Neutralization of Residual Chlorine Deposit by Sodium-dichloro-iso-cyanurate on Disinfected Water Sample using Ascorbic Acid and Sodium Ascorbate Derivative

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***Abstract:* - Water treatment has been a regulated approach in the purification of polluted water system getting rid of toxic and pathogenic agents before usage.**

Chlorination of water by Sodium-dichloro-iso-cyanurate is a common and cheap disinfection process with a limitation of depositing extra chlorine radical in the system after treatment which indirectly induces carcinogenic compounds as by-products in the living tissues.

This research exploited the neutralization and elimination of residual chlorine in chlorinated and treated water sample(TW) actively by commercial water disinfectant known as water guard in form of Sodium-dichloro-iso-cyanurate with Ascorbic acid(AA) and its derivative; Sodium ascorbate (SA).

Selected physicochemical parameters such as pH, in situ temperature, dissolved oxygen, turbidity, total dissolved oxygen, and fecal coliform were estimated on raw water sample (WS), mixture of raw water sample with water guard(WS+WG), mixture of raw water sample, water guard with the neutralizing agents(WS+WG+AA)/(WS+WG+SA) and the treated distilled water sample (TW).

SA presented a better pH adjustment of 7.2 to AA of 6 after distillation. Dissolved oxygen was better with AA at 9.2mg/l to 86.8mg/l; while SA was from 9.2mg/l to 87.3mg/l after treatment, neutralization and distillation.

Total chlorine in both cases was completely neutralized after distillation. Turbidity, TDS were significantly controlled below WHO standards. Fecal coliforms in both cases were completely cleared after treatment, neutralization, and distillation of the water sample.

Both Ascorbic acid (AA) and Sodium ascorbate (SA) to an extent proved to be cheap and safe dechlorinating agents in the treatment of water.

***Key words;* Water treatment, Dechlorination, Disinfectant, Sodium-dichloro-iso-cyanurate, Ascorbic acid, Sodium ascorbate.**

I. INTRODUCTION

Water pollution is a contamination of water with chemical agents or other foreign agents that are unfavorable to the general ecosystem.[1] [2] The major factors of pollution with water include a discharge of untreated raw sewage from households and factories, chemicals discarded from factories, agricultural run-offs that leached into surface waters and applications of synthetic substances such as pesticides which inhibit and induce cancer on nervous system due to the carbonates and organophosphates that are present in them.

The indices of pollution include nitrates which are particularly dangerous to children that consume formula milk. It restricts the level of oxygen to their brain and causes the "blue baby syndrome.

Lead, which when accumulated in the body tissues damage the central nervous system. Arsenic, which induces; arsenic, which damage the liver, causes skin cancer and vascular diseases; fluorides which in excess quantity causes damage to the spinal cord and teeth discoloration and petrochemicals at a very low concentration which cause cancer. Infectious diseases such as cholera, paratyphoid, typhoid, dysentery, malaria, fever, jaundice and amoebiasis are contacted from contaminated and polluted water. Hence, a strong reason to treat and disinfects our water systems. However, the formation of mutagenic and carcinogenic agents on polluted water with chlorine has encouraged research to seek alternative disinfecting methods that would curtail environmental and public health impacts.

The technologies, based on nonchemical methods, which are also available commercially, are undergoing rapid development. [3] [5].

Chlorination is a method of interacting chlorine its compounds with water or any other solvent. This kills certain bacteria and microbes in water due to chlorine are high toxicity to a living organism. Generally, chlorination curbs the spread of waterborne diseases such as cholera, dysentery, and typhoid.

It has been used for many years to treat domestic polluted and waste industrial water to control microorganism because of its capacity to inhibit most pathogenic microorganism quickly. The activity of chlorine in water treatment is basically dependent on its concentration, time of exposure and the pH of the polluted water.

Chlorine is used for treating potable water where a residual chlorine concentration near 0.5mg/l is commonly used. Chlorine is added with a reaction time of 20-30 min. A free residual chlorine concentration of 0.5-1.0mg/l should be maintained through the entire pretreatment system. The degree of chlorine activity depends on various sources of water. With an alkaline polluted water system, chlorination is a much faster process than at neutral or acidic condition.

Similarly, the process is also faster when iron or other transition metals are in the water as they catalyze the degradation of chlorine

Disinfection by chlorination can be challenging, in some circumstances though widely accepted, the use of water guard as a disinfectant has some limitation such as limited shelf life, the likelihood of adding chlorinated organic by-products namely chlorate, chlorite, chloroform and bromated collectively known as trihalomethane), corrosiveness and bad odor [6]. An additional limitation is based on the fact that chlorinated water destroys much of the intestinal flora, the friendly bacteria that help in the food digestion [7]. Chlorinated water also contains chemical compounds called trihalomethanes which are carcinogenically resulting from the combination of chlorine with organic compounds in water [8]. These chemicals are also known as organ chlorides, do not degrade very well and are stored in the fatty tissues of the body. Organo chlorides can cause mutations by altering DNA suppresses immune system function and interfere with the natural controls of cell growth [8].

In other findings, a by-product of chlorination in drinking water has been linked to cancer in rats; although these findings cannot be extrapolated to humans should be taken as an indication of the risk due to the use of Water Guard [9]. In another study carried out in Harare, Zimbabwe by Jaravaza [10], the health survey results have been made to link the prevalence of cancer and the consumption of drinking water containing trihalomethanes, however there was no clear association between the two variables since during the same period there was no analysis carried out for trihalomethanes, making this more complex.

It is, however, clear that case-control studies provided more conclusive information, especially where diagnosed people may be contacted to verify exposure a good opportunity to investigate the extent to which chlorination of water contributes towards the prevalence of above-mentioned cancer

Chlorine interacts with most organic species and compound in an aqueous system to produce disinfection by-products (DBPs) commonly as trihalomethanes (THMs) and haloacetic acids (HAAs). However, the major by-product of water chlorination are trihalomethanes such as bromoform and dibromochloromethane, which are both carcinogenic.

At a significant amount, bromoform retards the normal mental bioprocesses, which is evidenced with signals such as sedation. Persistent disclosure of both bromoform and dibromochloromethane can cause cancer, as well as cardiac disease, unconsciousness, or death in high doses [11]. The carcinogenic nature of these by-products instituted general regulations for the control and monitoring of these products and compounds in the water distribution and treatment systems According to WHO, the health hazards emanating by these by-products are insignificant compared to those associated with poor disinfection".[3][WHO].

Sodium dichloroisocyanurate is sodium derivative of chlorinated hydroxytriazine and a source of free available chlorine, in an aqueous state as hypochlorous acid, for the disinfection and treatment of water bodies. It is applied extensively to secure supply chlorine for disinfection of pools, reservoirs and in the food industry. It is as well used as a way of disinfecting drinking water, mainly in emergencies, when it gives an easy-to-use source of free chlorine, and as the form of chlorine for domestic point-of-use water treatment [18]. In Tanzania, the manufacturer of Water Guard recommends a dose of 0.375ml/1, which is equivalent to 5ml/1 (a cap-full of Water Guard bottle) in 20 liters of water.

But various studies suggest that the exact amount required depends on the water chemistry temperature, contact time, and the presence or absence of sediment e.g. water with turbidity values of 30-35 NTU chlorine dosage of 8.0-ml/20 liters container is recommended and this gives residue chlorine of 0.3-0.5mg/1. People should, therefore, be aware when disinfecting turbid water; the water has to settle overnight followed by filtration using a clean white piece of cloth. The use of-of chlorine-based disinfectants in domestic water although widespread has led to some controversy due to the formation of small quantities of toxic and carcinogenic by-products.

1.1 Chemistry of chlorination

Chlorine is usually available as chlorine gas and as hypochlorite of sodium and calcium. Generally, in an aqueous system, they hydrolyze instantly to hypochlorous acid and subsequently dissociates in water into hydrogen and hypochlorite ions:

$HOCl \rightarrow H^{+} + OCl^{-}$.

The activity and efficiency of available chlorine are directly linked to the level of undissociated HOCl. Hypochlorous acid is 100 fold effective than hypochlorite ion OCl^{-}. The portion of unhydrolyzed hypochlorite is inversely proportional pH.

At pH 7.5 (25°C), 40 mg/L TDS), only 50% of free residual chlorine is present as HOCl, but 90% is present at pH 6.5. The portion of HOCl also increases with decrease in temperature. At 5°C, the HOCl mole fraction is 62% (pH 7.5, 40 mg/L TDS). In high-salinity waters, less HOCl is present (30% at pH 7.5, 25°C, 40,000 mg/L TDS). [23]

Table l. WHO Guidelines for Drinking-water Quality, Geneva, 1993

WHO's drinking water standards 1993

WHO's Guidelines for Drinking-water Quality, set up in Geneva, 1993, are the international reference point for standard setting and drinking-water safety.

Element/ substance	Symbol/ formula	Normally found in fresh water/surface water/ground water	Health based guideline by the WHO
Aluminium	Al		0,2 mg/l
Ammonia	NH_4	< 0,2 mg/l (up to 0,3 mg/l in anaerobic waters)	No guideline
Antimony	Sb	< 4 µg/l	0.005 mg/l
Arsenic	As		0,01 mg/l
Asbestos			No guideline
Barium	Ba		0,3 mg/l
Berillium	Be	< 1 µg/l	No guideline
Boron	B	< 1 mg/l	0,3 mg/l
Cadmium	Cd	< 1 µg/l	0,003 mg/l
Chloride	Cl		250 mg/l
Chromium	Cr^{+3}, Cr^{+6}	< 2 µg/l	0,05 mg/l
Colour			Not mentioned
Copper	Cu		2 mg/l
Cyanide	CN^{-}		0,07 mg/l
Dissolved oxygen	O_2		No guideline
Fluoride	F	< 1,5 mg/l (up to 10)	1,5 mg/l
Hardness	mg/l $CaCO_3$		No guideline
Hydrogen sulfide	H_2S		No guideline

1.2 WHO standards for Disinfectants and disinfectant by-products

Group		Substance	Formula	Health-based guideline by the WHO
Disinfectants	Disinfectants	Chloramines	$NH_nCl^{(3-n)}$, where n=0, 1 or 2	3mg/l
		Chlorine	Cl2	5mg/l
		Iodine	I2	Nil
		Bromate	$Br\ O_3^{-}$	25ug/l
		Chlorate	$Cl\ O_3^{-}$	Nil
		Chlorite	$Cl\ O_2^{-}$	200ug/l
		Chlorophenols		
		Formaldehyde	HCHO	900ug/l
		2-Chlorophenol (2-CP)	$C_6\ H_5\ Cl\ O$	Nil
		2,4-Dichlorophenol (2,4-DCP)	$C_6\ H_4\ Cl_2\ O$	Nil
		2,4,6-Trichlorophenol (2,4,6-TCP)	$C_6\ H_3\ Cl_3\ O$	200ug/l
Disinfectant by-products		MX (3-Chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone)	$C_5\ H_3\ Cl_3\ O_3$	Nil
	Trihalomethanes	Bromoform	$C\ H\ Br_3$	100ug/l
		Dibromochloromethane	$CH\ Br_2\ Cl$	100ug/l
		Bromodichloromethane	$CH\ Br\ Cl_2$	60ug/l
		Chloroform	$CH\ Cl_3$	200ug/l
	Chlorinated acetic acids	Monochloroacetic acid	$C_2\ H_3\ Cl\ O_2$	Nil
		Dichloroacetic acid	$C_2\ H_2\ Cl_2\ O_2$	50ug/l
		Trichloroacetic acid	$C_2\ H\ Cl_3\ O_2$	100ug/l
		Chloral hydrate (trichloroacetaldehyde)	$C\ Cl_3CH(OH)_2$	10ug/l
	Chloroacetone		$C_3\ H_5\ O\ Cl$	Nil
		Dichloroacetonitrile	$C_2\ H\ Cl_2\ N$	90ug/l
	Halogenated acetonitriles	Dibromoacetonitrile	$C_2\ H\ Br_2\ N$	100ug/l
		Bromochloroacetonitrile	$CH\ Cl_2\ CN$	Nil
		Trichloroacetonitrile	$C_2\ Cl_3\ N$	1ug/l
	Cyanogen chloride		$Cl\ CN$	70ug/l
	Chloropicrin		$C\ Cl_3\ NO_2$	Nil

1.3 Ascorbic acid and Sodium ascorbate

Vitamin C, or ascorbic acid, chemically neutralizes chlorine. Hence by logic, ingesting lot of vitamin C than chlorine is solution and panacea against chlorine toxicities. It was established that one gram of vitamin C will neutralize almost 400L of water having 1mg/l of chlorine [15]. Vitamin C does not have the potential of lowering the dissolved oxygen compared to chemicals with sulfur components. Although it is slightly acidic but in higher concentration, the pH of the treated water will be lower. Sodium ascorbate is a sodium salt of ascorbic acid and It is biologically not available compared to other forms of vitamin C [19]. It is a food additive, with E number E301 and it is an antioxidant and an acidity regulator. It was recommended as an additive in the food industry in the EU,[20] the USA,[21]and Australia and New Zealand.[22] It is very neutral and does not alter the pH of the treated water

$C_5H_5O_5CH_2OH + HOCL \rightarrow C_5H_3O_5CH_2OH + HCl + H_2O$

Ascorbic acid + Hypochlorous acid → Dehydroascorbic acid + Hydrochloric acid + water

Just about 2.5 portions of ascorbic acid are needed to neutralize 1 portion of chlorine. As ascorbic acid is a weak acidic, the pH of the treated water may drop to some extent in low alkaline waters [5]. The products, dehydroascorbic acid, which is a weak acid, hydrochloric acid, and water, are formed as by-products. Sodium ascorbate will also neutralize chlorine. It is neutral to pH and will not affect the pH of the treated water.

$C_5H_5O_5CH_2ONa + HOCL \rightarrow C_5H_3O_5CH_2OH + NaCl + H_2O$

Sodium ascorbate + Hypochlorous acid → Dehydroascorbic acid + Sodium chloride + water

II. MATERIALS AND METHODS

6 liters of borehole water sample was gotten from the senior staff quarters of National Research Institute for Chemical Technology Zaria Kaduna State, Nigeria, Ascorbic acid and sodium ascorbate were of Analar Grade, Water guard granules which contain 4.3% chlorine as sodium-dichloro-iso-cyanurate and a set of distillation apparatus.

Methodology

Analyses were conducted in the Industrial and environmental pollution department of National Research for Chemical technology Zaria Kaduna state, Nigeria. Standard Methods (APHA 1992) were adopted for pH, temperature, dissolved oxygen, turbidity, residual and total chlorine, total dissolved solids and fecal coliform before and after treatment [17].

Dosage of 1mg of water guard(Sodium-dichloro-iso-cyanurate) was dissolved in 400L of the water sample for a period of 30 minutes. Ascorbic acid (AA) and Sodium ascorbate (SA) at the level of 3.22g and 8.05mg respectively by estimation were mixed in the resulting water guard treated water sample. The selected physic-chemical properties were conducted before treatment, after treatment, and with the distilled water sample.The reaction mixture afterward were distilled at 100°C for water, 390°C for dehydroascorbic acid and 109°C for hydrochloric acid.

III. RESULTS AND DISCUSSION

Table II. Treatment with Ascorbic Acid.

Table II. Treatment with ascorbic acid

	Ascorbic Acid (AA)			TW
Parameters	WS	WS + WG	WS+WG+AA	
pH	2.8	11.6	12.5	6.8
Ambient temperature (°C)	28.5	20.5	20.6	20
Dissolved oxygen (mg/l)	9.2	24.4	25.2	86.8
Total Chlorine (mg/l)	8.04	25.24	0	0
Turbidity (NTU)	95	106	113	7
TDS (mg/l)	226	475	645	9
Fecal coliform (colony density)	276	0	0	0

WS=Water sample (400L)
WG=Water guard (1mg)
AA=Ascorbic acid (1g)
TW=Treated water after distillation at 100°C (100ml)

Table III. Treatment with Sodium Ascorbate

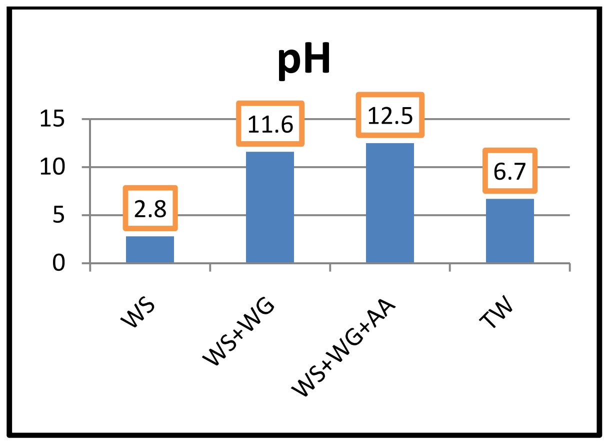
Table III. Treatment with sodium ascorbate

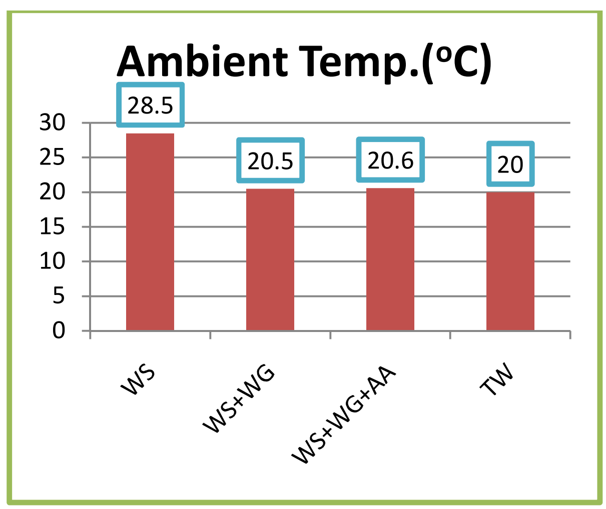
	Sodium Ascorbate (SA)			TW
Parameters	WS	WS + WG	WS+WG+SA	
pH	2.8	11.6	10.4	7.2
Ambient temperature (°C)	28.5	20.5	20.6	20
Dissolved oxygen (mg/l)	9.2	25.2	26.7	87.3
Total Chlorine (mg/l)	8.04	25.24	0	0
Turbidity (NTU)	95	106	110	6.1
TDS (mg/l)	226	475	645	6
Fecal coliform	276	0	0	0

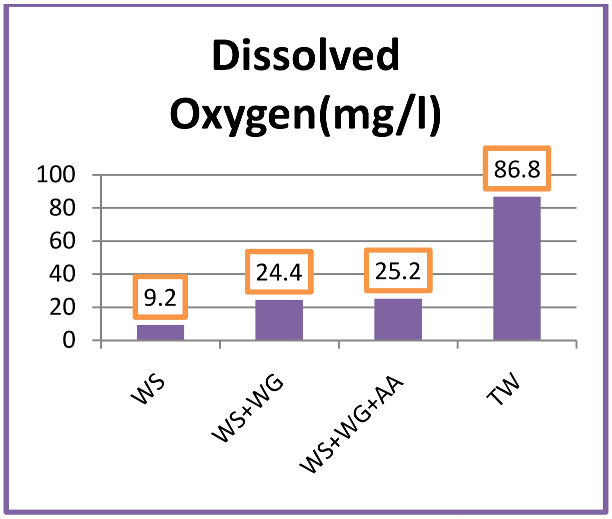
WS=Water sample (400L)
WG=Water guard (1mg)
SA=Sodium ascorbate(2.8mg)
TW=Treated water after distillation at 100°C (100ml)

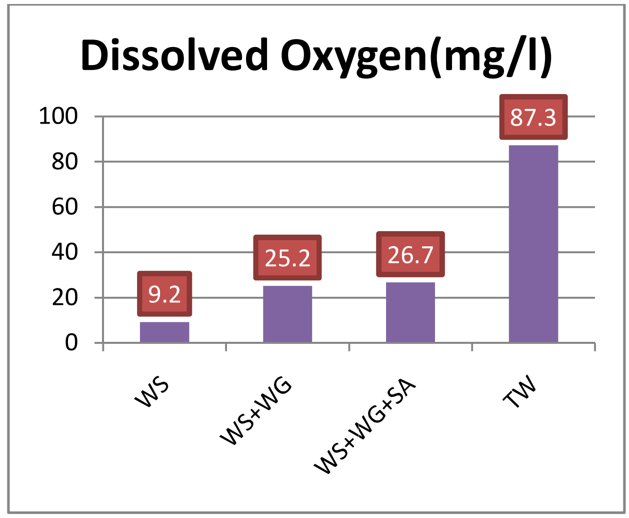
Figure I. Selected physicochemical evaluations of Ascorbic acid (AA) and Sodium Ascorbate (SA) residual chlorine neutralization in polluted water disinfection.

ASCORBIC ACID

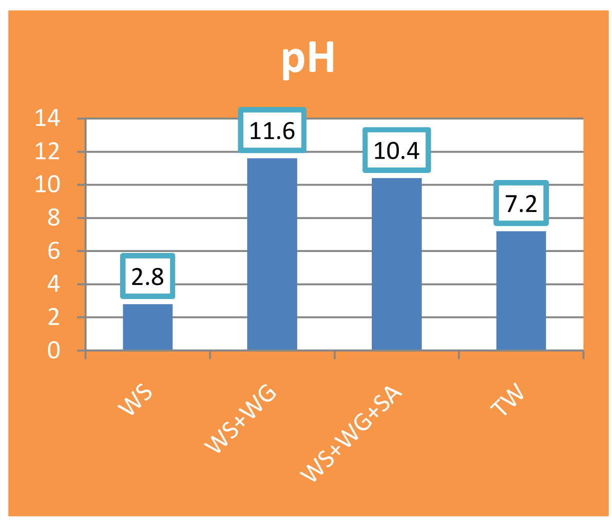


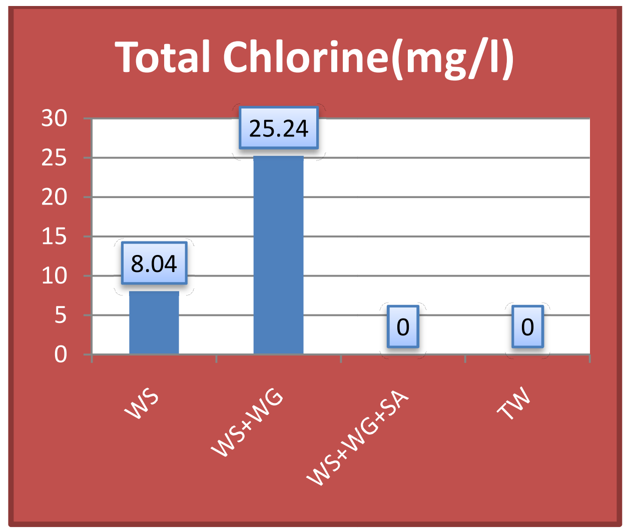


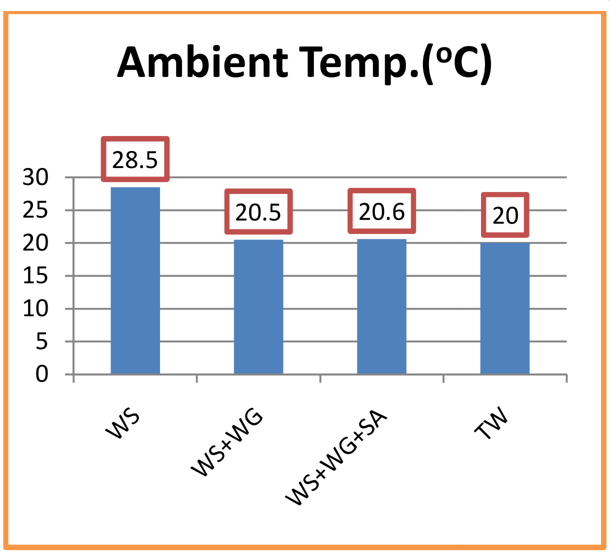


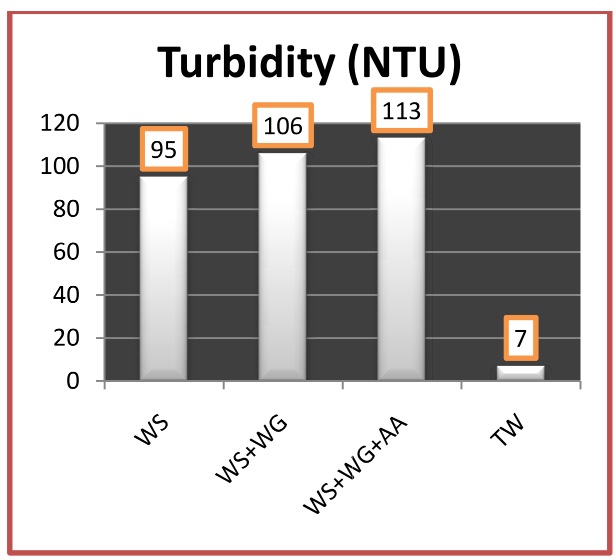


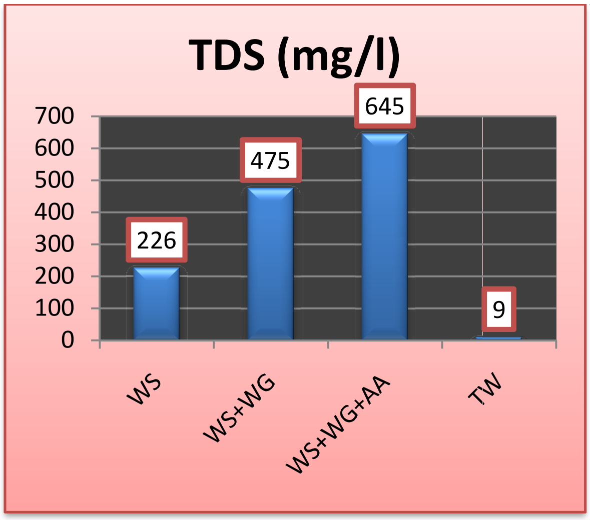
SODIUM ASCORBATE

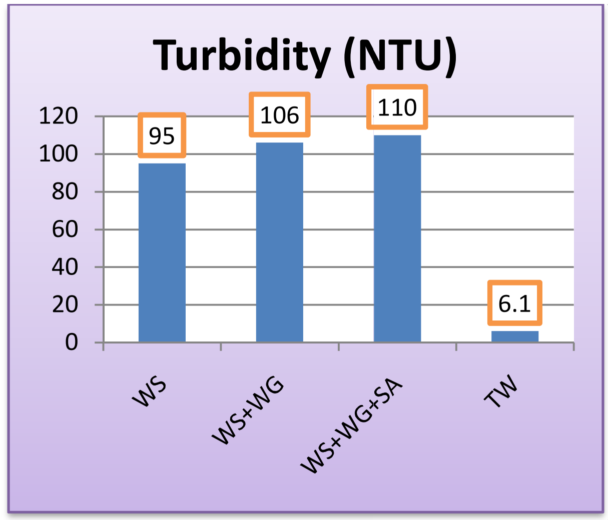


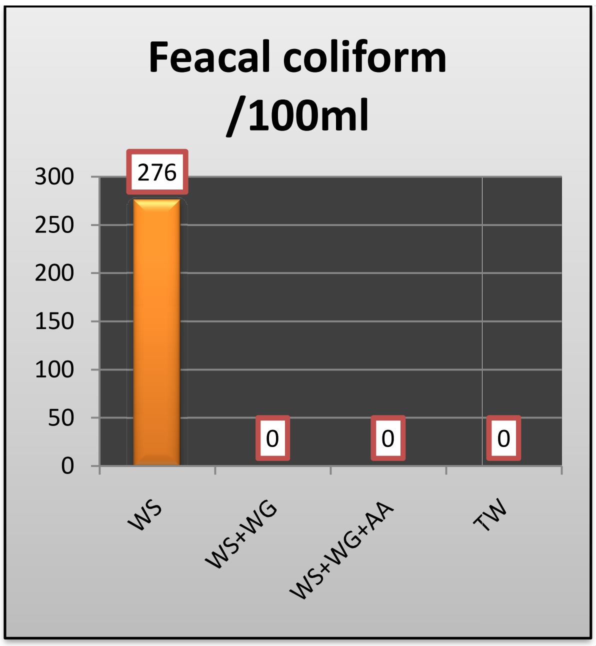


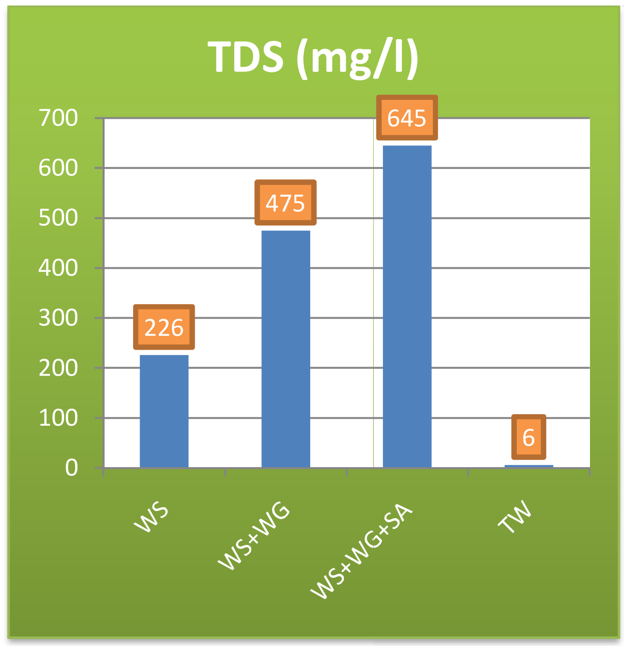


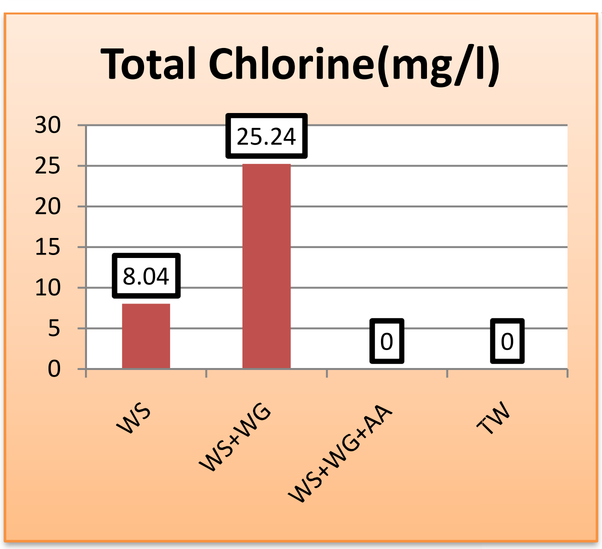


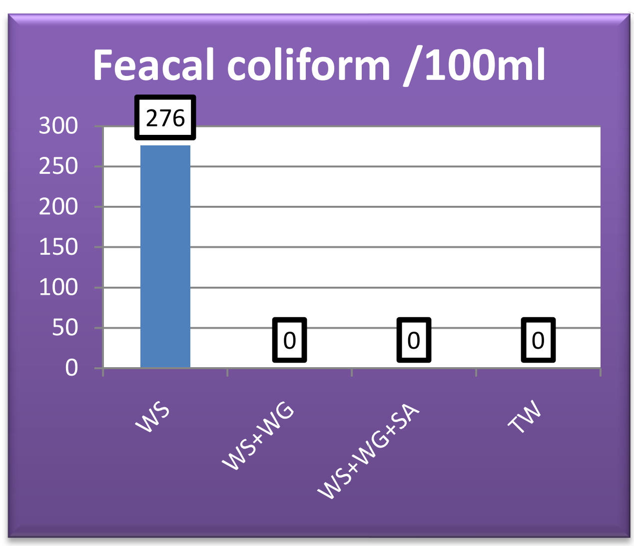

TDS (mg/l)
700
600
500
400
300
200
100
0
226
475
645
9
WS
WS+WG
WS+WG+AA
TW


Turbidity (NTU)
120
100
80
60
40
20
0
95
106
110
6.1
WS
WS+WG
WS+WG+SA
TW


Feacal coliform /100ml
300
250
200
150
100
50
0
276
0
0
0
WS
WS+WG
WS+WG+AA
TW


TDS (mg/l)
700
600
500
400
300
200
100
0
226
475
645
6
WS
WS+WG
WS+WG+SA
TW


Total Chlorine(mg/l)
30
25
20
15
10
5
0
8.04
25.24
0
0
WS
WS+WG
WS+WG+AA
TW


Feacal coliform /100ml
300
250
200
150
100
50
0
276
0
0
0
WS
WS+WG
WS+WG+SA
TW

IV. DISCUSSION

Ascorbic acid (AA) and Sodium ascorbate (SA) shifted the pH the treated water sample towards neutrality at 6.7 and 7.2 respectively with controlled ambient temperatures in both cases.

Dissolved oxygen was significantly compensated with Ascorbic acid (AA) by 89% after treatment and distillation (water separation) and with Sodium ascorbate (SA) by 89.5% after treatment and distillation.

Total chlorine in both cases with water guard (Sodium-dichloro-iso-cyanurate) raised the concentration by 68% and was completely neutralized under the two conditions after treatment and water distillation.

Turbidity and total dissolved solids in the case of Ascorbic acid were controlled by (4.3NTU) 94% and (124mg/l) 45% while in the case of Sodium ascorbate (4.7NTU) 94% and (113mg/l) 50% respectively after treatment. Fecal coliform tests strongly claimed that water guard is an effective antiseptic and antimicrobial inorganic chemical agent. This was evidenced in the termination of the microbial population estimated to be 476 colonies in the water sample and final inhibition of the pathogenic activities exhibited in the water sample.

V. CONCLUSION

Chlorinated agents that are applied in the treatment of water for wholesome purposes might not induce any toxic effects at the prime or initial stage but definitely with the possibilities of exceeding the WHO limit (5mg/l) overtime within the biological systems cumulatively.

Similarly, the organic chlorinated byproducts from these processes such as trihalomethanes are strongly carcinogenic.

In other words, it is not enough to disinfect water with chlorine but also to confidently neutralize it from such medium before using up for drinking and domestical activities. This is what ascorbic acid and sodium ascorbates which are both antioxidants and essential vitamins to our body system has been able to achieve.

They are very promising in the neutralization of residual chlorine in water systems.

As established with the fact that 5ml of water guard solution will treat about 20 liters of water without residual chlorine and 1g of ascorbic acid will neutralize 1mg/l of chlorine; 0.0014mg of ascorbic acid will neutralize 0.5mg of chlorine in 500ml of the water sample and if approximately 2.8mg of sodium ascorbate with 1mg/l of chlorine in water sample; 1.4mg of sodium ascorbate will neutralize 0.5mg of chlorine in 500ml water sample. However, it is of slight observation that sodium ascorbate regulated the pH, the turbidity and the total dissolved solids than ascorbic acid. But the dissolved oxygen was better with ascorbic acid.

As well, factors such the water chemistry, temperature, contact time, and the turbidity nature play key roles in the process.

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