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EVALUATION OF HEAVY METALS CONTAMINATION IN INDUSTRIAL EFFLUENTS USED FOR VEGETABLES AND CROPS IRRIGATION IN SEMI-ARID ECOLOGICAL ZONE OF NIGERIA

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Abstract – Heavy Metals (HMs) contaminated Industrial Effluents which are occasionally used as irrigation water, can be one of the major sources of qualitative irrigation water rich in nutrients when efficiently treated and reclaimed, and concomitantly augment the high water needs in agricultural irrigation from natural freshwater sources. The aim of this study is to assess if discharged metals contaminated effluents from different industries located in three phases in Sharada industrial area can improve water quality and be recycled for irrigation using Food and Agricultural Organisation (FAO), World Health Organisation (WHO), and other related international standards. Findings indicated that out of the analysed metals; Lead (Pb), Nickel (Ni), Zinc (Zn) and Cadmium (Cd), only Pb (0.054mg/l) and Zn (0.021mg/l) were above irrigation reuse limit all in phase I compared to other phases with high significant difference ($P<0.05$) observed between the former metal in the former phase than other phases while no significant difference ($P>0.05$) was recorded in the latter metal in all phases. Pertaining other water quality parameters; chemical oxygen demand (COD), nitrate-nitrogen (NO3-N), and ammonia nitrogen (NH4-N), results revealed that all the parameters were non-compliant to irrigation water quality standards of (0-146mg/l), (0-30mg/l), and (0-5mg/l) respectively in all the locations. Moreover, the COD and NO3-N variables showed highly significant difference ($P<0.05$) in phase I compared to other phases while highly significant variation ($P<0.05$) was noted in phase II for the NH4-N parameter in comparison to phases I and III. Though pH complied with irrigation re-use permissible limit, it recorded a highly significant difference ($P<0.05$) in phase I if compared with other phases. Overall, the outcome of this research implies that the effluents could not be relied on as an effective potential source of irrigation water rich in nutrients as believed by some farmers that can increase soil fertility and crop quality. Resultantly, this study may give useful scientific rationalization for not using and applying the effluent as an irrigation amendment for agricultural food production unless necessary proactive measures are put in place to improve the effluent quality.

Keywords: water quality, soil quality, industrial effluent, irrigation, environment

Introduction

Geometric industrial revolution with concomitant population increase has tremendously resulted in natural fresh water sources shortages in many arid and semi-arid countries globally owing to high consumption demand from the former and the latter. As a result, meeting the water demands for other challenges like irrigation becomes impossible without another alternative resources (Khaskhoussy et al., 2015; Sani et al, 2020) such as treated industrial effluents (Almuktar et al., 2018) which have the potential of reducing pressure demand on the natural fresh water sources, supplying irrigation water rich in appropriate nutrients for proper soil and crop quality improvement, saving economic cost of buying inorganic fertilizers by farmers and simultaneously protecting the environment from pollution by direct discharge of these effluents according to Food and Agricultural Organisation (FAO, 2012) provided the effluents are properly and adequately treated.

Industrial effluents are liquid wastewater discharged from industrial facilities either properly treated, untreated or poorly treated and depending on the sources, comprisematerials ranging from chlorides (Cl), phosphates (PO_4-P), nitrates (NO_3-N), hydrocarbons (H), total dissolve solids(TDS), suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), electrical conductivity (EC) and heavy metals (HMs) among others (Abdulmumini et al., 2015).

HMs are trace elements that are stable metalloids in nature and their density is greater than 4.5 g/cm^3. They include lead (Pb), Copper (Cu), nickel (Ni), cadmium (Cd), zinc (Zn), mercury (Hg) and chromium (Cr) etc. Moreover, they exhibit some characteristic features such as non-degradationor destruction making them accumulate in soils and sediments. They are also among the pollutants of concern globally due to their non-biodegradable nature, bio-accumulation effect and potential adverse impacts to humans, soil and water bodies (Chopra et al., 2009; Ali et al., 2013). For instance, they are carcinogenic, mutagenic, and teratogenic, and cause diseases like hair loss, brain and Kidney damage, liver cirrhosis, anxiety, depression, impaired development, reduced intelligence, loss of short-term memory, among others (Ali et al., 2013). Furthermore, many studies (Almuktar et al., 2018; Sani et al., 2020) have expounded that application of these metals contaminated effluents on soils as irrigation water causesreduction in soils aggregate stability, porosity and hydraulic conductivity, increased bulk density leading to poor texture and structure (Alkhais, 2001), increased soil salinity, electrical conductivity (EC), organic matter (OM), exchangeable cations, phosphorus (P), micronutrients and decrease in pH (Mojiri, 2011; Khaskhoussy et al., 2015; Sani et al., 2020).

Some studies in UK and Asia revealed that soilsirrigation with HMs contaminated effluentsdecreased soil microorganisms' population, degrade soil quality in terms of fertility, productivity and yield reduction, and contaminate food chain mostly through the vegetables consumption growing on the affected soils (Rattan et al., 2002; Gupta et al., 2008; Almuktar et al., 2018) due to their toxicity.However, a different study in UK, Al-Isawi et al.(2016) found out that, HMs in the irrigation effluents used for Chillies production were above irrigation and discharge limit but no apparent significant effect on the agronomic parameters of the grown vegetables.

Sharada is an industrial area of Kano metropolis, Kano state, Nigeria which covered about 600 Km^2 and located between longitude 8° and 9°E and latitude 10° and 12°N in the Semi-arid ecological Savannah zone of the country. The climate of the research area is the tropical wet and dry type, with dry and wet season months in between November to May, and June to October respectively.The temperature is 26^{o}C with the maximum value of 39^{o}C occurring in the month of April/May and the lowest of 14^{o}C in December according to Nuruddeen et al. (2016). The industrial effluents comprise of waste water from various industries ranging frombattery production factories, sacks and nylon manufacturing companies, oil and gas, textiles and tanneries, plastic industries and little component of domestic waste water. The industries are located in three phases; phase I, II and III respectively. The released effluents from these industries drain into gutters through the industries discharge outlets and empty into a concrete open sink, where the farmers in the area use them for the irrigation of vegetables, cereals, tubers and fruits. Examples of the common vegetables grown in the area are lettuce, spinach, onions, cabbage, tomatoes, peppers etc. maize is the only cereal crop grown, the tubers comprise of carrots and sweet potatoes while the fruits are sweet and lime oranges. Most of these vegetablescultivated in this area are supplied to the wholesale vegetable market within Kano metropolis and the rest enter the local markets.

This study may provide useful information to environmental, agricultural, health and other relatedwater industries with established interpreted data leading to understanding of different constituents in HMs contaminated effluentsand their discharge processes, allowing them to justify their application in their wastewater management and potential reuse as irrigation amendments into agricultural food production, water, soil and crop quality improvement with concomitant environmental protection particularly to agricultural sector..

Considering the negative implication of these metal compounds to irrigation agriculture, human health and environment, this study is aimed to evaluate the metals concentration in industrial effluents used for irrigation of vegetables and crops in semi-arid ecological savannah zone of Nigeria. Though, numerous investigations on quality of industrial effluents were carried out (Danazumi and Bichi, 2010; Abdulmumini et al., 2015; Sani et al., 2020) in the area, assessment of HMs compounds concentration in the effluents used for irrigation of vegetables and crops, and whether or not the effluents are within irrigation reuse and safe limit using international standards remains thinly implemented.

The overall aim of this study is to assess heavy metals contamination in discharged industrial effluents used for irrigation of vegetables and crops in semi-arid ecological zone of Nigeria with the following objectives;

- Assess the concentration of HMs in the Sharada industrial discharged effluents
- Compare the observed concentration of the metals and other pollutants with international standard for irrigation compliance

Materials and Methods

Effluent sampling

Discharged effluents samples were collected randomly in triplicate from Sharada industrial effluent collection sink where the farmers draw the wastewater for the irrigation during the months from October to December 2019 in order to estimate Cd, Ni, Pb Zn and other water quality parameters in the collected samples.

Laboratory analysis

The analysis of different effluent samples for some selected metals concentration was carried out in thelaboratory using Varian 720-ES Inductively Coupled Plasma—Optical Emission Spectrometer technology (ICP–OES (USEPA, 1994) manufactured by Agilent Technologies UK (Wharfedale Road, Wokingham, Berkshire, UK). pH was measured with sensION+Benchtop Multi-Parameter Meter (Hach Lange, Düsseldorf, Germany). Standard water quality analysis procedures were applied for variables including chemical oxygen demand (COD), ammonia-nitrogen (NH_4-N) and nitrate-nitrogen (NO_3-N). All the water quality analyses were performed according to APHA (2005) procedures.

Statistical analysis

To assess the contamination level of metals and other pollutants concentration in different phases and their corresponding differences, data mean values of the concentration in each phase were subjected to analysis of variance (ANOVA) using SPSS Statistical package. The treatment means were separated using Duncan Multiple Range Test (DMRT) at 5% level of probability.

Result and Discussion

Comparison of Heavy Metals (HMs) in the Industrial Effluents

Comparison of Lead (Pb)

Overall mean values with regards to all metals and other water quality parameters was shown in Table1. With regards to Pb, the result shows that, all phases recorded low Pb concentrations and complied with irrigation reuse standard (Tables 1and 2) of 0-5mg/l according to FAO (2003) and USEPA (2004).

The overall mean Pb concentration in phase I was highest compared to phase III which recorded higher values than phase II. This difference was statistically significant ($P<0.05$) as shown in Table 3which shows an assessment of the statistically significant differences betweenHMs and other water quality parameters concentration in the effluents in the three different industrial phases using one way Anova. Despite complying with permissible irrigation quality standard, the high Pb values recorded in Phase I compared to other phases could be attributed probably to much amount of Pb containing substances such asaerial emission of leaded petrol combustion, battery production, herbicides and insecticides that might have been released in the effluents from phase I industries in comparison to other phases**,** since several studies have expoundedthat aerial emission from combustion of leaded petrol, battery manufacture, herbicides and insecticides are major sources of Pb production in environment (Thangavel and Subbhuraam, 2004; Wuana and Okieimen, 2011; Ali et al., 2013). Consequently, this might have led to the elevated concentration of the metal observed in the former industrial phase compared to the latter ones.

The concentration of Pb in the industrial effluent of this research is below the values of concentration reported in some studies reported elsewhere (Danazumi and Bichi, 2010). The plausible reason for this difference could be attributed to lack of proper treatment of the Pb containing industrial effluents from the treatment facilities of the industries in the reported literature leading to the reported high Pb value, while adequate proper treatment of the effluents or and domestic sewage confluence in the effluent might have diluted the Pb concentration leading to the observed low concentration of the current study. Contrastingly, the data range of Pb concentration in the current research was within the range of data confirmed by the findings of Gupta et al. (2008).

High Pb concentration in wastewater used for irrigation leads to soil toxicity with subsequent quality and fertility reduction, accumulation in the leafy parts of vegetables and in the grain yield of some crops (Sidhu and Narwal, 2004; Chopra et al., 2009), and upon consumption of these crops, the accumulated Pb was released in the host body leading to disease problems such as impaired development, reduced intelligence, loss of short-term memory, learning disabilities and coordination problems, among others (Ali et al., 2013; Sani et al., 2020).

Comparison of Nickel (Ni)

The overall effluent concentrations of all phases with reference to Ni metal were relatively high and above irrigation reuse quality standard in phase I compared to other phases that were similar (Tables 1and 2). The statistical table 3 indicates that effluent waste water high in Ni metalresults in no statistically significant ($P>0.05$) difference in Phase I compared to other phases despite having higher values above irrigation reuse quality compliance of 0-0.2mg/l (Table 1) according to FAO (2003) and USEPA (2004) (Table 2) recorded in the former phase than the latter ones. Though, phases II and III recorded 0.17mg/l (Table 1), this value is almost equal to the irrigation threshold. This high Ni concentration observed could be ascribed probably due to improper treatment from the Ni producing industries leading to high amount of Ni containing substances in the released effluents (Tariq et al., 2006; Ali et al., 2013). The range in the mean values of Ni of the current research is within the range of data values reported in the literature (Gupta et al., 2008) and were non-compliant to irrigation reuse quality standards.

Application of wastewater high in Ni concentration contaminates the soil growth media with negative impact to the crops grown which can accumulate high concentration of the metal to cause serious health risks to consumers (Islam et al., 2007; Chopra et al., 2009; Ali et al., 2013) upon the consumption of the crops.

Comparison of Zinc (Zn)

The mean values of Zn as depicted in Tables 1and 2 were relatively low in all phases and withinirrigation quality threshold limit of 0-2.0mg/l according to the report of environment and agricultural regulatory agencies (FAO, 2003; USEPA, 2004). In the statistical analysis table however, phase II recorded highest concentration value of Zn fallowed by phases I and III respectively (Table 3). This difference was statistically significant ($P<0.05$). Despite Zn concentration inall phases were compliant with irrigation reuse permissible limit, the high concentration observed in phase II compared to other phases could be attributed tohigh amount of Zn originating substances that were not removed efficiently from the phase II industries treatment facilities and released in the discharged effluents (Ali et al., 2013). This has been confirmed by data elsewhere (Danazumi and Bichi, 2010), and attributed the high concentration of metals including Zn to inefficiency of the industries facilities to properly treat the metals, which as a result led to the elevation of the metals concentration in the discharged effluents. Furthermore, the ranges of mean values of Zn concentration reported in this study was within the range of data reported in some literatures (Gupta et al., 2008) and were compliant to irrigation quality standard for effluent recycling.

Crops irrigation with effluents containing high amount of Zn deteriorates soil quality and subsequent impediment of the crops grown in the growth media with apparent browning of collaroid roots andchlorosis particularly in vegetables (Islam et al., 2007) in addition to health risks associated problems such as dizziness and fatigue (Hess and Schmid, 2002) on their host animal.

Comparison of Cadmium (Cd)

The mean average concentration of Cd and other water quality parameters was depicted in Tables1and 2. The results indicated thatthe metal concentration was high and above compliance to irrigation quality permissible standard advocated by regulatory agencies in all phases with the exception of phase III which recorded the concentration equals to that of the recommended threshold of 0.01 (FAO, 2003) and USEPA (2004) respectively. The highest concentration of Cd metal was recorded in phase I followed by Phases II and III accordingly. This difference in concentration was statistically significant ($P<0.05$) as revealed in the statistical table (Table 3). The plausible reason for the high concentration of Cdmetal in the former phase compared to the other latter phases could probably be due to release of high amount of phosphate fertilizers in the discharged effluents as a result of farming activities in the area via leaching, release of Cd originating substances from the industries treatment facilities due to poor treatment or the combination of the two. It has been reported that phosphate fertilizers, paints and pigments, plastic stabilizers (Salem et al., 2000; Pulford and Watson, 2003; Ali et al., 2013) are sources of Cd and their increase in concentration increase the metal concentration and vice-vasa. The range of Cd concentration in the irrigation effluent reported in this research has been in conformity with the data reported in literature elsewhere (Gupta et al., 2008).

Application of high containing Cd effluent as irrigation amendment leads to Cd soil toxicity and subsequent transfer of the toxic effect on to the roots and shoots o the affected crop, consequently, this leads to the development of harmful effects such as oxidative stress, genotoxicity in addition to impediment of the photothynthetic processes, and root absorption mechanismto the grown crops. Furthermore, consuming the Cd metal via affected crops or vegetables by humans or animals has carcinogenic, mutagenic and teratogenic effect (Awofolu, 2005; Ali et al., 2013; Sani et al., 2020).

Table 1: Overall mean values of HMs and other parameters in all phases in mg/l except pH

Parameters	Phase I	Phase II	Phase III	Irrigation quality standard
Pb	0.054	0.038	0.048	0-5.0[a]
Ni	0.021	0.017	0.017	0-0.2[a]
Zn	0.017	0.021	0.015	0-2.0[a]
Cd	0.018	0.016	0.01	0-0.01[a]
COD	360.00	300.00	330.00	0-146[b]
NH_4-N	63.05	154.11	91.07	0-5[a]
NO_3-N	119.09	59.54	31.52	0-30[a]
pH	7.04	7.12	7.01	6.0-8.5[c]

Note; Pb, lead, Ni, nickel, Zn, zinc, Cd, cadmium, COD, chemical oxygen demand, NH_4-N, ammonium nitrogen, NO_3-N, nitrate nitrogen, HMs, heavy metals, [a]FAO (2003),[b]Radaideh et al. (2009) and [c]WHO (2008).

Comparison of Other Pollutants in the Industrial Effluents

Comparison of Chemical Oxygen Demand (COD)

The COD concentration of this research was relatively high and above irrigation quality compliance limit in all phases (Table 1). The highest concentration was observed in phase I compared to phases III and II respectively. Statistically, there was a significant difference in the concentration of COD recorded in phase I ($P<0.05$) compared to other phases which were statistically similar to each other (Table 3).

The irrigation quality standard set by regulatory agencies for COD concentrations from irrigation effluent was 0-146mg/l (Radaideh et al., 2009). All phases were none compliant (Table 1). The possible reason for this high concentration of COD reported in this study could be attributed to much recalcitrant chemicals that were not efficiently removed from the industries water treatment plants and has been confirmed elsewhere (Abdulmumini et al., 2015; Sani, 2015). Moreover, despite noncompliance to irrigation reuse standard, the high COD values recorded in Phase I compared to other phases could be attributed probably to much recalcitrant chemicals that escape biodegradation in the Phase I released wastewater in comparison to other phases (Abdulmumini et al., 2015; Sani et al., 2020).

COD values within the range of this study's concentration and noncompliant to irrigation reuse standard has been reportedin many studies elsewhere (Almuktar et al., 2015; Sani et al., 2020).

High concentration of COD in effluent used for irrigating crops, leads to nutrient toxicity and excessive morphological growth in crops (Almuktar et al., 2015, 2018).

Comparison of Nutrients variables (NH_4-N and NO_3-N)

The overall effluent concentrations of all phases with reference to ammonia-nitrogen were high and all above irrigation quality standard (Table 1). The statistical analysis of the NH_4-N variable in different phases (Table 3) indicates that effluent waste water high in NH_4-N results in a statistically significant ($P<0.05$) difference in Phase II in comparison to phases III and I respectively possibly due to convergence of animal wastes, high sewage and leached nitrogenous containing ammonium fertilizers from urban and agricultural sources (Paul, 2011; Sani et al., 2020) that might have raised the observed NH_4-N values in effluents of the former phase in comparison to latter phases.

With regard to the irrigation quality reuse standard, a typical standard advocated by FAO regulations set 0-5mg/l (FAO, 2003) for NH_4-N variable and all phases were non-compliant (Table 1). The findings of this high concentration of the NH_4-N in the industrial effluent of the present research are within the range of values reported in the literature elsewhere (Paul, 2011; Sani et al., 2020).

The use of industrial effluents rich in NH_4-N concentration above maximum irrigation threshold safe limit and applied as irrigation amendment leads to soil quality degradation and poor crop growth (Al-muktar et al., 2015, 2018).

Table 2: Overall mean values of HMs in the Industrial Effluents in different Phases (2019) and their corresponding USEPA standards. All parameters in mg/l except pH

Parameters	Phase I	Phase II	Phase III	Standard
Lead (Pb)	0.054	0.038	0.048	<0.05
Nickel (Ni)	0.021	0.017	0.017	<0.02
Zinc (Zn)	0.017	0.21	0.015	<2.0
Cadmium (Cd)	0.018	0.016	0.01	<0.01

Note; Pb, lead, Ni, nickel, Zn, zinc and Cd, cadmium

The NO_3-N effluent concentrations in all phases were high and all above irrigation reuse quality standards (Table 1). The statistical analysis (Table 3) indicates that industrial effluent high in NO_3-Nresults in a statistically significant ($P<0.05$) difference in Phase I compared to phases II and III respectively. This high difference in concentration could be attributable tohigh sewage, nitrogenous compound fertilizers and other wastes confluence in the former phase released effluents that might have elevated the concentration of the NO_3-N values observed compared to the latter phases discharged effluents (Paul, 2011; Sani et al., 2020). The values of NO_3-N observed in this study are within the range of values reportedin a recent research published by Sani etal. (2020).

Untreated or poorly treated effluent with high nitrate concentration has been reported to cause soil quality degradation, excessive crop growth and crops maturity extension under long-term extensive application as irrigation amendment (Almuktar et al., 2015; Sani et al., 2020).

The observed high NO_3-N concentration in the released effluents of the current researchcould be attributed to improper treatment of the effluent containing NO_3-N from industrial treatment facilities and convergence of high municipal sewage, animal wastes, leached nitrogenous fertilizers and runoff from urban and agricultural catchments (Danazumi and Bichi, 2010; Paul, 2011) and has been confirmed previously elsewhere (Abdulmumini et al., 2015; Sani et al., 2020).

Table 3: Overall Statistical differences between HMs and other parameters with different phases in mg/l

Parameters	Phase I	Phase II	Phase III	SE+/-
Pb	0.054^a	0.038^c	0.048^b	0.0017
Ni	0.021^{NS}	0.017^{NS}	0.017^{NS}	0.0013
Zn	0.017^{ab}	0.021^a	0.015^b	0.0018
Cd	0.018^a	0.016^b	0.01^c	0.0013
COD	369.30^a	311.70^b	338.30^b	14.64
NH_4-N	62.20^c	151.70^a	91.10^b	2.045
NO_3-N	119.34^a	59.58^b	33.90^c	1.985
pH	7.04^b	7.12^a	7.01^b	0.03

Note; means having the same letter are insignificant statistically at 5% level of confidence, NS, not significant. Means were separated using DMRT at 5% level of probability

Comparison of pH

The pH concentrations recorded from this study (Table 1) are generally within the irrigation reuse quality standard advocated by regulatory agencies of 6.5-8.5 (WHO, 2008) despite having significant difference ($P<0.05$) observed in different phases as indicated in the statistical analysis (Table 3), with phase II showing highest value compared to other phases that were similar statistically.

Acidic pH in effluents poses a threat to irrigation system corrosion particularly where sprinkler irrigation systems are used for crops irrigation while basic pH makes some nutrients such as heavy metals and sodium more soluble in the effluent. This effluent afterwards, will lead to high electrical conductivity (EC) and salinity, consequently, when these effluents are applied as irrigation amendment, disperse the soil texture and structure (Bauder et al., 2011; Sani et al.,2020) leading to the soil quality degradation.

The pH concentration values observed in the current research has been in consistent with the ranges of pH values reported in many studies elsewhere (Almuktar et al., 2015, 2018; Sani et al., 2020).

Conclusion and recommendations for further research

The main objective of this research was to assess the HMs contamination along other water quality parameters of the Sharada industrial effluents and whether they are fit for irrigation of some crops and vegetables in Kano state, a semiarid ecological zone of Nigeria. Findings indicated thatNi and Cd out of the assessed metalsexceeded the standard limit for reuse in irrigation agriculture as recommended by regulatory agencies. Furthermore, results of other water quality parameters analysed revealed that the industrial effluents are not fit for recycling in irrigation agriculture and cannot improve soil and crop quality, and protect the environment due to their toxicity.

Overall, the study findings indicated that Sharada industrial effluents are polluted with HMs and other conventional pollutants that cannot be relied as a source of irrigation water rich in nutrients capable of increasing soil fertility and crop quality as believed by some farmers in the area who apply the effluent as soil and water amendments to produce crops and vegetables as being a practice, because of the deleterious effects themetals and other pollutants in the effluents can cause such as diseases to both humans and animals upon consumption of the harvested crops and vegetables, soil and water quality degradation, crop growth and quality alteration.

Concerning recommendations, there is need for all industries in Sharada to discharge their effluents to the sewer system not through irrigation or discharge directly to the environment as has been the usual practice in the area. Moreover, these industries should be enforced by authority not to discharge the effluent till after an environmental impact assessment.In addition, research using the effluents be conducted on their impact on soil quality and fertility using some test crops and vegetables grown in the area to fully ascertain adequate assessment of the effluents effect on soil quality and fertility, and their correlation with different types of crops growth and yield parameters..

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