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DETERMINATION OF NITRITE IN WATER USING ANILINE SULPHATE AND NAPTHOl METHOD

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ABSTRACT
Nitrite (NO_2), occurs naturally in the environment as an intermediate of the nitrogen cycle through microbial decomposition of organic matter. The determination of concentration of nitrite in water body using Cadmium Reduction method test kit which is costly and not easily available is urgently needed alternatives. The aim of this research is to develop a new method using aniline sulphate and napthol for determination of nitrite concentration in water and compare it with the use of Cadmium Reduction method (Hach Dr890) test kit. The samples for the research were taken from F.U.T Minna fish ponds and seasonal stagnated pools from river that flow through the campus. The absorbance of standard nitrite concentration was scanned to determine the wavelength for aniline sulphate and napthol method colouration. The prepared standard concentration of nitrite absorbance and samples were observed at 390 nm. The Cadmium Reduction method was equally carried out on the prepared standard nitrite and the samples as well as with the new aniline sulphate and napthol method. Aniline sulphate and napthol method obeyed Beer-Lambert's law when tested on prepared standard nitrite. The Cadmium Reduction method did not obey Beer-Lambert's law on the prepared standard nitrite. Comparatively, the result obtained from different fish ponds water indicated that the new method had a concentration ranges from 44.8 to 2.7 ppm while the Cadmium Reduction method (Hach Dr890) was in the range of 19.82 to 0.011mg/l. This aniline sulphate/Napthol method could be considered as a new azo dye method that could be used for the analysis of nitrite in water sample.

Key Aniline Sulphate/Napthol, Beer-Lambert's law, Cadmium Reduction, Nitrite

Introduction

Nitrites are nitrogen species; they occur naturally in water and soil and are essential nutrients for plants. Nitrites contain a nitrogen atom joined to two oxygen atoms respectively. The anion O-N=O converge partial negative on oxygen and partial positive on Nitrogen. Hence, they easily associated with cations or ions with a positive charge to achieve neutral state. Sodium nitrite is used [1] for the synthesis organic nitrites and nitro-compounds and particularly in diazotization reaction leading to azo dyes and pharmaceuticals.

Nitrites are found commonly in ground water than in surface water, they are more commonly detected as contaminants in river, well water and fish pond. Principal sources of nitrite contamination are fertilizers, septic tank waste, livestock manure and erosion of natural deposits. The nitrite is concern because it is significantly more toxic than ammonia or nitrate. It is an environmental concern due to its harmful effects to aquatic plants, animals and human health [2, 3].

Nitrate and nitrite salt component are used as preservatives to influence the curing bacon and ham [4] colour and also extend meat shelf life. The combinations of nitrite with myoglobin result to the formation of nitrosohemoglobin, which is responsible red colour characteristic in cured meat and hence serve as meat preservative sometimes. The effluent from the industries and nitrogen cycle contribute to the contamination with nitrite [2, 5].
Owning to its toxicity, nitrite is unwanted in water. The level of concentration of nitrite in

portable water prescribes by US public health service is 0.06 mg/L [6, 7]. On a normal condition, the level of nitrite are generally low 0.1 ugmL^{-1}. However, the level of which nitrite are used in food industry as a corrosion inhibitor in industrial process has tentatively increase as result of increased level of nitrite in water bodies [6].

The high pollution of water due to nitrite has, become the major concern for infant less than 6 months of age and farm animals and infant food that are made with water containing more than 50 mg nitrite per liter is been confirmed to be the major causes of met-hemoglobin infants which causes reduction of hemoglobin ability to carry oxygen with symptoms such as cyanosis, coloration of the skin, hence known as blue baby syndrome [8].

Nitrite (NO_2), occurs naturally in the environment as an intermediate of the nitrogen cycle through microbial decomposition of organic matter. However, nitrite contains nitrogen in a reasonably unstable oxidation state and readily oxidizes to nitrate (NO_3). Nitrite is present at considerably lower concentrations in ground and surface waters than nitrate. Higher concentrations of nitrite are indicative of pollution by industrial wastewater or agricultural run-off. The USEPA established a maximum contaminant level (MCL) of 1 mg/L nitrite-nitrogen in drinking water to help prevent conditions including blue baby syndrome in infants [2]. In this application, the quantitative analysis of nitrite-nitrogen was performed using the LAMBDA™ 265 UV-Vis spectrophotometer and CHEMetrics nitrite test kit and Hach test kit [10].

Determination of nitrite in drinking water and environmental samples by ion exclusion chromatography with electrochemical detection. Interferences was presumably removed due to spectrophotometric method or by the ion exchange chromatographic method with either conductivity detection or UV detection. The detection limit in this method was 0.1 ppb without pre-concentration. Amounts of 19.1 ppm and 0.50 ppm nitrite were observed from fertilized and unfertilized soil, respectively [9]

A novel simple, sensitive and rapid kinetic-spectrophotometric method was proposed called spectrophotometric determination of nitrite by its catalytic effect on the oxidation of congo red with bromate for the determination of trace amounts of nitrite is proposed. The method is based on its catalytic effect on the oxidation of congo red (CR) by potassium bromate in acidic solution. The oxidation reaction is monitored spectrophotometrically by measuring the decrease in the absorbance of CR at a suitable λmax = 570 nm this method can be applied to water with a nitrite content of at least 0.025 mg/L [10].

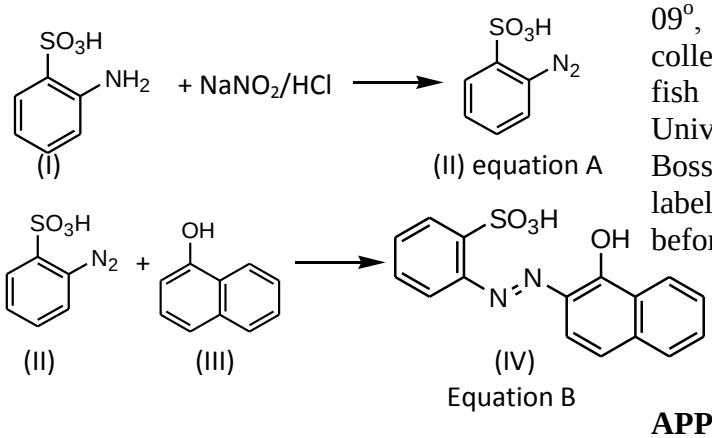
Another simple, sensitive, and specific spectrophotometric method for the measurement of nitrite in water was azo dye, -(1-methyl-1-mesitylcylobutane-3-yl)-2-(*p*-N, N-dimethylazobenzene)-1,3-thiazole was synthesized with the reaction of 4-(1-methyl-1-mesitylcylobutane-3-yl)-2-amin othiazole and N,N-dimethyl aniline in acidic medium. The dye shows an absorption maximum at 482 nm. At an analytical wavelength of 482 nm, Beer's law is obeyed over the concentration range 0.05 to 2.00 µg nitrite per mL analyses. The detection limit of the method is 0.012 µg ml^{-1} of nitrite ion. The method was successfully applied to the determination of nitrite in tap water and lake water [11].

Different type of methods had been used for determination of nitrite for example the azodye method. The method of determination of nitrite in water was first applied to studies of nitrite formation in the marine environment [12 ,13] The originality of Wada's method in 1972 was that, the content of nitrite was determined following the formation of azo dye

-N=N-, with sulfanine acid and N-1 napthylethylenediamine [13, 14] Olson (1981) and Horigan and Capon (1985) adopted the modification of this method in which aniline and 2- naphthol are used as a reagent due to the fact that, the reagent can only introduce one nitrogen atom to a dye molecules other than emanating from nitrite.. Sulfuric acid has been a common agent of nitrite of nitrate removal [14]. Preliminary studies has shown that, it has become difficult to achieve a constant and meaningful yield of Azo dye after sulfamic acid treatment, [14, 15].

GENERAL PRINCIPLE FOR NITRITES (NO_2) ANALYSIS

Aniline sulphate (I) reacts with $NaNO_2$ in an acidic medium, HCl to afford a diazonium salt (II) as shown in equation A. The diazonium salt further couples with 2- naphthol (III) to form an azo-dye (IV) as shown in equation B. The compound (IV) which is colored, is then quantitatively determined using a spectrophotometer.



Significance of the study

The essence of devising another new method which is the synthesis of diazonium salt (equation A) for the analysis of nitrile is to reduce the cost of use of sulphanilamide as an anti-bacterial agent, so that the diazonium salt replaces the sulphanilamide. The method would be affordable, quick and sensitive enough to be used for nitrite water determination in aquatic and domestic water bodies. This method would also stop the competitive therapeutic uses of sulphanilamide as a drug for man and water quality analysis.

This research is to develop aniline sulphate and napthol method to determine nitrite concentration in water and compare it with the conventional powder pillow Cadmium Reduction method test kit (Hach Dr890) [10] . The objective is to determine stiochiometric ratio of aniline sulphate and napthol, absorbance wavelength, concentration of nitrite in new developed method and compare with conventional Hach method of nitrite determination in water samples

MATERIALS AND METHOD

SAMPLE COLLECTION

The samples collection were gotten from Minna, Niger State north central region of Nigeria, the study area Minna, located on coordinate of longitude 06^o 30'E and latitude 09^o, 37'N. The water samples were all collected in sufficient amount from different fish ponds located behind the Federal University of Technology Minna boys hostel, Bosso campus and was poured into a well-labeled plastic bottle stored in refrigerator before the analysis.

APPARATUS USED

UV-Vis Spectrophotometer model 752 (200-1000nm) Guang1zhou guoheno electric machine limited, 50ml volumetric flask 100ml volumetric flask, 1 to 5ml pipettes, Spatula, soft tissue, 100ml measuring cylinder and Weighing balance.

REAGENTS

2-naphthol, Hydrochloric, Aniline Sulphate, Sodium Nitrite, Distilled water (H_2O), Methanol all were analytical grade.

Nitrite Stock Solution Preparation

The salt sodium nitrite was first dried in an oven for about 2 hours at temperature of 110^{o}C. Then 0.6g of dried anhydrous $NaN0_2$ was weighed and dissolved in distilled water and diluting this to 1L the nitrite standard (100ppm). The solution was homogenized properly and stored.

Preparation of working Nitrite Standard Solution from (100ppm)

The following concentration 2, 4, 6, 8 and 10 ppm were prepared from nitrite stock solution of 100ppm into 100 ml volumetric flask each.

Preparation of Naphthol Solution and Aniline Sulphate

The 10.0g of 2-naphthol powder was dissolve in 100ml of Methanol in 500ml conical flask and **0.3g of** Aniline Sulphate dissolved in 50ml of methanol in another 500ml conical flask

Determination of Nitrite Using Aniline Sulphate

Working standard of nitrite 0.0, 2, 4, 6, 8, and 10ppm were prepared in volumetric flask. These were prepared by taking each of the following 2, 4, 6, 8, and 10ml from standard nitrite solution into 100ml volumetric flask to obtain a calibration curve. To each of the volumetric flask solution, 2.5ml 6NHCl was added, 0.1ml of Aniline Sulphate was pipette and two drop of 2-napthol was added as well and homogenized thoroughly to azo formation. The absorbance was measured at 390nm against the blank, greenish colour was observed.

The 10ml of water samples was put into 100ml volumetric flask, 10ml of 6NHCl was added, 0.1ml of Aniline Sulphate and two drop of 2-napthol was added and mixed properly for colour development and then scan with a spectrophotometer to determine its wavelength at 390nm using UV-Vis Spectrophotometer model 752 (200-1000nm)

Conventional Determination of Nitrite using Cadmium Reduction method (Hach Dr890) test kits:

Working standard of nitrite was prepared using 2, 4, 6, 8, 10, 12, and 14ppm into 50ml volumetric flask. To the solution powder pillow (reagent) was added **(Hach Dr890)**. The mixture was properly mixed. The absorbance was measured at 600nm against the blank **(Hach Dr890)**. The colour observed was pink.

The 10ml of collected water samples, placed into 50ml volumetric flask and powder pillow (reagent) was added, and shocks properly. Pink coloured was observed after fifteen minutes reaction time showing different level of concentration of nitrite present in each water samples. It was scan with hach (DR 890) colorimeter at wavelength of 600nm.

RESULTS

The result obtained from using Aniline Sulphate and powder pillow are shown in table 1& 2 below. The absorbance against concentration at 390 & 600nm wavelength was reported and also comparative table involving the two methods are also shown below.

Table 1: The results of the reading of concentration of prepared nitrite (ppm) versus absorbance at 390 nm using aniline sulphate and napthol

S/N	ppm of $NaNO_2$	Absorbance
1	0.0	0
2	2.0	0.039
3	4.0	0.080
4	6.0	0.133
5	8.0	0.176
6	10.0	0.239

Table 2: The results of known prepared concentration of Nitrite ppm versus observed concentration Reading of Hach Dr890 method test kit of $NaNO_2$ (ppm).

S/N	prepared Standard Concentration of $NaNO_2$(ppm)	Observed Reading of Hach Dr890 method test kit of $NaNO_2$(ppm)
1	0	0
2	2	2.473
3	4	1.42
4	6	1.625
5	8	2.11
6	10	2.595
7	12	3.48
8	14	4.265

Table 3: The results Concentration of Nitrite ppm versus absorbance of water samples A - O using aniline sulphate and napthol obtained from prepared standard curve.

S/N	**Absorbance at 390nm**	**Concentration of $NaNO_2$ ppm**
A	0.129	5.4
B	0.077	2.7
C	0.105	4.2
D	0.213 x 4	39.2
E	0.209 x 2	19.2
F	0.138	5.80
G	0.233 x 3	32.4
H	0.111	4.4
I	0.240 x 4	44.8
J	0.141 x 3	19.2
K	0.145	6.2
L	0.099	2.80
M	0.111 x 4	17.6
N	0.154	6.7
O	0.161	7.0

Table 4: The results of concentration of Nitrite ppm of sample A - O using Cadmium Reduction method (Hach Dr890)

S/N	**HACH READING OF $NaNO_2$ (ppm)**
A	19.82
B	7.68
C	0.047
D	0.042
E	0.259
F	0.056
G	0.013
H	0.011
I	0.019
J	0.013
K	0.012
L	0.037
M	0.030
N	4.130
O	0.053

Table 5: Comparison of Concentration of Nitrite Aniline Sulphate and Cadmium Reduction method

S/N	ANILINE SULPHATE CONCENTRATION, ppm OF $NaNO_2$	HACH READING OF $NaNO_2$ (ppm)
A	5.4	19.82
B	2.7	7.68
C	4.2	0.047
D	39.2	0.042
E	19.2	0.259
F	5.8	0.056
G	32.4	0.013
H	4.4	0.011
I	44.8	0.019
J	19.2	0.013
K	6.2	0.012
L	2.8	0.037
M	17.6	0.030
N	6.7	4.130
O	7.0	0.053

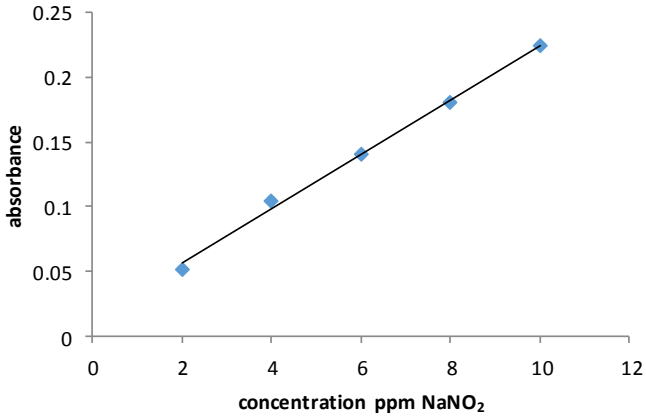


Figure 1: The standard curve of the absorbance versus concentration of aniline sulphate

Discussion of Result

Higher concentrations of nitrite are indicative of pollution by industrial wastewater or agricultural run-off. The USEPA established a maximum contaminant level (MCL) of 1 mg/L nitrite-nitrogen in drinking water to help prevent conditions including blue baby syndrome in infants2.Analysis of Nitrite in water has been taken seriously. The reason is that nitrite a source of pollution to tap water, drinking ground water and fish Pond. The present available methods for the determination of nitrite had never been consistent.

The concentration of prepared nitrite (ppm) versus absorbance at 390 nm using aniline sulphate and napthol method (table 1) was observed to obeyed Beer Lambert law. Meanwhile, when the prepared concentration of nitrite (ppm) were read using **Hach Dr890** test kit method it did not give us corresponding desired prepared concentration of nitrite (ppm) table2. Due to obedience of Beer Lambert's law aniline sulphate and napthol method, some water samples coded A –O were analyzed. Their absorbance from these samples were determined and their

corresponding concentration were determine from the standard curve (figure 1).

Comparatively, the result obtained from different fish ponds water from F.U.T Minna fish ponds samples indicated that aniline sulphate had a concentration ranges from 44.8 to 2.7ppm while the Cadmium Reduction method (Hach Dr890) is in the range of 19.82 to 0.011mg/l. This aniline sulphate and naphthol method had a concentration result ranges from 44.8 to 2.7ppm which was as a result of pollution due to defecation in the stagnated pool and the feed used for the fish respectively [9]. These observed value were not far from expectation because the some sampled ponds were polluted and stagnant (table 3). This method looked very sensitive and reliable since it obeyed Beer Lambert law (table 2 and figure 1). The Cadmium Reduction method (Hach Dr890) test kit result has no bases of comparison because the prepared standard did not follow any trend. The Cadmium Reduction method (Hach Dr890) test kit result did not obeyed the Beer-Lambert's law (table 2, 4 5). The prepared standard did not follow any trend for Cadmium Reduction method (Hach Dr890) test kit (table 2, 4 5).

CONCLUSION AND RECOMMENDATION

Conclusion

This study has shown that comparison of the Cadmium Reduction method (Hach Dr890) and aniline sulphate and naphthol method proven that aniline sulphate and naphthol method is more sensitive compared to that of the Cadmium Reduction method (Hach Dr890). From the result of different concentration obtained, the graph of aniline sulphate proves to be sensitive and its obeyed Beer Lambert law. The result obtained from different fish ponds water from F.U.T Minna fish ponds samples indicated that aniline sulphate had a wider application in concentration determination from 44.8 to 2.7ppm while the Cadmium Reduction method (Hach Dr890) is in the range of 19.82 to 0.011mg/l. This aniline sulphate method could be considered as a new method, although more analysis needs to be done before it could be published.

In all indication and observation I hereby concluded that the study has improved for the qualitative analysis in determination of nitrite in water most especially in comparison with the Cadmium Reduction method (Hach Dr890) test kit.

Recommendations

This study is to shown the role in which aniline sulphateand naphthol play in the cause of determining nitrite in water, either in drinkable water, waste water or pond water and there no bases for comparison with the Cadmium Reduction method (Hach Dr890). Hence, more effort is required to ensure that more work have to be done to improve and standardize this methods for effective determination of nitrite in water.

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