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Physicochemical Analysis and Heavy Metal Content of Effluent Discharge from a Steel Processing Plant in Ilorin, Kwara State, Nigeria

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Abstract

This study investigates the physicochemical characteristics and heavy metal concentrations of effluents discharge from a steel processing plant in Ilorin, Kwara State, Nigeria. The effluents parameters were monitored bi-monthly for six months to assess the quality level. Water Quality Index (WQI) and Metal Pollution Index (MPI) of the effluents were calculated using Weight Arithmetic Water Quality Index method. The mean ± Standard Deviation (SD) values recorded for the parameters were as follows: pH 1.38 ± 0.02, Electrical Conductivity (EC) 9824.75 ± 3.02 µs/cm, Total Suspended Solids (TSS) 85.25 ± 1.71 mg/L, Total Dissolved Solids (TDS) 2219.32 ± 2.33 mg/L and Dissolved Oxygen (DO) 5.19 ± 0.07 mg/L. Others are Biological Oxygen Demand (BOD) 97.30 ± 2.09 mg/L, Chemical Oxygen Demand (COD) 244.33 ± 2.49 mg/L, Chlorides 2456.35 ± 2.70 mg/L, Sulphates 491.25 ± 2.75 mg/L and surfactants 5.21 ± 0.06 mg/L. EC was found to correlate linearly with pH and TDS at moderate acidic pH. However, at pH < 0.7, EC was basically influenced by hydrogen ions concentration in respective of concentration of TDS. Mean ± SD values for heavy metal ions detected in the samples were: iron (235.64 ± 1.13 mg/L), zinc (38.22 ± 0.54 mg/L), lead (10.84 ± 0.30 mg/L), chromium (10.42 ± 0.15 mg/L) and manganese (0.37 ± 0.02 mg/L) respectively. The WQI and MPI calculated were above critical pollution index. These effluents are being discharged into a nearby Dam through a municipal drainage system and contained parameters that are above the permissible limits for industrial discharge.

Keyword: Steel, effluents, physicochemical parameters, heavy metals

Introduction

The expansion of industrial activities has resulted in increase in pollution and environmental degradation, especially through the unfettered discharge of industrial wastewater into water bodies that are often major sources of drinking water in a developing country like Nigeria and densely populated nations. Industrial effluents impact assessment has shown that, about 1,900 tons of toxic wastes are produced annually in Nigeria, and these come mainly from steel, pharmaceutical, textile and tanneries (Egbu, 2000).

Effluents from steel plants contribute greatly to the contamination of water bodies because of the content which include acidic waste, heavy metals and organic contaminants. In steel processing, high volumes of water in thousands of cubic meter are used daily for cooling of equipment, quenching, slag handling, coke-oven, acid pickling and metal finishing processes (Strugariu and Heput, 2012). Polluted water discharged from steel industries differs greatly in physicochemical parameters and heavy metal concentrations due to difference in nature of raw materials, by-product and efficiency of the operation system. Wastewater from coke-oven plants often contain high concentration of suspended solids, oil and grease phenolics, cyanides, thiocyanates, ammonia-nitrogen and poly aromatic hydrocarbon compounds and are thereby considered toxic. (Parimal and Ramesh, 2014; Sinha *et al*., 2014). Steel processing and metal finishing wastewater originates mainly from pickling, rinsing, enameling and electroplating processes. These processes involved the use of acidic or alkaline solutions to remove impurities, such as stains, heavy metals, precious metals and aluminum alloys (Chandra and Mandal, 2000; Baba *et al*., 2011; Anuradha *et al.*, 2013). Consumption of water containing high concentration of heavy metals such as lead, chromium, iron and zinc are usually associated with problems such as lead poisoning, respiratory diseases, tumor formation and alteration of metabolic activities (Majid, 2010; Momodu and Anyakora, 2010; Sagar and Pratap, 2012).

Studies have shown that a larger percentage of industries in Nigeria discharge their wastes without proper treatment (Egbu, 2000). To curtail these industrial menace, several efforts have been put in place by regulatory agencies such as National Environmental Standards and Regulations Enforcement Agency of Nigeria (NESREA), saddled with the responsibility of setting standards for discharge of industrial effluents, monitor and enforce compliance with effluents quality standards (NESREA, 2011).

Materials and methods

Samples of the effluents were collected bi-monthly from July to December 2016 and analyzed for some physicochemical parameters as outlined. The pH and Electrical conductivity (EC) were determined using PHS-3C Searchtech pH meter and Hana Hi2030 conductivity meter. Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Chlorides were determined using standard methods (Shun and Lee, 2004; De, 2012). Sulphate ions and surfactants (methylene blue method) were analyzed using a UV spectrophotometer (Beckman Coulter DU 730 model). Dissolved Oxygen (DO) was determined using Winkler method: the volume of $MnSO_4$ and KI-azide reagent were varied in accordance with the pH of the effluents to prevent interference from high concentration of iron present in the effluents sample. The concentrations of heavy metals were determined using Buck Scientific Atomic Absorption Spectrophotometer (AAS) 210 VGP.

Weighted Arithmetic Water Quality (WQI) and Metal Pollution (MPI) Indices was used to rate the wastewater quality level. The WQI/MPI parameters were determined using a published procedure (Boah *et al*., 2015). The results obtained were compared with permissible limits of World Health Organization (WHO) and National Environmental Standards Regulations and Enforcement Agency (NESREA) of Nigeria.

Results and discussion

The results obtained for the physicochemical parameters and heavy metal ion concentrations were shown in Figure 1-4 and Table 1 and the water quality rating index in Table 2 and 3 respectively.

pH: Acidic pH in the range of 0.32 ± 0.1-2.46 ± 0.02 were recorded during the period under investigation. All pH values were far below the permissible limit of 6.5-8.5 specified by WHO (2011). The acidic nature of the effluents was attributed to wastewater streams generated from operations such as acid pickling process for chemical descaling of the iron/steel roll bands raw materials, pickling rinse waters, fume scrubbing and residual acid as a result of acid spills or leaks from ageing equipment. Similar acidic effluents (pH < 1.0) from a steel plating facility has been reported (Sultan, 2011).

EC: The electrical conductivity of the steel effluents ranged from 2604 ± 1.73-42600 ± 2.0 µs/cm at 25^{o} C, an indication of high concentration of dissociated ionic species of elevated conductance. From this report, lower pH values < 1.0 has more influence on EC than TDS. This agrees with an earlier results that hydrogen ion poses the highest equivalent ionic conductance in solutions (David, 2006).

TSS and TDS: Low values of TSS (24 ± 1.0-248 ± 1.73 mg/L) and high amount of TDS (1212 ± 2.0-3232.3 ± 2.65 mg/L) were observed in the effluents. The TDS values were above the recommended standards of 500 mg/L (WHO, 2011). TDS represent a combination of all dissolved inorganic, organic or molecules in colloidal state (Weber-Scannell and Duffy, 2007), and the high concentration as observed, was attributed to the dissolution of metal dusts and other solid particles by the action of acid solution used during the pickling and grinding process.

Figure 1, shows pH values of 0.7 and above correlate linearly with EC and TDS. This agrees with EC and TDS linear relationship at moderate pH (Uwidia and Ukulu, 2013). EC sharp curve observed at pH < 0.7, indicates that at extreme acidic pH, EC is basically influenced by hydrogen ions irrespective of TDS concentration. However, the plot of EC relationship and TDS against 1/pH shows that EC is a function of both pH and TDS (Figure 2).

DO: Significant variation in the amount of DO (1.19 ± 0.04-8.40 ± 0.10 mg/L) was observed. Low levels of dissolved oxygen noticed in some of the samples can be attributed to depletion of oxygen in the effluents (Eneh, 1994). On the average, the dissolved oxygen concentration (5.19 ± 0.07 mg/L) of the effluents was within acceptable standard limit of 5.0 mg/L specified by WHO and considered as the average concentration for aquatic life sustainability (WHO, 2011; Sachchida *et al*., 2012).

BOD: BOD is a measure used to determine the rate of aerobic degradation of organic pollutant in wastewater by the action of microorganisms. Values in the range of 32.4 ± 1.70-163 ± 3.24 mg/L recorded for BOD, shows the effluents contains less organic pollutants. Nevertheless, the values were higher than the tolerance limit of BOD (5.0 mg/L) standards for drinking water and 30 mg/L for industrial discharge (NESREA, 2011; WHO, 2011). Low BOD trend is peculiar to steel processing and metal finishing wastewater effluents (Sahu *et al*., 2012; Monika *et al*., 2014).

COD: COD values in the range of 116 ± 2.0-398 ± 3.46 mg/L obtained for these effluents were above the recommended limit of 60 mg/L for discharging industrial effluents and 10 mg/L for drinking water (NESERA, 2011; WHO, 2011). This COD values obtained can be attributed to the discharge of lubricants and water proof coatings applied on surface of acid pickled metals to prevent rusting after pickling (Rao, 2006). From the results, the COD values were higher than the BOD values, an indication that the steel effluents contains more of biodegradable resistant organic compounds (Ram *et al*., 2011).

Chlorides and Sulphates: The observed values for chloride ions in the range of 683.5 ± 2.88-8008.8 ± 2.99 mg/L, confirm hydrochloric acid as the primary pickling agent used for the descaling process. These concentrations were beyond the permissible limit of 250 mg/L and 350 mg/L of WHO and NESREA. Chloride in excess of 250 mg/L imparts a salty taste to water and can cause death to living organisms (Ram *et al*., 2011; Wong *et al.*, 2013). High amount of chloride ions contributes significantly to high EC and TDS (McCulloch, 1993). This was observed in the sample with the highest value of EC (42600 ± 2.0 µs/cm), TDS (3232.3 ± 2.65 mg/L) and lowest pH of 0.32 ± 0.1 respectively. Sulphate ion concentrations in the effluent ranged from 38 ± 1.0-1800 ± 3.0 mg/L. In comparison, the average concentration of chloride (2456.31 ± 2.70 mg/L) was higher than sulphate ion (491.25 ± 2.75 mg/L).

Surfactants: The concentrations of surfactants detected in the range of 0.0-13 ± 0.10 mg/L, can be attributed to the use of detergents for cleansing operations.

Surfactant concentrations above 15 mg/L in water can result to persistent foaming (Yuan *et al*., 2014). Negative effect at such concentration can inhibit the degrading activities of microorganism in effluents treatment plants (Adewoye, 2010). It can also result to formation of insulating layers that reduces the amount of dissolved oxygen in water bodies (Yuan *et al*., 2014). Surfactant concentrations recorded in this report are below the level considered harmful.

Heavy Metal Ion Concentrations: Figure 4, shows the concentration of heavy metal ions present in the steel effluents. Fe was in the range of 32 ± 0.66-625.24 ± 2.56 mg/L; Zn 5.2 ± 0.03-73.5 ± 1.04 mg/L; Pb 0.11 ± 0.01-22.11 ± 0.64 mg/L; Cr 1.2 ± 0.01-20.3 ± 0.48 mg/L and Mn 0.02 ± 0.01-0.9 ± 0.02 mg/L respectively. With the exception of manganese, all other metal ion concentrations were above the recommended standard limits (WHO, 2011; NESREA, 2011). The high concentration of iron was attributed to chemical descaling of steel materials processed into other metallic products (Sultan, 2011). High concentration of zinc recorded was as a result of surface cleansing and processing of zinc roll bands into corrugated zinc roofing sheets. The amount of chromium recorded (1.2 ± 0.01-20.3 ± 0.48 mg/L) confirm chromium as one of the constituent of the steel products which can sometimes be up to 12% in steel product composition (Flenner, 2002).

Water Quality Index (WQI) and Metal Pollution Index (MPI): WQI and MPI, were calculated by aggregation of quality rating and unit weight of the 10 physicochemical variables and the 5 heavy metal ions detected in the effluents using their mean concentration (Table 2). From the calculations (Table 3 and 4), WQI and MPI values of 1,105.013 and 85,961.29 obtained were above the critical pollution index value of 100 and permissible level recommended by WHO for drinking water (WHO, 2011; Boah, *et al*., 2015). This shows the wastewater does not meet the requirement for industrial discharge and freshwater quality criteria for protection of aquatic life.

Conclusion

With the exception of Dissolved Oxygen and surfactants, all other parameters monitored were above the standard set by WHO and NESREA. The extreme acidic pH, high EC, TDS and heavy metal ion concentrations recorded indicates high amount of spent acid liquor in the wastewater. The WQI and MPI values were above the critical pollution index value of 100. Effluents from the steel plant constantly been discharge through a public drainage system, empties its content into a nearby Dam. Discharging this highly acidic and heavy metal-laden industrial wastewater, will have adverse effect on humans, aquatic organisms and ecosystem in general. It is therefore recommended that effluents treatment facility should be installed in the plant. The regulatory agencies should also monitor and enforce compliance on management and disposal of wastewater by steel industries in Nigeria.

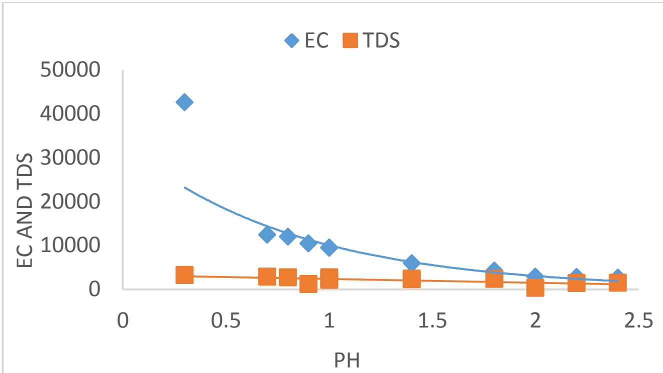

Figure 1. Variation of EC and TDS with pH

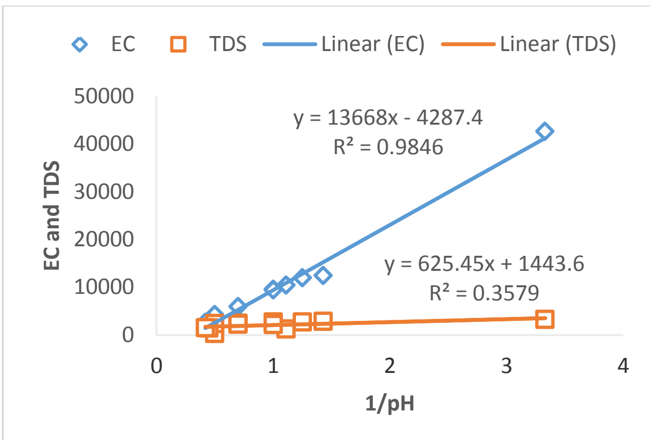

Figure 3. EC and TDS with 1/pH

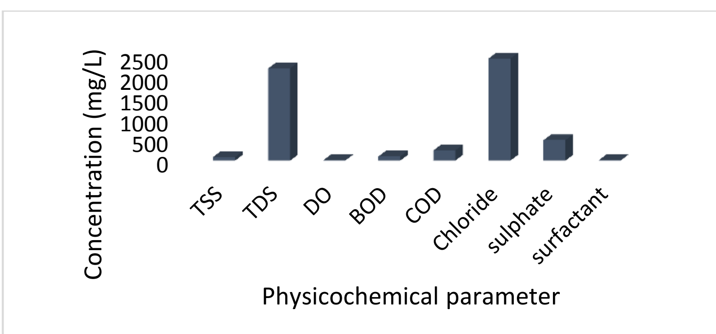

Figure 3. Average concentration of the effluent physicochemical parameters

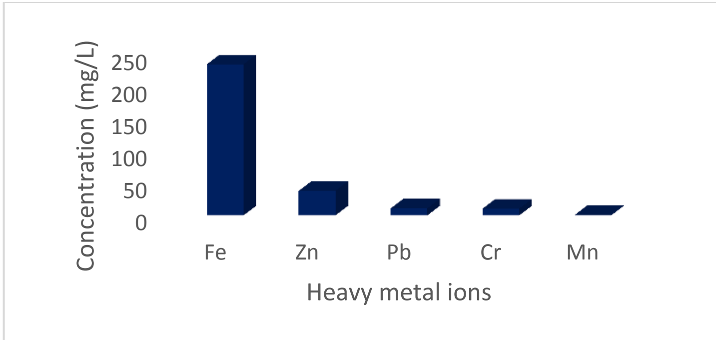

Figure 4. Average concentration of heavy metals present in the effluent

Table 1 Physicochemical analysis of effluent from the steel processing plant

Parameter	Range	Mean ± SD	NESREA Standard (industrial discharge)	WHO Standard (drinking water)
pH	0.32 ± 0.1-2.46 ± 0.02	1.38 ± 0.02	6.0-9.0	6.5-8.5
EC	2604 ± 1.73-42600 ± 2.0	9824.75 ± 3.02	-	300
TSS	24 ± 1.0-248 ± 1.73	85.25 ± 1.71	500	500
TDS	1212 ± 2.0-3232.3 ± 2.65	2219.32 ± 2.33	500	500
DO	1.19 ± 0.04-8.40 ± 0.10	5.19 ± 0.07	4.0	5.0
BOD	32.4 ± 1.70-163 ± 3.24	97.30 ± 2.09	30	5
COD	116 ± 2.0-398 ± 3.46	244.33 ± 2.49	60	10
Chloride	683.5 ± 2.88-8008.8 ± 2.99	2456.35 ± 2.70	350	250
Sulphate	38 ± 1.0-1800 ± 3.0	491.25 ± 2.75	500	250
Surfactant	0.0-13 ± 0.10	5.21 ± 0.06	-	-
Fe (mg/L)	32 ± 0.66-625.24 ± 2.56	235.64 ± 1.13	2.0	1.0
Zn (mg/L)	5.2 ± 0.03-73.5 ± 1.04	38.22 ± 0.54	5.0	4.0
Pb (mg/L)	0.11 ± 0.01-22.11 ± 0.64	10.84 ± 0.30	0.10	0.01
Cr (mg/L)	1.2 ± 0.01-20.3 ± 0.48	10.42 ± 0.15	0.5	0.05
Mn (mg/L)	0.02 ± 0.01-0.9 ± 0.02	0.37 ± 0.02	1.0	0.10

With the exception of pH and EC (μs/cm at 25^{o} C), unit for other parameters are expressed in mg/L

Table 2: Calculation of Water Quality Index (WQI) of the steel ef

Parameter	Observed value(V_o)	Standard value (S_V)	1/ S_V	Unit weight (W_p)	Quality rating (Q_r)	WpQr
pH	1.38	6.5	0.153846	0.209074	1124	234.999
Cond. (µs/cm)	9824.75	300	0.003333	0.00453	32.74917	0.148352
TSS (mg/L)	85.25	500	0.002	0.002393	0.1705	0.000408
TDS (mg/L)	2219.325	500	0.002	0.002393	4.43865	0.010621
DO (mg/L)	5.19	5	0.2	0.239278	98.02083	23.45427
BOD (mg/L)	97.3	5	0.2	0.239278	1946	465.6358
COD (mg/L)	224.33	10	0.1	0.119639	2243.3	268.3866
Cl^- (mg/L)	2456.349	250	0.004	0.004786	982.5396	4.70201
SO_4^{2-} (mg/L)	491.25	250	0.004	0.004786	196.5	0.940364
Surfact. (mg/L)	5.2125	15	0.066667	0.079759	34.75	2.771641
Total				**0.905916**		**1001.049**

WQI = $\sum_{i=1}^{10} W_p\, Q_r / \sum_{i=1}^{10} W_p$ = 1105.013

Table 3 Calculation of Heavy Metal Pollution (MPI) Index of the steel effluents

Parameter	Observed value(V_o)	Standard value (S_V)	1/ S_V	Unit weight (W_i)	Quality rating (Q_r)	WpQr
Fe	235.64	1	1	0.007486	23564	176.4001
Zn	38.22	4	0.25	0.001872	955.5	1.788218
Pb	10.838	0.01	100	0.7486	108380	81133.27
Cr	10.4225	0.05	20	0.14972	20845	3120.913
Mn	0.3717	0.1	10	0.07486	371.7	27.82546
Total				**0.982538**		**84460.20**

MPI = $\sum_{i=1}^{5} W_p\, Q_r / \sum_{i=1}^{5} W_p$ = 85961.29

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