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Pearson Correlation Analysis on the Assessment of ground and falls water Quality in Madurai, Thenkasi and Virudhunagar Districts

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Abstract
Water samples were collected from ground, falls and Corporation water sources in Madurai, Tenkasi, and Arupukottai. The parameters such as pH, TDS, alkalinity, acidity, hardness, COD, BOD, chloride, fluoride and conductivity were analyzed by standard methods and compared with WHO standards. COD was analyzed by COD analyzer, Total Hardness was analyzed by EDTA method pH and TDS were found using digital meters. Fluoride was measured by the SPONDAS method using HANNA Fluoride high range checker. Morinda Citrifolia-Manjanathi-
leaves were collected and processed as bio adsorbent in 1:1 ratio. Analyzed parameters for all the samples subjected to pearson correlation statistical Tool to derive meaningful data regarding pollution factors. Fluoride contaminated areas were identified from the data and bio adsorbents as Morinda Citrifolia-Manjanathi leaves were used in 0.2, .4, .6, .8, 1 g/ mL as into 25 mL of water sample. The adsorbent was used to carry out in the variation of Temperature, pH concentrations of samples and adsorbents respectively.

Key words: *Water quality parameters, Fluoride concentration, High range fluoride checker, Morinda Citrifolia-Manjanathi leaves.*

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I. Introduction

Water is the important natural source for the well-being of human life. Environmental pollution is one of the major problems faced by the population in today's world. Especially in the cities of the developing countries this not only experience a rapid growth of population due to increasing rate of rule – urban migration but also uncoupled industrialization and is accompanied by growth pollution levels. All the above factors not only lead to deteriorating environment condition, health of the people in such areas full an easy prey to the pollution and are infected by pollution related diseases.Water is one of the most important of all natural resources known on earth. It is important to all living organisms, most ecological systems, human health, food Production and economic development. The safety of drinking water is an on-going concern within the global village. Traditionally, the safety of potable water Supplies has been controlled by disinfection, usually by chlorination and coliformPopulation estimates. However, it has been reported that coliform-free potable Water may not necessarily be free of pathogens.[2-4] Many congenital diseases such as goiter and cancer have been associated with Presence of high concentration of a chemical or its inadequate supply in Water[3-6].This is the first attempt to reveal the meaningful correlation among the analysed falls and ground water qualities in Thirupalai G.W, Thirupalai CW, Muthulingapuram, Avaniyapuram

Avaniyapuram, Aaviyur, Alagar Koil-falls, Coutralam-falls, Papanasam-falls and grouped them to identify the polluted area. Low cost bio adsorbent was used to decrease the fluoride contamination.

II. Materials And Method

REQUIREMENT OF **EQUIPMENT**

Conductivity meter, volumetric flask, Conductivity meter, single pan balance Burettes, pipette, TDS Meter, COD analyser, Fluoride HR analyser

REQUIREMENT OF CHEMICALS

0.1 N Potassium dichromate , 0.1 N Thio, H_2SO_4 10% KI Strach(indicator) SPADNS solution zirconyl acid Potassium chromate indicator solution Standard silver nitrate solution 0.0141NPhenolphthalein indicatorStandard sodium hydroxide (0.02N)Standard sulphuric acid (0.02N)Methyl orange indicator standard solution of KClCalcium fluorideSodium carbonate$AgNO_3$

METHODOLOGY

Sample collection and preservation from the above-mentioned sites, water sample were collected water is Allowed to run of more than ten minutes and then the required quality of water sample was collected after rinsing the container for more than three times. The containers were polythene cans with capacity of three liters. Biochemical oxygen demand was determined in the laboratory within two of collection. Other parameters were analysed within 8 hours.the chemicals used for determining the quality parameters were analog or of equivalent grade. Double distilled water was used for all parameters.

CONDUCTIVITY:

Switch on the instrument and leave for 10 minutes to warm up. Rinse the electrode with distilled water and wipe off with tissue paper. After it, dip the electrode with a probe in the standard 0.01 M solution of KCl. Press calibration knob and wait for calibration completed and press continued knob check the displayed reading 1.412±0.01 at 250C. Rinse the electrode and dip in the sample and note the reading with temperature 0C. Rinse the electrode and dip in another sample respectively.

ALKALINITY (Titrimetric method)

Take a 100 ml sample in a volumetric flask and add 2-3 drops of Phenolphthalein indicator. If pink colour develops titrate with 0.02N H_2SO_4 till a colour disappears. Note the volume of sulphuric acid used. Add 2-3 drops of Methyl orange indicator to the same flask and continue titration till yellow colour changes to orange. Note the volume of sulphuric acid used.

FORMULA:

Phenolphthalein alkalinity (mg/l as $CaCO_3$) = A x N x 1000/ volume of sample

Total alkalinity (mg/l as $CaCO_3$) = B x N x 1000/ volume of sample

Methyl orange alkalinity (mg/l as $CaCO_3$) = (B-A) x 1000/ volume of sample

ACIDITY (Titrimetric method)

Take 100 ml sample in conical flask, add 2 drops of Phenolphthalein indicator and titrate with standard NaOH solution till pink colour appears.

FORMULA:

Acidity as $CaCO_3$ (mg/l) = ml titrant used (NaOH) x 1000/ ml sample

CHLORIDE (Argentometric method)

Take 100 ml sample in a conical flask and adjust the pH in the range of 7-10.Add 1 ml K_2CrO_4 indicator, titrate with $AgNO_3$ end point will be pinkish yellow. Note the reading, repeat the titration with distilled water blank.

TOTAL HARDNESS (EDTA Method)

20 ml of the given water sample is pipetted out into a clean conical flask. 5 ml ammonia buffer and 2 drops of EBT indicator are added and titrated against EDTA from the burette. The end point is the change of colour from wine red to steel blue. The titration is repeated to get concordant titre value.

Formula-Total Hardness (EDTA) mg/l= A x B x 1000/ volume of sample

TDS(Total Dissolved Substance)

- Remove the protective cap of the Digital TDS meter and switch it "ON".
- Immerse the electrode in the solution to be tested.
- Stir gently and wait for the reading to stabilize.
- Press the "C/F" button to switch between Celsius and Fahrenheit.
- After use,turn off the meter.Rinse the electrode with distilled water to minimize contamination.
- Always replace the protective cap after use.

Figure:2 TDS meter

pH OF WATER SAMLE

The pH meter was set to the temperature of the buffer solutionfirst. Then the pH scale of the instrument is preliminary against buffersolution after doing zero correction. The appropriate pH value of the solution being analysed in known, selected a buffer solution whosepH value is close to that of solution being analysed and the

instrument was set accordingly with the help of sot buffer knob. Then washed theel ectrodes with copious amount of distilled water and read the pH of the unfiltered water sample and reported to the nearest 0.1 units.

FLUORIDE(FLUORIDE HR CHECKER)
Preparation of the reagent: 958 mg of SPADNS is dissolved in distilled water and diluted to 500 ml. 133 mg of zirconyl chloride octahydrate ($ZrCl_2.8H_2O$) is dissolved in 25 ml distilled water and 350 ml of Conc.HCl is added and diluted to 500 ml with distilled water. Equal volumes of SPADNS solution and zirconyl acid solutions are mixed.

Figure:4 Fluoride HR checker

ADSORPTION FOR FLUORIDE CONTAMINATION
Fluoride contaminated areas identified from the data and bio adsorbents as *Morinda Citrifolia-Manjanathi* were collected and processed as adsorbents as were used in 0.2, .4, .6, .8, 1 g/ mL as into 25 mL of water sample. The adsorbent was used to carry out in the variation of Temperature, pH concentrations of samples and adsorbents respectively.

COD (CHEMICAL OXYGEN DEMAND)
20 ml of potassium dichromate in COD bottle (blank solution) and another COD bottle taken a 20ml of potassium dichromate and 20 ml sample of water and COD bottle is attached in the condenser of COD.COD flask is heated on 15min ..After heating the blank and sample solution titrated using sulphuric acid,0.1N Thio,KI, and Starch as an indicator.

Figure:5 COD analyser

III. Results And Discussion

In present investigation an attempt was made for assessment of Water samples collected from Thirupalai G.W, Thirupalai CW ,Muthulingapuram ,Avaniyapuram ,Avaniyapuram,Aaviyur ,Alagar Koil-falls ,Coutralam-falls and Papanasam-falls to determine the quality of the samples. Pearson correlation analysis was carried out on all the analysed data to find the correlation among the quality of samples and was discussed in figures and tables given below for each parameter. For assessing water quality, pH, total hardness, calcium, magnesium, chloride, total dissolved solids, calcium, magnesium and fluorides have been considered. For fluoride contamination remedial measures were introduced using bio adsorbent. Concentration of fluoride was decreased when the quantity of adsorbent increased and showed the R value as 0.942.

4.1. pH

Table 4.1: pH of the sample

Stations	Places	pH	Nature
1	Thirupalai G.W	8	Basic
2	Thirupalai CW	9	Basic
3	Muthulingapuram	7	Neutral
4	Avaniyapuram	9	Basic
5	Avaniyapuram	9	Basic
6	Aaviyur	8	Basic
7	Alagar Koil-falls	6	Acidic
8	Coutralam-falls	6	Acidic
9	Papanasam-falls	6	Acidic

The above table 4.1, showed the high medium and low pH values among the analysed samples. The pH values of all the stations show in the range. 6 to 9. (Figure 4.1) The PH values of the 4, 5 and 6 water samples were in the undesirable limit. The acidity many be due to mild organic salt. So the water sample from the polluted stations may not be used for drinking purpose.

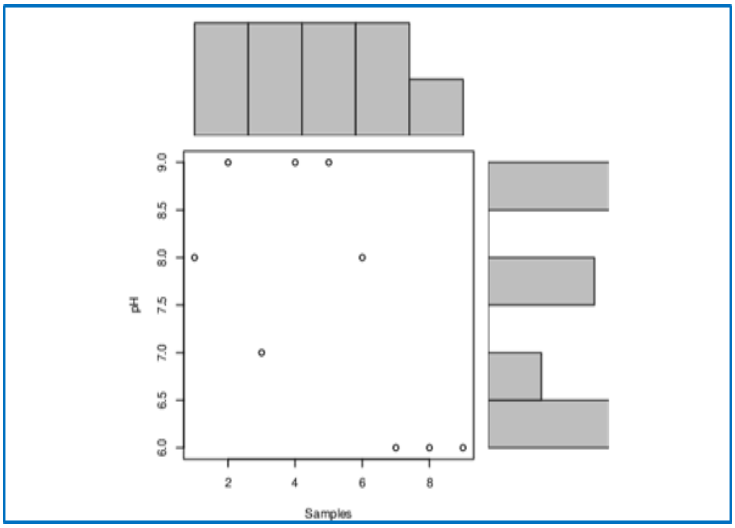


Figure-6 Pearson correlation diagram for pH

Number of Observations -9

Mean	7.5
Correlation	-0.684653196881458
T-Test	-2.48525060873854
p-value (2 sided)	0.0418868139372642
p-value (1 sided)	0.0209434069686321
95% CI of Correlation	[-0.927188663196403,

All the samples were correlated with 95% CI of Correlation [-0.927]. These results confirmed that all the samples came under the three different categories. Samples 7, 8 and 9 were grouped together and showed acidic nature. Samples 2, 4, and 5 grouped together and revealed the basic nature of the samples.1, 3 and 6 varied from all the samples and showed the neutral values.

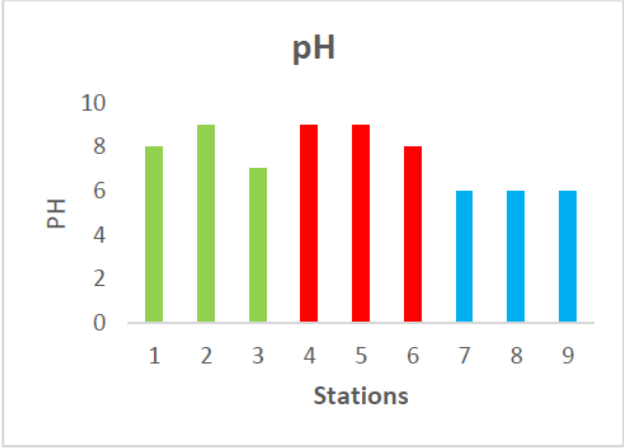


Figure- 7 Variation of pH with respect to stations

Figure 1.2 showed the higher and lower values of the analysed samples . Samples 2, 4,5 and 6 showed higher values than 7,8 and 9. It represented the acidity and alkalinity of the analysed samples.
The reason for the variations may lead to the appliances becomes encrusted with deposits, and it also depresses the effectiveness of the disinfection of chlorine, thereby generating the need for additional chlorine when pH is high. Low- pH water might corrode or dissolve metals and other substances. Pollution has the potential to change the pH of water, which might harm animals and plants living in the water.

4.2. ALKALINITY

Table 4.2: Alkalinity of the samples

Stations	Sample	Alkalinty
1	Thirupalai G.W	408.96
2	Thirupalai CW	612.48
3	Muthulingapuram	470.4
4	Avaniyapuram	854.4
5	Avaniyapuram	1351.68
6	Aaviyur	800.64
7	Alagar Koil	48
8	Coutralam	109.44
9	Papanasam	300

The above table 4.2 represents the high and low alkalinity values compared to falls water and corparation water. The alkalinity of all the stations shows in the range 100 – 1400mg/l. (Figure 9). The alkalinity of the station4, 5 and 6 are found to be high. This may due to more seepage of effluent, domestic sewage around the stations. Sample 5 showed highest value among all other samples. Alkalinity for WHO showed (20-200)

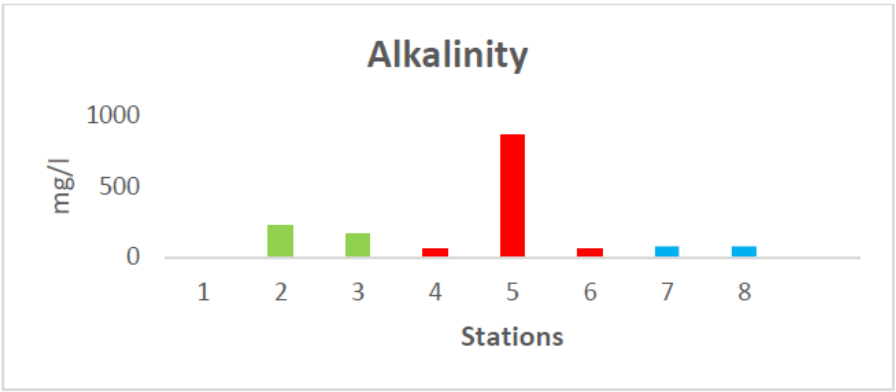


Figure 8. Variation of alkalinity with respect to stations

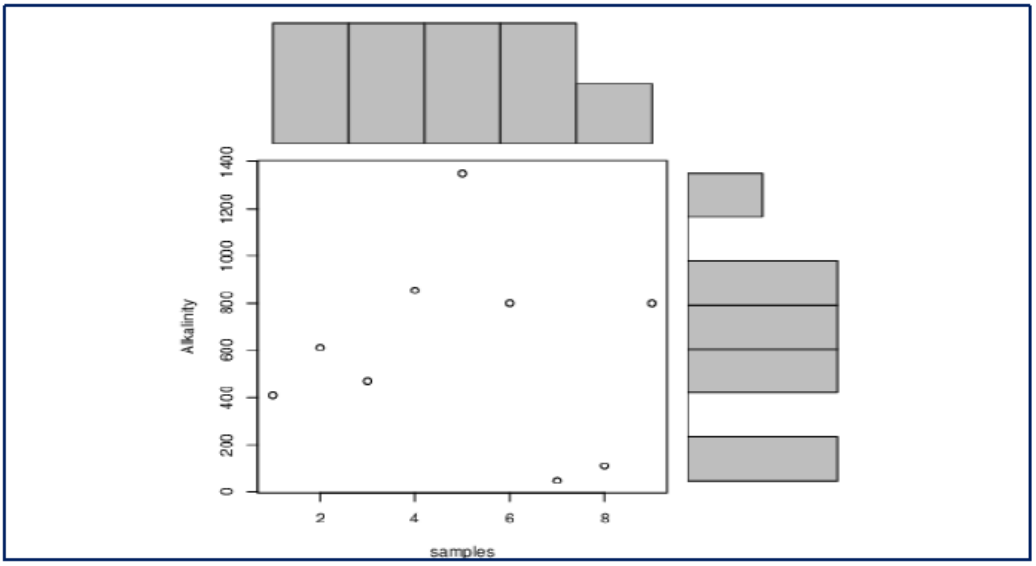


Figure-9Pearson correlation diagram for alkalinity

All the samples were correlated with 95% CI of Correlation [-0.927]. These results confirmed that all the samples have shown the four different categories. Samples 6 and 9 grouped together. Samples 7 and 8 were grouped together in a way. Samples 1, 2, 3and 4 grouped together and revealed the basic nature of the samples. 5 showed high value among all the samples.

4.3. CALCIUM AND MAGNESIUM

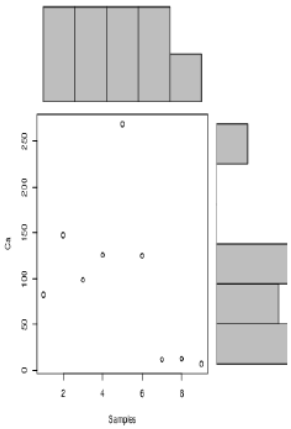
The table 4.3. represents the high and low values of calcium and magnesium quantities. Calcium values of all the stations are found to be in the range of 10 – 900mg/l (Figure 12). Where as the station 5 observed high calcium value of 897.22mg/l and stations1 to 4 and 6, 7,8 observed to be low calcium value.

The magnesium values of all the stations are found to be in the range 7 – 200 mg/l (Figure 12). All the station showed a low value of magnesium Concentration. The presence of calcium and magnesium may be due to the dissolution of Host granitic rock.WHO Standard value 80 mg/L.

Table 4.3: Calcium and Magnesium of the samples

Stations	Sample	Calcium (mg/l)	Magnesium (mg/l)
1	Thirupalai G.W	82.56	29.70
2	Thirupalai CW	147.49	43.83
3	Muthulingapuram	98.59	29.70
4	Avaniyapuram	125.85	54.54
5	Avaniyapuram	268.53	119.31
6	Aaviyur	125.04	20.45
7	Alagar Koil	12.02	7.30
8	Coutralam	12.82	3.89
9	Papanasam	7.21	2.43

Correlation	-0.479
Determination	0.229
T-Test	-1.44
p-value (2 sided)	0.19
p-value (1 sided)	0.096
95% CI of Correlation	[-0.8672470335, 0.27145941901372]
Degrees of Freedom	7



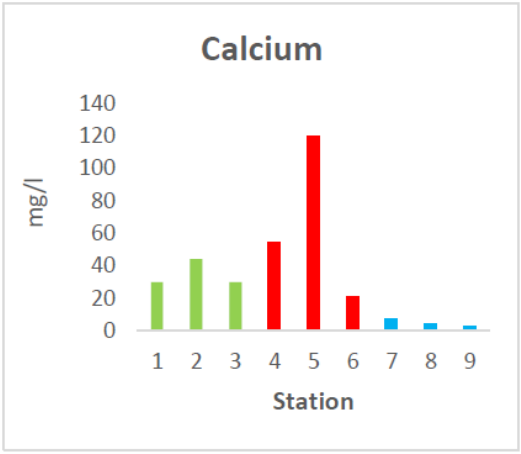


Figure-10 Pearson correlation diagram for Ca Figure 12. Variation of calcium with respect to stations

All the samples were correlated with 95% CI of Correlation [-0.86]. These results confirmed that all the samples have shown the four different categories. Samples 7,8 and 9 grouped together. Samples 1 and 3 were grouped inot another set .Samples 2, 3and 4 grouped together and revealed the high quantity of Ca in the water samples. 5 showed highest value among all the samples.

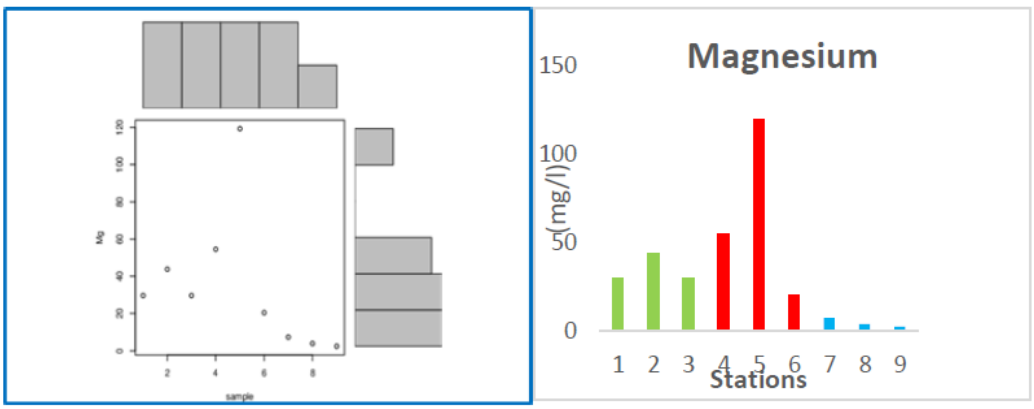


Figure-11 Pearson correlation diagram for Mg and Variation of magnesium with respect to stations

All the samples were correlated with 95% CI of Correlation [-0.86]. These results confirmed that all the samples have shown the four different categories. Samples 6, 7, 8 and 9 grouped together. Samples1, 2, 3 and 4 were grouped together .Sample 4 showed medium value. 5 showed highest value among all the samples and highly polluted by Mg ions.

If inorganic salts are high in the waster sample 5 it may be the reason for the high concentration of Ca and Mg. Alkalinity has also increased due to the high concentration of Ca, Mg and Chloride ions.

After revealing the Pearson correlation analysis, for all the water quality parameters, samples 5 Avaniyapuram showed the highest value. It showed that some geogenic and anthropogenic factors may affect the water quality. From this correlation, we observed that falls water collected from Coutralam, Papanasam and Alagar Kovil were showed the good quality in all the analysed parameters.

4.4. Chemical Oxygen Demand (COD)

The below table 4.4 represents Chemical Oxygen Demand for the analysed samples. This indicated that the value of chemical oxygen demand (COD) and observed from the experimental data that the range 4-900 (Figure 14). COD value of all water sample are above the limits (70 mg/l) prescribed by ISI. The COD test is helpful in indicating toxic condition and the presence of biological resistant organic substance. The test is widely used in the operation of treatment facilities, because of the speed which results can be obtained. WHO standard value is (250mg/L)

Table 4.4 : Chemical Oxygen Demand of the samples

Station	Sample	COD
1	Thirupalai G.W	4.6
2	Thirupalai CW	224.64
3	Muthulingapuram	163.8
4	Avaniyapuram	60.84
5	Avaniyapuram	861.12
6	Aaviyur	56.16
7	Alagar Koil	74.88
8	Coutralam	74.88
9	Papanasam	69.0

COD is the amount of O_2 demanded to oxidize biodegradable organic matter as well as non-biodegradable organic matter present in waste water using a strong chemical oxidant such as potassium dichromate. This test is widely used to determine the Degree of pollution in water bodies and their self-purification capacity. Efficiency of treatment of the plants Pollution loads. COD represents both biologically active and inactive organic matter.

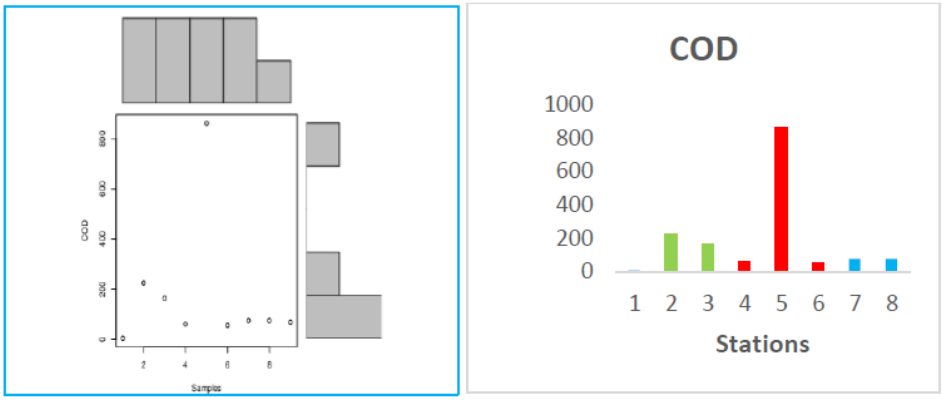


Figure-12 Pearson correlation diagram for COD and Variation of COD

Except sample 5, all the other samples showed the same values and correlated 95 % Pearson correlation with -.67 to .62.

Table-4.5 Analysis of Chloride

stations	sample	chloride
1	Cor.water	147.45
2	Cor.water	184
3	Cor.water	124.5
4	Tap water	162.8
5	Tap water	897.22
6	Tap water	177.44
7	Falls	9.99
8	Falls	27.4
9	falls	27.4

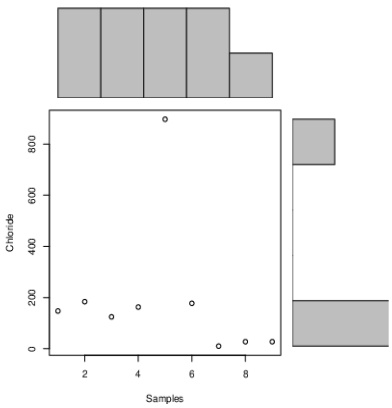


Figure-13Pearson correlation diagram for Cl-

After revealing the Pearson correlation analysis , All the samples were correlated with 95% CI of Correlation [-0.76] and +0.58. It showed that there were three groups . All the falls water comes under low qualntity of Chloride concentration . Samples forom 1,2,3,4 and 6 showed medium level of chloride concentration. Avaniapuram sample showed highly contaminated of Chloride . For all the water quality parameters, sample number -5 Avaniyapuram showed the highest value. It showed that some geogenic and anthropogenic factors may affect the water quality. From this correlation we observed that falls water collected from Coutralam, Papanasam and Alagar Kovil were showed the good quality in all the analysed parameters. WHO standard value of Cl- and F- were 130 mg/L and 1.5 mg/ L respectively

Table- 4.6 Analysis of Fluoride

Sample	Fluoride PPM
1	2.4
2	3.7
3	3.4
4	3.0
5	4.9
6	2.4
7	1.0
8	1.9
9	1.1

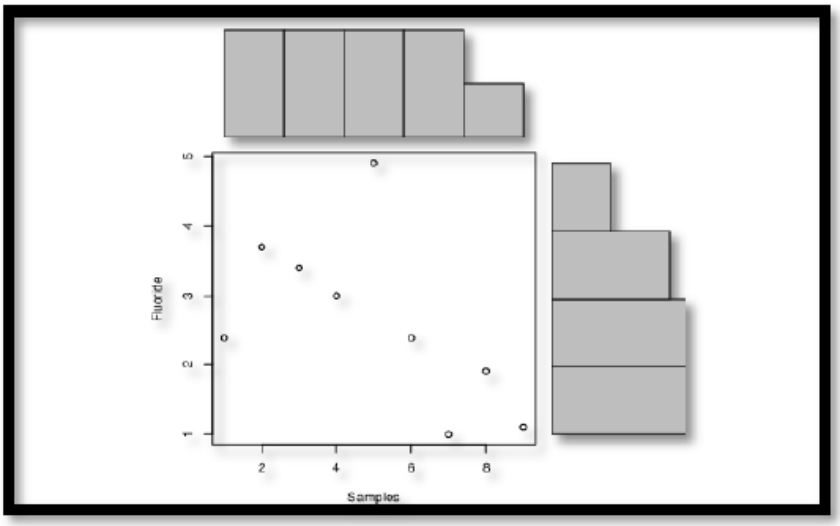


Figure-14 Pearson correlation diagram for F-

All the samples were correlated with 95% CI of Correlation [-0.89] and +0.28. It showed that there were three groups. Sample 7 and 9 showed low concentration of fluoride. All the other samples showed more or less same concentration. Avaniapuram showed high concentration of fluoride contamination. This may be due to the high population density, some natural fluoride genesis rock located under the ground. Some small scale dye factories for textiles were released the untreated water from the small scale industries.

Bio Adsorbent to minimize the fluoride in water

Stock solution of CaF_2 was prepared and the working solutions were prepared into various dilution. At 527 in spectrophotometry, Concentration of fluoride was decreased during the concentration of adsorbent increased for 0.2 to 1.0. After each addition, the adsorption % of fluoride was decreased. Fluoride contaminated areas were identified from the data and bio adsorbents as *Morinda Citrifolia-Manjanathi leaves* were used in 0.2, .4, .6, .8, 1 g/ mL as into 25 mL of water sample. The adsorbent was used to carry out in the variation of concentrations of samples and adsorbents respectively. It showed + correlation as $R^2 = 0.964$ at pH=7 for .1 M of CaF_2 in 10 ml of working solution.

Table : 4.7 Concentration of *Morinda Citrifolia-Manjanathi in decreasing fluoride*

Concentration of adsorbent	% of adsorption
0.2	64
0.4	51
0.6	40
0.8	32
1.0	28

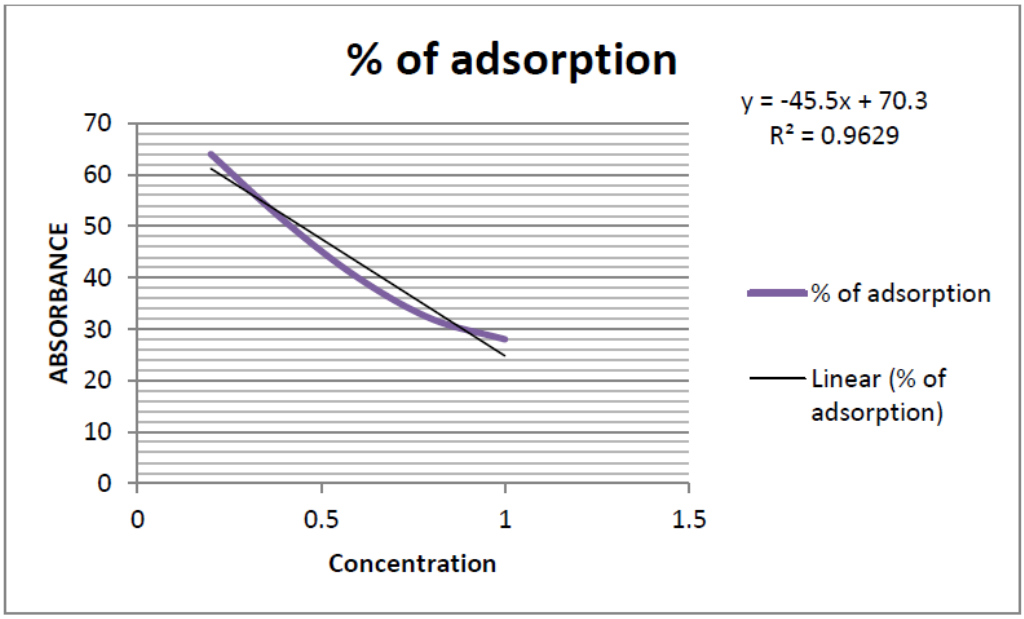


Figure- 15 The value of adsorbent increased with decrease of % of adsorption at = 527nm at pH=7 for .1 M of CaF_2 in 10 ml .

IV. Conclusions

The water samples collected from Thirupalai G.W, Thirupalai CW, Muthulingapuram, Avaniyapuram, Avaniyapuram Aaviyur , Alagar Koi,l Coutralam Papanasam in Madurai, Tenkasi, and Virudhunagar district respectively were carried out to determine the quality of the water. For assessing water quality, pH, total hardness, calcium, magnesium, chloride, total dissolved solids, calcium, magnesium and fluorides have been considered. The data values obtained were compared with the standard values prescribed by WHO. From the above values, we have concluded that samples collected from falls have good quality in drinking purpose when compared to other samples (corporation water & ground water). The higher values have been found to be mainly in Total hardness, chloride, fluoride, calcium and magnesium in Avaniyapuram sample (Number 5). To decrease the fluoride contamination, *Morinda Citrifolia-Manjanathi leaves* was used as bio adsorbent. Different concentration of adsorbents was used to carry out adsorption in the various concentrations of samples. It showed positive correlation as $R^2 = 0.964$ at pH=7 for 0.1 M of CaF_2 in 10 ml of working solution.

The analysis revealed that the groundwater of the Avaniyapuram area needs some degree of treatment before consumption, and it also needs to be protected from the external anthropogenic contamination. Various government and NGO based awareness programs should be tried in Avaniyapuram region.

Acknowledgement

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