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Ground Water Quality Status with Respect to Fluoride Contamination in Vinukonda Mandal, Guntur District, Andhra Pradesh, India and Defluoridation with Activated Carbons

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Abstract: The present work is a comprehensive study on the quality assessment of the ground water of 13 villages of Vinukonda Mandal, Guntur District, Andhra Pradesh in India, a fluorosis-*prone area.* Various physicochemical parameters such as pH, EC, TDS, TA, TH, Turbidity, Ca^{2+} Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^-, HCO_3^-, SO_4^{2-}, PO_4^{3-}, DO along with Fluoride have been assayed and the values obtained have been compared with WHO and BIS guide lines. A systematic calculation of correlation coefficient (r) and regression analysis have shown significant linear relationship among different pairs of water quality parameters. The results have indicated that the ground waters are un-suitable for drinking as they have fluoride concentration ranging from 3.28 to 4.27 mg/lit and the waters need treatment before consumption. Application of batch mode of adsorption process with activated carbons: NVNC, NSOC, NAbIC and NAcIC derived from some plant materials, on ground water samples has been found to reduce the concentrations of all physicochemical parameters to less extent and the concentration of fluoride has been reduced to permissible limits
Keywords: ground water quality, physicochemical parameters, correlation, regression, activated carbons, de-fluoridation

1. Introduction

Ground water is one of the most broadly distributed and essential natural sources for domestic, industrial and agricultural purposes in all over the world. In India, most of the population use ground water as its primary source of drinking water[1-2]. The ground water is polluted due to the rapid urbanization, improper disposal of industrial effluents and sewage in urban areas, hazardous wastes, increasing mining and petroleum operations, agricultural development activities particularly excessive application of pesticides and fertilizers and unsanitary conditions[3-4]. In addition, variations in natural and human activities are reflected in the hydro chemical parameters of the groundwater. The relationship between the ground water flow systems and ground water quality is an important aspect of ground water analysis. The differences in concentrations of dissolved ions in ground water are generally governed by lithology, groundwater flow, geochemical reactions, the solubility of salts, and human activities[5-6]. The quality of ground water is stated by its quantitative and qualitative composition of suspended solids and dissolved minerals or organic compounds[7].

In India, research on the assessment of ground water quality especially with reference to fluoride has been carried out by various workers[8-9]. Both fluoride (F^-) and hydroxyl (OH^-) ions have the same ionic radii and are roughly of the same size and hence they can easily replace each other in many rocks forming processes[10]. Fluoride exists naturally in a number of different minerals[11]. The major fluoride containing minerals are: Fluorite (CaF_2), Fluorapatite [Ca_2F (PO_4)], Cryolite (Na_3AlF_6) and Topaz [Al_2SiO_4 (OH.F)$_2$]. So, fluoride ions are widespread in lithosphere as compared to hydrosphere, atmosphere and the biosphere since most of the fluoride exists bound in different minerals[12].

The quality of water in ground waters is a major concern for the mankind because human welfare is directly linked with it and so, the water quality regulating authorities such as WHO and BIS gives the fixed desirable and permissible limits of various physicochemical parameters of water[13-14]. The desirable limits are safe limits and permissible limits are allowed only in the event of the absence of alternative sources.

The correlation and regression coefficients of the water quality parameters help to assess the overall water quality. The correlation coefficient measures the degree of association that exists between two variables, one taken as dependent variable. The correlation study provides an excellent tool for the prediction of parametric values within a reasonable degree of accuracy[15].

In the present work a well known fluoride affected area, Vinukonda Mandal of Guntur District of Andhra Pradesh, India has been chosen for ground water quality assessment with an emphasis on the fluoride levels and for investigating the remedial methods for the de-fluoridation of ground waters using active carbons derived from the plant materials of *Vitex Negundo (NVNC), Senna Occidentali (NSOC), Abutilon Indicum (NAbIC) and Acalypha Indica (NAcIC) plants*.

2. Materials and Methods

2.1: Materials:

2.1.1: Study area:

The Vinukonda Mandal of Guntur District, Andhra Pradesh has rocks of Cryolite, a major source of fluoride and moreover, it has other deposits comprising of limestone (of cement grade), iron ore, copper and lead minerals, diatomaceous earth, gypsum, granite, kankar, quartz and white clays. The soils of this area are wetted by the famous Naguleru, a rivulet of Krishna River. It has hot summer temperature between 34°C to 47°C and winter around 25°C.

2.1.2: Water samples collection:

Thirteen villages of the selected area, ear-marked for the sample collections were given in the Table 1. Ground water samples were collected in polyethylene bottles with necessary precautions[16-17], to avoid unpredictable changes in their characteristics as per standard procedures of APHA [18].

Table 1: Names of the samples collected villages

S.No :	Sample Number	Village Name
1	1	Peda kancherla
2	2	Narasarayanipalem
3	3	Dondapadu
4	4	Vinukonda
5	5	Gokana konda
6	6	Enugupalem
7	7	Surepalli
8	8	Ummadivaram
9	9	Perumallapalli
10	10	Nayanipalem
11	11	Settupalli
12	12	Vithamrajupalli
13	13	Neelagangavaram

2.1.3: Sample preservation and handling:

The collected samples were stored in an icebox and brought to laboratory for determining both physical and chemical parameters. Preservation is essential for retarding biological action, deterioration with aging due to various interactions, hydrolysis of chemical compounds and complexes, and reduction of volatility of constituents. The preservation techniques of various parameters of water were given by U.S. Environmental Protection Agency[19].

2.1.4: Preparation of Nitric acid activated carbons:

The barks/stems of ***Vitex Negundo, Senna Occidentalis, Abutilon Indicum and Acalypha Indica plants*** were collected, cut into small pieces, washed with double-distilled water and dried under sunlight for two days. In the absence of air at 500^0C, the dried plant materials were carbonized for 4 hours in muffle furnace. After carbonization, the carbons were washed with double-distilled water and they were dried in an air oven at 110^0C and sieved into desired particle sizes. The carbonized materials were subjected to liquid phase oxidation by treating with 0.1N HNO_3 and boiled for 2 to 3 hours for the removal of unwanted materials. The acid treated carbons were thoroughly washed with double-distilled water to remove the excess acid and thus prepared active carbons were dried at 150^0C for 12 hours in an air oven. These Nitric acid activated carbons prepared from barks/stems of ***Vitex Negundo, Senna Occidentalis, Abutilon Indicum and Acalypha Indica*** plants were named as ***NVNC, NSOC, NAbIC and NAcIC respectively***.

2.2: Methods:

2.2.1: Methods of analysis of various water quality parameters other than fluoride:

The collected ground water samples were tightly corked to avoid any entry of foreign particles and brought to the laboratory. They were analyzed for pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), Total Alkalinity (TA), Total Hardness (TH), Turbidity, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^-, HCO_3^-, SO_4^{2-}, PO_4^{3-}, F^- and Dissolved Oxygen (DO) as per the standard methods available in literature [18, 20] and the methods used for the analysis of TH, TA, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^- and DO were by Titrimetry, pH was by pH-metry, EC was by Conductometry, TDS was by TDS analyzer, Turbidity was by Turbidity meter, Na^+ and K^+ were by Flame photometry and NO_3^-, SO_4^{2-}, PO_4^{3-} and F^- were by Spectrophotometry. All the chemicals used were of AR grade of pure quality. Double distilled water was used for the preparation of all the reagents and solutions. The average values of three replicates were taken for each determination.

2.2.2: Removal of fluoride by Nitric acid activated carbons:

Batch experiments were designed to investigate the efficiency of fluoride removal with varying conditions of extraction. 100 ml of ground water from one of the samples was pipette out into a 250ml conical flask and to it, weighed quantity of the prepared active carbon adsorbent was added, pH (=7) was adjusted and the solution was stirred for desired period at 200 rpm on a mechanical shaker at room temperature 30 ± 1^0C. Then the solution was filtered through Whatman No: 42filter paper. The fluoride concentration in the sample after de-fluoridation was determined by SPADNS method using U.V-Visible Spectrophometer (Model No: Elico U.V-2600) as described in the "Standard Methods for the Examination of Water and Waste water[18]" at λ_{max} 570 nm. The same procedure has been adopted for the experiments carried out with different active carbon adsorbents: NVNC, NSOC, NAbIC and NAcIC at the optimum conditions of pH (=7), contact time (50min for both NVNC and NSOC and 60 min for both NAbIC and NAcIC) and adsorbent dosage. It has been observed that the amount of active carbons required for defluoridation of 1 m^3 (1000 liters) water are: 2.61 kg for NVNC, 3.09 for NSOC, 3.61 for NAbIC and 3.72 kg for NAcIC.

2.2.3: Fluoride ion analysis:

The percentage removal of fluoride ion and amount adsorbed (in mg/g) were calculated using the following equations.

$$\% \text{ Removal } (\%R) = \frac{(Ci-Ce)}{Ci} X100$$

$$\text{Amount adsorbed } (q_e) = \frac{(Ci-Ce)}{m} V$$

where C_i = Initial concentration of the fluoride solution in mg/lit
C_e = Equilibrium concentration of the fluoride solution in mg/lit
m = mass of the adsorbent in grams
V = Volume of fluoride test solution in liters

2.3: Correlation coefficient and linear regression:

Statistical investigation offers more attractive decisions in environmental science. The systematic calculation of correlation coefficient between water quality variables and the study of regression analysis provide indirect means for rapid monitoring of water quality. Correlation is the mutual relationship between two variables. Direct correlation exists when increase or decrease in the value of one parameter is associated with a corresponding increase or decrease in the value of other parameter[21]. The greater the value of regression coefficient, the better is the fit and more useful the regression variables[22]. In statistics, correlation is used for the measurement of the strength and statistical significance of the relation between two or more water quality parameters[23]. The relationship between two variables 'x' and 'y' is given by correlation coefficient (r) which is defined by the formula:

$$r = \frac{n.\sum x.y - \sum x.\sum y}{\sqrt{\left(n\sum x^2 - (\sum x)^2\right)\left(n\sum y^2 - (\sum y)^2\right)}}$$

Larger is the value of correlation coefficient, greater will be the correlation between two variables x and y and in such cases, the equation describing the line on the graph is called a regression equation and is given as:

$y = a + b\,x.$

The value of empirical parameters '*a*' and '*b*' are calculated with the help of the following equations

$$a = \frac{\sum y - b\sum x}{n}$$

$$b = \frac{n.\sum x.y - \sum x.\sum y}{n\sum x^2 - (\sum x)^2}$$

In the present study, we tried to correlate the various parameters found for the 13 samples in the area of study using these statistical methods.

3. Results and Discussion

3.1: Ground water quality status in the study area before de-fluoridation:

The results obtained for various physicochemical parameters of the 13 Ground waters samples collected from the chosen 13 villages were presented in the Table 2. These results were compared with the desirable and permissible values given by WHO and BIS to assess the potability of the water.

pH is considered as an important ecological factor in assessing the water quality. In the present study, pH values are in the range from 7.4-8.5 (vide 2nd Column of Table 2) and the results have shown that the pHs lie in the range (6.5-8.5) prescribed by the Indian Standards and WHO. Higher pH value 8.5 is observed for the Sample No.5 of Gokanakonda, while lower pH value 7.4 is observed for the Sample No.1 of Peda kancherla.

The EC is dependent on the nature and numbers of the ionic species in that solution and is directly proportional to the total dissolved matter. The EC values for the samples are in the range from 595-1218(μ S/cm) (vide 3rd Column of Table 2). The results have shown that the electrical conductivity values of all the samples are exceeded to the desirable limit (300 μS/cm) but the values are within the maximum permissible limit (1500 μS/cm) prescribed by Indian Standards and WHO. Maximum EC value 1245μS/cm is observed for the Sample No. 7 of Surepalli, while minimum EC value 595μS/cm is observed for the Sample No.4 of Vinukonda.

The concentration of TDS decides the quality of drinking water. In the present study, TDS is ranged from 524-1042 mg/lit (vide 4th Column of Table 2). The results have shown that the TDS values of all the samples are exceeded to the desirable limit (500 mg/lit) but the values are within the maximum permissible limit (2000 mg/lit) prescribed by Indian Standards and WHO. Maximum concentration of the value: 1042 mg/lit is found in ground water Sample No.7, collected from Surepalli, while minimum concentration of value: 524 mg/lit is found in the ground water Sample No.4, collected from Vinukonda. Robinove et al., [24] have classified the water as non-saline, slightly saline, moderately saline and very saline as given in Table 3. As per this salinity classification, it has been observed that all the ground water samples are non-saline except one sample which is slightly saline.

Table 2: Physicochemical characteristics of ground water of villages of Vinukonda Mandal, Guntur Dist.: before defluoridation

Sample Number	pH	EC	TDS	TH	TA	Turbidity	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^-	HCO_3^-	SO_4^{2-}	PO_4^{3-}	DO	F^{-}
1	7.4	660	656	542	423	2.38	175	58	181	4.56	717	88	312	241	0.11	3.68	3.68
2	7.8	684	678	456	346	1.76	166	55	174	4.78	658	44	267	239	0.09	2.49	3.52
3	8.2	918	715	477	479	1.58	178	36	193	3.04	565	20	338	248	0.32	3.95	3.95
4	7.9	595	524	424	309	1.98	149	36	180	6.23	515	15	235	217	0.07	3.48	3.62
5	8.5	1218	945	524	587	2.73	184	53	212	7.01	626	31	482	295	0.18	5.12	4.21
6	8.3	950	735	535	532	2.47	189	48	185	3.14	615	47	418	305	0.14	4.32	3.69
7	7.6	1245	1042	586	585	2.83	201	65	166	6.89	789	25	474	330	0.17	7.33	3.45
8	8.1	851	808	359	487	2.21	105	45	178	3.18	674	43	359	249	0.07	4.69	3.59
9	7.8	1034	935	499	496	2.65	178	52	199	4.72	667	76	382	307	0.09	5.01	4.12
10	7.5	975	778	422	342	1.58	148	60	182	2.51	708	31	332	229	0.07	2.78	3.68
11	8.2	1189	997	638	328	1.76	137	84	186	7.24	985	54	295	316	0.20	6.51	3.72
12	7.5	1056	786	512	301	1.39	112	61	163	3.81	728	24	257	212	0.18	4.32	3.43
13	8.4	995	857	492	309	2.28	130	46	173	2.92	674	32	264	304	0.25	6.42	3.49

Units: Except pH, EC (µ S/cm), Turbidity (NTU) all parameters are measured in (mg/lit)

Table 3: Classification of groundwater on the basis of salinity values

TDS (mg/lit)	Description	No. of Samples
<1000	Non-saline	12
1000-3000	Slightly saline	01
3000-10000	Moderately saline	00
>10000	Very saline	00

Table 4: Classification of water on the basis of Total hardness

TH (mg/lit)	Description	No. of Samples
0-60	Soft	00
61-120	Moderate	00
121-180	Hard	00
>180	Very hard	13

The Total Hardness is an important parameter of water quality. The hardness is due to the dissolution of alkaline earth metal salts from geological matter. The total hardness has been found to be ranging between 359 to 638 mg/lit (vide 5th Column of Table 2). The results have shown that the TH values of all the samples are within the maximum permissible limit (600 mg/lit) prescribed by Indian Standards and WHO except Sample No.11. Maximum concentration: 638 mg/lit is found in ground water Samples No.11, collected from Settupalli, while minimum concentration: 359 mg/lit is found in ground water Samples No.8, collected from Ummadivaram. Durfor and Becker, [25] have classified the water as soft, moderate, hard and very hard as given in Table 4. As per this classification it has been observed that all the samples are very hard in nature.

The Total Alkalinity value in water provides an idea of natural salts presents in water. The alkalinity values have been found to be ranging from 301 to 587mg/lit (vide 6th Column of Table 2). The results showed that the TA values of all the samples are exceeded to desirable limit (200 mg/lit) but the values are within the maximum permissible limit (600 mg/lit) prescribed by Indian Standards and WHO. Maximum TA value of 587 mg/lit is observed for the Sample No.5 of Gokana konda, while minimum TA value of 301 mg/lit is observed for the Sample No.12 of Vithamrajupalli.

In the present investigation, the turbidity values are varied from 1.39 to 2.83 NTU (vide 7th Column of Table 2). The results have shown that the turbidity values of all the samples collected from study area are below the maximum permissible limit (10 NTU) given by Indian Standards and WHO. Maximum Turbidity value of 2.83 NTU is observed for the Sample No.7 of Surepalli while minimum Turbidity value of 1.39 NTU is observed for the Sample No.12 of Vithamrajupalli.

Calcium is an essential nutritional element for human beings. In ground waters of the study area, the calcium (Ca^{2+}) content has been found to be varying from 105 to 201 mg/lit (vide 8th Column of Table 2). Maximum calcium content, 201 mg/lit is observed for the Sample No.7 of Surepalli, while minimum calcium content, 105 mg/lit is observed for the Sample No. 8 of Ummadivaram. The results have shown that the calcium content of all the samples is found to be exceeding the desirable limit (75 mg/lit) but the values are within the permissible limit (200 mg/lit) given by Indian Standards and WHO, except for the Sample No: 7.

A large number of minerals contain magnesium and is a constituent of bones and its deficiency may lead to protein energy malnutrition. The values of magnesium (Mg^{2+}) of the ground water samples in the study area have been found to be ranging from 36 to 84 mg/lit (vide 9th Column of Table 2). The results have shown that magnesium content of all the samples collected from study area is below the maximum permissible limit (100 mg/lit) given by Indian Standards and WHO. Maximum concentration of 84 mg/lit is found in groundwater Sample No.11, collected from Settupalli, while minimum concentration, 36 mg/lit is found in ground water Sample No's.3 and 4, collected from Dondapadu and Vnukonda.

Ground water usually has higher sodium concentrations than in surface waters. The sodium (Na^{+}) content of the ground water in the study area is found to be ranged from 163 to 212 mg/lit (vide 10th Column of Table 2). The results have shown that the sodium content of all the samples is above the maximum permissible limit (50 mg/lit) described by Indian Standards and WHO. Maximum concentration of 212 mg/lit is found in ground water Sample No.5, collected from Gokana konda, while minimum concentration of 163 mg/lit is found in ground water Sample No.12, collected from Vithamrajupalli.

Potassium is an essential nutrient for humans, plants and animals. The potassium (K^{+}) content of the ground water in the study area is found to be ranged from 2.51 to 7.24 mg/lit (vide 11th Column of Table 2). The results have shown that the potassium content of all the samples are within the maximum permissible limit (10 mg/lit) described by Indian Standards and WHO. Maximum concentration of 7.24 mg/lit is found in ground water Sample No.11, collected from Settupalli, while minimum concentration of 2.51 mg/lit is found in ground water Sample No.10, collected from Nayanipalem.

Chloride ions are present naturally in ground water and widely distributed in all types of rocks and soils. Chloride present in ground water samples of study area is in the range of 515-985 mg/lit (12th Column of Table 2). The results have shown that the chloride content of all the samples is exceeded the desirable limit (250mg/lit) but below the maximum permissible limit (1000 mg/lit) described by Indian Standards and WHO. Maximum concentration:985 mg/lit is found in ground water Sample No.11, collected from Settupalli, while minimum concentration: 515 mg/lit is found in ground water Sample No.4, collected from Vinukonda.

The ground water contamination is due to the leaching of nitrate present on the surface with percolating water. High concentrations of nitrates in drinking water can cause methemoglobinemia (blue baby disease),

gastric cancer, goiter etc.[26]. In ground waters of the study area, the nitrate concentration is varied from 15 to 88 mg/lit (vide 13th Column of Table 2). The results have shown that the nitrate concentration of Sample No's: 1, 6, 9 and 11 collected from study area is above the permissible limit and for the remaining samples, the values are within the maximum permissible limit (45 mg/lit) given by Indian Standards and WHO. Maximum nitrate concentration of 88 mg/lit is observed for the Sample No.1 of Pedakancherla, while minimum nitrate concentration of 15 mg/lit is observed for the Sample No.4 of Vinukonda.

Alkali bicarbonates and most of the bicarbonates of other metals are soluble in water and contribute to total dissolved salts which are a common parameter for assessing water quality. In the ground water of the study area, the bicarbonate concentration has been found to be varied from 235 to 482 mg/lit (vide 14th Column of Table 2). The results showed that the bicarbonate concentration of all the samples collected from study area is below the maximum permissible limit (600 mg/lit) given by Indian Standards and WHO. Maximum bicarbonate concentration of 482 mg/lit is observed for the Sample No.5 of Gokanakonda, while minimum bicarbonate concentration of 235 mg/lit is observed for the Sample No.4 of Vinukonda.

The sulphate content in ground water generally occurs as soluble salts of calcium, magnesium and sodium. In the present study, the sulphate content in all the ground water samples is varied from 212 to 330 mg/lit (vide 15th Column of Table 2). The results indicate that the values of sulphate in all the samples are within the maximum permissible limit (400 mg/lit) as given by Indian Standards and WHO. Maximum sulphate concentration of 330 mg/lit is observed for the Sample No. 7 of Surepalli, while minimum sulphate concentration of 212 mg/lit is observed for the Sample No.12 of Vithamrajupalli.

Phosphate may occur in ground water due to the domestic sewage, detergents, agricultural run-off with fertilizers and from the sugar manufacturing process[27]. In the present study, the phosphate concentration in all the ground water samples is varied from 0.07 to 0.32 mg/lit (vide 16th Column of Table 2). The results indicate that the values of phosphate concentration in all the samples are within the maximum permissible limit (10 mg/lit) as given by Indian Standards and WHO. Maximum phosphate concentration of 0.32 mg/lit is observed for the Sample No. 3 of Dondapadu, while minimum phosphate concentration of 0.07 mg/lit is observed for the Sample No's. 4, 8 and 10 of Vinukonda, Ummadivaram and Nayanipalem respectively.

Dissolved oxygen is an important parameter in water quality assessment. The higher value of dissolved oxygen can impart good aesthetic taste to drinking water[28]. In our present study DO content is monitored in all ground water samples and the obtained results are presented in the 17th Column of Table 2 and the DO content in all the ground water samples is varied from 2.49 to 7.33 mg/lit. The results indicate that the values of DO content in all the samples, except Sample No's: 7, 11 and 13, are within the maximum permissible limit (6.0 mg/lit) and for these three samples the values are above the permissible limit as given by Indian Standards and WHO. Maximum DO content of 7.33 mg/lit is observed for the Sample No. 7 of Surepalli, while minimum DO content of 2.49 mg/lit is observed for the Sample No.2 of Narasarayanipalem.

Fluoride concentrations in natural water are depending on the geological setting[29-30] and high dissolved fluoride concentrations can be found in various geological settings of igneous and metamorphic rocks[31]. In ground water of the study area, the fluoride concentration is varied from 3.43 to 4.21 mg/lit and the observations are presented in the 18th Column of Table 2. The results have shown that the fluoride concentration of all the ground water samples collected from study area is above the maximum permissible limit (1.5 mg/lit) given by Indian Standards and WHO. Maximum fluoride concentration of 4.21 mg/lit is observed for the Sample No. 5 of Gokana konda, while minimum fluoride concentration of 3.43 mg/lit is observed for the Sample No.12 of Vithamrajupalli. These results indicate that the fluoride concentration is very high in the ground waters of this study area.

3.2: Statistical Analysis:

The correlation coefficient (r) and regression coefficients are very important to evaluate the quality of water[32-33]. The correlation matrix for different water quality parameters of ground water samples collected from study area is presented in Table 5. In the present correlation regression study, all the parameters are more or less correlated with each other. For the ground water samples of collected study area, significant positive correlations are observed between different water quality parameters. The discussions are made based on the positive correlations and the higher numerical value of parameter indicated the linear relationship between the two parameters. Highly positive correlation is observed between Na^+ and F^- (0.9743).

3.3: Regression analysis

For some pairs of water quality parameters having higher correlation coefficients, linear regression analysis has been carried out and the obtained regression equations have been presented in the Table 6. Further, using thus developed regression equations, values of related parameters of the water samples have been predicted and they are presented in the Table 7 along with the experimentally observed values. It is observed from the values that the observed and predicted values of the chosen parameters (having the high correlation coefficient) are comparable (Table 7). Thus it may be inferred that the correlation studies are significant in the water quality assessment studies.

Table 7: The observed and predicted (using regression equation developed from better correlated parameters) values of water samples

	Na^+		Mg^{2+}		TA		EC		TDS	
S. No:	O	P	O	P	O	P	O	P	O	P
1	181	181	58	57	423	390	660	758	656	726
2	174	173	55	50	346	333	684	787	678	628
3	193	195	36	41	479	423	918	835	715	749
4	180	178	36	35	309	292	595	587	524	710
5	212	209	53	47	587	605	1218	1135	945	845
6	185	182	48	46	532	524	950	861	735	779
7	166	169	65	64	585	595	1245	1261	1042	1028
8	178	176	45	52	487	449	851	956	808	810
9	199	204	52	51	496	478	1034	1122	935	836
10	182	181	60	56	342	415	975	917	778	652
11	186	183	84	85	328	368	1189	1202	997	960
12	163	168	61	58	301	320	1056	928	786	779
13	173	171	46	52	309	329	995	1020	857	952

Note: O - Observed value, P- Predicted value

3.4: De-fluoridation of ground water samples collected from study area:

All the ground water samples collected from study area have been found to contain excess levels of fluoride beyond the permissible limit (1.5 mg/lit). So, de-fluoridation studies have been made using the active carbons NVNC, NSOC, NAbIC and NAcIC at optimum extraction conditions. The obtained values have been presented in the Table No's: 8, 9, 10 and 11.

3.5: Concentrations of the studied water quality parameters after de-fluoridation:

After the de-fluoridation experiments, the pH values of the ground water samples were decreased due to the decrease in fluoride levels, TA and TDS which were positively correlated with pH. The EC values of the ground water samples were decreased due to the positively correlation of EC with all the water quality parameters except NO_3^- which were decreased in the analysis. The decrease in TDS and TH values was due to the positive correlation of TDS and TH with all the water quality parameters whose concentrations were decreased after de-fluoridation experiments. The total alkalinity of the ground water samples collected in study area was decreased. This is because of positive correlation of TA with fluoride concentration and particularly with HCO_3^- and the small decrease in pH values were also observed after de-fluoridation of the ground water samples. The turbidity values were decreased after de-fluoridation due to the positive correlation of turbidity with fluoride concentration and other turbidity contributing ions, whose concentrations were decreased in de-fluoridation of the ground water samples.

Table 5: Correlation matrix of various water quality parameters of ground water samples collected from study area

	pH	EC	TDS	TH	TA	Turbi-dity	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^-	HCO_3^-	SO_4^{2-}	PO_4^{3-}	DO	F^{-}
pH	1																
EC	0.2646	1															
TDS	0.2047	0.9195	1														
TH	0.0494	0.5689	0.5485	1													
TA	0.2458	0.3966	0.4193	0.1694	1												
Tur-bidity	0.2245	0.2692	0.4219	0.2533	0.7378	1											
Ca^{2+}	0.0102	0.1402	0.1289	0.4139	0.6590	0.5567	1										
Mg^{2+}	-0.2725	0.5269	0.5989	0.6865	-0.1247	-0.0579	-0.0459	1									
Na^{+}	0.5106	0.1928	0.1608	0.0529	0.4681	0.3207	0.4021	-0.1649	1								
K^{+}	0.0667	0.3078	0.3780	0.5576	0.2002	0.3591	0.3179	0.4481	.2119	1							
Cl^{-}	-0.1704	0.5303	0.6472	0.6475	-0.1492	-0.0669	-0.1866	0.9472	-0.2318	0.3591	1						
NO_3^-	-0.2257	-0.1569	0.0879	0.2642	0.1195	0.3305	0.1697	0.3111	0.2234	0.0107	0.3122	1					
HCO_3^-	0.2271	0.5948	0.5851	0.2681	0.9461	0.7228	0.6322	0.0790	0.4564	0.2561	0.0170	0.0592	1				
SO_4^{2-}	0.4615	0.6809	0.7854	0.6344	0.5279	0.6857	0.4399	0.3453	0.2629	0.3763	0.4116	0.2159	0.6131	1			
PO_4^{3-}	0.4662	0.4366	0.2818	0.4305	0.0751	-0.1347	0.1034	-0.0272	0.0921	-0.0366	0.0930	-0.3222	0.0531	0.3069	1		

Table 6: Linear correlation coefficient and regression equation for some pairs of parameters which have significant value of correlation

Pair of Parameters	r	Regression equation y = a + bx	Regression coefficient	
			a	b
Na^{+} and F^{-}	0.9743	Na^{+} = 52.42 (F^{-}) - 11.71	-11.71	52.42
Mg^{2+} and Cl^{-}	0.9472	Mg^{2+} = 0.105 (Cl^{-}) - 18.75	-18.75	0.105
TA and HCO_3^-	0.9461	TA = 1.265 (HCO_3^-) - 4.818	-4.818	1.265
EC and TDS	0.9195	EC = 1.302 (TDS) - 95.68	-95.68	1.302
TDS and DO	0.8083	TDS = 82.50 (DO) + 422.80	422.80	82.50

The concentration of Ca^{2+} ions in the ground water samples was decreased after de-fluoridation of the ground water samples collected in study area. This is because after de-fluoridation, the concentrations of fluoride, EC, TDS, TA, TH and HCO_3^- , which were positively correlated with the Ca^{2+} ions were decreased. After de-fluoridation experiments, the Mg^{2+} ions concentration of the ground water samples was decreased. This is due to the positive correlation of Mg^{2+} ions with EC, TDS, TH and with other ions like K^+, Cl^-, and SO_4^{2-} which were decreased after de-fluoridation experiments. The concentration of Na^+ ions was decreased after de-fluoridation due to the positive correlation of Na^+ ions with fluoride, EC, TDS, TH, TA and with other ions like Ca^{2+}, K^+, HCO_3^- and SO_4^{2-} whose concentrations were also decreased in de-fluoridation of the ground water samples. The concentration of K^+ ions in the ground water samples was decreased due to the decrease in concentrations of fluoride, EC, TDS, TH, TA and other ions like Ca^{2+}, Mg^{2+}, Na^+, Cl^- and SO_4^{2-} which were positively correlated with the K^+ ions.

After de-fluoridation experiments, the Cl^- ions concentration of the ground water samples was decreased due to the decrease in concentrations of EC, TDS, TH, Mg^{2+} and K^+ which were positively correlated with the Cl^- ions. The NO_3^- ions concentration of the ground water samples was decreased due to the positive correlation of NO_3^- ions with the ions like Ca^{2+}, Mg^{2+}, Na^+, K^+ and fluoride which were decreased in de-fluoridation of the ground water samples. The concentrations of both HCO_3^- and SO_4^{2-} ions were decreased due to the positive correlation of these ions with all the water quality parameters whose concentrations were decreased in de-fluoridation of the ground water samples. The PO_4^{3-} ions concentration of the ground water samples was decreased due to the positive correlation of TDS, TH, Ca^{2+}, Na^+ and fluoride with the PO_4^{3-} ions. The DO content of the ground water samples was also decreased after de-fluoridation experiments.

After de-fluoridation with the four activated carbons at optimum conditions of parameters, the fluoride concentration in the ground water samples was reduced and it was in the range of 0.391-0.655 with NVNC, 0.607-0.758 with NSOC, 0.662-0.989 with NAbIC and 0.775- 0.993 with NAcIC. The fluoride content in all the ground water samples was within the permissible limits. The de-fluoridation capacity of the adsorbents was in the following increasing order: NAcIC < NAbIC < NSOC < NVNC.

3.6: Assumptions based on positive correlation of fluoride with water quality parameters

A good correlation coefficient has been found between F^- and lithogenic Na^+ and this indicates that the lithogenic Na^+ can be used as an index of weathering of minerals[34]. Due to the alternative wet and dry conditions of the climate prevailing in the present study area the leaching of F^- from the soils occurs mainly through the ion-exchange mechanism[35-36]. Moreover, the intensive and long-term irrigation causes the waters to have easy access to the weathering minerals that contributes leachable F^- to the groundwater[37-38].

A good positive correlation between F^- ion and TA/TH suggests the solubility of CaF_2 with the increase TA in the ground waters[39-40]as per the equations:

$$CaF_2 + CO_3^{2-} \rightleftharpoons CaCO_3 + 2F^-$$

$$CaF_2 + 2HCO_3^- \rightleftharpoons CaCO_3 + 2F^- + H_2O + CO_2$$

Further, TH precipitates as carbonates[41] and thus formed $CaCO_3$ also favours the dissociation of F^- from F^-containing minerals due to the difference in their solubility products. The contact or residence time between waters with minerals also influence the F^- concentrations in the ground waters[39-40,42]while the presence of intrusive bodies causes ground water barriers[43-44]. The increase in contact time increases the ion-exchange between OH^- in water to F^- in the mineral and these results in enhancing the concentration of F^- in ground waters. Further, higher values of TDS also increase the dissolution of CaF_2 in the ground water[45]. The slow weathering and fixation of K^+ ions in the clay minerals may be a reason for the low concentrations of K^+ in the ground waters. The heavy use of fertilizers for higher crop yields[46-47] is a characteristic of the positive correlation of SO_4^{2-} and NO_3^- with F^- in the ground waters.

Table 8: Physicochemical characteristics of ground water of villages of Vinukonda Mandal, Guntur Dist.: after defluoridation with activated carbon, NVNC

S. No:	pH	EC	TDS	TH	TA	Turbidity	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^-	HCO_3^-	SO_4^{2-}	PO_4^{3-}	DO	F^{-}
1	7.1	643	629	521	385	2.05	149	38	159	3.77	264	73	278	214	0.04	3.23	0.545
2	7.4	671	654	436	326	1.16	138	33	152	3.75	231	25	238	208	0.03	1.86	0.538
3	7.6	901	686	453	451	1.07	162	22	162	1.18	306	13	309	214	0.14	3.49	0.545
4	7.2	581	498	395	280	1.09	112	23	158	6.09	211	09	208	189	0.03	3.11	0.391
5	7.5	1203	929	494	563	1.31	168	38	194	5.80	448	22	458	257	0.10	4.76	0.531
6	7.3	935	715	514	487	1.72	161	29	167	2.28	386	31	391	263	0.07	4.05	0.523
7	7.2	1232	1017	565	561	2.25	102	49	148	5.14	431	18	446	301	0.09	7.08	0.521
8	7.4	839	775	336	462	1.87	89	29	161	2.11	323	31	317	212	0.03	4.31	0.582
9	7.3	1021	912	471	471	2.26	158	32	178	3.95	349	58	357	268	0.04	4.61	0.655
10	7.0	961	751	387	311	1.12	123	41	163	1.53	322	18	306	183	0.03	2.56	0.592
11	7.2	1178	974	602	301	1.13	112	63	168	6.52	561	39	254	249	0.02	6.21	0.513
12	7.0	1045	761	478	270	1.11	91	46	143	2.72	231	13	239	182	0.11	4.11	0.579
13	7.7	984	836	461	281	1.67	114	33	151	1.81	241	21	233	264	0.15	6.21	0.520

Table 9: Physicochemical characteristics of ground water of villages of Vinukonda Mandal, Guntur Dist.: after defluoridation with activated carbon, NSOC

S. No:	pH	EC	TDS	TH	TA	Turbidity	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^-	HCO_3^-	SO_4^{2-}	PO_4^{3-}	DO	F^{-}
1	7.2	648	634	526	392	2.10	154	42	163	3.89	271	79	289	227	0.06	3.36	0.648
2	7.5	674	661	441	331	1.44	147	35	159	4.19	239	29	241	215	0.05	1.98	0.644
3	7.7	904	692	460	457	1.21	174	27	165	1.86	312	15	319	227	0.16	3.58	0.758
4	7.3	583	504	402	285	1.21	119	28	161	6.19	219	10	213	197	0.04	3.18	0.619
5	7.8	1208	931	501	568	1.42	172	41	196	5.95	453	25	469	263	0.11	4.85	0.707
6	7.5	939	721	521	503	1.82	169	32	169	2.49	393	33	402	274	0.09	4.11	0.719
7	7.3	1235	1021	573	569	2.29	109	51	151	5.34	447	19	458	309	0.10	7.12	0.638
8	7.6	841	786	340	469	1.89	92	33	167	2.23	331	35	325	228	0.04	4.37	0.693
9	7.4	1023	916	482	476	2.46	162	39	182	4.16	352	61	365	275	0.05	4.68	0.729
10	7.3	965	758	398	325	1.25	129	47	165	1.68	327	19	314	192	0.03	2.62	0.669
11	7.5	1180	981	614	309	1.34	119	69	172	6.82	569	41	268	274	0.03	6.28	0.651
12	7.2	1047	765	486	276	1.22	99	49	145	2.76	238	16	241	187	0.12	4.16	0.655
13	7.9	986	841	468	285	1.77	117	39	157	1.97	245	23	248	271	0.17	6.27	0.607

Table 10: Physicochemical characteristics of ground water of villages of Vinukonda Mandal, Guntur Dist.: after defluoridation with activated carbon, NAbIC

S. No:	pH	EC	TDS	TH	TA	Turbidity	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^-	HCO_3^-	SO_4^{2-}	PO_4^{3-}	DO	F^{-}
1	7.3	653	641	531	402	2.15	165	49	168	3.95	282	82	294	234	0.08	3.43	0.762
2	7.6	678	668	446	337	1.56	157	42	162	4.34	243	32	257	219	0.06	2.29	0.662
3	7.8	909	698	465	465	1.44	176	32	176	2.88	324	17	321	238	0.18	3.75	0.841
4	7.5	589	512	413	294	1.86	128	31	168	6.21	226	11	222	209	0.05	3.26	0.731
5	8.0	1211	937	513	576	1.65	179	43	205	6.31	469	27	478	279	0.14	4.91	0.989
6	7.9	942	726	528	514	1.94	176	38	178	2.61	407	39	409	289	0.10	4.18	0.838
7	7.4	1239	1027	576	574	2.45	114	56	159	5.45	459	21	465	315	0.12	7.18	0.759
8	7.7	845	792	346	473	2.01	96	35	172	2.86	347	38	337	235	0.05	4.49	0.779
9	7.6	1028	921	487	483	2.54	169	41	186	4.46	361	68	376	298	0.06	4.74	0.849
10	7.4	969	765	402	331	1.32	132	53	171	1.97	331	23	323	207	0.04	2.73	0.701
11	7.7	1182	985	626	315	1.45	121	74	179	6.93	575	47	279	289	0.04	6.34	0.714
12	7.3	1050	778	494	281	1.24	101	51	151	2.79	247	19	249	198	0.14	4.23	0.792
13	8.1	989	847	475	294	1.78	123	41	164	2.27	251	26	254	284	0.19	6.31	0.743

Table 11: Physicochemical characteristics of ground water of villages of Vinukonda Mandal, Guntur Dist.: after defluoridation with activated carbon, NAcIC

S. No:	pH	EC	TDS	TH	TA	Turbidity	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^-	HCO_3^-	SO_4^{2-}	PO_4^{3-}	DO	F^{-}
1	7.3	657	647	537	414	2.25	173	54	172	3.98	304	84	304	237	0.09	3.56	0.832
2	7.7	682	671	451	341	1.68	162	46	165	4.49	258	37	263	227	0.07	2.38	0.887
3	7.9	913	711	472	472	1.54	177	34	187	2.97	331	19	332	242	0.29	3.87	0.976
4	7.7	592	519	420	301	1.89	136	35	177	6.22	232	13	228	211	0.06	3.39	0.883
5	8.3	1213	940	521	582	1.67	182	48	209	6.56	476	29	480	283	0.16	5.07	0.993
6	8.1	947	731	531	529	1.98	187	42	182	3.10	412	43	412	302	0.12	4.27	0.948
7	7.5	1242	1035	583	581	2.65	119	61	162	5.79	463	23	471	326	0.15	7.29	0.790
8	7.9	848	801	352	481	2.09	98	42	176	2.94	351	41	343	242	0.06	4.54	0.840
9	7.7	1031	930	494	492	2.56	175	49	194	4.66	374	72	378	302	0.07	4.88	0.981
10	7.4	972	772	413	338	1.42	146	56	177	2.49	338	28	329	213	0.05	2.76	0.924
11	8.0	1185	992	631	322	1.68	128	80	181	7.13	589	51	287	303	0.05	6.49	0.949
12	7.4	1053	784	502	287	1.31	107	54	156	2.89	251	21	252	209	0.16	4.28	0.775
13	8.3	992	851	487	301	1.98	128	44	167	2.78	259	28	259	293	0.21	6.35	0.834

4. Conclusions

The quality of ground water samples collected from 13 villages of Vinukonda Mandal, Guntur Dist., A. P. is analyzed. The quality of ground water samples is observed with respect to some physicochemical parameters like pH, EC, TDS, TA, TH, Turbidity, Ca^{2+} Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^-, HCO_3^-, SO_4^{2-}, PO_4^{3-}, F^{-} and DO. To assess the quality of ground water each parameter is compared with the standard desirable limits prescribed by World Health Organization (WHO) and Bureau of Indian Standard (BIS). For some ground water samples these parameters are above the maximum permissible limits, while for some samples the values are within the permissible limits. The reason for decreasing quality of water in this region may be due to over consumption for drinking, domestic and agricultural purposes. Hence, rapid and reliable monitoring measures are essential for keeping a close watch on water quality and health environment. Based on the correlation regression study, it can be concluded that the good correlations among various water quality parameters are observed in all samples. The linear correlation is very useful to get fairly accurate idea of quality of the groundwater by determining a few parameters experimentally.

It is disheartening to note that fluoride content is found beyond the WHO limit in all samples. De-fluoridation process is suggested to make study area water portable. Batch mode adsorption process is adopted for the removal of fluoride from ground water samples with the activated carbon adsorbents: NVNC, NSOC, NAbIC and NAcIC. After treatment with these activated carbon adsorbents, the fluoride concentration is successfully reduced to below the permissible limit and the concentrations of other water quality parameters are also reduced to less extent. Thus the active carbons developed in this work are highly successful in the de-fluoridation.

5. References

1 Jain C.K. et al., Ground water quality in Sagar district, Madhya Pradesh, Indian Journal of Environmental Health, 2000, 42(4), 151-158.

2 Lilly Florence P., Paulraj A. and Ramachandramoorthy T., Water Quality Index and correlation Study for the Assessment of Water Quality and its Parameters of Yercaud Taluk, Salem District, Tamil Nadu, India, Chem Sci Trans., 2012, 1(1),139-149.

3 Meenakshi and Maheshwari R. C., Fluoride in drinking water and its removal, J. Haz Mater, 2006, B137,456-463.

4 Ramakrishnaiah C.R., Sadashivaiah C. and Ranganna G., Assessment of Water Quality Index for the Groundwater in Tumkur Taluk, Karnataka State, India, E. J. Chem., 2009, 6(2), 523-530.

5 Bhatt K.B. and Salakani S., Hydrogeochemistry of the upper Ganges River, India, J. Geol Soc. India, 1996, 48, 171-182.

6 Karanth K.B., Groundwater assessment, development and management, Tata McGraw-Hill Publishers, New Delhi, 1997.

7 Jain P., Sharma J.D., Sohu D. and Sharma P., Chemical analysis of drinking water of villages of Sanganer Tehsil, Jaipur Dist, Int. J. Env. Sci. Tech., 2005, 2(4), 373-379.

8 Paramesha Naik D., Usha M. and Somashekar R.K., High fluoride content in groundwater-a case study in Bagepalli, Kolar District, Karnataka State, Eco Environ & Cons., 2007, 13(2),303-305.

9 Handa B.K., Geochemistry and genesis of fluoride containing ground water in India, Groundwater, 1975, 13(3), 275-281.

10 Gupta S., Mondal D. and Bardhan A., Geochemical provenance and spatial distribution of fluoride in Groundwater in parts of Raniganj coal field, West Bengal, India, Archives of Applied Science Research, 2012, 4 (1), 292-306.

11 Muggler L., Fluoride in soil solution. An assessment of fluoride availability and uptake by plants in fluoride contaminated soils, Term paper, 2009, 1-3.

12 Devi S.B. and Kamble R.K., Groundwater fluoride in East Imphal district of Manipur, IJEP, 2006, 26(10), 885-891.

13 BIS, Bureau of Indian Standards, Specifications for Drinking Water, IS: 10500, New Delhi, India, 1991.

14 WHO, World Health Organization, Guidelines for drinking water quality, Geneva, 1993.

15 Gajendran C. and Thamarai P., Study on statistical relationship between ground water quality parameters in Nambiyar river basin, Tamilnadu, India, Poll Res., 2008, 27(4), 679-683.

16 Sudhakar G. and Latha S.G., Seasonal Variation of Ground-Water Analysis from Bapatla Mandal, Guntur District, Andhra Pradesh, Int. J. Sci & research, 2013, 10.12.

17 Brown E., Skougstad M.W. and Fishman M.J., Method for collection and analysis of water sample for dissolved minerals and gases, US Department of Interior, 1974, Book No. 5.

18 APHA, American Public Health Association, Standard Methods for Examination of Water and Waste Water, 20 th edn., Washington, D.C., 1998.

19 USEPA, U. S. Environmental Protection Agency, In Methods for Chemical Analysis of Water and Wastes, Sample preservation, pp.xv-xx, EPA-600/4-79-020, Cincinnati, Ohio, USA. 1983.

20 NEERI, National Environmental Engineering Research Institute, Course manual on water and waste water analysis, Nagpur, 1984, 134.

21 Patil V.T. and Patil P.R., Groundwater quality of open wells and tube wells around Amalner town of Jalgaon, district, Maharashtra, India, Electronic Journal of Chemistry, 2011, 8(1), 53-78.

22 Kumar N. and Sinha D.K., Drinking water quality management through correlation studies among various physicochemical parameters: a case study, International Journal of Environmental Sciences, 2010, 1(2), 253-259.

23 Meta K.V., Physicochemical characteristics and statistical study of groundwater of some places of Vadgam taluka in Banaskantha district of Gujarat state, India, Journal of Chemical Pharmaceutical Research, 2010, 2(4), 663-670.

24 Robinove C.J., Langford R.H. and Brookhart J.W., Saline water resource of North Dakota, In US Geological Survey Water Supply, 1958, Paper No. 1428, pp.72.

25 Durfor C.N. and Becker E., Public water supplies of the 100 largest cities in the United States, In Geological Survey Water Supply, U.S. Government Printing Office, Washington, 1964, Paper No. 1812, pp. 364.

26 Majumdar D. and Gupta N., Nitrate pollution of groundwater and associated human health disorders, Indian J. Environ Health, 2000, 42, 28-39.

27 Dhembare A. J., Pondhe G. M. and Singh C., Ground water characteristics and their significance with special reference to public health in Pravara area, Maharashtra, Poll. Res., 1998, 17, 87- 90.

28 Mehta M.B., Drinking water quality of Ground water from selected sample points around Thane District of Maharashtra, J. Indust. Poll Control, 2003, 19 (2), 153-157.

29 Brunt R., Vasak L. and Griffioen J., Fluoride in groundwater: probability of occurence of excessive concentration on global scale, International Groundwater Resources Assessment Centre (IGRAC), Report SP 2004-2, Utrecht, 2004.

30 Jha S.K., Nayak A.K., Sharma Y.K., Mishra V.K. and Sharma D.K., Fluoride accumulation in soil and vegetation in the vicinity of brick fields, Bull Environ Contam Toxicol, 2008, 80(4), 369-373.

31 Ozsvath D.L., Fluoride concentrations in a crystalline bedrock aquifer Marathon County, Wisconsin. Environ Geol., 2006, 50(1), 132-138.

32 Somasekhara Rao K. and Someswara Rao B., Correlations among water quality parameters of ground waters of Musunur mandal, Krishna District, Indian J. Environ. Prot., 1995, 14(7), 528-532.

33 Kannan N. and Rajasekharan N., Correlations of water quality parameters of printing industry effluents in Sivakasi (South India), Ind. J. Env. Hlth., 1993, 33(3), 330-335.

34 Ramesam V. and RajagopalanK., Fluoride ingestion into the natural water of hard rock areas, peninsular India, J. Geol. Soc. India, 1985, 26, 125-132.

35 Robinson W.D. and Edington G., Fluorine in soils, Soil Sci., 1946, 61, 341-353.

36 Hem J.D., Study and Interpretation of the Chemical Characteristics of Natural Water, Book 2254, third edn, Scientific Pub, Jodhpur, India, 1991.

37 Sahu N.K. and Karim M.A., Fluoride incidence in natural waters, Gujarat, India, J. Geol. Soc. India, 1989, 6, 450-456.

38 Wenzel W.W. and Blum W.E.H., Fluoride speciation and mobility in fluoride contaminated soil and minerals, Soil Sci**.,** 1991,153, 357-364.

39 Ramamohana Rao N.V., Suryaprakasa Rao K. and Schuiling R.D., Fluorine distribution in waters of Nalgonda Dist, A.P., India, Env. Geol., 1993, 21, 84-89.

40 Saxena V.K. and Ahmed S., Dissolution of fluoride in groundwater: a water-rock interaction study, Environ. Geol., 2001, 40, 1084-1087.

41 Gaciri S.J. and Davis T.C., The occurrence and geochemistry of fluoride in some natural waters of Kenya, J. Hydrol., 1993,143, 395-412.

42 Wodeyar B.K. and Sreenivasan G., Occurrence of fluoride in the ground waters and its impact in Peddavankahalla Basin, Bellary District, Karnataka, India-a preliminary study, Current Sci., 1996, 70, 71-74.

43 Singh R.P. and Jamal A., Dykes as groundwater loci in parts of Nashik district, Maharashtra, India, J. Geol. Soc. India**,** 2002, 59, 143-146.

44 Subba Rao N., Factors affecting optimum development of ground waters in crystalline terrain of the Eastern Ghats,Visakhapatnam area, Andhra Pradesh, India, J. Geol. Soc. India, 1992, 40, 462-467.
45 Perelman A.I., Geochemistry of Elements in Supergene Zone, Keter Pub. House, Jerusalem, Israel, 1977.
46 Subba Rao N., Geochemistry of groundwater in parts of Guntur district, Andhra Pradesh, India, Environ. Geol., 2002, 41, 552-562.
47 Subba Rao N., Prakasa Rao J., John Devadas D., Srinivasa Rao K.V., Krishna C. and Nagamalleswara Rao B., Hydrogeochemistry and groundwater quality in a developing urban environment of a semi-arid region, Guntur, Andhra Pradesh, India, J. Geol. Soc. India, 2002, 59, 159-166.

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