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Synthesis of Carbon Dots & Detection of Fluoride Ions Using Spectrophotometry

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Abstract - *Water is essential for sustainment of life on earth. But with growing industrial and commercial sector the water available for drinking is not safer any more. It is contaminated with various pollutants. Among these pollutants Fluoride Ions are identified as one of the major contaminant in water. Higher concentration of these in water can cause fatal effects on our body. Thus it becomes necessary to develop electronics for detection of Fluoride ions in water. In this paper a new novel technique has been explored wherein instead of the traditional techniques, an optical light source and detector based system is proposed where fluorescent carbon dots and its metal conjugates are synthesized to detect fluoride ions using fluorescent quenching. Carbon dots were synthesized using calcium citrate as carbon source. Optical analysis of Fluorescence of Carbon Dots was done using fluorescent spectrophotometer.*

Key Words: **Fluoride, Carbon Dots, Optical Light Source, Spectrophotometer**

1. INTRODUCTION

The importance of water for sustenance of life cannot be overemphasized. Whether it is in use of running water in our homes, rearing cattle and growing crops in our farms, or the increased use in industry, remain immeasurable. It is important therefore, to note that depletion of this commodity either through contamination, or careless use results in serious consequences.

Water is considered polluted if some substances or condition is present to such a degree that the water cannot be used for specific purpose [1]. Olaniran (1995) defined water pollution to be the presence of excessive amount of a hazard (pollutants) in water in such a way that it is no long suitable for drinking, bathing, cooking or other uses according to webmaster.com 2010. According to webmaster.com 2010, Pollution is the introduction of contamination into the environment. It is created by industrial and commercial waster, agricultural practices, everyday human activities and mode notably models of transportation.

Thus, detection of such pollutants is essential for monitoring of water quality [1]. Water quality monitoring defined by the International Organization for Standardization (ISO) as: "the programmed process of sampling, measurement and subsequent recording or signaling, or both, of various water characteristics, often with the aim of assessing conformity to specified objectives". Thus, the surveillance of source water quality and the detection of toxic elements present, simultaneously treating the water and making it fit for drinking[3,4]. The objective of this thesis work is to detect one such pollutant, i.e. Fluoride.

1.1 Fluoride Ion

Fluoride ion (F^-) is widely found in biological systems and the external environment. Fluoride ions basically comes from fluorine atoms. Due to their high reactivity fluorine atoms exists in the form of fluorides in a number of minerals, for e.g. Fluorspar, cryolite and fluorapatite and it covers about 0.3 g/kg of the Earth's crust[5]. Fluorite (CaF2) is a common fluoride mineral of low solubility occurring in both igneous and sedimentary rocks. Fluoride is commonly associated with volcanic activity and fumarolic gases.The accepted value of fluoride in water is set to be 1.5 mg/litre (i.e. 1.5 ppm) by WHO in 1984 and reaffirmed in 1993 [5]. The fluorides ions are not harmful if their concentration is 1.5 ppm or lesser. Fluoride is often added to drinking water at a concentration of 1.0 ppm to prevent tooth decay.

For optimal dental health, the World Health Organization recommends a level of fluoride from 0.5 to 1.0 mg/L (milligrams per liter), depending on climate[48]. Adverse effects become possible at fluoride levels far above this recommended dosage. The United States Health and Human Services Department recommends 0.7 milligrams of fluoride per liter of water — the lower limit of the current recommended range of 0.7 to 1.2 milligrams.

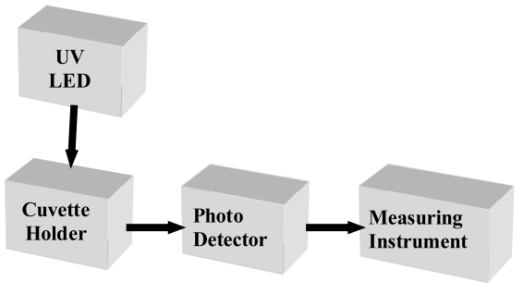
The effects of fluoride on human health can be either positive or negative depending on the amount of fluoride that has been ingested. The main source for fluoride intake is usually the drinking water, which supplies 75-90 % of the daily intake (Meenakshi et al. 2004). Therefore the concentration of fluoride in drinking water is an important factor controlling daily fluoride intake. It is, however, the sum of all ingested fluoride over a period of time that is relevant when looking at health effects, and not just the concentration in drinking water. Thus, in a temperate climate the effects of 1.0 mg/L fluoride in water might be positive while the same concentration in a warmer climate might, due to larger water intake, be negative. Excessive intake of fluoride affects the teeth and the bones. This is

because fluorine is very electronegative and thus easily binds to the positively charged calcium ions in teeth and bone. In large quantities fluoride can also affect the kidneys and the thyroid gland and in the most extreme cases it can lead to death.

There have been various methods and techniques to determine the concentration of fluoride ion in water. For detection of fluoride ion particular range of wavelength is required. There is certain equipment available in the market for the above purpose. But the equipment are not as cost effective and easily available for the common man to use in India, So there is a necessity to come up with a product that is portable, cheap as well as readily available for general daily use. In the current research, for getting a solution to the above problem, there is a need to come up with an effective design for a portable carbon dot based sensor for fluoride ion detection and concentration determination. Here a new novel technique has been explored wherein instead of the traditional techniques, an optical light source and detector based system is considered. The design of the system can be done in Solid Works software.

2. EXPERIMENTAL DETAILS

Very few studies have concentrated on coming with an optical technique to determine the fluoride ion concentration. Most of them have either used ion selective electrode method or colorimetric method. In this paper, UV light source based optical method has been studied. The basic setup consists of a LED light source, the sample to be tested and a photo detector. The principle of photoluminescence has been used. Photoluminescence (abbreviated as PL) is light emission from any form of matter after the absorption of photons (electromagnetic radiation). It is one of many forms of luminescence (light emission) and is initiated by photo excitation (excitation by photons), hence the prefix photo [2]. Following excitation various relaxation processes typically occur in which other photons are re-radiated. Time periods between absorption and emission may vary: ranging from short femtosecond-regime for emission involving free-carrier plasma in inorganic semiconductors [3] up to milliseconds for phosphorescent processes in molecular systems; and under special circumstances delay of emission may even span to minutes or hours. Observation of photoluminescence at a certain energy can be viewed as indication that excitation populated an excited state associated with this transition energy. In general, three different excitation conditions are distinguished: resonant, quasi-resonant, and non-resonant. For the resonant excitation, the central energy of the laser corresponds to the lowest exciton resonance of the quantum well. No or only a negligible amount of the excess energy is injected to the carrier system. For these conditions, coherent processes contribute significantly to the spontaneous emission [5,6].



Samples prepared:

A number of samples were prepared containing different concentrations of fluoride ion and different quantities. They are properly stirred and mixed till the fluoride ion is completely dissolved in water. They were introduced in the cuvette already containing carbon dots solution one after the other separately and the corresponding readings noted down .The fluoride ion sources taken were sodium fluoride (NAF). Standard pipettes with volumes ranging from 120ul are used to introduce the fluoride sample into the carbon dots solution. The step by step procedure is as below:

Step 1: Carbon dots solution is taken in a cuvette.

Step 2: Cuvette is placed between the led source and the OPT101.

Step 3: The system is switched on with a voltage supply supplied to the UV led source and the photo detector.

Step 4: The multimeter is connected to the output terminal of the OPT101 and the voltage reading noted down.

Step 5: The above steps are repeated for all the samples.

The samples selected for the experiments are given below

I. Carbon dot solution
II. CDS with 1ppm NAF
III. CDS with 5ppm NAF
IV. CDS with 10 ppm NAF
V. CDS with 40 ppm NAF

UV analysis:

UV analysis is used to determine maximum absorbing wavelength, absorbing intensity. By the UV analysis, we can also determine energy band gap of carbon dots with the help of TAUC plot. Here, I took 60ul carbon dots and mixed in water containing by cuvette. Then I placed

this cuvette in spectrophotometer and took its UV. The UV result has shown below.

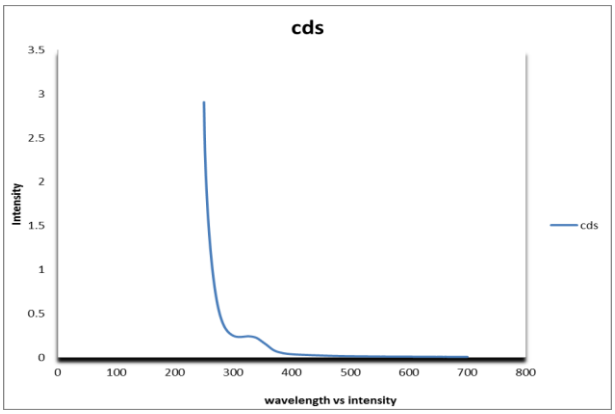


Fig-1: UV Ananlysis

IRJET sample template format ,Define abbreviations and acronyms the first time they are used in the text, even after they have been defined in the abstract. Abbreviations such as IEEE, SI, MKS, CGS, sc, dc, and rms do not have to be defined. Do not use abbreviations in the title or heads unless they are unavoidable.

Fluoride Sensitivity graph:

In this graph, different concentration of fluoride ion spectrum plotted on same graph and compared with CDS spectrum. I found that, there is intensity changes takes place when I increased amount of fluoride concentration. For different fluoride concentration, different intensity changes takes place. As we see from graph, there is lowest intensity change for 1ppm and highest intensity change for 40ppm. So we can say that when I increased fluoride concentration then intensity changes also increased. Fluoride sensitivity graph has been shown below.

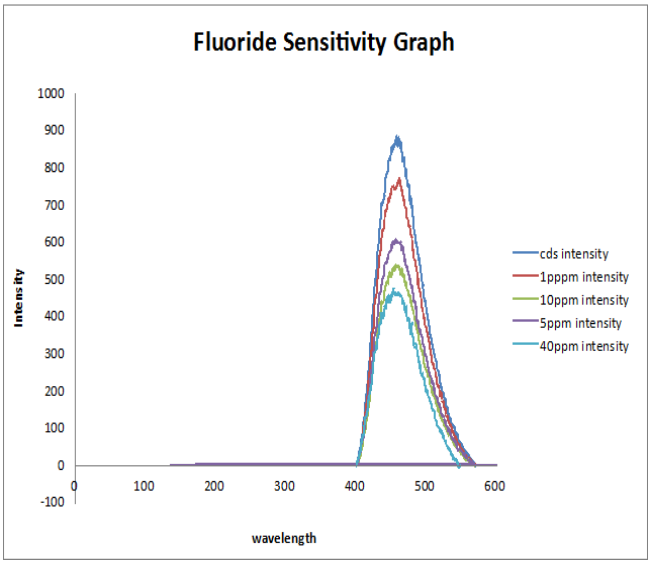


Fig-2: Wavelength Vs Intensity Graph

Design of Experimental Set-Up:

The proposed design set-up is shown below. This set-up consists of UV LED, cuvette holder and photo detector. In this fig. cuvette contains only water and there is no luminescence takes place when UV light passes through cuvette.

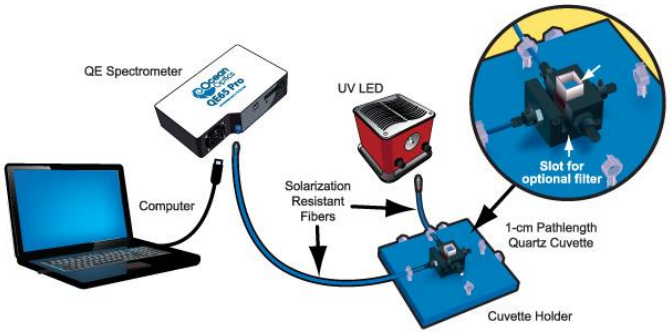


Fig -3: Proposed Experimental Set-up

3. CONCLUSIONS

With the growing number of fluorosis cases and other health problems arising due to fluorine overdose in India and the vast number of people being affected due to the same, there was definitely a need to produce a cost effective measuring device which was portable, easy to handle and operate. The traditionally methods are in use but they have certain disadvantages and have not reached out to the general public.

In this work we have used minimal of components which are cost effective and provide the results the without much time consuming. It has been shown in the experimental results that the method can successfully determine fluoride concentration. From the experiments, it is seen that different samples of NAF were used simultaneously and the readings observed. In the cases, from the results, the intensity of the sample is seen to reduce whenever the concentration of fluoride ion is increased. This method is proposed for its simplicity, portability, rapid response, and ability to directly measure with a good range of sensitivity.

It is also be possible to analyze and calculate the values of fluoride in water by interfacing the output of the transducer i.e., photo detector with computers. Smart detection processes using Artificial Neural Networks will be designed in the same project in the future work.

The novel optical sensor can be optimally used for water pollution level information in fluoride affected regions and also equally at other places as it is versatile and one can test any heavy metal ion or any anion simply by varying the source excitation frequency. This sensor system can be used by many sectors such as tourism, environmental department; public sectors and others related sectors. This can be of great help in estimating fluoride content of water bodies in both urban and rural areas.

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