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Implications of carbonates and chlorides contamination in groundwater: Examples from textile tie and dye markets in some parts of Southwestern Nigeria

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Abstract

Objectives: To evaluate the impact of common mineral dyes in effluents from dyeing processes on the quality of groundwater at Itoku and Asero, Abeokuta in Nigeria. **Methods:** Thirty-two (32) samples were examined by determining the In-situ parameters: Total Dissolved Solids (TDS), Electrical Conductivity (Ec) and pH with the aid of a multi-parameter portable meter(model Testr-35); Chemical parameters were determined with Atomic Absorption Spectrometry (AAS)and Titration methods for both cations and anions. Collected samples were analyzed for heterotrophic bacteria load using standard method. **Findings:** Elevated Ec-1830 μS/cm and TDS-1020mg/l values at Odutola-8 exceeded the WHO permissible limit with bicarbonate, carbonate and chlorides presence, in the water sample. DO at Ifote-6.0, Asero-6.8, Ifote-7.1, Asero carwash-7.9 was greater than WHO standard, specifying water that can support aquatic life and micro-organisms. However, other areas had low dissolved oxygen below the specified permissible limit. The results of the physicochemical parameters including; Chloride and Carbonate levels in effluent and groundwater in most of the studied sites were higher than the World Health Organization (WHO) permissible limits. Dye effluents and well water samples displayed high microbial loads. Predominant bacteria isolated from the effluent and groundwater included *Aspergillus spp. Pseudomonas aeruginosa* and *Bacillus subtilis*. Polycyclic aromatic hydrocarbon (PAHs) observed indicated probable human carcinogens found where dye fabrication processes were high and effective. **Novelty:** Dye effluents have high bacterial and fungal loads. Similarity in the predominant bacteria isolated from effluent and groundwater from the hand-dug wells indicated that the effluent from the dyeing processes is negatively impacting the groundwater and this may pose a risk to public health. High levels of Carbonates, bicarbonates and chlorides in groundwater indicate contamination; making the water unfit for human and animal consumption.

Keywords: Minerals; dyes; contamination; groundwater; carbonates; chlorides

1 Introduction

Nigeria is very popular for tie and dye activities as well as numerous other international markets all over the world. Abeokuta is foremost among the three regions popular for the tie and dye activity in Nigeria. Diverse age groups are engaged in this tie and dyeing business while other sets are occupied with sourcing of raw materials, production, and distribution, sales and marketing of the final products.

Dyeing extract can be derived from three major sources such as (i) dye derived from rock minerals (ii) dye producing plants (iii) synthetic Organic/inorganic types. These dye yielding materials can be extracted and processed to acquire diverse colours with varying degree of tone and adherence. Dyes from plants have been extracted from tree leaves, barks, roots, flowers and young shoots [1]: but dyes from rock minerals such as: copper carbonate hydroxide mineral-Malachite-($Cu_2CO_3(OH)_2$, Ochre-$FeO(OH)\cdot nH_2O$, Manganese-MnO_3, Mn_2O_3, Mn_3O_4, Mn_2O_7 and Cinnabar-HgS have been used for these purpose as an age long practice. Some of these dyes are mineral salts inform of carbonates, chlorides sulphates, oxides, hydroxides and others [2].

1.1 Description of some rock mineral dyes

1.1.1 Malachite

Malachite is a monoclinic green-banded copper carbonate hydroxide mineral ($Cu_2CO_3(OH)_2$of variable habit which include botryoidal and fibrous (Figure 1). In addition, it occurs as masses in fractures and deep-underground spaces through chemical precipitation. It also appears as pseudomorphs in blue blocky and acicular prisms of Azurite. Naturally, it exists as crystalline aggregates always banded in appearance with high similarity to agates. They are found from weathering of copper ores and is often found with azurite ($Cu_3(CO_3)_2(OH)_2$), goethite $Fe(OH)_2$, and Calcite. It is typically associated with copper deposits around limestone which act as the source of the carbonate. Malachite is used as a mineral pigment in green paints [1,3]. Although, the pigment thickness and viscosity become reduced, with the introduction of acid, which turn these pigments to varying colours.

Fig 1. Mineral Dyes of Malachite, Pyrolusite and Ochres

1.1.2 Iron Minerals (Ochres-Limonite-Hematite-Goethite)

Iron oxides (Ochres) are the most widespread minerals found on earth(Figure 1) which display various colours that range from Yellow or gold/limonite-$FeO(OH)\cdot nH_2O$, Red/hematite-Fe_2O_3, Purple, Brown/goethite- FeO(OH). These colours contrast significantly in different countries, depending upon on the concentration of limonite and the reddish hematite contents [4]. In order to make ochres to become dark, they are combined with manganese oxide (MnO) in a little quantity of less than 6% to develop a new mixture and further addition of manganese (6-20%), revealed a dark brown colouration of pigments. Iron oxides were employed as good pigments and still in use in some parts of Africa countries. This has become good additives or colouring agents for the purpose of decoration in dyes and paints [5], [6].

1.1.3 Cinnabar

Cinnarbar (HgS) occured with scarlet to brick-red colour(vermilion) and associated red mercury pigments [7]. It occurs as minerals in veins and bears a resemblance to quartz with hardness and refractive index that has been a supportive character to the colour for the production of dyes and paints. It can also be found as earthy, massive or granular material displaying adamantine luster.

1.1.4 Manganese (Pyrolusite-Hausmannite)

Manganese oxides formed various minerals (Pyrolusite-MnO_2; Hausmannite-Mn_2O_3, Mn_3O_4; and Mn_2O_7) and display different colours that range from blue-purple (Figure 1). It is relevant as dyes/pigments and fungi prevention. Some of these minerals occur in association in their ores and consist of heavy metals/toxic metals of various forms in their minerals which include Cd-Greeneckite, As-Orpiment, Pb-Minium, Co-Aurelium and Sn-Cassiterite. They release these toxic metals into the environment during extraction and production processes since they occur in form of salt and other compounds. These metals find their way into both surface and underground water sources thereby contaminating these water sources. Wastes materials from dyes in different forms find their routes into effluent /waste water in the area.

1.2 Ground water and effluents assessment

Water is an essential part of human life which is being used for many purposes, however, for it to be used for consumption purposes: it must be free from both chemical and microbiological contaminants. Groundwater was hitherto, considered to be clean and safe in the past but in recent times, rapid industrialization have caused severe environmental problems in most of the countries, due to the infiltration of effluents into groundwater by industries such as textile, dyeing, leather, tannery, pulp and paper processing industries. The effluent discharged by these industries lead to serious contamination and pollution issues which alter the geochemical parameters of surface water and ground water resources [8]. Ground water refers to water located beneath the ground surface soil pore spaces and in fractures of rock formations [9]. It is about 20% of the world's fresh water supply, which is about 0.61% of the entire world's water, including oceans and permanent ice [9].

Water contamination due to the activities of the dyeing industry in the study area and some other parts of Abeokuta is a matter of great concern since large quantities of effluents is being discharged into the water bodies and the environment (Figure 2). Central Pollution Control Board had listed the dyeing industry as one of the heavily polluting industries [10] of this generation. The dye effluent is highly contaminated in nature as it contains high suspended solids, dye and chemicals along with high concentration of heavy metals like Cu, Cd, Zn, Ni and Pb. The dye effluent contains certain chemicals that could be toxic, carcinogenic or mutagenic to human beings [11]. Wastes from dyeing activities disposed both in liquid and solid forms on land and water bodies that percolate into the groundwater and get transported in the direction of groundwater flow. The rate of percolation and transportation of contaminants from

Fig 2. Scenes of tie and dye local processes atItoku and Asero

mineral dyes in groundwater flow direction increases in arid and semi-arid conditions due to high permeability of the soil and rocks. As a result, different pollutants from mineral dyes reaching into the groundwater system have posed a threat to groundwater quality, which ultimately affects the socio-economic life of the people, who depend on groundwater sources for various purposes in the area [12].

This study therefore investigates the geochemical influence of these wastes (mineral dyes) on groundwater resources of Itoku and Asero areas of Southwestern Nigeria which are known for dyeing activities. Abeokuta and other parts of Ogun State experience a tropical climate with conspicuous wet and dry seasons with the dry period covering a period of 130 days [13]. The major occupation of the inhabitants of the study area is the production of fabrics with 'Adire' designs (tie and dye business). This activity is the major source of groundwater pollution and the basis for this study.

1.3 Geology of the area

Geologically, Abeokuta is part of transition zones within the Southwestern Nigeria; underlain and bounded by crystalline basement rock at the northern while in the south by the sedimentary rocks of the eastern Dahomey basin. At the south-eastern part of the area is the outlier of the Ise formation of Abeokuta group. The basement rock of the area is unconformable overlained by organically rich friable reddish sand. The basement rock consists of ancient gneisss-migmatite suite (Complex) which has been distinguished into three major divisions due to the penetration of Pan-African (600Ma) bodies of granodiorites, Porphyritic granites, Quartz diorites and pegmatites. The major rock units that underlain the area include: Biotite Granite Gneiss, Porphyroblastic Gneiss, Porphyritic Biotite Granite, Biotite Schist and Migmatites [14]. The remaining small portion are covered by the Ise Formation of the Abeokuta Group which consists of conglomerates and grits at base and in turn overlain by coarse to medium grained loose sands. This formation is notable in the south-eastern and south-western parts of the study area. The study area is covered by pegmatites, older granites and gneisses (Figure 3).

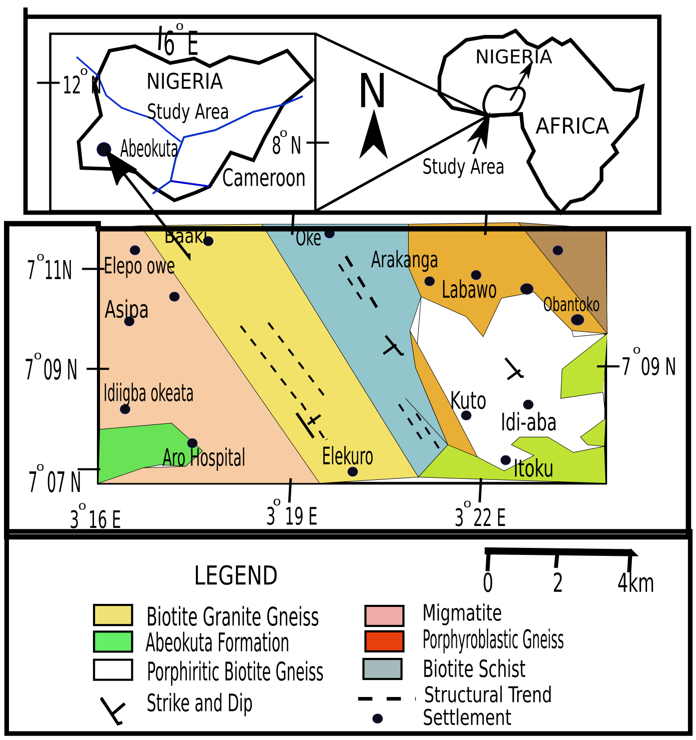

Fig 3. Geologic Map of the Study Area: Adapted from Nigerian GeologicalSurvey Agency (NGSA)

1.4 Dyeing activities in the study area

In order to achieve dyeing processes, the material to be dyed must first be bleached. Bleaching removes existing colouring from the fabric thereby preparing it to be dyed. During this process, the cloth is soaked in caustic soda slurry so as to remove starch. It is then passed through a solution of bleaching powder and washed and this cloth is heated with dilute acid and sodium sulphate. After heating, the cloth is washed with detergent and whitening agent and spread out to dry up. After which is the addition of chemicals to fix a new colour on the textiles and clothings. The three commonly used dye fixing processes in the study area are Diazotization process (common chemical used is sulphuric acid or hydrochloric acid), Silicate process (using sodium silicate) and Patri Process (which uses sodium bicarbonate as a secondary reagent after diazotization process).

2 Materials and Methods

2.1 Field and laboratory procedures

2.1.1 Microbial assessment of groundwater and effluents

For the purpose of Microbiological examination and to check well-water vulnerability to contamination by discharged effluent: A total of thirty-two samples were collected from 16 hand-dug wells located within the dye processing sites (Figure 4) as well as a well about 500m away from the processing site(s). The depths of these wells were mostly less than 5m (Table 1). Discharged tanning effluents around at each area were also collected. These samples were taken from three spaced out points on effluent discharge points and were later pooled to form composite samples at each sampling time. Sampling for both groundwater and effluents followed aseptic procedure and was in accordance with the Standard Methods for the Examination of Water and Wastewater [15]. Samples were maintained in ice packed containers and transported to the laboratory within 8hours of collection for microbiological analysis. The perimeters of the dye sites are all bounded by regular homes where wells are sited for domestic purpose.

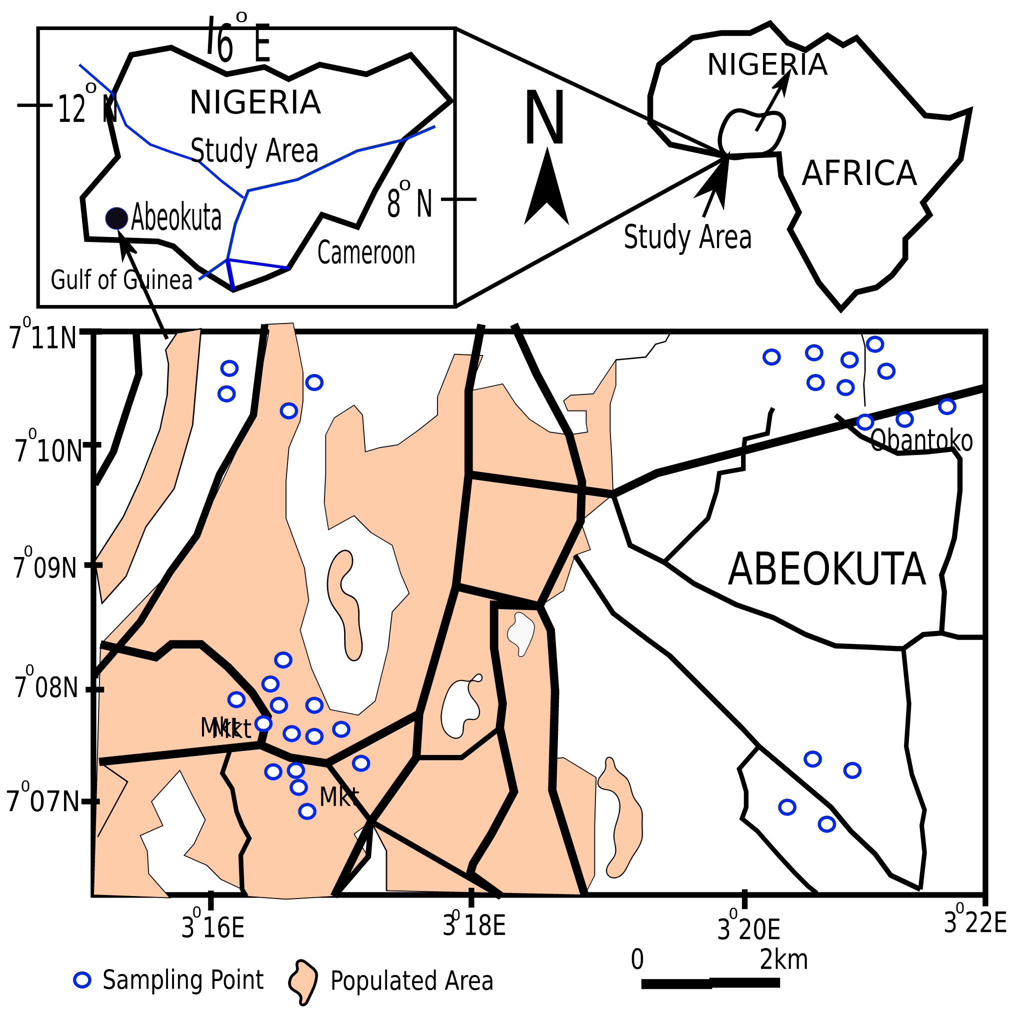

Fig 4. Map of the Study Area Showing the Sample Locations

2.1.2 Physico-chemical tests of collected samples

Field procedures water-level meter were used to determine the static water level, water column thickness and the depth to the basement were recorded at each location. In-situ measurement of Total Dissolved Solids (TDS), Electrical Conductivity, Dissolved Oxygen, Temperature and pH were carried out on the field and all the physical parameters were measured by the multi-parameter portable meter (model Tester-35).Atomic Absorption Spectrometer was used to determine the cations present in the water samples. Trace metal evaluation and appropriate trace metal concentration reports are not included in this work. Also, the Polycyclic Aromatic Hydrocarbons (PAHs) compounds were

Table 1. Physical parameters values compared with well depth

Well	ELV	TD	Temp	EC	TDS	pH	DO	DTWT	WC/Thk
1 Ifote	71	3.2	28	1430	750	6.7	7.1	2.5	0.7
2 Ifote	67	12	28	1350	650	7.1	2.3	2.4	9.6
3 Ifote	66	11	28	1700	850	7	3.9	10.5	0.3
4 Idi Ape	64	18	28	1220	610	7.9	1.9	17.5	0.5
5 Idi Ape	71	3.2	28	1090	540	6.8	1.01	2.66	0.55
6 Kenta	75	1.8	28	1270	640	7.3	6	1.5	0.3
7 Better life	63	2.3	28	1410	700	7.4	2.1	2.1	0.2
8 Odutola	60	13	27	1830	1020	8.4	2.09	12	0.8
9 Imoo	83	4.5	28	1400	700	7.4	4.12	0.3	4.2
10 Kampala Mkt	115	5.5	26	1150	560	7.2	3.1	2.56	2.94
11 Garage Asero	111	5.5	26	1150	560	7.2	3.1	2.56	2.94
12 Asero Carwash	124	2.5	26	440	220	6.3	7.9	2.3	0.2
13 Market House	137	3	26	350	170	6.9	2.03	1.1	1.9
14 Adeyanju	123	3.1	26	800	400	6.8	2.12	1.5	1.58
15 Matt Close	119	2.7	26	590	290	7.2	1.32	0.9	1.75
16 Asero	130	4.1	27	900	440	6.7	6.8	3.9	0.2
WHO (2011)	-	-	20-33	1500	1000	6.5-8.5	>5	-	-

Elev-Elevation(m); TD-Total Depth(m); Temp-Temperature(°C); EC-Electrical Conductivity(μs/cm);
Total Dissolved Solids(mg/l); pH; Dissolved Oxygen(mg/l);DTWT-Depth to Water Table(m);
WC/Thk-Water Column Thickness(m)

determined in wastewater samples from the tie and dyeing sites at Itoku and Asero using: Gas Chromatography-Mass Spectrometer (GC-MS) to test for the dangerous organic radicals of organic dyes that did not fix to the fabric of the textile material being used at Itoku area.

2.2 Microbial analysis

Collected samples were analyzed for heterotrophic bacteria load thus; Briefly, 1ml from effluent composite sample which had been thoroughly mixed was suspended in 9ml of sterile normal saline solution. This was serially diluted until appropriate dilution was obtained. 1ml aliquot of this was plated using the pour plate method in Nutrient agar (Oxoid, Basingstoke UK). The procedure was repeated for the analysis of microbial load of groundwater samples as well. Plates were incubated at 37°C for 24 hours. Subsequently, plates were read by counting the colony forming units and recording these in CFU (colony forming units per ml). Isolation of bacteria was done by standard spread plate method by inoculating sterile nutrient and MacConkey agar plates with 0.2ml aliquots of appropriate dilutions. Following incubation, sub-culturing was done until discreet colonies were obtained. Isolated organisms were stored on nutrient agar slants for further studies. Potato dextrose agar (PDA) was used for the isolation of fungal strains using 0.1 ml aliquot of appropriate dilution. Standard spread plate technique and plates were incubated for 3-5 days at 25°C.

The identities of isolated bacteria were confirmed based on biochemical characterizations tests [16]. These tests included Gram staining, citrase, methyl red, motility, oxidase, presence of endospores, urease, heamolysis, nitrate reduction, indole and an array of sugar fermentation tests.

3 Results and Discussion

3.1 Physical parameters

The results of the physical parameters which were measured on the field are shown on Table 1. The pH values of the water samples range from 6.3 - 8.4. The values are within the WHO range [17]. The lowest was recorded at Asero Car Wash-12 with pH of 6.3is moderately acidic while Idi Ape-4, Odutola-8, Garage Asero-11 are slightly alkaline others are neutral.

The Electrical Conductivity (EC) values range from 350-1830 μS/cm with peak values in Ifote-3 and Odutola-8 exceeded the WHO permissible limit and could be as a result of dyes and other contamination carrying electrolytes in dissolved constituents. These high values might indicate that the examined waters are receiving large quantities of industrial contaminants. These two areas are populated with dyeing activities and are significantly active in the study area.

The Total Dissolved Solids (TDS) of water sample is the sum of concentrations of all dissolved solid chemicals or minerals [18]. Among all the sampled wells, only Odutola-8 falls above the set limit of WHO with 1830 μS/cm and 1020 mg/l for EC and TDS value respectively (Figure 5). This might specify the presence of high bicarbonate, carbonate and chloride in water sample. Groundwater from Garage, Asero-11, Asero car wash-12, Mart House-13 and Mart close-15 fall into excellent water, signifying its degree of potability possibly as a result of low tie and dyeing processes in that vicinity. Adeyanju-14, Asero-15, Idi Ape-5 and Kampala Market-10 fall into good water. Water samples from Ifote 1-3, Idi Ape, Kenta, Better life and Imoo fell into fair water signifying the presence of moderate tie and dyeing processes in that vicinity; while groundwater collected from Odutola falls into poor water; this must have been caused by infiltration of domestic effluents due to its close proximity to dyeing processing areas. In terms of Dissolved Oxygen, only four locations met the WHO permissible limit; these were: Ifote-1, Kenta, Asero car wash and Asero having 7.1, 6, 7.9 and 6.8mgs/l respectively (Figure 5) while others fall below 5mg/l which is the set limit. The DO at Ifote-6.0, Asero-6.8, Ifote-7.1, Asero carwash-7.9 was greater than the WHO specified limit; specifying water that can support aquatic life and micro-organisms. The DO of other areas ranged from 1.01-4.12mg/l which include Odutola-2.09mg/l due to dyeing activities indicating the water's non-support to aquatic life which might have resulted from excessive algae growth caused by phosphorus and its decomposition consumes dissolved oxygen that may be available for fish and other aquatic life. However, Odutola had the highest pH-8.4, temperature-27°C, the highest electrical conductivity of 1830μS/cm and highest Total dissolved solid of 1020mg/l suggesting this site as the most vulnerable water with minimal capacity to support aquatic life and laden with both chemical and biological contaminants (Figure 5). Conversely, since conductivity is used in appraising salinity and TDS, which affect water quality and aquatic life because they interfere with dissolved oxygen solubility; therefore, the higher the TDS level, the lower the dissolved oxygen concentration indicating that the well water at Odutola is not safe or fit for potable purposes. The Levels recorded for some of these physical parameters are similar to the results of Idowu et al.[11] and Bhatia et al.[12]

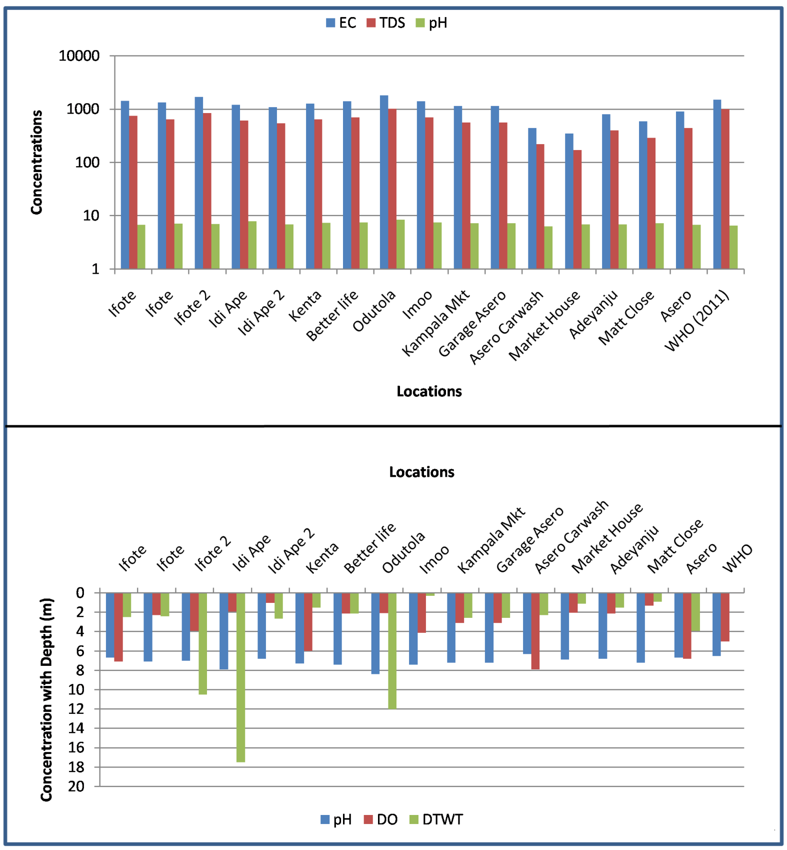

Fig 5. Physical Parameter Comparison with WHO Standards

3.2 Chemical parameters

The results of the analyzed chemical parameters for both anions and cations were presented in Table 2. Most of the values of anions and cations are within the WHO limit and other quality standards with the exception of chloride and carbonates.

Table 2. Comparison of cations and anions concentration with standards (mg/l)

Well	F-	Cl-	NO_3^-	PO_4^{3-}	SO_4^{2-}	CO_3^{2-}	HCO_3^-	Ca^{2+}	K^+	Mg^{2+}	Na^+
1	0.8	993.96	0.45	0.2	3.2	210.1	427.4	0.35	6.67	3.8	0.4
2	0.5	923.01	1.08	0.8	8.2	390.1	793	0.35	5.99	3.5	0.9
3	1.2	923.1	0.98	0.8	7.8	390	763	0.33	7.25	2.9	0.5
4	1.1	993.96	0.65	0.5	7.6	300	610.1	0.29	7.25	2.3	0.5
5	0.79	781.01	0.6	0.4	0.76	150	305.1	0.44	6.33	4.4	0.5
6	0.9	710.1	0.32	0.3	6.9	300	610	0.27	6.95	4.3	0.4
7	0.9	851.1	0.6	0.3	1.7	390	793	0.39	5.68	3.7	0.5
8	0.87	639.1	0.7	0.6	0.76	300	610	0.55	6.47	4.6	0.6
9	0.68	993.96	1.2	1.1	8.7	210	427.1	0.29	6.72	4.6	0.4
10	0.6	781.01	0.76	0.8	9.7	420	671	0.27	6.95	4.3	0.4
11	1.3	497.1	0.3	0.4	0.54	270	549	0.33	4.85	2.9	0.5
12	1.4	852.1	0.5	0.8	0.84	150.1	305	0.28	6.64	3.4	0.7
13	0.35	355	1.01	1.2	0.87	300	610.1	0.27	5.78	3.5	0.8
14	1.1	923.01	0.8	0.3	3.9	330	671.1	0.34	5.63	2.7	0.7
15	0.18	710.1	0.8	0.2	8.1	300	610	0.42	5.88	2.7	3.8
16	0.6	710.05	0.8	0.4	4.6	240	488.9	0.43	6.75	3.3	0.8
WHO(2011)	1.5	250	50	5	400	240	500	75	12	150	200

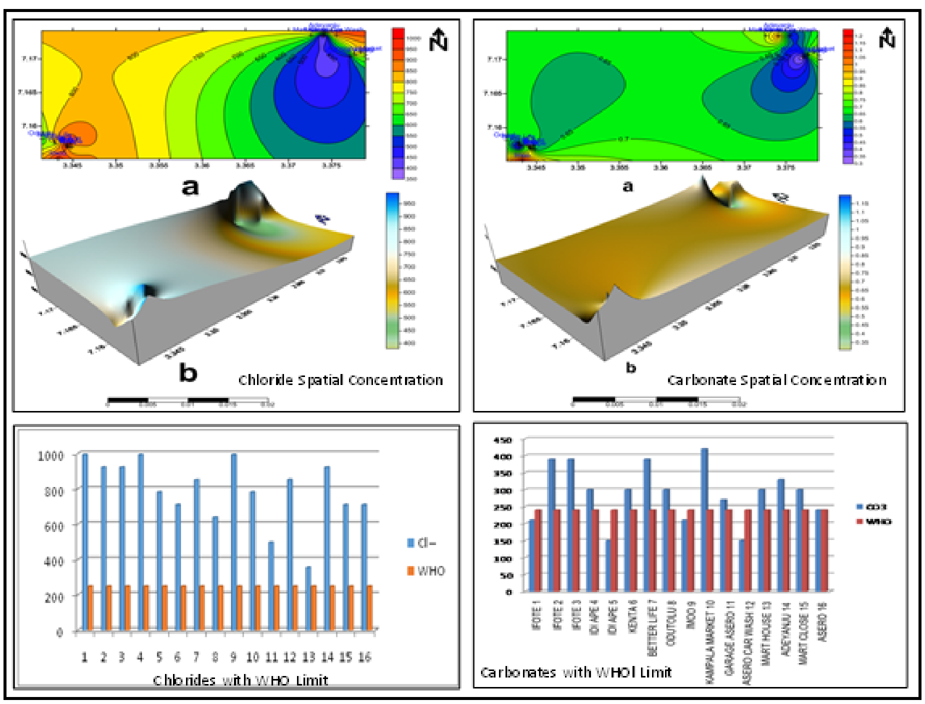

Fig 6. Comparison of Cl^- and CO_3^{2-} Concentration with WHO standards

3.2.1 Chloride

On the other hand, compared with the chemical results of the anions the values of chloride ion are higher than the WHO standards signifying higher input from mineral dyes/salts or the chlorinated types. Chloride in drinking water could originate from natural sources or processes which may include weathering of feldspars and other minerals. Similarly, influx of sewage, domestic and micro-industrial effluents (dye wastes) may correspondingly contribute to this phenomenon. Therefore, chloride concentrations above 250mg/l can give rise to a detectable taste in water. In this area, chloride concentrations of all the sampled wells exceed the permissible limit of 250mg/l[19] and the source could be traced to excessive addition and use of NaCl and other salts in varying quantities during dyeing activities. The high concentration of Cl observed in the water of the study area can as well emanate from additives of various dyes that were being used in the area. Medically, people who regularly drink water containing high level of chloride have a great risk of developing bladder and rectal cancer (Figure 6).

3.2.2 Fluoride

The values of fluoride lie between 0.35 to 1.4 mg/l for the groundwater samples with the highest concentration at Car wash Asero-12 specifying safe values of fluoride that may increase beyond limit with time or when dyes containing fluoride are in use. The WHO permissible limit of fluoride is 1.5 mg/l for all the groundwater samples. However, with increase and continuous activities that influence fluoride concentration in the groundwater, the WHO limit could be exceeded, especially at locations where fluoride observed values are very close to the permissible level and this would totally render the water useless for consumption purposes. Dyeing activities, chemical decomposition of rocks, and sewage inputs are the likely sources of fluoride in the groundwater of the area.

3.2.3 Nitrates

The values of nitrate concentration are found to be in the range of 0.32 - 1.2 mg/l which is below the WHO standard. This is the most significant parameter used to measure contamination and pollution in water. If the WHO permissible limit of 50 mg/l is exceeded, it would be considered unfit for domestic uses. This could be as a result of infiltration of septic tank leakages into the groundwater sources.

3.2.4 Phosphate

The values of phosphate recorded are in the range of 0.2 to 1.2 mg/l which were below WHO-5.0mg/l standard value. The presence of phosphate in drinking water may lessen the exposure of the consumer to lead contamination from plumbing pipes. However, excessive content of this parameter in water leads to a considerable decrease in Dissolved Oxygen content thereby increased the mineral and organic nutrients (eutrophication).

3.2.5 Sulphate

The sulphate values are recorded in the range of 0.32 - 9.7 mg/l and they are quite below the set limit of WHO-400mg/l at all locations. If this limit is exceeded, it could result elevated bitterness of the water thereby causing laxative effects in humans.

3.2.6 Carbonates

The results also indicated that values of carbonate and bicarbonate are in excess and above the WHO permissible limits indicating hard water with combination of Ca, Mg and other trace metals. This clearly suggests that both the carbonate and bicarbonates are derived from trace metal carbonates in the dyes. The carbonates concentration in the water range from 150 - 420mg/l while that of the bicarbonate is in the range of 305 - 793mg/l: signifying hard and acidic to alkaline water. The WHO limits for these anions are 240 mg/l and 50 mg/l respectively. These specify excess anions concentrations than the WHO limit. These high values also revealed corresponding low values of calcium and magnesium in the water. This clearly implied that the carbonate and bicarbonates might have originated from another source (Figure 6).

3.2.7 Calcium

is usually found in or near areas with sedimentary lithologies and igneous or metamorphic terrains whose rocks are rich in silicate minerals. The values in the water range from 0.27 - 0.55 mg/l which are far below the WHO permissible limit of 75 mg/l. If excess or high calcium intake is observed it could be a pointer to the development of kidney stones.

3.2.8 Potassium

Potassium values observed in the water range from 4.85 - 7.25 which are also in the range specified by [19] as safe. Meanwhile [20] has established that high potassium intake by healthy individuals might not pose any health risk.

3.2.9 Magnesium

The magnesium values observed are in the range of 2.3 - 4.6 mg/l in the groundwater samples of the area. The values of sulphate are quite below set limit of the WHO (150 mg/l) at all locations. Excessive intake of magnesium has been linked to laxative effects.

3.2.10 Sodium

The recorded values of sodium concentration lie between 0.4 to 3.8 mg/l in the groundwater samples which are very low compared to WHO-200 mg/l limit. Excessive sodium intake in healthy adults does not account for any serious health hazard. However, children and adults who have been placed on sodium - restricted diet need caution because of other side effects of this feat.

3.3 Organic contaminants

The result of Polycyclic aromatic hydrocarbon (PAHs) compounds that was examined in the water samples from the tie and dyeing sites indicated the presence of the following compounds: Naphthalene, Acenaphthylene, Anthracene, Fluoranthene, Benzo[c]phenanthrene, Benz(a)anthracene, Benzo[b+]fluoranthene, Dibenzo[a,h]pyrene, Benzo[e]pyrene, and Benzo[a]pyrene. Some have been classified as probable human carcinogens that serve as live threatening ailments that eventually cause death. These compounds were significantly high where the processes of production were high and effective. This is proportional to the toxic organic compounds produced.

3.4 Microbial load and bacteria isolates

Generally, the dye effluents had high bacterial and fungal loads. The counts fell between the ranges: $0.39\text{x } 10^7$ and $2.35\text{x}10^7$ for bacterial counts. Mean fungal count ranged between $1.2 \text{ x } 10^3$ and $1.8\text{x}10^3$CFU/ml. There was a distinctly lower count in the microbial population of the sampled hand-dug well in comparison where mean total heterotrophic bacteria count ranged between $0.35 \text{ x } 10^3$CFU/ml and $2.56 \text{ x } 10^3$CFU/ml and fungi count was zero (0). The least of these counts was observed at the well far located away from the dye impacted sites and this was closely followed by the Ifote wells. Wells at Odutola had the highest total heterotrophic counts. The high microbial load of the effluents is thought to be as a result of the inherent microbial status of the water used in dyeing activity as well as those from follow up activities involved in the process. The bacterial load of the groundwater though lower in comparison to the sampled effluent is still on the high side. This may in part, be due to the low attenuative capability of shallow hand-dug wells. To further buttress this, most of the studied wells were visibly coloured with dye, an evidence of enhanced infiltration via soil strata overlying the groundwater. Studies have reported high vulnerability of hand-dug shallow wells to infiltration due to their low attenuation capacity[21]. The visibly coloured groundwater in this study suggests the infiltration of toxic dye components and microbial contaminants that could have been in dye effluent. Besides, wells in this study were observed to be very poorly maintained; some were uncovered, while some were partially covered water fetchers were unhygienically handled. All of these could have been source of additional contaminants to the water. Bacteria specie isolated from the effluent include; *Escherichia coli, Pseudomonas aeruginosa, Bacillus cereus, Bacillus subtilis and Proteus sp. Fungal spp. isolated include: Aspergillus niger and Aspergillus flavus*. The most predominant of these isolated organisms were *Aspergillus niger, Pseudomonas spp. and Bacillus spp.* This is similar to the report of Idowu et al[11]. From the groundwater sampled, *Bacillus spp. and Pseudomonas sp.* were the most predominant as these organisms were recovered from n=12 of the sampled wells. The similarity in the predominant bacteria isolates from effluent and hand-dug wells suggests that the microbial population of the effluent may have impacted the shallow hand-dug wells and the presence of these microbes in the water poses a risk to public health. Moreover, there is a peculiarity in the isolates that constituted predominant organisms in this study, in that they have been well reported by other investigators as being highly adaptive in their capacity to survive in toxic environment such as dye impacted areas[22],[23]. Their ability to adapt, accumulate and utilize toxic polluting compounds as energy sources had been widely reported. This may have made these species well adapted in the study sites.

Table 3. Microbial load and bacteria isolates of groundwater and wastewater samples

Sampled site	Source/Microbial count	Source/ Organisms isolated
1 Ifote	Well: 0.35x 102 Effluent: 5.9x 107	Well: *E. coli, Pseudomonas aeruginosa, Bacillus subtilis* Effluent: *E. coli, Pseudomonas aeruginosa., Bacillus cereus, Bacillus subtilis and Proteus sp. Aspergillus niger and Aspergillus flavus*
2 Ifote	Well: 13.5x 103	Well: *Pseudomonas aeruginosa, Bacillus cereus, E. coli*
3 Ifote	Well: 10.5x 103	Well: *Pseudomonas aeruginosa, Bacillus cereus, Proteus sp.*
4 Idi Ape	Well: 8.5x 102 Effluent: 0.38x 107	Well: *Escherichia coli, Bacillus subtilis and Proteus* Effluent: *E. coli, Bacillus subtilis and Proteus sp. Bacillus cereus, Aspergillus niger*
5 Idi Ape	Well: 2.03x 102	Well: *Pseudomonas aeruginosa. Bacillus subtilis*
6 Kenta	Well: 10.6x 102 1.23x 107	Well: *Escherichia coli, Pseudomonas aeruginosa, Bacillus spp.* Effluent: *E. coli, Bacillus subtilis, Pseudomonas aeruginosa, Proteus sp. Aspergillus niger and Aspergillus flavus*

Continued on next page

Table 3 continued

7 Better life	Well: 0.85x 102	Well: *Pseudomonas aeruginosa, Bacillus cereus, Bacillus subtilis and Proteus sp*
8 Odutola	Well: 15.6x 103 Effluent: 2.35x107	Well: *Pseudomonas aeruginosa., Bacillus cereus, Bacillus subtilis and Proteus* Effluent: *E. coli, Pseudomonas aeruginosa., Bacillus cereus, Bacillus subtilis and Proteus sp. Aspergillus niger and Aspergillus flavus*
9 Imoo	Well: 23.3x 102 Effluent: 0.42x 107	Well: *Escherichia coli, Bacillus subtilis and Proteus* Effluent: *Bacillus subtilis and Proteus sp. Pseudomonas aeruginosa, E.coli, Aspergillus flavus*
10 Kampala Mkt	Well:10.2x 102 Effluent10.22x 107	Well: *Pseudomonas aeruginosa, and Proteus* Effluent: *E. coli, Bacillus subtilis and Proteus sp. Pseudomonas aeruginosa, E.coli, Aspergillus flavus*
11 Garage Asero	Well: 2.5x 102 Effluent:0.34x 107	Well: *Pseudomonas aeruginosa and Proteus sp.* Effluent: *E. coli, Bacillus subtilis and Proteus sp. Pseudomonas aeruginosa, Aspergillus niger*
12 Asero Carwash	Well: 8.5x 103 Effluent: 0.56x 107	Well: *Enterobacter sp.* Effluent: *E. coli, Bacillus subtilis and Proteus sp.*
13 Market House	Well: 1.9x 102 Effluent: 4.8x 107	Well: *Escherichia coli, Pseudomonas aeruginosa.* Effluent: *Pseudomonas sp, Bacillus subtilis and Proteus sp. Aspergillusniger, Aspergillus flavus*
14 Adeyanju	Well: 3.1x 103 Effluent:1.08x 107	Well: *Bacillussubtilis and Proteus, E. coli* Effluent: *E.coli, Bacillus subtilis and Proteus sp. Aspergillus niger and Aspergillus flavus*
15 Matt Close	Well: 0.45x 103 Effluent: 15.7x 107	Well: *Proteus, Bacillus sp.* Effluent: *E. coli, Proteus sp. Enterobacter sp.*
16 Asero	Well: 0.95x 102 Effluent: 10.7x 107	Well: *Pseudomonas aeruginosa., Bacillus cereus, Bacillus subtilis* Effluent: *E. coli, Bacillus subtilis and Proteus sp. and Aspergillus niger*

3.5 Contaminants routes into groundwater sources

Discharged effluents from dyes leads to serious contamination problems because they link up to water under the ground through soil pore spaces and in fractures of rock formations. Both liquid and solid forms of Wastes generated from tie and dye disposed on land and water bodies that percolate into the ground-water and get transported in the direction of groundwater flow (Figure 7). Percolation rate supported transportation of pollutants from mineral and organic dyes in groundwater flow direction increases in tropic conditions due to high permeability enhanced by pore in the soil and fractures in rocks. Thus, contaminants are transported from place to place through groundwater flow pattern generated by the pores, joints and fractures.

Groundwater resources contamination takes place when anthropogenic materials and chemicals get into the groundwater and cause it to become unsafe and unfit for human use. Some of these substances can move about or travel from the ground surface through the soil into the groundwater sources. Spills of these dyes' contaminants can in the long run move through the soil and get into the groundwater. Apart from this, an exposed rock with or without thin overburden but laden with joints and fractures also serves as transporting routes for these contaminants into the groundwater. Rain water, wash-offs and floods can also move dyes, chemical salts and other chemicals through soil pores into the ground and eventually into the water. The size of pores, joints and fractures with the interconnection pattern has been the major factors that enhance contamination of ground water sources.

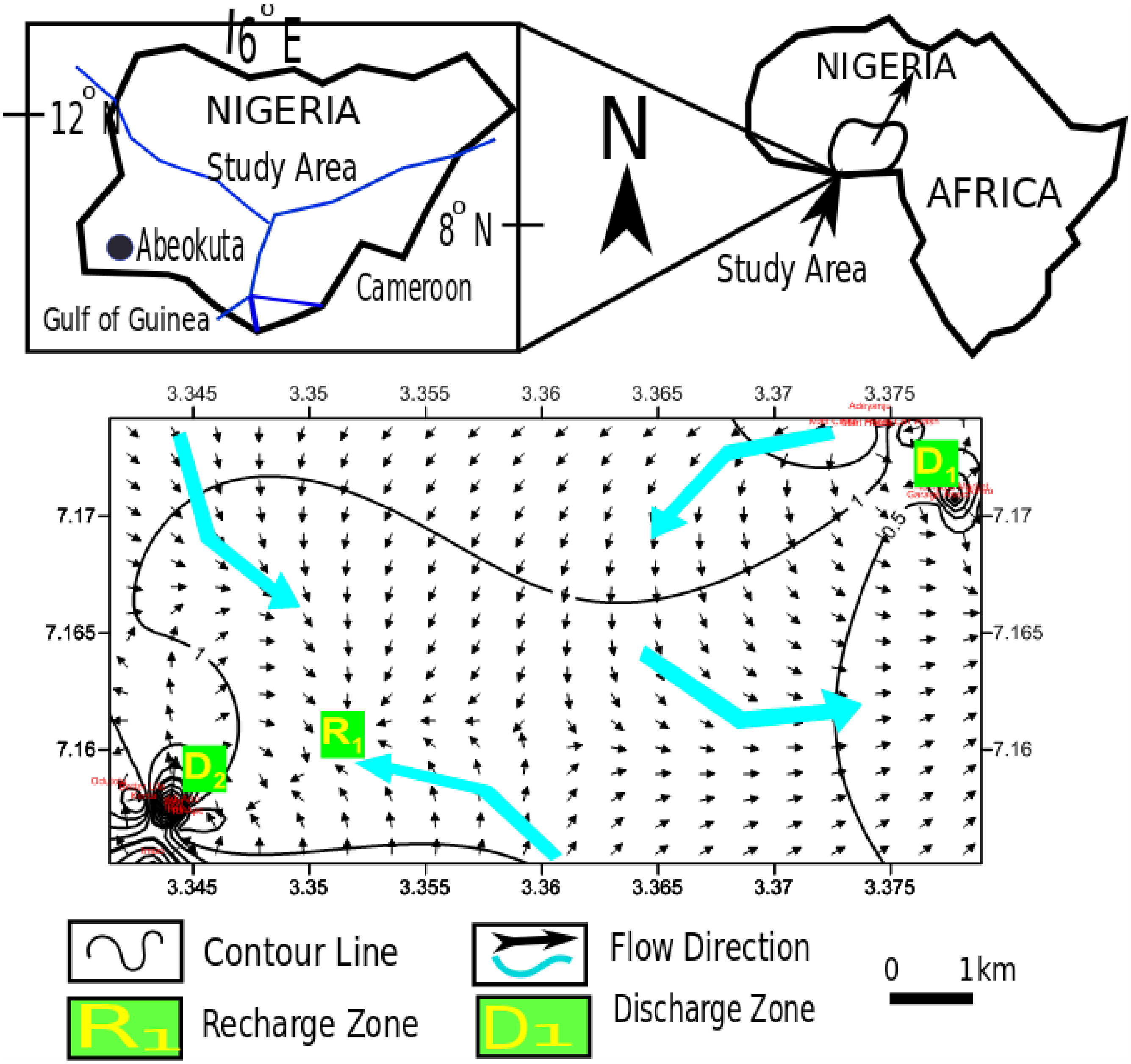

Fig 7. Ground water flow in the study area.

3.6 Impact and harmful effects of dyes on the environment

Dyes are mostly initiated into the environment and groundwater through waste waters and industrial effluents [24]. They have created myriads of problems in the environment where they are used and this depends on the exposure duration and the type, coupled with the adverse effects the concentration of the waste dyes can have on the ecosystem. The elevated thermal and photo stability at standard conditions can be kept in the environment for an extended period of time. Organisms are seriously affected because the incidence of minute measure of dyes in water (< 1 ppm) is exceedingly perceptible due to their vividness. This greatly affects the food chain since photosynthetic activity of algae is reduced through light absorption changes. Most often, the breakdown products of dyes are devastating based on their toxicity; because they are carcinogenic and mutagenic to life. Some of the dyes were used in their crude form without any further purification was attempted when it concerns rock minerals natural dyes. The systematic back-tracing of the flows of wastewater from neighborhoods to the small scale textile industries led to the identification of textile dyes as a cause of strong contamination effects.

Dyes affect water by causing contamination/pollution. The effluent from textiles industrial zones are classified as the most polluting in terms of the nature, volume and contents that is significant [24]; and the waste-water from Itoku and Asero cannot be an exception that contaminates groundwater sources. Textile industry is big and synonymous to world population indicating that; the more the increase in population, the more the increased demand of textile products and the greater the increase in the use of dyes which is directly proportional to the volume of waste-water generated. This is visible at itoku and Asero area where soil, rock, shallow-well water and other materials in the environment have been stained with different colouration of dyes.

3.7 Toxicological effects

Rock mineral dyes can cause different allergies such as contact dermatitis and respiratory diseases, skin irritation, allergic reaction in eyes and respiratory mucous membrane with upper respiratory region [24]. General public awareness and insight of water quality as regards contamination is greatly influenced by the colour and odour which may be generated by either fungi or microbial growth. Therefore, the removal of colour from wastewater will be more imperative than any other substance/parameter but the total removal of dyes from the wastewater will be very costly.

There are a wide range of toxicological effects of dyes which can be connected to the use of malachite green. The histo-pathological disturbances and harm of malachite green on multi-organ tissue damage can be unlimited to various checks. Soil-worm-transmitted disease (helminth) and serious infections is common with the use of malachite green; mostly found in areas with warm and moist climates with poor hygiene and sanitation [25]. The infectious disease increases with the levels of exposure of people to malachite green which might lead to no symptoms to ominous contagious illness that may root out a range of health distress such as: abdominal pain, diarrhoea, blood and protein loss and rectal prolapsed in Itoku and Asero area. It is applicable as a preventive tool on fungal assault, worm infections and some other diseases in aquatic animals caused by helminths-worms according to some other reports. However, it also has wide application in food, health, textiles and paint industries through which it can eventually have their way into human system. The toxicity of dye has created a lot of anxiety [24] based on the reported cases and based on its increasing usage from siting of dyes and textile industries. Based on these findings from various usages, medical effects have been observed to have a link to carcinogenesis, mutagenesis, chromosomal fractures, teratogenecity and respiratory lethal symptoms [26]. Biochemical in human system could also be affected with significant alterations which occur in biochemical restrictions of blood that damage organs and tissues through a long exposure to dye residues thereby, causing live threatening diseases [26]. This occurrence may also manifest with malachite green dye residues in the study. However, this incidence may also be possible or related to a developmental toxicity expression that comes up in embryo through the introduction of enhancement that create constant occurrence of structural mess in offspring from intake of different materials derived from dye contaminated/toxic food, water or drug during pregnancy and lactation [26]. From the observation of the small-scale tie and dye industries at Itoku and Asero; there is possibility of direct ingestion of dyes by workers if they have their hands stained with dyes when they failed to use any personal protective materials.

Mercury containing dyes (mineral) are also harmful for both animals and human being which calls for putting proper safety measures in place [27] in order to safeguard workers from poisoning. Mercurialism as an occupational disease with its toxicity is uncommon and its associated diseases include shaking of nerves, loss of sense, and death. It is highly connected to extraction and processes which can lower life expectancy [28], [29].

Manganese laden dyes are prone to cause manganese toxicity and this can represent serious health vulnerability including nervous system damage. Permanent crippling in the form of neurological disorder known as Parkinson's disease is greatly connected with this. In less pronounced form, the toxicity can manifest as incoordination, hallucination and hyperirritability [30]. Slight signs to Mn-toxicity is apparent at 1mg m^{-3} to >5 mg m^{-3}. Toxicity of this metal may be manifested in people who consumed high quantity of manganese supplements for a number of years and in individuals who have consumed water containing high levels of manganese especially, those people that engage themselves in tie and dye business. These toxicity states in humans have only been reported for adults. Oral interview / personal communication revealed this as a common disease among the aged workers and operators of this business [31].

3.8 Remediation procedures

The use of activated carbon can be adopted for the absorption of chemicals in waste from the process which can trim down some of the pollutant in the waste. Oxidation process [31], membranes filtration techniques can also be adopted and the use of manganese oxides-modified diatomite (MOMD) for the removal of colour from textile waste-waters by making use of the size, and its surface charge in the adsorption and attachment of the dyes to the birnessite layers of MOMD [32], [33]. Birnessite layers can also be found as an oxidation product of several other minerals, such as rhodonite (Mn, Fe, Mg, $CaSiO_3$) and rhodochrocite ($MnCO_3$) which exists in different geological formations [34], [35]. Since the quantity or magnitude of waste water from textile, tie and dye which goes into different water bodies carried different toxic materials that can possibly and unfavourably affect ground water systems and implicate environmental and public health through their percolation and infiltration into soil materials [36]; therefore earthy pond or pool should be created for wastewater treatment in order to guide against aquiferous zone contamination. Various studies and observations have shown that natural (plant) dyes are better than natural (mineral) and synthetic dyes [36], because these two dyes holds more of toxins that are carcinogenic; since mixtures of both natural and syntentic dyes are been used in the study area therefore caution should be applied.

4 Conclusion

Generally, the groundwater is slightly acidic to slightly alkaline at Itoku and Asero areas this might be as a result of dyes contamination to groundwater systems. The high concentrations of chloride (Cl^-) and carbonates in the groundwater were due to the excessive addition of NaCl and caustic soda coupled with dyes laden with chloride (Cl^-) anionic part in the tie and dye processes. The unusually high concentrations of Cl^-, HCO_3^- and CO_3^{2-} in groundwater of Itoku and Asero areas of Abeokuta southwestern Nigeria might have been derived through the type of dye in use. The highest concentration of Cl^-, HCO_3^- and CO_3^{2-} revealed exceedingly high values beyond the standard specifying groundwater system contaminated with chlorides and carbonates that might have been derived from mineral dyes. In all, from the visual assessment of ground water both in terms of colour and odour; these may suggest that the water is not fit for drinking because it can cause serious health hazard but it may be good for industrial purposes. The coloured shallow well water may also suggest the presence of some toxic metals in this water sources.

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