A KINETIC MODEL FOR FLUORIDE UPTAKE IN A LOW COST DOMESTIC DEFLUORIDATOR USED IN RURAL WATER SUPPLY

by

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Abstract:

Several defluoridation methods have been known to remove the excess of fluoride in drinking water to avoid endemic fluorosis. Some of these methods are not suitable for rural communities in regions where the groundwater is fluoride rich, as they are not sustainable in those socio-economic conditions. A low -cost domestic defluoridator was developed by the National Water Supply and Drainage Board of Sri Lanka and was tested in several villages in the Dry Zone using over one thousand domestic units. Broken pieces of freshly burnt bricks or laterite were used as filter media in these units. A kinetic model for fluoride uptake in the filter with broken bricks as defluoridating agent, was considered and the model parameters were estimated using experimental data. This model was extended for simulating the filter behaviour under the real conditions in a rural set-up. This model is used to predict the fluoride concentration of the effluent for given seasonal variation of fluoride concentration in groundwater used as the influent. This extended model was applied to two filters, one having freshly burnt broken bricks as the filter medium and the other having laterite as the same and the model performance was found to be satisfactory in comparison with observed field data. Thus the proposed extended model is an useful tool in the design and operation of low cost defluoridators.

1. Introduction

1.1 Fluoride in Groundwater:

Environmental fluoride has received much attention on account of the fact that an optimum concentration was found to reduce the incidence of dental caries. Low levels of fluorides are required for humans as it has beneficial effects on tooth and bone structures. However ingestion of excessive fluorides, mainly through drinking water, causes, dental and skeletal fluorosis, (WHO 1970). The chronic toxicity by excessive fluoride intake has long been observed as skeletal abnormalities. The most common manifestation of the toxicity of fluoride in drinking water is dental fluorosis. Long term ingestion of excessive fluoride has a chronic effect on the kidneys as well. The optimal level suggested by the WHO, (1990) is 0.7 mg/l from infancy to 16 years. Studies done in Sri Lanka recommend 0.8 mg/l for Sri Lanka (Warnakulasuriya et al. 1990).

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Fluorosis is related to the geology and climatic conditions of the place and the levels of fluoride. There is a distinctly geographical pattern in the incidence of fluorosis in Sri Lanka.

The fluoride rich and fluoride poor areas have been demarcated and are closely linked with climate and geology. Geochemical surveys on the fluoride content of grounwater in Sri Lanka reveals that in the Dry Zone areas in Polonnaruwa and Anuradhapura in the North-Central Province, Uda-Walawe and Wellawaya in the Southern Province and in Maho have high fluoride content, (Dissanayake 1979). High fluorides are in the plains especially in the Dry Zone, while the low fluoride areas are in the central highlands and in the western plains where the rainfall is high. With the rainfall, fluoride is leached from rocks and soils and carried away in solution whereas in the Dry Zone, evaporation causes upward capillary action of fluoride ions. The fluoride content of water obtained from lakes, artesian wells and rivers is mostly below 0.5 mg/l.

1.2 Prevension of Fluorosis:

Dental fluorosis is irreversible and therefore treatment is sophiticated and expensive. Thus the prevention of fluorosis is the best and only form of treatment in Sri

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Lanka. Excessive fluoride content in water can be reduced to a desired limit by precipitation and absorption. The absorption method involves the contact of the fluoride containing water with a suitable absorbent. Various substances such as activated carbon, activated alumina, activated bauxite, zeolite, hydroxyapatite, etc., have been used for fluoride removal from water, (Choi et al. 1979). Ion-exchange, absorption and precipitation are the usual means of defluoridation. However, most of the available materials for defluoridation are expensive and technically non-feasible in rural communities in Sri Lanka. Hence the need to find locally available defluoridation media for safe and easy use at both household and small community levels is desirable. The National Water Supply and Drainage Board has distributed low cost defluoridators among people in the affected areas. Easily available, laterite and freshly burnt bricks broken into pieces have been used as filter medium. The upward flow technique has been used to get more retention time. The performance of the sampled filters has been monitored at regular intervals to see how well they are functioning. It was observed that at certain sites the desired effluent qualities were not obtained. In this study, various factors affecting the filter media is looked into. Fluoride uptake in broken bricks as a filter medium was modelled from experimental data. This kinetic model was extended for usage in a rural set-up where filter performance could be simulated considering seasonal variation of fluoride concentration of well water. Thus, it is envisaged to determine the suitability of the extended kinetic model for prediction of the performance of defluoridators under conditions that are prevalent in a rural set-up.

2.0 Model Description

2.1 Review of models developed:

There have been various attempts to establish a mathematical model to describe the fluoride uptake in a defluoridating agent in the past few decades. Initially, let us consider the following three models from research studies done on various defluoridating materials.

- *Larsen*, (1974), using dental enamel and *Bhargava et al*, (1991), using bone char, described the uptake as a simple first order process kinetics with respect to fluoride concentration in water(*S*) as described by :

$$\frac{dS}{dt} = -k_1.S \qquad (1)$$

- *Christoffersen et al.*, (1984), described the uptake as first order with respect to the fluoride concentration in water and with respect to the fluoride saturation deficit (f_{mb} - f) in the defluoridating agent namely, Synthetic Hydroxy Apatite (Hap) as given by:

$$\frac{dS}{dt} = -k_1.X_{DA}.(f_{mb} - f)S - k_2.X_{DA}.f \qquad (2)$$

- *Stumm*, (1992), used a semi-infinite linear diffusion model to describe diffusion limited sorption in porous media in general, where the uptake is proportional to the concentration of fluoride in water and dosage of defluoridating agent and also the reciprocal of the square root of contact time as described by :

$$\frac{dS}{dt} = -kX_{DA}.S.t^{-0.5} \qquad (3)$$

These tested models fit some of the data collected, but none of them seem to fit in general, for all the different experimental conditions. Therefore the development of a general model to describe the change in fluoride concentration in water in batch as a function of time by means of an explicit mathematical equation was envisaged by *Bregnhφj et al.* (1995).

2.2 A kinetic model to describe fluoride uptake in batch

Bregnhφj et al. (1995) developed a model to address the situation of treatment of water in fluoride affected areas in developing countries. So the number of experimental variables and rate parameters were to be kept as few as possible and the advanced characteristics of the filter media such as bulk density, grain size, particle spherity etc., were to be avoided. The following differential equation to describe the change of fluoride concentration was thus developed by *Bregnhφj et al* (1995) using a trial and error approach with many different models.

$$\frac{dS}{dt} = -k.X_{DA}.(f_{mb} - f).S.t^{-0.5} \qquad (4)$$

As f is the concentration of fluoride uptaken in the defluoridating agent and f_{mb} is a measure of maximum concentration of possible uptake, (f_{mb} - f) would represent a deficit towards saturation of the defluoridating agent (DA), where X_{DA} is the mass of defluoridating agent per litre of water in the filter. Thus X_{DA} (f_{mb} - f) is the total potential uptake per volume of defluoridating agent. This equation express that the rate of fluoride uptake is first order with respect to the fluoride concentration in water (S), first order with respect to saturation of defluoridating agent X_{DA} (f_{mb} - f), as well as first order with respect to the inverted square root of time $t^{-1/2}$. This model seems to fit various defluoridating media. Assuming that the initial concentration of fluoride in the defluoridating agent is negligible (f=0), f may at any time be given as,

$$f = \frac{(S_0 - S)}{X_{DA}} \qquad (5)$$

By substitution into the equation(4) and integration, the concentration of fluoride in the water is given as a simple function of time,

$$S = \frac{X_{DA}.f_{mb} - S_0}{\left[\dfrac{X_{DA}.f_{mb}.e^{2k.(X_{DA}.f_{mb} - S_0)t^{0.5}}}{S_0} - 1 \right]} \qquad (6)$$

Let β be expressed as:

Then

$$\beta = \frac{X_{DA}.f_{mb}}{S_0}$$

$$S = \frac{S_0(\beta - 1)}{[\beta.e^{2.(\beta-1).S_0.k.t^{0.5}} - 1]}$$

Thus the S-t curve of uptake of fluoride in a defluoridating agent(DA) is characterized by only two parameters β and k., For a given defluoridating agent, these parameters could be determined by an optimization technique (Wijesundara, 1999).

2.3 Extention of the Model to simulate a domestic defluoridator.

In the case of a low-cost defluoridator used in fluoride affected areas, raw water is retained in the filter for considerable time and then withdrawn for drinking and cooking. Initially let us assume that the 16 litres of water in a filter is retained for 24 hours and then withdrawn. After the i-th day, let the fluoride concentration of the raw water(influent) be $S_{0,i}$ and the fluoride concentration of the water withdrawn from the filter at the end of 24 hours be $S_{f,i}$. Assuming that the initial concentration of fluoride in the deflopidating agent in negligible, the flopide concentration (f) in the DA at the end of the first day in given by:

$$f_{f,1} = \frac{(S_{0,1} - S_{f,1})}{X_{DA}} \qquad (7)$$

The fluoride concentration ($f_{f,i}$) in the DA at the end of ith day is given by:

$$f_{f,1} = f_{0,i} + \frac{(S_{0,1} - S_{f,i})}{X_{DA}} \qquad (8)$$

So, during the first day, the fluoride concentration in defluoridating agent $f_{t,1}$ is given by:

$$f_{t,1} = \frac{(S_{0,1} - S_{t,1})}{X_{DA}} \qquad (9)$$

Thus during i-th day, the concentration of fluoride in the DA $f_{t,i}$ is

$$f_{t,i} = f_{0,i} + \frac{(S_{0,i} - S_{t,i})}{X_{DA}} \qquad (10)$$

The deficit towards saturation of the defluoridating agent(DA) at the beginning of the i-th day, denoted by *f,m,i* could be expressed as:

$$f_{m,i} = f_m - f_{0,i} \qquad (11)$$

where f_m is the capacity parameter for fluoride uptaken by the defluoridating agent in mg/g. Thus the kinetic model for the fluoride uptaken during i-th day could be given by:

$$\frac{dS_{t,i}}{dt} = -k.X_{DA}.(f_{m,i} - f_{t,i}).s_{t,i}.t^{-0.5} \qquad (12)$$

where

$$f_{t,i} = \frac{(S_{0,i} - S_{t,i})}{X_{DA}}$$ is the fluoride uptaken during the i-th day

By integrating the equation(12), the concentration of fluoride in water during the i-th day is expressed as:

$$S_{t,i} = \frac{X_{DA}.f_{m,i} - S_{0,i}}{\left[\dfrac{X_{DA}.f_{m,i}.e^{2k.(X_{DA}.f_{m,i} - S_{0,i}).t^{0.5}}}{S_{0,i}} - 1 \right]} \qquad (13)$$

This expression could be written as:

$$S_{t,i} = \frac{S_{0,i}(\beta_i - 1)}{[\beta_i.e^{2.(\beta_i - 1).S_{0,i}.k.t^{0.5}} - 1]} \qquad (14)$$

where

$$\beta_i = \frac{X_{DA}.f_{m,i}}{S_{0,i}} \qquad (15)$$

Once the capacity parameter f_m and the reaction rate parameter *k* are determined for a defluoridating agent, given the fluoride concentration of the influent $S_{0,i}$ the effluent quality could be estimated using the equations, (14,15).

3.0 Application of the kinetic model to low cost defluoridating materials

3.1 The requirements of low-cost defluoridation methods

Simple, inexpensive methods of fluoride removal have been the quest for many years. The general requirements for household defluoridation methods are (i) the required capital investment should be modest and should be affordable by the affected community; (ii) The maintenance cost of the method should be low; (iii) The equipment should be simple in design and the villagers should be able to operate it; and (iv) the metod should be able to reduce the fluoride content to low levels within a day or so and should improve the quality of water in general. Clay, being an indigenous and inexpensive material in the high fluoride regions, the fluoride binding potential of clay and clayware was investigated by several researchers.

3.2 The effect of firing temperature

An important factor in the choice of clayware as the defluoridating agent is its firing temperature. The firing of clays causes a series of physical and chemical changes in the material. Free water in clay is driven off by gently increasing the temperature to about 100 °C. Chemically bound water, namely, water of crystallization, escapes at 400°C to 550°C. Changes in crystalline structure of clay minerals take place about 350°C. Carbonaceous matter in clay is burnt out at at 800°C to 900°C and a fussion of particles takes place making it less porous. Hauge et al, (1994), examined the efficacy of.clay pots and crushed clay pots in removing fluoride from water. In the experiments the fluoride adsorption declined as the firing temperature increased and when heated above 800°C, pots were rendered unfit for defluoridation purposes. The parameters of the kinetic model fitted to the data obtained for crushed clay pots with different firing temperature are shown in Table 1.

in the range of 900°C to 1000°C had very little effect on fluoride removal.

3.3 Defluoridation in a Low-cost Domestic Defluoridator with Broken Bricks of different size.

The typical low-cost domestic defluoridators distributed by the National Water Supply and Drainage Board is shown in Fig.1. Raw water is poured in through the funnel attached to a 25 mm diameter PVC pipe which runs to the bottom compartment. Thus raw water enters the defluoridator through the bottom compartment and moves upward as the water is removed from the the tap at the top. This defluoridator has a capacity of about 16 litres and this quantity of water could be used by a household for cooking and drinking purposes.

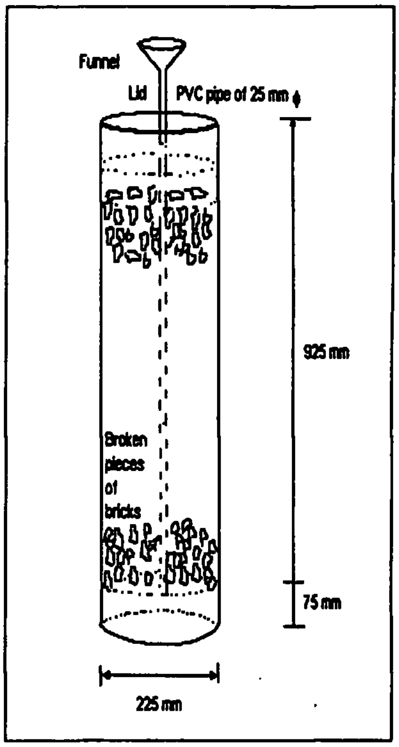


Figure 1: Low-Cost Domestic Defluoridator

Table1 The effect of Temperature on crushed pottery

Fired Temperature°C	500	600	700	800	900
k (l mg^{-1} $h^{-0.5}$)	0.0125	0.011	0.011	0.0037	0.0006
f_m (mg/g)	0.068	0.075	0.043	0.039	0.036

Though f_m decreases by about 50%, the reaction rate parameter k reduces drastically from 0.0125 to 0.0006 beyond 700°C. Thus, from the observation it could be seen that the pottery fired in the range of 500°C to 700 °C has the greatest removal capacity, while clay fired

A series of experiments were conducted by Wijesundera, (1999), using different sizes of broken bricks. Two trials were performed with a batch of raw water brought from a fluoride rich area (Thambuththegama-Dambulla). This water contained fluoride 6-6.5 mg/l and the bricks used were also brought from a fluoride rich area. It was observed that even after a week in the defluoridator, the residual fluoride was above the permissible level of 0.7 mg/l.

The performance of the defluoridator in the final trial with broken bricks of size 12-16 mm, using raw water having fluoride concentration of 2.0 mg/l is shown in Fig. 2. Estimated values of the concentration of fluoride using kinetic model are also shown in the same figure. Here it could be seen that the permissible level is reached by 4 hours of retention. The kinetic model parameters for all these trials are given in Table 2. It is observed that the parametrer B and k are dependent on the initial fluoride concentration. Further better values for β and k were obtained for smaller size of broken bricks as they have a larger contact surface.

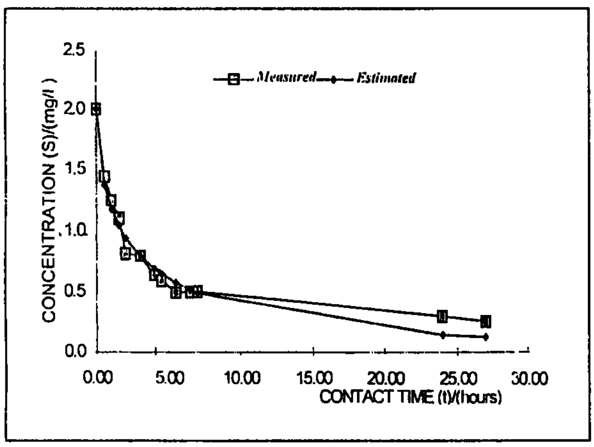


Figure 2: Measured and Estimated Coneentrations of Fluoride

season and low during wet season. Large quantities of low cost domestic defluoridators developed by the National Water Supply and Drainage Board are distributed in fluoride rich areas in Sri Lanka. Fluorine when present in water is colourless and odourless and detection of its presence requires chemical analysis. So the users will not be able to find out easily whether the defluoridators are effectively removing the excess fluoride. The National Water Supply and Drainage Board has deployed a monitoring program where influent and effluent fluoride concentrations are observed every 10 or 15 days on a sample of defluoridators distributed by them. In this study it was attempted to use the extended kinetic model to simulate the behaviour of the domestic defluoridator in the conditions under which it is used to see how well this model simulates the performance of the same. The extended model mentioned in section 2.3 was used to simulate the behaviour of the defluoridator. Two domestic defluoridators distributed by the National Water Supply and Drainage Board were considered, one with broken pieces of bricks and the other with laterite as defluoridating agents. The defluoridator with broken pieces of bricks, used by a family of five at Kithulhitiyawa was considered where measurements of fluoride levels of influent and effluent observed approximately every 15 days for the period from 15 August 1995 to 6 January 1996 were taken. Similarly defluoridator with laterite, used by a family of six at Madatugama was considered where measurements of fluoride levels of influent and effluent observed approximately every 10 days for the period from 11 December1994 to 6 July 1995 were also taken. In both

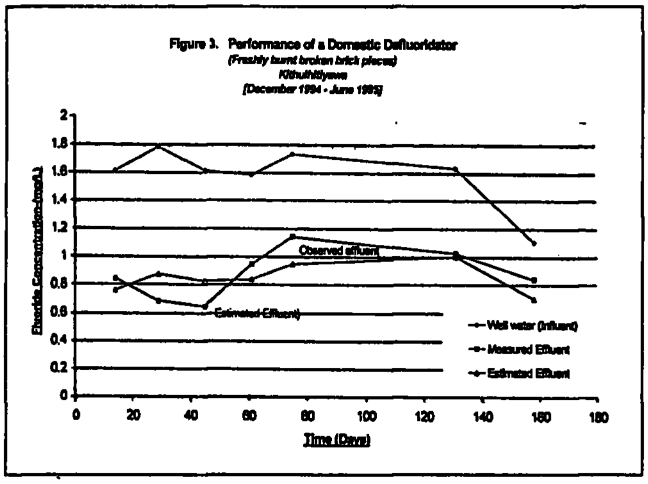
Table 2. Kinetic model parameters for broken brick pieces as defluoridating agent

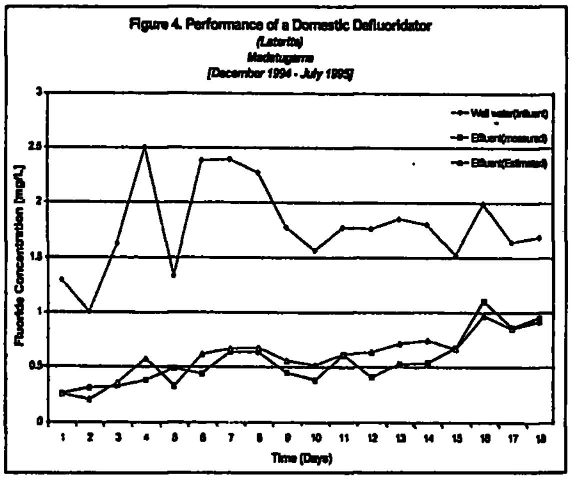
Trial size (mm)	Broke brick So (mg/l)	Initial concentration (g/l)	X_{BP}	β (mg/g)	f_{mb} (l/(mg.$h^{0.5}$))	k
1	12-16	6.20	1593.75	37.23	0.145	0.00067
2	5-8	6.20	1846.23	42.50	0.167	0.00064
3	12-16	2.00	1591.25	81.25	0.102	0.00165

4.0 Simulation of Low-cost Defluoridator using the Extended Kinetic Model

The defluoridators are used in areas where well water contains fluoride above permissible levels. These defluoridators contain about 16 litres of water and it is retained for about 24 hours. It is expected that the fluoride concentration drops below 1.0 mg/l during this retention period. Generally fluoride concentration varies from season to season being rather high during dry

these units it was assumed that the raw water was retained in the defluoridator for nearly 24 hours before it was consumed. Since the concentration of fluoride in the raw water was not observed every day, it was approximated to vary linearly during periods between the observations. With these simplifying but reasonable assumptions the extended model was used for predicting the concentration of fluoride in the effluent. Figures 3 and 4 show the performance of the extended model for these two cases respectively. In both these cases one could observe that the measured value of effluent quality tally with the values predicted by the model, in spite of various constraints and limitations.





5.0 Conclusions

The capacity parameter f_m mainly depend on the quality of bricks, specially the firing temperature of bricks, the optimal range of which is from 500 C to 700 C. The reaction parameter k, which depends on the initial concentration of fluoride (S0) in raw water seems to decrease rapidly as S0 increases from 2.0 mg/l to 6.2 mg/l. Since bricks demonstrate poor fluoride removal quality for raw water containing high concentration of fluoride, they are not suitable as filter medium to achieve the desired level of fluoride in the effluent under these conditions. Although the rate of removal of fluoride is better in smaller sized brick pieces as they have larger surface area for absorption, the water storage capacity decreases in the defluoridator with decrease in porosity. The kinetic model extended to simulate the behaviour of a low cost defluoridator under a rural set-up was proposed and tested. It was assumed that the raw water was retained in the defluoridator for a day before consumption. The predicted quality of the effluent in these defluoridators with these low cost agents such as laterite and freshly burnt broken brick pieces seems to tally reasonably well with the measured data, in spite of the various limitations encountered. Thus the extended kinetic model is a useful tool in the design and operation of low cost defluoridators.

6.0 Acknowledgement

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7.0 References

1. Bhargava, D.S., Killedar D.J.(1991) "Batch studies of water defluoridation using fish bone charcoal", *Research Journal of the Water Pollution Control Federation*, 63, pp 848-858.

2. H Bregnhφj and E Dahi, (1995) "Kinetics of uptake of fluoride on bone char in batch". Proceedings of the First International Workshop on Fluorosis and Defluoridation of Water. The International Society of Fluoride research editorial office, pp 55-83.

3. E Dahi, J J Singano and J M Nielsen,(1995) "Kinetics of defluoridation of water by Calcined Magnesia and clay". Proceedings of the First International Workshop on Fluorosis and Defluoridation of Water. The International Society of Fluoride research editorial office, pp 58-66.

4. Dissanayake, C.B. (1979) "Geochemical provinces and incidences of dental fluorosis in Sri Lanka", *The Science of the Total Environment*, 13, pp47-53.

5. Larsen M J (1974) "In vitro studies of fluoride uptake in human enamel", *Scandinavian Journal of Dental Research*, 82, pp 448-454.

6. Stumm, W (1992), "Chemistry of the solid-water interface", John Wiley & Sons, New York, p 103.

7. Warnakulasuriya, S., Balasuriya, S. Perera, P A J (1990), *Ceylon Medical Journal*, 35, pp 125-128.

8. Wijesundara, TWMLP (1999), " Defluoridation of Water", Undergraduate Project No: C/99/24., Dept. of Civil Engineering , University of Peradeniya.

9. C Zevenbergen , LP Van Reeuwijk, G. Frapporiti, R D Schuiling, "A simple method for defluoridation of drinking water at village level by absorption on Ando soil in Kenya". *The Science of the Total Environment*, 188(1996) pp 225-232.

10. S Hauge, R Osterberg, K Bjorvatn and KA Selvig (1994), "Defluoridation of drinking water with pottery: effect of firing temperature". Department of Chemistry, University of Bergen, Norway., pp 329-333.

11.. I.Rathnayaka (1996), "Fluorosis in the settlement schemes", Proceedings of the Sri Lanka Association for the Advancement of Science, 52(2), pp 27-45.

12. J P Padmasiri (1997), "Low cost defluoridation using broken pieces of bricks as filter media". National Water Supply and Drainage Board. pp 47-55.

Appendix I: Notations.

I. Kinetic Model:

f = Concentration of fluoride uptaken in the Defluoridating Agent(DA)

f_m = Capacity parameter for fluoride uptaken in the Defluoridating Agent (DA)

k = Reaction rate parameter (L mg -1h-0.5)

S = Fluoride concentration in water phase (mg/L)

X_{DA} = Mass of defluoridating agent per litre of water in the filter.

II Extended Kinetic Model used for domestic defluoridators:

$f_{f,i}$ = Fluoride concentration in the defluoridating agent(DA) at the end of i-th day

$f_{m,i}$ = Deficit towards saturation of the DA at the beginning of i-th day

$f_{t,i}$ = Fluoride uptaken in the DA during t hours on the i-th day

$S_{t,i}$ = Fluoride concentration of water in the defluoridator after t hours on the i-th day