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Monitoring and Assessment of Fluoride Contamination in Industrial Environment [South India] and Removal of Fluoride

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ABSTRACT

In the present work detailed studies were carried out to understand the effect of adsorbent dose [Ball clay], temperature on kinetics, and competing anion concentrations. Characterization studies on the adsorbent by XRD, SEM and FT-IR analysis before and after fluoride adsorption were carried out to understand the adsorption mechanism. XRD and FT-IR studies revealed significant changes after fluoride adsorption and showed formation of new complexes on adsorbent surface. Applicability of different sorption kinetic models was studied. The surface sites are heterogeneous in nature and followed heterogeneous site binding model. The presence of phosphate, sulphate and arsenate showed adverse effect on fluoride removal efficiency of ball clay adsorbent. The efficiency of material towards ground water samples treatment was tested with and without adjusting pH, and the results are discussed.

Key words: Adsorption; Effects of Fluoride; Fluoride contamination; Fluoride removal; Kinetics; South India.

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INTRODUCTION

Water is one of the abundant available substances in nature. Although earth is a blue planet and 4/5th of its surface is covered by water, the hard fact of life is that about 97% of it is locked in the oceans which is too saline so it cat be used for drinking and agricultural purposes. Of what is left, about 80% is trapped in polar ice caps and giant glaciers. Another 10% of it is locked in rock crevices lying deep as 800 m below the earth's surface which is very expensive to pump out. This leaves only about 0.3% of the world's water resources that man can tap for domestic, agricultural and industrial use [1, 2]. Water is an essential ingredient of all animals, plants and human beings. So it is also called ELIXIR. The water requirement of a community may be grouped under the following categories. Domestic purpose, commercial and industrial purpose, civil and public purpose, and loss and waste. The quantity of water required for domestic purpose viz., drinking, cooking, bathing, washing, sanitary purposes, private gardening, domestic animals etc. This demand depends upon the living conditions of the community. Also, essential for commercial and industrial purpose includes manufacturing plants, hotels, dairies, offices, business centres, stores, refineries, breweries etc [3, 4]. The requirement depends upon the character of the town or city, used for civic or public purpose includes sprinkling street, fountains, ornamental displays, swimming pools, lawns etc. loss and waste includes the careless use of water, leakage in mains, valves, other fittings etc. The requirement of water is also essential for the growth of crops. Water is very important in aquaculture systems. Water plays an important role in the manufacture of electric power.

Thus water can be considered as the most important raw material of civilization because of the fact that without water, human being cannot live and industry cannot thrive. With ever growing population and industrial developments, the demand for water is also increasing day by day and hence every country has to take necessary action to make use of the available water resources. The water resources are certainly inexhaustible gift of nature. But to ensure their services for all the time to come, it becomes necessary to maintain, conserve and use the water resources very carefully. It is an established fact that proper maintenance, conservation and wise use of water resources will definitely avoid the chance of water famine for future generation for an indefinite period. Natural waters may be broadly divided into the following categories. Surface waters: Flowing waters e.g. streams and rivers; Still waters e.g. ponds, lakes, and reservoirs; underground water supplies: Water form shallows and deep springs and wells; Water form lower measures of coal mines: Rain water; Estuarine and sea water. Fluoride is an essential micronutrient for human health [5]. However, excessive body intake of fluoride leads to dental fluorosis and crippling skeletal. High groundwater fluoride concentrations associated with igneous and metamorphic rocks which have been reported from India, Pakistan, West Africa, Thailand, China, Sri Lanka, and Southern Africa. The maximum permissible level of fluoride in drinking water as regulated by the World Health Organization is 1.5 mg/L. Excellent technologies are available for defluoridation. These technologies are not always applicable in rural area due to cost and technology requirements [6]. The adsorbents derived from natural minerals and by-product from industrial activities such as clay minerals and bleaching powder has been developed for defluoridation. Many researchers used adsorbents in a powder form for adsorption study. Excess intake of fluoride is responsible for dental caries, bone fluorosis, and lesions of the thyroid, endocrine glands, and brain. Fluoride is a naturally occurring element in minerals, geochemical deposits, and natural water systems and enters food chains through either drinking water or eating plants and cereals. High fluoride levels in groundwater are a worldwide problem, including various regions in Africa and Asia, as well as China. Many parts in India have been reported fluoride concentrations in water above the permissible limits. The material properties before and after fluoride adsorption were studied by following XRD, FT-IR and SEM techniques. Effects of experimental parameters like different particle size of ball clay and temperature on fluoride removal were studied to understand its applicability in treating water samples.

MATERIALS AND METHODS

History of collection of adsorbent:

The adsorbent is collected at Neyveli Thermal Power Station, Neyveli. Lignite and coal is used as raw material for producing power in the thermal power station. When the process is completed the clay substance is obtained as effluent. Such clay substance is called as ball clay. This substance is used as adsorbent material in our studies. The physico-chemical properties of the three materials are studied. The clay substance has high amount of aluminium, magnesium and calcium. Such metals are present in the form of silicates. In addition to this, some other metal species are present in trace quantities. Analar grade chemicals are used in this study. Batch adsorption method is carried out of the removal of fluoride from drinking water [7]. For preparing artificial fluoride solution NaF sample [BDH 99% pure] is used. The required amount of sodium fluoride is weighed accurately for preparing the concentration of fluoride as 100 ppm per litre. From this stock solution, the fluoride concentration of 3 ppm is prepared freshly. Take 100 ml of 3 ppm solution is taken with 5mg of adsorbent into the numbered 250 ml iodine flasks. The experiments are carried out at different time intervals, viz., 10, 20, 30, 40, 50, 60, 80 and 90 min.

The size of the adsorbent particles is separated by using molecular sieves. This is available at Department of Rural Technology, Gandhigram Rural University, Gandhigram. 3 gm of adsorbent is weighed accurately and taken in to the Iodine flasks. Now, all the iodine flasks are put in the regulator attached mechanical shaker. The flasks are shaken vigorously. The rotation of the flask is 150 rounds per min. After the completion of the experiment at different time intervals, the flasks are taken out and filtrate of the content is collected in a 100 ml beaker. The water quality parameters of this filtrate are noted. The detailed procedures are given below.

Determination of pH:

Preparation of buffer solution: a] pH: 4.0 and b] pH: 9.2

Buffer solution of pH 4.0 is prepared by dissolving the buffer tablet 4.0 [s.d. Fine – Chem. Ltd.,] is dissolved in a 100 ml beaker with minimum amount of double distilled water. This solution is quantitatively transferred into a 100 ml SMF. The content is made upto the mark by adding double distilled water. Buffer tablet 9.2 dissolved in a 100 ml beaker with minimum amount of double distilled water. Then this solution is quantitatively transferred into a 100 ml SMF. The content is made upto the mark by adding double distilled water.

The pH measurements of the water samples were carried out suing an analog pH meter, systronics make. The pH meter was calibrated first with buffer solution of pH 4 and gain cross checked with another buffer solution pH 9.

Electrical Conductivity

The conductance of fluoride treated sample is measured with the help of EQUIP – TRONICS, digital conductive meter model No EQ-660. The measurements are made at room temperature and the values are tabulated.

Determination of total alkalinity

10ml of the sample was taken in a conical flask. Added 2 to 3 drops pf Methyl orange indicator and the contents of the conical flask were titrated against hydrochloric acid taken in the burette. The end point of the titration was shown by a sharp colour change from yellow to red. The total Alkalinity values for all the samples were calculated using the following formula.

$$\text{TA as Calcium carbonate [mg / L]} = \frac{\text{B x Normality of HCl x 1000 x 50}}{\text{ml of sample}}$$

Where, B = ml of total HCl used with methyl orange.

Determination of total hardness – EDTA method

10ml of the water sample was taken in a conical flask. 2 to 3 drops of buffer solution were added to this sample. The contents in the conical flask were titrated against EDTA solution taken in the burette using EBT as indicator. The end point of the titration is shown by a sharp colour change from red to blue. Total hardness of the samples was determined using the following formula.

$$\text{Hardness [mg/L]} = \frac{\text{ml of EDTA x 1000}}{10}$$

Determination of Fluoride by Electrode method

The amount of fluoride present in the solution was measured using expandable ion analyzer EA 940, the fluoride ion sensitive electrode 9409 and the reference electrode [all Orion, USA make]. The fluoride electrode is a selective ion sensor. The key element in the fluoride electrode is the laser type doped lanthanum fluoride crystal across which a potential is established by fluoride solutions of different concentrations. The crystal is in contact with the sample solution at one face and an internal reference solution at the other.

Reference Electrode

The fluoride electrode can be used with a standard calomel reference electrode and almost any modern pH meters having and expanded millivolt scale. The fluoride electrode measures the ion activity of fluoride in solution rather than the concentration. Fluoride ion activity depends on the total ionic strength of the solutions pH and on fluoride complexity species.

Interference

Fluoride forms complexes with several polyvalent cations, notably aluminium and iron. The extent to which the complexation takes place depends on the solution pH and relative levels of fluoride and complexion species. In acidic medium [pH<=5.5] fluoride ion forms a poorly ionized HF. The LaF_3 based electrode is unresponsive to HF. In alkaline medium [pH>5.5] hydroxyl ion also can interfere with electrode response to fluoride ion, whenever the hydroxyl ion concentration is greater than one tenth of the concentration of fluoride ion.

Remedy

Adding an appropriate amount of buffer solution to the sample. Provide a uniform ionic strength background. Maintain the pH between 5 and 5.5. 1, 2 - cyclohexylene dinitrilo tetra acetic acid [CDTA], one of the components of the buffer preferentially complexes with the interfering cations and releases free fluoride ions.

Detection Limits

Upper detection limit: 100 mg/L; Lower detection limit: 0.002 mg/L

Preparation of standard Sodium fluoride solution:

A stock solution of sodium fluoride containing 100 mg F^-/L was prepared using analog sodium fluoride and fluoride free double distilled water. The procedure is given below.

Total ionic strength Adjustment Buffer – [TISAB-III]:

About 500 ml of fluoride free double distilled water was taken in a one litre beaker. To this 211 ml of concentrated hydrochloric acid was added, followed by 383 ml. of ammonium acetate and 19.8 g of 1, 2-cyclohexylene dinitrilo tetra acetic acid [CDTA]. A calibrated pH electrode was immersed into the solution and the pH was adjusted between 5 and 5.5 by adding the required amount of sodium hydroxide solution. The beaker was kept in a water bath for cooling. The contents of the beaker were transferred into a one litre standard measuring flask and the solution was made up to the mark using fluoride free double distilled water.

Measurement of fluoride

Direct measurement is an easy procedure for analyzing large number samples. The method involves the calibration of the meter with two standards of known concentrations selected in such a way that the unknown has a concentration in between these two standards can be ten times. Concentrations of unknown samples were read directly from the meter.

First two solutions of sodium fluoride with fluoride concentration of 0.5 mg/L and 5 mg/L respectively were used for calibrating the instrument. 25 ml of the standard sodium fluoride sample with concentration of 0.5 mg/L was mixed with 2.5 ml of TISAB-III buffer solution. The electrodes were then immersed in this solution. After calibrating the meter with this standard fluoride solution and again the calibration was done.

Take 25 ml of water sample and 2.5 ml of buffer solutions were mixed and the mixture was stirred for about five minutes. After stirring the electrodes were immersed in the solution. The fluoride ion concentration of the sample was read directly from the meter.

Evaluation of Defluoridation Capacity

Defluoridation experiments were carried out by the Batch equilibration method. 3 gm. of the adsorbent material was added to 100 ml. of water sample at a fluoride concentration of 3.00 mg. F/L. The contents were shaken thoroughly using a shaker rotating at a speed of 120 rpm. The solution was then filtered through Whatmann 42 filter paper and the filtrate was analyzed for fluoride. The deflouridation capacity of the adsorbent was calculated as follows.

$$\text{Defluoridation capacity} = \frac{\text{mg of fluoride removed x 1000}}{\text{Amount of the adsorbent taken in grams}} \text{ [mg F/kg]}$$

RESULTS AND DISCUSSION

The samples are collected in the villages of Vellarkulam, Thallarkulam and Elanthaikulam of Mukkudal block, Tirunelveli district. The examinations are carried out on water samples, cow milk children's urine and adult's urine. The water samples are obtained from tube wells and wells of the above villages. The physico-chemicals characters of the water samples are analyzed and given in table 1. The pH of the water samples is almost neutral. The other parameters viz., EC, TH and TA are in the permissible limit. The value of fluoride is somewhat above the tolerance level. In the Elanthaikulam village, the concentration of fluoride of the tube well is 1.982 ppm. Comparison with W.H.O. the value is greater than the permissible limit [1 ppm]. In the Vellarkulam village, the value is 1.32 / ppm. From this analysis, the above two villages are fluoride endemic areas of the block, where the pupils are affected by fluoride toxicity [1, 2]. Thallarkulam village has lesser fluoride concentration value, ie. 0.923 ppm. This is less than the permissible limit. So, the toxicity due to fluoride in the drinking water is very minimum level. Similarly, the level of fluoride in cow milk, urine of children and urine of adult were also determined. Among the three villages, Elanthaikulam village has a greater amount of fluoride concentration in cow's milk and urine of 0.157 and 3.31 ppm respectively. This data reveals that, the above village is the highest fluoride endemic area of the block. The other villages have minimum values of fluoride ion concentration. The data are given in table 2.

From the two water bodies, the well water has maximum amount of fluoride. The people, who drink well water, are affected by the fluoride toxicity and leads to the disease are known as "fluorosis". The main types of dental fluorosis and skeletal fluorosis are occurred is that areas. This is confirmed by the further analysis of the dental and skeletal of the people. The status of the dental fluorosis of the above three villages are givens in table 3. The surveys are made on nearly 110 residents. In Elanthaikulam village, the moderate level of dental fluorosis is only 55. The parentage of dental fluorosis is 50. The severe attack of dental fluorosis is 27.27% and acute level of fluorosis is 22.72%. This is evidenced by the presence of high level of fluoride ion concentration in drinking water of the village. The level of fluoride in the cow's milk, urine of children and adults is highly pronounced. Due to prolong ingestion of fluoride, 22.72% of peoples are affected acute dental fluorosis. Thallarkulam is another fluoride endemic area where the children, men and women were also affected by fluoride pollutant in drinking water. The percentage of dental fluorosis for moderate, severe and acute cases is 41.17, 31.76 and 27.05 respectively. The values are less than the Elanthaikulam village due to less value of fluoride concentration in drinking water.

Table .1. Physico-Chemical Parameters

Name of Village	*Source*	pH	Electrical conductivity (μmho)	Total Alkalinity	Total Hardness	Chloride	Fluoride (ppm)	TDS (ppm)
Vellarkulam	Well	7.3	2.500	700	30	4260	-	120
	Hand Pump	7.4	6.11	550	780	4970	1.34	280
	River Water	7.8	0.205	250	80	5325	-	10
Thallarkulam	Well	7.2	1.248	1450	250	4260	-	60
	Hand Pump	7.3	0.144	750	150	2485	0.93	100
	River Water	7.4	0.176	450	120	7455	-	10
Elanthaikulam	Well	6.9	2.710	1250	120	4260	-	130
	Hand Pump	7.5	2.460	600	860	5680	194	120
	River Water	7.5	0.200	150	130	5325	-	10

Table.2.Fluoride analysis

S.No.	Village	Fluoride concentration ppm		
		Cow milk	Urine (Child)	Urine (adult)
1	Elanthaikulam	0.157	1.22	3.31
2	Vellarkulam	0.143	0.157	0.931
3	Thallarkulam	0.098	0.006	0.825

Table.3. Dental Fluorosis status among the Fluoride affected people in different village

S.No.	Name of the Village	Status of dental Fluorosis					
		1+ moderate	%	2 + Severe	%	3 + acute	%
1	Elanthaikulam	55	50	30	37.27	25	32.72
2	Thallarkulam	35	41.17	27	31.76	23	27.05
3	Vellarkulam	23	38.33	18	27.0	19	21.66

In addition to drinking water, the fluoride levels in cow's milk and urine samples are also noticed. The values are highly supported to the nature of the toxicity in the above villages. Drinking water is an essential commodity for human and animals. So we concentrated on the study of fluoride in drinking water and its residual substances like milk and urine. The obtained information are complied and analyzed and further evidenced with the help of photo for children, adult and aged people. The photos for moderate, severe and acute cases for dental fluorosis and skeletal fluorosis for aged peoples are also shown in this report. We found that the Elanthaikulam village is the highest endemic area for fluorosis compared to the other villages. We also made an analysis of distribution of fluorosis in the different age groups of peoples who are living in Elanthaikulam village. The total numbers of affected person is 110, the age group from 5 to 90. The data are given in table 4. The fluoride toxicity is mainly affected is women society than the men. In the case of children the ratio of boys and girls is 1:5 for the age group between 5 to 10 years. For adults, the ratio is 1: 4. For the age group betweens 40 to 50, the ratio is 1:6. Above the age group 55, we identified that both dental and skeletal fluorosis of men and women, while women are higher numbers than men. In the third village Thallarkulam, where the value of fluoride level is less than the tolerance limit where the toxicity leads to dental and skeletal fluorosis are very minimum. This indicates that, the drinking water contains only lesser amount of fluoride, is good for drinking. The defluoridation efficiency of ball clay was studied under different experimental conditions like contact time of the adsorbent for maximum defluoridation, particle size of the adsorbent, dose of the adsorbent, effect of pH and effect of temperature. A similar type of study has been reported on to fire clay

Table 4: Distribution of fluorosis in the different age group of population living in Elanthaikulam (Total No. of affected person 110)

Age	Affected men	Affected Women
5-10	2	10
10-15	1	5
15-20	-	2
20-25	3	2
25-30	-	-
30-35	-	1
35-40	4	3
40-45	5	-
45-50	2	12
50-55	8	11
55-60	3	-
60-65	5	5
65-70	2	3
70-75	-	-
75-80	3	5
80-85	6	10
85-90	-	-

Adsorption Kinetics

Effect of temperature

The sorptive behaviour noticed the three temperatures for systems is shown in figure 1. The sorption rate increased at higher temperatures as the intra particle diffusion is the governing factor of the adsorption process [12-14]. At higher temperatures mobility of fluoride ions increased so the complex formation also increased. A similar behaviour has been observed by other workers also for the adsorption of Hg [II] on to different adsorbents [15-16].

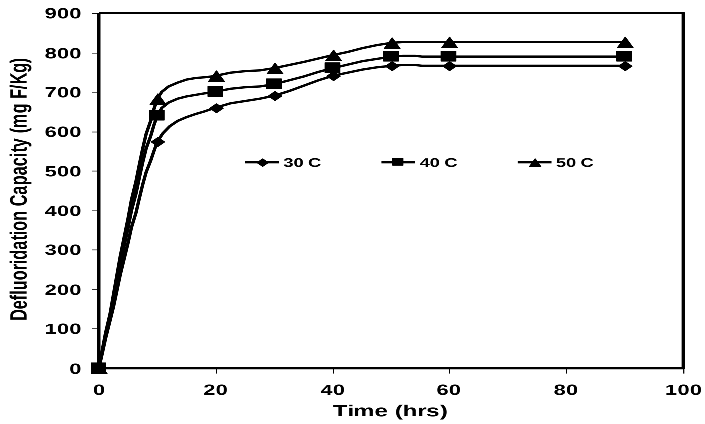

Fig. 1. Amount of fluoride adsorbed with time at different temperatures

Effect of particle size

The defluoridation studies were carried out with three particle sizes viz., 75, 150 and 300 µ as shown in Fig.2. The results indicated that there was a significant increase in defluoridation capacity with a decrease in particle size of ball clay [18-19]. This is obvious, because any adsorption process depends upon the number of active surface sites. The particle size 75 µ has maximum defluoridation capacity [767 mg/Kg] and hence it was used in all laboratory experiments. This is due to a given mass of ball clay; smaller particle size would increase surface area availability hence the number of sites increased.

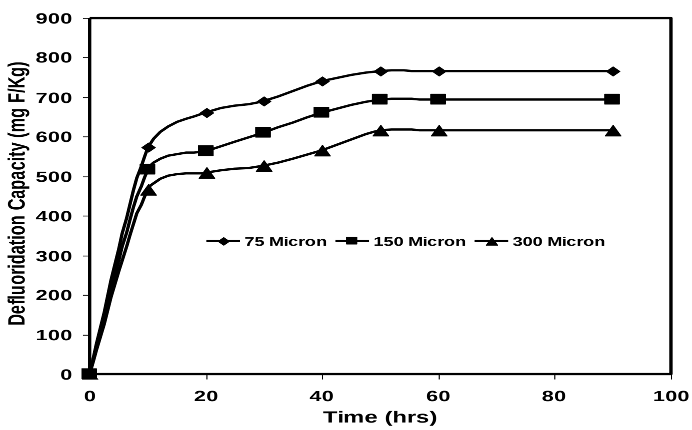

Fig. 2. Amount of fluoride adsorbed with time at different ball clay

The removal of fluoride by Ball clay at three temperatures was also determined using the following first order expression by Lagergren.

$$\log [qe - q] = \log qe - [Kad / 2.303] \times t \quad [1]$$

The Lagergren plots of the reactions at the three Ball clay and temperatures are given in Fig. 3 and 4. The values of Kad at three temperatures were calculated from the slopes of the respective linear plots and are given in table 5 and 6 along with the thermodynamic parameters as shown in Fig 3 and 4. The sorption of fluoride from aqueous solutions plays a significant role in water pollution control. The naturally occurring ball clay has been identified as potential defluoridating agents, functioning through ion exchange, adsorption and chemical processes [9 -11]. Detailed investigations under different conditions were carried out to determine the defluoridation capacity of ball clay and to understand the mechanism of adsorption. The effect of various factors like contact time, particle size, and temperatures governing the defluoridation capacity of ball clay has been experimentally studied in the laboratory by batch equilibration method.

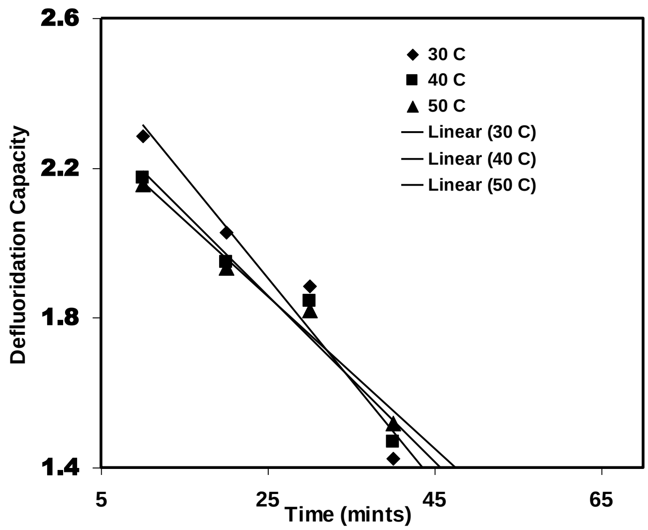

Fig.3. Effect of Temperature on Lagergren plots

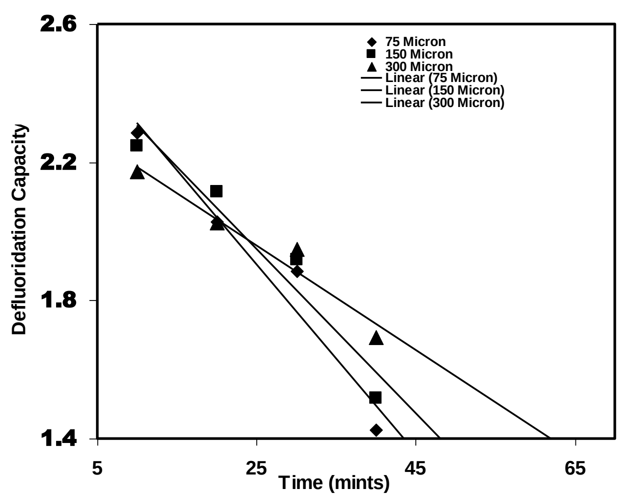

Fig. 4. Effect of ball clay on Lagergren plots

Instrumental Studies

For understanding the nature of fluoride sorption XRD and FTIR studies were performed using the raw and treated adsorbents. The XRD pattern of pure ball clay and fluoride loaded ball clay are shown in Fig. 5a and 5b.

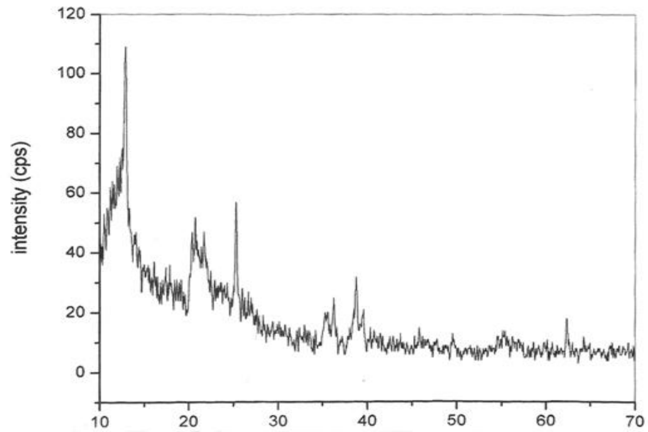

Fig. 5a. XRD pattern of pure ball clay

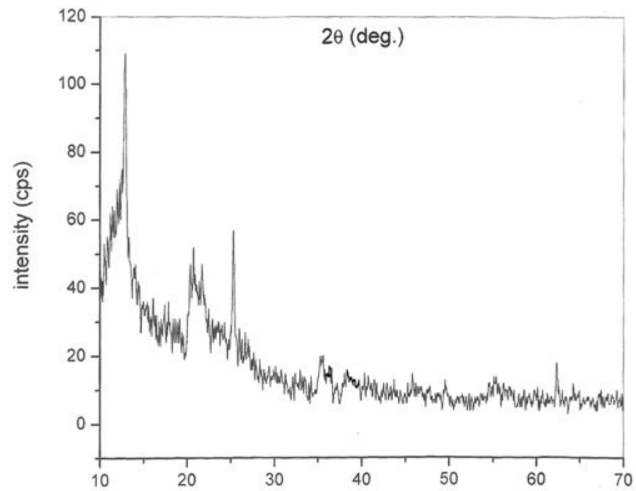

Fig. 5b. XRD pattern of fluoride adsorbed ball clay

The crystal dislocation takes place on fluoride adsorbed material. This is evidenced by the disappearance of 2θ value at 35^{o}. This shows the strong adsorption of fluoride on the surface of the adsorbent. FTIR analysis of the sorbent surface before and after the sorption reaction has provided the information regarding the surface groups that might have participated and also about the surface sites at which sorption might have taken place [Fig 6a, 6b]. The shift of stretching frequency, corresponding to the presence of – OH groups from 3600 to 1100 cm-1 is due to the exchange of - OH group in the aqueous solution of the adsorbent with fluoride ion in the solution.

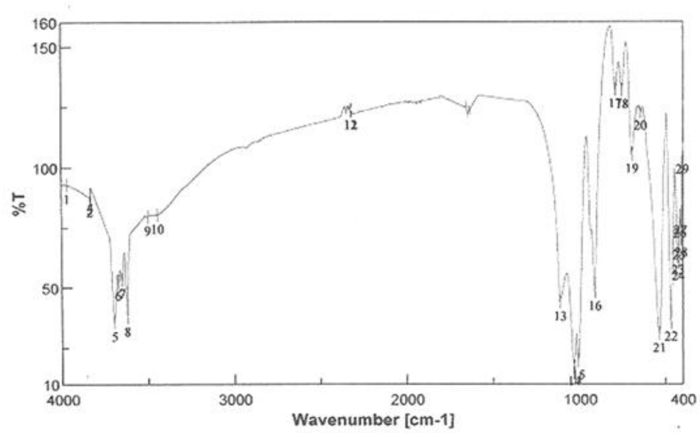

Fig.6a. FTIR spectra of pure ball clay

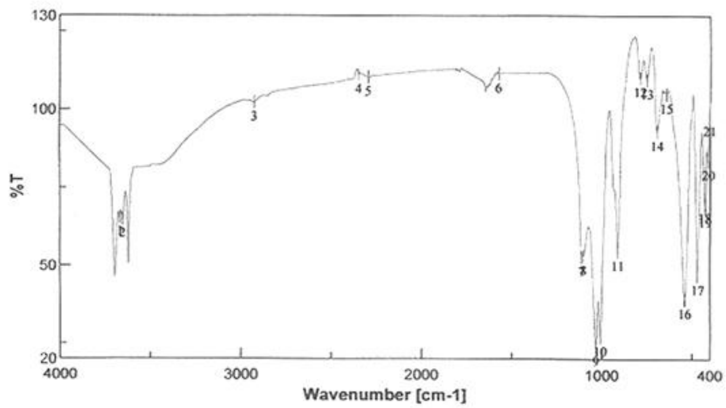

Fig. 6b. FTIR spectra of fluoride adsorbed ball clay

CONCLUSION

The survey and analysis were made on fluoride endemic areas and identified three villages in the block. Among the villages, Elanthaikulam village had highly pronounced the fluoride disease. This is due to high level of fluoride content in well water and tube-well waters. These are the sources for drinking purpose. The dental fluorosis and skeletal fluorosis were highly noticed in the above village. The data were analyzed and explained. The other two villages had the diseases only in minimum level. From the analysis made on the above studies, we concluded and suggested that, the people who are living in the Elathaikulam village should drink only boiled water and also eat food stuffs containing enriched calcium. The order of fluorosis in the three villages was Elanthaikulam> Vellarkulam> Thallarkulam. Defluoridation experiments were carried out by batch equilibration method and ball clay was used as adsorbent. The maximum contact time between adsorbate and adsorbent was fixed as 50 min. The minimum particle size of 75 µ exhibits the maximum efficiency of fluoride removal. This is due to the greater availability of surface area of the adsorbent. The mechanism of adsorption process was explained in terms of pH of the medium. At lower pH ranges, the defluoridation capacity is the maximum in the adsorbent. That is, chemisorption dominates an important role. At higher ranger, the value decreases, where chemisorption along with physisorption takes place. In both cases, the adsorption process follows monolayer coverage. This is evidenced by the linear Lagergren plots. Hence, Ball clay has maximum efficiency of in terms of removal of fluoride in aqueous solution. The experimental data were further confirmed with XRD and FTIR analysis.

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