DE-FLUORIDATION OF WATER USING LOW COST AND LOCALLY AVALABLE RAW MATERIALS

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF

MASTER OF TECHNOLOGY
IN
ENVIRONMENTAL ENGINEERING

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<u>CERTIFICATE</u>

This is to certify that the research work embodied in this dissertation entitled "**De-fluoridation of water using low-cost and locally available raw materials**" has been carried out in the Department of Environmental Engineering, Delhi Technological University, New Delhi. This work is original and has not been submitted in part or full for any other degree or diploma to any university or institute. The work is approved for submission.

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It was my mother's dream, my father's vision and my grandparents' undying faith which has brought me this far. I dedicate my thesis to my parents and my grandparents.

Abhas Jain
MTech-Environmental Engineering

Dedicated to my parents and grandparents…

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Chapter 1
Introduction

We all know that about 70% of the earth's surface is covered with water. Most of the water is in the oceans (96.5%) in the unusable form and some of it is frozen (1.74%). Lakes, swamp water and rivers hold 0.014% and soil moisture accounts for 0.001%. Water also exists in the form of vapor in the air (0.001%) and as groundwater beneath the sub surface in the aquifers (1.7%). World's water needs are met from the surface and groundwater resources. However, groundwater use is advantageous as it is comparatively fresh and widely distributed unlike the surface water. Threats to groundwater have been increasing everyday due to rise in population and demand of water. Thus with increasing demand of groundwater for domestic, industrial and agricultural needs, the pressure on this resource has become huge. Improper management and over exploitation has also lead to contamination of this resource. The degradation of groundwater may be due to natural or anthropogenic processes. Anthropogenic causes include contamination from wastewater from sewage treatment plants, discharge from industries, improper solid waste disposal, agrochemicals, runoff from agricultural fields, leakage from underground storage tanks etc. while natural cause are inherent geological conditions. When the chemical composition of groundwater is not within the prescribed limits for drinking or irrigation or industrial water, they become unsuitable. Arsenic, fluoride, iron, nitrate, manganese, boron, most heavy metals and radionuclides are few contaminants that are of great concern if not present within permissible limits. In my thesis, the causes and implications due to presence of increased fluoride in groundwater used for drinking purpose has been discussed. Also, I have discussed about measures to be adopted to mitigate the problem.

Natural waters contain fluorides in varying amounts. Consumption of water that contains fluoride in a concentration of approximately 1 mg/liter is found to be effective against tooth decay. For the same reason, salts with Fluoride concentration are added to public water supplies which contain Fluoride less than the desired concentration. In some places, where Fluoride concentration in drinking water supply has been in the permissible limits,

tooth decay has been found to be 65% less than in communities with less or zero Fluoride. Most un-fluoridated waters contain less than 0.3 mg/l fluoride. Excessive exposure to fluoride, however, may cause fluorosis. Fluorosis is condition in which the teeth become mottled, discolored, and pitted during their development. Skeletal fluorosis, characterized by increased bone density and abnormal bone growths, may result from long-term consumption of water containing 8 to 20 mg/l of fluoride (Hodge, H.C., 1954). The consumption of fluorides in excess of 20 mg/day over a period of 20 years or more could result in crippling fluorosis (Roholm, K. 1937). Dental health is of primary consideration for the control of fluoride in water. The USEPA National Interim Primary Drinking Water Standards have indicated that the allowable level of fluoride should not exceed 1.4 to 2.4 mg/l. This level is dependent upon the average maximum daily air temperature since the amount of water, and consequently the amount of fluoride ingested, is primarily influenced by the air temperature of the area. In general, most municipal water supplies contain less fluoride than the amount that is considered to be beneficial to dental health; however, many water supplies are found to exceed this limit.

Concern about elevated fluoride levels in drinking water is not based so much on acute toxicity effects, but rather on the long-term exposure to low levels of fluoride. In Rajasthan, a number of projects have been carried out on a variety of treatment methods for the removal of fluoride from potable water supplies.

The methods for fluoride removal that have been tried or proposed have been divided into two basic groups: (a) precipitation methods based upon the addition of chemicals to the water during the coagulation or softening processes and (b) methods in which the fluoride is removed by adsorption or ion exchange on a medium which can be regenerated and reused. The activated alumina column is a noteworthy example of this latter group. The primary objective of this project was to determine whether or not the fluoride level in any water sample (groundwater or lab synthesized) with high fluoride content (5-10 mg/L) could be reduced to an acceptable level by chemical treatment.

The second objective of this project was to find out the materials which are economically available and to determine the most advantageous method for reducing fluoride at various natural levels. Emphasis, in this study, was placed upon adsorption methods in which the

removal of fluoride was carried out by using different adsorbents and passing fluoride rich water from the adsorbent and letting Fluoride adsorption. Some materials showed appreciable adsorption whereas results of some materials were unsatisfactory.

This study was also intended to investigate the removal of fluoride from potable water by column adsorption but due to some technical reasons, column process could not be carried out and results were obtained by batch process itself. The adsorbents that I have used are Tulsi, Eucalyptus leaves and stem, kattha, marble slurry, brick powder and Alum. The adsorbents that I have used are Tulsi (Ocimum tenuiflorum, also known as Ocimum sanctum, Holy basil, or tulsī), Eucalyptus (*Eucalyptus globules, Eucalyptus citriodora, Eucalyptus dives, Eucalyptus polybractea, Eucalyptus radiate)* leaves and stem, kattha (Acacia catechu), marble slurry, brick powder and Alum. Of these, results obtained by using Alum and brick powder have been satisfactory. Alum is used in Nalgonda Technique (Nawlakhe WG, 1975) in many parts of India and the world. But it has certain limitations. It adds Aluminum to water and also increase the dissolved salts content. Though cumbersome, it is still being used for defluoridation as it is an economic method. Brick powder has a large surface area and presence of Aluminum and Silica enhances Fluoride adsorption. Brick is heated at a high temperature which activates the brick particles and hence more surfaces for adsorption are created. I have also performed experiments on Alum impregnated on brick powder. The purpose of this combination was to utilize the de-fluoridation capacity of both the materials and to ensure that output water has less dissolved Aluminum content and solids. Success rate was appreciable. But using this combination in column process shall yield better outcome.

1.1   Problem Statement

Rajasthan is located in the North-western part of India. It is more than 40% desert. Groundwater hence, contains fluoride above permissible levels. People in many parts of Rajasthan consume water with fluoride above 10 mg/L. People of all age groups have mottled teeth, skeletal fluorosis, painful and restricted joint, deformities in limbs and hunch back. Providing safe drinking water in interior parts of has been a challenge since the beginning. Efforts have been taken to avenge the problem. But most of the rural people still do not have access to safe drinking water.

1.2   Motivation:

As mentioned earlier people in some parts of Rajasthan consume water with high Fluoride content. My project is an attempt towards devising an adsorbent which is low cost and locally available so that it can be easily be put to use. Fluoride has been a menace as far as drinking water quality is concerned. Hence I have attempted to look for simple methods of treatment which can be practiced in emergencies or in areas still deprived of safe or alternative water supplies.

1.3   Objective of the study:

1. To study the occurrence of Fluoride in nature.

2. To study the health effects of Fluoride on human beings.

3. To study the problem of Fluoride in Rajasthan state.

4. To study the removal of Fluoride by different low cost materials such as brick, alum impregnated brick, tulsi and Eucalyptus.

5. To compare and recommend best low cost and locally available material for fluoride material.

Chapter 2
Literature review

2.1   Existence in Nature:

2.1.1   Chemical Properties of Fluorine: Fluorine is an element of Halogen group with molecular weight 18.998 and atomic number 9. It is the most electro negative of all elements. It occurs as a diatomic gas in its elemental forms and has a valence number 1. This fluorine has remarkably low dissociation energy (38 K cal/mole). As a result it is highly reactive and has strong affinity to combine with other elements to produce compounds known as **Fluoride**. Fluoride belongs to halogen family represented as 'F' with atomic weight 18.998 and atomic number 9. It is the most electronegative and the most reactive when compared to all chemical elements in the periodic table. It has an oxidation state of -1 and occurs as both organic and inorganic compounds. It is the 13th most abundant element in the earth's crust. Its natural abundance in the earth's crust is 0.06 to 0.09% (Fawell et al., 2006) and the average crustal abundance is 300 mg/kg. Fluoride does not exhibit any color, taste or smell when dissolved in water. Hence, it is not easy to determine its presence through physical examination. Only chemical analysis of the groundwater samples can determine the concentration of this ion.

2.1.2   Sources of Fluoride in nature

Sources of fluoride in environment- Usually the surface water is not contaminated with high fluoride, whereas ground water may be contaminated with high fluoride because the usual source of fluoride is fluoride rich rocks. When water percolates through rocks it leaches out the fluoride from these rocks. Table 2.1 shows the value of fluorides in various rock types.

Table 2.1: Value of Fluorides in various rock types (Hussain J, Sharma, KC)

Rocks	Fluoride range (in ppm)	Average (in ppm)
Basalts	20-1060	360
Granites and Gniesses	20-2700	870

Shales and Clasy	10-2700	800
Line stones	0-1200	220
Sandstones	10-880	180
Phosphorite	24000-41500	31000
Coal (ash)	40-480	80

The rocks rich in fluoride are **Flurospar**- CaF_2 (Sedimentary rocks, lime stones, sand stones); **Cryolite**- Na_3AlFPO_6 (Igneous, Granite); **Fluorapatite**- $Ca_3(PO)_2$ $Ca(FCl)_2$

Table 2.2: Sources of Fluoride in groundwater. (Hussain J, Sharma KC)

Minerals	Chemical composition	Rocks of these minerals
Fluorite (Fluorspar)	CaF_2	Pegmatite Pneumatolitic deposits as vein deposit
Flurapatite (Apatite)	$Ca(F_2Cl)PO_4$	Pegmatite & metamorphosed limestone.
Mica Biotite Muscovite	$K(MgFe^{+2})_3(AlSi_3)O_{10}(OHF)_2$ $KAl_2(AlSi_3O_{10})(OHF)_2$	Basalts Permatites, Amphiboites
Amphiboles Hornblende Tremolite Actinolite	$NaCa_2(MgFe+2)_4(AlFe+3)(SiAl)_8O_{22}(OHF)_2$ $Ca_2(MgFe+2)_5(Si_8O_{22})(OHF)_2$	Gneisses, schists, shales, Clay Aklaline rocks etc.
Topaz	$Al_2SiO_4(OHF)_2$	Acid, Igneous rocks, schists, gneisses etc.
Rock Phosphate	$NaCa_2(MgFe^{+2})_4(AlFe^{+3})(SiAl)_8O_{22}(OHF)_2$	Limestone, fossils etc.

2.2   The Hydro-geochemical cycle of Fluorine

The fluoride occurs mainly as fluorspar (CaF_2), sellaite (MgF_2), fluorapatite [$3Ca_3(PO_4)_2$ $Ca(F,Cl_2)$] and cryolite (Na_3AlF_6). As fluorspar it is found in sedimentary rocks and as cryolite it is found in igneous rocks. These fluoride minerals are nearly insoluble in water. Hence fluorides will be present in groundwater only when conditions favor their dissolution or when effluents containing high fluoride are discharged to the water bodies from industries. The hydro-geochemical cycle of fluorine is illustrated in Figure 2.1 (Mike Edmunds, 1998). The cycle involves the transfer of fluorine in nature by volcanic emissions, evaporation, marine aerosols, and industrial pollution. In the geosphere,

uptake and release of fluorine are controlled by various water-rock interactions and by inputs from anthropogenic sources (Ashley, 1994). Rainfall constitutes an important component of the fluorine cycle. Fluorine sources in rainfall include marine aerosols,
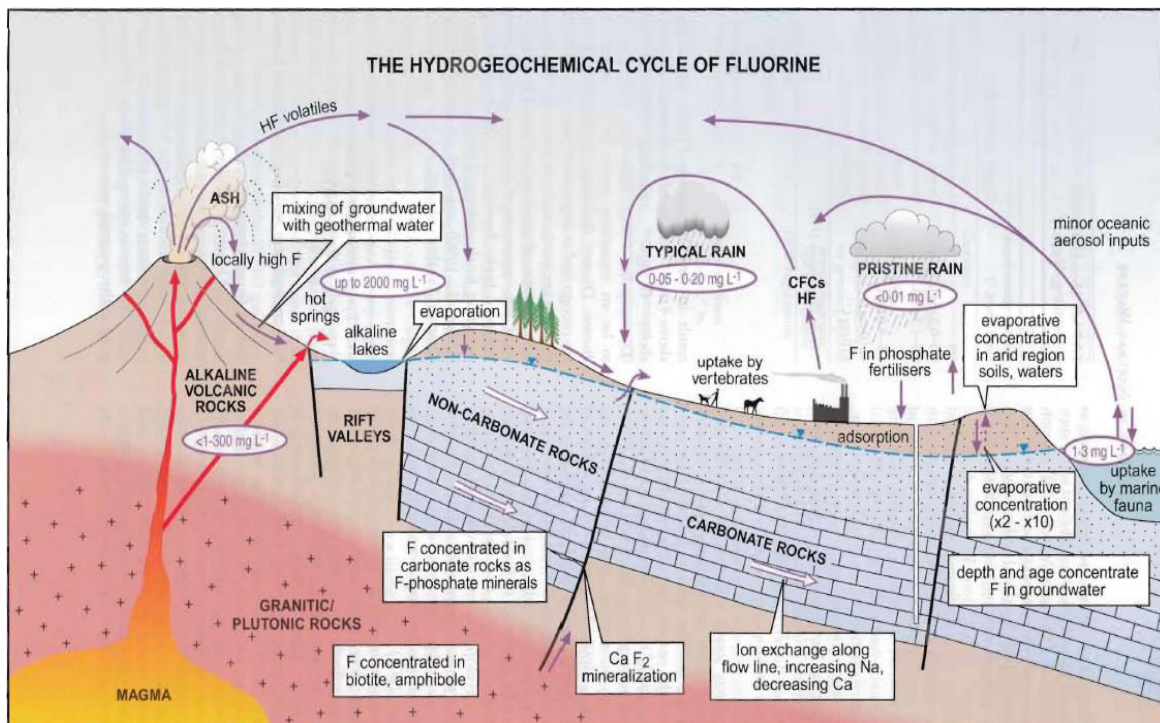
Figure 2.1: Schematic diagram showing the fluorine Hydro-geochemical cycle

volcanic emissions, recent introduction of (chlorofluorocarbons (CFCs), and industrial emissions. The industrial aerosols include production from coal burning, brick making, and aluminum smelting (Fuge, 1988). In many continental areas where the rainfall chlorine concentrations are near or below 1 mg/L, fluoride inputs to streams and ground waters from rainfall should be or below 0.1 µg/L. In fact, fluoride concentrations in the rainfall tend to be higher than these estimates, implying that some fractionation favors greater uptake of the more volatile fluoride at the sea surface or that the ratio is increased by atmospheric fluoride inputs.

The concentrations of fluoride in pristine rainfall are quite difficult to assess because the impacts due to human are likely to dominate in most areas. Comparative studies at inland and coastal sites in Virginia in the United States found median values of 4 and 9 µg/L, respectively (Table 2.3) and marine aerosol inputs were considered to be small (Barnard & Nordstrom, 1982). Such values are likely to reflect a large contribution from marine

aerosols. Neal (1989) reported typical fluoride concentrations in rainfall from Wales of 20-70 µg/L, which reflects in part marine influences. Occasional higher values up to 220 µg/L were interpreted as increased atmospheric inputs, presumably of anthropogenic origins. Saether and Andreassen (1989) found concentrations in Norwegian precipitation up to 253 µg/L. They used the correlation between sulfate and fluoride to suggest that anthropogenic contributions amount to as much as 98% of the total fluoride, which is derived principally from industrial aerosols.

Concentrations of fluoride in surface waters are generally much higher than in rainfall, though still typically in the l mg/L range. In the Bengal Basin, the Ganges Brahmaputra river system has mean fluoride concentrations in the range of 66-154 µg/L (Table 2.3) and rivers from southern Ghana have concentrations of around 30-140 µg/L (Table 1) (Botchway et al, 1916). In most cases, concentrations in surface waters are less than 300 µg/L. Despite these generally low concentrations, fluoride in surface waters can be much higher in geothermal areas and volcanic lakes in the East African Rift Valley, for example, have concentrations of the order of tens to hundreds of mg L-I (up to 1980 mg L-J; Table 2.3)

Table 2.3: Range of Fluoride in Various Natural Waters (Mike Edmund, 1998)

Country	Region/aquifer	Range of F (mg L⁻¹)	Average (mg L⁻¹)	Number of analyses	Reference
Rainfall					
Norway		0.0–0.253	0.013–0.025		Saether & Andreassen (1989)
USA	Virginia—coastal	0.002–0.02	0.009		Barnard & Nordstrom (1982)
	Virginia—inland		0.004		
Sri Lanka	Anuradhapura	<0.02–0.08	0.03	6	BGS (unpublished data)
UK	Chilton, southeast England		0.096	24	Edmunds et al. (1987)
UK	Mid Wales	0.02–0.22	0.02		Neal (1989)
UK	Loch Fleet, Scotland	<0.05	<0.05	10	Cook et al. (1991)
Surface waters					
India	Ganges River		0.154		Datta et al. (2000)
India	Meghna River		0.066		Datta et al. (2000)
India	Brahmaputra River		0.120		Datta et al. (2000)
UK	Hafren river, Wales	0.03–0.07	0.05		Neal (1989)
Ghana	Rivers, Accra region	0.03–0.14	0.09	5	Botchway et al. (1996)
Ghana	Ponds, Accra region	0.07–0.30	0.18	5	Botchway et al. (1996)
Surface waters in high-fluoride regions					
Tanzania, Kenya, Uganda	Lakes on alkaline volcanic rocks and others	0.2–1627		200	Kilham & Hecky (1973)
Ethiopia	River Awash	0.9–1.3	1.1	2	Ashley & Burley (1994)
Kenya	Streams bordering Lake Magadi	0.1–1.9	0.6	14	Jones et al. (1977)
Kenya	Lake Naivasha	1.7–1.8	1.75	2	Jones et al. (1977)
Tanzania	Lake Magadi	759–1980	1281	13	Jones et al. (1977)
Tanzania	Little Magadi Lake	668–754	711	2	Jones et al. (1977)
Tanzania	Lakes, alkaline volcanic area	60–690		9	Nanyaro et al. (1984)
Tanzania	Rivers, alkaline volcanic area	12–26		9	Nanyaro et al. (1984)
Soil water					
UK	Upland Wales	0.02–0.30	0.05		Neal (1989)

Country	Region/aquifer	Range of F (mg L⁻¹)	Average (mg L⁻¹)	Number of analyses	Reference
Geothermal springs					
Tanzania	Mbulu springs	up to 99			Bugaisa (1971)
Tanzania	Lake Natron thermal springs	330			Bugaisa (1971)
Kenya	Hot springs (>50°C) bordering Lake Magadi	141–166	7	155	Jones et al. (1977)
Kenya	Warm springs (<50°C) bordering Lake Magadi	50–146	14	82	Jones et al. (1977)
Tunisia	Hot springs	up to 4			Travi (1993)
USA	Western states	0.8–30.8			Nordstrom & Jenne (1977)
USA	Wister mudpots, Salton Sea	14–15			Ellis and Mahon (1977)
Iceland	Spring, Reykjavik	1.0			Ellis and Mahon (1977)
Iceland	Spring, Hveragerdi	1.1–1.9			Ellis and Mahon (1977)
Kamchatka	Spring	0.8			Ellis and Mahon (1977)
Former USSR	Spring, Makhachkala, Dagestan	0.4			Ellis and Mahon (1977)
New Zealand	Springs	0.3–8.4			Ellis and Mahon (1977)
Taiwan	Spring, Tatun	7.3			Ellis and Mahon (1977)
France	Vichy water	3.8–8.0			Goni et al. (1993)
France	Mont Dore springs	0.07–3.6			Jacob (1975)
France	Plombières springs	1.9–7.0			Fritz (1981)
China	Springs, Shixingsian, Guangdong	up to 45			Fuhong & Shuquin (1988)
Portugal	Rio Vouga hot springs	0.04–20.5	11.0	6	Ten Haven et al. (1985)
Groundwater: crystalline basement rocks					
Norway	Caledonian basic and ultrabasic rocks		1.89		Banks et al. (1998)
	Precambrian granite		1.69		Banks et al. (1998)
	Precambrian anorthosite, charnockite		<0.05		Banks et al. (1998)
Norway	Igneous and metamorphic rocks, Hordaland	0.02–9.48	0.30	1063	Bårdsen et al. (1996)
Ghana	Crystalline basement, including granite and metasediment	0.09–3.8	1.07	118	Smedley et al. (1995)
Senegal	Granitoids, pelites, schists, amphibolites	0.1–3.5			Travi (1993)
India	Crystalline basement, Andhra Pradesh	up to 20			Rao (1974)
India	Archaean granites and gneisses, east and southeast Karnataka	0.80–7.4	3.5	25	Suma Latha et al. (1999)
India	Archaean banded gneiss, southeast Rajasthan	<0.1–16.2	1.28	2649	Gupta et al. (1993)
India	Archaean granite	0.3–6.9		188	Vijaya Kumar et al. (1991)
Sri Lanka	Crystalline basement, including granite and charnockite	<0.02–10			Dissanayake (1991)
South Africa	Western Bushveld Complex	0.1–10	143	3485	McCaffrey (1998)
Groundwater: volcanic rocks					
Ethiopia	Volcanic bedrock (Wonji/Shoa area)	6.1–20.0	12.9	14	Ashley & Burley (1994)
Ethiopia	Pleistocene sediment above volcanic bedrock (Wonji/Shoa)	2.1–4.6	3.4	6	Ashley & Burley (1994)
Ethiopia	Pleistocene sediment above volcanic bedrock (Metahara)	2.7–15.3	5.9	15	Ashley & Burley (1994)

Country	Region/aquifer	Range of F (mg L^{-1})	Average (mg L^{-1})	Number of analyses	Reference
Tanzania	Ngorongoro Crater and Lemagrut volcanic cone	40–140			Bugaisa (1971)
Tanzania	Kimberlites, Shinyanga	110–250			Bugaisa (1971)
Groundwater: sediments and sedimentary basins					
China	Quaternary sands, Hunchun Basin, northeast China	1.0–7.8		19	Woo et al. (2000)
Argentina	Quaternary loess, La Pampa	0.03–29	5.2	108	Smedley et al. (2002)
India	Quaternary alluvium Agra, Uttar Pradesh	0.11–12.8	2.1	658	Gupta et al. (1999)
UK	Cretaceous Chalk, Berkshire	<0.1–2.4	0.74	22	Edmunds et al. (1989)
	Cretaceous Chalk, London Basin	0.11–5.8	1.44	21	Edmunds et al. (1989)
	Cretaceous Lower Greensand, London	<0.1–0.35	0.17	26	Edmunds et al. (1989)
	Triassic Sandstone, Shropshire	<0.1–0.17	<0.1	40	Edmunds et al. (1989)
	Triassic Sandstone, Lancashire	<0.1–0.14	0.1	16	Edmunds et al. (1989)
	Triassic Sandstone, Cumbria	<0.1–0.26	<0.1	23	Edmunds et al. (1989)
Canada	Carboniferous clastic rocks, Gaspé,	0.02–28	10.9	20	Boyle & Chagnon (1995)
	Alluvial/glacial (<30m depth)		0.09	39	Boyle & Chagnon (1995)
Canada	Non-marine Upper Cretaceous sediments, Alberta Basin	0.01–22.0	1.83	469	Hitchon (1995)
Germany	Cretaceous Chalk Marls	<0.01–8.9	1.28	179	Queste et al. (2001)
Libya	Miocene, Upper Sirte Basin	0.63–3.6	1.4	11	Edmunds (1994)
Sudan	Cretaceous, Nubian Sandstone (Butana area)	0.29–6.2	1.8	9	Edmunds (1994)
Senegal	Palaeocene sediments	1.5–12.5		26	Travi (1993)
Senegal	Maastrichtian sediments	1.1–5.0		32	Travi (1993)
Tunisia	Cretaceous to Quaternary sediments	0.1–2.3		59	Travi (1993)
USA	Carboniferous sediments, Ohio	0.05–5.9		255	Corbett & Manner (1984)

2.3   Fluoride prevalence in the world

Groundwater is one of the major sources for various usages, specially drinking in most parts of the world. Presence of low or high concentration of certain ions is a major issue as they make the groundwater unsuitable for different purposes.

Fluoride is one such ion that causes health problems in people living in more than 25 nations around the world. Fluoride concentration in water, of at least 0.6 mg/l is required for human consumption as it will help to have stronger teeth and bones. The figure shows the Fluoride presence in the water above 1.5 mg/L. Fluoride in water is mostly of
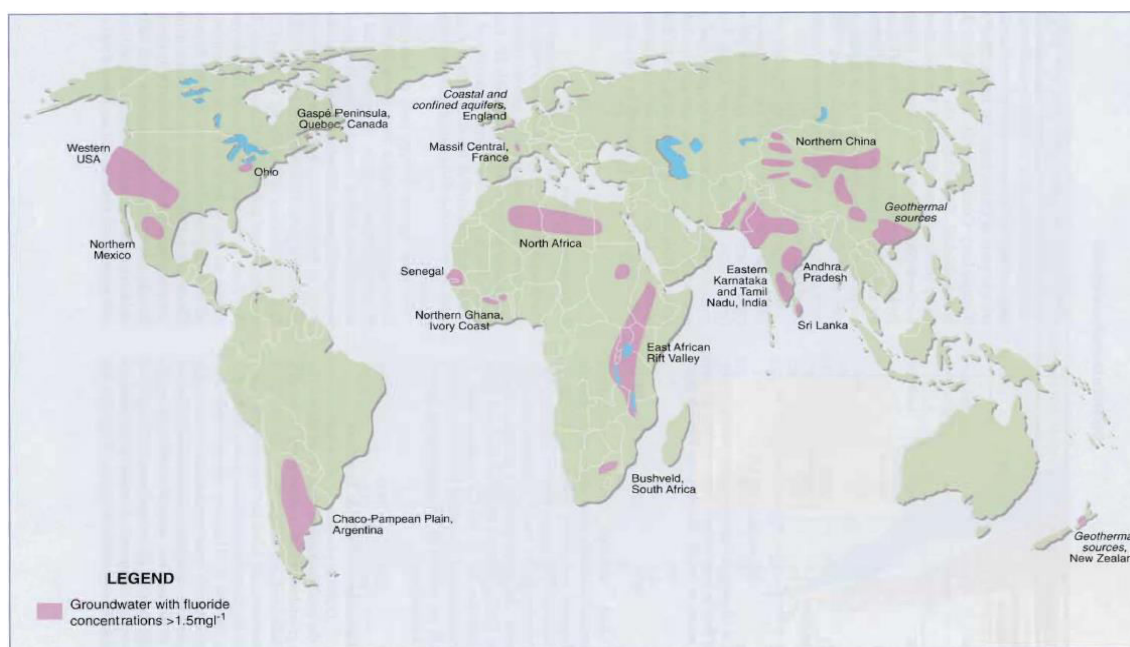
Figure 2.2: Map of the world showing areas with Fluoride above 1.5 mg/L (Mike Edmund.1998)

geological origin. Waters with high levels of fluoride content are mostly found at the foot of high mountains and in areas where the sea has made geological deposits. Known fluoride belts on land include: one that stretches from Syria through Jordan, Egypt, Libya, Algeria, Sudan and Kenya, and another that stretches from Turkey through Iraq, Iran, Afghanistan, India, northern Thailand and China. There are similar belts in the Americas and Japan. In these areas fluorosis has been reported (WHO). Figure 2.2 shows the distribution of fluoride in the world. Presence of high or low concentration of fluoride in groundwater is because of natural or anthropogenic causes or a combination of both

natural sources are linked to the geological conditions of the area. Several rocks have fluoride bearing minerals like apatite, biotite, fluorite and hornblende. The weathering of these rocks and infiltration of rainfall through it increases fluoride concentration in groundwater. Fluoride which is present in high concentration in volcanic ash is readily soluble in water and forms another natural source. Anthropogenic sources of fluoride include agricultural fertilizers and combustion of coal. Phosphate fertilizers contribute to the fluoride in irrigation lands which washes in the groundwater and nearby surface water resource. Coal, which is a potential source of fluoride, is used for combustion in various industries and in brick kilns. The aerial emission of fluoride in gaseous form during these activities reaches the surface by fall out of particulate fluorides and during rainfall they percolate with the rainwater thus reaching the groundwater table. Also the improper disposal of fly ash on ground surface contributes to fluoride in groundwater.

Since ingestion of high fluoride has a long term effect on human health it is essential to monitor its concentration in groundwater used for drinking periodically and take steps to bring them within permissible range of 0.6 to 1.5 mg/l. There are several in-situ and ex-situ methods available for the removal of fluoride from groundwater. To dilute the groundwater contaminated with fluoride, artificial recharging structures can be built in suitable places which will decrease its concentration.

Rainwater harvesting through existing wells also will prove effective to reduce the groundwater fluoride concentration. Ex-situ methods which are conventional treatment methods like **adsorption, ion exchange, reverse osmosis, electro dialysis, coagulation and precipitation** etc. can be practiced at community level or at households to reduce fluoride concentration before ingestion. But the choice of each method depends on the local conditions of the region such as the quality of groundwater and the source of contamination whether it is natural or anthropogenic. Fluoride contamination is a prominent and wide spread issue in several parts of the world. The causes for this are mostly natural and unpreventable; hence educating people about fluoride is essential for a healthy world.

2.4   Fluoride in Indian States

An attempt has been made to trace the State-wise geological reasons for high fluoride content in Indian waters:

Jammu and Kashmir and Himachal Pradesh:

Geologically, the area where form the high fluoride concentration is reported has three distinct belts separated by major tectonic features. The Southern belt essentially consists of gneiss, schist, granite, lensoid of Proterozoic age and represents the Indian plate. Several phases of igneous intrusions have been identified in these rocks. Therefore, in all probabilities, the high concentration of fluoride could be due to the presence metamorphic gneiss present in the region.

Rajasthan:

Fluorides in drinking water of Rajasthan have been found to originate from indigenous rocks, which extend from Delhi to Gujarat. The geological distribution of rocks in Rajasthan reveals that fluorotic ores occupy large areas of eastern and southeast parts of this state, in constricted synclinal bands in the central region of Aravali synchronium. Secondly, around the mica mines, ground water is rich in fluorides and Rajasthan is a rich source of mica. All the 32 districts have been declared as fluorosis prone areas. The worst affected districts are Nagaur, Jaipur, Sikar, Jodhpur, Barmer, Ajmer, Sirohi, Jhunjhunu, Churu, Bikaner, Ganganagar etc. The presence of Bundel gneiss complex appears to be the cause of high fluoride content in waters from the Bhilwara region.

Table 2.4: Fluoride affected states (D.D. Ozha, 2003)

Percentage extent	Affected States
50-100%	Andhra Pradesh, Tamil Nadu, Uttar Pradesh, Gujarat, Rajasthan
30-50%	Bihar, Haryana, Karnataka, Maharashtra, Madhya Pradesh, Punjab, Orissa, West Bengal
< 30 %	J & K, Delhi, Kerala

Haryana:

In Sohna, the main rock types are quartzite, schist, siliceous limestone, slate and phyllite (Singh et al., 1996) where from the water sample analysis results have been picked up does not show the presence of high fluoride due the absence of hornblende gneiss in the region.

Bihar and West Bengal:

The high fluoride values in the water may be due to leaching of fluoride from the hornblende gneiss and granulites (Mukhopadhyay, 1996) reported and well documented in the region.

Chattisgarh:

The area is covered by Proterozoic and Gondwana Group of rocks. The Proterozoic comprises grey, pink gneiss and hornblende gneiss. Therefore, the leaching of fluoride from the hornblende gneiss of Proteozoic age appears to be main source of fluoride in thermal water at Tattapani (Sarolkar, 1996).

Orissa and Maharashtra:

Composition of solution in these two areas appears to be the result of reaction of volcanic rocks like Basal, Andesite and Dacite with water at high temperature and pressure (Girhe, 1996) thus giving rise to high content of fluoride in the water.

2.5   Fluoride prevalence in Rajasthan

Rajasthan is located in the North-West part of India. The status of availability and
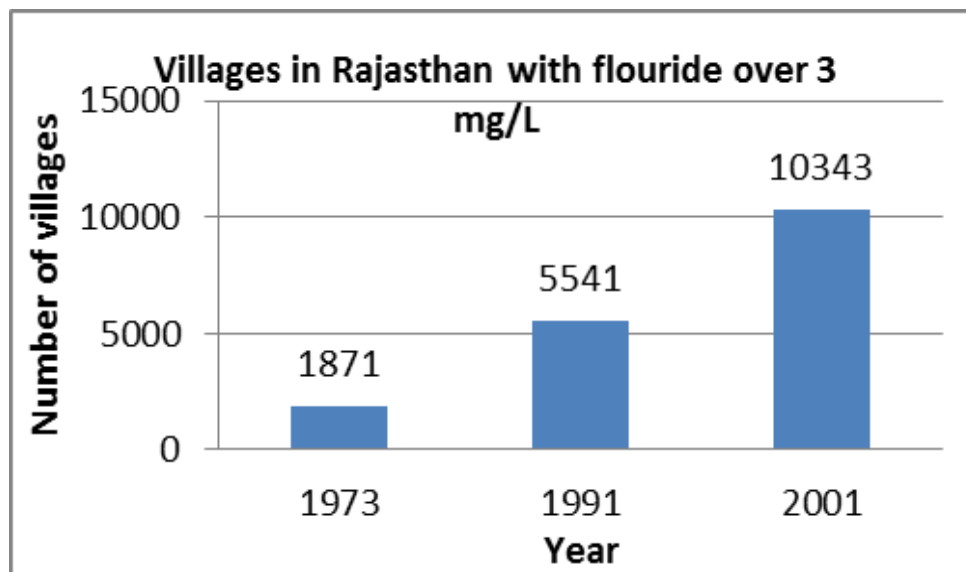
Figure 2.3: Increase in Fluoride in villages of Rajasthan above 3 mg/L
(PMSC, 2013)

utilization of water in Rajasthan is quite critical. Rajasthan is the largest State of the country. It has about 10.5% area; 5.5% population and 18.7% livestock of the country but has only 1.16% surface water and 1.72% ground water of the country (Dhingra, 2001). The ground water condition in the Rajasthan is quite alarming. The stage of ground water exploitation, which was just 35% in the year 1984, has reached a level of 125% in 2004. Only 25 of the 243 blocks in the State are categorized as "safe" with respect to groundwater availability. (JICA, 2001)

A recurring feature in the State is the uncertainty of rainfall, which only aggravates the drought and famine conditions. The situation is worst in the eastern part of Rajasthan, which is adjacent to the Thar Desert. With ever growing population and water demand, the water availability (per capita) is also dwindling year after year. As per present estimation, per capita water availability is about 640 cum per year against international standards of 1000 cum per year. It is apprehended that this may further reduce to 440 cum by the year 2025. (WHO, 1994)

Fluorides in drinking water of Rajasthan are found to originate from various rocks. These rocky belts extend from Delhi to Gujarat. The geological distribution of rocks in Rajasthan reveals that the fluoride yielding ores occupies large areas of eastern and southeast parts of the state. Also, Rajasthan has mica mines, where the ground water is rich in fluorides.
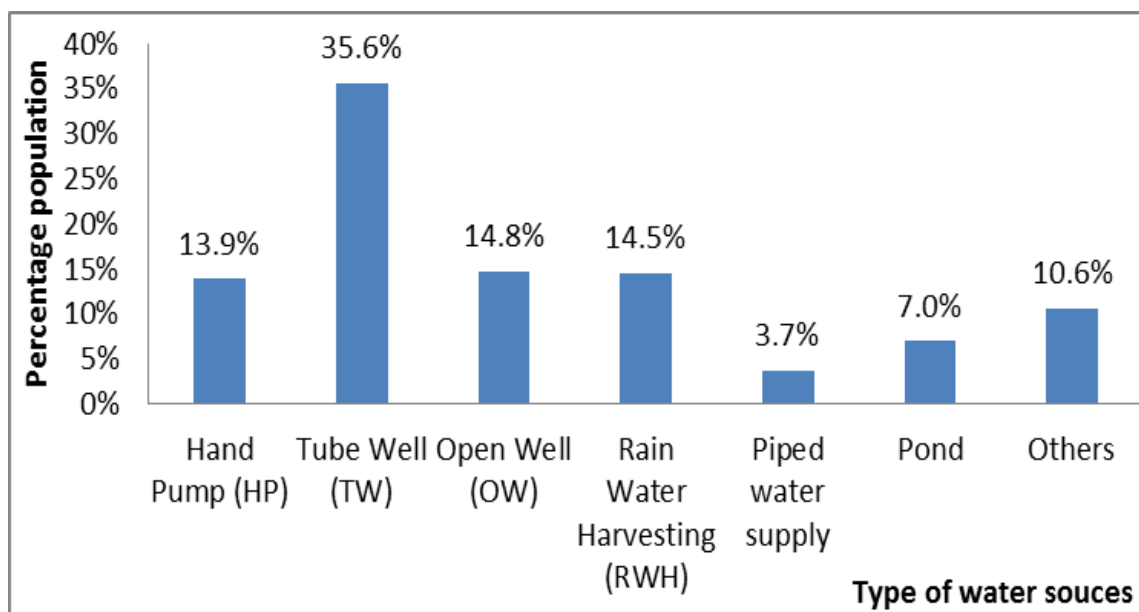
Figure 2.4: Water sources and its usage in excess Fluoride regions in Rajasthan (PMSC, 2013)

As seen in Figure, the number of villages affected by fluoride has increased over time. In 1973, there were 1,871 villages with fluoride levels over 3mg/l. By 2001, this number had risen to 10,342 villages, an increase of more than five times. This makes Rajasthan the most severely affected state in India, with millions crippled as the result of consuming excessive amounts of fluoride (Hindu, 2008). All the 32 districts have been declared as fluoride prone areas. Among all the districts worst affected are Nagaur, Jaipur, Sikar, Jodhpur, Barmer, Ajmer, Sirohi, Jhunjhunu, Churu, Bikaner, Ganganagar etc. People in some of these districts in Rajasthan are consuming water with fluoride concentrations up to 24 mg/l. Rajasthan has more than 51 per cent of the affected villages in the country. Table 2.3 in the last gives the detail about the district with fluoride re than 1.5 mg/L and 3 mg/L Figure 2.4 shows the major water sources for drinking, cooking and other

household demands (HP- Hand Pump,, TB-Tube Well, OW- Open Well, RWH- Rain Water Harvesting, PWS- Piped Water Supply).

2.6   Mitigation of Fluoride problem in Rajasthan:

The people of western Rajasthan have been practicing rain water harvesting, by collecting rainwater from roof tops or pucca surfaces or collecting it in small surface
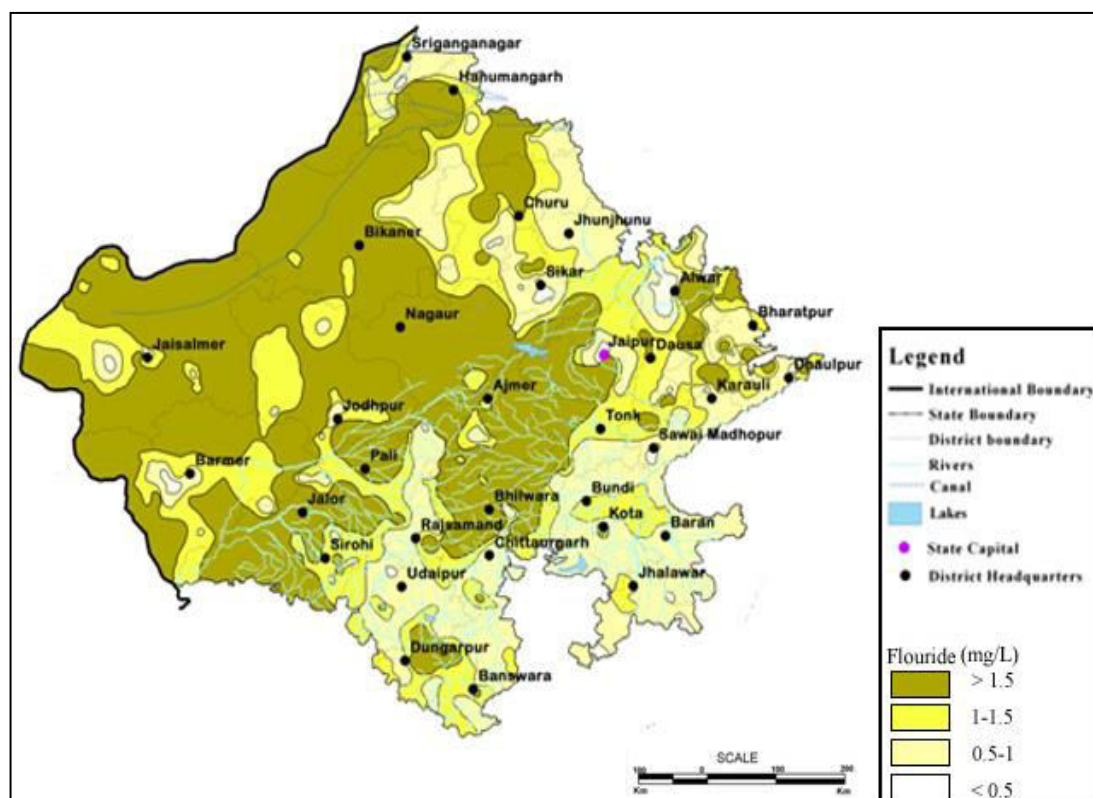
Figure 2.5: Map of Rajasthan showing Fluorde variation in the state.

ponds. The salinity in ground water has been the major cause of this practice and not much was known about fluoride in particular, except for the fact that they knew about the ill effects of the ground water on body which the rain water didn't have. In the last few decades, thousands of tube wells and hand pumps have been dug in all the districts to provide drinking water to rural areas. The other districts didn't know about the wise water practice of rain water harvesting and hence fell victim to the ill effects of fluoride as the ground water quality has gradually deteriorated throughout the state. Figure 2.5 shows the distribution of fluoride throughout the state.

The government with support of NGOs like UNICEF and others took up the issue and

launched massive community awareness programme and implemented ways and methods to provide safe drinking water. Efforts were made to treat fluoride through user friendly methods.

The Nalgonda technique (using lime and alum to treat fluoride) developed by NEERI

Figure 2.6: A DDFU unit

proved to be too cumbersome and failed. The only alternative available was to depend on

Figure 2.7: Rainwater harvesting tank (popularly called *taanka*) on a road side in one of the fluoride hit area of Rajasthan

surface water sources, which was too expensive and was likely to take years to cover each and every village. Also, there were not many dependable surface sources. Figure 2.7 shows a RWH tank near a road way. This catchment is called as *taanka* in the local language.

Then the adsorption method of fluoride using Activated Alumina was introduced. It was developed by IIT-Kanpur with UNICEF support. The government launched Rajasthan Integrated Fluoride Mitigation Programme (RIFMP). The habitations having more than 5 mg/L fluoride in ground water were targeted in RIFMP Phase-I and those having 3-5 mg/L were addressed to in the phase-II. In both the phases, Domestic De-fluoridation Units (DDFUs) (Figure 2.6) based on adsorption by activated alumina were distributed through NGOs, who were supposed to educate people and train them in using the DDFUs.

Despite huge effort, phase-I and phase-II couldn't bring the desired success except for

Figure 2.8: A filter from a large size De-fluoridation and De-salination plant at Nagaur (Rajasthan)

increased awareness in almost all the rural areas of Rajasthan. The major issues linked with the failure were; regeneration of AA, free distribution of DDFUs to BPL and on payment to APL, the people looking at the government for piped water supplies etc. On the basis of learning from the phase-I and II, the government launched the phase-III wherein the hand pump and tube well attached large size DDFUs have been installed through private agencies who would operate and maintain the units for 10 years in addition to educating the people. This has brought appreciable success. Figure 2.8 shows a DDFU unit.

Under the GoI supported NRDWP, rain water harvesting and ground water recharge have also been taken up in a big way. But using rain water for drinking hasn't been popular in most of the districts due to the habit and socio cultural reasons. Installation of large size RO plants has also been taken up wherein a private agency installs and operates and maintains the units and the villagers are required to pay 10 paisa per liter for the treated drinking water.

The mega RO plant at Matasukh (Nagaur) (Figure 2.8), treating 10 MLD saline water from coal mines, is one of its own kind in the country. After all the experience and learning the government of Rajasthan aims at covering the whole state by providing safe drinking water from surface sources.

The spot treatment of ground water is likely to continue as an interim measure till all the villages start getting water supply from major projects depending on surface water. Bisalpur dam, IGNP canal, River Chambal and a number of other dams are the major surface sources of water for most of the major projects. Figure 2.7 shows a roadside small Rain water harvesting tank. Water gets collected in the tank

2.7   Effect of Fluoride on human health:

Fluoride in drinking water has a profound effect on teeth and bones. Up to a small level (1–1.5 mg/L) this strengthens the enamel. Concentrations in the range of 1.5–4 mg/L result in dental fluorosis whereas with prolonged exposure at still higher fluoride concentrations (4–10 mg/L) dental fluorosis progresses to skeletal fluorosis. High fluoride concentrations in groundwater, up to more than 30 mg/L, occur widely, in many parts of the world.

Table 2.5: Fluoride concentration and effect on human health (Sengupta, 1937)

F⁻ concentration, (mg/L)	Health outcome
<0.5	Dental caries
0.5–1.5	Optimum dental health
1.5–3.0	Dental fluorosis/ mottled enamel
3.1-6.0	Osteoporosis
20-80 mg/day or more in water or air	Crippling skeletal fluorosis
50 mg/l in food or water	Thyroid change
100 mg/l in food or water	Growth retardation
More than 125 mg/l in food or water	Kidney change
2.5 – 5.0 gm in actual dose	Death

2.7.1   Main sources of fluoride for humans:

Water: Although there are several sources of fluoride intake, it is roughly estimated that 60% of the total intake is through drinking water. This is the most assimilable form of fluoride and hence the most toxic.

Food: The fluoride of food items depends upon the fluoride contents of the soil and water used for irrigation, therefore the fluoride content of the food items may vary from place to place. (Sengupta, 1937)

Drugs: Prolonged use of certain drugs has been associated with the chronic adverse effects of fluoride e.g. sodium fluoride for treatment of osteoporosis, Niflumic acid for the treatment of rheumatoid arthritis, use of fluoride mouth rinse (Proflo) to render the tooth stronger. (Lakdawala, 1973)

Air: The use of fluorides in industry leads to occupational exposure e.g. inorganic

Figure 2.9: Mottled teeth and deformed legs due to consumption of
water with excessive Fluoride concentration.

fluoride compounds are used in the production of aluminum. Fluorides are also released during the manufacture and the use of phosphate fertilizers.

Figure 2.9 show three images of a kid having deformed legs and mottled teeth due to consuming fluoride rich water.

Cosmetics viz. Toothpaste's & Mouth Rinses: Highly significant associations were found between estimated fluoride ingestion from toothpaste and fluorosis. (Rock-WP, 1997) The fluoride content arising from the raw material used for the manufacturing of paste viz. calcium carbonate, talc and chalk have high fluoride arising as a contaminant from raw materials; can be as high as 800-1000 ppm. In the fluoridated brands, there is a deliberate addition of fluoride, which may range form 1000-4000 ppm. (Levy SM, 1997)

2.8   Methods used for de-fluoridation of water:

The main objective in fluoride removal is to treat the contaminated water so as to bring down fluoride concentration to acceptable limits. The de-fluoridation techniques can be broadly classified into two categories; **Membrane technique and Adsorption techniques.**

(High concentrations of fluoride in **industrial effluents** are usually brought down to about 30 mg/L following precipitation method making use of calcium/magnesium/barium hydroxide slurry to reject fluoride as CaF_2, MgF_2 or BaF. These methods are not being discussed as these are beyond the scope of this review)

2.8.1   Membrane technique

Membrane technique comprises of **reverse osmosis, nano-filtration, dialysis and electro-dialysis**:

2.8.1.1 Reverse osmosis and nano-filtration

This process produces water of extremely high purity (Schneiter and Middlebrooks, 1983). It was observed that the rejection of fluoride ion was typically higher than 98%, considering that the RO membrane was fully regenerated after each set of experiments (Arora, 2004). Nano filtration technology uses the same overall phenomenon as reverse osmosis (RO). For nano-filtration, the membranes have slightly larger pores than those used for RO and offer less resistance to passage both of solvent and of solutes. As a consequence, pressures required are much lower, energy requirements are less, removal of solutes is much less exhaustive, and flows are faster. Retention of solutes is attributed mainly to steric and charge effects and although fluoride is a very small ion it is more strongly hydrated than other monovalent anions because of its high charge density, and the consequent steric effect leads to fluoride being more strongly retained on nano-filtration membranes than the competing monovalent anions such as chloride or nitrate, a particular advantage in de-fluoridation of brackish waters. Many configurations are used: simple pass, double pass with one type of membranes and combination of two types of membranes and supplied batch configuration. The water parameters are followed as a

function of the running conditions (time, pressure, fluoride content, etc.) in order to follow the behavior of the membranes tested.

2.8.1.2 Dialysis and electro-dialysis

Dialysis separates solutes by transport of the solutes through a membrane rather than using a membrane to retain the solutes while water passes through it as in reverse osmosis and nano-filtration. The membrane pores are much less restrictive than those for nano-filtration, and the solute can be driven through by either the Donnan effect (Donnan, 1911) or an applied electric field. In the Donnan dialysis process a counter current flow system is established in which the anion-exchange membrane is loaded with sodium chloride and the fed is 0.001 M NaF together with other sodium salts. Fluoride migrates into the receiver as other ions migrate into the feed. This technique was later used to de-fluoridate solutions made to simulate high fluoride African ground waters (>30 mg/L fluoride) and whatever other ions were present the fluoride in the feed could be brought below 1.5 mg/L (Hichour et al., 2000). It was observed that the transport of fluoride was maximum at pH 6 of feed phase and at pH 1 of receiver phase.

Electro-dialysis is the removal of ionic components from aqueous solutions through ion exchange membranes under the driving force of an electric field. De-fluoridation using natural chitosan as an absorbent and electro-dialysis has been compared, and both approaches have been found to bring the fluoride level to within WHO guidelines (Annouar et al., 2004). In other projects for de-fluoridation of high fluoride groundwater, the efficiency study of the process by linking electro-dialysis in tandem with chitosan adsorption has been studied. Results have showed that electro-dialysis can de-fluoridate water with 3000 mg/L total dissolved salts and 3 mg/L fluoride.

2.8.2   Adsorption technique

Although membrane methods have successfully reduced fluoride concentration to acceptable levels, surface adsorption retains a major place in de-fluoridation research and practice because of its general greater accessibility and lower cost. Thus even in the past decade, when interest in alternative de-fluoridation approaches has been increasing rapidly, many researchers have continued to explore the development of low-cost and

effective adsorbents and to improve the efficiency of all adsorbents (Biswas et al., 2007). The nature of adsorption of fluoride on some adsorbents, especially clays which contain oxides of iron, Aluminum and silicon, has been reviewed by Puka (2004) as background for his own experimental studies to improve the understanding of fluoride–adsorbent interactions. Theoretically, the adsorption of fluoride on to solid particles normally takes three essential steps (Fan et al., 2003):

- Diffusion or transport of fluoride ions to the external surface of the adsorbent from bulk solution across the boundary layer surrounding the adsorbent particle, called external mass transfer;

- Adsorption of fluoride ions on to particle surfaces;

- Adsorbed fluoride ions probably exchange with the structural elements inside adsorbent particles depending on the chemistry of solids, or the adsorbed fluoride ions are transferred to the internal surfaces for porous materials (intra particle diffusion).

Evaluating an adsorbent for practical purposes, however, requires consideration of adsorption capacity in dilute solutions, pH, time for fluoride removal, stability of adsorbent, regeneration, and loading capacity in presence of other anions and cation and finally the overall cost for fluoride removal. But various adsorbents cannot be readily compared with respect to adsorbent loads, initial fluoride concentrations, and the varied dependent parameters reported. A wide variety of adsorbents have been used for the removal of fluoride from water. These include activated and impregnated alumina (Fan et al., 2003), rare earth oxides (Raichur and Basu, 2001), activated clay, impregnated silica (Wasay et al., 1996b), carbonaceous materials, solid industrial wastes like red mud, spent catalysts and fly ash, zeolites and related ion exchangers (Rao and Bhaskaran, 1988) bio adsorbents (Mohan et al., 2007) alum, alum sludge (Sujana et al., 1998) and modified chitosan (Jagtap et al., 2009) in addition to those considered under the heading of membrane techniques and more recently including layered double hydroxides.

While many adsorption systems have been studied, few adsorbents take the concentration of fluoride down to or below the 1.0–1.5 mg/L level which is required for drinking water

and for effluent water that could find its way into drinking water sources (Tripathy et al., 2006). However, less stringent limits for effluent that is not to be released in sensitive locations are readily reached. For example in New South Wales a fluoride concentration of 20 mg/L is the maximum concentration permissible before the waste becomes a controlled liquid waste requiring a license for transport and disposal (EPA, 1999).

2.8.2.1 Alumina and Aluminum based adsorbents

Alumina. In early experiments it was investigated that the interaction of fluoride ion with amorphous Aluminum hydroxide ($Al(OH)_3$), gibbsite (naturally occurring Aluminum hydroxide) and Aluminum oxide (Al_2O_3) over a range of pH values from 3 to 8 was high. Gibbsite displayed the same dissolution trends, but reacted at a much slower rate. Little F- was adsorbed by this substrate (10–20 mmol/kg or 0.2–0.4 mg/g). The study has confirmed the ability of fluoride to mobilize Al and the capacity of $Al(OH)_3$, to scavenge F^- from aqueous phases in the pH 4–7 region. It was reported that the adsorption characteristics of fluoride onto hydrous alumina. To be an effective adsorbent, alumina must be activated by heating. It is the less crystalline product that is the most rapid and effective adsorbent for fluoride, as it has a surface area well over 200 m^2 per gram of alumina. The selectivity sequence of anion adsorption (Johnston and Heijnen, 2002) on activated alumina in the pH range of 5.5–8.5 has been reported to be:

$$OHL > H_2AsOL_4 > SiOH_3OL > HSeOL_3 > FL > SO_2L_4 > CrO_2L4 >> HCOL_3 > ClL > OL_3 > BrL > IL$$
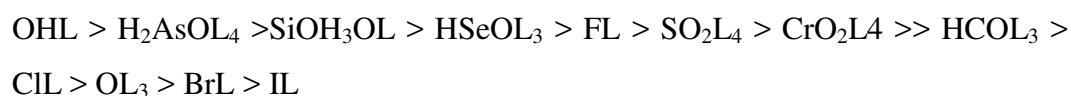
Activated alumina can be regenerated by flushing with a solution of 4% sodium hydroxide which displaces fluoride from the alumina surface (Schoeman and MacLeod, 1987). This procedure is followed by flushing with acid to re-establish a positive charge on the surface of the alumina. A major disadvantage of adsorption on activated alumina is that pH needs to be on the acid side of 7 and dissolution of some Aluminum oxide/hydroxide is inevitable, releasing toxic Aluminum ions.

The efficacy of alum-impregnated activated alumina (A/AA) in removal of fluoride from water was found to be 92.6% at pH 6.5, contact time 3 h, A/AA dose of 8 g/L, when 25 mg/L fluoride was initially present (Tripathy et al., 2006). This left 1.9 mg/L fluoride in

solution. The EDAX analysis showed that the uptake of fluoride at the A/AA/water interface is due only to surface precipitation.

2.8.2.2 Alumina plus manganese dioxide.

Maliyekkal (et al. 2006) reported that a new adsorbent manganese oxide-coated alumina (MOCA) was able to bring fluoride concentration below the statutory 1.5 mg/L for drinking water and was faster-acting than activated alumina and had a greater fluoride load capacity (2.85 mg/g compared with 1.08 mg/g for activated alumina). Tripathy and Raichur (2008) found that manganese dioxide-coated activated alumina could bring fluoride concentration down to 0.2 mg/L when the initial concentration of fluoride in water is 10 mg/L. Maximum adsorption relative to adsorbent dose took place at pH 5.5. From observation of kinetics and zeta-potential measurements, isotherm modelling and energy-dispersive X-ray analysis (EDAX) the authors concluded that the uptake of fluoride occurred through physical adsorption as well as initial intra particle diffusion at the porous surface. The adsorption of fluoride was found to decreases in the presence of other ions.

2.8.2.3 Alumina plus magnesium oxide.

Recently Maliyekkal et al. (2008) described a magnesia-amended activated alumina (MAAA) prepared by impregnating alumina with magnesium hydroxide and calcining the product at 450°C. MAAA adsorbed fluoride from drinking water more effectively than activated alumina. More than 95% removal of fluoride (10 mg/L) was achieved within 3 h of contact time at neutral pH, bringing concentration down to only 0.5 mg/L. Adsorption of fluoride on to MAAA was found to be pH-dependent and a decrease in sorption was observed at higher pH. The maximum sorption capacity for fluoride was 10.12 mg/g. Most of the co-existing ions found in the natural water source studied had negligible effect on fluoride sorption by MAAA. However, higher concentrations of bicarbonate and sulphate reduced the fluoride sorption capacity.

2.8.2.4 Alumina plus iron oxide.

When Aluminum and iron(III)vhydroxides are co-precipitated from a chloride mixture in equimolar quantities using ammonia, the resulting mixed hydroxide, after aging and

drying, is a better adsorbent for fluoride than either Aluminum hydroxide or iron(III) hydroxide (Biswas et al., 2007). It was showed that the pplymer has almost irregular surface morphology with high porosity, indicative of a high surface area. The monolayer adsorption capacity of the mixed hydroxide, derived from Langmuir isotherms, was greater than for the pure hydroxides. Chubar et al. (2005) studied the anion adsorption capacity of an adsorbent precipitated from equimolar Aluminum and iron(III) chloride by addition of ammonia. The anions investigated were fluoride, chloride, bromide and bromate. At pH 4, fluoride was the most strongly adsorbed at 88 mg per gram of adsorbent.

2.8.2.5 Alumina plus calcium minerals.

The Nalgonda technique, named after the village in Andhra Pradesh, India, where the method was pioneered, is based on adsorption of fluoride on flocs of Aluminum hydroxide as they are formed in solution. Long back Nawlakhe et al. (1975) reported on this technique. Two chemicals, alum (Aluminum sulphate or potassium Aluminum sulphate) and lime (calcium oxide) are rapidly mixed with the fluoride-contaminated water. Induced by subsequent gentle stirring, ''cotton wool''- like flocs develop (Aluminum hydroxides) which carry most of the dissolved fluoride and are removed after being allowed to settle. The Nalgonda technique has been introduced in many countries, e.g. India, Kenya, Senegal and Tanzania. One household version uses a pair of 20–liter buckets, with a settling time of one hour but not more than two hours: after coagulation and settling are complete, the treated water is withdrawn through a tap 5 cm above the bottom of the first bucket, safely above the sludge level, and stored for the day's drinking in the second bucket. The adopted dosages of 12.8 g alum and 6.4 g lime in the villagers' 20-L buckets had been reducing the fluoride concentration to 0.7-2.1 mg/L which was still above the WHO-recommended limit of 1.5 mg/L. Although it has been claimed that the Nalgonda process is the most effective technique for fluoride removal, critics have identified disadvantages:

- The process removes only a smaller portion of fluoride (18–33%) in the form of precipitates and converts a greater portion of ionic fluoride (67–82%) into soluble

Al3þ–F⁻ complex ions which are themselves toxic (Apparao and Kartikeyan, 1986).

- The concentration of the SO4 2- ion from the Aluminum sulphate coagulant reaches high levels, and in a few cases it crosses the maximum permissible limit of 400 mg/L.

- The residual Aluminum in excess of 200 ppb in treated water is believed to cause dementia and also affects musculoskeletal, respiratory and cardiovascular systems.

- Many users do not like the taste of the treated water.

- Regular analysis of feed and treated water is required to calculate the correct dose of chemicals to be added, because the water matrix fluctuates with time and season.

- The maintenance cost of a community plant is high. On an average as experienced in the recent years, a plant of 10,000 L per day capacity requires Rs. 3000 every month.

- The process is not automatic. It requires a regular attendant during treatment process.

- Large space is required for drying of sludge.

- Silicates have adverse effect on de-fluoridation by Nalgonda technique. Temperature also affects the de-fluoridation capacity.

2.8.2.6 Bauxite.

Das et al. (2005) studied the adsorption of fluoride on thermally activated titanium-rich bauxite (TRB). Thermal activation at moderate temperatures (300–450$^{\text{o}}$C) greatly increased the adsorption capacity of TRB. Adsorption was rapid and maximum level was attained within 90 min. The uptake of fluoride increased with increasing pH, reaching a maximum at pH 5.5–6.5 and thereafter decreased. The presence of common interfering

ions in drinking water did not affect the uptake of fluoride from aqueous solution indicating fluoride-specific sorption behavior of TRB.

2.8.2.7 Red mud

Aluminum and iron oxides are major components of red mud, and this mixed adsorbent has been studied extensively as an adsorbent for anionic pollutants, especially anions from arsenic(III) and arsenic(V), because of its availability and low cost (White et al., 2003). Table 2 shows a typical composition of an Australian red mud. As recovered from the Bayer process, red mud is too alkaline (pH 10–12) for use as an adsorbent for anions. The alkalinity can be reduced by washing with sea water (White et al., 2003), and on a laboratory experiments the pH can be adjusted with strong acid or base. After treatment for two hours at the optimum pH of 5.5, the activated red mud could remove only 77% of 21 mg/L fluoride, leaving 2.7 mg/L fluoride in solution which was still higher than the acceptable levels.

2.8.2.8 Lateritic ores.

Nickel laterites and chromite mine overburden usually contain high content of iron and small amounts of alumina, chromium, cobalt, nickel, manganese. Due to their high iron content in the form of goethite, some studies have been reported for fluoride adsorption (Sarkar et al., 2006). Recently Sujana et al. (2009b) have compared the fluoride uptake capacity of various goethite containing geo materials of India. Effect of various experimental parameters such as time, temperature, pH, and adsorbent and adsorbate concentration has been reported. The kinetic, isothermic and thermodynamic parameters were evaluated. Groundwater samples were also tested for fluoride removal.

2.8.2.9 Clays and soils

The first comprehensive study of fluoride adsorption on to minerals and soils was published in 1967 (Bower and Hatcher, 1967). Since then there have been a large number of studies including the use of Ando soils of Kenya, Illinois soils of USA, Alberta soil, illite-goethite soils in China, clay pottery, fired clay, fired clay chips in Ethiopia, bentonite and kaolinite and fly ash.

a.   Clay

Bower and Hatcher (1967) had indicated that the adsorption of fluoride on to minerals and soils is accompanied by the release of OH^- ions. It was also found that the fluoride adsorption is concentration-dependent and it is described by the Langmuir adsorption isotherm. The structure of the clay plays a key role in determining the charge on the clay surface and type of exchange that can occur with ions in solution (Puka, 2004). In general the more positive the surface the better the sorption will be for negatively charged ions, such as fluoride. Adsorption capacity is strongly pH-dependent as pH modifies the charges on edge positions in phyllosilicates and also those of variably charged minerals such as gibbsite, haematite and goethite. Charges are generally positive under acid conditions and negative in an alkaline environment. The specific pH range for positive and negative surface charge will depend on the pKa values of the conjugate acids of the metal hydroxides present. (Puka, 2004).

b.   Fired clays

Researchers have studied the removal of fluoride using fired clays (Hauge et al., 1994). Hauge's group investigated the effect of firing temperature on fluoride adsorption by pottery. The rate and capacity of F^- binding in the clayware varied with the firing temperature. Clay fired at approximately $600^\circ C$ was most effective. Temperatures over $700^\circ C$ caused a decline in F-binding, and pottery fired at $900^\circ C$ and above seemed unable to remove F^- from water. Pots fired at $500^\circ C$ or less cracked in water.

c.   Coated clays

Chemical pre-treatment which includes the use of dilute sodium carbonate and hydrochloric acid improves the adsorption capacity of many types of clay and soils (Srimurali et al., 1998). Further improvement can be achieved by chemical coating introduced by stirring the pre-treated clay with solutions containing ions such of Aluminum or Iron and adjusting pH to precipitate the adsorbed cations as hydroxides.

2.8.2.10   Related low-cost materials

Srimurali et al. (1998)investigated the removal of fluoride using low-cost materials such as **kaolinite, bentonite, charfines, lignite and nirmali seeds**. Their results show that fluoride adsorption using nirmali seeds and lignite is low (6–8%). The removal of fluoride by kaolinite is slightly better (18.2%) while charfines and bentonite give higher fluoride removal capacity of 38 and 46% respectively. Also, bentonite was found to have a higher fluoride adsorption capacity than kaolinite. Fluoride removal using China clay has also been studied (Chaturvedi et al., 1988). Low fluoride concentration, high temperature and acidic pH are factors favoured the adsorption of fluoride. It was concluded that the alumina constituent of the China clay is responsible for fluoride adsorption. In 1990, Chaturvedi went on to study the de-fluoridation of water by adsorption on fly ash. Again low fluoride concentration, high temperature and acidic pH favoured the adsorption of fluoride (Chaturvedi et al., 1990).

2.8.2.11   Soils

Several research groups have studied the adsorption of fluoride on soils (Wang and Reardon, 2001) investigated the effect of varying levels of exchangeable sodium on the adsorption of fluoride onto sodic soils. At equilibrium fluoride concentration, a decrease in adsorption of fluoride with increase in the soil exchangeable sodium percentage was observed. Also the adsorption of fluoride by Illinois soils was studied. It was reported that at low concentrations fluoride adsorption onto soils was described by both Langmuir and Freundlich isotherms. It was also suggested that fluoride adsorption on soils was due to the presence of amorphous Aluminum hydroxides.

2.8.2.12   Calcium

Fan et al. (2003) studied fluoride adsorption on to a number of minerals such as fluorite, calcite, quartz, iron activated quartz and compared their fluoride uptake capacities. Their experimental data suggested that among the selected materials, calcite is a surface fluoride adsorbent within that low fluoride concentration range and less effective than all the other solids except untreated quartz. The fluoride did not appear to exchange with carbonate beyond an initial surface reaction. Turner et al. (2005) extended this lead to a

range of fluoride concentrations in which (unlike Fan's conditions) the solubility product of calcium fluoride is readily exceeded.

2.8.2.13   Carbon

The three best-known allotropes of carbon are diamond, graphite and fullerene. Diamond is not relevant to adsorption of fluoride, but graphite and fullerene can be good adsorbents when suitably treated and amended.

2.8.2.14   Graphite

Fan et al. (2003) have reported the fluoride uptake capacity of various carbon based adsorbents in the order:

bone char > coal charcoal > wood charcoal> carbon black> petroleum coke.

Bhargava and Killedar (1992) studied the fluoride adsorption on fish-bone charcoal through a moving media adsorber. They also studied fluoride adsorption on activated rice straw which produced a low density and highly porous activated product. The activated rice straw carbon was treated with the strong oxidants nitric acid, hydrogen peroxide and potassium permanganate. The adsorption capacity was greatly increased relative to similarly activated carbon which had not been treated with oxidants.

2.8.2.15   Alumina-impregnated graphitic carbon

Ramos et al. studied adsorption of fluoride from an aqueous solution on plain and alumina-impregnated activated carbons, prepared by stirring with an Aluminum nitrate solution at a fixed pH, followed by calcination under nitrogen at temperatures $300^{o}C$ (Ramos et al., 1999). The adsorption of fluoride on impregnated carbon was shown to be dependent upon both the pH of the impregnating solution and the temperature of calcination. Impregnated carbon was shown to have a fluoride adsorption capacity of 3 to 5 times that of plain activated carbon. With the increase in calcination temperature from 300 to $1000^{o}C$, uptake of fluoride decreased.

2.8.2.16   Carbon nanotubes.

Exploring the application of carbon nanotubes to adsorbing fluoride, a team led Ramos (1999) prepared aligned carbon nanotubes (ACNT), by the decomposition of xylene,

catalyzed by ferrocene. The authors found this material to adsorb 4.5 mg/g fluoride from 15 mg/L fluoride at pH 7, and the adsorption capacity to increase with increasing acidity owing to the increasing positive charge on the surface. The adsorption isotherms generated under identical conditions for activated carbon, g-Al_2O_3, a typical soil and carbon nanotubes showed that the order of adsorption was:

carbon nanotubes > soil > g-Al_2O_3 > activated carbon.

2.8.2.17   Alumina-impregnated carbon nanotubes.

Ramos (et al., 1999).   group also investigated adsorption of fluoride on alumina supported on carbon nanotubes. Constant charges of adsorbent (0.2 g per 100L solution) were shaken for 12 hours with sodium fluoride solutions after pH was adjusted with small amounts of sodium hydroxide or nitric acid. The effect of pH on adsorption isotherms was determined. The adsorption capacity of the Al2O3/carbon nanotubes was found to be 13.5 times higher than that of AIC-300 carbon and four times higher than that of g-Al_2O_3.

Chapter 3

Materials and methods

3.1 **Materials and Reagents**

Synthetic test water was used in the majority of these tests and was referred to as the "standard test water." This was prepared by adding 0.211 grams NaF (Sodium Fluoride) in the water supply sample to prepare a stock solution of Fluoride content 100 mg/L. The water quality parameters of the Public Supply water are as follows:

Table 3.1: Water Quality parameters of Public supply water used for experimental work.

Parameter	Value
1. Total Dissolved Solids	230 mg/L
2. Fluoride	0.3 mg/L
3. Nitrate	4 mg/L
4. Chloride	40 mg/L
5. Total Hardness	120 mg/L

The water samples used in the experiments were from a surface water source, the parameters of which are mentioned above.

Laboratory grade reagents: Alum [$KAl(SO_4)_2 \cdot 12H_2O$], Sodium Hydroxide (NaOH) and Hydrocholric acid (HCl) were used in my experiment. Single distilled water prepared in the laboratory was used for all experiments. Reagents were made available in the laboratory itself. Apparatus used were standard Jar Test apparatus, Fluoride meter (Thermo Scientific, American grade 500), Conductivity meter, Thermo scientific Oven and standard borosil glassware such as pipette (5 ml, 10 ml), beaker (50 ml, 100 ml, 500 ml and 100 ml.) were used.

3.2 **Procedure:**

Experiments were carried out in batch process varying the following parameters.

- Optimum pH.

- Optimum Dose of adsorbent.
- Optimum contact time.
- Stirring time

Identification of appropriate adsorption isotherm for different materials was done.

3.3   Synthesis of adsorbent:

The different adsorbents used in the experiments i.e. tulsi, eucalyptus and brick powder were washed with distilled water and dried in natural sunlight and in oven at 60°C. Sieve

Figure 3.1: Eucalyptus leaves being converted to smaller particles to facilitate adsorption.

Figure 3.2: Converting brick into smaller particles and then passing through sieve (150-300 microns)

analysis was done and appropriate particle size was chosen to facilitate maximum adsorption.

Figure 3.3: Drying the brick powder in open sunlight

3.4   **Isotherm Modeling**: Information involving the adsorption process, the effects of the previously mentioned parameters and the favorability of adsorption can be quantified using equilibrium isotherm modeling. Many named isotherms exist that describe the adsorption process. Each isotherm is characterized by a unique set of assumptions and operating parameters. Fitting experimental data to a wide range of isotherms allows for the appropriate isotherm(s) to be selected which best describe the specific adsorbent/adsorbate combination of interest. For this study of fluoride adsorption to active alumina and bone charcoal five isotherms were selected for comparison including: Freundlich, Langmuir, Temkin, Harkins UJura, and Halsey.

3.4.1   Freundlich Isotherm:

The Freundlich isotherm is empirically derived and suitable for modeling adsorption on heterogeneous surfaces in dilute solutions (Freundlich H.,1907). Freundlich was the first to develop a mathematical model for adsorption onto solid surfaces and his equation

currently remains as one of the most cited adsorption isotherms. The Freundlich isotherm is commonly seen in its condensed and linearized forms as shown in the equations below:

$$q_e = \frac{x}{m} = K_f C_e^{\frac{1}{n}}$$

Equation 1

$$\log(\frac{x}{m}) = \log K_f + \frac{1}{n} \log C_e$$

Equation 2

Where,

q_e = equilibrium sorption capacity (mg/g)

K_f (mg adsorbate/g adsorbent) and n (g adsorbent/ L solution) are empirical constants ($K_f > 1$: Favorable Adsorption)

x/m = Mass of adsorbate per unit mass of adsorbent (mg/g)

C_e = Equilibrium Concentration of Adsorbate (mg/L)

Freundlich model or van Bemmelon equation has been developed for adsorption system with emphasis on two factors, namely the lateral interaction between the adsorbed molecules and the energetic surface heterogeneity. The equation has the general form (Freundlich 1906)

$$q_e = K_f C_e^{\frac{1}{n}}$$

but it is well cited in logarithmic form as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where K_f and n are empirical constant. Here, $K_f \propto RT$ nb $\exp(\Delta H/RT)$. Equation above suggests that with increase in C_e, adsorption capacity (q_e) would increase without restriction, which is practically impossible. The model may simulate concentrations far outside the range of the defining batch experiment. Extrapolating equation into such concentration regions hence may give results of unknown, but potentially very large error. However in practical situation, adsorption process are sufficiently dilute and one never encounters the region where Freundlich equation breaks down for this region and

Freundlich isotherm equation implies that the energy distribution of adsorption site is of exponential (Cooney 1999).

In order to identify the best fit isotherm model, Chi square test was done by the following equation (Ho et al, 2005)

$$\chi^2 = \Sigma \frac{(q_e - q_{em})^2}{q_{em}}$$

Where, q_e is the experimental data of the equilibrium fluoride uptake (mg/g) and q_{em} is the equilibrium uptake calculated from isotherm models (mg/g).
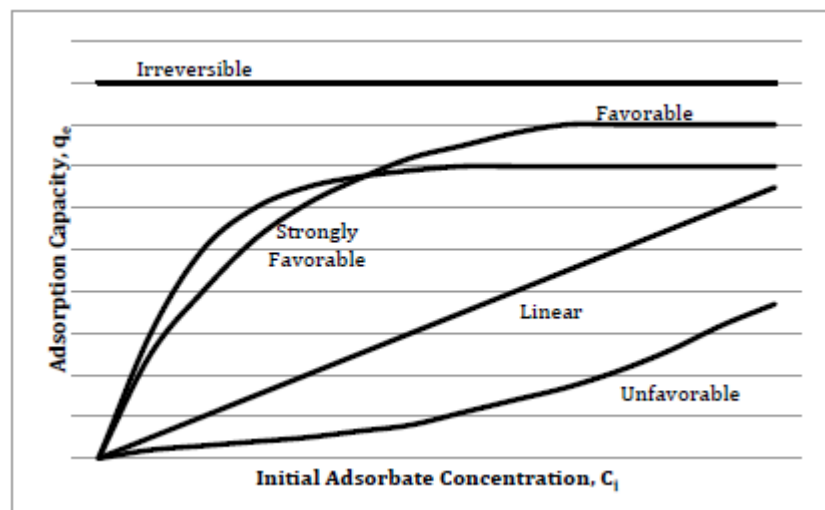
Figure 3.4: Graphical representation of adsorption capacity and concentration

3.4.2 **Langmuir Isotherm:** The Langmuir isotherm is a semi-empirical correlation for adsorption modeling (Langmuir I., 1918). Langmuir developed the correlation in 1916 using four main assumptions: All adsorption sites are equal in energy, Adsorbed molecules do not interact with each other, Adsorption is limited to a monolayer, and Desorption can occur. The condensed and linearized forms of the Langmuir isotherm are shown in

Equation 3 (Z.V.P. Murthy):
$$q_e = \frac{x}{m} = \frac{q_m K_L C_e}{1 + K_L C_e}$$

Equation 4 (Z.V.P. Murthy):
$$\frac{1}{q_e} = \frac{m}{x} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m}$$

Where,

> KL (Liters of solution / mg of adsorbate) is an empirical constant qm (mg/g) is the theoretical maximum adsorption capacity for the system.

A dimensionless separation factor, RL, for the Langmuir isotherm, as presented in Equation 5, provides a measure of the favorability of specific adsorbate/adsorbent systems. The reaction is termed favorable when RL < 1 (Hall K.R.,1966).

Adsorption can be classified on a continuum from unfavorable, which is characteristic of little removal even at high concentrations to irreversible, which is characteristic of high removal at all concentrations. Favored adsorption will lead to greater removal of the adsorbate per unit mass of adsorbent resulting in greater adsorption efficiency, but higher difficulty of regeneration (SJSU, 2011). The favorability of adsorption is determined by the shape of the curve formed by its equilibrium adsorption capacity, q_e, versus initial adsorbate concentration C_i. The relationship between the favorability of adsorption and the shape of the curve on the q_e vs. C_i plot is shown in Figure above.

> Langmuir isotherm is based on the following assumptions. It states that each surface site can be singly occupied. There are no lateral interactions between adsorbed species. The enthalpy of adsorption is independent of surface coverage and energy of adsorption is constant thus creating homogeneity of energy on the surface (there is dynamic equilibrium between the adsorption and desorption processes).

$$K_d \theta = K_a C_e (1-\theta)$$

or, $\theta = \dfrac{K_a C_e}{K_d + K_a C_e} = \dfrac{bC_e}{1+bC_e}$

The adsorption coefficient $b = \dfrac{K_a}{K_d}$, is related to the enthalpy of adsorption (ΔH) by

$$b = b_0 \exp^{-\Delta H / RT}$$

where b_0 is constant related to entropy, R is the universal gas constant, T is the temperature (^{0}K) (Voice and Weber 1983).

As q_e is proportional to θ, therefore, equation (4.13) can be written as,

$$q_e = \frac{bQ_mC_e}{1+bC_e}$$

where q_m is the maximum adsorption for a complete monolayer coverage. Equation (4.14) can be rearranged in variety of linear forms.

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}$$

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m C_e}$$

$$q_e = Q_m - \frac{q_e}{bC_e}$$

3.4.3   Temkin Isotherm: The Temkin isotherm is a thermodynamically based model that assumes the enthalpy of adsorption varies linearly with the concentration of the adsorbate (Temkin M.J.). The Temkin isotherm is commonly used in its condensed and linearized forms as depicted in Equations 6 to 8 below (Z.V.P. Murthy). The unitless

$$q_e = \frac{x}{m} = \frac{RT}{b}\ln(K_T C_e) \qquad\qquad \text{Equation 5}$$

$$q_e = \frac{x}{m} = B_1 \ln(K_T) + B_1 \ln(C_e) \qquad\qquad \text{Equation 6}$$

$$B_1 = \frac{RT}{b} \qquad\qquad \text{Equation 7}$$

constant B1 is formed from the gas constant, temperature, and model constant for the Temkin isotherm and is related to the enthalpy of adsorption. Although related, the value of B1 cannot be assumed to be equal in magnitude or sign to that of the ΔHabs.

Where:

R = universal gas constant (8.314 J/(mol K))

b = model constant (J/mol)

T = absolute temperature (K)

KT = equilibrium binding constant, and

B1 = unit less constant related to the enthalpy of adsorption.

3.4.4 **Harkins-Jura and Halsey Isotherms:** The Harkins-Jura and Halsey Isotherms account for the possibility of multilayer adsorption and heterogeneous pore distribution and are represented in their linearized forms as shown in Equations an 10 (Z.V.P Murthy). The Harkins-Jura Isotherm has been used to effectively model the adsorption of red dye on tea waste, fluoride on activated alumina (Z.V.P Murthy), and crystal violet dye on watermelon rind. The Halsey isotherm has been shown to display a good description of fluoride adsorption on Activated Alumina (Z.V.P Murthy), red dye on tea and palm kernel waste. (Z.V.P Murthy,

Harkins-Jura: $\frac{1}{q_e^2} = \left(\frac{B'}{A}\right) - \left(\frac{1}{A}\right)\log(C_e)$

Halsey: $\ln(q_e) = \left[\left(\frac{1}{n_H}\right)\ln(k)\right] - \left(\frac{1}{n_H}\right)\ln\left(\frac{1}{C_e}\right)$

Where:

A, B and k are empirical constants.

Chapter: 4

Results and Discussion

In the experiments I performed, four materials were tested in laboratory for the adsorption of fluoride under different conditions. The bio adsorbents i.e. Tulsi and Eucalyptus showed unsatisfactory results, but brick powder, Alum and Alum impregnated on brick powder yielded satisfactory results. The aim with which the experiments were done was to find out or modify the adsorbent so that it can be used locally for removal of fluoride. Fluoride contamination in ground water in India and in different parts of the world is serious problem. De-fluoridation method especially for developing and underdeveloped countries should be economic, sustainable and easy to operate. I have used brick powder which adsorbs fluoride up to some extent and renders water fluoride free. Brick powder with Alum impregnated on its granules further enhances fluoride removal. Alum is used in Nalgonda technique but it has certain limitations. Aluminum is released in the water and it is quite toxic. So with permissible Aluminum content fluoride removal is limited, up to 20-30 %.

4.1   Tulsi and Eucalyptus:

4.1.1   **Effect of pH** on bio-adsorbents- Tulsi and Eucalyptus are medicinal plants of great importance. Tulsi is a sacred Indian plant and is used for disinfection and in many
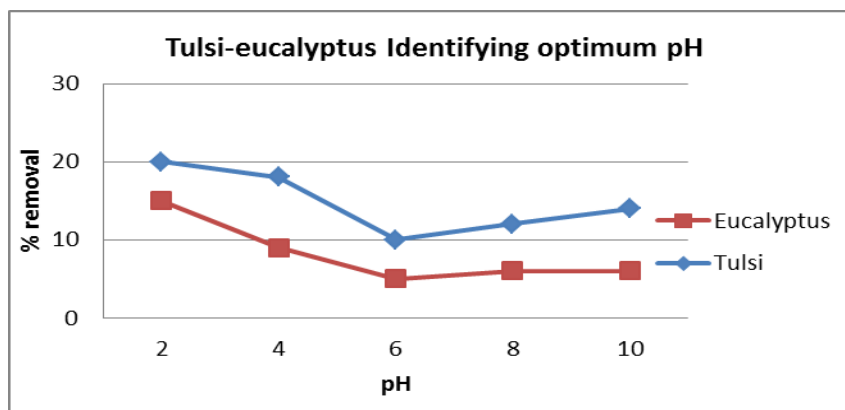
Figure 4.1: Effect of pH on fluoride removal: Contact time and initial fluoride concentration are 40 min, 10 mg/L for both Tulsi and Eucalyptus Adsorbent doses are 1.0 g/100 ml for both adsorbents.

house hold and ayurrvedic medicines. Eucalyptus is used in manufacturing of many allopathic and ayurvedic medicines. They have been selected based on their marvelous capacities in treatment of diseases. Although the results were quite unsatisfactory. As shown in Figure 4.2 and figure 4.3, Tulsi removed upto 20-25% fluoride; eucalyptus dry leaves precipitated 4-5 % fluoride and Eucalyptus bark adsorbed 10-12%.

4.1.2 **Identifying optimum dose-** The effect of adsorbent dosage on adsorption of fluoride at pH 7.0 for both the bio adsorbents was studied. Contact time was maintained
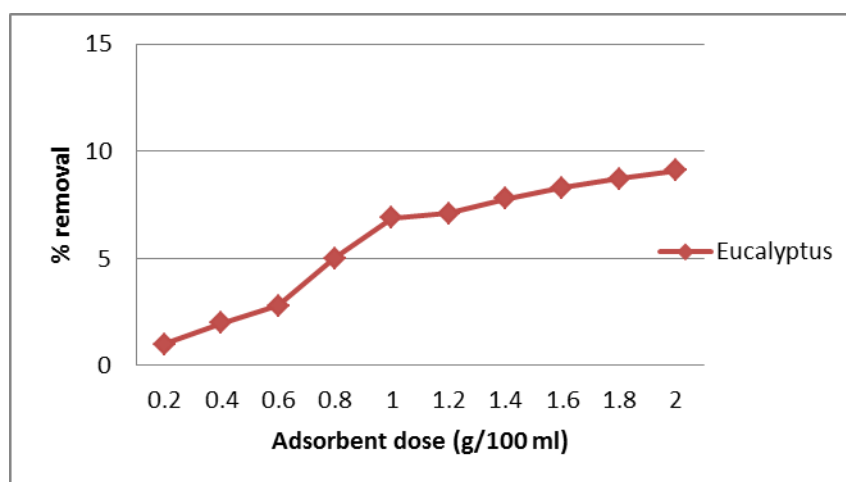
Figure 4.2: Effect of adsorbent dose on fluoride removal: (Contact time is 40 min and pH 7for Eucalyptus.
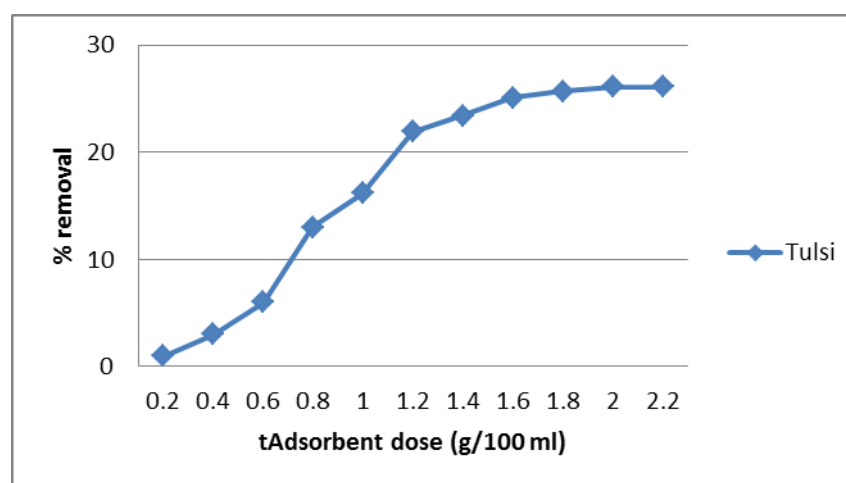
Figure 4.3: Effect of adsorbent dose on fluoride removal: (Contact time is 40 min and pH 7 for Tulsi)

at 40 minutes for both adsorbents. The results are presented as percentage removal of fluoride versus adsorbent dosage in Figure. The removal of fluoride increased in case Eucalyptus was maximum 9% at 2 grams per 100 ml quantity. But there was no appreciable change in the adsorption after 1 grams dose was put which showed 7 % removal of fluoride. On the other hand Tulsi showed some better results. Removal was 26 % maximum at 2.2 grams per 100 ml, but the increase almost remained constant after 1.2 grams in 100 ml. So 1.2 grams /100 mL was chosen as optimum dose in case of Tulsi.

Although the results were unsatisfactory, as the maximum adsorption in both the cases was not satisfactory. It was 26 % for Tulsi and 9% for Eucalyptus.

4.2   Brick Powder:

4.2.1   Effect of pH- The effect of pH on removal of fluoride was studied in the pH range of 2.0–13.0 and results are shown in Fig below. pH played a major role in fluoride adsorption on brick powder. Maximum adsorption of fluoride was found to be 49.0–54.1% in pH range between 6.0 and 8.0. Percentage removal fell sharply as pH varied on either side of 6 and 8 pH. The lower adsorption efficiency of fluoride in acidic medium
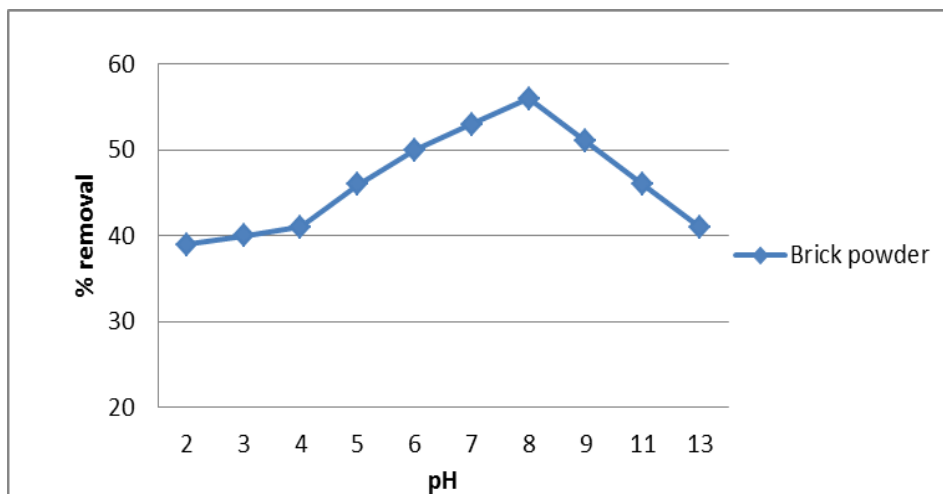
Figure 4.4: Effect of pH on fluoride removal: Fluoride concentration is 10 mg/L, dose is 1.6 grams/100 mL and contact time is 60 minutes.
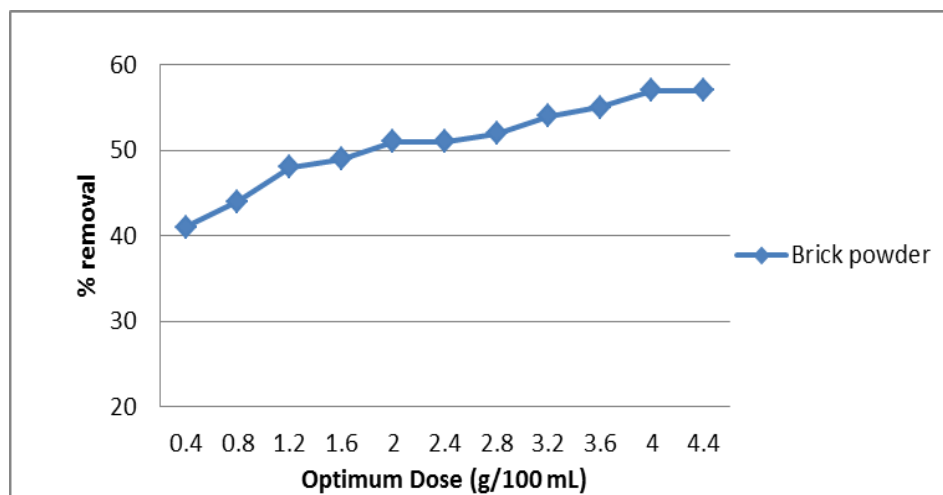
Figure 4.5: Effect of dose on fluoride removal: Fluoride concentration is 10 mg/L, pH is maintained at 7 and contact time is 60 minutes.

might be due to the formation of weakly ionized hydrofluoric acid, which reduces availability of free fluoride for adsorption. In alkaline conditions, lower adsorption may

be due to the competition of OH− ions with F− ions for adsorption because of similarity in F− and OH− in charge and ionic radius. The obtained results for maximum adsorption were similar, as reported for fluoride removal by rare earth oxides as adsorbent (Raichur AM, 2001).

4.2.2 **Identifying optimum dose:** The effect of adsorbent dosage on adsorption of fluoride at pH 7.0 for brick powder for 60 min was studied. The results are presented as percentage removal of fluoride versus adsorbent dosage in Figure. The removal of fluoride increased from 41 to 58 % for 0.4–4.4 g/100 ml dosages of brick powder. However, it is hereby observed that after dosage of 1.6 and 2 g/100 ml there was no
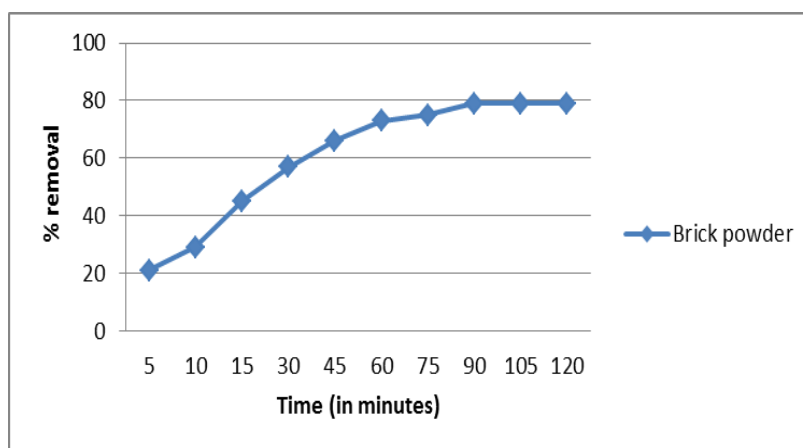
Figure 4.6: Effect of contact time on fluoride removal: Fluoride concentration is 10 mg/L and pH is maintained at 7.

significant change in percentage removal of fluoride. It was due to the overlapping of active sites at higher dosage, thus, reducing the net surface area (Killedar. D.J.1990). So, 2 grams per 100 mL was taken for further study.

4.2.3 **Effect of contact time**: Figure shows the progression of adsorption reaction, the percentage removal of fluoride by brick powder at different contact times. As contact time was increased, initially, percentage removal also increased, but after some time, it gradually approached an almost constant value, denoting attainment of equilibrium. It was assumed that the equilibrium time is that at which curves appear nearly asymptotic to the time axis. In the present case, the equilibrium time was obtained at 60 min for brick powder. The changes in the rate of removal might be due to the fact that initially all

adsorbent sites were vacant and the solute concentration gradient was high. Later, the fluoride uptake rate by adsorbent had decreased significantly, due to the decrease in number of adsorption sites. Decreased removal rate, particularly, towards the end of experiment, indicates the possible monolayer of fluoride ions on the outer surface, pores of both the adsorbents and pore diffusion onto inner surface of adsorbent particles through the film due to continuous shaking maintained during the experiment.

4.2.4   **Adsorption isotherms**: An adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent, qe, to the concentration of the solute in the liquid, Ce, with which it is in contact. The adsorption isotherm is also an equation relating the amount of solute adsorbed onto the solid and the equilibrium concentration of the solute in solution at a given temperature. The adsorption data was fitted on Langmuir and Freundlich isotherm equations to find out the maximum R^2. Results showed that the data follows Langmuir assumptions.

Table 4.1: Adsorption data for De-fluoridation using brick powder.

Fluoride (initial conc.) C_0	Fluoride (Final Conc.) C_e	Adsorbent dose (m)	% removal F	q_e (mg/g)	$1/C_e$	$1/q_e$	log q_e	log C_e
10	5.9	**0.4**	41	1.025	0.17	0.98	0.02	1.77
10	5.6	**0.8**	44	0.550	0.18	1.82	-0.60	1.72
10	5.2	**1.2**	48	0.400	0.19	2.50	-0.92	1.65
10	5.1	**1.6**	49	0.306	0.20	3.27	-1.18	1.63
10	4.9	**2**	51	0.255	0.20	3.92	-1.37	1.59
10	4.9	**2.4**	51	0.213	0.20	4.71	-1.55	1.59
10	4.8	**2.8**	52	0.186	0.21	5.38	-1.68	1.57
10	4.6	**3.2**	54	0.169	0.22	5.93	-1.78	1.53
10	4.5	**3.6**	55	0.153	0.22	6.55	-1.88	1.50
10	4.3	**4**	57	0.143	0.23	7.02	-1.95	1.46
10	4.3	**4.4**	57	0.130	0.23	7.72	-2.04	1.46

Table 4.2: Calculations of (chi) square (Langmuir isotherm):

q_e	q_{em}	$(q_e - q_{em})^2/q_{em}$
1.025	1.698805	0.267255
0.550	1.688261	0.76744
0.400	1.672556	0.968218
0.306	1.668296	1.112014
0.255	1.659325	1.188513
0.213	1.659325	1.261539
0.186	1.654599	1.304015
0.169	1.644618	1.324433
0.153	1.639344	1.348027
0.143	1.628174	1.355646
0.130	1.628174	1.37939
		12.27649

Table 4.3: Coefficients of Langmuir and Freundlich's isotherm

Langmuir				Freundlich			
R^2	Q_m(mg/g)	b (L/mg)	λ^2	R^2	K_f	N	λ^2
0.9963	1.932	1.2843	12.28	0.8939	0.552	-5.461	11.12
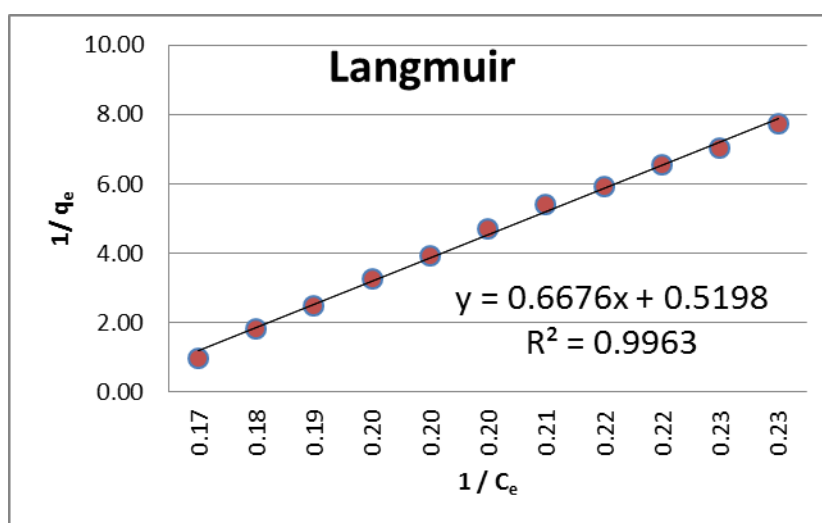
Figure 4.7: Plot of Langmuir's isotherm for adsorption of Fluoride by brick powder
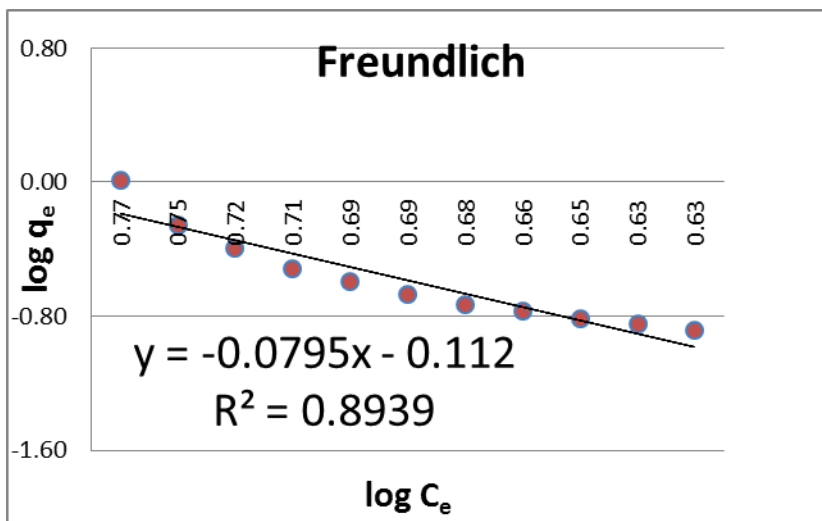
Figure 4.8: Plot of Freundlich's isotherm for adsorption of Fluoride by brick powder

From the values of the Langmuir and Freundlich, we see that R^2 value is maximum for Langmuir isotherm which is 0.98. Value is greater than that of the Freundlich. It can be concluded that the adsorption follow Langmuir isotherm and hence, assumptions by Langmuir shall be applicable. Langmuir isotherm is based on the following assumptions:

- Each surface site can be occupied singly,

- There are no lateral interactions between adsorbed species,

- The enthalpy of adsorption is independent of surface coverage and

- Energy of adsorption is constant thus creating homogeneity of energy on the surface (there is dynamic equilibrium between the adsorption and desorption processes).

Alum impregnated in brick powder: 0.5 grams Alum was mixed in 1 litres of distilled water and brick powder was put in the solution for 24 hours at room temperature. Solution was then in sunlight till dryness. The idea is based on the fact that Alum and Brick has been found to remove Fluoride from drinking water. But Nalgonda process (Alum + lime) has its limitations. It adds Aluminum and hardness causing salts which
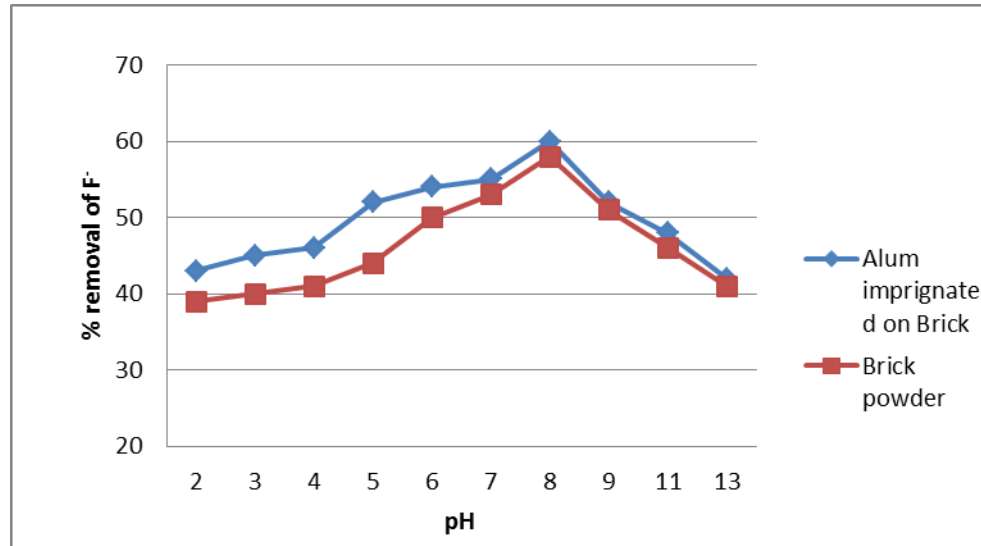
Figure 4.9: Effect of pH on fluoride removal: Fluoride concentration is 10 mg/L, pH is maintained at 7 and contact time is 60 minutes.
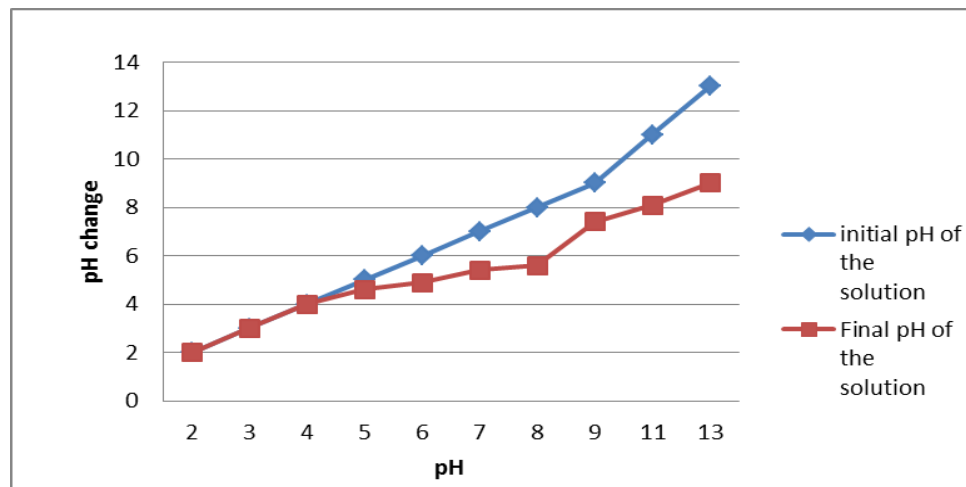
Figure 4.10: Initial and Final pH of the solution using Alum impregnated brick as the adsorbent.

may become toxic at high Alum content. So impregnating Alum on Brick powder shall enhance the fluoride removal as it will utilize adsorption power of brick powder and
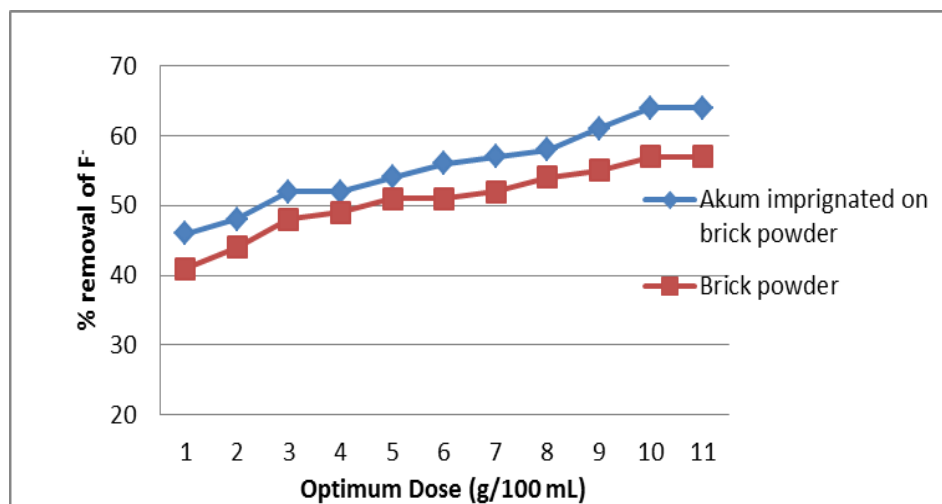
Figure 4.11: Effect of dose on fluoride removal: Fluoride concentration is 10 mg/L, pH is maintained at 7 and contact time is 60 minutes.

precipitation capacity of Alum. Also, hardness and Aluminum added in water is also below toxic levels.

4.2.5 **Identifying pH-** Overall, Alum impregnated on brick powder showed 4-5 % increase in Fluoride adsorption. Although Alum renders solution acidic and hence the final pH of the solution was on the left side of the pH scale. The pH dropped by 1-2 units in each sample. But maximum removal was obtained in pH range 6-8.

4.2.6 **Identifying optimum dose-** The effect of adsorbent dosage on adsorption of fluoride at pH 7.0 for Alum impregnated on brick powder for 60 min was studied. The results are presented as percentage removal of fluoride versus adsorbent dosage in Figure. The removal of fluoride increased by 4-5 % in this case. Earlier obtained values were from 41 to 58 % for brick powder which increased to 46-64 % for alum impregnated on brick powder for 0.4–4.4 g/100 ml dosages for both. However, it is hereby observed that after dosage of 1.6 and 2 g/100 ml there was no significant change in percentage removal of fluoride. It was due to the overlapping of active sites at higher dosage, thus, reducing the net surface area (Killedar. D.J.1990). So, 2 grams per 100 mL was taken for further study.

4.2.7　**Effect of contact time-** In the Figure as contact time was increased, initially, percentage removal also increased, but after some time, it gradually approached an almost constant value, denoting attainment of equilibrium. The graph followed almost the same line as that for brick powder.

4.2.8　**Adsorption isotherms:** The Brick and Alum combination too followed Langmuir isotherm giving maximum value of R^2. Figure 4.13 and Figure 4.14 shows the Plot of Langmuir and Freundlich isotherms for adsorption of Fluoride by Alum impregnated on brick powder.

Table 4.4: Adsorption data for De-fluoridation using Alum impregnated brick powder.

Fluoride (initial conc.) C_0	Fluoride (Final Conc.) C_e	Adsorbent dose (m)	% removal F	q_e (mg/g)	$1/C_e$	$1/q_e$	log q_e	log C_e
10	5.4	**0.4**	46	1.150	0.185	0.870	0.06	0.73
10	5.2	**0.8**	48	0.600	0.192	1.667	-0.22	0.72
10	4.8	**1.2**	52	0.433	0.208	2.308	-0.36	0.68
10	4.8	**1.6**	52	0.325	0.208	3.077	-0.49	0.68
10	4.6	**2**	54	0.270	0.217	3.704	-0.57	0.66
10	4.4	**2.4**	56	0.233	0.227	4.286	-0.63	0.64
10	4.3	**2.8**	57	0.204	0.233	4.912	-0.69	0.63
10	4.2	**3.2**	58	0.181	0.238	5.517	-0.74	0.62
10	3.9	**3.6**	61	0.169	0.256	5.902	-0.77	0.59
10	3.6	**4**	64	0.160	0.278	6.250	-0.80	0.56
10	3.6	**4.4**	64	0.145	0.278	6.875	-0.84	0.56
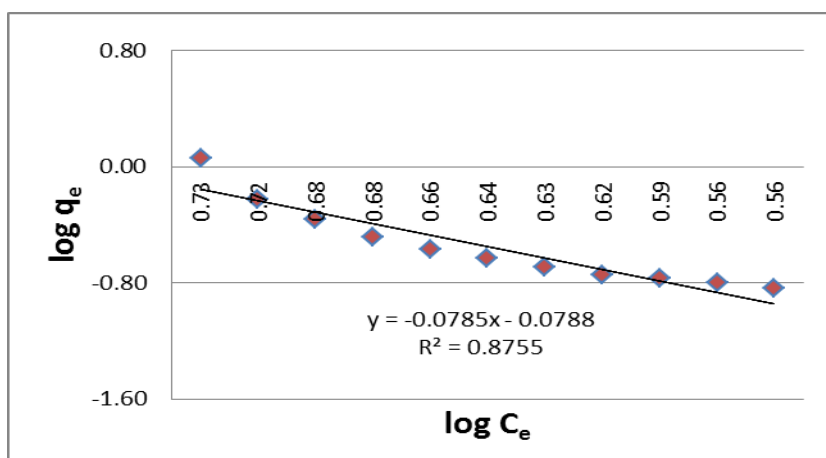
Figure 4.13: Plot of Freundlich Isotherm for adsorption of Fluoride by Alum impregnated on brick powder

Table 4.5: Coefficients of Langmuir and Freundlich's isotherm

Langmuir				Freundlich			
R^2	Q_m(mg/g)	b (L/mg)	λ^2	R^2	K_f	N	λ^2
0.9835	1.837	0.8981	11.18	0.8735	0.4311	-1.332	6.11
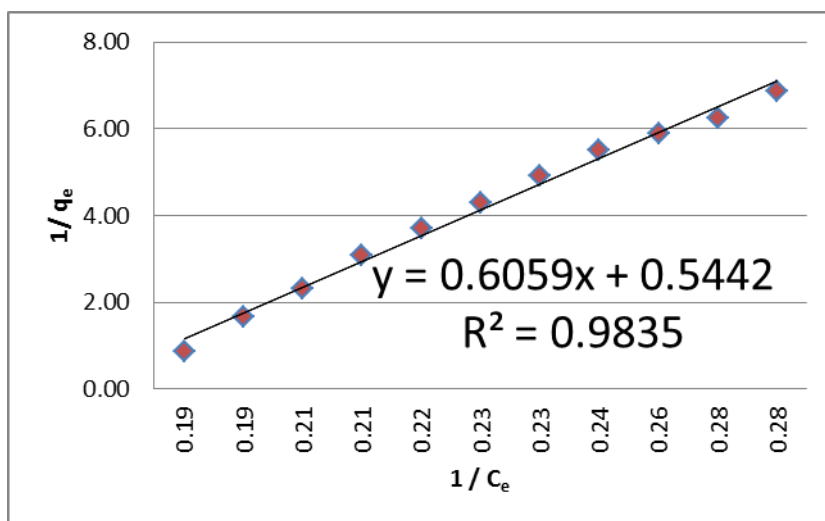
Figure 4.12: Plot of Langmuir isotherm for adsorption of Fluoride by Alum impregnated on brick powder

From the values of the Langmuir and Freundlich, we see that R^2 value is maximum for Langmuir isotherm which is 0.98. Value is greater than that of the Freundlich. It can be concluded that the adsorption follow Langmuir isotherm and hence, assumptions by Langmuir shall be applicable. Langmuir isotherm is based on the following assumptions:

- Each surface site can be singly occupied,.

- There are no lateral interactions between adsorbed species,

- The enthalpy of adsorption is independent of surface coverage and

- Energy of adsorption is constant thus creating homogeneity of energy on the surface (there is dynamic equilibrium between the adsorption and desorption processes).

Chapter 5
Conclusions and Recommendations

In my present study, tulsi, eucalyptus, brick powder and alum impregnated brick powder has been studied for removal of fluoride from synthetic as well as from public water supply of different fluoride concentrations. The conclusions drawn from the above study are given below:

1. Most of the organic materials have some functional group that can exchange F^-, but not at a high level. Introducing organic material to water may further result in proliferation of bacteria on storage and hence require extra treatment. Some bio adsorbents have been successfully used for de-fluoridation. *Moringa Oleifera* Seed has been successful in de-fluoridation with removal percentage was upto 92% in treated water. Tulsi and Eucalyptus are medicinal plants of great importance but fluoride adsorption was found to be quite low. Percent removal for both was observed to be 24% and 9% respectively.

2. Adsorption of fluoride on brick powder from aqueous solution was found to be first order reaction and mechanism of fluoride removal on adsorbent was found to be complex. The surface adsorption as well as intra-particle diffusion contributes to the rate-determining step. The optimum pH was found to be in range of 6.0–8.0 for maximum adsorption of fluoride, which makes it very suitable for use in drinking water treatment, especially in rural areas. Presence of others ions in groundwater did not significantly affect the de-flouridation process thereby indicating that brick powder is selective adsorbent for fluoride. Effective Fluoride removal percentage was found to be 46-52% under optimum pH and 1 hour contact time with optimum dosage of 2 grams per 100 mL.

3. Alum impregnated brick powder was used as the fourth adsorbent and yielded most satisfactory results. Fluoride removal was throughout 4-5 % more than brick powder when used alone. Also, it is beneficial as Alum removes 20-30% fluoride and if used in high quantity renders water unfit for drinking as Aluminum and

hardness causing salts are added to water above permissible levels. Both adsorbents (brick powder and Alum impregnated brick powder) followed Langmuir plot with maximum R square values i.e. 0.99. Alum impregnated on brick powder can proved to be an improved method over Alum or brick individually.

Recommendations:

1. Ideally using a bio-adsorbent is not suggested for de-fluoridation because this may remove fluoride but may give rise to other impurities in water. They can be used only with prior treatment with acid or base or by exposure to high temperature. Results from Tulsi and Eucalyptus were less satisfactory hence these materials cannot be used for de-fluoridation at local levels.

2. Brick powder is a good de-fluoridating agent and experiments with brick powder yielded satisfactory results. Alum impregnation on brick powder improved the results by 4-5 %. Hence brick powder and alum impregnated brick powder can be used effectively for fluoride removal in the rural areas.

3. In order to test the method/material further it is recommended to take a real life pilot project where in well/tube well water is subjected to treatment and performance of the material is evaluated

Chapter 6

Scope for Future work

A better approach on the Fluoride removal using brick and Alum impregnated on brick shall be Column process. Column studies at advanced level shall make it usable at root level. Removal is continuous and it is less cumbersome.

Alum adsorption on other popular adsorption materials like burnt clay, husk, jute etc. can be studied. There can be a number of plants/vegetation which could be tried as an adsorbent to remove fluoride. All such locally available herbs can be experimented upon to come out with an effective fluoride remover.

The need for user friendly, economic and simple methods based on use of locally available material and methods is the need of the hour. A real life pilot project shall be useful to analyze the treatment and performance of the material.

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