



## Potential impacts of Effluent from Non-Industrial Dyehouses in Kano Metropolis on Groundwater Quality in the Vicinity

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### ABSTRACT

Water supplied by treatment plants in Kano Metropolis is far less than the demand and therefore low-income communities meet their water demands mostly through dug wells in households. Dyehouses operate in the neighbourhood of residential houses where the wastewater discharged has a propensity to contaminate the groundwater sources. A total of 18 dyehouses were investigated where residual vat dyebaths were collected. Groundwater samples were collected within a 100 m radius of the dyehouses. Sample collection, handling and analysis of physicochemical parameters were carried out as described by standard methods for the examination of water and wastewater. Heavy metals were measured using a Microwave Plasma Atomic Emission Spectrophotometer. Among the physicochemical parameters investigated in dye effluents, pH, colour, biological oxygen demand, chemical oxygen demand, total dissolved solids and sulphate were above the limits set by the Federal Environmental Protection Agency (FEPA). Except for Pb, all heavy metals investigated are within FEPA limits. Sodium is not listed but has an excessively high concentration (856.72 mg/l) Among the physico-chemical parameters studied in groundwater samples, temperature, conductivity and total dissolved solids with mean concentrations of 30.94 °C, 1112.2 µs/cm and 786.22 mg/l respectively have exceeded permissible limits specified by standards organization of Nigeria (SON) and world health organization (WHO) for drinking water quality. The mean values of pH and DO were 6.45 and 4.05 mg/l respectively and are indicative of poor water quality. The mean concentrations of sodium, iron, nickel, chromium, and lead were 808.75, 1.23, 0.1, 0.08, and 2.27 mg/l respectively which were above SON and WHO permissible limits. It may be concluded that the groundwater in the proximity of the dyehouses is not safe for drinking and irrigation.

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### INTRODUCTION

Dyes can be classified into different application classes namely disperse, acid, basic, direct, fibre reactive, pre-metallized, mordant, solubilized, sulphur, azoic, and vat dyes (Wardman, 2018). Occupational dyers in Kano

Metropolis use synthetic vat dye as the colour, hydros as reducing agent, and caustic soda as solubilising agent to formulate the dyebath (Abdullahi *et al.*, 2021a). Vat dyes belong to either indigo or anthraquinone type. Anthraquinone based vat dyes require more synthetic steps than

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the acid, basic, direct, disperse and reactive dye classes with increase in the consumption of raw-materials resulting in vat dyes being the highest generator of wastewater and hazardous waste compared to other dye classes (Baptista, 2009). Vat dye in the non-soluble form do not represent an environmental risk as regards to its toxicity (Bozic and Kokol, 2008) but is the main cause of pollution in the wastewaters of textile and other industrial effluents (Rapo and Tonk, 2021) which some countries classified as the most toxic class of wastewaters (Bozic and Kokol, 2008). Typically, released vat dyebath contains spent caustic soda and hydros (Bechtold and Turcanu, 2009), residual dye, and heavy metals (Baptista, 2009).

Due to surface water contamination, groundwater is the major source of fresh water worldwide (Raji and Abdulkadir, 2020; Aghazadeh *et al.*, 2017) where approximately one third of global population depend on this water source for drinking (Li *et al.*, 2021). The number of individuals living in water scarce areas will increase to around 3.9 billion by 2030 as assessed by world water council (Velusamy *et al.*, 2021). Groundwater quality depends on chemical constituents and their concentration which are mostly derived from the geological data of a particular region. In addition to geological data, groundwater quality also depends on a number of factors such as the degree of chemical weathering of rocks, quality of

recharge water, and water-rock interactions (Aghazadeh *et al.*, 2017). The relative proportions of various dissolved ion concentration in groundwater depends largely on the solubility of rocks in aquifers (Feng *et al.*, 2020).

Contaminated surface water, industrial effluent, underground storage tanks, sewage, fertilizers, pesticides used for agriculture, and landfills constitute anthropogenic sources of groundwater contamination (Brindha *et al.*, 2020). In 2016, there were about 270 factories in the 4 industrial estates of Kano metropolis where tanneries and textiles dominated and generated more than 90 % of liquid and solid wastes mostly discharged into open drains thereby contaminating natural waters in the vicinity (Nabegu, 2016). Non-industrial dyehouses in Kano Metropolis comprised of large informal groups of young people working in the neighbourhood of residential houses (Abdullahi *et al.*, 2021b) with majority disposing wastewater in to nearby shallow drain as shown in Figure 1 (Abdullahi, 2023). The volume of effluent discharged weekly could be up to 240,000 l due to the fact that dyeing of 5 yards of material requires 30 l of water for dyeing and additional 30 l for rinsing (Abdullahi *et al.*, 2021c) and, as at 2015, a particular dyehouse could process over 20,000 yards within 1 week (Abdullahi, 2023).



**Figure 1:** Shallow drainage (Abdullahi, 2023)

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The threat of water scarcity in the near future has necessitated the need for an extensive study on the quality of groundwater used for drinking and irrigation. Groundwater quality parameters have been evaluated in many places worldwide e.g., China (Zhang *et al.*, 2020), India (Brindha *et al.*, 2020), Iran (Aghazadeh *et al.*, 2017), and in Nigeria such as in Ogun (Zacchaeus *et al.*, 2020), Lagos (Popoola *et al.*, 2019), Gombe (Yusuf *et al.*, 2018), Jigawa (Tukur *et al.*, 2020), and Kano metropolis (Balogun *et al.*, 2020; Suleiman *et al.*, 2020; Shawai *et al.*, 2018; Yahaya *et al.*, 2017). For the first time this study investigates the potential dangers the effluent discharged by non-industrial dyehouses pose to the immediate environment by characterizing both the residual wastewaters as well as groundwater from hand-dug wells in the vicinity.

## MATERIALS AND METHODS

### Materials

The materials used include 100 % cotton fabric, 3 different dyes viz. C. I Vat Blue 4 (RSN, lot No. 101-196, Hangzhou Tiankun Chemical Co. Ltd., China), C. I Vat red 1 (VR1, lot No. 261-308, Hangzhou Tiankun Chemical Co. Ltd., China), and C. I. Vat Violet 1 (VRR, lot No. 1-40, Shaoxing Shangyu Haohua Chemical Industrial Co. Ltd., China) as well as Commercial grades of sodium hydroxide (caustic soda) (99 %, UN No. 1823, Tianya chemicals, China) and sodium dithionite (hydros) (85 %, UN No. 1384, Jinhe hydrosulphite Factory Co. Ltd., China).

## METHODOLOGY

### Sample collection

For the effluent samples, each of 18 dyehouses was presented with 20 g of sized cotton fabric, 2 g of either RSN, VR1, or VRR and large amounts of caustic soda and hydros. The dyers were asked to dye the fabric in an open 2 l-beaker for 10 min. using liquor to goods ratio (LR) of 100:1. After dyeing, residual dyebath wastewaters, 2 l each, containing spent caustic soda and hydros, and residual VR1 (18 samples among DA to DF), RSN (18 samples, DG to DL), and VRR (18 samples, DM to DR) were collected by convenient sampling technique in triplicates (a

total of 54 samples) before disposal while the colour of the effluent from each dyehouse was randomly selected. For the groundwater samples, 2 l each from hand-dug wells were collected within 100 m radius of some of the dyehouses. Samples were collected using the same material that is used to fetch water from each well which is usually a 2-l paint rubber tied to a long rope or a rubber container made from motorbike and car wheel tube attached to a long chord. The wells were agitated to obtain homogeneous, representative samples.

The collection and handling of effluent and water samples were carried out as described in the standard methods for the examination of water and wastewater published by American Public Health Association (APHA, 1985). Specifically, samples were collected in triplicate using clean plastic containers which were covered with black polyethene bags to prevent growth of algae. One set of the samples for heavy metal analysis were acidified with few drops of nitric acid to prevent adsorption of ions on the wall of the containers and to prevent bacterial activity. The samples were labelled and transported to the laboratory in a cooler with ice packs within few hrs. of collection and samples that were not analysed immediately were stored in a refrigerator at 4 °C. Sampling was conducted between 14 and 28 August, 2018. The samples were filtered through Whatman no. 1 filter paper to remove solid and suspended materials.

### Determination of physico-chemical parameters

The pH and temperature of water samples were determined in-situ at the point of sample collection. pH was determined using pH metre (Jenway 3310, UK) after the metre had been calibrated using buffer at pH 7.0. The electrode was then immersed into the samples and the reading was recorded. Temperature was determined using a thermometer. The colour of the dye containing effluent was measured at wavelength of maximum absorption value using a UV-Visible spectrophotometer and according to American dye manufacturers institute (ADMI)

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method as per the procedure outlined in standard methods (APHA, 1998).

Dissolved oxygen (DO) was measured using DO meter (HANA model HI9143). Biological oxygen demand (BOD) was obtained by deducting the value of initial DO from the final DO (after incubating in the dark at 20 °C for 5 days) and multiplying the value with the dilution factor (APHA, 1998). Chemical oxygen demand (COD) was determined by titrimetric method according to standard methods (APHA, AWWA, WEF, 1997). Electrical conductivity and total dissolved solids (TDS) were measured using digital conductivity meter which has been previously standardized using 0.1 N potassium chloride at 25 °C (APHA, 1992). Sulphate concentration in effluent and groundwater samples was determined by turbidimetric method as described by APHA (1985) where the concentration was obtained from the constructed calibration curve of 5 known concentrations of standard sulphate solution.

#### Determination of metal content

Effluent and water samples, acidified at the time of collection, were acid digested by adding 0.5 ml of concentrated hydrochloric acid and 0.2 ml of concentrated nitric acid to 10 ml

sample aliquots in 16 by 125 mm polypropylene tubes at 90-100 °C in a sand bath on a hot plate until the final digested volume was 10 ml. If the sample volume was less than 10 ml, distilled water was added to make up the sample volume to 10 ml mark. All measurements were performed using Agilent 4210 MP-AES. The sample introduction system consisted of polyvinyl chloride (PVC) peristaltic pump tubing, a single pass cyclonic spray chamber, and a oneNeb nebulizer.

The Agilent MP Expert software was used to automatically subtract the background signal from the analytical signal. A background spectrum from a blank solution was recorded and automatically subtracted from each standard and sample solution analyzed. The software also optimizes the nebulization pressure and viewing position for each wavelength selected to maximize sensitivity. Heavy metal content was determined sequentially by the equipment under optimized conditions except for the determination of sodium which was carried out separately. The machine operating conditions are shown in Table 1 and the wavelength of maximum absorption at which determinations were made are shown in Table 2.

**Table 1:** MP-AES operating conditions

Parameter	Setting
Replicates	3 (except for Na, 4)
Background correction	Auto
Read time (s)	3
Viewing position	0
Nebulizer flow (l/min.)	0.45-0.95 (depending on the element)
Pump speed (rpm)	15
Uptake time (s)	60 (E/H <sub>2</sub> O) (except for Na, 15 s)
Stabilization time (s)	15 (E/H <sub>2</sub> O)
Calibration fit	Linear weighted
Rinse time (s)	30 (E/H <sub>2</sub> O)
Calibration correlation coefficient limit	0.999

Uptake time:80 s, rinse time:40s and calibration fit:0.995 (for dye powders), Replicates:4, uptake time:25 s, rinse time:25 s, stabilization time:10 s, calibration fit:0.995 (for hydros and caustic soda), Instrument type: MY17380004, Current software: version 1.6.0.9255

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**Table 2:** Wavelengths at which concentrations of heavy metals are determined

Analyte	Wavelength (nm)
Chromium	425.433
Lead	405.781
Sodium	588.995
Iron	373.713
Nickel	352.454

**RESULTS AND DISCUSSION**

The concentration of metals in groundwater and effluent samples were determined by using calibration curves which were found to be linear starting from the origin with regression coefficient greater than 99%. Tables 3 shows physico-chemical parameters and heavy metals in residual VR1, RSN, and VRR wastewaters. VRR was found to contain more

pollutants with more biological oxygen demand, higher conductivity and TDS due to higher metal content. Table 4 shows mean effluent pollutants measured in this study compared to values obtained in previous studies and National standard. Table 5 shows mean water pollutants compared to values obtained in previous studies, national and international standards.

**Table 3:** Pollutants found in 3 different colours of wastewaters

Parameter	Mean± SD (VR1)	Mean± SD (RSN)	Mean± SD (VRR)
pH	11.57±0.07	11.58±0.01	11.36±0.14
Colour	649±157.68	555.39±151.8	645.75±64.78
DO	1.49±0.08	1.46±0.12	1.51±0.10
BOD	376.53±60.58	419.92±44.54	420.99±69.07
COD	1618.24±425.53	1566±377.45	1466.71±257
Cond.	2080.37±49.06	2076.06±98.16	2286.85±198.5
TDS	4239.12±414.38	4207.41±785.75	4756.59±417
Sulphate	53.17±9.39	55.22±7.88	51.23±9.55
Sodium	740.53±584.7	562.74±631.96	1266.9±107.25
Iron	0.73±0.39	0.83±0.36	1.01±0.18
Nickel	0.13±0.03	0.13±0.04	0.14±0.02
Chromium	0.17±0.29	0.05±0.03	0.19±0.22
Lead	1.56±1.08	2.64±1.08	3.14±1.13

pH: no units, Colour: pt-co, Cond.: µs/cm, All other parameters: mg/l

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**Table 4:** Mean effluent pollutants concentrations

Parameters	Mean± SD (DA-DR)	Mounteer et al. (2018)	Santhi and Moses (2008)	Abebe and Galebo (2019)	Rahman et al. (2020)	FEPA (1991)
pH	11.50±0.15	11	11.87	11.89	11.64	6-9
Colour	616.71±131.58	1230	-	-	-	5
DO	1.49±0.10	-	-	-	-	NS
BOD	405.81±59.33	-	462	480	-	50
COD	1550.32±344.72	2412	1560	1590	-	80
Conductivity	2147.76±159.30	1656	-	-	1,439.29	NS
TDS	4401.04±591.93	-	6811	7895	18,015.0	2000
Sulphate	53.21±8.60	24.1	159	-	68.75	50
Sodium	856.72±562.18	-	3125	-	-	-
Iron	0.85±0.33	-	-	-	7.109	20
Nickel	0.13±0.03	-	-	-	-	<1
Chromium	0.14±0.21	-	-	-	0.212	<1
Lead	2.45±1.23	-	-	-	0.938	<1

pH: no units, Colour: pt-co, Conductivity: µs/cm, All other parameters: mg/l, FEPA: Federal Environmental Protection Agency

**Table 5:** Mean water pollutants concentrations

Parameters	Mean± deviation (WA-WL)	Standard	Yahaya et al (2017)	Tahir et al (2015)	Dabo and Saleh (2017)	SON (2007)	WHO (2011a)
pH	6.45±0.45		7.7	6.32	7.3	6.5-8.7	6.5-8.5
Temperature	30.94±0.90		27.85	33.6	27	-	27-28
DO	4.05±0.80		4.67	-	2.64	-	7.5
BOD	1.49±0.55		1.25	-	0.93	-	-
Conductivity	1112.26±162.28		590.9	558	504	1000	1000

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Parameters	Mean± deviation (WA-WL)	Standard	Yahaya et al (2017)	Tahir et al (2015)	Dabo and Saleh (2017)	SON (2007)	WHO (2011a)
TDS	786.22±481.70		119.13	312	1056	500	500
Sulphate	20.78±2.85		-	22.2	-	100	-
Sodium	808.75±312.40		-	35	-	200	-
Iron	1.23±0.91		0.6	0.3	0.25	0.3	0.3
Nickel	0.10±0.01		-	0.018	-	0.02	0.07
Chromium	0.08±0.04		0.57	0.04	0.56	0.05	0.05
Lead	2.27±0.06		0.11	0.11	0.25	0.01	0.01

pH: no units, Temperature: °C, Conductivity: µs/cm, All other parameters: mg/l, SON: Standard organization of Nigeria, WHO: World Health Organization

#### PHYSICO-CHEMICAL PARAMETERS IN EFFLUENT AND GROUNDWATER SAMPLES

##### pH

The pH measured in effluent ranged from 11.11 to 11.8 with mean value of 11.50±0.15 (Table 4) which indicates a basic nature. The average pH value determined in this study was beyond Federal environmental protection agency (FEPA) recommended limits. Vat dye wastewaters investigated previously by Mounter *et al.* (2018), Santhi and Moses (2008), and Abebe and Galebo (2019) have measured mean pH values similar to the values obtained in this study. This may be due to the fact that leuco vat dyeing is usually carried out in an alkaline pH region (Chakraborty, 2010). Mean pH of a vat dye wastewater analysed in Bangladesh was found to be 11.64 (Rahman, 2020). pH in groundwater ranged from 5.54 to 7.20 with an average of 6.45±0.45. The mean pH value was beyond permissible limits set by standards organization of Nigeria (SON) and World health organization (WHO). Previous studies reported slightly alkaline pH of groundwaters in the same study area (Yahaya *et al.*, 2017; Dabo and Saleh, 2017). Tahir *et al.* (2015) reported a more acidic pH than the value measured in this study.

Strength of pH alters the rate of biological reaction for the survival of microorganisms and also affects the soil permeability which results in contaminating groundwater sources (Elango *et al.*, 2017). Although pH usually has no direct impact on consumers, it is one of the most important operational water quality parameters as toxicity of metals increases with the basic pH (Mandour, 2012). Acidity of water samples may be attributable to the fact that water undergoes anaerobic fermentation processes as a result of formation of ammonia and organic acids where hydrolysis of those acidic materials decreases the pH value and make the water more acidic (Elango *et al.*, 2017). Acidic waters can cause corrosion of pipes and may pose negative effects on gastrointestinal tracts when consumed resulting in diarrhea (Zacchaeus *et al.*, 2020).

##### Dissolved oxygen

DO concentration in effluent samples ranged from 1.31 to 1.68 mg/l with a mean value of 1.49±0.1 mg/l. FEPA did not specify limits for DO of industrial effluent. Concentration of DO in groundwater ranged from 2.93 to 5.40 mg/l with an average of 4.05±0.8 mg/l. The mean DO value is lower than the recommended limit set by WHO. SON did not recommend any limit for DO of

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drinking water. The mean DO concentration measured in this study is higher than that reported by Dabo and Saleh (2017) and lower than that measured by Yahaya *et al.* (2017). DO test measures the concentration of oxygen dissolved in water or wastewater and is significantly affected by temperature, salinity, and atmospheric pressure. Saturation concentration of oxygen in deionized water at 1 °C and standard air pressure is 14.2 mg/l. Species that live in water are sensitive to relatively small changes in the already extremely low quantity of oxygen available. Trout fish died when the DO concentration was less than 5 mg/l (Woodard, 2001). The presence of organic substances in water also affects the DO. Decrease in DO levels does not only affect the ecological balance but also poses environmental problems as it reduces the population of beneficial microorganisms that naturally degrade harmful organic substances (Ratna and Padhi, 2012).

#### **Biological oxygen demand**

BOD concentration in effluent ranged from 307.32 to 490.44 mg/l with an average value of 405.81±59.33 mg/l. The average value exceeds the FEPA limit of 50 mg/l. Santhi and Moses (2008) and Abebe and Galebo (2019) have reported the BOD of effluent from vat dyebaths as 462 and 480 mg/l, respectively which corroborates with the value measured in this study. A BOD of 3,670 mg/l was found in dyebath wastewater containing C. I. Vat Blue 4 from a dyeing unit in India (Olaganathan and Patterson, 2009). BOD concentration in groundwater ranged from 0.69 to 3.44 mg/l with a mean value of 1.49±0.55 mg/l. No BOD limit is set by both SON and WHO. Previous studies reported lower mean BOD values (Yahaya *et al.*, 2017; Dabo and Saleh, 2017) indicating that the water samples investigated in this study may be more contaminated. Low or nil BOD shows good quality water while high BOD indicates that the water is highly contaminated and not suggested for drinking purposes. Increase in BOD also leads to microbial oxygen demand reducing DO which may induce hypoxia conditions with subsequent adverse effects on aquatic biota (Elango *et al.*, 2017).

#### **Conductivity**

Conductivity in effluent ranged from 1958.22 to 2540.0 µs/cm with an average of 2147.76±159.3 µs/cm. No Conductivity limit is set by FEPA. Munteer *et al.* (2018) and Rahman (2020) reported conductivity of 1656 µs/cm and 1,438.29 respectively in raw textile mill effluents containing residual vat dye. Conductivity in groundwater ranged from 923.32 to 1358.49 µs/cm with a mean value of 1112.26±162.28 µs/cm. The mean conductivity value obtained in groundwater is almost twice the values reported previously (Yahaya *et al.*, 2017; Tahir *et al.*, 2015) and exceeds the limit of 1000 µs/cm set by SON and WHO. Conductivity reflects the total amount of salt in water (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>) and is used to determine salinity of water (Hussain, 2013). High conductivity level recorded could be linked to sewage materials as well as leaching of inorganic contaminants. It can also be related to high sodium content in effluent and groundwater samples.

#### **Total Dissolved Solids**

TDS in effluent ranged from 3168.4 to 5104.32 mg/l with a mean value of 4401.04±591.93 mg/l. Mean TDS value in effluent was above FEPA recommended limit of 2000 mg/l. It is lower than mean values reported by Santhi and Moses (2008) and Rahman *et al.* (2020) the higher TDS value recorded may be due to spent caustic soda and hydros used in the dyeing process. TDS in groundwater ranged from 18.78 to 1678 mg/l with an average of 786.22±481.70 mg/l which exceeds the maximum permissible limit of 500 mg/l set by SON and WHO. The mean TDS is higher than that reported by Yahaya *et al.* (2017) and Tahir *et al.* (2015) but lower than the value measured by Dabo and Saleh (2017). Water with high TDS value of water is not recommended for drinking and irrigation purposes as it may cause salinity problem (Elango *et al.*, 2017).

#### **Sulphate**

Concentration of sulphate in effluent ranged from 32.18 to 64.3 mg/l with a mean value of 53.21±8.60 mg/l. The mean value in effluent exceeds the maximum of 50 mg/l set by FEPA.

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Santhi and Moses (2008) reported sulphate concentration of 159 mg/l from a Jade Green XBN vat dye bath and Rahman (2020) recorded 68.75 mg/l from a raw vat dye wastewater. Use of hydros as reducing agent in vat dyeing is being criticized for the formation of environmentally unfriendly oxidation byproducts such as sulphite ( $\text{SO}_3^{2-}$ ), sulphate ( $\text{SO}_4^{2-}$ ), thiosulphate ions ( $\text{S}_2\text{O}_3^{2-}$ ) and toxic sulphur (Shi, 2014). The sulphide ions released from hydros and sodium sulfide decompositions affect the environment detrimentally by noxious odors, toxicity and high chemical oxygen demand of the wastewater (Bozic and Kokol, 2008). Some vat dyes have tendency to biodegrade and produce intermediate products more toxic than the original dye (Arcanjo *et al.*, 2018).

Sulphate concentration in groundwater ranged from 13.37 to 26.77 mg/l with an average of  $20.78 \pm 2.85$  mg/l. Mean sulphate concentration obtained in groundwater is within the maximum permissible limit of 100 mg/l set by SON. Tahir *et al.* (2015) reported a higher sulphate concentration in groundwater. Sulphate is widely distributed in nature and may be present in natural waters in concentration ranging from a few to thousands mg/l. Bacteria and dissolved oxygen play leading roles in determining the fate of sulphur containing compounds in aquatic systems where sulphate reducing bacteria use sulphate ion as an oxygen source for the assimilation of organic matter in the same way DO is used by aerobic bacteria (Kularatne *et al.*, 2003).

Natural source of sulphate is linked to the dissolution of sulphate/evaporites minerals such as gypsum and anthropogenic sources such as municipal and industrial effluents mainly due to sulphur-based waste products (Aladejana *et al.*, 2020). Sulphates are sulphuric acid products used in the production of fertilizers, chemicals, dyes, glass, paper, textiles etc. and are discharged into water from mines and smelters from kraft pulp, paper, textile mills and tanneries (WHO, 2004). During vat dyeing process, hydros is converted into sulphite (toxic to fish and bacteria) and in some cases this is further oxidized into sulphate which may cause corrosion of concrete pipes

(Chavan, 2011). Equation 1 shows decomposition of hydros under oxidative condition. Accumulation of sulphate in water may lead to increase in water pH causing acidosis (Popoola *et al.*, 2019).



Equation 1: Decomposition of hydros under oxidative condition (Chakraborty, 2010)

### Colour

Colour in effluent ranged from 405.3 to 920.12 pt-co with a mean value of  $616.71 \pm 131.58$  pt-co. The mean colour value is above FEPA limit and lower than 1,230 pt-co reported by Munteer *et al.* (2018). Colour of effluent is one of the major problems in the textile industry and it is a widely accepted primary pollutant in wastewater. Colour diminishes the photosynthetic activity of aquatic life and affects other parameters such as DO, BOD etc., Colour is difficult to remove by conventional treatment methods (Elango *et al.*, 2017) and high colour renders water unfit for use at the downstream of the disposal point and threatens the biodiversity (Karim *et al.*, 2018).

### Chemical oxygen demand

Concentration of COD in effluent ranged from 1203.84 to 2218.44 mg/l with an average value of  $1550.32 \pm 344.72$  mg/l. The mean value far exceeds FEPA recommended limit of 80 mg/l and is in the same range as values reported previously (Munteer *et al.*, 2018; Santhi and Moses, 2008; Abebe and Galebo, 2019). COD test oxidizes materials that microorganisms cannot metabolize in 5 days (Scholz, 2016). COD is a measure of the amount of oxygen required to oxidize organic matter and possibly some inorganic materials in a sample and also provides a direct measure of the potential impact of oxygen consumption on oxygen content of water body (Walker *et al.*, 2019).

High COD value recorded may be due to the use of hydros as reducing agent in an open bath. Excess air oxidizes a part of the total hydros to sulphate and the rest contributes to COD. The quantity of hydros converted to sulphate and the rest left in the bath are nearly 50:50 (Chakraborty,

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1992). In the case of biodegradable organics, COD is 1.3 to 1.5 times the BOD and when the ratio is twice, there is good reason to suspect that a significant portion of the organic material in the samples is not biodegradable by ordinary microorganisms (Woodard, 2001). The COD measured in effluent samples is almost 4 times the BOD which indicates that the wastewater is not readily biodegradable and may be toxic to microorganisms.

### Temperature

Temperature in groundwater ranged from 29 to 33 °C with an average value of 30.94±0.9 °C. The mean temperature exceeds WHO recommended limit of 27-28 °C and is higher than the temperature measured by Yahaya *et al.* (2017) and Dabo and Saleh (2017) but lower than that obtained by Tahir *et al.* (2015). Temperature is one of the most essential parameters of water. It is significant for the growth and activity of ecological life as it affects the solubility of oxygen in water (Shawai *et al.*, 2018).

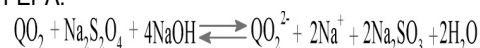
### METAL CONTENT IN EFFLUENT AND GROUNDWATER SAMPLES

In recent years, there has been an increasing ecological and global public health concerns associated with environmental contamination by heavy metals and although they are found naturally, most environmental contamination and human exposure result from anthropogenic activities such as industrial activities, domestic and agricultural use of metals etc. (Tchounwou *et al.*, 2012). The heavy metals investigated in dye effluent and groundwater samples include sodium, iron, nickel, chromium and lead as shown in Table 4 and Table 5 respectively.

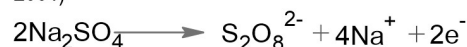
### Sodium

High level of sodium in a sample may cause interferences in atomic spectrometric methods because sodium is one of the so-called easily ionized elements which is a well-known and common interferent (Baranyai *et al.*, 2020). According to the authors, sodium concentration naturally present in human blood serum samples

affected the intensity values of other measured elements. The concentration of sodium in effluent ranged from BDL to 1398.91 mg/l with an average value of 856.72±562.18 (Table 4). The high sodium content may be attributable to the fact that caustic soda and hydros are known to have high sodium content which will invariably contribute to the overall sodium concentration in the dyebath. Reduction of vat dye in an alkaline solution produces sodium as shown in Equation 2. Oxidation of sulphate also gives rise to sodium as shown in Equation 3. Santhi and Moses (2008) found sodium concentration of 3,125 mg/l in Jade Green XBN vat dyebath wastewater in which hydros was used as the reducing agent. The limit of sodium in effluent samples has not been set by FEPA.



Equation 2: Reduction of quinone (QO<sub>2</sub>) with hydros to give leuco dye (QO<sub>2</sub><sup>2-</sup>) (Broadbent, 2001)



Equation 3: Oxidation of sulphate (Kariyajanavar *et al.*, 2013)

Sodium concentration measured in groundwater samples ranged from BDL to 1187.36 mg/l with an average of 808±312.4 (Table 5). The mean sodium level obtained in this study is higher than that reported previously and exceeded the limit of 200 mg/l set for safe drinking water quality by SON. WHO, however, has not set limit for sodium in drinking water. Tahir *et al.* (2015) reported 35 mg/l as the mean sodium concentration in deep and shallow boreholes in Kano Metropolis. Sa'eed and Mahmoud (2014) detected mean Na conc. in Fagge local government area as 3.7 mg/l while Suleiman *et al.* (2020) determined the concentration of 23.3 mg/l in Gwale. However, a maximum level of sodium up to 863 mg/l was measured in a shallow tube well of Barguna district, Bangladesh (Islam *et al.*, 2017).

Sodium occurs naturally in groundwater and is believed to have been released by weathering of plagioclase feldspars. The rock

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types in Kano Metropolis are characterized by enrichment in sodium, calcium, and potassium ions (Tahir *et al.*, 2015). Frequent discharge of the vat dye effluent with high sodium content in to shallow drainages which are in close proximity to groundwater source (not more than 91 m away) may be responsible for the high sodium content. Aghazadeh *et al.* (2017) also attributed the high concentration of sodium to cation exchange among minerals, anthropogenic activities, and poor drainage conditions. sodium is one of the leading constituents of blood plasma of humans and because of that, alteration of its normal concentration in the body may have direct effects on the osmotic pressure of the plasma, plasma volume, acid-base balance, and on the maintenance of electric activity of body cells (Hasan *et al.*, 2020). Elevated sodium intake has been associated with hypertension, cardiovascular disease and stroke. Sodium intake for adults equals to 2 g/day which is equivalent to 5 g salt/day (WHO, 2012).

#### **Iron**

Iron concentration in effluent samples ranged from 0.1 to 1.30 mg/l with an average of  $0.85 \pm 0.33$  mg/l. The mean iron content detected in this study is within FEPA permissible limit of 20 mg/l. Rahman (2020) reported 7.109 mg/l as mean iron concentration in composite vat dye effluent from 28 dyeing units in Bangladesh. Iron in groundwater samples ranged from 0.81 to 3.99 mg/l with an average of  $1.23 \pm 0.91$  mg/l. Mean iron level is higher than these reported previously and is above permissible limit set by SON and WHO for drinking water quality. Yahaya *et al.* (2017) found 0.6 mg/l mean iron concentration in groundwater samples from wells located in industrial areas of Kano Metropolis. A mean iron concentration of 0.3 mg/l was found around residential areas in Kano Metropolis (Tahir *et al.*, 2015). Mean iron concentration in drinking water sources in Kano Metropolis (boreholes, wells, and tap water) was reported as 0.25 mg/l (Dabo and Saleh, 2017).

High iron content is a characteristic of groundwater in significant proportions practically in all states of Nigeria (Ezeigbo, 1988). Iron levels

found in some states ranged from 0.3-1.5 mg/l in coastal aquifer in Ogun State (Aladejana *et al.*, 2020) to 2.2-4.71 mg/l in industrial and residential areas of Lagos Metropolis (Popoola *et al.*, 2019). Even though concentration of iron in effluent is within FEPA permissible limit for effluent discharge, frequent dumping of the wastewaters in to a shallow drain may accumulate and increase iron content in the groundwater because of its proximity to the source of contamination. High level of iron may also be attributable to the dissolution of iron bearing rocks and/or soils (Popoola *et al.*, 2019). It can also be due to leaching from rusting in the old galvanized metal pipe work in the distribution channel (Audu and Idowu, 2015) since iron is used in coatings of many pipes and can deteriorate and find its way into the water supply (Mandour, 2012).

Iron exists in its natural form as ores (magnetite taconite and hematite) in rocks, soil, and minerals making about 5 % of the earth's crust (Popoola *et al.*, 2019) and can be dissolved and transported into groundwater (Mandour, 2012). Iron is an essential element that is required by all forms of life. It is a natural constituent of all nutrients of plant and animal origin (Geiger and Cooper, 2010). In humans, it is an essential element for haemoglobin and myoglobin, and its deficiency leads to anaemia and loss of wellbeing. Overload of iron causes severe health problems such as liver cancer, diabetes, cirrhosis of liver, heart disease, etc. (Zhang *et al.*, 2020).

#### **Nickel**

Nickel concentration in effluent ranged from 0.08 to 0.19 mg/l with an average of  $0.13 \pm 0.03$  mg/l. The mean nickel level is within FEPA permissible limit. The concentration of nickel in groundwater ranged from 0.09 to 0.14 mg/l with a mean value of  $0.1 \pm 0.01$  mg/l. The average nickel concentration is above the SON and WHO limits which may be deleterious to consumers of the water samples tested. Mean nickel level of 0.018 mg/l was reported to be present in groundwater samples around Kano Metropolis (Tahir *et al.*, 2015). Nickel is a naturally occurring metal existing in various mineral forms and it is present in all compartments of the

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environment and ubiquitous in the biosphere (EPSA, 2015). The primary source of nickel in drinking water is leaching from metals in contact with the water such as pipes and fittings and it may also be present in some groundwater as a consequence of dissolution from nickel ore bearing rocks (Tiwari *et al.*, 2013). The source of nickel measured in this study may be attributable to municipal waste scattered virtually all around the study area. nickel present in dye effluent may also contribute to its concentration in groundwater. Nickel is used as alloy in nickel-plating and in the manufacture of batteries. Its toxicity is usually enhanced by the presence of other metals such as cobalt, copper, iron, and zinc in drinking water (Mandour, 2012).

Nickel is present in a number of enzymes in plants and microorganisms. In humans, it influences ion adsorption, metabolism, and may be an essential component of the haemopoietic process (Tiwari *et al.*, 2013). Short-term inhalation exposure causes damage to the lungs and kidneys. Effects of ingestion through drinking water include gastrointestinal diseases e.g., nausea, vomiting, diarrhea, and neurological effects. Long-term exposure via skin contact can result in nickel dermatitis consisting of itching of the fingers, hands, and forearms (Geiger and Cooper, 2010).

### Chromium

Chromium concentration in effluent samples ranged from 0.02 to 1.24 mg/l with a mean value of  $0.14 \pm 0.21$  mg/l. Mean chromium concentration found in the effluent studied is within FEPA limit. Rahman *et al.* (2020) have detected 0.212 mg/l in effluent from loom dye effluent in Bangladesh. Concentration of chromium in groundwater ranged from 0.04 to 0.18 mg/l with an average value of  $0.08 \pm 0.04$  mg/l. The mean chromium value is above the limit set by SON and is lower than that previously measured in groundwaters around Kano Metropolis (Yahaya *et al.*, 2017; Dabo and Saleh, 2017) except for values reported by Tahir *et al.* (2015). Chromium exists naturally as element in rocks, soils, volcanic emissions, plants, and animals. Natural deposits erosion and coating removal from water pipes may

contribute to chromium present in groundwater samples (Popoola *et al.*, 2019). Chromium has several oxidation states, the common ones being divalent ( $\text{Cr}^{+2}$ ), trivalent ( $\text{Cr}^{+3}$ ), and hexavalent ( $\text{Cr}^{+6}$ ) where  $\text{Cr}^{+3}$  is an essential nutrient while  $\text{Cr}^{+6}$  is listed as a known human carcinogen (Walker *et al.*, 2019). Hexavalent Chromium is widely used in numerous industrial processes including chrome pigment production, chrome plating, stainless steel manufacturing, leather tanning, etc. (Sun *et al.*, 2015). Trivalent Chromium is required by human body for insulin secretion that helps to maintain normal glucose metabolism in the body (Vetrimurugan *et al.*, 2017).

The short-term effects of hexavalent Chromium include shortness of breath, coughing, wheezing, and other effects on the respiratory tract. Inhalation and ingestion may also cause gastrointestinal effects including abdominal pain, vomiting, and hemorrhage (Geiger and Cooper, 2010). The long-term exposure to Chromium could cause kidney damage, lung cancer, high blood pressure, and bone defects (Popoola *et al.*, 2019). Chromium contaminated water in Greece indicated increased incidence in liver cancer, mortality, lung cancer, cancer of the kidney, and other genitourinary organs among women (Linos *et al.*, 2011).

### Lead

Concentration of lead in effluent ranged from 0.05 to 4.09 mg/l with an average of  $2.45 \pm 1.23$  mg/l. The mean lead concentration far exceeded the FEPA permissible limit. Lead concentration in groundwater ranged from 2.16 to 2.38 mg/l with an average value of  $2.27 \pm 0.06$  mg/l. The mean lead content far exceeds SON and WHO permissible limits of 0.01 mg/l and is also higher than the results obtained in previous studies. Previous mean concentration of lead found in groundwater samples in Kano Metropolis include 0.11 mg/l (Yahaya *et al.*, 2017; Tahir *et al.*, 2015) and 0.25 mg/l (Dabo and Saleh, 2017). The groundwater samples investigated are not fit for drinking due to excess lead levels.

Lead is used in the production of lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors etc. Uncontrolled disposal

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of lead acid batteries can cause relative high levels of lead in groundwater (Oyeku and Eludoyin, 2010). High lead concentration may originate from corrosion of brass fitting of certain types of submersible pumps used in groundwater wells (Sa'eed and Mahmoud, 2014). High concentration of lead could also be as a result of composed manure deposited on farms, littered petrol in cars, generators, and water pumps (Yusuf *et al.*, 2018). High lead level can also be attributed to leaching of natural deposits of lead ores in the soil into the groundwater (Popoola *et al.*, 2019).

Presence of lead in water beyond permissible level could result in hypertension, interference of vitamin D and calcium metabolism, and damage to tissues and organs (Popoola *et al.*, 2019). Exposure to lead results in significant behavioural and cognitive deficits such as impairment of activity, attention, adaptability, learning ability and memory, as well as increased distractibility. Acute intoxication with lead results in headaches, muscle tremor, abdominal cramps, kidney damage, etc. while chronic lead intoxication causes tiredness, irritability, joint pain, and gastrointestinal symptoms (WHO, 2011b).

## CONCLUSION

Effluent from non-industrial dyehouses was found to be non-biodegradable as the COD was about 4 times higher than the BOD. The effluent also contains high amounts of lead and sodium which could be responsible for the high values measured in groundwater samples. Groundwater investigated contain high levels of TDS, low concentration of DO (DO is vital to aquatic life), and heavy metal concentrations above the limits set by SON and WHO for drinking water quality. Lead content which is far above FEPA limits is alarming due to potential effects on children growth and development. Based on some physico-chemical parameters and heavy metals measured, the groundwater within 100 m radius from the dyehouses is not suitable for drinking and irrigation. The study recommends that the dyehouses should be relocated to industrial areas of the state where their activities can be closely monitored. Stringent environmental laws should

be created and existing ones should be enforced with regards to waste management. To mitigate harmful effects of dyes and auxiliaries, the dyers should be encouraged to revert to the use of eco-friendly natural indigo dyes which could be less polluting for sustainable development.

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