

Determination of Chemical Oxygen Demand of Some Selected Wells and Ponds in Bayero University, Kano and its Environs

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Abstract: *Chemical oxygen demand measurements of eight different ponds and wells were determined by back titration method. All samples were analyzed immediately and Chlorides and nitrites interferences were eliminated. The work is aimed at evaluating the pollutional strength of the waters so as to recommendations concerning the detrimental effects that may arise from various uses of such waters. The ponds have 216.59 ± 12.07 while the wells have 74.26 ± 23.31 . This further justify the notion that due to a number of factors like washings, agricultural practices and making local bricks ponds were more polluted than wells. Drinking water its high COD directly could results in water borne diseases such as cholera, typhoid, dysentery, etc.*

Keywords: Back titration, Chemical oxygen demand, chlorides, nitrites

1. Introduction

Water is one of the most common substances known and it is a good solvent for many substances, due to this property it does not occur in its pure form. Its natural forms include rainwater, spring water, well water, river water, lake, sea etc. Of these rain water is most the purest form of water, formed by the condensation of water vapor in the atmosphere i.e. it is called natural distilled water [1]. It is essential for any form of life and account for about 70% of Human body by weight and about 80% of the earth's surface [2]. It provides the medium for metabolic reactions in the living cells; convey food substances from place to place within the body of living organisms, helps in getting rid of waste and excretory products in living system. Water is also a medium for the transportation of goods and people. Its other uses include hydroelectric power generation, municipal water supply, recreation, irrigation, fishing, discharge of industrial and domestic wastes, etc. Hence the need to avoid the accumulation of foreign substances in our waters became imperative.

To deal this we have to look into the gigantic water cycle (hydrological cycle). The term hydrological cycle simply refers to a natural process of cycling water from the atmosphere down (and through) the earth and back to the atmosphere [3]. It has five parts as sources of water. A largest portion of water is found in the oceans. Another fraction present as a vapor in the atmosphere. Some is contained in the solid state as ice and snow in snow packs, glaciers and polar ice caps. Surface water includes lakes, streams and reservoirs. Groundwater is located in the ground water aquifers underground.

There is a strong connection between the hydrosphere, where water is found and the lithosphere, which is accessible to water. Human activities affect both for example, agricultural production may reduce the vegetation cover, decreasing transpiration (loss of water molecules by plants) and affecting the microclimate. These resulted in

increased rain runoff, erosion and accumulation of slits in bodies of water [4].

Solar energy especially in the tropics evaporates water from ocean surface, filling mass above with large quantities of water vapors. When this warmed, moist maritime masses come in contact with cold dry air over large land areas, some of the water vapor precipitates out as rain or snow. 70% of the annual precipitation evaporates or is transpired by plants while the remaining 30% goes into the stream flow [5].

These water bodies are often contaminated or polluted by several foreign substances either in dissolved or an undissolved form by a human activity. With the exploding population and increasing industrialization and urbanization, water pollution by agricultural, municipal and industrial sources has become a major concern for the welfare of mankind [2]. It is also regarded as the addition into water of harmful or objectionable materials and substances in large quantities to adversely affect the water usefulness [3]. Therefore water whether from underground or surface sources found in nature is polluted and the pollution may be due to various reasons, namely from sewage, industrial waste or from natural contaminant [4]. The use of polluted water may result in water borne diseases and its epidemics when consumed directly, deteriorates its aesthetics, agricultural and industrial uses [2], [4]. Such waters may also introduce into a human food chain harmful substances that may result in ill health.

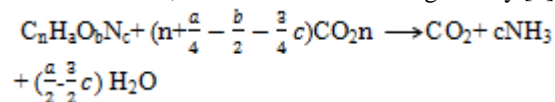
There are various types of water pollutants and in this study we are particularly interested in organic pollutants (particularly oxygen demanding waste). They include a wide range of substances such as domestic sewage, biodegradable and industrial wastes from food processing plants, meat-packing plants, slaughter houses, paper and pulp mills, tanneries etc. as well as agricultural run-off, microbes synthetic organic compounds (e.g. elastomers, plastics) and oil from spillage to mention few [2]. It is on this note that oxygen is demanded uncomprehendingly for the conversion (oxidation) of organic

pollutants in water into carbon dioxide, water and ammonia [2], [6], [7].

A significant portion of the total damage caused by the discharging of waste water into lake or rivers is because many of these discharges deplete the oxygen contents of ecosystem [8]. This oxygen depleting potential is usually expressed and quantified by biological oxygen demand (BOD), chemical oxygen demand (COD) or total oxygen demand (TOD) measurements [8]. The general term that describes all these parameters is called oxygen demand, which for a sample of water is the amount of elemental oxygen required to react with biodegradable material that dissolved and suspended in the sample. This amount is expressed in milligram of oxygen per liter of sample. When the oxidation is carried out with a chemical oxidizing agent such as potassium chromate/dichromate, the oxygen equivalent is called the chemical oxygen demand (COD) [8].

Chemical oxygen demand is a measure of the oxygen equivalent to that portion of organic matter present in the waste water sample that is susceptible to oxidation by potassium dichromate [2]. This is an important and quickly measured parameter from sewage and industrial waste samples to determine their pollution strength. For many years, the strong oxidizing agent potassium permanganate (KMnO_4) was used for measuring chemical oxygen demand. The potassium permanganate effectiveness at oxidizing organic compounds varied widely and in many cases biochemical oxygen demand (BOD) were often much greater than results from COD measurements [9]. This indicated that potassium permanganate was not able to effectively oxidize all the organic in water-rendering it a poor oxidizing agent for COD determination. Since then, other oxidizing agents such as ceric sulfate, potassium iodate and potassium dichromate have been used to determine COD and of these potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) has been found to be the most effective. It is relatively cheap, easy to purify and is able to nearly completely oxidize almost all organic compounds [6].

The basis for the COD test is that nearly all organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions. The amount of oxygen required to oxidize an organic compound to carbon dioxide, ammonia and water is given by [6].



The ammonia that is being formed reacts with oxygen subsequently to form nitrate (nitrification). This method is very effective because the oxidation of most organic compounds is 95-100% of the theoretical value with the exception of pyridine and its related compounds and some other volatile organic compounds which are only oxidized to the extent they remain in contact with oxidant [10].

2. Materials and Methods

2.1 Apparatus

The apparatus that were used are three 500ml Erlenmeyer flask, burette, funnel, spatula, three 100ml measuring cylinders, three 250ml beakers and a refluxing set-up: 300ml heat resistance round bottom flasks, reflux condenser, hot plate and retort stand.

2.2 Chemicals

All the chemicals used were of analytical grade and Sigma-Aldrich brand. The chemicals used in this study were potassium dichromate, silver nitrate, sulfuric acid, mercury sulfate, sulfamic acid, Ferroin indicator and ferrous ammonium sulfate (FAS).

2.3 Preparation of Standard potassium dichromate solution, 0.00833M:

2.450g of $\text{K}_2\text{Cr}_2\text{O}_7$ A.R. grade was weighed and dried in an oven for two hours at 103°C . It was then transferred into 1000ml volumetric flask containing some distilled water. Distilled water was then added slowly around the neck of the flask; thereby ensuring all the reagent that was retained on the neck is washed down to the bottom. This was continued till the solution reaches the mark.

2.4 $\text{AgNO}_3\text{-H}_2\text{SO}_4$

10g of silver nitrate was weighed and transferred into 500ml of concentrated sulfuric acid (s.g. 1.84) in a standard flask. It was left overnight to dissolve completely.

2.5 Standard ferrous ammonium sulfate solution, 0.05M

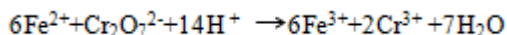
19.60g of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ was weighed in a beaker and 2.5ml of concentrated sulfuric acid was added. It was then cooled and emptied into 1000ml volumetric flask and distilled water was added thereafter up to the mark. This solution is secondary standard and thus requires standardization daily before used.

2.6 Sample Collection

Samples were collected from in a clean 120ml plastic bottles (sample bottles). Each bottle was first rinsed with the water to be sample before deepened completely into it. After each bottle is completely filled with the sample it is then capped before taken out. This is to ensure that no air is entrapped in the sample.

2.7 Standardization of Ferrous Ammonium Sulfate

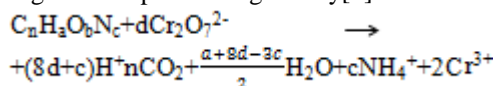
10ml of standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution was measured and then transferred completely into 500ml Erlenmeyer flask. This was diluted to 95ml with distilled water followed by addition of 30ml concentrated sulfuric acid. The mixture was allowed to cool. After it was cooled 3 drops of ferroin indicator were added. The solution becomes blue green and was titrated against FAS solution to a reddish brown end point. The equation of the reaction is as follows [11]:



2.8 Determination of chemical oxygen demand

1g of HgSO₄ was weighed and poured into a refluxing flask. This was followed by 50ml of water sample, 5mg of sulfamic acid, 80ml of AgNO₃-H₂SO₄ solution and finally 10ml of 0.00833M K₂Cr₂O₇ solution. The flask was shaken and fitted into the reflux condenser. The mixture was boiled for 15 minutes. This was then removed and poured into 500ml Erlenmeyer flask and the refluxing flask was rinsed with 50ml of distilled water through the condenser. This was poured into the refluxed solution already in 500ml Erlenmeyer flask and then allowed to cool to the room temperature. After it was cooled 3 drops ferroin indicator were added and the solution turned blue-green. It was then titrated with FAS to red brown end point. The procedure repeated two more times for each sample.

The procedure was in triplicate carried out on blank sample by adding all the reagents to 50ml distilled water instead of the sample [12]. The reaction of potassium dichromate with organic compounds is given by [6]:



Where $d = 2n/3 + a/6 - b/3 - c/2$.

3. Results and Discussion

3.1 Standardization of ferrous ammonium sulfate

The variation of molarity of FAS can be seen in table 3.1 below

Table 1: Standardization of FAS

Trial	Volume of FAS Titrated in cm ³	Molarity of FAS, M
1	20	0.025
2	18.50	0.027
3	18.00	0.028
4	20.5	0.024
5	17.50	0.029
Average molarity of FAS	0.027M	
Standard deviation	0.002	

3.2 Chemical oxygen demand results

Table 2: COD for the various ponds examined

S/N	Sampling Site	Average titre (cm ³)	COD, mg/L
1	Blank sample	67.35	
2	A	15.61	206.96
3	B	14.67	210.72
4	C	16.00	205.40
5	D	12.40	219.80
6	E	15.03	209.28
7	F	9.77	230.32
8	G	7.67	238.72
9	H	14.47	211.52
	Average COD	216.59	
	Standard deviation	12.07	
	Relative standard deviation (RSD)	0.06	
	Coefficient of Variation (CV)	5.57%	

A=Kafinga pond E=Lulga pond
 B=Afinga pond F=Duck pond
 C=kagoshi pond G=Ramin tsakuwa
 D=Janbolu pond H=Zakara pond

Table 3: COD for the various wells examined

S/N	Sampling site	Average titre (cm ³)	COD mg/L
1	P	45.20	88.60
2	Q	46.97	81.52
3	R	44.80	90.20
4	S	46.52	83.32
5	T	61.44	23.64
6	U	45.00	89.40
7	V	46.85	82.00
8	W	53.51	55.36
	Average COD	74.26	
	Standard deviation	23.31	
	Relative standard deviation (RSD)	0.31	
	Coefficient of variation (CV)	31.39%	

P=Danbare well T=Janbulu well
 Q=Tudun muntsira U=Kankare well
 R=Rimingata well V=Rijiyar zaki
 S=BUK botanic garden W=BUK new site

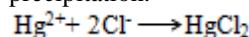
In each case COD was determined as follows:

$$\text{COD} = \frac{(B-A) \times M \times 8000}{\text{sample volume}}$$

Where B=volume of FAS consumed by the blank sample
 A=Volume of FAS consumed by the water sample
 M=Molarity of FAS solution

3.2 Roles of the reagents used

The addition of H₂SO₄-AgNO₃ solution serves two functions: the sulfuric acid provides the acid medium needed for oxidation process to occur while AgNO₃ catalyzed the reaction [2]. Mercury(II) sulfate removes chlorides ions by precipitation.



While sulfamic acid liberate nitrogen gas from nitrites [13]

$$\text{HO.SO}_2.\text{NH}_2 + \text{HNO}_2 \rightarrow \text{N}_2 + 2\text{H}^+ + \text{SO}_4^{2-} + \text{H}_2\text{O}$$

The ponds appears to have very high COD as compare to wells because they are being maltreated by their host communities apart from some other additional natural processes that takes place viz: dumping of refuse, washing cloth, irrigation, source of drinking water by animals, fishing, as well as discharge of domestic sewages, decaying death flora and fauna among others. This is particularly important as it was even observed that all the ponds that were sampled are green (algal bloom). All these activities introduce organic compounds into the water.

Despite that the fact that wells were observed to have low COD values and are used for drinking and cooking because they are sourced from ground water and are more protected from contamination than ponds. There is fear that high COD values indicate the presence of microbes which most a times are pathogenic. Water borne diseases like typhoid and cholera are believed to have occurred due to organic pollution.

4. Conclusion

The World Health Organization(WHO) standard for drinking (portable) water shows that for chemical oxygen demand (COD), the maximum permitted or allowable limit is 10mgL^{-1} [2]. And the results so far obtained were all above the standard value and hence not recommended for drinking. As for the wells examined, some were always open with no perfect cover to prevent the slipping of materials into it. So the same also with the ponds the very high COD level was observed due to activities of the people of their host communities like washing, irrigation, dumping of refuse and dead animals among others as earlier mentioned.

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