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AN IMPACT ASSESSMENT OF DYE WASTEWATER OF SELECTED SITES IN URBAN KANO, NIGERIA

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ABSTRACT
The discharge of unprocessed dye wastewater is one of the main sources of severe pollution problems worldwide. This study characterized dye wastewater by measuring physicochemical characteristics and concentrations of some selected heavy metals. The average pH values of wastewater for the three dyeing sites were, Kofar Mata; 11.14, Kofar Na'isa, 12.03 and Zawaciki, 11.95, all exceeding the acceptable limit. The average electric conductivity values were 2657.50µS/cm, 3198.91µS/cm and 4141µS/cm respectively, also exceeding standard limit. The average concentrations of selected heavy metals analyzed were higher than the standard limits set by the FEPA (1991). Temperature, dissolved oxygen, biochemical oxygen demand, total suspended solids, total dissolved solids, alkalinity, chloride and phosphate were found to be within the FEPA acceptable limits. The values for turbidity and chemical oxygen demand also exceeded acceptable limits. Nitrate value in Kofar Na'isa was within acceptable limit while, Kofar Mata and Zawaciki values exceeded the acceptable limit. This calls for further monitoring of both people exposed to these dyes and their associates as well as the environment to detect possible symptoms of related ailment and take appropriate measures to prevent further damages.
Key words: textile dyes, dye wastewater, physicochemical parameters, heavy metals

INTRODUCTION

Human actions and activities have created several environmental problems with varying magnitude from one place to another. In the last 15 years, a new dyeing practice has emerged in urban Kano. The increasing spread of this secondary dyeing processing activity is causing some concern to the population. In urban Kano, it has become very common to see places where this re-dyeing of textile materials (clothes) is taking place. The interest to change the colour of one's textile material to another seems personal, because people generally have different colour preferences. Similarly, the impact of the discharged wastewater from this activity on land (soil) organisms, aquatic flora and fauna (species, composition, distribution and diversity), public health and environmental safety at present and in the immediate future needs to be given due consideration (Sani, 2015).

Dye is a natural or synthetic substance that can be used to colour something, e.g. a textile or hair, and is most often applied as a liquid (Kuberan *et al*., 2011). Dyeing is the process of adding colour to materials, such as textile fibers, yarns, and fabrics, so that the colouring matter becomes an integral part of the dyed material (Jayanth *et al*., 2011). Dyeing is normally done in a special solution containing dyes and particular chemical material. After dyeing, dye molecules have uncut chemical bond with fiber molecules, and about 10-20% of the dye remains in the dye bath which is discharged along with other residual chemicals as exhausted dye wastewater (Sajjala *et al*., 2008). In addition to imparting colour, dye wastewater also contributes to organic and inorganic load of the receiving streams. The dye wastewater is typically characterized by residual colour, alkaline pH, excess TDS content, high COD with relatively low BOD values (Sajjala *et al*., 2008).

The wastewater from the dyeing process is usually discharged on open land or soil nearby or into drains that subsequently flow to ditches, burrow pits, ponds and other important aquatic ecosystems. It is estimated that 10 to 15 % of the dye is lost in the effluent during dyeing process (Kuberan *et al*. 2011).

There are areas particularly where the wastewater is used for irrigation by peri-urban vegetable growers at Kofar Na'isa or seep into shallow public wells used for drinking and other domestic activities (Sani, 2015).

One of the main source of severe pollution problems worldwide is the textile industry and its dye-containing wastewater (i.e. 10,000 different textile dyes with an estimated annual production of 7.105 metric tonnes are commercially available worldwide; 30% of these dyes are used in excess of 1,000 tonnes per annum, and 90% of the textile products are used at the level of 100 tonnes per annum or less) (Baban *et al*., 2010). About 10-25% of textile dyes is lost during the dyeing process, with 2-20% directly discharged as aqueous effluents in different environmental components (Baban *et al*., 2010).

In particular, the discharge of dye-containing wastewaters into the aquatic environment is undesirable, not only because of their colour, but also because many of the dyes released and their breakdown products are toxic to living organisms mainly because they contain carcinogens, such as benzidine, naphthalene and other aromatic compounds (Suteu *et al*., 2009). Many investigators reported several cases of tumor, cancer, effect on liver and kidney after long-term exposure (Sajjala *et al*., 2008). The most obvious impact of the discharge of dye wastewater is the persisting nature of the colour, which is stable and fast, difficult to degrade, toxic and inhibitory, rendering the receiving water bodies unfit for their intended use (Sajjala *et al*., 2008). Without adequate treatment these dyes can remain in the environment for a long period of time. For instance, the half-life of hydrolysed Reactive Blue 19 is about 46 years at pH 7 and 25°C (Hao *et al*., 2000).

Excess salts used in the dyeing process, to increase fixation of reactive dyes to fibers, as well as heavy metal components of some dye wastewater may adversely affect the aquatic biota of the receiving streams (Law, 1995).

Dyes undergo chemical as well as biological changes in the aquatic system, consume dissolved O_2 and thus disturb the aquatic ecosystem (Rahman *et al*., 2009). Consequently, survival of fishes and other lives becomes difficult depending on their structural complexities and metabolic efficiency. Since large quantities of dyes are used, such pollution due to dyes may occur on a significant scale (Nupur *et al*., 2012).

In addition to the aforementioned problems, the textile industry consumes large amounts of potable and industrial water as processing water (90-94%) and a relatively low percentage as cooling water (6-10%) (in comparison with the chemical industry, where only 20% is used as process water and the rest for cooling) (Baban *et al*., 2010).

The main routes of human exposure to dyes includes: oral ingestion, dermal absorption, inhalation and direct contact with skin, which might cause incurable diseases (Joe, 2001).

The study is aimed at assessing the level of contamination of dye wastewater and its ecological impacts in urban Kano.

MATERIALS AND METHODS

Study Area

Urban Kano is located at the central western part of Kano State between latitude 11°59´59.57° – 12°02´39.57°N of the equator and between longitudes 8°33´19.69° – 8°31´59.69°E. It lies in the northern central boundary of Nigeria and is located some 840km away from the edge of the Sahara desert and 1,140km from the Atlantic Ocean. The Kano urban area covers 137sq.km (Oseiki, 2009).

A survey of the sites where this activity takes place was conducted using a GPS device (12 model - Garmin, USA) and the geographical co-ordinates were transferred onto a digital map of Kano to produce a map showing the specific selected sites of these dyeing processes (Figure 1).

Sampling sites includes the Kofar Mata, Kofar Na'isa, Zawaciki dyeing pits.

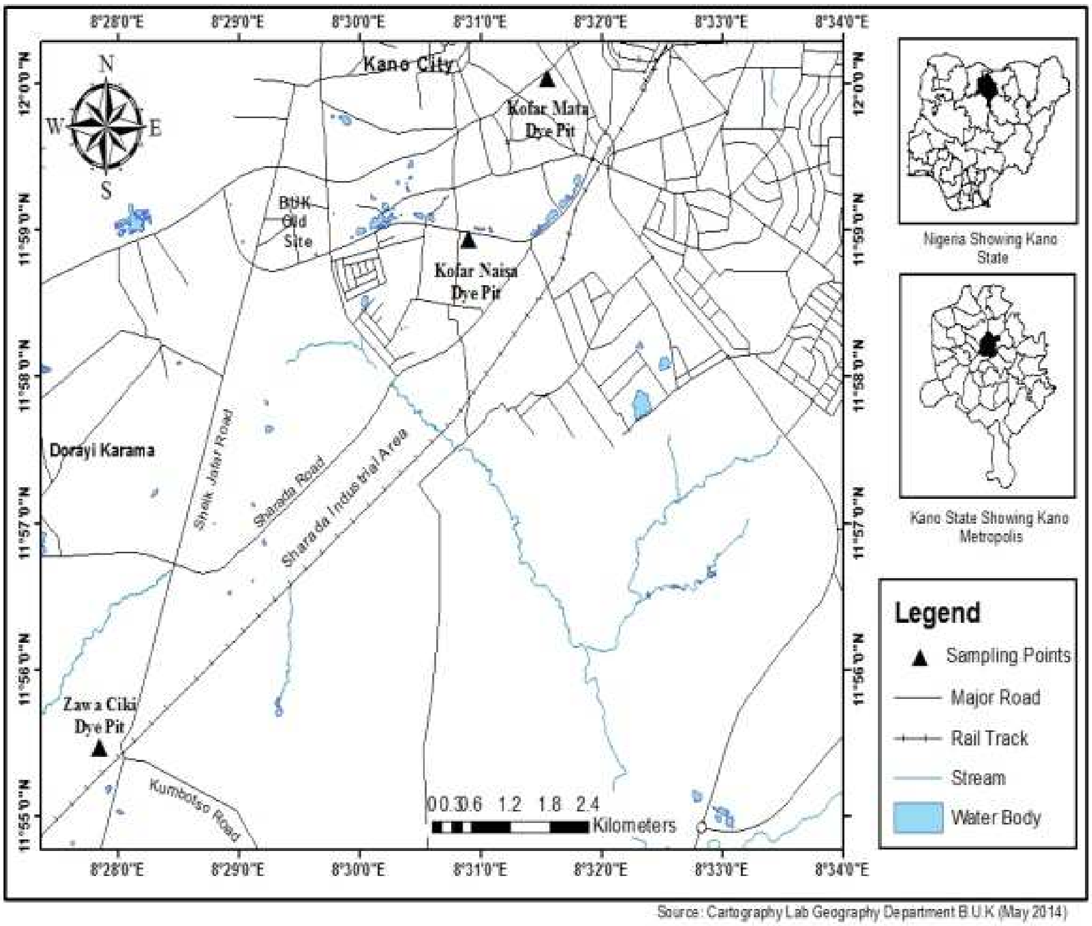

Figure 1: Map of Kano state showing the three dyeing activity sites; Kofar Mata, Kofar Na'isa and Zawaciki

Sample Collection

Dye wastewater from the sites was collected systematically using sterilized sampling bottles as described by APHA (1992). The samples were taken to the Soil Science Department, Faculty of Agriculture, Bayero University Kano, and also to the Department of Pollution Control, Ministry of Environment, Kano, laboratories for physico-chemical and heavy metals analyses.

Physicochemical Analysis of Dye Wastewater Samples

Temperature was measured *in situ*, using a 0-100°C mercury-in glass thermometer as described by Bannet and David (1974). Standard laboratory pH meter (model 3150) was used to determine the pH of the samples as described by Ademoroti (1996). Turbidity was determined using LP 2000 turbidity meter as described by Owen (1979). A platinum electrode conductivity meter (model HI 8733) was used to determine the electrical conductivity as described by Black *et al*., (1965). Dissolved oxygen (DO) was measured using Dissolved Oxygen meter (model 200) as described by Ademoroti (1996). A five days incubation method was employed to determine the Biochemical oxygen demand (BOD) level of the samples as described by APHA (1992). Chemical oxygen demand (COD) was determined spectrophotometrically (wavelength, 357.9nm) according to the method of Raed (2006) by measuring the absorbance of the Cr^{+3} formed due to the addition of an acid-dichromate solution in the presence of silver sulfate catalyst to the dye wastewater. To determine total solids (TS), the initial weight of an empty dish was recorded; then, well-mixed samples were placed in the dish and dried to constant weight in an oven at 103 - 105°C. The final weight of the dish after drying was taken, to which the initial weight was subtracted. The reading obtained after subtraction represents the total solids (Raed, 2006). Total dissolved solids (TDS) was measured by filtering the samples through standard fibre filters, and the filtrates were evaporated and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids (Raed, 2006).

For total suspended solids (TSS), the samples were filtered through weighed standard fibre filters and the residue retained on the filters was dried to a constant weight at 103 – 105°C. The increase in weight of the filters represents the total suspended solids (Raed, 2006). Chloride was determined using Atomic Absorption Spectrophotometer (AAS) (wavelength, 455nm) as described by Ademoroti (1996). Nitrate was determined using multi-specific meter (wavelength, 500nm) as described by Ademoroti (1996). Phosphate was determined using multi-specific meter (Hanna C-2000 model) (wavelength, 890nm) as described by APHA (1992).

Dye Wastewater Heavy Metals Analysis

The wastewater samples were digested for heavy metals analysis. Five millilitre of conc. HNO_3 was added to 2ml of the dye wastewater sample. The solution was evaporated to near dryness on a hot plate, making sure the sample does not boil. The sample was allowed to cool and another 5ml of conc. HNO_3 was added. The sample was covered with a watch glass and returned to the hot plate. A gentle refluxing action of the solution was set by increasing the temperature of the hot plate. Subsequent heating and addition of conc. HNO_3 acid was continued until a light coloured residue was obtained (digestion completed). Again, 1.2ml of conc. HNO_3 was added to dissolve the residue which was then washed with distilled water and filtered to remove silicate and other insoluble materials. The volume of the solution was adjusted to 2ml in a volumeric flask. A reagent blank determination was carried out. Samples and reagent blank was analyzed for total heavy metals with the flames (Njosi, 2005). Heavy metals (zinc, copper, lead, chromium and cadmium) in the wastewater were then determined spectrophotometrically (at wavelength (nm); Zn = 213.8, Cu = 324.8, Pb = 217, Cr = 357.9 and Cd = 228.8) using Atomic Absorption Spectrophotometer (AAS) as described by Ademoroti (1996).

Statistical Analysis

The data was subjected to General Linear Model (GLM) using SAS version 9.3. Means were separated using SNK (Student-Newman-Keuls Test) at 5% level of significance.

RESULTS

The table below presents the result for the physico-chemical analysis of the dye wastewater samples. All the parameters analyzed, with the exception of pH, chemical oxygen demand and nitrates, were found to be within acceptable limits set by FEPA (1991) for the discharge of wastewater into the environment.

Table 1: Mean Values for Physico-Chemical Parameters of Dye Wastewater Samples from Three Dyeing Activity Sites in Urban Kano

Sites / Parameters	Kofar Mata	Kofar Na'isa	Zawaciki	FEPA (1991)
Temperature (°C)	29.00 ± 2.00	26.00 ± 1.00	27.00 ± 2.00	<40.00
pH	11.14 ± 0.21	12.03 ± 0.07	11.95 ± 0.22	6.00-9.00
Dissolved Oxygen, DO (mg/l)	6.93 ± 0.08	6.60 ± 0.10	6.30 ± 0.33	-
Biochemical Oxygen Demand, BOD (mg/l)	3.07 ± 0.02	2.73 ± 0.83	3.10 ± 0.03	50.00
Chemical Oxygen Demand, COD (mg/l)	857.25 ± 37.25	524.75 ± 32.75	601.35 ± 44.65	80.00
Total Solids, TS (mg/l)	15.11 ± 3.50	17.60 ± 6.40	31.13 ± 3.87	2000.00
Total Suspended Solids, TSS (mg/l)	42.88 ± 13.42	6.41 ± 1.48	23.81 ± 9.13	30.00
Total Dissolved Solids, TDS (mg/l)	13.49 ± 4.19	19.85 ± 3.81	30.15 ± 3.15	2000.00
Electrical Conductivity, EC (µS/cm)	2657.50 ± 664.51	3198.91 ± 668.26	4141.00 ± 815.01	-
Turbidity (NTU)	3619.00 ± 110.00	463.83 ± 58.68	274.00 ± 71.00	-
Alkalinity (mg/l)	100.00 ± 3.00	447.33 ± 92.61	68.00 ± 6.00	-
Nitrate, NO_3 (mg/l)	64.80 ± 20.82	8.40 ± 3.07	104.00 ± 21.70	20.00
Chloride, Cl^- (mg/l)	89.38 ± 0.63	68.24 ± 18.88	251.62 ± 80.05	600.00
Phosphate, PO_4 (mg/l)	1.20 ± 0.33	2.65 ± 0.86	2.58 ± 0.87	5.00

The table below shows that dye wastewater have very high concentration of heavy metals which have exceeded acceptable limits. The concentration of copper was found to be high in all the sites, with cadmium having the least.

Table 2: Mean Values for Selected Heavy Metals Determined in Dye Wastewater Samples Collected from Three Dyeing Activity Sites in Urban Kano

Heavy Metals \ Sites	Kofar Mata	Kofar Na'isa	Zawaciki	FEPA (1991)
Cadmium, Cd (mg/l)	1.50 ± 0.54	0.85 ± 0.17	1.40 ± 0.20	<1.00
Chromium, Cr (mg/l)	8.98 ± 2.92	2.80 ± 0.81	5.37 ± 1.77	<0.10
Copper, Cu (mg/l)	13.91 ± 3.37	12.48 ± 4.96	8.41 ± 1.43	<1.00
Lead, Pb (mg/l)	3.12 ± 1.11	6.24 ± 2.17	7.33 ± 2.20	<1.00
Iron, Fe (mg/l)	$3.70 \pm 5.44E^{-16}$	7.41 ± 0.00	$3.70 \pm 5.44E^{-16}$	2.00
Zinc, Zn (mg/l)	3.91 ± 1.51	6.00 ± 2.02	28.43 ± 7.13	<1.00

DISCUSSION

The results for the physicochemical analysis of dye wastewater samples collected from the three dyeing sites (Kofar Mata, Kofar Na'isa and Zawaciki) are presented in Table 1. The mean temperature values were 29.00°C, 26.00°C and 27.00°C respectively, which were within the set limit by the Federal Environmental Protection Agency (FEPA, 1991). Temperature in Kofar Na'isa and Zawaciki had no significant difference, but there was significant difference with Kofar Mata at p≤0.05. This may be due to the fact that in Kofar Mata the wastewater is released into a closed constructed channel, while in Kofar Na'isa and Zawaciki the wastewater is released in open drains and constructed reservoirs, resulting in speedy cooling due to exposure (Sani, 2015). The average pH values for the three sites were 11.14, 12.03 and 11.95 respectively (all alkaline) which agrees with the report of Sajjala *et al*. (2008) that dye wastewater usually have an alkaline pH, because of the frequent use of alkaline salts (such as caustic soda, sodium hydrosulphite, etc.) as dye associates during dyeing processes. Dissolved oxygen (DO) had mean values of 6.93mg/l, 6.60mg/l and 6.30mg/l respectively (Zawaciki had a significant difference with both Kofar Mata and Kofar Na'isa). This is because the dye wastewater in both Kofar Mata and Kofar Na'isa is discharged in street drains; as such there is continuous mixing with wastewater from other domestic activities (Sani, 2015). Biochemical oxygen demand (BOD) had mean values of 3.07mg/l, 2.73mg/l and 3.10mg/l respectively (there was no significant difference within the sites at p≤0.05), which may be as a result of organic pollution in the wastewater due to percolation of effluents containing soluble organic compounds (Sastry *et al*., 2003). This also indicates that there could be low oxygen available for living organisms in the wastewater during utilization of organic matter. Chemical oxygen demand (COD) had mean values of 857.25mg/l, 524.75mg/l and 601.35mg/l respectively (showed significant difference within the sites), which implies toxic condition and presence of biologically resistant organic substances (Sawyer and McCarty, 1978). Mean values for total solids (TS) were 13.11mg/l, 17.60mg/l and 31.13mg/l respectively (Zawaciki had a significant difference with both Kofar Mata and Kofar Na'isa), this is because in Zawaciki the dye wastewater is discharged in a constructed pit, with no chance of receiving effluents from other activities, thus, most of the solids sediment at the bottom of the pit (Sani, 2015). Total suspended solids (TSS) were, 42.88mg/l, 6.41mg/l and 23.81mg/l respectively, there was significant difference between Kofar Mata and Kofar Na'isa, which may be due to the fact that re-dyeing processes in Kofar Mata involves both the traditional dyeing (using plants extracts) and modern (using synthetic dyes), and the wastewater generated for both contains different compounds, and is discharged through the same channel (Sani, 2015). Total dissolved solids (TDS), were 13.49mg/l, 19.85mg/l and 30.15mg/l respectively, and there was no significant difference within the sites at p≤0.05. The TDS values indicates high salinity in the dye wastewater (Balakrishnan *et al*., 2008), also TSS and TDS detected could be attributed to the high colour from various dyestuffs which may be the major sources of heavy metals. Kambole (2003) stated that increased heavy metal concentrations in river sediments could increase suspended solid concentrations. The three sites had average electrical conductivity values of 2657.50 µS/cm, 3198.91µS/cm and 4141.00µS/cm respectively, which may be due to the presence of different ionic compounds as a result of chemical reactions occurring between the dyes and their associates (Suteu *et al*., 2009).

There was no statistical significance in the electrical conductivity values within the sites. Mean values for turbidity were 3619.00NTU, 463.83NTU and 274.71NTU respectively (there was significant difference within the sites at $p \leq 0.05$). High turbidity may be as a result of mixing of the wastewater with other industrial and domestic effluents/sewages containing various sediments (Sani, 2015). Alkalinity had mean values of 100.00mg/l, 447.33mg/l and 68.00mg/l respectively (Kofar Na'isa had significant difference with both Zawaciki and Kofar Mata), thus, shows the capacity of the wastewater to neutralize acids, which is said to be undesirable (Yusuff and Sonibare, 2004). The mean values for Nitrate (64.80mg/l, 8.40mg/l and 104.00mg/l respectively) showed statistical significance within the sites at $p \leq 0.05$. Chloride had mean values of 89.38mg/l, 68.24mg/l and 251.62mg/l respectively, where Zawaciki had significant difference with both Kofar Mata and Kofar Na'isa. The mean values for phosphate were 1.20mg/l, 2.65mg/l and 2.58mg/l respectively, where Kofar Na'isa and Zawaciki showed statistical significance. The mean values for nitrate, chloride and phosphate were all above the permissible limit, and Sastry *et al*. (2003) reported that high concentration of these substances in water indicates industrial pollution, as lesser amount of nitrate, chloride and phosphate comes from natural resources.

The results for the detection of some selected heavy metals from dye wastewater samples collected from the three dyeing sites (Kofar Mata, Kofar Na'isa and Zawaciki) are presented in Table 2. The mean cadmium values of the three samples were 1.50mg/l, 0.85mg/l and 1.40mg/l respectively. Hazel (2010) reported that high levels of cadmium concentration in water results in its accumulation in plant and animal tissues through uptake and ingestion causing serious damage. Mean values for chromium were 8.98mg/l, 2.80mg/l and 5.37mg/l respectively. Mean values for copper were 13.91mg/l, 12.48mg/l and 8.41mg/l respectively. High levels of both chromium and copper in water cause various health effects to humans and other animals over a relatively short period of time through bioaccumulation (Sharma *et al*., 2009). Lead had mean values of 3.12mg/l, 6.24mg/l and 7.33mg/l. This may be as a result of corrosion of leaded pipelines, because motorized borehole pumps and pipe borne water transporting system serve as the main source of water used for these dyeing processes (Sani, 2015). Accumulation of lead in human and animal tissues through uptake or direct contact may affect the kidney, brain cells and permeability of liver membrane (Sharma *et al*., 2009). The mean values for iron were 3.70mg/l, 7.41mg/l and 3.70mg/l respectively. The presence of excess iron in water may cause decolourization of clothes washed in such waters (Kesavan and Parameswari, 2005), this means that high iron content in the dye wastewater may be attributed to its mixing with other domestic effluents containing iron compounds (Sani, 2015). Mean values for zinc were 3.91mg/l, 6.00mg/l and 28.43mg/l respectively. This may be due to the presence of zinc compounds that come from other domestic and industrial activities. Excess zinc concentration in water may also increase its acidity (Hambidge and Krebs, 2007).

CONCLUSION

In conclusion, the result of the study indicated contamination in dye processing activity sites in urban Kano due to discharge of untreated dye wastewater directly into the environment. The dye wastewater contained high levels of heavy metals, most of which have exceeded the recommended limits and have been proven to pose serious risks to humans, animals and plant growth through ecological interaction in the ecosystem.

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