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Detection of Nitrates in Water Sample by Voltammetric Analysis on Modified Carbon Nanotube Electrode

J. Rathidevi[1], H. Mary Helen[2,*]

[1]*Research Scholar (Reg. No. 12197), Department of Chemistry, S.T. Hindu College, Nagercoil, Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli – 627 012, Tamilnadu, India.*
[2]*Department of Chemistry, S.T. Hindu College, Nagercoil, Kanyakumari District – 629 002, Tamilnadu, India.*

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ABSTRACT

The present study was carried out to determine the physico-chemical characteristics of water from selected tourist spots of Kanyakumari district during the period of twelve months from June 2016 to May 2017. Five sampling stations were selected and water samples were collected for the study. Surface water temperature varies from 24.2 to 31.5 °C and pH is ranged as 6.23 to 8.12. Variation of dissolved oxygen content was 4.2 to 6.7 mg/L. The ranges of chloride from 10 to 21100 mg/L. TDS value ranges from 30 to 41234 mg/L. Total hardness ranges from 12 to 17300 mg/L. Nitrite monitoring is particularly important in drinking water and food because of its increased relative toxicity to humans. High nitrite concentrations in humans have been linked to methemoglobinemia and stomach cancer. Nanoparticle-based materials have played an important role in the development of new electrochemical sensors and have recently gained enormous attention for the detection of hazardous ions such as nitrate compounds. The modified carbon nanotube were made by a simple citrate technique and then prepared with black carbon powder on a glassy carbon electrode for the measurement of nitrate ions in water using cyclic voltammetry and differential pulse voltammetry. CNTs electrocatalytic reduction of NO^{3-} in acid solution was used to calculate the concentration of NO^{3-} in water samples by measuring the reduction current on the working electrode during the NO^{3-} reduction reaction on the surface of carbon nanotube. The ranges of nitrate, nitrite and phosphate were found to be 0.5 to 4 mg/L, 0.03 to 0.43 mg/L and 0.1 to 1.05 mg/L respectively. Electrical conductivity ranges from 45 to 62114 µs/cm.

1. Introduction

Water is a precious resource on our earth and is a vital component for human being and animals for their day today survival. Its quality is likely to change day by day and from source to Source 1. Any change in the natural quality may disturb the equilibrium system and would become unfit for designated uses Water quality has become an important water resource issue due to rapid increase in population, industrialization, unplanned urbanization, discharge of pollutants and much use of fertilizers and pesticides. During the last decade it was observed that the surface water get polluted because of increased human activities [1-3].

In recent years, various methods have been explored to develop real-time nitrate monitoring systems that incorporate analytical techniques such as chromatography, colorimetry, electrochemistry, and spectroscopy. Among these methods, electrochemical analysis has emerged as a promising approach due to its simplicity, high sensitivity, accuracy, wide measuring range, affordability, user-friendliness, and suitability for field-deployable applications. As a result, researchers have begun to view electrochemical sensing as a favorable alternative to the more expensive conventional analytical techniques [4].

The present study is to assess and interpret the water quality of various tourist spots of Kanyakumari district like Thiruparappu Falls (S_1), Muttom Beach (S_2), Mandaikadu Beach (S_3), Chothavilai Beach (S_4) and Kanyakumari Beach (S5) due to their utility by tourists and other domestic activities. Electrochemical sensing electrode was prepared based on MEMS technology.

2. Experimental Methods

The samples were collected from all the five stations for physico-chemical examinations, different methods of collection and handling were adopted based on standard procedures [5]. The samples were collected in plastic cans of 5 liter capacity without any air bubbles. The temperatures of the samples were measured in the field itself at the time of sample collection. The study period was from June 2016 to May 2017. Standard methods were used for the analysis of various water quality parameters [6-8]. All the reagents used were AR grade and double distilled water was used for the preparation of solutions. The water sampling stations are shown below. Station I is Thiruparappu Falls (S_1), Station II is Muttom Beach (S_2), Station III is Mandaikadu Beach (S_3), Station IV Chothavilai Beach (S_4), Station V is Kanyakumari Beach (S_5)

All the electrochemical measurements were carried out by CHI 650C electrochemical work station (CH Instruments, Inc., U.S.A). Electrochemical studies were carried out in a conventional undivided three electrode cell using modified glassy carbon electrode (GCE) as a working electrode (area 0.0341 cm^2), Ag|AgCl as a reference electrode and Pt wire as a counter electrode. Prior to each electrochemical experiment, the electrolyte solutions were deoxygenated with pre-purified nitrogen for 10 min unless otherwise specified. Were prepared and used for different pH solution as supporting electrolyte for throughout the electrochemical studies. All the experiments are carried out three times and the average value is used to plot figures and calibration plots.

3. Results and Discussion

3.1 Physico-Chemical Analysis

During the study period from June 2016 to May 2017 temperature varied from 24.2 °C to 31.5 °C. The minimum was observed during post monsoon at station III and maximum during pre-monsoon at station IV. In general all the five stations showed similar seasonal variations. The

*Corresponding Author:helencolombus@gmail.com(H. Mary Helen)

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surface water temperature was inflamed by the intensity of solar radiations, evaporation, fresh water influx and flow from, adjoining neritic water [9]. The low value during monsoon may be due to rainfall and sea breeze.

The variation in the pH of the water may be due to photosynthesis or due to the variation in salinity. In the study period maximum pH was recorded during pre monsoon at stations IV and minimum during monsoon at station I. Decrease in pH value during the period were related to the factor like removed of CO_2 by photosynthesis, dilution of water with fresh water that reduces salinity.

Electrical conductivity is high at station IV during pre-monsoon and low at station I during monsoon season. Increase in temperature increases conductivity and drastic increase or decrease in conductivity indicates the presence of pollutants in water.

DO is a very important indicator of water body's ability to support aquatic life [10]. They also indicate the degree of pollution in water bodies. In the study period DO level varied as 4.2 - 6.7 mg/L. The maximum 6.7 mg/L found at the station I monsoon and minimum 4.2 mg/L found at station IV during pre-monsoon season. The combined effect of winter cooling and high photosynthetic activity leads to increase of DO [11, 13]. Bacteria, fungi and other decomposer organisms reduce dissolved oxygen level because they consume oxygen while breaking down organic matter.

The nitrate content in the study period is varied from 0.5 to 4 mg/L, given in Fig. 1. It doesn't show any significant variation during the sampling periods. Nitrate pollution will cause Eutrophication which reduces the water quality, even though the values not exceed the permissible limit.

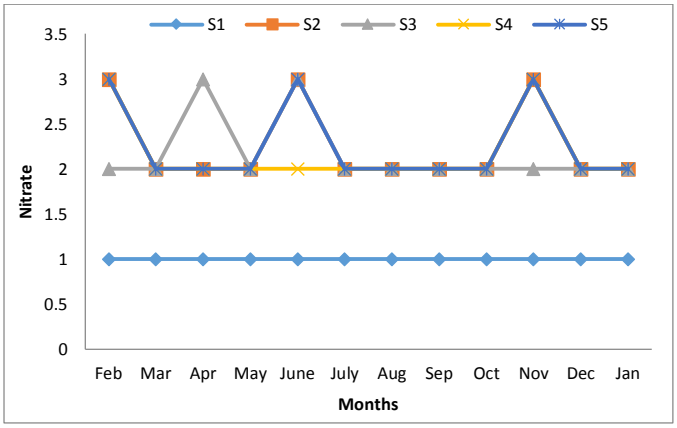

Fig. 1 Concentration of nitrates at different duration

In the present study nitrite varied from 0.03 mg/L to 0.43 mg/L given in Fig. 2. Maximum was found at Station V during monsoon and minimum found at station I during pre-monsoon season. Nitrite that present in fertilizers applied to land dissolved in rain water and flows into water bodies.

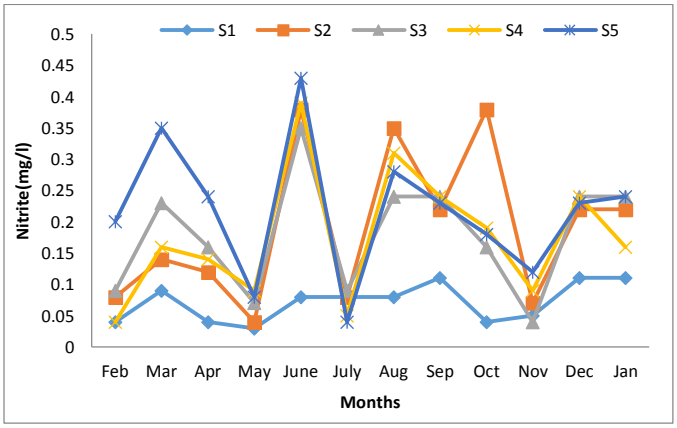

Fig. 2 Concentration of Nitrites at different duration

In the present study total hardness varied from 12 mg/L to 17300 mg/L. The maximum was observed during pre-monsoon at station IV and minimum was observed during monsoon at station I. Bicarbonates, chlorides, nitrates, phosphates and sulphates are present in the form of Na^+, K^+, Mg^{2+} and Ca^{2+} are mainly responsible for alkalinity and hardness of water[14].

In the present study period the chloride content was varied from 10 mg/L to 21100 mg/L. The maximum was observed during pre-monsoon season at station IV and minimum was observed during monsoon season at station I. The present study the chloride content were beyond the limit except station I. The higher content of chloride may be due to the contamination of inflow of wastes from the terrestrial runoff or of anthropogenic activities.

Phosphorous is necessary nutrient for the plants to live but it is a limiting factor for plant growth. In the present study period phosphate varied from 0.1 mg/L to 1.05 mg/L. The maximum value was observed during monsoon at station I and minimum was observed during pre-monsoon at station IV. High value of phosphate may be due to detergents, industrial, domestic runoff and usage of fertilizers.

3.2. Electrochemical Analysis

The electrochemical methods, oxidation or reduction are used to produce a current to detect a particular analyte [15]. The primary element of any electrochemical sensor is an electrochemical transducer. A transducer consists of a sensing element that reacts with the target analyte and transforms the chemical reaction into an analytical signal. Typically, the electrochemical sensor is a three-electrode system that includes a reference electrode (RE), sensing/working electrode (WE), and counter electrode (CE). The electrolyte reaction occurs at the working electrode. This electrode is generally modified with a nanomaterial to accelerate the electrolytic reaction. The reference electrode allows the correct application of the working electrode potential. The counter electrode is used to complete the circuit and helps continue the electron flow.

The current response properties of micro-sensing electrodes changed by continuous voltage deposition to various concentrations of nitrate standard solutions were investigated using voltage linear scanning. In all experiments, 0.1 mol/L H_2SO_4 solution with pH 1.0 was used as the supporting electrolyte. The microsensor was immersed in the test solution containing different concentrations of NO^{3-} for linear scanning test. The relationship between the concentration of NO^{3-} and the reduction peak current was studied. Fig. 3 shows the microsensor's linear scan response curve at various concentrations of standard nitrate. The figure shows that the sensor's current response signal grows with increasing NO^{3-} concentration in the test solution.

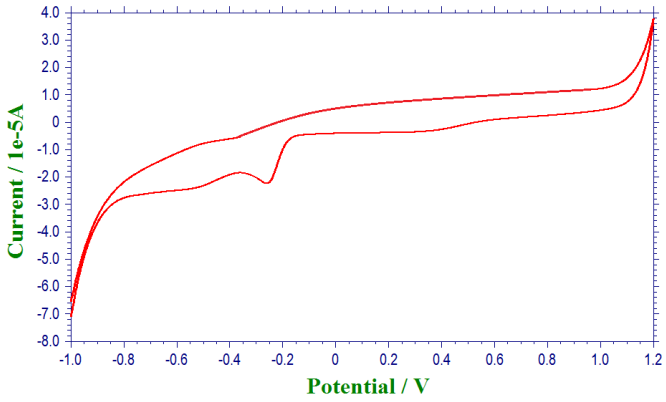

Fig. 3 Cyclic voltammetric behavior of nitrate ions at 100 mV/s in pH 1.0

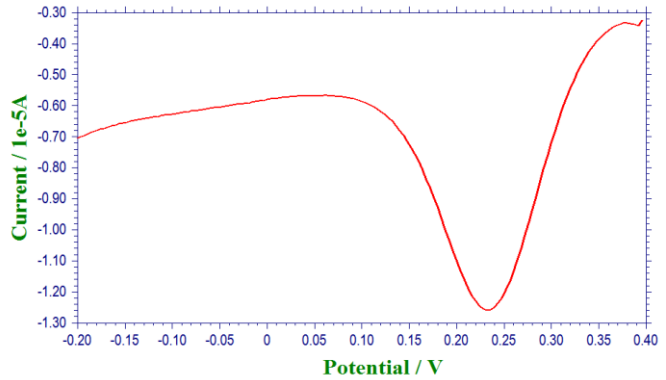

Fig. 4 Typical differential pulse voltammetric behavior of nitrates

Under the optimum experimental conditions, the pulse form applied to the stripping of the nitrates yielded a good analytical signal than the differential pulse (Fig. 4) form for an assayed concentration of 100 ppm. This may be due to the use of increased scan rate, with a significant improvement in sensitivity achieved by employing a pulse scan. Differential pulse stripping voltammograms were recorded at various

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concentrations of nitrates using the optimum conditions. From them, a linear calibration plot was obtained for this compound at a concentration between 20 ppm and 200 ppm. The calibration plots obtained are presented in Fig. 5. The reproducibility of the stripping signal was ascertained in terms of relative standard deviation for five measurements carried out at a concentration of 100 ppm for 2.2%. The results given by the sensors were in good agreement with the data obtained by different pulse voltammetric method for nitrate measurement.

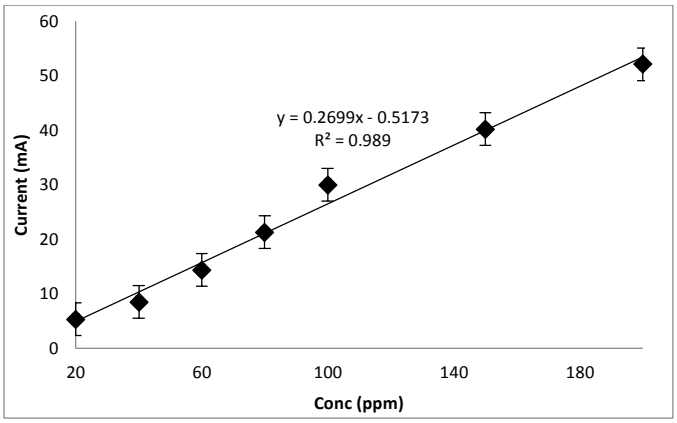

Fig. 5 Calibration plot of different concentration nitrates

4. Conclusion

In this study different physico-chemical parameters were studied and compared with standard values to analyze the water quality of various tourist pots of Kanyakumari district. From the study it was observed that except station I, all other stations electrical conductivity, total dissolved solids, total hardness and chloride content were high. All other parameters determined were within the permissible limit. The results reveals that all the tourist spots and the depended organisms and human beings near by the tourist spots were highly disturbed by the waste water discharged through the sewage from the tourist resorts and other anthropogenic activities. This will cause serious health problems to the people living in the environment. It is the responsibility of the humans to avoid the entering of wastes into the water. So few years from now serious water quality determination could take place. Hence rapid and reliable monitoring measures are essential for keeping a close watch on water quality and health environment. The electrocatalytic reduction characteristics of CNT were used to nitrate ions in an acidic solution and realized the detection of nitrate concentration in the solution. Good detection sensitivity and linearity were obtained in the standard concentration range of 20 ppm and 200 ppm.

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