Studies on estimation of fluoride and defluoridation of drinking water

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by

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Chapter 1

Introduction

Fluorine, the 13th most abundant element of the earth's crust, represents about 0.3g / kg of earth's crust. It occurs mainly in the form of chemical compounds such as sodium fluoride or hydrogen fluoride, which are present in minerals fluorospar, fluorapatite, topaz and cryolite. The physicochemical properties of fluorides available in the form of sodium fluoride and hydrogen fluoride are given in Table. 1.1. In India, fluorite and topaz are widespread and contain a high percentage of fluoride. Fluoride pollution in the environment occurs through two channels, namely natural and anthropogenic sources (Cengeloglu et al. 2002). Fluoride is frequently encountered in minerals and in geochemical deposits and is generally released into subsoil water sources by slow natural degradation of fluorine contained in rocks.

Fluorine is an important element for human beings, as it helps in growth and prevents the enamel of the teeth from dissolving under acidic conditions. Various dietary components influence the absorption of fluorides from gastrointestinal tract and the absorbed fluorides are distributed throughout the body. Drinking water and sea food are good sources of fluoride.

Fluoride is beneficial to health if the concentration (C_F) of the fluoride ion (F^-) in drinking water is less than 1.5 mg/L (WHO 1994). A higher concentration causes serious health hazards. The disease caused manifests itself in three forms, namely, dental, skeletal, and non-skeletal fluorosis. Dental fluorosis produces widespread brown stains

Table 1.1: Physicochemical properties of common forms of fluoride

Property	Sodium fluoride (NaF)	Hydrogen fluoride (HF)
Physical state	white, crystalline powder	colourless liquid or gas with biting smell
Density (g/cm^3)	2.56	–
Water solubility	42 g/ L at 10 °C	readily soluble below 20 °C
Acidity	–	strong acid in liquid form; weak acid when dissolved in water

on teeth and may cause pitting (Bulusu and Nawlakhe, 1992). Skeletal fluorosis causes crippling and severe pain and stiffness of the backbone and joints (Bulusu and Nawlakhe, 1992).

Even though extensive studies have been conducted, there seems to be no effective cure for these diseases. Therefore, it is desirable to drink water having a fluoride concentration less than certain value. Hence, drinking water with $C_F > 1.5$ mg/L (1 mg / L in India) needs treatment (WHO 1994).

1.1 Fluoride in India

In India, the states of Andhra Pradesh, Bihar, Chattisgarh, Haryana, Karnataka, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh and West Bengal are affected by fluoride contamination in water. This involves about 9000 villages affecting 30 million people (Nawalakhe and Paramasivam, 1993). The fluoride content of the water in some villages is given in Table 1.2.

It must be noted that the problem of excess fluoride in drinking water is of recent origin in most parts. Digging up of shallow aquifers for irrigation has resulted in declining levels of ground water. As a result, deeper aquifers are used, and the water in these aquifers contains a higher level of fluoride (Gupta and Sharma, 1995).

1.2 Present work

The aims of the present work are to (i) to develop a low-cost device for the estimation of fluoride at the field level, and (ii) examine the performance of various adsorbents for defluoridation of water.

Development and performance of the device is discussed in chapters 2 – 4 and defluoridation studies are discussed in chapter 5. The results are summarized in chapter 6, which also suggests topics for future work.

Table 1.2: Concentration of fluoride in water (C_F) at different locations in India

Village	C_F (mg / L)	Reference
Sheshpur(Gujarat)	6.2	Bulusu &Nawalakhe, 1992
Fazilpur (Haryana)	2.5	Bulusu &Nawalakhe, 1992
Bellary (Karnataka)	4.25	Central ground water board, 1997
Jato wali dhani (Rajasthan)	7.2	Public health engineering Rajasthan,1997

Chapter 2

Estimation of fluoride

Some of the common methods of estimation of fluorides are discussed below:

2.1 Titrimetry

A titrant usually containing a rare earth metal, such as thorium, is added to the solution containing fluoride. The fluoride ions are allowed to react with the titrant and then the solution is treated with an indicator dye, such as Alizarin Red S or SPADNS. A colour change which occurs when excess thorium reacts with indicator dye, is detected either visually or by using instrumentation techniques (Jacobson and Weinstein, 1977). The pH and the composition of the solution must be carefully controlled and interference of other substances is avoided by prior separation. It is an accurate method, but is tedious. Further, the results are highly dependent on the skills and experience of the analyst.

2.2 Potentiometric Methods

Fluoride in drinking water can be easily estimated by direct potentiometric analysis using fluoride ion selective electrodes (Jacobson et al. 1977). The single crystal lanthanum electrode was introduced by Frant and Ross (1968), and it has provided a reliable method for measuring the fluoride activity (Snell and Ettre, 1971). The sensor used is a single crystal of lanthanum fluoride which has been doped with 0.5 – 1.0 % europium (II) and is fixed at the bottom of a cylindrical glass tube which houses the reference electrode and the reference solution. The reference solution is usually 0.001M sodium fluoride in 0.1M potassium chloride, and it fills the fluoride electrode. Silver – silver chloride electrode as the reference electrode anddips into this solution to provide contact. The electrode can be used to measure the activity or the concentration of the fluoride present in water by the use of an appropriate calibration curve. The electrode does not respond to bound or complexed fluoride. To overcome this, a buffer solution of high ionic strength must be added to it, so that the fluoride ions bound to complex molecules are liberated.

When the concentration of fluoride present in the solution is low (less than 15 mg/L), direct potentiometric methods can be used. This method is less susceptible to interferences from other metals than titrimetry and spectrophotometry. Hence tedious preliminary techniques like crushing and interfering ion separation can be avoided in this case.

2.3 Spectrophotometric methods

In this method, a compound of a metal such as aluminium, iron, thorium, zirconium, lanthanum or cerium reacts with an indicator dye to form a complex of low dissociation constant. This complex reacts with fluoride to give a new complex (Jacobson et al. 1977). Due to the change in the structure of the complex, the absorption spectrum also shifts relative to the spectrum for the fluoride-free reagent solutions. This change can be detected by using a spectrophotometer.

One of the important dyes used is trisodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6- napthalene disulfonate, commonly known as SPADNS . Erichrome Cyanine R is another commonly used dye. The dye reacts with metal ions to give a coloured complex. In the SPADNS method, zirconium reacts with SPADNS to form a red coloured complex. Fluoride bleaches the red colour of the complex and hence the change in absorbance can be measured using a spectrophotometer.

2.4 Selection of the method

Though there are many methods available for the estimation of fluoride, our aim is to develop an inexpensive and portable device, which can be used to estimate fluoride at the field level. The methods described in the above sections require sophisticated instruments, and hence are expensive. Apart from this, if we want the device to work at the field level, it should be small in size. We use the SPADNS method, as it does not involve sophisticated instruments and expensive chemicals. Interference from other ions such as aluminium, iron, hexametaphosphate and orthophosphate which are commonly found in raw water samples, is less for the SPADNS method compared to other methods such as the Cerium (III)- alizarin complexone method. Hence the former method is chosen for estimation of fluoride in drinking water. It requires either a spectrophotometer or a colorimeter to make the estimation. Hence our aim is to develop a simple and inexpensive colorimeter, which can give fairly accurate results. Sen et al. (1998) have developed such a colorimeter. It is shown here that a modification of the circuit used gives better results.

Chapter 3

Development of a device for estimation of fluoride

The device is a low cost colorimeter, which detects the change in the fluoride concentration of a solution depending upon the change in colour of the solution. The method is based on the principle of colorimetry

When light falls on a coloured system, a part of the light will be absorbed and reflected by it and the rest is transmitted. We choose a coloured chemical system whose colour changes when water containing fluoride comes in contact with it. The intensity of the transmitted light depends on the colour of the solution and hence the amount of fluoride present in the solution. The intensity can be measured using a detector and can be correlated with concentration of fluoride ions in the solution (C_F). When the intensity of the transmitted light changes, the signal from the detector changes accordingly, and this in turn changes the output voltage. This change in voltage is measured and is correlated with C_F.

3.1 Previous work

A colorimeter for measuring fluoride concentration in water was developed by Sen et al. (1998). The circuit diagram is given in Figure 3.1. The colorimeter consists of a sample holder of square cross section, a light source (LED), a detector (phototransistor) and associated electronics. The sample holder is made of M – Seal and is placed inside an opaque plastic box along with the electronic circuit and 9V battery. An aluminium lid covers the box. The LED and the photo detector are placed in opposite faces of the sample holder (Fig. 3.2). Light from the LED is incident on the sample holder containing the solution and a part of it is absorbed. The rest of the light is transmitted and falls on the phototransistor, which is located on the other side of the cuvette. The phototransistor converts the incident light to a measurable quantity (voltage). The output of the phototransistor is then amplified using a non–inverting operational amplifier, and measured using a digital multimeter connected to the device through jacks.

3.2 Present work

The device developed by Sen et al. (1998) did not function as reported. The calibration curve reported by Sen et al. (1998) could not be reproduced. A replica of the device made by Sen et al. (1998) was assembled, but the calibration curve obtained from it had too much scatter. Hence Professor Gunasekaran was contacted. He suggested a modified circuit, which was used in the present work.

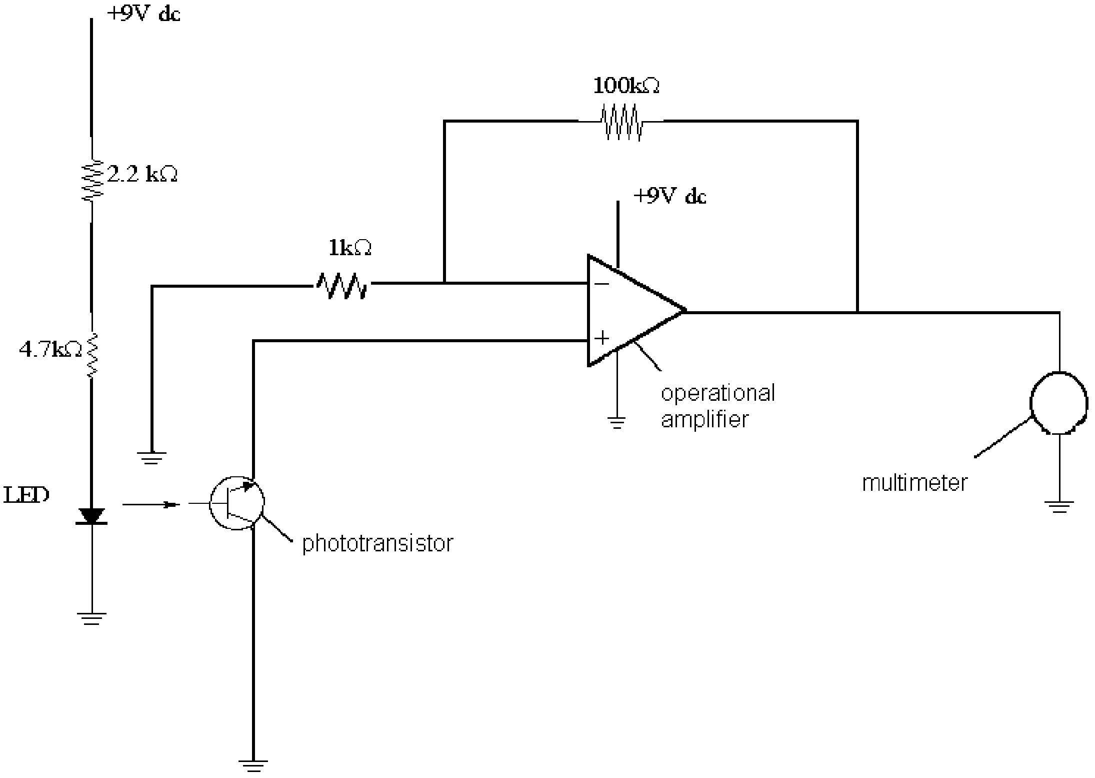

Figure 3.1: Circuit diagram of the fluoride colorimeter developed by Sen et al. (1998)

3.2.1 Design of the colorimeter

The circuit diagram of the device is shown in Figure 3.3. The circuit was designed by Gunasekharan (private communication, 2003). The fluoride containing coloured solution is placed in between the LED and phototransistor. Light from the LED passes through the solution and falls on the phototransistor which generates a voltage across its terminals. The output voltage of the phototransistor is quite small in magnitude and hence is amplified by a non-inverting amplifier. The output is taken across the operational amplifier output and a reference ground. As the operational amplifier is being operated by a single power supply a reference ground has to be created above ground. The reference voltage is generated by a 2.5 V Zener diode connected to a 9 V battery. Capacitive coupling is essential to prevent the output and the input voltage levels from equalling the reference voltage.

The cost estimate of the box is given in Table 3.1. The cost of a plastic cuvette is not included in the estimation.

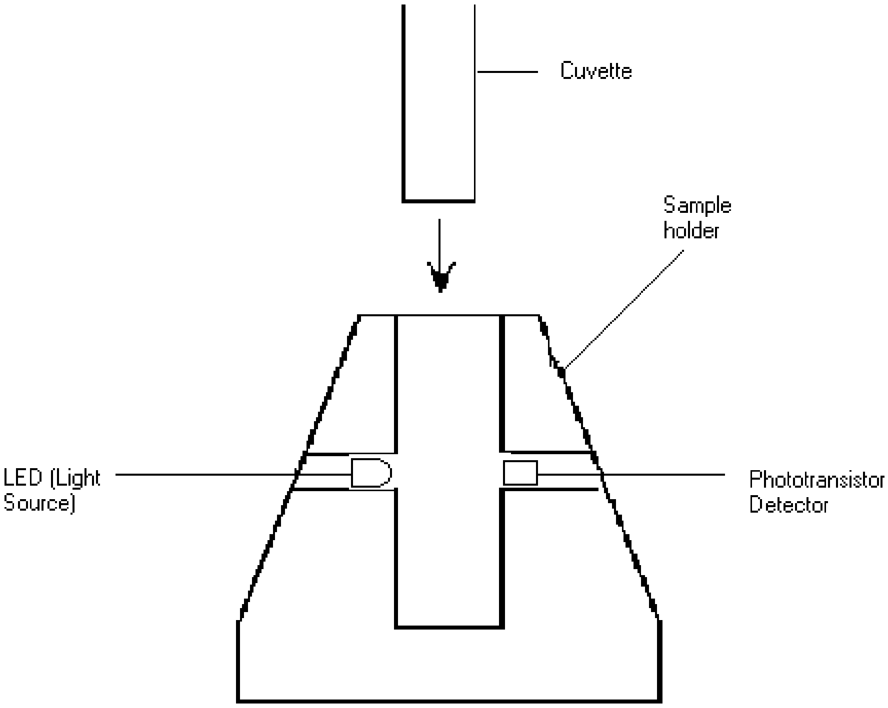

Figure 3.2: Cross section of a cuvette stand (sample holder)

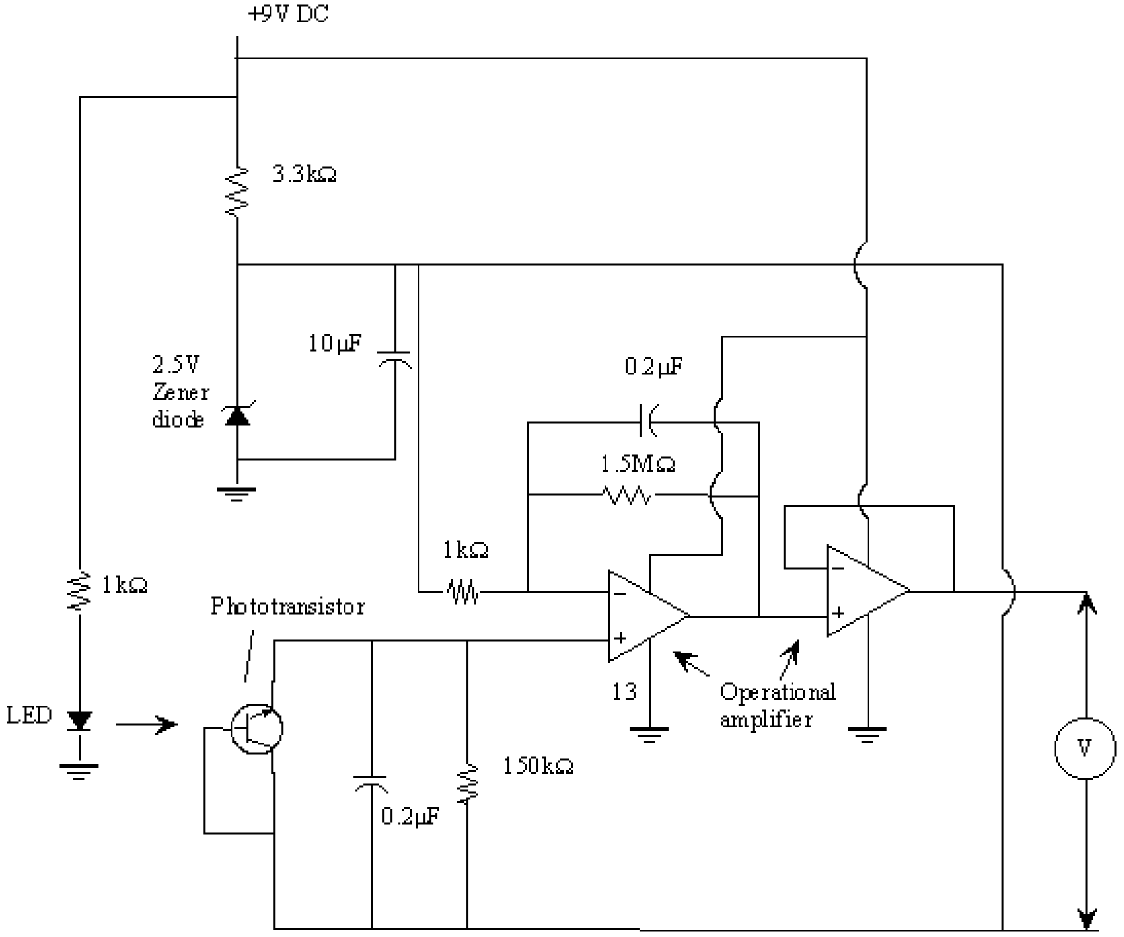

Figure 3.3 Circuit diagram for fluoride colorimeter

Table 3.1: Cost estimation of the fluoride colorimeter

Component	Quantity	Cost (Rs)
phototransistor (L14G2)	1	30
operational amplifier (LM 324)	1	10
9 V battery	1	150
LED	3	3
box	1	40
M-Seal		20
resistors	5	5
capacitors	3	10
jack	2	2
multimeter	1	200
Zener diode	1	10
other expenses		40
	total	520

Chapter 4

Estimation of fluoride using the SPADNS method

4.1 Introduction

The SPADNS (trisodium 2-parasulfophenylazo- 1,8-dihydroxy –3,6-napthalene disulfonate or 4,5 –dihydroxy-3- paraphenylazo-2,7 –napthalenedisulfonic acid trisodium salt) method of determination of fluoride in drinking water is a simple and a rapid technique with high accuracy. It can be applied directly to most water samples without prior pre-treatment, and is not very sensitive to the other ions which are usually found in potable water (Jacobson and Weinstein 1977). The reagent used in this method i.e. SPADNS – $ZrOCl_2$ is a red coloured complex, which changes colour when it reacts with fluoride. The change in concentration of SPADNS – $ZrOCl_2$ causes a change in the transmitted light, which is detected by the colorimeter.

The reaction between fluoride and SPADNS reagent is rapid and hence the samples can be tested within 10 minutes after adding them to the reagent. SPADNS reacts with zirconyl chloride to give a wine - red coloured complex which further reacts with fluoride to give a new complex (Fig. 4.1).

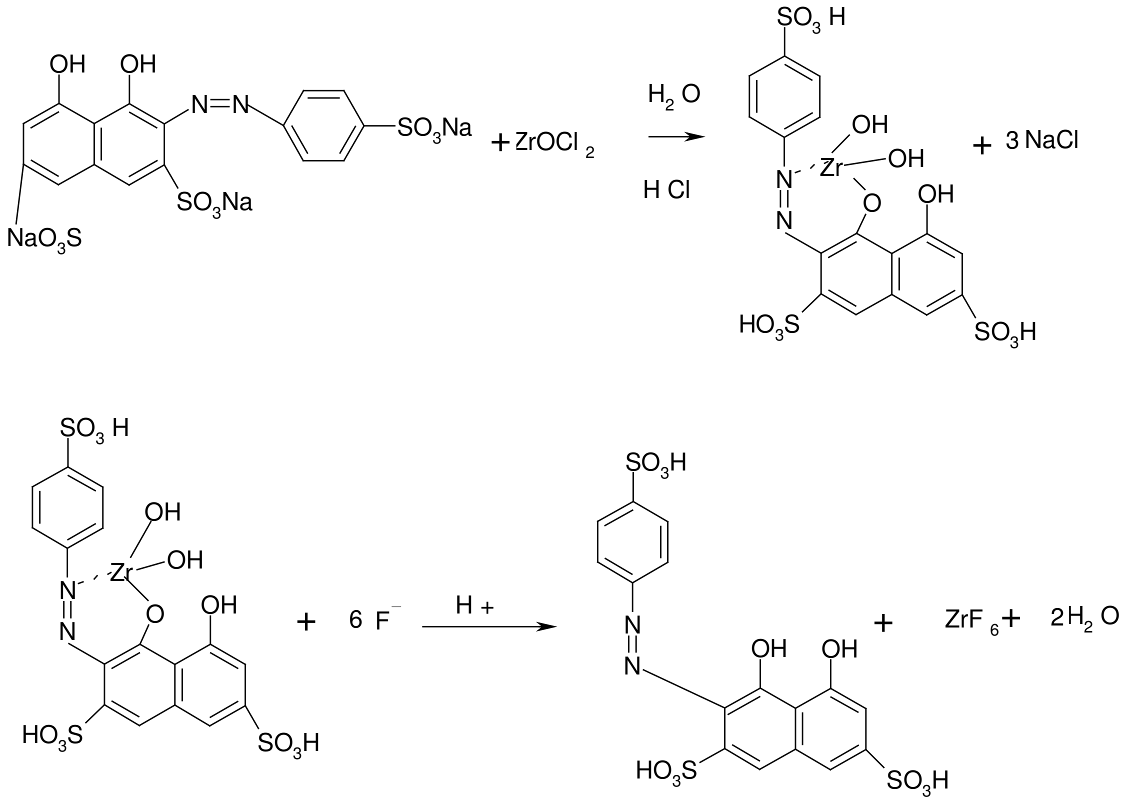

Figure 4.1: Reactions involved in the SPADNS method for estimation of fluoride (Bellack and Schouboe. 1958): (a) formation of the SPADNS – $ZrOCl_2$ complex, (b) reaction of the complex with fluoride ions

4.2 Apparatus and reagents

All measurements were made using the colorimeter assembled in our laboratory. A plastic cuvette was used as the sample holder. The reagents were prepared as follows (Bellack and Schouboe 1958):

Standard fluoride solution: A 100 mg/L solution was prepared by dissolving reagent grade sodium fluoride in distilled water. This was then diluted to obtain solutions with a fluoride concentration (C_F) in the range 1-6 mg/L.

Reagent A: SPADNS (0.958 g) was dissolved in 100 mL of distilled water and diluted to 500 mL. This solution is stable indefinitely if protected from direct sunlight.

Reagent B: Zirconyl chloride octahydrate (0.133 g) was dissolved in 25 mL of distilled water. Concentrated hydrochloric acid (LR grade) (350 mL) was added to it. The mixture was then diluted with water to make up the volume to 500 mL.

Reagent S: Equal volumes of reagent A and B were mixed to make a single reagent, henceforth referred to as reagent S. This reagent is stable for more than 2 years when kept away from light (APHA, 1975).

Reference solution: Reagent S (5 mL) was mixed with 20 mL of distilled water to obtain the reference solution.

4.3 Determination of fluoride

4.3.1 Calibration

Reagent S (5 mL) is taken in a 50 mL standard flask and 5 mL of the sample containing known amount of fluoride is added to the reagent. The final volume is then made up to 25 mL (Bellack and Schouboe 1958). After allowing the reaction to attain equilibrium, the mixture is transferred to the cuvette and the voltmeter reading, M (C_F) is recorded.

The voltmeter reading may vary when the test is repeated using samples of water taken from same source. This may be caused by errors in measuring the volume, differences in mixing etc. Apart from this, there may be some defects in the design of the device. To reduce these errors, we use the relative meter reading, $D = M(C_F=0) - M(C_F)$ for calibration purpose. Here $M(C_F=0)$ and $(M(C_F))$ denote the meter readings obtained with the reagent S plus fluoride free water sample, and with the water sample containing fluoride plus reagent S, respectively.

The calibration curve is obtained by plotting D versus C_F (Fig. 4.2). From the figure it can be seen that the data is linear for $C_F \leq 5$ mg/L. For $C_F > 5$ mg/L, the slope decreases as C_F increases. Hence the data for $C_F \leq 5$ mg/L was fitted by linear least squares, using a line passing through the origin (Fig. 4.3). The equation of the line is

$$D = b\,C_F \qquad (4.1)$$

where b is the sample regression coefficient given by

$b = \dfrac{\Sigma\left(C_{F_i} D_i\right)}{\Sigma\left(C_{F_i}\right)^2}$, C_{F_i} and D_i are the fluoride concentration and relative meter reading, respectively for the i^{th} data point (Snedecor and Cochran, 1968, p 166).

4.3.2 Estimating the fluoride concentration of a sample

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The procedure discussed in the last section is used to obtain the relative meter reading D, and the fluoride concentration C_F is calculated using (Eqn. 4.1). An estimate of the uncertainty in C_F is obtained by calculating the 95% confidence limits for the predicted value.

The limits are given by

$$C_{Fi} = \frac{\dfrac{D_i}{b} \pm \dfrac{t_{0.05,n-1}s}{b}\sqrt{\left(1-c^2\right) + \dfrac{D_i^2}{b^2\sum\limits_{i=1}^{n} C_{Fi}^2}}}{1-c^2} \qquad (4.2)$$

$$c^2 = \frac{1}{\Sigma C_{Fi}^2}\left(\frac{t_{0.05,n-1}s}{b}\right)^2 \qquad (4.3)$$

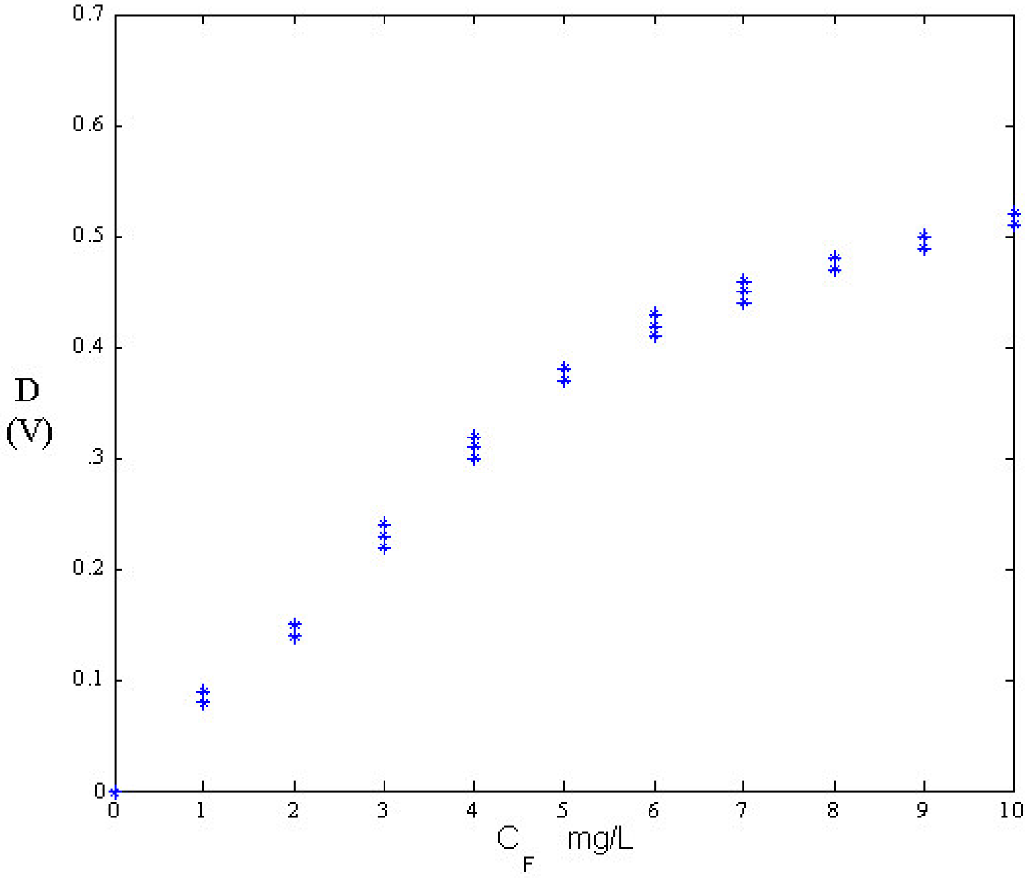

Figure 4.2: Calibration curve for the colorimeter . Here D is the relative meter reading and C_F is the fluoride concentration in the water sample.

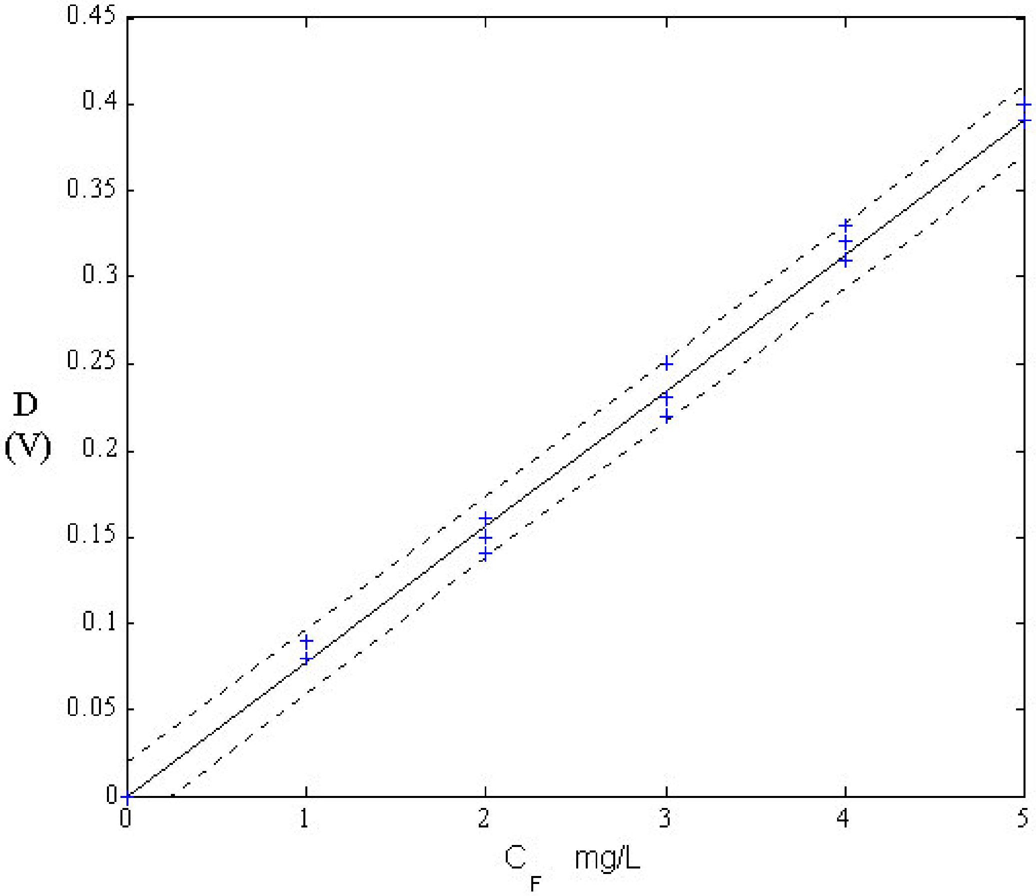

Figure 4.3: Calibration curve for the colorimeter: +, data for solutions containing 5 mL of reagent S, 5 mL of standard fluoride solution of concentration C_F and 15 mL of distilled water; — linear regression of relative meter reading D = M (C_F = 0) – M (C_F) on the fluoride concentration (C_F). ----------- 95% confidence limits for C_F.

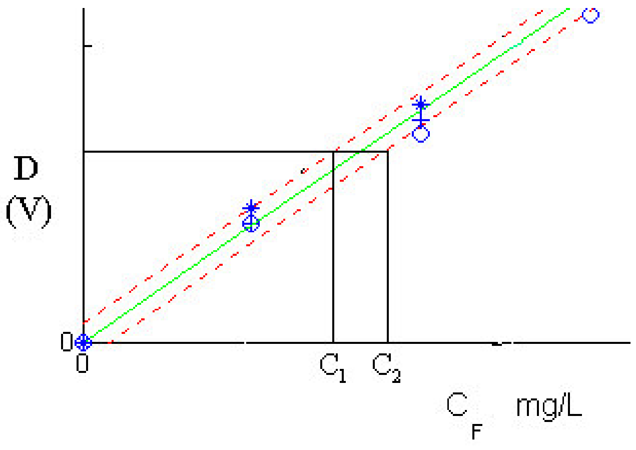

Figure 4.4: Schematic diagram showing the confidence limits for a typical value of D.

where s = sample standard deviation from regression, given by

$$s = \frac{1}{n-1} \sum_{i=1}^{n} \left(D_i - bC_{Fi} \right)^2 \qquad (4.4)$$

Here n is the number of data points and $t_{0.05\,,\,n-1}$ denotes the tabulated value (Snedecor and Cochran, 1968, p 549) of the statistic t which satisfies the Student's distribution with (n-1) degrees of freedom, such that the probability that the modulus of t exceeds $t_{0.05,\,n-1}$ is 0.05 (Snedecor and Cochran, 1968, p 59).

4.4 Results

The meter readings obtained using the colorimeter are reported in the table 4.1for two sets of tests. The tests were carried out on different days. The meter readings for the similar sample for two different tests are different, but the relative meter readings are comparable. The solid line and the broken curves in Fig 4.3 represent the sample regression line (Eqn. 4.1) and the confidence limits for C_F (Eqn. 4.2), respectively. For any value of D the 95 % confidence limit may be represented graphically as shown in Figure 4.4. There is 95 % chance that the value of C_F corresponding to D lies in the range (C_1, C_2).

It is found that the sample regression coefficient (b) is 0.074 V/ (mg/L), and the uncertainty in the estimation of C_F is about ± 0.25 mg/L.

Finally the effect of the volume of distilled water added to the SPADNS-fluoride water mixture was studied. Bellack and Schouboe (1955) suggested that 20 mL of distilled water should be added to 5 mL of reagent S and 5 mL of raw water. In the present work 0 mL, 10 ml and 15 mL of distilled water were added and then the meter readings were recorded. The results show that the calibration curve is not affected significantly by the volume of distilled water added (Fig 4.5). Hence, distilled water need not be added, eliminating the need to carry it during field tests.

Table 4.1: Meter reading (M) and the relative meter reading (D) for standard fluoride solutions. Run 1 and run 2 are two different runs conducted on different days.

C_F (mg/L)	Run 1		Run 2	
	M (C_F) (V)	D= M(C_F=0) - M(C_F) (V)	M (C_F) (V)	D = M(C_F = 0) - M(C_F) (V)
0	3.89	0	4.91	0
1	3.81	0.08	4.83	0.08
2	3.74	0.15	4.77	0.14
3	3.65	0.24	4.69	0.22
4	3.57	0.32	4.62	0.31
5	3.51	0.39	4.57	0.4

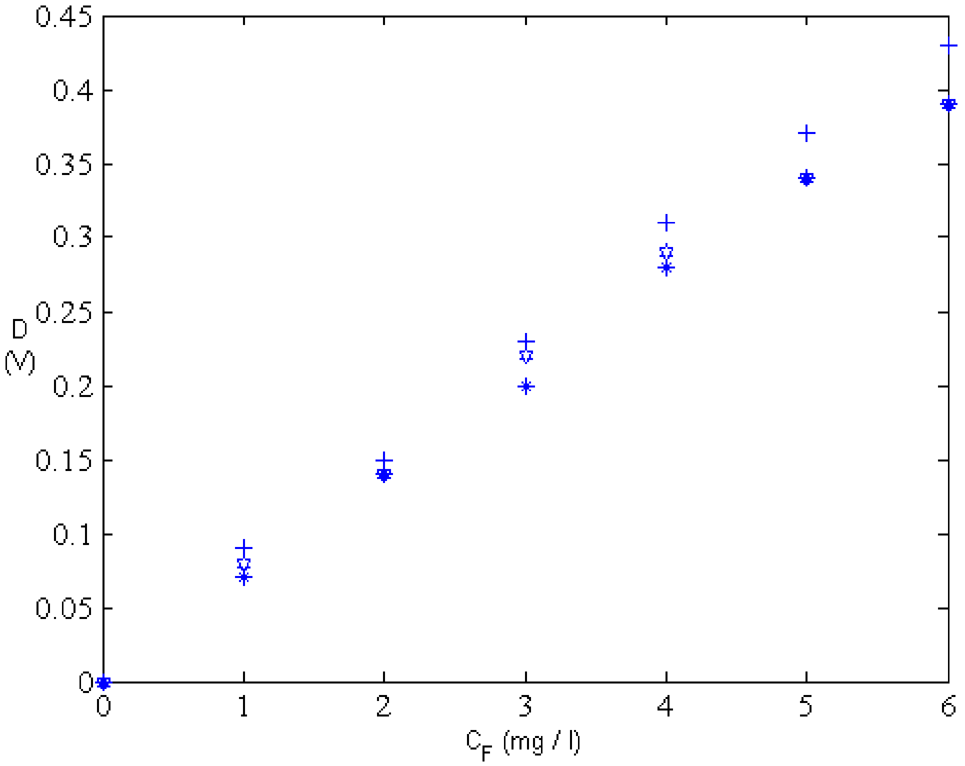

Figure 4.5: Effect of volume of distilled water added (V_w) on the relative meter reading D = M (C_F = 0) – M(C_F) for solutions containing 5 mL of reagent S, 5 mL of standard fluoride solution of concentration C_F, and V_w mL of distilled water. The meter reading M(C_F=0) corresponds to a solution containing 5 mL of reagent S and (V_w + 5) mL of distilled water: V_w = 15 mL(+), 10 mL (*), 5 mL (✡).

Table 4.2: Comparison of the calibration curves of Sen et al. (1998) and the present work

Parameters	Sen et al.(1998)	Present work
sample regression coefficient (b) (V/(mg/L))	0.046	0.074
Confidence limits for C_F (mg/ L)	± 1	± 0.25

4.5 Replication of the colorimeter

Several attempts had been made to replicate the circuit shown in Figure 3.3. But we found it difficult to procure the phototransistor needed for the circuit. Several phototransistors bearing different part numbers were purchased, but many of these did not work. Two of the phototransistors (No L14G2 and MQ314) worked well in the circuit and the corresponding calibration curves are shown in Figure 4.3 and Figure 4.6, respectively. Subsequent attempts to procure more phototransistors having either of these part numbers were not successful.

4.6 Comparison of calibration curves

Comparison of calibration curves for the present device (Fig 4.3 and Fig 4.6) with the calibration curve of Sen et al. (1998) shows that the scatter is more in the later case (Fig 4.7). Table 4.2 shows that the present device performs better than Sen's device as the slope of the calibration curve is higher and the uncertainty in the estimate of C_F is smaller in the present case.

4.7 **Field testing of the colorimeter**

The colorimeter developed in the present study was used for field level testing of fluoride in drinking water. At the request of Samuha (a non-governmental organisation), I visited a few villages in North Karnataka (Koppal district), collected water samples, and tested them on the spot. In all the cases the fluoride concentration is seen to be well above the permissible limit of 1 mg/L (Table 4.3). Hence there is a pressing need for defluoridation of the drinking water used in these villages.

4.8 Testing of water samples from Rajasthan

Water samples from Rajasthan were also tested in our laboratory and the results were compared with the results obtained from fluoride-ion selective electrode. Once again the fluoride concentration is seen to be above the permissible limit (Table 4.4). Further, it is encouraging that the values of C_F estimated by the colorimeter and the electrode are comparable.

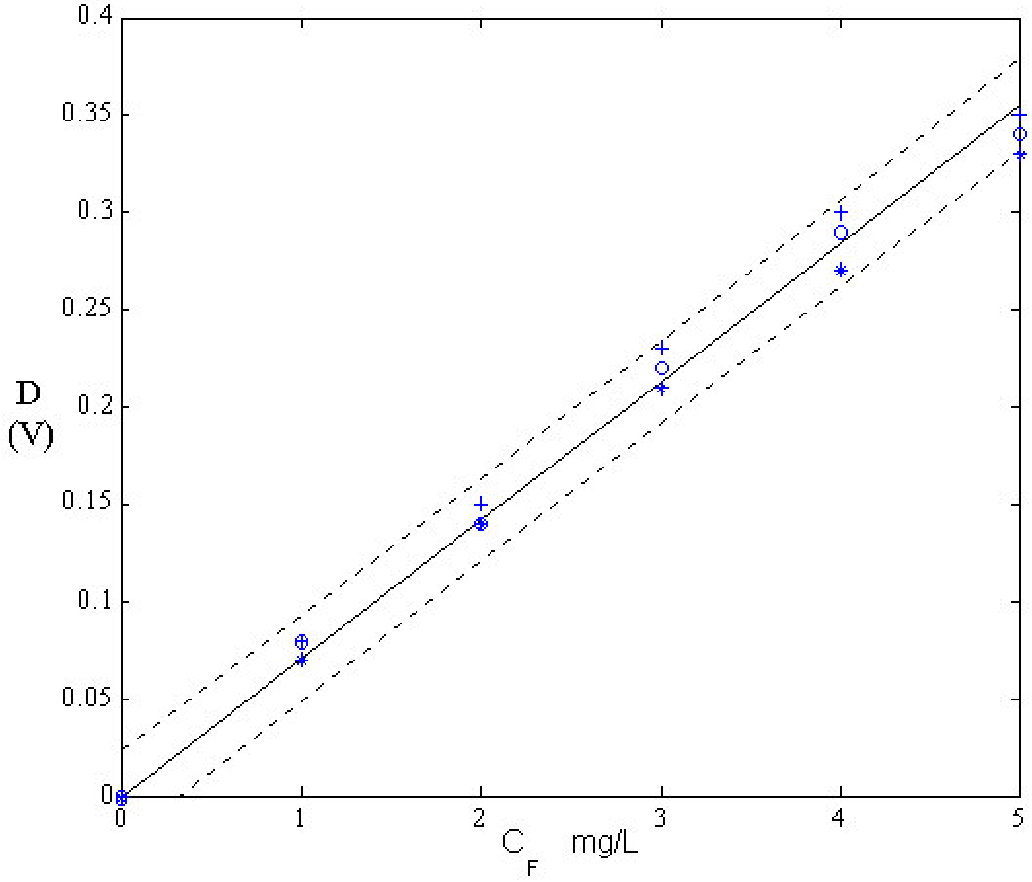

Figure 4.6: Calibration curve for the colorimeter: +, *, ○ data for solutions containing 5 mL of reagent S, 5 mL of standard fluoride solution of concentration C_F and 15 mL of distilled water; — linear regression of relative meter reading D = M (C_F = 0) – M (C_F) on the fluoride concentration (C_F). ----------- 95% confidence limits for C_F..

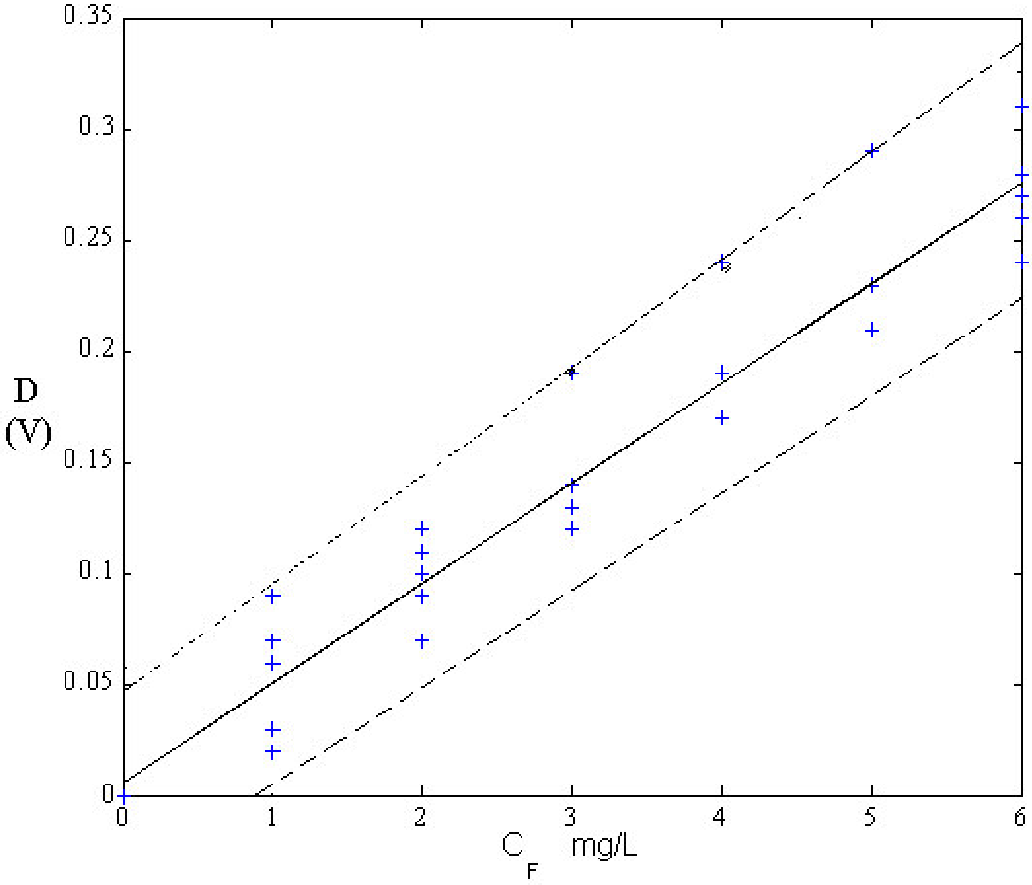

Figure 4.7: Calibration curve reported by Sen et al. (1998) for their colorimeter: +, data for solutions containing 5 mL of reagent S, 5 mL of standard fluoride solution of concentration C_F and 15 mL of distilled water; — linear regression of relative meter reading $D = M(C_F = 0) - M(C_F)$ on the fluoride concentration (C_F). ----------- 95% confidence limits for C_F.

Table 4.3: Field test results of the colorimeter

Village	Source of water	C_F (mg/L)
Chattar	Bore well	12.6± 0.5
	Tap water	12.5 ±0.5
	Hand pump	12.1 ±0.5
Vandali	Bore well	10.5± 0.48
	Tap water	10.8 ±0.49
	Hand pump	9.8 ±0.48
	Bore well	10.1 ±0.48
Tavargere	Bore well	3 ±0.25
	Hand pump	2.7 ±0.25
	Hand pump	2.8 ±0.25
Mendhali	Bore well	3.5 ±0.25
	Hand pump	3.4 ±0.25
	Tap water	3.9 ±0.25

Table 4.4: Test results of the samples from Rajasthan

Village	C_F (colorimeter) (mg/ L)	C_F (fluoride ion-selective electrode) (mg /L)
Agrasen nagar	5.2 ±0.25	5.4
Sagjer	1.8 ± 0.25	1.9
Tonk fatak	1.1 ±0.25	1.2

Chapter 5

Defluoridation of drinking water

5.1 Introduction

There are many methods of removing fluoride from drinking water. Some of them which could possibly be used at the village level have been studied in the present work. We have chosen fired clay chips, mud and fly ash as adsorbents for fluoride. Fired clay chips have a tendency to bind fluorides (Moges et al.1996) and are easily available in village communities, thereby making it a proper choice for fluoride adsorption. Fly ash and mud are known to be good adsorbents of fluoride. Investigations are carried out for adsorption properties of fired clay chips, mud and fly ash and are reported in the later sections.

Many methods have been developed for removal of fluoride from drinking water. These methods can be broadly classified into four basic groups.

- Ion exchange or adsorption methods
- Coagulation and precipitation methods
- Electro – chemical defluoridation or electro dialysis
- Reverse osmosis

Some of these methods are explained in the next section.

5.2 Methods of defluoridation

5.2.1 Defluoridation using activated alumina

Activated alumina is the common name for γ- aluminium oxide. The crystal structure of alumina contains cation lattice discontinuities giving rise to localized areas of positive charge (Clifford et al.1978). This makes alumina attract various anionic species. The maximum capacity of activated alumina is found to be 3.6 mg F^- / g of alumina (Bulusu and Nawalakhe 1988). In treatment processes, the more preferred ions can be used to displace the less preferred ions. Alumina has a high preference for fluoride compared to other anionic species, and hence is an attractive adsorbent. In practice, alumina is first treated with HCl to make it acidic.

$$\text{Alumina}\cdot H_2O + HCl \longrightarrow \text{Alumina}\cdot HCl + H_2O$$

This acidic form of alumina when contacted with fluoride ions displaces the chloride ions and gets attached with the alumina.

$$\text{Alumina}\cdot HCl + NaF \longrightarrow \text{Alumina}\cdot HF + NaCl$$

To regenerate the adsorbent a dilute solution of sodium hydroxide is mixed with the adsorbent to get a basic alumina.

$$\text{Alumina}\cdot HF + 2NaOH \longrightarrow \text{Alumina}\cdot NaOH + NaF + H_2O$$

Further treatment with acid regenerates the acidic alumina.

$$\text{Alumina}\cdot NaOH + 2\,HCl \longrightarrow \text{Alumina}\cdot HCl + NaCl + H_2O$$

A disadvantage of this process is that the regeneration steps result in an aqueous solution containing fluoride. On the other hand, if the spent alumina is discarded, the cost of the defluoridation increases. Apart from that, spent alumina may leach out fluoride ions when it comes in contact with alkali (Bulusu and Nawalakhe. 1988). In India activated alumina was used in some places in Andhra Pradesh and Maharashtra (Nawalakhe 1988).

5.2.2 Defluoridation using serpentine

Serpentine is a material containing one or both of the minerals chryostile and antigorite. These minerals contain mainly silica and magnesium oxide. Jindasa et al. 1989 noted that serpentine could be used as a suitable adsorbent for defluoridation. Serpentine is first of all powdered to less than 30 mesh size and then treated with concentrated HCl. Treated serpentine is then dried and then mixed with fluoride water. Studies show that the capacity of serpentine is about 0.1 mg F^-/g of serpentine. Maximum fluoride adsorption is achieved when acid is used along the fluoride containing water in the ratio 1:5.

This method has some disadvantages. Serpentine tends to be deactivated with repeated use. When used in acidic conditions, other ions such as aluminium, magnesium or iron leach out into the water. Further, the pH of the treated water must be increased before it can be used for drinking.

5.2.3 Alum coagulation

Studies show that alum ($Al_2(SO_4)_3$ 18 H_2O) can be used to coagulate fluoride, which then be removed by filtration. Alum, in the presence of sodium carbonate reacts with fluoride ions to give a complex, as indicated below (Nawalakhe and Paramasivam 1993). Alkalinity supplemented by the addition of sodium carbonate or sodium bicarbonate, ensures effective hydrolysis of aluminium salts leaving no residual aluminium in the treated water.

$$2\ Al_2(SO_4)_3\ 18\ H_2O + NaF + 9\ Na_2CO_3 \rightarrow [5\ Al(OH)_3\ Al(OH)\ 2F] + 8\ CO_2 + 9\ Na_2SO_4 + NaHCO_3 + 45\ H_2O$$

$$3\ Al_2(SO_4)_3\ 18\ H_2O + NaF + 17\ NaHCO_3 \longrightarrow [5\ Al(OH)_3\ Al(OH)\ 2F] + 9\ Na_2SO_4 + 17\ CO_2 + 18\ H_2O$$

Experiments show that 250 mg alum is required to reduce the C_F from 3.6 mg/L to 1.5 mg/L in 1 L of water(Nawlakhe and Paramasivam 1993). It has been shown that this method can be used to treat water with high values of C_F.

5.2.4 Defluoridation of water using fired clay chips

Fired clay chips are reported to have good fluoride removal capacity (Moges et al.1996). The maximum capacity of the adsorbent was found to be 0.2 mg F^- / g of the adsorbent. Studies show that 5 – 20 mg/L of fluoride solution can be reduced to less than 1.5 mg/L using fired clay chips.

One of the disadvantages of this process is that the contact time required for the completion of the process is very high (150 hours).

5.2.5 Defluoridation by carbonaceous adsorbents

Fluoride can be removed by carbonaceous adsorbents such as wood charcoal or bone charcoal, which are obtained either by direct carbonisation or by sulphuric acid treatment of saw dust, coconut coir or animal bones. However, the maximum removal of fluoride from the water samples using these methods was found to be about 80% and their removal capacity reduces sharply in saline conditions (Sivasamy et al. 2001). But use of coal - based adsorbents such as lignite, bituminous coal and fine coke gives better results (Sivasamy et al. 2001). The adsorbents are washed, sieved to a size 80 µm, dried at 110 °C, and then mixed with water containing fluoride. The contact time required for reducing C_F from 10 mg/L to 1 mg/L is found to be a few hours. It is being found that at acidic pH, the fluoride uptake is much higher compared to neutral or basic pH limits. The fluoride adsorption capacity of the coal - based sorbents is around 7 mg F^- / g of adsorbent.

5.3 Present experiments

In the present work, some materials which are easily available, inexpensive and are known to be adsorbents of fluoride have been used.

5.3.1 Defluoridation studies using fired clay

A solution with C_F = 100 mg/L was prepared, and diluted to the desired concentrations. Clay pots were purchased from the market, crushed in a ball mill and analysed using sieve to obtain particles in the size range 50-80 μm. Both batch and continuous experiments were conducted. These are discussed below.

For the batch experiments, 50 g of clay powder was taken in a 1 L plastic beaker and 1L of water having an initial fluoride concentration in the range 5 to 100 mg/L was added to the beaker. The mixture was thoroughly agitated. A sample was periodically taken out of the flask and analysed using the colorimeter or fluoride ion - selective electrode.

For the continuous experiments, 250 g of clay powder was taken in a glass tube of length 200 cm and diameter 2.5 cm (Fig 5.1). A set of filter papers was placed at the bottom of the tube to retain the powder in the tube, while permitting the water to flow. The tube was filled with water containing sodium fluoride, and the filtrate was collected in a beaker. The fluoride concentration (C_{Fb}) of the water in the beaker was analysed at various times(t_b). Each experiment was repeated two times, and each time a fresh batch of clay powder was used. The surface area of fired clay was estimated in Combustion Gasification and Propulsion Laboratory and was found to be 29 m^2/ g.

From the Figure 5.2, it can be seen that the contact time required for attaining the desired level of defluoridation is quite high for the batch process. The contact time can be effectively reduced by increasing the amount of adsorbent. This is shown in Figure 5.3. The time required for attaining a certain level of defluoridation decreases by one third when the amount of adsorbent taken was increased by five times. Another way of decreasing the contact time is by agitating the mixture or by using continuous flow system.

The effect of initial concentration has been studied and the result is shown in Figure 5.2. According to the figure the amount of fluoride removed [C_F/ C_0] decreases with the increase of initial fluoride concentration for a given mass of adsorbent. This may be because the less accessible sites of the adsorbing medium bind more fluoride as the concentration of fluoride increases.

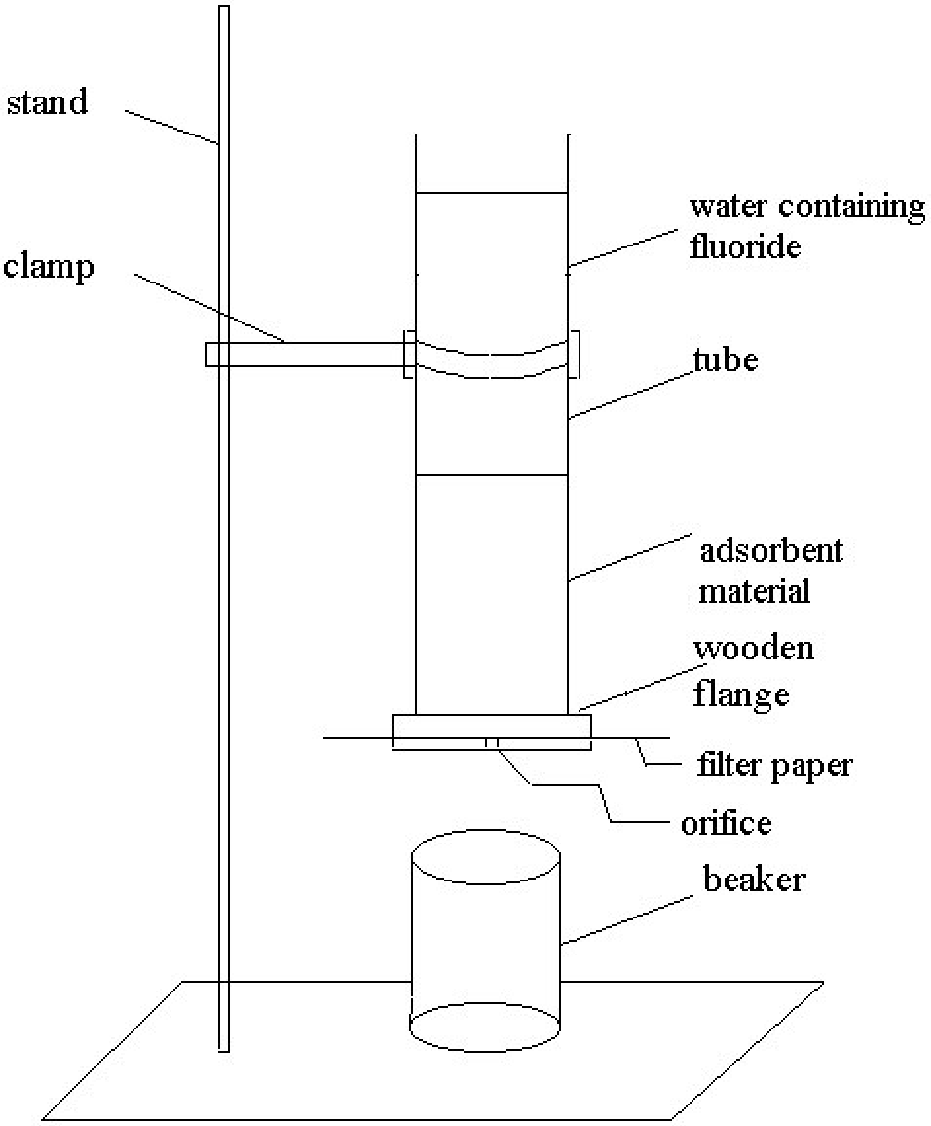

Figure 5.1: Experimental setup for the studies of adsorbents in continuous flow

As expected, the quantity of adsorbent significantly influences the extent of defluoridation achieved (Figure 5.3). The amount of fluoride removed was 0.1032mg F /g of fired clay for 50 g of adsorbent and 0.0368 mg F / g of clay for 250 g of adsorbent. The corresponding adsorption isotherm is given in figure 5.4. For a typical value of C_F = 10 mg / L the amount of adsorbent needed to decrease C_F to 1 mg/L is 450 g for a litre of water.

5.3.1.1 Model for predicting the variation of the concentration with time

Assuming that both the solid and liquid phases are well mixed, the mass balances for fluoride in the solid and the liquid phases are given by:

Liquid phase balance:

$$\frac{d}{dt}(\varepsilon C_F)=-ka\left(C_F-C_F^*\right) \tag{5.1}$$

Solid phase balance:

$$\frac{d}{dt}\left[\rho_p(1-\varepsilon)q_F\right]=ka\left(C_F-C_F^*\right) \tag{5.2}$$

where ε = porosity of the bed, k = mass transfer coefficient, a = surface area of the adsorbent / volume of liquid, C_f^* = interfacial concentration of fluoride in the liquid phase (mg/L), q = concentration of fluoride in the solid phase (mg F^- / g adsorbent), ρ_p = density of the adsorbent.

Addition of (Eqn. 5.1) and (Eqn. 5.2) and integrating using the boundary conditions C(0) = C_0, q(0) = 0 gives

$$\varepsilon C_F+\rho_p(1-\varepsilon)q_F=\varepsilon C_0=\text{ constant} \tag{5.3}$$

For $C_F \leq$ 10 mg/L the adsorption isotherm (Fig 5.4) may be approximated by

$$Q_F = K\, C_F^*;\quad K=\text{constant} \tag{5.4}$$

Substituting (Eqn 5.3) and (Eqn. 5.4) in (Eqn. 5.1) and integrating, we obtain

$$\frac{C_F}{C_0}=G+e^{-At}(1-G) \tag{5.5}$$

where $A = \frac{ka}{\varepsilon}\left(1+\frac{\varepsilon}{m\,K}\right)$, $G= \frac{\frac{\varepsilon}{m\,K}}{1+\frac{\varepsilon}{m\,K}}$ and $m = \rho_p\left(1\text{-}\varepsilon\right)$

Simplification of Equation 5.3 gives

$$\ln\left(\frac{C}{C_0}\text{-}G\right)=\ln F - At$$

where F = 1 - G. A plot of $\ln\left(\frac{C}{C_0}\text{-}G\right)$ versus t should give a straight line of slope –A and intercept ln F.

Results obtained from the semi batch column are shown in Table 5.1. Inspection of the results shows that the fluoride adsorption capacity, defined as the mass of fluoride adsorbed per unit mass of adsorbent, of fired clay increases with the increase of initial fluoride concentration which is also observed in the batch process. An interesting result obtained from the experiment is that the concentration of water in the beaker (C_{Fb}) decreases with time. If we analyse the process intuitively we would expect C_{Fb} to be minimum at the beginning as the clay powder would be fresh. A simple mass balance of fluoride in the beaker (Fig 5.1) is given by

$$\frac{d}{dt}\left(VC\right) = Q\,C_e \qquad (5.6)$$

where V = volume of water in the beaker, C = concentration of fluoride in the beaker, Q = volumetric flow rate of water, C_e = concentration of fluoride in the outlet stream.

Also,

$$\frac{dV}{dt} = Q \qquad (5.7)$$

Using (Eqn. 5.6) and (Eqn. 5.7), we get

$$\frac{dC}{dt} = \frac{Q[C_e(t) - C]}{V(t)} \qquad (5.8)$$

Equation 5.8 could not be solved as we do not have the data showing the variation of C_e, V and Q with time t. Hence, results shown in Table 5.1 could not be justified.

The results also show that though the inlet stream is free of fluoride we get an outlet concentration of 0.1 mg/L. This may be due to the fact that the clay might have some impurity which is interfering with the estimation of fluoride or there might be small amount of fluoride present in the clay which was leaching out. By using a continuous flow tube we decrease the contact time or residence time as compared to the batch experiment where there is no flow of fluid.

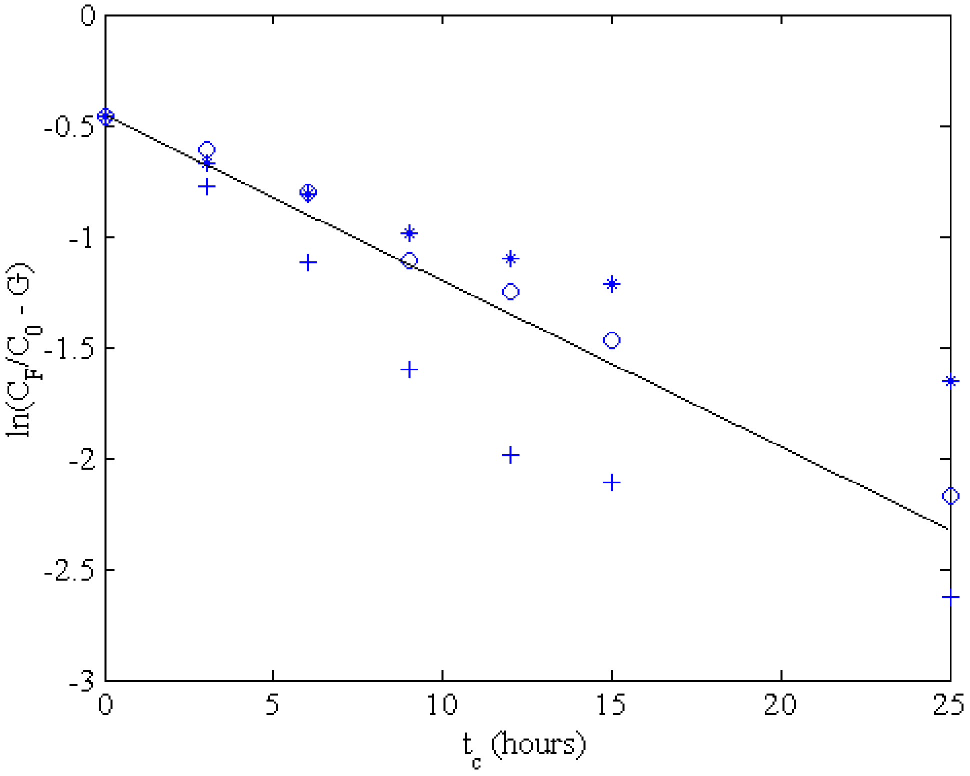

Figure 5.2: Variation of fluoride concentration in water (C_F) with the contact time (t_c) for clay powder. Parameter values: mass of powder = 50 g, volume of water = 1 L, initial concentration of fluoride in water (C_{F0}) = 20 mg/L (+); 10 mg/L (○); 5 mg/L (*). G = 0.31. — linear regression of the data points.

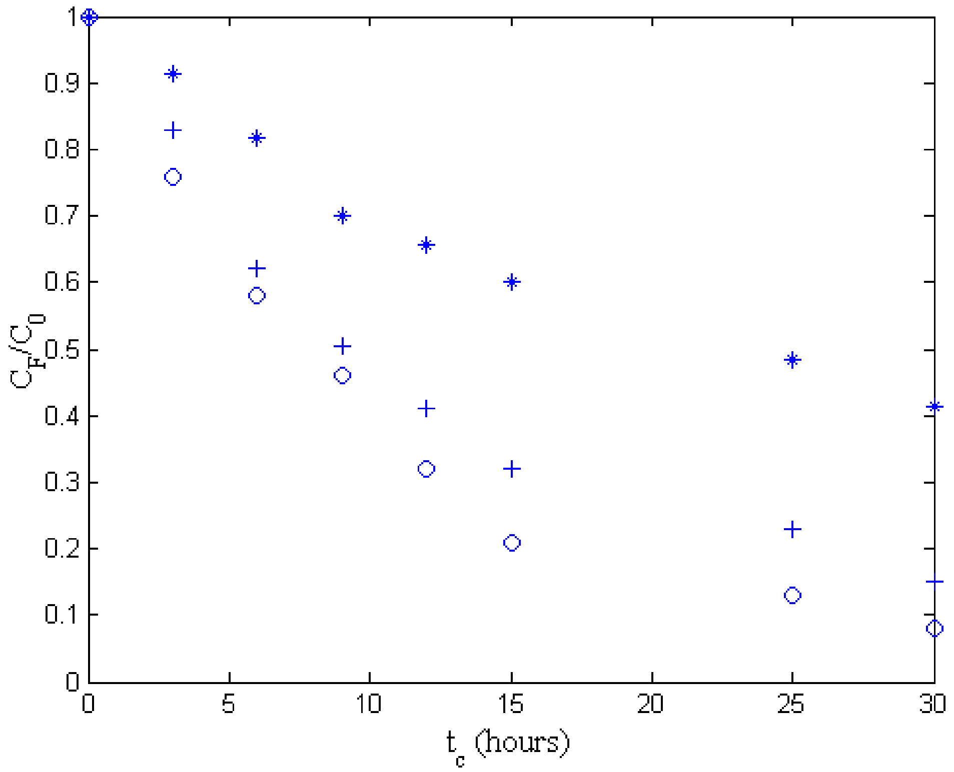

Figure 5.3: Variation of the dimensionless fluoride concentration (C_F / C_{F0}) with the contact time (t_c). The mass of clay used was 250 g (○), 150 g (+), 50 g (*).

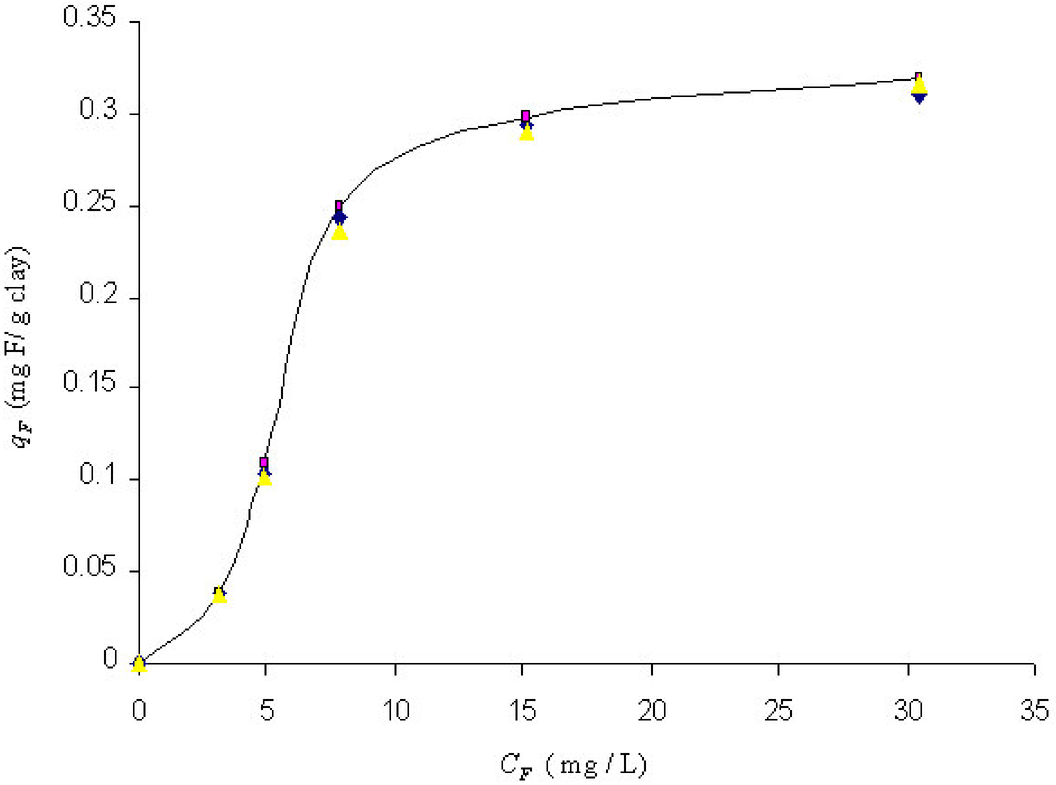

Figure 5.4: Adsorption isotherm for the fluoride – water - fired clay system. Here q_F is the concentration of fluoride in the solid phase, which is in equilibrium with water having a fluoride concentration (C_F).

Table 5.1: Variation of the fluoride concentration of the filtrate collected in the beaker (C_{Fb}) (Fig 5.1) with time. The experiments were conducted using a column packed with 250 g of clay powder. The initial volume of water added to the column was50 mL and its fluoride concentration was C_{Fc}.

C_{Fc} (mg/L)	t (hr)	C_{Fb} (mg/L)
0	8	0.1
	16	0.12
	24	0.12
5	12	3.9
	24	3.3
	36	3.1
	48	2.95
10	12	6.15
	24	4.9
	36	3.4
	48	3.1
20	12	10.6
	24	8.1
	36	6.8
	48	5.6
	60	5.5

5.3.2 Defluoridation studies using mud

Red mud was obtained from the hostel surroundings and stones and gravel were separated from it. The cleaned mud was used for batch experiments.

5.3.2.1 Procedure

Mud (100 g) was washed with water and taken in a plastic beaker. One litre of a solution containing a known concentration of fluoride (C_F) was added to it. The mixture is kept undisturbed during the course of experiment. A sample was periodically taken out of the beaker and analysed using the colorimeter or the fluoride – ion selective electrode.

5.3.2.2 Results

The variation of the fluoride concentration in the water (C_F) adsorbed with time is shown in Figure 5.5. It was observed that the amount of fluoride adsorbed increases with time upto 140 hours after which equilibrium is attained.

The adsorption isotherm of fluoride on mud is shown in Figure 5.6. From the figure we find that the capacity of mud in contact with 1 mg/L solution of fluoride in water is 0.01 mg F / g mud.

The extent of adsorption of anions by mud is a function of the pH of the system. The adsorption is highly dependent on pH (Figure 5.7). It reveals that the maximum adsorption of fluoride is for pH = 4.5 to 5. For pH greater than 5.5, fluoride removal decreases sharply.

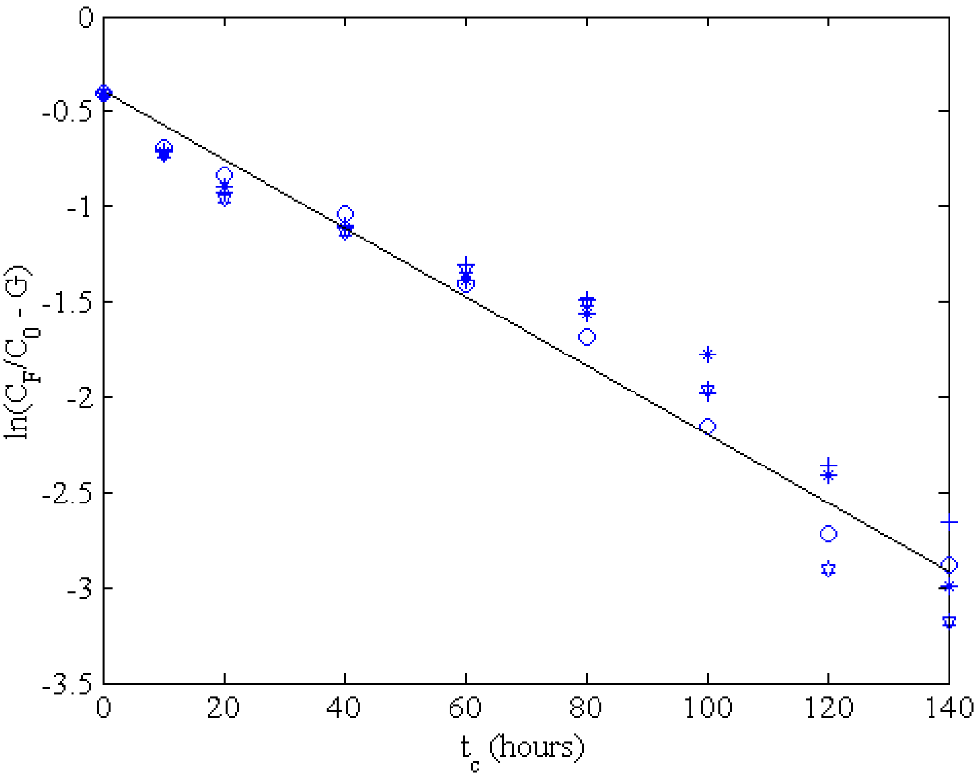

Figure 5.5: Variation of fluoride concentration in water (C_F) with the contact time (t_c) for clay powder. Parameter values: mass of mud = 100 g, volume of water = 1 L, initial concentration of fluoride in water (C_{F0}) = 3 0 mg/L (✡); 20 mg/L (+); 10 mg/L (○); 5 mg/L (*). G = 0.34. — linear regression of the data points.

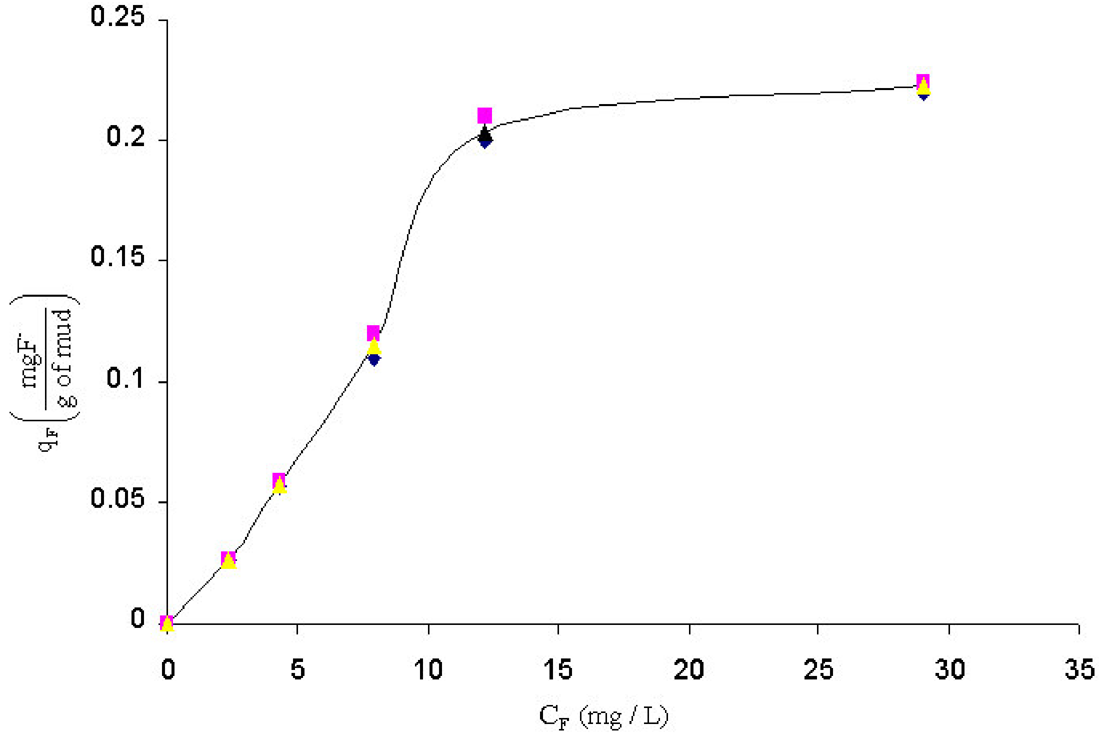

Figure 5.6: Adsorption isotherm for the fluoride – water - mud system. Here q_F and C_F denote the fluoride concentrations in the solid and aqueous phases, respectively. The symbols used are for repeated sets of readings.

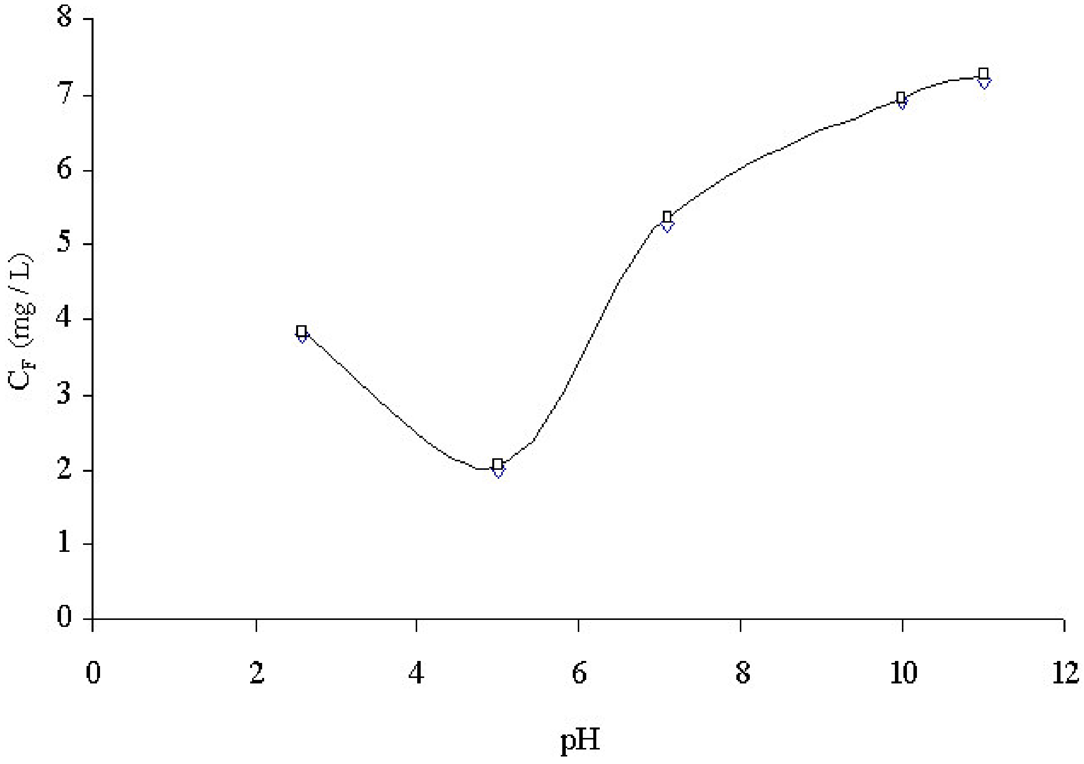

Figure 5.7: The effect of pH on the equilibrium fluoride concentration for the fluoride – water – mud system. Mass of mud = 50 gm, volume of water = 1 L, concentration of fluoride in water = 10 mg/L

5.3.3 Defluoridation studies using fly ash

Fly ash is a major solid waste by–product of coal fired power plants. It is produced as a fine residue carried off with the flue gases and deposited in the electrostatic precipitator. The particle size of fly ash ranges from 10 microns to a few mm (Agarwal et al. 2003). The main components of fly ash are silica, alumina, iron oxides, calcium oxide and residual carbon (Yadawa et al. 1989). The presence of unburnt carbon and surface area of 1 $m^2 g^{-1}$, make it a good candidate for utilization as an inexpensive adsorbent.

5.3.3.1 Procedure

Fly ash was obtained from the Raichur thermal power plant. Sieve analysis of the fly ash showed that the size range of the particles was between 10 – 80 µm. Adsorption studies were conducted at room temperature in a batch process with 25 g of fly ash and 1 L of sample solution containing known concentration of fluoride (C_F). The fly ash in a beaker is mixed with 1L of sample solution and then kept idle. Samples were withdrawn periodically from the beaker for estimating the value of C_F.

5.3.3.2 Results

The variation of C_F with time is shown in Figure 5.8. As in the earlier cases, we can see that the fluoride adsorption ability of fly ash is higher at higher concentration levels. This remarkable property can be explained by the fact that at higher concentrations the less accessible sites of the adsorbents are more likely to adsorb fluoride. The corresponding adsorption isotherm is shown in Figure 5.9. From the figure we can see that the adsorption capacity of fly ash is much higher (3.5 mg F/ g fly ash) than the previously studied adsorbents. This may be because of the presence of unburnt carbon particles in the fly ash which are known to be very efficient adsorbing materials.

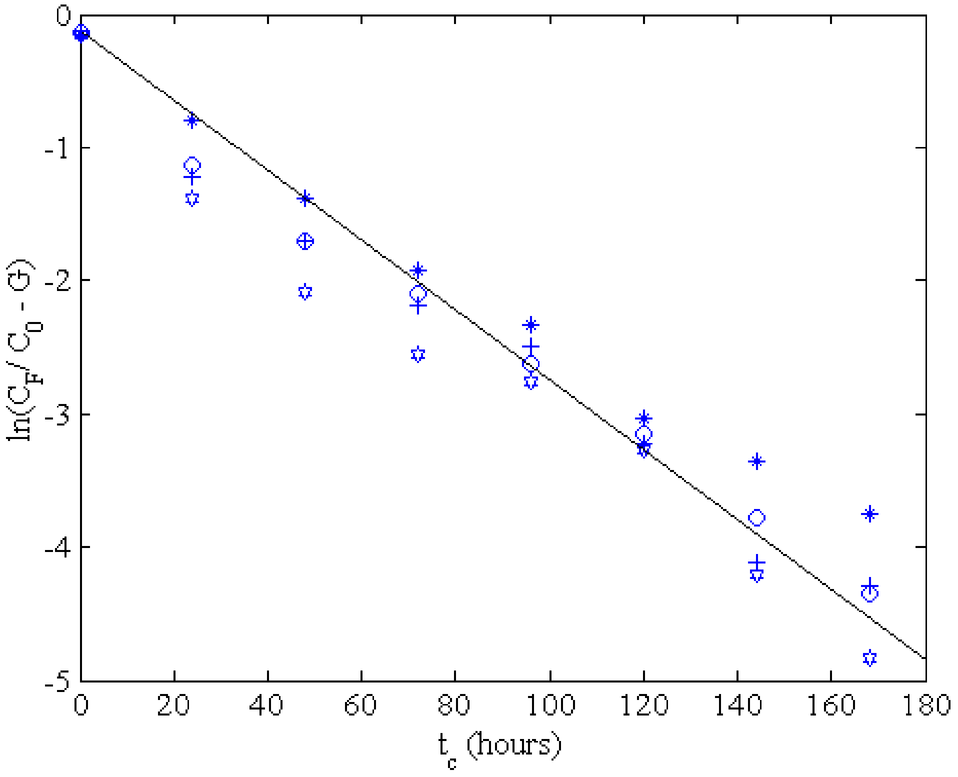

Figure 5.8: Variation of the fluoride concentration in water (C_F) with contact time. Parameter values: mass of fly ash = 25 g, volume of water = 1 L, initial concentration of fluoride in water (C_{F0}) = (*) 5 mg/L; (+) 10 mg/L; (○) 30 mg / L; (✡) 100 mg/L. G = 0.137. — linear regression of the data points.

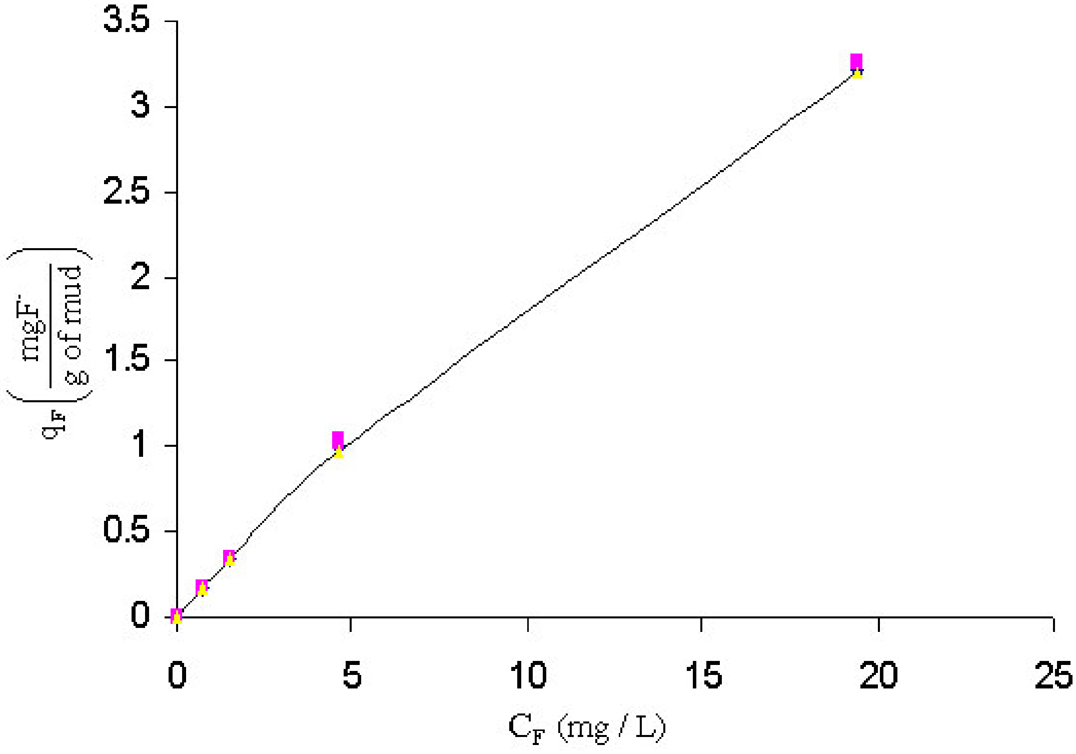

Figure 5.9: Adsorption isotherm for fluoride – water – fly ash system. Here q_F and C_F denote fluoride concentration in the solid and aqueous phases, respectively. The curve shows the equilibrium relationship of fluoride ions in both the phases.

5.4 Comparison of adsorbents

Comparison of the adsorbents studied in the present work shows that fly ash is better adsorbent compared to fired clay and red mud (Table 5.2). The adsorption capacity as well as the contact time required for reaching equilibrium is much lower in case of fly ash as compared to the other two adsorbents.

Table 5.2: Comparison of adsorbents studied in the present work

Parameters	Q_F at C_F = 1 mg/L (mg F/ g)	Contact time (t_c) (hr)
Fired clay	0.015	140
Red mud	0.01	150
Fly ash	0.2	50

Chapter 6

Discussion and suggestions for future work

6.1 Discussion

The purpose of this work was to develop a device, which can conveniently measure the fluoride concentration in water. The device works on the principle of colorimetry. SPADNS- $ZrOCl_2$ method was used as the analysing media. Results show that a linear calibration curve can be obtained for concentration (C_F) less than 5 mg/L with an uncertainty of ± 0.25. For C_F greater than 5 mg/L the calibration curve deviates from linearity. Overall, it is shown that an inexpensive colorimeter can be constructed, which can provide a reasonable estimate of the fluoride concentration in drinking water.

An inexpensive material such as fly ash has been found which can still be used to remove fluoride ions from drinking water upto certain extent.

The adsorption capacity of fly ash is much higher than the other adsorbents studied in this work and is an industrial waste in nature. Hence we can conclude that fly ash is a potentially good adsorbent of fluoride at the field level. However the amount of fly ash required is fairly large. Consider a family of five people, which consumes about 20 L of water per day for drinking and cooking. If the fluoride concentration of the raw water is 10 mg/L, than the amount of fly ash needed to reduce C_F to 1 mg/L is 330 kg/year.

6.2 Suggestions for future work

In the present study three adsorbents have been studied, there are many more adsorbents, which can be used for defluoridation purposes. Hence, further study can be done on other adsorbents as well. Future work also involves, studying the effect of hydrodynamic conditions on the adsorption efficiency, to reduce C_F to 1 mg/L and to reduce the contact time of the operation.

In the semi batch experiment, further study can be carried out to determine the variation of Q, V and C_e with time.

Notations

A	non dimensional constant occurring in (Eqn 5.5)
C_e	concentration of fluoride in water at the exit of the column
C_F	concentration of fluoride in water
C_f^*	interfacial concentration of fluoride in the liquid phase (mg/L)
C_{Fb}	concentration of fluoride in effluent stream
C_{Fc}	concentration of fluoride in inlet stream
C_0	initial fluoride concentration in water
D	relative meter reading = $M (C_F = 0) – M (C_F)$
D_i	relative meter reading for ith data point
G	non dimensional constant occurring in (Eqn 5.5)
M	voltmeter reading
Q	volumetric flow rate through the column
V	volume of water in the beaker
a	surface area of the adsorbent / volume of liquid
b	sample regression coefficient
c	non dimensional constant occurring in (Eqn. 4.2)
k	mass transfer coefficient
q	concentration of fluoride in the solid phase (mg F^- / g adsorbent)
t	tabulated values of Student's distribution
s	sample standard deviation
ε	porosity of the bed
ρ_p	density of the adsorbent.

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