F$  and  $n$  are the amount of fluoride adsorbed at equilibrium ( $\text{mg/g}$ ), the fluoride concentration at equilibrium ( $\text{mg/L}$ ), the Freundlich adsorption capacity ( $\text{mg/g}$ ) and adsorption intensity, respectively. The values of  $K_F$  and  $n$  were determined from the intercept and slope of the linear plot of  $\ln(q_e)$  vs.  $\ln(C_e)$ .

##### 2.4.1.4.2 Langmuir isotherm

Langmuir isotherm assumes that sorption occurs on homogeneous surface. The Langmuir isotherm can be written as Eq. (2.8)<sup>289</sup>:

$$C_e/q_e = C_e/Q_o + 1/bQ_o \quad (2.8)$$

where  $Q_0$  and  $b$  are the adsorption capacity (mg/g) based on Langmuir isotherm and the Langmuir isotherm constant (L/mg) related to the affinity of the binding sites, respectively. The  $Q_0$  and  $b$  values were calculated from slope and intercept of the plot of  $C_e/q_e$  vs.  $C_e$ .

#### 2.4.1.4.3 Dubinin-Radushkevich (D-R) isotherm

Dubinin-Radushkevich (D-R) isotherm equation helps in understanding whether the adsorption is physisorption or chemisorption<sup>290</sup>. This equation is expressed in the linear form as:

$$\ln(q_e) = \ln(Q_D) - B_D \varepsilon^2 \quad (2.9)$$

where,  $Q_D$  is the adsorption capacity (mg/g),  $B_D$  is the activity constant related to mean sorption energy ( $\text{mol}^2/\text{kJ}^2$ ) and  $\varepsilon$  is the Polanyi potential which is defined by Eq. (2.10)<sup>290</sup>:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (2.10)$$

where,  $R$  is the gas constant (J/Kmol) and  $T$  is the temperature in K. The mean free energy of adsorption,  $E$  (kJ/mol) can be calculated from  $B_D$  using Eq. (2.11)<sup>290</sup>.

$$E = 2B_D^{-0.5} \quad (2.11)$$

The values of  $Q_D$  and  $B_D$  are calculated from the slope and the intercept of the plot  $\ln(q_e)$  vs.  $\varepsilon^2$ , respectively. If the value of mean free energy of adsorption ( $E$ ) ranges from 1.0-8.0 KJ/mol, then the sorption process is physisorption and if it is in between 9.0-16.0 KJ/mol, then the sorption process is chemical in nature<sup>290</sup>.

#### 2.4.1.4.4 Temkin isotherm

The Temkin isotherm model describes that the heat of adsorption of all molecules decreases linearly with coverage due to adsorbate-adsorbate interactions, and that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy<sup>291</sup>. The Temkin isotherm equation can be written as Eq. (2.12)<sup>291</sup>:

$$q_e = B_T \ln(A_T) + B_T \ln(C_e) \quad (2.12)$$



$A_T$  (L/g) is the binding constant that represents the maximum binding energy and  $B_T = (RT)/b$  is the Temkin constant related to heat of sorption. These constants have been evaluated from the plots of  $q_e$  vs.  $\ln(C_e)$ .

#### 2.4.1.5 The thermodynamics of adsorption

The thermodynamic parameters were evaluated by conducting the batch experiments at five different temperatures, *viz.*, 298, 303, 308, 318 and 328 K for fixed adsorbent dose of 0.5 g/100 mL with  $[F]_0$  of 5 mg/L. The thermodynamic parameters such as standard free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) of adsorption were calculated using the following equations (2.13) and (2.14)<sup>292</sup>.

$$\Delta G^\circ = -RT \ln(K_c) \quad (2.13)$$

$$\ln(K_c) = \Delta S^\circ/R - \Delta H^\circ/RT \quad (2.14)$$

where,  $K_c$  is the standard equilibrium constant of adsorption.  $K_c$  is the ratio of the adsorption capacity ( $q_e$ ) to the equilibrium concentration of fluoride ( $C_e$ ). The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  have been calculated from the slope and the intercept of plot of  $\ln(K_c)$  vs.  $1/T$ .

### 2.4.2 Methods of fluoride removal by hydrothermally modified limestone powder using PA

#### 2.4.2.1 Hydrothermal modification of limestone powder

PA solution with different known molar concentrations, *viz.*, 0.30 M, 0.60 M and 0.90 M were prepared by taking known volume of 85% (W/V) PA in appropriate volume of double distilled water. Initially, definite amount of limestone powder ( $\leq 170 \mu\text{m}$ ) was kept in a Teflon-lined stainless autoclave reactor and PA solution was added drop-wise. The PA solutions of different concentrations were put separately into autoclaves containing limestone powder. In all the experiments, the Ca/P molar ratio was kept constant at 1.66 as this is the ratio of Ca/P in HAP. The reaction mixture was kept in oven for 12 h at  $120^\circ\text{C}$  for hydrothermal treatment. After 12 h, the autoclave was cooled slowly and the reacted powders (modified limestone) were collected and filtered through a Whatman 42 filter paper. The modified limestone was dried by keeping in desiccators for 24 h and used for characterization by FTIR, XRD and SEM-EDX analysis.

#### ***2.4.2.2 Batch experiments of fluoride adsorption***

Batch adsorption experiments were carried out in 250 mL Erlenmeyer flasks. A known amount of the modified limestone powder was added to 150 mL of known concentration fluoride solution. The mixture was then shaken in the thermostated shaker at a fixed temperature at a speed of 200 rpm for a predetermined time interval. After that the suspensions was filtered through a Whatman 42 filter paper. The residual fluoride concentrations were measured using a fluoride ion selective electrode.

The defluoridation capacity of the prepared materials at time ( $q_t$ ) and at equilibrium ( $q_e$ ) was determined by using Eqs. (2.1) and (2.2), respectively.

#### ***2.4.2.3 Desorption study***

For study of desorption of fluoride from fluoride-loaded material, 2 g of the modified sample was taken in a 250 mL conical flask with 150 mL of water containing 1000 mg/L of  $[F^-]_0$ . The mixture was shaken for 12 h in a thermostated shaker at 200 rpm. After the equilibration, the supernatant solution was separated by a Whatmann 42 filter paper. The fluoride-loaded residue was washed with distilled water until fluoride concentration in the effluent water reached equilibrium. After that the residue was dried in desiccators. 0.25 g of the fluoride-loaded dry residue was taken in 250 mL conical flasks with 75 mL of distilled water at varying pH. The pH was adjusted in the range from 3 to 12 using 0.10 M HCl and 0.10 M NaOH. The mixtures were allowed to equilibrate for 3 h at  $298 \pm 1$  K and filtered. The concentration of the desorbed fluoride in the filtrate was measured.

#### ***2.4.2.4 Characterization of the modified limestone***

The characterization of unmodified and modified limestone powder, prepared by hydrothermal treatment of limestone powder in presence of PA was investigated using FTIR, XRD and SEM-EDX analysis.

#### ***2.4.2.5 Fluoride removal by modified limestone***

The batch experiments on fluoride removal were studied using unmodified (L0) and modified limestone powder in presence of PA concentrations of 0.30 M (M3), 0.60 M (M6) and 0.90 M (M9) at fixed dose of adsorbent and  $[F^-]_0$  of 10 mg/L with varying treatment time.

#### **2.4.2.6 Effect of process parameters**

To see the effect of contact time and initial fluoride concentration on fluoride removal, the batch experiment was studied as a function of contact time at different  $[F^-]_0$ , viz., 5 mg/L, 10 mg/L and 20 mg/L. The effect of dose of M9 on fluoride removal from aqueous solution has been investigated by performing the batch experiments at fixed  $[F^-]_0$  of 10 mg/L with contact time of 3 h.

#### **2.4.2.7 Adsorption kinetics**

For kinetics study of fluoride sorption on M9 sample, the batch experiments were performed using fixed dose of M9 (0.5 g/150 mL) at different  $[F^-]_0$  range of 3-20 mg/L. The mixtures were agitated at 200 rpm and each samples were collected after different treatment time and filtered through Whatman 42 filter paper and the suspension was used for measurement of residual  $[F^-]$  and pH. The experiment was maintained at a fixed temperature of  $298 \pm 1$  K. The kinetics of fluoride removal by M9 was investigated through pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich kinetic models using Eqs. 2.3-2.6.

#### **2.4.2.8 Adsorption isotherms**

For adsorption isotherm study of fluoride removal by unmodified and modified limestone (M9) sample, the batch experiments were conducted at different  $[F^-]_0$  of 3-20 mg/L for fixed adsorbent dose of 0.5 g/150 mL at  $298 \pm 1$  K. The samples were withdrawn after 3 h and used for measurement of residual  $[F^-]$  in filtrate solutions. Adsorption isotherms were studied using Freundlich, Langmuir, Dubinin-Radushkevich (D-R) and Temkin isotherm models using Eqs. 2.7-2.12.

#### **2.4.2.9 The thermodynamics of fluoride sorption**

The batch experiments were conducted at five different temperatures, viz., 298, 303, 308, 318 and 328 K for fixed adsorbent dose of 0.5 g/150 mL with  $[F^-]_0$  of 10 mg/L to evaluate the thermodynamic parameters. The thermodynamic parameters such as standard free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) of adsorption were calculated using Eq. 2.13 and Eq. 2.14. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were evaluated from slope and intercept of van't Hoff plots of  $\ln(K_c)$  vs.  $1/T$ .

### 2.4.3 Methods of continuous-flow column experiment

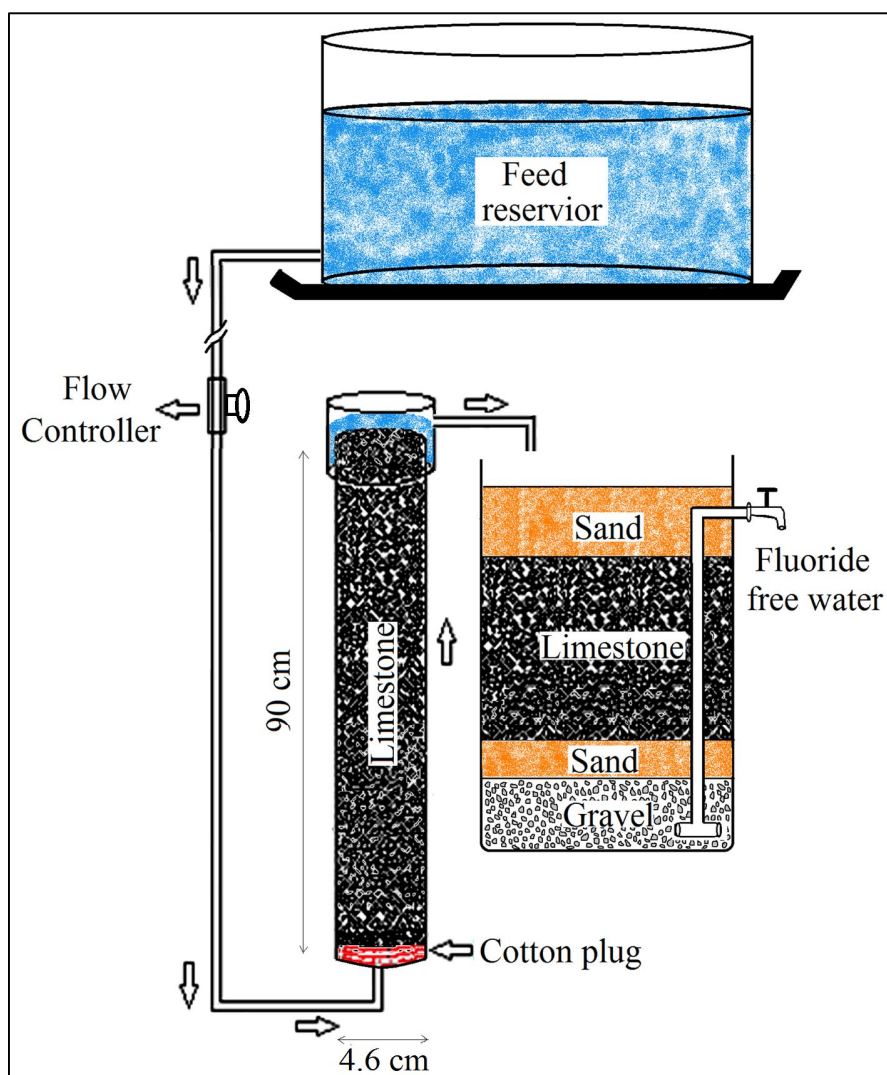
For continuous-flow experiment, a plexiglass columns of length 90 cm and radius 2.3 cm containing crushed limestone chips was placed vertically as shown in Figure 2.1. The column was filled with 1.0-1.5 cm size limestone chips. The void (empty bed) volume in such a fixed bed column was approximately 1500 mL. The pore volume ( $V$ ) of the column filled with limestone was 650 mL which was about 43% of the void volume of the column. The experiments were carried out at three different flow rates, *viz.*, 100, 200 and 300 mL/h. The empty bed contact time (EBCT) or residence times of the influent water in the column, as obtained from Eq. 2.16, were 900 min, 450 min and 300 min at the flow rates of 100 mL/h, 200 mL/h and 300 mL/h, respectively. Flow channelling was assumed to be absent at the slow experimental flow rates in the present study though there might have been some flow channelling still occurring in the column.

The influent water was prepared by mixing known quantity of fluoride and PA in freshly withdrawn groundwater. A large flat plastic of low-density polyethylene (LDPE) container, kept at about 1.5 m above the column to minimise variation in flow rate, was used as a feed reservoir for influent water containing fluoride and PA. The feed reservoir was placed at a level above the outlet at the top of the column to maintain a nearly constant gravity feeding in an up-flow mode. The influent water was allowed to enter the column from its bottom with different flow rate controlled by a flow controller. A plastic container of radius 8 cm open at the bottom towards the column and having a hole at its bottom side wall was placed at the top of the column for collecting the overflowing effluent water. Further, the effluent water, so collected can be used for treatment in a four layered sand-limestone-sand-gravel filter for pH correction as shown in Figure 2.1.

#### 2.4.3.1 Effect of process parameters

The effect of influent PA concentrations on fluoride removal by phosphoric acid-crushed limestone treatment (PACLT) in continuous-flow mode was studied with  $[PA]_0$  of 0.01 M, 0.03 M and 0.05 M at fixed  $[F^-]_0$  of 5 mg/L at the flow rate of 100 mL/h.

The fluoride removal by PACLT in continuous-flow mode was studied at different  $[F^-]_0$  of 5, 7 and 10 mg/L at a fixed  $[PA]_0$  of 0.01 M by maintaining the flow rate at 100 mL/h.



**Figure 2.1.** The experimental set up for continuous-flow test.

The fluoride removal performance was examined at different flow rates of the feed, and hence of the output also at 100 mL/h, 200 mL/h and 300 mL/h, at  $[F^-]_0$  of 5 mg/L in presence of 0.01 M  $[PA]_0$ .

The service time at breakthrough ( $t_b$ ) and empty bed contact time (EBCT) have been evaluated using the following equations<sup>293, 294</sup>:

$$t_b = V_B/Q \quad (2.15)$$

$$EBCT = V_v/Q \quad (2.16)$$

where,  $V_v$  (mL) and  $Q$  (mL/h) are void volume and flow rate. EBCT is defined as the time a fluid spends in the empty column<sup>293</sup>.

### **2.4.3.2 The effect of co-existing ions**

To investigate the interference of co-existing ions, i.e.,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  on fluoride removal in continuous-flow mode, respective sodium salts for  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  and potassium salt for  $\text{NO}_3^-$  have been added to the fluoride containing water pre-acidified with PA and influent water was used for PACLT in continuous-flow mode.

### **2.4.3.3 Mechanism of fluoride removal**

The mechanism of fluoride removal by PACLT in continuous-flow mode has been studied by using saturation index, FTIR, XRD and SEM-EDX analysis.

#### **(i) Calculation of saturation index of fluorite**

The fluorite Saturation Index ( $\text{SI}_f$ ) has been calculated using the equation below<sup>242</sup>:

$$\text{SI}_f = \log_{10} (Q/K_{sp}) \quad (2.17)$$

where,  $Q = (\text{activity of Ca}^{2+})(\text{activity of F}^-)^2$  and  $K_{sp}$  is the solubility product of fluorite,  $3.5 \times 10^{-11}$ .

#### **(ii) Analysis of the precipitate**

The limestone sample before used and the precipitate collected after breakthrough in continuous-flow PACLT method has been analyzed by FTIR, XRD and SEM-EDX analysis.

### **2.4.3.4 Column regeneration**

After breakthrough, the exhausted limestone columns were fed with 0.30 M NaOH (pH = 12.00) solution in the up flow mode at different flow rates. The cycle was continued until the concentration of fluoride in the effluent water attained equilibrium. After the alkali treatment, the column was flushed with fluoride free water to remove the remaining alkali from limestone and was used for further fluoride removal experiment without drying the regenerated limestone. The fluoride removal experiment was then repeated until the breakthrough was observed. All the experiments are done in triplicate.

### **2.4.3.5 Toxicity characteristics leaching procedure (TCLP) test**

Leaching behaviour of precipitate was studied by toxicity characteristics leaching procedure<sup>295</sup>. For TCLP test, a extraction fluid was prepared by adding 5.7 mL glacial acetic acid and 64.3 mL of 1 M NaOH and the volume made up to 1 L with distilled

water. The solid waste and extraction fluid were taken in the ratio of (W/V) 1:20, in a 250 mL glass conical flask and shaken at 30 rpm for 18 h. After shaking, the suspension was allowed to settle for 5 min and filtered through Whatman 42 filter paper and the filtrate was analyzed for residual  $[F^-]$ . The precipitate was settled at the bottom of the container after PACLT was dried at room temperature and used for the TCLP test.

#### 2.4.4 Methods of the laboratory-scale pilot test of PACLT

For the laboratory-scale pilot experiments, bucket-shaped LDPE containers (11 L) were used. The containers were filled up with fixed bed of crushed limestone chips. Though smaller size of limestone particles gives better removal<sup>264-267</sup>, the author used larger size, *viz.*, 1.0-1.5 cm diameter particles in the pilot test to increase the pore volume of the limestone-bed reactor to a practically acceptable value of 45%, *i.e.*,  $\approx 5$  L. Synthetic fluoride-containing groundwater was prepared by addition of known quantity of fluoride to freshly withdrawn groundwater. The synthetic fluoride-containing water with  $[F^-]_0$  of 10 mg/L preacidified with different  $[PA]_0$  of 0.001 M, 0.005 M and 0.01 M (Figure 2.2).



**Figure 2.2.** The experimental set up for laboratory-pilot experiment.

The influent water was then added to the container to fill up the vacant pores up to the top level of limestone particles. In the plug-flow column experiments, fluoride removal by crushed limestone in presence of PA attained equilibrium at 3 h<sup>267</sup>. Therefore, the water was allowed to react with crushed limestone bed for a residence time of 3 h in laboratory-scale pilot test. The water was removed from a tap at the base of the container after 3 h and filtered using Whatman 42 filter paper and used for the measurement of the respective parameters. The experiments are done in triplicate.

#### ***2.4.4.1 Regeneration of used limestone***

The activity of used limestone, which gave less than 80% removal from 10 mg/L (0.526 mM) in the pilot test, was regenerated by three different ways: (i) simple scrubbing, (ii) soaking in 0.30 M (300 mM) Ca(OH)<sub>2</sub> for 24 h and (iii) soaking in 0.30 M (300 mM) NaOH for 24 h followed by rinsing with fluoride free water. The regenerated limestone was used for further fluoride removal experiments without drying it.

#### ***2.4.4.2 Study of the relevant water quality parameters before and after PACLT treatment***

The relevant water quality parameters *viz.*, pH, dissolved solids, suspended solids, alkalinity and hardness as calcium carbonate, concentration of other ions such as calcium, potassium, sodium, iron, chloride, nitrate, phosphate, sulphate, concentration of heavy metal ions such as cadmium, calcium, chromium, cobalt, copper, lead, magnesium, manganese and zinc of the water samples were measured before and after the PACLT method were determined using standard methods.

#### **2.4.5 Field trial**

The field trial of the phosphoric acid-crushed limestone treatment (PACLT), named '***Fluoride Nilogon***' ('*Nilogon*' for removal) was started in a phased manner at six spots water sources which included five household units with 15 L and one small community unit with 220 L water holding capacity at different fluoride affected villages in Karbi Anglong District of Assam, India. The author felt the necessity of a suitable name for the method to make it familiar to the users whose participation in the field trial was vital for the study as well as for popularity of the method. Therefore, the PACLT method was



named as '*Fluoride Nilogon*', where, '*Nilogon*' (নিলগন) is the local Assamese equivalent for removal.

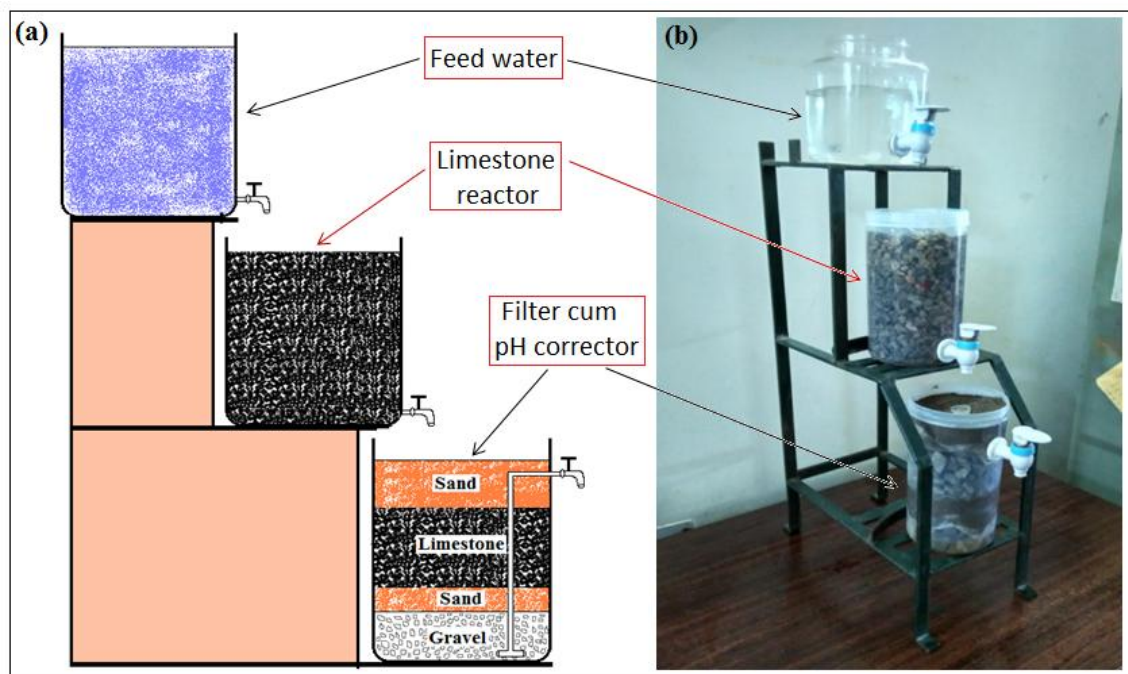
#### **2.4.5.1 Selection of site**

Groundwater of some areas of Karbi Anglong district is reported to be highly contaminated with fluoride<sup>35</sup>. Occurrence of large scale fluorosis is also reported in the fluoride contaminated areas of the district<sup>36</sup>. The author has also performed an initial survey of water used by the people of the chosen areas, namely, Dengaon and Bagpani (Tekelang Jung) area, at the start of the field trial. The author visited some fluoride affected villages in Assam during October, 2012. The water samples were collected in plastic sample bottles from the source of the selected places and fluoride concentration, pH and other relevant water quality parameters were measured. Most people in the area were using groundwater from hand tube wells contaminated with excess fluoride up to 20 mg/L for drinking purpose. At Dengaon, the drinking water supplied by the local public health department was also found to have excess fluoride of about  $4.8 \pm 0.2$  mg/L. The author noticed moderate to severe dental fluorosis of the users of the fluoride containing water. The village selected for the user trial of the small community unit was Dengaon. The villages selected for the user trial of the domestic units were, Napakling, Kehang Inglang, Sarik Teron and Kat Tisso in the Bagpani area.

#### **2.4.5.2 Methods of fluoride removal from groundwater model unit**

A small replica test was done using fluoride containing groundwater collected from selected field trial site in order to pre-assess the performance of the field units. The experiment was designed to resemble as far as possible a traditional household filter used in rural areas (Figure 2.3a). For replica test in laboratory, three 1.0 L LDPE containers were used as mixture, reactor and four-layered, i.e., sand-limestone-sand-gravel filter cum pH corrector (Figure 2.3b). The reactor container was filled with crushed limestone of 1.0-1.5 cm chip size. Groundwater containing  $4.8 \pm 0.2$  mg/L  $[F^-]_0$  was acidified with optimized  $[PA]_0$  in the mixture container and added to reactor containing crushed limestone of 1.0-1.5 cm chip size for a residence time of 3 h. After 3 h, the treated water was filtered through a four layered sand-limestone-sand-gravel filter to adjust the pH up to the level for drinking purpose. The water was allowed to remain in the four-layered

filter for a residence time of 1 h. The water collected after four layered filter was used for the measurement of residual  $[F^-]$  and pH.



**Figure 2.3.** A schematic diagram of replica unit (a) and a real picture of a replica unit (b).

#### ***2.4.5.3 Dose optimization and pre-assessment of performance***

The small replica of the field units was also used PA-dose optimization and for pre-assessment of the performance of the field units using feed water collected from the field source of the small community unit. This piped groundwater with varying fluoride concentration between  $4.8 \pm 0.2$  mg/L during the year has been being supplied by government Public Health Engineering Department (PHED) for years. Three 1.0 L low-density polyethylene containers were used to make the replica: as mixer, reactor and four-layered filter cum pH corrector (Figure 2.3b). The container was filled with crushed limestone of 1.0-1.5 cm chip size.

#### ***2.4.5.4 Regeneration and disposal of used limestone***


Regeneration of exhausted limestone in replica test was done by simple scrubbing and rinsing with fluoride free water and by soaking in 0.30 M lime solution for 24 h followed by rinsing with fluoride free water. The regenerated limestone was used for further PACLT to see the activity towards fluoride removal. The author did not use any drying process on regenerated limestone for further PACLT experiments.

#### **2.4.5.5. TCLP test**


The solid sludge obtained in the PACLT in replica test was analyzed by TCLP test to check the leaching behaviour of fluoride.

#### **2.4.5.6 User training and demonstration**

During the field study the author faced some problems mainly due to the lack of awareness of people about fluoride contamination and toxicity. Therefore, the author made some attempts for creating awareness about fluoride contamination and the importance of fluoride removal from drinking water among the affected rural people. The author demonstrated the method to the villagers and taught them how to use the method. The author also trained them to set up the units for removal of fluoride from groundwater at household and small community level. The author has also supplied one page instruction manual and poster to the users describing the ill effects of fluoride and the procedure of the *Fluoride Nilogon* method in details in English, Assamese and Karbi (local) languages (Figure 2.4.-2.9).



## ☺ Fluoride Nilogon ☺




**What is Fluoride?**  
 Fluoride is an invisible chemical contaminant of drinking water. A small amount of fluoride is good for health. But excess fluoride of drinking water causes various health problems including damage of tooth and bone.

**What is Fluoride Nilogon?**  
 Fluoride Nilogon is a simple, efficient and low-cost method of removing excess fluoride from water. In this method, crushed limestone is used along with a very small amount of a solution of a weak acid called phosphoric acid. Please note that the use of phosphoric acid in water purification is safe. Phosphoric acid is used in packaged food and soft drinks like Pepsi. The Fluoride Nilogon method has been developed by a research group lead by professor Dr. Robin Kumar Dutta in the Department of Chemical Sciences, Tezpur University.

Fluoride Nilogon removes the excess fluoride retaining only a small amount of fluoride (0.7 ppm) required for good health. The treated water does not contain any residual chemical added from outside. Its pH is about 7.5 which is very safe for drinking. However, the treated water should be consumed only after boiling.

**The Procedure for Fluoride Nilogon:**  
 Please see the picture and follow the instructions as given below:

1. Make sure that the tap of the upper crushed-limestone container is closed.
2. Take 15 liter water in a bucket.
3. Add 7 ml of the dilute phosphoric acid solution to it and mix.
4. Then, pour this water into the upper crushed limestone container and leave it for at least 3 hours.  
*(There is no harm if you leave it like that for longer time even for a day. Fluoride is removed here along with neutralization of the acid.)*
5. After 3 hours, open the upper tap of the upper container to allow the water to go to the lower container which is a specially designed four-layered sand-limestone-sand-gravel filter. *(This filter ensures neutralization of the acid in addition to purifying the water. It can also store some water.)*
6. Now you can collect fluoride-free water from the lap of the filter.



**Precautions to be taken:**  
 The solution used in the method is a dilute solution (8.5%) of an acid even though it is a weak acid. Please handle and keep it carefully. Keep it away from children. Wash with water in case of its contact with hand, skin or eye.

*For more information on Fluoride Nilogon and in case of facing any difficulty in using the method, you may contact:*

*Dr. Robin Kumar Dutta - 9435006674*  
*Ms. Sweety Gogoi - 9954490668,*  
*Department of Chemical sciences, Tezpur University, Tezpur -784028;*






\*\*\*


Figure 2.4. Instruction manual that the author supplied to users in English language.




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**ফ্লাইডনো কি?**

ফ্লাইড এবিধ ভূজলৰ অদূষক। সামান্য পৰিমাণৰ ফ্লাইড সুস্বাদুৰ বাবে দৰকাৰী যদিও খোৱাপানীৰ অত্যাধিক ফ্লাইডে মানুহৰ হাঁড় আৰু দাঁত বেয়া কৰাকে ধৰি বিভিন্ন ধৰণে স্বাস্থ্য হানি কৰে।

**ফ্লাইড নিলগননো কি?**

ফ্লাইড নিলগন হৈছে পানীত থকা অত্যাধিক ফ্লাইড গুচুৱা এটা অতি সক্ষম, সহজ আৰু কম খৰচী উপায়। এই পদ্ধতিত সৰুকৈ ভঙা চূপশিলৰ টুকুৰা আৰু সামান্য পৰিমাণে ফছফ'ৰিক এচিড নামৰ এবিধ দুৰ্বল অম্লৰ পনীয়া দ্ৰৱ ব্যৱহাৰ কৰা হয়। উল্লেখনীয় যে পানী পৰিশোধনত ফছফ'ৰিক এচিড ব্যৱহাৰ কৰাটো নিৰাপদ। ফছফ'ৰিক এচিড বজাৰৰ পেকেটত পোৱা খাদ্য আৰু পেপচিৰ দৰে পানীয়তো কমকৈ ব্যৱহাৰ হয়। ফ্লাইড নিলগন পদ্ধতিটো অধ্যাপক ড° ৰবিন কুমাৰ দত্তৰ নেতৃত্বত এটি গৱেষকৰ দলে তেজপুৰ বিশ্ববিদ্যালয়ৰ ৰসায়ন বিজ্ঞান বিভাগত উদ্ভাৱন কৰা।

এই ফ্লাইড নিলগন পদ্ধতিৰে পৰিশোধন কৰা পানীখিনিৰ প্ৰয়োজনীয় ফ্লাইডকণহে (প্ৰায় ০.৭ নিয়ুতাংশ বা পিপিএম) ৰাখি বাকীখিনি দূৰ কৰি দিয়া হয়। শেষত পানীখিনিৰ অম্লতা প্ৰায় ৭.৫ থাকে, যিটো খোৱাৰ কাৰণে অতি নিৰাপদ। পানীখিনিৰ বাহিৰৰ পৰা যোগ কৰা কোনো ৰসায়নিক পদাৰ্থ থাকি নাযায়। তথাপি এইদৰে পৰিশোধন কৰা পানী উতলাইহে খোৱাহে উচিত।

**সংক্ষেপে ফ্লাইড নিলগনৰ পদ্ধতিটো:**

কাষৰ চিত্ৰটি চাই লওক আৰু তলত বৰ্ণনা মতে কামটো কৰক।

- ১) ওপৰৰ চূপশিল থকা পাত্ৰটোৰ টেপটো বন্ধ থকাটো নিশ্চিত কৰক।
- ২) এটা বাস্টিত ১৫ লিটাৰ পানী লওক।
- ৩) এতিয়া আঙ্গিক দ্ৰৱটোৰ পৰা ৭ মিলিলিটাৰ লৈ পানী বাস্টিত মিহলাই দিয়ক।
- ৪) তাৰপিছত পানীখিনি চূপশিল থকা পাত্ৰটোত ঢালি দিয়ক আৰু কমেও তিনি ঘণ্টা সময় তেনেকৈয়ে থাকিবলৈ দিয়ক। *(তেনেকৈ বেছি সময়, আনকি এদিন থাকিলেও কোনো কথা নাই। ইয়াতে ফ্লাইড নিলগন হোৱাৰ লগতে পানীখিনিৰ অম্লতাও প্ৰশমিত হয়।)*
- ৫) তিনি ঘণ্টাৰ পাছত, ওপৰৰ পাত্ৰটোৰ টেপটোৰে পানীখিনি বিশেষ ভাৱে নিৰ্মিত বালি-চূপশিল-বালি-শিলৰ চাৰি তৰঙ্গীয়া ফিল্টাৰটোত পৰিবলৈ দিয়ক। *(এই পাত্ৰটোত পানীৰ বিশুদ্ধিকৰণ হোৱাৰ উপৰিও পানীৰ অম্লতা প্ৰশমণ নিশ্চিত হয়। পাত্ৰটোত অল্প পৰিমাণৰ পানী জমা কৰিও ৰাখিব পৰা যায়। মন কৰিব যাতে পাত্ৰটোৰ পৰা পানী ওপৰেদি বাগৰি নাযায়।)*
- ৬) এতিয়া তলত থকা বালি-চূপশিল-বালি-শিলৰ পাত্ৰটোৰ পৰা টেপটোৰে ফ্লাইড মুক্ত পানী সংগ্ৰহ কৰিব পাৰে।

**ল'বলগীয়া বিশেষ সাৱধানতা:**


আপুনি ব্যৱহাৰ কৰা দ্ৰৱটো দুৰ্বল অম্ল ফছফ'ৰিক এচিডৰ (৮.৫%) পনীয়া আঙ্গিক দ্ৰৱ। এইটোৰ ব্যৱহাৰ আৰু সংৰক্ষণ সাৱধাননেৰে কৰিব। এইটো সৰু ল'ৰা-ছোৱালীৰ পৰা আঁতৰাই ৰাখাটো জৰুৰী। কেনেকাকৈ হাতত, চকুত বা ছালত পৰিলে লগে লগে পানীৰে ধুই পেলাব।

*ফ্লাইড নিলগনৰ বিষয়ে যিকোনো কথা জানিবৰ বাবে বা এই পদ্ধতিৰে পানীৰ পৰা ফ্লাইড নিলগন কৰোতে কিবা অসুবিধা পালে তলৰ ঠিকনাত যোগাযোগ কৰক:*


ড° ৰবিন কুমাৰ দত্ত - ৯৪৩৫০০৬৬৭৪  
প্ৰীমতী চুইচ গ'প - ৯৯৪৪৯০৬৬৮  
ৰসায়ন বিজ্ঞান বিভাগ, তেজপুৰ বিশ্ববিদ্যালয়, মগাম, তেজপুৰ, অসম।

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Figure 2.5. Instruction manual that the author supplied to the village people in local language, Assamese.



## ☺ Fluoride Nilogon ☺



**Fluoride Kopilo?**

Fluoride ke eisi a-mek pen theklongle alang along aketer a chemical lo. A sap-o a fluoride ke a-ok a-prang aphan ke meseng. Chetame ongdung a fluoride kejun alang alongke a-ok a-prang aphan me-me, a-so mate a-repi aphan meme.

**Fluoride Nilogon Kopilo?**


Fluoride Nilogon esi joike lapen ador kekom abidi lo . A-ke ongdung a fluoride lang pen kepakak aphanlo. Laso abidi along sainsi aduk lapen a sap-o phosphoric acid jokdung nangji. Phosphoric acid ke kejun alang aphan me-o. Phosphoric acid ke a-hom arlo kecho lapen lang kangsam kejun along ta pidun- Pepsi ason. Fluoride Nilogon abidi ke esi a research group keja pon abang ke Dr. Robin Kumar Dutta, enut a professor ,Department of Chemical Sciences, Tezpur University.

Fluoride Nilogon ke ongdung a fluoride lang pen kepakak aphanlo .Pipotma a-ok, a-prang aphanke (0.7 ppm) a fluoride anta chok. Kapachithingtang alang ke hon pen thang aketear ta avelo. 7.5 pH ke kejun alang aphan me-o lo. Sitame lang paso det aphi si kechithingtang alangta jun nangji.

**Fluoride Nilogon abidi ke lapuhanlo:**

Laso a picture langra abidi klem eknoi

- 1) Angson sainsi aduk a container a tap abang ke bongchet nangji.
- 2) 15 liter alang bucket along ang nangji
- 3) Laso alang along 7ml phosphoric acid jok si pangvoi nangji
- 4) Lapen laso ke pangvoitang alang ke angson sainsi aduk a container along chor si 3 khonta an binangji. *(Bongsitame ajirkeding aphan le bita thangta henoneh. Acid aphan kapalam kapali aphanngsi fluoride enponlo)*
- 5) Khonta kethom aphi , angson a-tap a container inpu se a room a container along lang pali nangji .Laso a room alang a container along indeng phli a filter lang kechithing aphan bi lake sangti-sainsi-sangti lapen arlongso si kebi. *(Laso a filter ke acid aphan kepalam kapali lapen lang kechithing ta me. labangso a filter ke lang ta chopangpeng me.)*
- 6) Nonke fluoride a-vepin alang filter a tap pen an melo.





**Kechere nangsok nangji ke lahenlo je:**

*Laso ke pangvoi tang alang along (8.5%) a acid do. Lasi elitum cherepeme nangji. Osomar pen heloving se bi nangji. A-mek along mate a-reng along nang chedat lote lang pen chechamvek nangji.*

**Jongsi an sose abirta Fluoride Nilogon aputhak nangji pulote .Mate pineh akesung do pulote laso amonet aphan ariu eknoi:**

Dr. Robin Kumar Dutta- 9435006674  
Ms. Sweety Gogoi, - 9954490668  
Department of Chemical sciences, Tezpur University, Tezpur –784028.


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**Figure 2.6.** Instruction manual that the author supplied to the village people of Karbi Anglang in their local language, Karbi.





**FLUORIDE NILOGON**  
**PACLT pen**  
(Phosphoric Acid-Crushed Limestone Treatment)

**Fluoride ke Kopilo?**  
 ◊ Arlo alang along ke fluoride do-a.  
 ◊ Fluoride arlo alang along pen kepakat sung-a.  
 ◊ Fluoride ojainsi a-ok a-pran aketora detek se do:  
**DENTAL FLUOROSIS** lapen **SKELITAL FLUOROSIS**.

**Fluoride alang kejun pen akeso kelong meme ke**  
 ◊ 1-3ppm (mg/L)- kote Dental fluorosis (aso kear) akeso anthek.  
 ◊ 4-10ppm late- skelital fluorosis (aripi akeso) akeso anthek doji.  
 ◊ 10ppm pen akeong late akeng akeso,esi akeso, akenghu akeso, avag akeso akeso lapen jasemetpet puloto keche-akeso akeso mandeji.

**Arlo alang along fluoride ake-onkdunk si do**  
 Langroi, pukhuri, ring alang lapen arve alang alongke fluoride ave  
 Elitum kejun alang alongke Fluoride 1ppm pen arum si do nangji. Dongkol alang along fluoride doma avensa asat langnangji.

**Thihek pen PACLT abidi ke lapuhanlo.**  
 Fluoride kedo alang. Saini pankjr nangji. Filter. Lang kama.  
**A community Fluoride Nilogon Unit** **A Domestic Fluoride Nilogon unit**

**Fluoride alang kejun pen akeso kelong meme ke**  
 Hydroxyapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ] Fluoroapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ]  
 A-so pen A-tipi ke Hydroxyapatite pen si kema.

**Fluoride ki pame un-a bonseta chere ke un!**  
 Fluoride do-o alangke jun nangne, chotun-chodunk-e nangne lapen ink-lo checheruk-e nangne.

**Pisi klem unjima?**  
 Thihi (ingri ak-e-k koro) Anti-oxidant Vitamin C Chulung Akarhor adheene e-g, jame ng theso kholok.

**Fluoride ki pame un-a bonseta chere ke un!**  
 Fluoride do-o alangke jun nangne, chotun-chodunk-e nangne lapen ink-lo checheruk-e nangne.

**PACLT abidi ke Tezpur University along**  
 Dr. Robin K. Dutta, Dr. Suresh K. Nath lapen Ms. Sweetsy Gogoi alonglitum se kepaklang chenglo.

**Hem anut aphan fluoride akeso pen pejok nangji!**  
 Ansoe chini ji aphan, contact: Dr. Robin K. Dutta (9435006674) or Ms. Sweetsy Gogoi (9954490668) Dept. of Chemical Sciences, Tezpur University

**Abidi ke:**  
 Bidi 1. Thik-vet pen PA lang along pangvui dun nangji  
 Bidi 2. Laso alang saini kepankjr tang along pangvui dun nangji. Laso alang 3 khonta bak bi nangji.  
 Bidi 3. 3 khonta pen ake-onkdunk le bi ta chot  
 Step 4. Ladetpen sangti pen saini a filter mate lang kepankpat along pangvui dun nangji.

**Laso alang kechahiti ahut kechere nangsof ke.:**  
 Phosphoric acid ke-ot ahut chere nangji pipotma a-reng ink-thak det ta thek. Osomar aphan pe-ot longie det nangji.

**Pipotsi sainsi lo?**  
 ◊ Pipotma saini ke fluoride pekat un.  
 ◊ Nahokta longlok ahormu. Ador kekom.  
 ◊ Ador kekom.

**Pipotsi Phosphoric acid (PA) lo?**  
 ◊ PA pen saini fluoride pachiti un.  
 ◊ Hydroxyapatite semar nangji pipotma hydroxyapatite ke fluoride inkcip un.  
 ◊ Hydroxyapatite kecho pen mesen.  
 ◊ Kalketa chover ahormu asone chota chok.  
 ◊ Salt dihal-coca cola lapen pepsi  
 ◊ USE PA arunta lang keme kechahiti aphanlo para chekroi dunlo.

**◊ 0.7 ppm fluoride alang ke jun un.**  
**◊ 6.5-7.0 kechahitang tang pH alang ke jun un**

**Figure 2.9.** The poster that the author provided to the users of Karbi Anglang in their local language, Karbi.

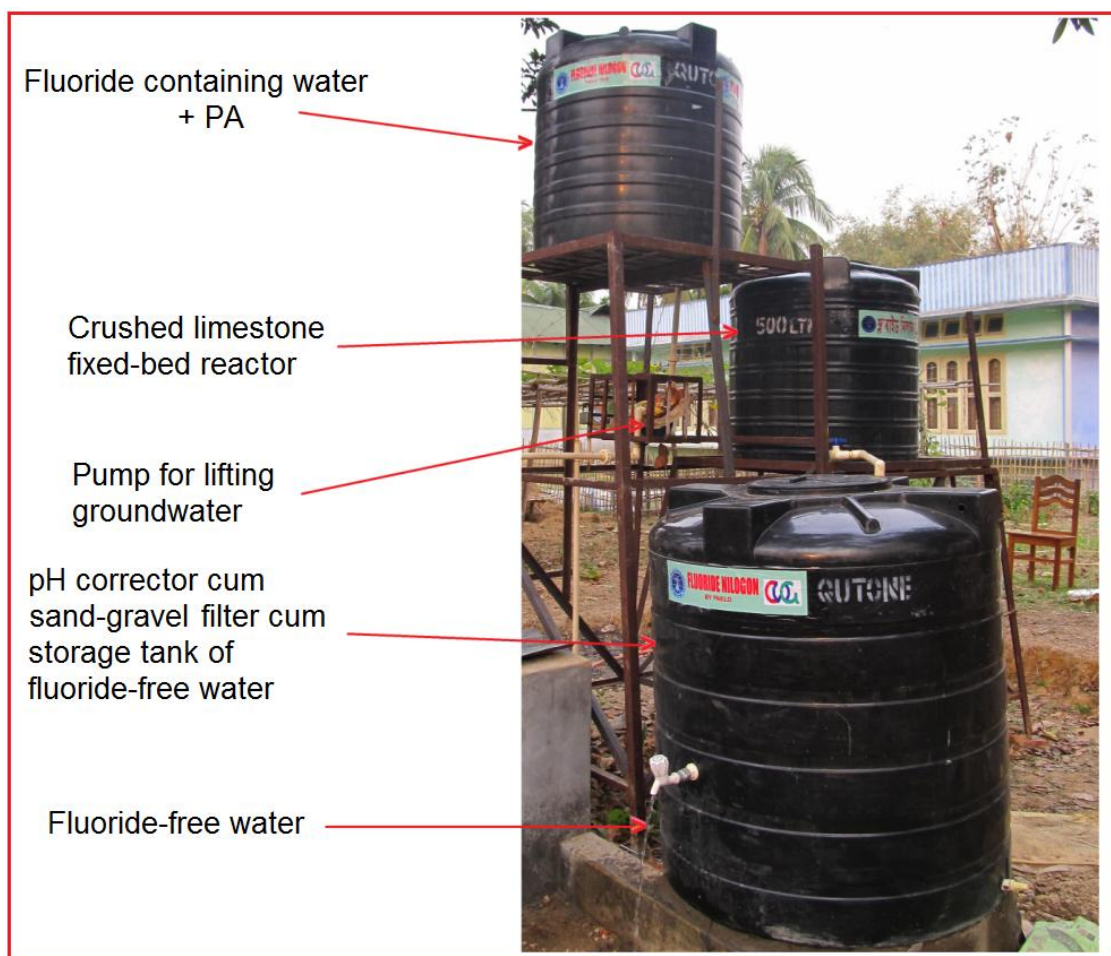
#### 2.4.5.7 Design and fabrication of Fluoride Nilogon systems of different capacities

##### (A) A small community system:

The author, at first, selected a village, viz., Dengaon in Karbi Anglang district of Assam to carry out a small community system user trial. The people in this village are used fluoride contaminated water of  $4.8 \pm 0.2$  mg/L fluoride supplied by public health water scheme. In the small community system, installed on 16 March 2013, two 500 L and one 1000 L plastic tank was used. The first tank was used to collect fluoride contaminated water supplied by the local public health water supply scheme and for mixing PA before feeding the reactor containing crushed limestone bed. The second tank, i.e., reactor was filled with crushed limestone of 0.2-2.0 cm chip size gave a void volume of 220 L. A 1000 L plastic tank was used as a four layered filter cum pH corrector (Figure 2.10). Fluoride containing field water, after mixing with dilute PA, was fed to the reactor and kept for a residence time of 3 h. After 3 h, the water was transferred to the filter. The first time treated water occupied the void volume of the filter cum pH corrector and filtered water could be collected only from the second time treatment onwards. This allowed



enough residence time of at least 6 h to the treated water to finally come to a pH of around 7.80.



**Figure 2.10.** A picture of a *Fluoride Nilogon* plant installed on 16<sup>th</sup> March, 2013, at Dengaon, a fluoride-affected place in Karbi Anglong district of Assam, India.

### (B) Household systems:

In the next step, the author has carried out the *Fluoride Nilogon* user trial in five household systems in which groundwater contains fluoride level within the range of 2.8-20 mg/L. The author selected four villages viz., Napakling, Kehang Inlang, Sarik Teron and Kat Tisso villages in Bagpani area of Karbi Anglong district. For a household system, a 40 L capacity bucket was used as a treatment chamber in which crushed limestone was packed through which the author can obtain 15 L void volume. About 2 inches below the container, another 40 L capacity bucket was placed. This bucket was typically made with four layered, i.e., sand-limestone-sand-gravel layer which worked as a pH corrector along with filtration. The household unit H1 was installed at 12 October

2014 and units H2, H3, H4 were installed on 6 December 2014. The household unit H5 was installed by a local villager trained by us at Tezpur University on 15 October 2015. The domestic units have been shown in Figure 2.11.



**Figure 2.11.** Photographs of *Fluoride Nilogon* plant in five household systems at (H1) Napakling, (H2) Kehang Inlang and (H3) Sarik Teron and (H4) Kat Tisso villages installed by us and at (H5) Napakling household unit installed by a villager in Karbi Anglong district, Assam.

#### **2.4.5.8 Monitoring of user trial**

The author supplied PA to the users after 10 times dilution of 85% W/V PA with distilled water. The author also supplied plastic sample bottles to collect the water samples after each treatment. Filtered water samples were collected from community system and households and were analyzed for residual  $[F^-]$ , pH and other relevant water quality parameters.

