Physicochemical and Heavy Metal Analysis of Effluent from Selected Food and Pharmaceutical Industries in Kano Metropolis

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Abstract

Industrial pollution has been and continues to be a major threat to the environment affecting the water we use, the air we breathe and the soil we live on. Among the various industries, foods and pharmaceutical industries are one of the largest and most important based industries in Kano State, Nigeria. In this study, the content of Physicochemical (pH, Conductivity, Temperature, COD, BOD, TDS, TSS, DO, TOC, Turbidity, Total hardness, Nitrate and Nitrite) and heavy metals (Cd, Cr, Ni, Pb, Co, Zn, Fe, As and Cu) in the samples of effluent were analysed quantitatively between the year 2020 and 2021 for both wet and dry seasons respectively using standard analytical methods. All the parameters were more or less higher for the pharmaceutical than the food industries. The pH ranged between 7.34 to 7.89, conductivity was higher in the dry season to the wet season, the presence of nitrate and nitrite in all the samples is an indication the effluents are untreated. The presence of heavy metals like arsenic, cadmium, copper, lead, mercury, zinc, chromium was detected in all the samples analyzed. Availability of Fe was highest is sample GE (4.001±0.003 mg/kg) and Co was least (0.014±0.0004 mg/kg). In sample PA, 12.611±0.0060 and 0.040±0.0005 mg/kg was recorded as highest and lowest values for Cr and Co. Amount of Fe was the most in sample UG, and Cr the least (5.236±0.0024 and 0.058±0.0002 mg/kg). sample MY reported Cr as having the highest concentration (13.343±0.0052 mg/kg) while the least concentration (0.066±0.0011 mg/kg) was documented for Co. samples PA and AM showed Fe to be highest available metal with concentrations ordering as 1.531±0.0021, 1.376±0.001, 3.364±0.0022, 2.196±0.0002, 7.973±0.0052, 4.466±0.0021, 2.944±0.002, 2.418±0.0032, 1.889±0.0003, 7.804±0.009, 1.020±0.0013, 1.326±0.0020 and 9.103±0.005 mg/kg; lowest concentrations following the same sample arrangement order is listed as 0.044±0.0010, 0.004±0.0003, 0.032±0.0007, 0.051±0.0003, 0.029±0.0017, 0.015±0.0004, 0.012±0.001, 0.027±0.001, 0.024±0.0009, 0.037±0.0014, 0.015±0.0002, 0.031±0.0003 and 0.010±0.001 mg/kg for the elements Mn, Co, Co, Mn, Co, Pb, Pb, Mn, Co, Co, Mn, Mn and Cr. On the whole, the content of investigated physicochemical and heavy metals varied in different sampling sites and different parameters had different variations. The analysed contents indicated that the effluent

indicates that it may be become major source of water, soil and air pollution which will affect the flora and fauna inhabiting such environments.

Key words: Industrial Pollution, Food Industries, Pharmaceutical Industries, Effluents, Physicochemical Analysis, Heavy Metal Analysis

Introduction

Pollution has been documented as one of the most important problems in the world today as millions of world inhabitants suffer health problems related to industry and atmospheric pollutants. Recent years have witnessed significant attention being paid to the problems of environmental contamination by wide variety of chemical pollutants including heavy metals. Route for Heavy metals exposure into our environment have been determined to be both from natural and anthropogenic sources where they contaminate food source and are able to accumulate in both agricultural products and seafood products via water, air and soil pollution. Environmental pollution as anthropogenic phenomenon, is as a consequence of industrialization process, and constitutes one of the major problems that has to be solved or controlled [3]. Which if not, can lead to the contamination of freshwater and marine environment. Heavy metal ions are nowadays among the most important pollutants in surface and ground water [4; 5; 6].

Studies have related metal distribution between soil and vegetation as a key issue in assessing environmental effect of metals in the environment. Heavy metal toxicity has been documented to have an inhibitory influence on the growth of plants, enzymatic activity, photosynthetic activity and accumulation of other nutrient elements, and also damages the root system [8; 9].

This work is aimed at determining the physicochemical and heavy metals level of effluents in selected food and pharmaceutical industries of Kano State.

Materials and Methods:

The entire chemicals used were Analar grade.

Study Area

Manufacturing Industries and Industrial Estates in Kano metropolis very little, if anything, is mentioned of pre-colonial Kano industries. But most of the commodities taken away from Kano city included leather (the renowned Moroccan leather), dyed cloths (yan Kura) and plain-woven cloths [43-36] and are sufficient proof of the traditional industries that existed particularly in leather, textiles and dyeing. Modern industrial activities came with colonial administration. Just as the traditional dyeing industry was harmful in many ways and so the activity was concentrated in one place and usually at the outskirts of the city or the ward ("Karofi" in Hausa) so is the modern industrial set-up of the time polluting to the environment by way of its discharge or noise and so had to be secluded in estates. Economic reasons, in the form of benefits of agglomeration and economies of scale, also dictate the formation of industrial estates. Although industries don"t have to be concentrated in one place any more, Kano metropolis already has the Bompai, Challawa,

Sharada, and Tokarawa Industrial Estates which in design could be home to 1,200 Industries. In terms of organization, the Manufacturers" Association of Nigeria (MAN) is, so far, the voice of industrialists in Nigeria. In Kano MAN has an Executive Secretary and two chairmen managing the two industrial zones. The Bompai Industrial Zone (BIZ) is made up of the Bompai and *Tokarawa* (*Gunduwawa)* industrial estates, including all industries located outside the estates in the northern parts of Kano metropolis (*Dala, Fagge*, Nassarawa, and Tarauni LGAs). The Challawa/Sharada Industrial Zone (CIZ) comprises the Challawa and Sharada industrial estates, including all industries located outside the estates in the southern parts of Kano metropolis (Gwale, Kumbotso and Municipal LGAs). These are shown in Figure 3.1. The Bompai industrial estate was created in the 1950s (Olukoshi, 1996). Being the oldest industrial estate in Kano metropolis, it is home to some of the oldest industries in Kano. The estate is bordered in the south by the northern edge of the CBD, in the west by Sabon Gari and the Bompai G.R.A in the east. It was so successful that the Dakata industrial area was planned. However, Dakata industrial estate was only partially implemented. Thus the newly established industries were considered extensions of the Bompai industrial area**.**

Figure 1. Map of the Study Area, Kano State industrial area

Collection of Samples

Random sampling technique was employed to collect samples of the effluents in the industrial site listed. They were collected during irrigation and wet season.

Samples and their codes: PAL Pharmaceuticals (PA), Ugo Lab (UG), ASAD Pharmaceutical (AS), Chizy Foods (CH), Myer Foods (MY), Zhizou Industries (ZH), FECCOX Pharmaceuticals (FE), Gerawa Oil Mills (GE), Aminu Dawaki Industries (AM), Dala Foods (DA), Dangote Foods (DG), L and Z Foods (LZ), Seven up Bottling Company (SE), Santex industries (SA), Marley Shery Pharmaceuticals (MA)

Treatment of the Soil and Plant samples for Mineral analysis.

Appropriate quantities samples were digested by addition of 15.0 mL nitric acid, 20.0 mL perchloric acid and 15.0 mL hydrofluoric acid and placed on a hot plate for three (3 hour). On cooling, digest was filtered into a 100.0 mL volumetric flask and shall be made up to the mark with distilled water. Similarly, dry powdered samples were digested with 60% HClO4, concentrated $HNO₃$ and $H₂SO₄$. All the samples were treated in triplicates. The measurements were performed in vacuum using different filters (between the source and sample) for optimum detection of elements. A 0.05-mm-thick Ti filter was used in front of the source for Cu, Zn, As, Co, Fe, Pb, Cd, Ni and Cr with an applied voltage of 14 kV and a current 900 mA. The X-ray fluorescence spectra were quantitatively analysed by the, $nEXt$ ^{**}, system software runs under the Windows NTTM operating system integrated with the system [3], [23], [27], and [31].

Physicochemical Studies of the Samples

All equipment and meters for *in-situ* measurements was calibrated and checked according to the manufacturer's instruction before being put to use. Temperature $({}^{0}C)$, salinity, pH, electrical conductivity (EC), total dissolved solids (TDS) total suspended solid (TSS) was determined using probe instruments. Biochemical oxygen demand (BOD) and Chemical oxygen demand (COD) was evaluated following methods described by APHA standard method for the examination of water and wastewater (method 5210B and method for chemical analysis of water and wastes, EPA-600/4-79-020, USEPA, method 405.1), turbidity was measured using a turbidimeter. The concentration levels of nitrate, nitrite, phosphorus and phosphate, sulphate, chloride, and ammonium content as well as acidity and alkalinity were estimated using method recommended by [3]. Total organic carbon (TOC) was determined using the methods described by [27], [28] and [31]. The samples were collected and analysed in triplicates.

RESULTS:

SNO	Parameter	PA	UG	AS	CH	MY	ZH	FE	GE	AM	DA	DG	LZ	SE	SA	MA	WHO
	\mathbf{s}	$X\pm SD$	$X\pm S$	$X \pm SD$	$X \pm S$	$X \pm S$	$X \pm S$	$X \pm SD$	$X \pm SD$	$X \pm SD$	$X \pm SD$	$X\pm SD$	$X \pm SD$	$X\pm SD$	$X \pm SD$	$X \pm SD$	Limit
			D		\mathbf{D}	D	D										
$\mathbf{1}$	pH	$7.11+0$	$7.01 \pm$	$7.32+$	$7.42+$	$7.15+$	$7.24 \pm$	7.35 ± 0	8.19 ± 0	7.41 ± 0	$7.34 \pm 0.$	$7.31 \pm 0.$	7.34 ± 0	7.41 ± 0.0	$7.39 \pm 0.$	$7.36+0.$	$6-9$
		.00	0.01	0.02	0.11	0.10	30.11	.00.	.11	.11	10	00	.11	Ω	01	$00\,$	
$\overline{2}$	Conductivit	1120.0	1133.	1006.	1112.	1009.	1112.	1121.0	1431.0	1321.0	$1121.0\pm$	$1211.0+$	1367.0	1123.0 ± 0	$1003.0+$	$1101.0+$	1000
	y	± 0.11	0 ± 0.1	0 ± 0.1	$0 + 0.2$	0 _± 0.1	0.0010	± 0.11	± 0.00	± 0.02	0.11	0.00	± 0.00	.11	0.10	0.10	
	$(\mu s/cm)$		2	$\overline{1}$		1	$\overline{0}$										
3	TDS	$134.0 \pm$	234.0	242.0	167.0	253.0	245.0	$234.0+$	$301.0+$	$245.0+$	$208.0 + 0$	$213.0 + 0$	$289.0+$	$245.0 \pm 0.$	254.0 ± 0	$256.0+0$	2000
	(mg/L)	0.00	± 0.10	± 0.00	± 0.11	$\pm .010$	± 0.11	0.00	0.11	0.10	.00.	.00	0.00	$00\,$.10	.11	
4	Temp (°C)	$29.8 + 0$	$30.0 +$	$29.8 +$	$30.1\pm$	$29.9+$	$29.7+$	$30.1 + 0$	$29.9 + 0$	$30.0 + 0$	$29.8 \pm 0.$	$29.9 + 0.$	$29.7 + 0$	$30.0 + 0.0$	$28.9 + 0.$	$29.6 \pm 0.$	40.0
		.00.	0.00	0.00	0.00	0.00	0.00	.00	.00.	.00	$00\,$	$00\,$.00	θ	00	$00\,$	
5	Salinity	$1.07 + 0$	$1.01\pm$	$0.67 \pm$	$0.56\pm$	$0.78 +$	$1.01\pm$	$0.62 + 0$	1.11 ± 0	$1.04 + 0$	1.10.	$1.11 \pm 0.$	$1.12 + 0$	1.15 ± 0.0	$1.10+0.$	$1.13 \pm 0.$	\leq 250
	(mg/L)	.01	0.00	0.00	0.01	0.00	0.01	.00	.00	.00	± 0.00	00	.10	Ω	0 ⁰	$00\,$	
6	Sulphate	$105.0\pm$	121.0	126.0	111.0	101.0	113.0	$121.0+$	$124.0+$	$101.0+$	112.0 ± 0	$103.0 + 0$	$107.0+$	$127.0 + 0.$	$122.0 + 0$	$108.0 + 0$	200.0
	(mg/L)	$00\,$	± 0.11	± 0.00	± 0.10	± 0.11	± 0.11	0.00	0.12	0.00	.10	.00	0.00	$00\,$.00	.00	
7	Phosphate	0.51 ± 0	$0.52 +$	$0.43\pm$	$0.43 +$	$0.56 +$	$0.78 +$	0.77 ± 0	0.65 ± 0	$0.76 + 0$	$0.81 + 0.$	$0.75 + 0.$	$0.55 + 0$	0.73 ± 0.1	$0.45 \pm 0.$	$0.65 \pm 0.$	5.0
	(mg/L)	.00	0.00	0.00	0.00	0.01	0.10	.00.	.11	.10	10	00	.10		00	11	
8	DO(mg/L)	$2.08 + 0$	$2.80 +$	$2.34+$	$3.11 \pm$	$2.99 +$	$2.07 +$	$3.02 + 0$	3.45 ± 0	$2.89 + 0$	$3.01 \pm 0.$	3.77 ± 00	$2.98 + 0$	3.11 ± 0.0	$2.79 \pm 0.$	$3.40 \pm 0.$	$2 - 5$
		.00.	0.01	0.10	0.00	0.10	0.10	.00	.01	.10	01	Ω	10		$00\,$	10	
9	BOD	$1.98 + 0$	$2.33+$	$2.43+$	$2.33\pm$	$2.64 \pm$	$1.99 \pm$	2.91 ± 0	$2.89 + 0$	$2.91 + 0$	$2.55 \pm 0.$	$2.92 \pm 0.$	$2.92 + 0$	$2.88 + 0.1$	$2.90 \pm 0.$	$2.69 \pm 0.$	50.0
	(mg/L)	.00	0.10	0.00	0.00	0.10	0.11	.00	.00	.01	00	11	.00	Ω	11	0 ⁰	
10	COD	$388.1 \pm$	411.0	398.0	$501\pm$	201.0	811.0	389.0±	$878 + 0.$	$541.0+$	549.0±0	679.0 ± 0	$362.0 \pm$	$541.0 \pm 0.$	442.0 ± 0	621 ± 0.1	1000.0
	(mg/L)	0.11	± 0.10	±011	0.00	± 0.00	± 0.11	0.11	12	0.11	.12	.11	0.11	10	.11	$\overline{2}$	
11	Alkalinity	7.11 ± 0	$5.01 \pm$	$6.23 \pm$	$5.56 \pm$	$6.45 \pm$	$7.34+$	$5.01 + 0$	6.23 ± 0	4.11 ± 0	$6.76 \pm 0.$	$7.77 + 0.$	5.99 ± 0	6.77 ± 0.0	$6.99 \pm 0.$	$7.34 \pm 0.$	
	(mg/L)	.11	0.11	0.01	0.11	0.00	0.01	.11	.11	.01	01	01	.01		11	00	
12	Turbidity	15.0 ± 0	$31.0+$	$17.0 \pm$	$22.0+$	$28.0+$	$32.0+$	$23.0 + 0$	$27.0 + 0$	$25.0 + 0$	$19.0 + 0.$	$26.0 + 0.$	$28.0 + 0$	$19.0 + 0.1$	$32.0 \pm 0.$	$35.0 + 0.$	
	(NTU)	Ω	0.01	0.01	0.10	0.01	0.00	.10	.01	.01	01	10	.01	Ω	01	10	
13	Nitrate	$1.9 \pm 0.$	2.1 ± 0	$1.1 \pm 0.$	1.19±	$1.21 +$	$1.01\pm$	1.11 ± 0	$1.17 + 0$	1.12 ± 0	$1.34 \pm 0.$	$1.04 \pm 0.$	1.03 ± 0	132 ± 0.11	$1.17 + 0.$	$1.21 \pm 0.$	
	(mg/L)	01	.10	$00\,$	0.10	0.10	0.00	.00.	.01	.10	01	00	.00		$00\,$	$00\,$	
14	Total	30.3 ± 0	$37.8+$	$55.3+$	$41.0 \pm$	$32.6 \pm$	$29.8 \pm$	33.6 ± 0	$61.0 + 0$	$31.0 + 0$	$48.0 \pm 0.$	$32.9 + 0.$	42.6 ± 0	36.8 ± 0.0	$39.8 \pm 0.$	$42.7 \pm 0.$	
	Hardness	.01	0.10	0.00	0.10	0.00	0.00	.10	.11	.12	$00\,$	11	.00	Ω	11	$00\,$	
	(mg/L)																

Table 2: Results of Physicochemical analysis of waste water from selected industries in Kano (Wet season 2020)

Table 3: Results of Physicochemical analysis of waste water from selected industries in Kano (Dry season 2021)

SNO	Parameters	PA	UG	AS	CH	MY	ZH	${\bf F}{\bf E}$	GE	AM	DA	DG	LZ	SE	SA	MA	WHO
		$X\pm SD$	$X\pm SD$	$X\pm SD$	$X\pm SD$	$X \pm SD$	$X \pm SD$	$X \pm SD$	$X \pm SD$	$X \pm SD$	$X \pm SD$	$X\pm SD$	$X\pm SD$	$X\pm SD$	$X\pm SD$	$X\pm SD$	Limit
	pH	$7.77 \pm 0.$	$7.82 +$	7.99 ± 0	$8.01 + 0$	$7.97 + 0$	8.02 ± 0	$7.85 \pm 0.$	$8.87 \pm 0.$	$7.89 \pm 0.$	7.87 ± 0.1	7.72 ± 0.0	$7.98 \pm 0.$	7.95 ± 0.00	8.09 ± 0.0	8.12 ± 0.0	$6-9$
		0 ⁰	0.01	.02	.11	.10	.11	0 ⁰	11	11	Ω	Ω	11			Ω	
	Conductivity	$1143.0\pm$	1475.	1287.0	1396.0	1349.0	1228.0	$1555.0 \pm$	$1656.0\pm$	$1477.0+$	1305.0 ± 0	$1399.0 + 0$	$1402.0 \pm$	$1422.0 \pm 0.$	$1288.0 + 0$	1441.0 ± 0	1000
	$(\mu s/cm)$	0.11	0 ± 0.1	± 0.11	± 0.21	± 0.11	± 0.00	0.11	0.00	0.02	.11	.00	0.00	11	.10	.10	
			2														
3	TDS (mg/L)	299.0 ± 0	343.0	$333.0+$	$321.0 \pm$	$377.0 \pm$	$356.0 \pm$	$398.0 + 0$	409.0 ± 0	411.0 ± 0	$378.0 \pm 0.$	$388.0 \pm 0.$	$398.0 + 0$	399.0 ± 0.0	$365.0 \pm 0.$	$391.0 \pm 0.$	2000
		.00.	± 0.10	0.00	0.11	.010	0.11	.00	.11	.10	$00\,$	00	.00	Ω	10	-11	
	Temp $(^{\circ}C)$	$29.2 \pm 0.$	$30.1\pm$	29.9 ± 0	30.6 ± 0	29.3 ± 0	29.6 ± 0	$30.0 \pm 0.$	$29.9 \pm 0.$	$30.2 \pm 0.$	29.9 ± 0.0	29.9 ± 0.0	$29.3 \pm 0.$	29.0 ± 0.00	28.4 ± 0.0	29.9 ± 0.0	40.0
		00 ¹	0.00	.00	.00	.00	.00	0 ⁰	0 ⁰	0 ₀	Ω	Ω	0 ₀		Ω	Ω	
5	Salinity	$2.41 \pm 0.$	$2.11 \pm$	1.23 ± 0	.99 \pm 0	$1.98 + 0$	$1.97 + 0$	$2.02 \pm 0.$	$1.98 \pm 0.$	$1.87 \pm 0.$	2.11.	2.03 ± 0.0	$1.98 \pm 0.$	2.06 ± 0.00	$1.78 + 0.0$	1.88 ± 0.0	\leq 250
	(mg/L)	01	0.00	.00	.01	.00	.01	$00\,$	$00\,$	$00\,$	± 0.00	Ω	10		$\mathbf{0}$	θ	
6	Sulphate	168.0 ± 0	176.0	$177.0+$	$182.0 \pm$	$167.0 \pm$	$189.0+$	156.0 ± 0	189.0 ± 0	178.0 ± 0	145.0 ± 0	$159.0 \pm 0.$	153.0 ± 0	154.0 ± 0.0	$155.0 \pm 0.$	$156.0+0.$	200.0
	(mg/L)	$\overline{0}$	± 0.11	0.00	0.10	0.11	0.11	.00	.12	.00	10	0 ⁰	.00	Ω	$00\,$	$00\,$	
7	Phosphate	$0.98 \pm 0.$	$0.91 \pm$	$0.79 + 0$	0.92 ± 0	1.05 ± 0	$0.89 + 0$	$0.89 \pm 0.$	$1.22 \pm 0.$	$0.87+0.$	0.96 ± 0.1	0.84 ± 0.0	$0.77 \pm 0.$	0.89 ± 0.11	0.76 ± 0.0	0.81 ± 0.1	5.0
	(mg/L)	00	0.00	.00	.00	.01	.10	$00\,$	11	10	Ω	Ω	10		Ω		
8	DO(mg/L)	2.1 ± 0.0	$2.86 \pm$	2.51 ± 0	3.34 ± 0	2.67 ± 0	2.54 ± 0	$3.76 \pm 0.$	$3.61 \pm 0.$	$2.98 \pm 0.$	3.22 ± 0.0	3.70 ± 000	2.93 ± 01	3.34 ± 0.01	2.89 ± 0.0	3.77 ± 0.1	$2 - 5$
		Ω	0.01	.10	.00	.10	.10	0 ⁰	01	10			Ω		0	0	
9	BOD (mg/L)	$1.98 \pm 0.$	$2.22+$	1.95 ± 0	2.34 ± 0	2.34 ± 0	2.35 ± 0	$2.78 \pm 0.$	$2.43 \pm 0.$	$2.88 \pm 0.$	2.23 ± 0.0	2.56 ± 0.1	$2.34 \pm 0.$	2.32 ± 0.10	2.79 ± 0.1	2.87 ± 0.0	50.0
		$00\,$	0.10	.00	.00	.10	.11	$00\,$	$00\,$	01	$\mathbf{0}$		$00\,$			θ	
10	COD (mg/L)	381.9 ± 0	419.9	$399.5+$	$522.0 \pm$	$223.4+$	819.4 \pm	389.5 ± 0	889.7±0	549.9±0	599.8 \pm 0.	$688.2 \pm 0.$	377.7 ± 0	567.6 ± 0.1	$456.5 \pm 0.$	676 ± 4.12	1000.0
		.11	± 0.10	011	0.00	0.00	0.11	.11	.12	.11	12	11	.11	Ω	11		
11	Alkalinity	$7.32 \pm 0.$	$5.56\pm$	$6.28 + 0$	5.66 ± 0	6.76 ± 0	7.44 ± 0	$5.56 \pm 0.$	$6.99 \pm 0.$	$4.78 \pm 0.$	6.77 ± 0.0	7.87 ± 0.0	$6.11 \pm 0.$	6.98 ± 0.01	7.32 ± 0.1	7.88 ± 0.0	
	(mg/L)	11	0.11	.01	.11	.00	.01 $66.0+0$	11	11	01		65.0 ± 0.1	01			Ω	
12	Turbidity	56.0 ± 00	$67.0+$ 0.01	76.0 ± 0 .01	$76.0 + 0$.10	69.0 ± 0 .01	.00	$76.0 \pm 0.$ 10	$66.0+0.$	$65.0+0.$	67 ± 0.01		$56.0+0.$	68.0 ± 0.10	78.0 ± 0.0	59.0 ± 0.1	
13	(NTU)	3.4 ± 0.0	$4.6 \pm 0.$	$2.4 \pm 0.$	3.43 ± 0		$2.4 \pm 0.$	$3.41 \pm 0.$	01	01	2.99 ± 0.0	Ω 2.73 ± 0.0	01	3.53 ± 0.11	3.98 ± 0.0	Ω 4.11 ± 0.0	
	Nitrate			0 ⁰	.10	3.22 ± 0 .10	0 ⁰	00 ²	$2.22 \pm 0.$	$4.33 \pm 0.$ 10			$3.51 \pm 0.$ 0 ₀		0		
14	(mg/L)		10 $44.8 \pm$	55.9 ± 0	49.9 \pm 0	45.7 ± 0			01 $90.8 + 0.$			Ω 54.7 ± 0.1	$41.8 \pm 0.$	56.1 ± 0.00		Ω	
	Total Hardness	$39.9 \pm 0.$ 01	0.10	.00	.10	.00	45.1 ± 0 .00	$46.9 \pm 0.$ 10	11	$44.5 \pm 0.$ 12	557 ± 0.00		00		59.2 ± 0.1	51.3 ± 0.0 Ω	
	(mg/L)																

Table 4: Results of Physicochemical analysis of waste water from selected industries in Kano (Wet season 2021)

Table 5: Mean Concentration of heavy metals in wastewater from selected industries in Kano (dry season 2020)

Table 6: Mean Concentration of heavy metals in wastewater from selected industries in Kano (wet season 2020)

Table 7: Mean Concentration of heavy metals in wastewater from selected industries in Kano (dry season 2021)

Table 8: Mean Concentration of heavy metals in wastewater from selected industries in Kano (wet season 2021)

DISCUSSIONS

Industrial pollution has continue to be a major factor causing the degradation of the environment in developing countries like Nigeria, affecting the water we use, the air we breathe and the soil we live on [12] and [23]. The exponential increase in industrialization is not only consuming large areas of Agriculture lands, but simultaneously causing serious environmental degradation as well as to soil. Water originating from various industries is finding their place in Agriculture. Random samples of water were collected with the waste effluent, plants and soil samples from the industrial site listed for both dry and wet season during the 2020 and 2021 season. All samples were analysed in triplicates and the outcome values are presented as "mean concentration" as revealed in Table 1 to 8.

Table 1 shows the results of physicochemical analysis of waste water from selected industries in Kano (Dry season 2020); pH is an important parameter in evaluating the acid–base balance of water. The pH of the samples ranges between 7.34 \pm 0.11 (sample ZH) to 8.99 \pm 0.11 (Sample GE). The pH values of the samples were within the permissible limits $(6.0 - 9.0)$ set by FEPA and WHO. The average pH of the effluent was found to be within the range set by FEPA and WHO similar to that of [6] [25] and [36]. This could explain the high counts of microorganisms because most of them thrive well in such pH value. However, pH of the treated effluent is slightly alkaline. Discharge of such effluent with alkaline pH into ponds, and rivers for irrigation may be detrimental to aquatic biota such as zooplankton and fishes. [37], [38] and [39] revealed that alkaline nature of the industrial effluent may be due to the presence of carbonates and bicarbonates present in the effluent.

Conductivity: Electrical conductivity is the measure of water capacity to convey electric current. Electrical conductivity of water is directly proportional to its dissolved mineral matter content [12], [15], [24] and [38]. The source of conductivity may be an abundance of dissolved salts due to addition of table salt in food materials, actual salt present in pure water, and other mineral discharges. The conductivity values were found to range from 1045.0 ± 0.11 (sample PA) to 1631 ± 0.00 μs/cm³ (sample GE). The conductivity values for the samples were above the FEPA and WHO guideline value of 1000 μ s/cm³ for the discharge of wastewater. Total dissolved solids of untreated effluent was found to be between 279.0 ± 0.11 (sample SA) to 397.0 ± 0.11 mg/L (sample GE). The value was within the tolerance limits (2000 mg/L) by FEPA and WHO. Total Dissolved Solids (TDS) is the measure of total inorganic salts and other substances that are dissolved in water [24] and [30]. High levels of TDS are aesthetically unsatisfactory and may also produce distress in human and livestock [31]. Total dissolved solids are mainly due to carbonates, bicarbonates, chlorides, sulphates, phosphates, nitrates, nitrogen, calcium, sodium, potassium and iron [32] [33] and [34]. Temperature: Temperature is basically important for its effect on other properties of wastewater. Release of high temperature waste water into water bodies may speed up some reactions in the water body. It will also reduce solubility of oxygen and amplified odour due to anaerobic reaction (less oxygen). The temperature values for the various samples ranged from 28.9 ± 0.01 (sample SA) – 30.0 ± 0.01 °C (sample AM). The temperature values of all the samples analyzed were within the permissible limits of FEPA and WHO. Salinity:

The salinity values of all the samples were found to range between 0.98 ± 0.00 (sample AM) to 1.51 ± 0.00 (mg/L) sample GE. The Salinity of all the samples analyzed were far below the FEPA limit of \leq 250 mg/L

Sulphate and Phosphate: Sulpates are formed due to the decomposition of various sulfur-containing substances present in water bodies. Phosphates are mostly from fertilizers, pesticides, industry, and cleaning compounds. Natural sources include phosphate-containing rocks and solid or liquid wastes [35]. The Sulphate values of the samples ranges between 119.0 \pm 0.00 (sample DG) to 162 \pm 0.00 mg/L (sample GE). The Phosphate ranged from 0.57 \pm 0.00 (sample SA) to 0.98 mg/L (sample MY). The mean sulphate and phosphate concentrations of all the samples were below the 200mg/l for sulphate and 5mg/l for phosphate acceptable limit set by FEPA and WHO. Chemical Oxygen Demand (COD) test is used as an alternative to the Biological Oxygen Demand (BOD) test which is a measure of the polluting organic matter present in a sample. When effluents are discharged into water bodies, some of the waste is oxidized by the micro-organisms present, and this creates an oxygen demand. Consequently, the dissolved oxygen level and the saturation percentage fall and an oxygen deficit is created. If the deoxidation rate exceeds the reoxidation rate from the atmosphere then the oxygen deficit persist and these are the conditions of water pollution and disruption of the aquatic ecosystem. From the results of analysis, (Table 1) there was a high Chemical Oxygen Demand (COD). Samples GE had an average value of 878.0 ± 0.12 mg/l which is the highest value recorded. The reason for this very high value is because it is the point of poor handling of waste by the company. The nitrate contents of the effluents were very low to cause significant health problem. The [35] stipulates that nitrate value above 10.0 mg/L in water will cause a problem known as methaemoglobinaemia which is usually common in new born babies, hence the name Blue Baby Disease. This is a situation in which the nitrate reacts with the oxygen-carrying pigment, haemoglobin, reducing the ability of the pigment to transport oxygen to the body. This can lead to anorexia. The average nitrate values of the effluents ranged from 2.03 ± 0.11 mg/L for sample DG to 4.22 ± 0.12 mg/L for sample MA. The values recorded are however, capable of having an indirect effect on the aquatic ecosystem and humans. This indirect effect is called eutrophication [36]

Wet Season (2020). pH: The pH of the samples ranged from 7.01 ± 0.01 (sample UG) to $8.19\pm$ 0.11 (sample GE) as presented in Table 2. Sample GE has the highest pH value of 8.19, while sample UG has the lowest pH value of 7.01. All the pH values were within the permissible limits for industrial effluents set by FEPA $(6.0 - 9.0)$. The pH is an important parameter in evaluating the acid–base balance of water. The pH for the wet season (2020) is however lower due to leaching of the dissolved minerals by rain in the wet season. Electrical conductivity (EC), TDS, Total alkalinity, sulphate and phosphate, DO and COD ranged from Electrical conductivity; 1006 ± 0.11 (sample AS) to 1431.0 ± 0.11 µs/cm for Sample GE, TDS; 134 ± 0.11 (sample PA) to 301 mg/L \pm 0.10 (sample GE). The Total alkalinity ranged from 4.11 ± 0.00 (sample AM) to 7.77 (sample DG), DO ranged from 2.07 ± 0.11 (sample ZH) to 3.77 ± 0.00 mg/L (sample DG), COD ranged from 201 \pm 0.00 (sample MY) to 878 \pm 0.11 mg/L (sample GE). Generally there is increase in the EC, TDS, Alkalinity, DO and COD of the analysed samples during the wet season which could be attributed to accumulations. The analysed physicochemical parameters for 2021 season (dry and wet) showed similar trend as in the 2020 season (dry and wet), indicating higher accumulations in the dry season and lower levels in the wet season. Total dissolved solids are mainly due to carbonates, bicarbonates, chlorides, sulphates, phosphates, nitrates, nitrogen, calcium, sodium, potassium and iron. The presence of high level of TSS and TDS may be due to the insoluble organic and inorganic present in the effluent [37]. In our study, maximum level (318.5 mg/L) of potassium was recorded in untreated effluent of one year under study which was very much higher than the previous study conducted by [38], where the level was 600 mg/L. It was reported that the levels of exchangeable cations (sodium and potassium) in the soil irrigated with tannery waste water were found to be high [39]. The waste discharged from food and pharmaceutical processing industries are degradable waste, though it is hazardous to microorganism in the costal water. The extent of pollution was high as expressed by physicochemical properties. Analysis of industrial effluent discharge showed that the various parameters are beyond the permissible limit. The effluent from two industries shows acidic pH while remaining samples have alkaline pH. These values are generally due to the decomposition of the proteinaceous matter and emission of ammonia [40]

Investigated mineral deposits ($m g / k g$) in the industrial effluents of various industries (dry season 2020) is presented in Table 5. The composition of metals in the wastewater samples ranged from Zn; 0.92 ± 0.01 (sample GE) to 5.44 ± 0.01 (sample PA), Cd; 0.82 ± 0.10 (sample AS) to 2.22 ± 0.04 (sample SA), Fe; 49.55 ± 0.02 (sample SE) to 100.62 ± 0.00 (sample PA), Cu; 0.12 ± 0.00 (sample CH) to 0.36 ± 0.01 (sample PA), Ni; 0.01 ± 0.00 (sample AS) to 0.22 ± 0.00 (sample CH), As; 1.32 ± 0.00 (sample AS) to 9.63 ± 0.07 (sample MA), Co; 0.21 \pm 0.00 (sample DG) to 0.44 \pm 0.02 (sample DA), Pb; 0.05 \pm 0.01 (sample CH) to 1.17 \pm 0.02 (sample PA) and Cr; 0.45 ± 0.01 (sample UG) to 0.92 ± 0.00 (sample MA). The concentrations (mg/kg) of metals in the samples analysed are in the following order Fe>As>Zn>Cd>Pb>Cr>Co>Cu>Ni. While Fe and Ni can improve crop yield, only trace amount of Zn is required but, Pb and Cd are toxic. Highest amount of all the heavy metals analysed were found in sample PA and MA. while, the lowest amount of Cd and Pb were found in sample CH and AS. The concentration of heavy metals (Pb, Cd and Zn) in all the samples analysed were far above the maximum permissible level recommended by [35]. Wastewater discharge from industrial processing industries are major component of water pollution, contributing to oxygen demand and nutrient loading of the water bodies, promoting toxic algal blooms and leading to a destabilized aquatic ecosystem. The presence of oil and grease in an effluent was mainly due to the processing operations. It should be removed since they usually float and affect the oxygen transfer to the water and also objectionable from an aesthetic point of view.

The pollution by minerals in the wet season of 2020 was more than that of the dry season as revealed in Table 6. The higher concentrations of the minerals could be attributed to deposit and accumulation over time by wet season on the soils [41]. The trend of the mineral pollution in the

dry and wet season of 2021 is similar to the pattern of 2020 with the same elements having higher concentrations above the limit set by FEPA and WHO in both seasons. The results of physicochemical analysis of soil samples from selected industries in Kano (Dry season 2020) showed that the pH of the samples ranged from 7.77 ± 0.10 (sample DA) to 8.99 ± 0.11 (sample GE) which are closely within the set level by WHO, conductivity (μ S/cm); 0.234 \pm 0.11 (sample PA) to 0.431 \pm 0.11 (sample AS), Organic carbon (OC %); 0.89 \pm 0.11 to 1.42 \pm 0.10 (sample AM), Salinity (mg/L); 65.33 ± 0.00 (sample UG) to 98.28 ± 0.10 (sample LZ), Sulphate (mg/L); 141.0 ± 0.11 (sample UG) to 187.0 ± 0.00 (sample MA), phosphate (mg/L); 0.81 ± 0.10 (sample AM) to 0.99 ± 0.10 (sample DA), Nitrate (mg/L); 3.07 ± 0.01 (sample GE) to 4.9 ± 0.10 (sample PA). The presence of nitrates in the samples is a clear indication that the effluents from the industries are untreated and contaminations. The total hardness (mg/L) ranged from; 129.3 ± 0.00 (sample ZH) to 164 ± 0.11 (sample GE). The physicochemical analysis of the wet season for 2020 showed that is an important parameter in evaluating the acid–base balance of water. The pH of the samples ranges between $8.6 - 8.7$. Sample A has the highest pH value of 8.7, while samples B and C have the same pH value of 8.6. The pH values of the samples were within the permissible limits $(6.0 - 9.0)$ set by FEPA and WHO. Conductivity: Electrical conductivity is the measure of water capacity to convey electric current. Electrical conductivity of water is directly proportional to its dissolved mineral matter content [32]. Salinity: The salinity values of all the samples were found to be the same (0.05ppt). The Salinity of all the samples analyzed were far below the FEPA limit of ≤250.0 ppt. Total Dissolved Solids: The concentration of TDS of the samples ranges from 163.0 to 180.0 mg/L. Sample A recorded the highest TDS concentration, while the lowest concentration of TDS was recorded in samples analysed. These values obtained for TDS in all the samples were found to be below the WHO standard of 2000.0 mg/L for the discharge of waste water into surface water. Sulphate and Phosphate: Sulfates are formed due to the decomposition of various sulfur-containing substances present in water bodies. Phosphates are mostly from fertilizers, pesticides, industry, and cleaning compounds. Natural sources include phosphatecontaining rocks and solid or liquid wastes.

Dissolved Oxygen: DO is a measure of the degree of pollution by organic matter and the destruction of organic substances, as well as the self-purification capacity of the water body. The maximum tolerance limit for fish is 5.0 mg/L, and below 2.0 mg/L leads to death. Dissolved oxygen (DO) values obtained for the samples varied between $0.8 - 2.4$ mg/L. The DO value of sample A is the lowest, while Sample C has the DO value of 2.4 mg/L. The DO values of all the samples were within the $2 - 5$ mg/L minimum and maximum tolerance limits, except for sample AM which is below this range.

All samples were analysed in triplicates and the outcome values are presented as "mean concentration" (Table 5 to 8) in mg/kg; generally, Fe recorded the highest metal concentration $(115.02\pm0.00 \text{ mg/kg})$ in sample PA wet season 2020, while lowest metal concentration $(0.05\pm0.00 \text{ m})$ mg/kg) was recorded by Pb in sample FE dry season 2020. The concentration of Ni raged between 0.378 ± 0.0003 mg/kg (sample PA) to 0.003 ± 0.002 mg/kg (sample AS). Concentration for Pb ranged from 1.116 ± 0.001 mg/kg in sample UG to 0.011 ± 0.001 mg/kg in sample ZH. Fe concentration ranged between 40.947±0.007 to 0.896±0.0010 mg/kg in samples DA and LZ

respectively. Mn has concentration ranging between 1.262±0.002 mg/kg (sample DG) and similar values of 0.015±0.001 mg/kg for samples GE and MY. Values recorded for Zn ranged between 3.323±0.0041 mg/kg and 0.044±0.0014 mg/kg. Cd has concentration range between 0.3210±0.002 and 0.241±0.0010 mg/kg (samples MA and SE). For Co, concentration recorded ranged between 0.208 ± 0.0012 mg/kg in sample CH and 0.002 ± 0.0004 mg/kg in sample AM. Cr has values ranging between 62.232±0.004 and 0.002±0.002 mg/kg (samples UG and CH).

For elements measured in sample FE, Fe recorded the highest concentration (2.426 ± 0.001) mg/kg) while Co had the least (0.254±0.001 mg/kg). In sample AS, Fe also recorded the highest concentration (1.955 \pm 0.0010), and Mn the lowest (0.037 \pm 0.001). Samples GE and SA also revealed highest metal concentrations for Fe (2.429±0.001, 5.878±0.0072, 5.581±0.003, 3.562±0.002, 12.774±0.003, 2.066±0.002 mg/kg), with corresponding least concentrations of 0.040 \pm 0.0002, 0.106 \pm 0.002, 0.085 \pm 0.0011, 0.023 \pm 0.0004, 0.045 \pm 0.0013, 0.015 \pm 0.0003 mg/kg for Mn, Zn, Mn, Co, Co and Cr respectively. Cr gave highest in sample 9 (62.232±0.004) and Ni lowest (0.010±0.0014). The highest elemental concentrations in samples 10-17 was recorded by Fe as 1.525 ± 0.0014 , 2.087 ± 0.0004 , 3.567 ± 0.002 , 3.365 ± 0.008 , 4.795 ± 0.003 , 7.506 ± 0.006 , 1.918±0.0012 and 1.078±0.0003 mg/kg, while the lowest values recorded following same order was documented for the elements Mn, Co, Mn, Pb, Pb, Ni, Ni and Mn with their corresponding values of 0.035±0.001, 0.016±0.0013, 0.017±0.001, 0.058±0.0004, 0.108±0.0004, 0.003±0.002, 0.022 \pm 0.001 and 0.011 \pm 0.0003 mg/kg. In sample SA, Cr concentration was 4.990 \pm 0.0014, and Co reported a lowest value of 0.072±0.0011 mg/kg. Again, Fe was estimated highest in samples 19- 40 with concentrations of 6.978±0.005, 15.600±0.010, 1.601±0.001, 1.672±0.001, 2.725±o.oo1, 11.248±0.006, 1.364±0.0003, 6.130±0.0033, 14.911±0.007, 27.505±0.008, 19.171±0.009, 3.103 ± 0.0020 , 40.947 ± 0.007 , 1.453 ± 0.001 , 39.311 ± 0.007 , 9.701 ± 0.0041 , 2.830 ± 0.002 , 2.602±0.002, 3.082±0.002, 0.896±0.0010, 2.312±0.002 and 2.307±0.0012 mg/kg; their corresponding least concentrations were validated following same order are listed as 0.032 ± 0.0012 , 0.067 ± 0.001 , 0.002 ± 0.0004 , 0.057 ± 0.0001 , 0.021 ± 0.0014 , 0.085 ± 0.0004 , 0.049 ± 0.0004 , 0.023 ± 0.0002 , 0.013 ± 0.0006 , 0.018 ± 0.0002 , 0.020 ± 0.001 , 0.042 ± 0.002 , 0.081 ± 0.0013 , 0.015 ± 0.0011 , 0.011 ± 0.0005 , 0.002 ± 0.002 , 0.009 ± 0.0010 , 0.061 ± 0.001 , 0.072 ± 0.0003 , 0.006 ± 0.0017 , 0.046 ± 0.0015 and 0.076 ± 0.0001 for the elements Co, Pb, Co, Cr, Co, Cr, Mn, Co, Co, Cr, Ni, Ni, Co, Co, Co, Cr, Co, Mn, Mn, Co, Co and Pb. In Sample DA, Cr reported the highest concentration $(24.434\pm0.0011 \text{ mg/kg})$ while Pb was the lowest $(0.011\pm0.001$ mg/kg). Availability of Fe was highest is sample GE $(4.001\pm0.003 \text{ mg/kg})$ and Co was least $(0.014\pm0.0004 \text{ mg/kg})$. In sample PA, 12.611 ± 0.0060 and $0.040\pm0.0005 \text{ mg/kg}$ was recorded as highest and lowest values for Cr and Co. Amount of Fe was the most in sample UG, and Cr the least (5.236±0.0024 and 0.058±0.0002 mg/kg). sample MY reported Cr as having the highest concentration (13.343 \pm 0.0052 mg/kg) while the least concentration (0.066 \pm 0.0011 mg/kg) was documented for Co. samples PA and AM showed Fe to be highest available metal with concentrations ordering as 1.531±0.0021, 1.376±0.001, 3.364±0.0022, 2.196±0.0002, 7.973±0.0052, 4.466±0.0021, 2.944±0.002, 2.418±0.0032, 1.889±0.0003, 7.804±0.009, 1.020±0.0013, 1.326±0.0020 and 9.103±0.005 mg/kg; lowest concentrations following the same sample arrangement order is listed as 0.044 ± 0.0010 , 0.004 ± 0.0003 , 0.032 ± 0.0007 , 0.051 ± 0.0003 , 0.029 ± 0.0017 , 0.015 ± 0.0004 , 0.012 ± 0.001 , 0.027 ± 0.001 , 0.024 ± 0.0009 , 0.037 ± 0.0014 ,

 0.015 ± 0.0002 , 0.031 ± 0.0003 and 0.010 ± 0.001 mg/kg for the elements Mn, Co, Co, Mn, Co, Pb, Pb, Mn, Co, Co, Mn, Mn and Cr. On the whole, the content of investigated heavy metals varied in different sampling sites and different heavy metals had different variations.

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