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Assessment of ground water quality and application of activated carbons in the removal of fluoride from ground waters of Vinukonda Mandal in Guntur District, Andhra Pradesh, India

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ABSTRACT

The present study deals with the ground water quality with respect to fluoride in villages of Vinukonda Mandal, Guntur District, Andhra Pradesh, India. Ten ground water samples are collected from ten different villages for determining 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-}, F^{-} and DO. The observed values of these parameters of the samples are compared with standard values recommended by Indian Standards and World Health Organization (WHO). Fluoride concentration in the study area is ranged between 3.28 to 4.27 mg/lit. Overall water quality is found unsatisfactory for drinking purposes without any prior treatment. A systematic correlation and regression study shows a significant linear relationship between different pairs of parameters to identify the highly correlated and interrelated water quality parameters. After treatment with activated carbons, NVNC, NSOC, NAbIC and NAcIC, the concentrations of all physicochemical parameters of the samples are reduced to permissible levels.

Keywords: ground water**,** physicochemical parameters, correlation analysis, activated carbons, de-fluoridation

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INTRODUCTION

Ground water quality includes the physical, chemical, and micro-biological characteristics of ground water [1]. Since most ground water is colourless, odourless, and without specific taste, we are typically most concerned with its chemical and biological qualities. Naturally, ground water contains mineral ions. These ions slowly dissolve from soil particles, sediments, and rocks as the water travels along mineral surfaces in the pores or fractures of the unsaturated zone and the aquifer. They are referred to as dissolved solids. Water quality is based on the physical and chemical soluble constituents due to weathering of parent rocks and anthropogenic activities [2]. Ground water quality has become an important water resources issue due to rapid increase of population, rapid industrialization, unplanned urbanization, flow of pollution from upland to lowland, and too much use of fertilizers, pesticides in agriculture [3] and the polluted water may have an impact on the health and economic status of the consumers [4]. The major problem with the ground water is that once contaminated, it is difficult to restore its quality. Hence there is a need and concern for the protection and management of ground water quality. It is well known that no straight forward reasons can be advanced for the deterioration of water quality, as it is dependent on several water quality parameters [5, 6].

Drinking waters for human consumption should contain some level of minerals, but these levels should not be excessive or otherwise, they are hazardous or cause ill effects. The desirable and permissible limits of various physicochemical parameters in ground waters are presented in the Table 1 as per the ISI and WHO standards.

Table 1: Drinking Water Specifications [7-10]

S.No:	Water quality parameter*	Desirable limit	Permissible limit
1	Hydrogen ion concentration (pH)	6.5-8.5	---
2	Electrical Conductivity (EC)	300	1500
3	Total Dissolved Solids (TDS)	500	2000
4	Total Hardness (TH) as $CaCO_3$	300	600
5	Total Alkalinity (TA) as $CaCO_3$	200	600
6	Turbidity	5	10
7	Calcium (Ca^{2+})	75	200
8	Magnesium (Mg^{2+})	30	100
9	Sodium (Na^+)	---	50
10	Potassium (K^+)	---	10
11	Chloride (Cl^-) (Argentometric method)	250	1000
12	Nitrate (NO_3^-)	---	45
13	Bicarbonate (HCO_3^-)	---	600
14	Sulphate (SO_4^{2-})	200	400
15	Phosphate (PO_4^{3-})	---	10
16	Dissolved Oxygen (DO)	---	6.0
17	Fluoride (F^-)	1.0	1.5

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

The acceptable limits are to be implemented and the values in excess of these, render the water not acceptable, but still may be tolerated in the absence of an alternative source but up to the limits indicated under permissible limit.

A systematic study of correlation and regression coefficients of the water quality parameters helps to assess the overall water quality and also quantify the relative concentration of various pollutants in water. Therefore, statistical correlation technique is used to compare the physicochemical parameters.

1.1: Geohydrological conditions in villages of Vinukonda Mandal, Guntur District, A.P.:

Ground water is the main source for drinking purposes in these villages and high concentrations of fluorides are found in the underground water reserves and hence, potable water is highly affected and making it undrinkable. The local people in these villages of Vinukonda Mandal suffers from a major problem of very high fluoride levels in the water which causes a bone disease called Fluorosis. These villages in Vinukonda Mandal mainly contain rocks of Cryolite which is the major source of fluoride.

Mostly the villagers are suffering from enamel fluorosis, bow legs, symptoms similar to polio and deformity in muscle and bones and 30% of the people in these villages are disabled because of the high intakes of fluoride. Apart from the health aspect, the people are not inclined to have matrimonial relationship with the females of this area. So, it is essential to carry out a systematic study on fluoride contamination of ground waters in the villages of Vinukonda Mandal and to find methods to reduce the fluoride concentration below the harmful levels.

The main objective of this study is to investigate the fluoride levels in the real ground water samples collected from ten villages of Vinukonda Mandal of Guntur District, Andhra Pradesh and its removal by the application of batch method using activated carbons namely NVNC, NSOC, NAbIC and NAcIC which are prepared from barks/stems of *Vitex Negundo, Senna Occidentalis, Abutilon Indicum* and *Acalypha Indica* plants respectively. The work deals with the study of 17 physicochemical parameters like pH, EC, TDS, TA, TH, Turbidity, Ca^{2+}, Mg^{2+}, Na^+, K^+, F^-, Cl^-, $NO_3^-, HCO_3^-, SO_4^{2-}, PO_4^{3-}$ and DO of ground water samples of study area to analyse correlation and regression study of various physicochemical parameters.

MATERIALS AND METHODS

2.1: Study area

The ten villages, chosen for study, are in Vinukonda Mandal of Guntur District which has 57 Mandals under 3 divisions namely Narasaraopet, Guntur and Tenali [11] and of which the Narasaraopet division is well known fluoride affected area. Vinukonda Mandal is one of the 20 Mandals of Narasaraopet divisions (Figure 1). It is bounded by Savalyapuram Mandal towards East, Nuzendla Mandal towards South, Bollapalle Mandal towards North and Ipur Mandal towards North.

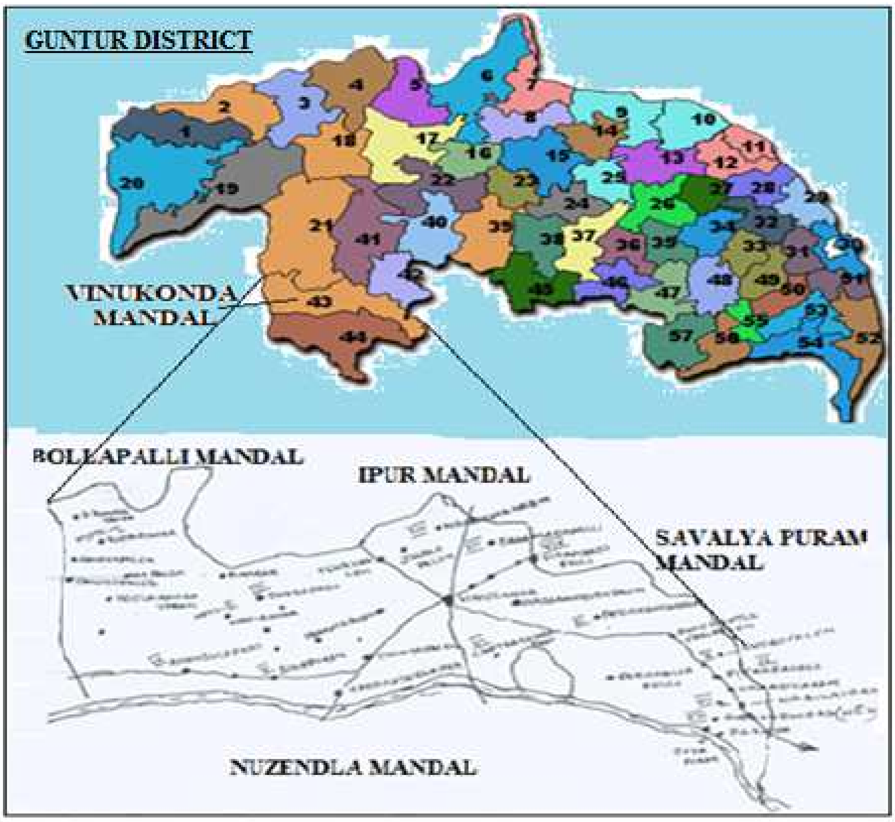

Figure 1: Location of Vinukonda Mandal

The study area is covered mostly with red soils contains immense economic reserves of cement grade limestone, diatomaceous earth, gypsum, granite, kankar and white clays as nature's gift. The climate is very hot in summer and the highest day temperature is in between 34°C to 47°C and in winter it is around 25°C. The Naguleru, rivulet of the river Krishna, passes through the study area.

MATERIALS

2.2.1: Ground water samples collection

In the present study ten ground water samples were collected from ten different villages of Vinukonda Mandal of Guntur District. The names of the ten villages in Vinukonda Mandal, where the ground water samples collected were listed in Table 2. The ground water samples were collected carefully in one-litre capacity polyethylene bottles with necessary precautions [12-15] to avoid unpredictable changes in characteristics as per standard procedures of APHA, [16]. They were further rinsed with sample water before collection.

Table 2: Names of the samples collected villages

S. No:	Sample Number	Village Name
1	1	Sivapuram
2	2	Koppukonda
3	3	Thimmayapalem
4	4	Narasayapalem
5	5	Brahmanapalli
6	6	Mada manchipadu
7	7	Andugulapadu
8	8	Tsoutapalem
9	9	Venkupalem
10	10	Nagulavaram

These bottles were labelled with respect to collecting points, date and time in order to avoid any error between collection and analysis. The collected samples were stored in an icebox and brought to laboratory for determining both physical and chemical parameters. All the chemicals used were AR grade of pure quality. Double distilled water was used for the preparation of all the reagents and solutions.

2.2.2: Preparation of activated carbons:
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. They were used in the defluoridation studies.

The barks/stems of above said *bio-materials* were collected separately in bulk, crushed in to small pieces, washed with fluoride free water and completely dried under sunlight for two days. The dried materials were carbonized separately in muffle furnace in the absence of air at 500^0C for 4 hours. After carbonization, the carbons were washed with fluoride free water; the process was repeated for several times and then filtered. Then the carbons were dried separately in air oven at 110^0C and were sieved into desired particle sizes. The carbons were subjected to liquid phase oxidation separately by mixing with 0.1N HNO_3 and boiled for 2 to 3 hours on flame. Then the carbons were washed with double distilled water to remove the excess acid and dried at 150^0C for 12 hours.

METHODS

2.3.1: Methods used for the determination of water quality parameters except fluoride ion:
For the assessment of ground water quality, seventeen physicochemical parameters were selected and analyzed according to the standard methods of chemical analysis as prescribed in literature [14, 16-18] and the methods for each parameter, except fluoride ion, were listed in Table 3. The average values of three replicates were taken for each determination.

Table 3: Methods used for the determination of water quality parameters

S.No:	Water quality parameter	Method of determination
1	Hydrogen ion concentration (pH)	pH-metry
2	Electrical Conductivity (EC)	Conductometry
3	Total Dissolved Solids (TDS)	TDS analyzer
4	Total Hardness (TH) as $CaCO_3$	EDTA-Titrimetry
5	Total Alkalinity (TA) as $CaCO_3$	Titrimetry
6	Turbidity	Turbidity meter
7	Calcium (Ca^{2+})	EDTA-Titrimetry
8	Magnesium (Mg^{2+})	EDTA-Titrimetry
9	Sodium (Na^+)	Flame photometry
10	Potassium (K^+)	Flame photometry
11	Chloride (Cl^-) (Argentometric method)	Titrimetry
12	Nitrate (NO_3^-)	Spectrophotometry
13	Bicarbonate (HCO_3^-)	Titrimetry
14	Sulphate (SO_4^{2-})	Spectrophotometry
15	Phosphate (PO_4^{3-})	Spectrophotometry
16	Dissolved Oxygen (DO)	Titrimetry

2.3.2: Analysis of fluoride ion by batch mode adsorption studies:
Batch mode of adsorption studies were adopted [19-21]. 100 ml of ground water from one of the samples was pipette out into a 250 ml conical flask at room temperature 30 ± 1^0C and to it, weighed quantity of the prepared active carbon adsorbent was added. Then the conical flask along with test solution (at pH: 7) and adsorbent was shaken in horizontal shaker at 120 rpm. At the end of desired contact time, the conical flask was removed from shaker and allowed to stand for 2 min for settling the adsorbent and the adsorbent was filtered using Whatman No.42 filter paper. The filtrate was analyzed for residual fluoride concentration by SPADNS method by measuring absorbance at λ_{max} 570 nm as described in Standard Methods of Water and Waste Water Analysis [16].

The optimum conditions for the de-fluoridation were found to be: pH: 7, contact time: 50 min for both NVNC and NSOC and 60 min for both NAbIC and NAcIC. The active carbons required for maximum defluoridation of 1 m^3 (1000 liters) water were found to be: 2.61 kg for NVNC, 3.09 Kg for NSOC, 3.61 Kg for NAbIC and 3.72 kg for NAcIC.

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

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

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

where C_i = Initial concentration of the fluoride ion in mg/lit

C_e = Final concentration of the fluoride ion in mg/lit
m = Mass of the adsorbent in grams
V = Volume of fluoride test solution in liters

2.4: Correlation coefficient and linear regression
The strong correlations among different parameters indicate the water quality. The statistical regression analysis has been found to be a highly useful tool for correlating different parameters. The developed regression equations for the parameters having significant correlation coefficients can be successfully used to estimate the concentration of other constituents.

Determination of correlation is important in finding out the strength of the relationship between the two inter dependent variables. If x and y are the two variables then the correlation coefficient (r) between the two variables is given by,

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

If the values of correlation coefficient ‘r’ between two variables x and y are fairly large, it implies that these two variables are highly correlated. 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 statistics, correlation is used for the measurement of the strength and statistical significance of the relation between two or more water quality parameters [22].

RESULTS AND DISCUSSION

3.1: Ground water quality status in the study area before defluoridation:
Ground water quality assessment was carried to determine its suitability in terms of drinking purposes. The physical and chemical parameters of the analytical results of groundwater were compared with the standard guideline values recommended by the Indian Standards and World Health Organization (WHO) for drinking and public health purposes. The results of physicochemical analysis of the ground water from five villages of Vinukonda Mandal were presented in Table 4. All the ground water samples collected in the study area were colourless.

The pH value of drinking water is an important index of acidity or alkalinity. A number of minerals and organic matter interact with one another to give the resultant pH value of the sample. In the present study, pH ranges from 7.2-8.4 and the observations are presented in the Table 4. The results showed that the pHs lie in the range prescribed by the Indian Standards and WHO (Table 1).

The EC values for the samples are in the range from 765-1145(μ S/cm) and the observations are presented in the Table 4. The EC value is directly proportional to the total dissolved matter. The results showed that the electrical conductivity values of all the samples are exceeded to desirable limit but the values are within the maximum permissible limit prescribed by Indian Standards and WHO (Table 1).

The level of TDS is one of the characteristics, which decides the quality of drinking water. In the present study, TDS ranged from 620-926 mg/lit and the observations are presented in the Table 4. The results showed that the TDS values of all the samples are exceeded to desirable limit but the values are within the maximum permissible limit prescribed by Indian Standards and WHO (Table 1).

Table 4: Physicochemical characteristics of ground water of villages of Vinukonda Mandal, Guntur Dist.: before defluoridation

	Sample Number									
Water quality parameter	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
pH	8.2	7.2	7.8	8.1	8.4	7.9	8.2	7.8	8.1	8.2
EC	976	765	936	912	1145	943	954	988	909	987
TDS	815	620	745	715	926	746	764	875	710	898
TH	506	557	423	515	620	414	603	496	475	595
TA	408	395	410	304	610	520	571	508	496	456
Turbidity	1.67	1.89	1.54	2.12	3.34	1.34	2.45	1.42	2.23	2.45
Ca^{2+}	125	166	115	165	209	112	206	118	158	194
Mg^{2+}	66	74	56	69	72	58	74	58	46	54
Na^{+}	188	190	176	172	221	191	184	196	161	157
K^{+}	2.34	1.58	5.65	4.21	5.12	3.89	2.54	1.71	2.12	3.10
Cl^{-}	769	695	865	696	986	642	814	774	809	799
NO_3^-	25	94	46	28	42	47	58	42	35	46
HCO_3^-	365	272	405	296	584	367	481	364	355	372
SO_4^{2-}	276	201	288	279	301	221	245	218	245	226
PO_4^{3-}	0.26	0.45	0.25	0.20	0.15	0.16	0.24	0.12	0.11	0.10
DO	2.56	3.25	4.76	4.67	5.48	4.68	2.89	4.45	3.23	4.57
F^{-}	3.75	3.82	3.56	3.48	4.27	3.88	3.69	4.09	3.37	3.28

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

The Total Hardness is an important parameter of water quality whether it is to be used for domestic, industrial or agricultural purposes. The hardness is due to dissolution of alkaline earth metal salts from geological matter. The total hardness ranges between 414-620 mg/lit and the observations are presented in the Table 4.The results showed that the TH values of all the samples are exceeded to desirable limit but the values are within the maximum permissible limit prescribed by Indian Standards and WHO (Table 1).

The Total Alkalinity of water is defined as the ionic concentration, which can neutralize the hydrogen ions. The alkalinity values ranges between 304-610mg/lit and the observations are presented in the Table 4. The results showed that the TA values of all the samples are exceeded to desirable limit but the values are within the maximum permissible limit prescribed by Indian Standards and WHO (Table 1).

In the present investigation, the turbidity values are varied from 1.34 to 3.34 NTU and the observations are presented in the Table 4. The results showed that the turbidity values of all the samples collected from study area are below the maximum permissible limit given by Indian Standards and WHO (Table 1).

In the studied area, the concentrations of the cations, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and potassium (K^{+}), are varied from 112-209, 46-74, 157-221 and 1.58-5.65 mg/lit respectively and the observations are presented in the Table 4. In human body Hypocalcaemia causes coma and death if serum calcium level rises to 160 mg/lit. Too high magnesium causes nausea, muscular weakness and paralysis in human body [23]. The results showed that the Ca^{2+} and Mg^{2+}contents of all the samples are exceeded to desirable limit but the values are within the maximum permissible limit; sodium content of all the samples is above the maximum permissible limit and the potassium content of all the samples is within the maximum permissible limit described by Indian Standards and WHO (Table 1).

In the present study the amounts of ions, Cl^{-}, $NO_3^-, HCO_3^-, SO_4^{2-}, PO_4^{3-}$, F^{-}, are varied from 642-986, 25-94, 272-584, 201-301, 0.10-0.45 and 3.28-4.27mg/lit respectively and the observations are presented in the Table 4. The value of chloride content in four samples has been found to be high, which can cause corrosion and pitting of iron plates or pipes. The results showed that the chloride content of all the samples is exceeded the desirable limit but below the maximum permissible limit; the bicarbonate, sulphate, phosphate concentrations of all the samples are below the maximum permissible limit; the nitrate concentration is above the maximum permissible limit for all the samples except for the sample No.5 and the fluoride concentration of all the ground water samples is above the maximum permissible limit as described by Indian Standards and WHO (Table 1). These results indicated that the fluoride concentration is very high in the ground waters of this study area because the villages of Vinukonda Mandal mainly contain rocks of Cryolite which is the main cause of fluoride.

The Dissolved oxygen in the water samples ranges from 2.56 to 5.48mg/lit and the observations are presented in the Table 4. The higher value of dissolved oxygen can impart good aesthetic taste to drinking water [24]. The results indicate that the DO content of all the samples, except Sample No: 5, are within the maximum permissible limit as given by Indian Standards and WHO (Table 1).

3.2: Statistical Analysis:

In this study, the numerical values of correlation coefficient, r, for the seventeen water quality parameters are tabulated in Table 5. It is evident that the significant positive correlations (r > 0.6) are observed between different water quality parameters. Positive correlation is obtained between 124 unions (i.e., 81.0% of the total number) and rest of the 29 unions (i.e., 19.0% of total number) demonstrates negative correlation. Highly positive correlation is observed between Na^+ and F^- (0.9766).

3.3: Regression analysis:

The linear regression analysis is carried out for the water quality parameters which are found to have better and higher level of significance in their correlation coefficient. The regression equations obtained from the analysis are given in the Table 6. The different dependent characteristics of water quality are calculated using the regression equation and by substituting the values for the independent parameters in the equations. The experimentally estimated and calculated values using the regression equations are given in Table 7. Hence it can be concluded that the correlation studies of the water quality parameters have a great significance in the study of water resources.

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

	pH	EC	TDS	TH	TA	Turb	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	HCO_3^-	SO_4^{2-}	PO_4^{3-}	DO
pH	1															
EC	0.7976	1														
TDS	0.6571	0.9011	1													
TH	0.3128	0.3042	0.3816	1												
TA	0.3817	0.6049	0.5070	0.3134	1											
Turb	0.5662	0.5163	0.3918	0.8108	0.4284	1										
Ca^{2+}	0.3983	0.2589	0.2235	0.9093	0.3365	0.9159	1									
Mg^{2+}	-0.0828	-0.0092	-0.1003	0.5671	0.0027	0.3235	0.4319	1								
Na^+	0.0064	0.4572	0.3115	0.2222	0.4950	0.2067	0.0450	0.5814	1							
K^+	0.3391	0.4605	0.2164	-0.1606	0.0119	0.2339	0.0163	0.0151	0.1714	1						
Cl^-	0.5125	0.7053	0.5889	0.4325	0.5201	0.6785	0.4456	0.0274	0.3208	0.4178	1					
NO_3^-	-0.7471	-0.5629	-0.4592	0.2566	0.0604	-0.0139	0.2182	0.3909	0.1507	-0.3017	-0.1889	1				
HCO_3^-	0.6343	0.8306	0.6359	0.4321	0.7953	0.6504	0.4659	0.2183	0.5489	0.4607	0.8250	-0.1703	1			
SO_4^{2-}	0.6084	0.5681	0.2897	0.0424	-0.0305	0.3988	0.1229	0.1546	0.2152	0.7212	0.6231	-0.5951	0.5288	1		
PO_4^{3-}	-0.6861	-0.6545	-0.6569	0.0669	-0.3985	-0.1982	-0.0356	0.6179	0.1742	-0.1922	-0.2751	0.6958	-0.3344	-0.1548	1	
DO	0.1615	0.5003	0.4413	-0.0539	0.1341	0.2077	0.0227	-0.1211	0.2641	0.7243	0.2847	-0.1752	0.3173	0.2819	-0.4413	1
F^-	-0.0686	0.4247	0.3316	0.1444	0.5188	0.0870	-0.0600	0.4709	0.9766	0.0586	0.2461	0.1558	0.4710	0.0718	0.1008	0.26 94

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^-	0.9766	Na^+ = 57.88 (F^-) - 31.68	-31.68	57.88
Ca^{2+} and Turbidity	0.9159	Ca^{2+} = 56.93(Turbidity) + 40.36	40.36	56.93
TH and Ca^{2+}	0.9093	TH = 1.738(Ca^{2+}) + 247.80	247.80	1.738
TDS and EC	0.9011	TDS = 0.922 (EC) - 95.96	-95.96	0.922
pH and EC	0.7976	pH = 0.002 (EC) + 5.252	5.252	0.002
TA and HCO_3^-	0.7953	TA = 0.812 (HCO_3^-) + 154.20	154.20	0.812
EC and Cl^-	0.7053	EC = 0.679 (Cl^-) + 418.20	418.20	0.679

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

	Na^+		Ca^{2+}		TH		TDS		pH		TA		EC	
	O	**P**	**O**	**P**	**O**	**P**	**O**	**P**	**O**	**P**	**O**	**P**	**O**	**P**
1	188	185	125	135	506	465	815	804	8.2	7.2	408	451	976	940
2	190	189	166	148	557	536	620	611	7.2	6.8	395	375	765	890
3	176	174	115	128	423	448	745	767	7.8	7.1	410	483	936	1006
4	172	170	165	161	515	535	715	745	8.1	7.1	304	395	912	890
5	221	215	209	231	620	611	926	960	8.4	7.5	610	628	1145	1088
6	191	193	112	117	414	442	746	773	7.9	7.1	520	452	943	854
7	184	182	206	180	603	606	764	784	8.2	7.2	571	545	954	971
8	196	205	118	121	496	453	875	815	7.8	7.2	508	450	988	944
9	161	163	158	167	475	522	710	742	8.1	7.1	496	442	909	968
10	157	158	194	180	595	585	898	814	8.2	7.2	456	456	987	961

**Note: O - Observed value, P- Predicted value*

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

The results of physicochemical analysis of all the ground water samples collected from the five villages of Vinukonda Mandal indicated that these samples contain excess of fluoride beyond the permissible limit (1.5 mg/lit). For this reason, all the ground water samples collected from study area were treated with the prepared activated carbon adsorbents: NVNC, NSOC, NAbIC and NAcIC, in order to reduce the fluoride concentration below the permissible limit. The defluoridation studies of these ground water samples were carried out at the optimum conditions of pH, contact time and adsorbent dosage and the values obtained were summarized in Table No's: 8, 9, 10 and 11 respectively.

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

	Sample Number									
Water quality parameter	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
pH	8.0	7.0	7.4	7.9	8.1	7.4	7.4	6.9	7.9	7.6
EC	949	743	910	892	1077	922	937	968	893	973
TDS	806	610	739	705	917	731	745	861	689	881
TH	487	536	401	496	596	397	584	481	453	581
TA	382	377	381	282	586	482	547	482	476	438
Turbidity	1.38	1.45	1.22	1.37	2.81	1.22	2.16	1.13	2.12	2.19
Ca^{2+}	111	145	102	142	161	92	185	107	138	169
Mg^{2+}	58	63	41	56	59	49	63	48	39	42
Na^{+}	169	167	165	165	211	165	167	187	153	148
K^{+}	1.43	1.18	4.88	3.46	3.57	3.51	2.36	1.63	1.85	2.58
Cl^{-}	341	255	384	388	526	348	458	346	324	345
NO_3^-	19	85	39	21	31	32	51	33	28	38
HCO_3^-	347	252	384	275	571	341	456	339	318	347
SO_4^{2-}	254	176	276	258	295	203	226	194	219	204
PO_4^{3-}	0.10	0.27	0.15	0.12	0.08	0.09	0.16	0.07	0.07	0.04
DO	2.34	2.82	4.34	4.45	4.67	4.46	2.36	4.12	3.08	4.48
F^{-}	0.589	0.657	0.591	0.529	0.845	0.671	0.601	0.765	0.654	0.610

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

	Sample Number									
Water quality parameter	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
pH	7.9	6.9	7.3	7.8	7.9	7.3	7.2	6.8	7.8	7.4
EC	936	739	904	889	1065	915	932	962	890	969
TDS	803	607	736	701	913	727	741	854	681	874
TH	482	531	393	491	592	393	578	475	449	573
TA	376	371	374	275	581	473	536	473	472	431
Turbidity	1.08	1.35	1.12	1.34	2.51	1.20	2.13	1.02	2.06	2.16
Ca^{2+}	108	131	99	139	153	89	173	101	129	161
Mg^{2+}	55	58	39	51	56	47	59	41	37	36
Na^{+}	167	163	164	163	207	161	162	181	149	142
K^{+}	1.39	1.15	4.76	3.28	3.45	3.21	2.16	1.53	1.80	2.47
Cl^{-}	338	251	374	376	514	342	451	332	302	341
NO_3^-	17	81	36	20	29	31	47	31	26	36
HCO_3^-	343	248	369	263	566	339	449	317	309	341
SO_4^{2-}	248	165	272	247	294	196	221	187	214	197
PO_4^{3-}	0.09	0.25	0.11	0.10	0.07	0.07	0.14	0.06	0.05	0.03
DO	2.18	2.75	4.20	4.34	4.59	4.30	2.31	4.02	3.01	4.43
F^{-}	0.454	0.554	0.495	0.432	0.743	0.442	0.432	0.483	0.377	0.538

3.5: Concentrations of the studied water quality parameters after defluoridation:

After the de-fluoridation experiments (Vide Table No's: 8, 9, 10 and 11), the pH values of the ground water samples are decreased and this might be due to the decrease in EC, TDS, TA and TH which are positively correlated with pH. The EC values of the ground water samples are decreased due to the positively correlation of EC with TDS, Na^+, K^+, F^- and Cl^- which are decreased in the analysis. The TDS values are decreased due to the positive correlation of TDS with EC, TH, TA, Ca^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, F^- and Cl^- whose concentrations are decreased after defluoridation. The decreased TH values of the ground water samples is due to the decrease in concentration of TDS, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}, PO_4^{3-} and F^- which contribute to total hardness to ground water and these ions are positively correlated with TH. The total alkalinity of the ground water samples is decreased due to the positive correlation of TA with all water quality parameters except with SO_4^{2-} and PO_4^{3-}. The turbidity values are decreased due to the positive correlation of turbidity with other turbidity contributing ions, whose concentrations are decreased after defluoridation.

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

	Sample Number									
Water quality parameter	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
pH	8.1	7.1	7.5	8.0	8.2	7.6	7.6	7.0	8.0	7.8
EC	958	751	918	898	1092	932	942	979	897	979
TDS	810	614	740	708	920	736	752	867	694	886
TH	492	543	409	501	604	403	591	486	461	587
TA	389	384	387	286	593	489	556	491	482	446
Turbidity	1.47	1.55	1.52	1.67	2.93	1.25	2.36	1.33	2.20	2.42
Ca^{2+}	113	155	108	153	178	107	197	109	149	175
Mg^{2+}	62	65	48	58	62	51	68	51	42	48
Na^{+}	170	179	166	167	213	176	174	191	154	151
K^{+}	2.23	1.38	5.25	3.96	4.68	3.73	2.46	1.66	1.93	2.93
Cl^{-}	348	268	389	393	556	356	465	352	339	359
NO_3^-	21	88	42	22	34	38	53	36	31	40
HCO_3^-	354	267	389	284	579	343	468	342	336	355
SO_4^{2-}	268	189	282	265	297	212	231	205	225	212
PO_4^{3-}	0.14	0.39	0.18	0.15	0.10	0.11	0.18	0.09	0.09	0.06
DO	2.49	2.94	4.54	4.52	4.89	4.59	2.75	4.19	3.11	4.50
F^{-}	0.806	0.795	0.726	0.689	0.961	0.830	0.760	0.793	0.714	0.725

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

	Sample Number									
Water quality parameter	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
pH	8.1	7.1	7.7	8.0	8.3	7.8	7.8	7.6	8.0	8.0
EC	967	759	929	905	1114	938	949	984	902	981
TDS	812	617	743	711	923	742	758	870	702	891
TH	501	550	416	512	613	409	597	490	468	590
TA	401	391	401	292	601	511	564	497	490	451
Turbidity	1.58	1.59	1.53	1.89	2.99	1.29	2.38	1.36	2.21	2.43
Ca^{2+}	117	161	110	163	193	112	201	110	152	189
Mg^{2+}	64	68	53	62	69	54	72	54	44	51
Na^{+}	171	182	168	172	216	185	176	194	156	153
K^{+}	2.31	1.49	5.49	3.99	4.87	3.82	2.48	1.69	1.99	2.99
Cl^{-}	356	273	403	397	563	361	478	361	346	368
NO_3^-	23	91	44	26	37	42	56	38	33	41
HCO_3^-	363	269	395	287	581	355	472	354	346	368
SO_4^{2-}	272	198	286	272	299	219	243	215	236	218
PO_4^{3-}	0.22	0.42	0.21	0.18	0.13	0.14	0.21	0.10	0.10	0.08
DO	2.52	3.21	4.65	4.64	5.39	4.62	2.82	4.36	3.16	4.54
F^{-}	0.930	0.905	0.862	0.804	0.974	0.912	0.893	0.908	0.829	0.764

The concentration of Ca^{2+} ions in the ground water samples is decreased due to the decrease in concentrations of TDS, TH, NO_3^-, HCO_3^- and SO_4^{2-} which are positively correlated with the Ca^{2+} ions. The Mg^{2+} ions concentration of the ground water samples is decreased due to the positive correlation of Mg^{2+} ions with TH, TA, Ca^{2+}, Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}, PO_4^{3-} and F^-. The concentration of Na^+ ions is decreased due to the positive correlation of Na^+ ions with all water quality parameters whose concentrations are decreased after de-fluoridation. The concentration of K^+ ions in the ground water samples is decreased due to the decrease in the concentrations of EC,TDS,Ca^{2+},Mg^{2+},Na^+, HCO_3^-, SO_4^{2-}, F^- and Cl^- which are positively correlated with the K^+ ions

The Cl^- ions concentration of the ground water samples is decreased due to the decrease in concentrations of all water quality parameters which are positively correlated with the Cl^- ions except NO_3^- and PO_4^{3-}. The NO_3^- ions concentration of the ground water samples is decreased due to the decrease in ions like Ca^{2+}, Mg^{2+}, Na^+ and F^- which are positively correlated with the NO_3^- ions. The HCO_3^- ions concentration of the ground water samples is decreased due to the positive correlation of all water quality parameters except NO_3^- and PO_4^{3-} with the HCO_3^- ions. The SO_4^{2-} ions concentration of the ground water samples is decreased due to the positive correlation of all water quality parameters except TA, NO_3^- and PO_4^{3-} with the SO_4^{2-} ions. The PO_4^{3-} ions concentration of the ground water samples is decreased due to the positive correlation of TH, Mg^{2+}, Na^+, and F^- with the PO_4^{3-} ions. The DO content of the ground water samples is also decreased due to the positive correlation of DO with some other water quality parameters.

Before de-fluoridation, the fluoride concentration in the ground water samples is varied from 3.28-4.27mg/lit whereas after de-fluoridation with four activated carbons at optimum conditions of parameters, the fluoride concentration is reduced and it is in the range of 0.377-0.743, 0.529-0.845, 0.689-0.961 and 0.764-0.974 mg/lit for the activated carbon adsorbents: NVNC, NSOC, NAbIC and NAcIC respectively. The fluoride content in all the ground water samples is within the permissible limits after defluoridation with the four activated carbons. The maximum percentage removal was observed with the adsorbent, NVNC while minimum percentage removal was observed with the adsorbent, NAcIC. The maximum percentage removals, 88.8, 84.8, 80.6 and 76.9 % were observed with the activated carbon adsorbents: NVNC, NSOC, NAbIC and NAcIC respectively. The de-fluoridation capacity of the adsorbents in terms of their percentage removal is in the following increasing order: NAcIC < NAbIC < NSOC < NVNC. The results of the de-fluoridation experiments of the ground water samples are listed in Table 12.

Table 12: Results of defluoridation of the ground water samples collected in study area

S. No.	Fluoride before Defluoridation, (mg/lit)	Fluoride after defluoridation, (mg/lit)				% Removal			
		1	2	3	4	1	2	3	4
1	3.75	0.454	0.589	0.806	0.930	87.9	84.3	78.5	75.2
2	3.82	0.554	0.657	0.795	0.905	85.5	82.8	79.2	76.3
3	3.56	0.495	0.591	0.726	0.862	86.1	83.4	79.6	75.8
4	3.48	0.432	0.529	0.689	0.804	87.6	84.8	80.2	76.9
5	4.27	0.743	0.845	0.961	0.974	82.6	80.2	77.5	77.2
6	3.88	0.442	0.671	0.830	0.912	88.6	82.7	78.6	76.5
7	3.69	0.432	0.601	0.760	0.893	88.3	83.7	79.4	75.8
8	4.09	0.483	0.765	0.793	0.908	88.2	81.3	80.6	77.8
9	3.37	0.377	0.654	0.714	0.829	88.8	80.6	78.8	75.4
10	3.28	0.538	0.610	0.725	0.764	83.6	81.4	77.9	76.7

**Note: 1-NVNC, 2-NSOC, 3-NAbIC and 4-NAcIC*

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

A high positive correlation of F^- with the Na^+ was observed. The positive correlation value suggested that the Na^+ concentration had a direct influence on fluoride concentration. The positive correlation of the lithogenic Na^+ indicated that the lithogenic Na^+ could be used as an index of weathering of clay minerals [25]. During weathering, the clay minerals promote ion exchange among the elements present in the soils and also among those present in the circulating waters [26-27]. This is probably responsible for the formation of the sources of F^- in the soils [28-31].

The F^- ion was found to have a positive correlation with TA and TH and hence, the amount of TA and TH was increasing with the increasing in F^- and this indicated a greater relationship between F^- and TA/TH. This is because of precipitation of TH as carbonates [32]. The solubility of CaF_2 increases with the increase in TA in the ground waters [33-34], according to the following reactions:

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

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

Thus, a positive relationship of TA with F^- suggests the dissolution of F^- bearing minerals in the ground waters. In these reactions, the concentration of dissolved ionic species and the pH of the water play important roles. The presence of $CaCO_3$ also favours the dissociation of F^- from F^- containing minerals. These reactions are as follows:

$$CaCO_3 + H^+ + 2F^- \rightarrow CaF_2 + HCO_3^-$$

$$CaF_2 \rightarrow Ca^{2+} + 2F^-$$

The residence times of waters with the aquifer materials also significantly regulate the F^- concentrations in the ground waters [30-31, 33-35]. The occurrence of intrusive bodies creates ground water barriers [36-38]. With the increase in residence time between the waters and aquifer materials due to the weathered zone and intrusive bodies, the dissolution of minerals, including that of F^- bearing minerals, and ion exchange activity between OH^- and F^- also increase, thus contributing to the concentration of F^- in the ground waters. A higher concentration of TDS enhances the ionic strength, leading to an increase in the solubility of CaF_2 in the ground water [39].

The resistance to weathering of K^+ and its fixation in the clay minerals causes low concentrations of K^+ among the cations in the ground waters of the area. The positive correlation of SO_4^{2-} and NO_3^- with F^- in the ground waters is attributed to the heavy use of fertilizers for higher crop yields [40-41].

CONCLUSION

The results of the quality status of the ground water samples collected from ten villages of Vinukonda Mandal, Guntur Dist., A.P., confirmed the necessity of the treatment of ground water samples prior to utilization. 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. Most of these parameters are above the maximum permissible limits for some ground water samples while for some samples the values are within the permissible limits. In correlation analysis, positive correlations are observed among various water quality parameters. When activated carbon adsorbents: NVNC, NSOC, NAbIC and NAcIC are used for de-fluoridation studies, the concentrations of these parameters are also reduced to less extent.

Before treatment all the ground water samples have the fluoride concentration above the permissible limit 1.5 mg/lit but after treatment with activated carbon adsorbents, the fluoride concentration is successfully reduced to below the permissible limit. The maximum percentage removals, 88.8, 84.8, 80.6 and 76.9 % are observed with the activated carbon adsorbents: NVNC, NSOC, NAbIC and NAcIC respectively and the increasing order of adsorbents with respect to defluoridation capacity is NAcIC < NAbIC < NSOC < NVNC. The de-fluoridation studies revealed that all samples are in the permissible limits of fluoride after de-fluoridation with indigenously prepared carbons.

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