ASSESSMENT OF EFFLUENT FROM HERBAL MIXTURE INDUSTRY ON THE PHYSICO- CHEMICAL PARAMETERS OF NEARBY WELL WATER

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ABSTRACT

This study investigated effluent from herbal mixture industry and well water nearby effluent drainage. Effluent was sampled twice while well waters were sampled four times (July, August, December and January). All the samples collected were analysed for parameters including water temperature, apparent colour, turbidity, conductivity, total suspended solids (TSS), total dissolved solids (TDS), dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), SO_4^{2-}, NO_3^-, PO_4^{3-} and Cl^- using standard methods. Sodium, K, Mg, Ca Cd, Cr, Cu, Fe, Mn, Pb and Zn were also determined using Atomic Absorption Spectrophotometry (AAS). The study revealed that the colour of the untreated herbal mixture effluent was black, and turbid in appearance with unpleasant odour. Ranges of turbidity (140.8±0.057 – 144.11±0.157 NTU), apparent colour (1579.35±0.071 – 1643.32±0.821 Pt.-Co.), BOD (20.05±2.828 – 24.40±0.566 mg/L), COD (297.87±0.431 – 301.01±0.041 mg/L), TSS (639.0±12.73 – 643.0±1.414 mg/L) and PO_4^{3-} (6.571±0.071 – 6.793±0.004 mg/L) were above Nigerian standards- National Environmental Standards and Regulations Enforcement Agency (NESREA). However, well water alkalinity, pH, water temperature, apparent colour, turbidity, conductivity, TSS, TDS, COD, SO_4^{2-}, NO_3^-, PO_4^{3-}, Cl^-, Ca and Fe values were significantly ($p < 0.05$) different between and within the wells. The mean vales of pH, DO, BOD, TSS, PO_4^{3-}, and Pb of some wells located close to the effluent drainage were above World Health Organisation (W.H.O.) drinking water quality standard. The range of values obtained in the entire wells for apparent colour, turbidity, COD, Cd and were above W.H.O. standard.

The study concluded that the level of pollution of herbal mixture effluents negatively impacted the well water in the study area.

Key words: effluent, groundwater, herbal mixture, NESREA, physico-chemical, well-water.

INTRODUCTION

According to WHO, in both developed and developing countries, a considerable percentage of people use medicinal plant remedies and the number is on the increase as population increase especially among younger generation Nandy *et. al*., (1998). Before millennium, herbal medication was household practices in Nigeria, as the importance of the medicine was known, its production increased by leaps and bounds everyday. The widespread of herbal medicines cottages in the country posed challenges of health and environmental issues. Health issues are safety of the consumers because some of these herbal products cut-corners of regulated agencies in charge of drug viability, originality and safety; also concern is the environmental issues. Flowers, stems, bark, nuts, fruits, resins, seeds, roots, leaves for herbal medicines are from plants which pose potential risks to plant ecology. In addition, herbal medicines production generates both solids and liquid wastes with disposal attentions. Solid wastes usually comprises of unused plant materials, spent plant materials, un-sales medicines, packaging material and damaged bottles (Kavitha, *et al.,* 2012). During manufacture of herbal medicines, a large volume of wastewater generation takes place is highly polluted because of presence of substantial amounts of organic pollutants (Vanerkar *et al.*, 2013).

Different types of pollutants are present in the wastewater generated during the manufacturing process of herbal drugs, the water is discharged as a waste and this waste contains many soluble and insoluble pollutants (Savita and Deepa, 2013). The wastewater discharged is highly polluted in nature with capricious characteristics such as colour, total suspended solids, biological oxygen demand and chemical oxygen demand. Discharge of effluent on land might result in obnoxious condition in the area and affects the groundwater quality around. Effluent discharge with high temperature can affect both fauna and flora system of the water bodies. Hence, the effluent presents significant disposal and treatment problems (Savita and Deepa, 2013). The discharge of waste water into drainages will finally enter the nearby water bodies creating extensive pollution and threatening to the aquatic life and health of surrounding human population (Singare and Dhabarde, 2014).

According to W.H.O. (2011), access to safe drinking water is important as a health and development issues at a national, regional and local level as well is essential to sustain life and a satisfactory (adequate, safe and accessible) supply must be available to all. UNESCO (2003) estimated that globally, groundwater provides about 50% of current portable water supplies, 40% of the demand of self-supplied industries and 20% of water use in irrigated agriculture. In almost African countries, groundwater is the most realistic water supply option for meeting dispersed water need (Foster, *et. al,.* 2000; Ocheri and Ahola, 2007). UNICEF, (2008) affirmed that groundwater is the most common water sources, especially in urban, rural and sub-urban areas in developing countries. Also, Edet *et al.,* (2011), groundwater plays an important role in the social and economic life of the people in terms of domestic, industrial and agricultural use.

However, at Surulere area, Osogbo southwestern Nigeria, groundwater is more widely available beside rain water and less expensive to extract. Effluent from herbal mixture industry is being discharged into an open drainage close to some wells in Surulere area of Osogbo. Water from the wells are coloured indicating possible effluent pollution. There is therefore the need to assess the effect of the effluent on the water quality, hence this study.

MATERIALS AND METHODS

This study was carried out at Surulere Community (Kasmo Area), Oke-Baale, Osogbo, Osun State Southwestern Nigeria. The descriptions are as shown in the Table 1 below.

Table 1: Location of Sampling Points and their Description

S/N	Station ID	GPS Coordinates of the Stations	Elevation	Rough Well Depth	Well Distance Relative to Drainage
1	HME	N 07º 46' 20.6'', E 004º 34' 52.8''	350 m	-	-
2	W_1	N 07º 46' 22.4'', E 004º 34' 50.3''	335 m	9.68 m	2.7 m (Same side as effluent drainage)
3	W_2	N 07º 46' 22.7'', E 004º 34' 50.2''	349 m	10.56 m	> 100 m (Other side of effluent drainage)
4	W_3	N 07º 46' 22.3'', E 004º 34' 49.4''	342 m	11.43 m	3.9 m (Same side as effluent drainage)
5	W_4	N 07º 46' 22.1'', E 004º 34' 46.7''	339 m	9.72 m	1.3 m Same side as effluent drainage

6	W_5	N 07° 46' 21.9'', E 004° 34' 44.2''	335 m	7.04 m	19.0 m (Same side as effluent drainage)
7	W_6	N 07° 46' 22.7'', E 004° 34' 44.4''	337 m	7.12 m	8.4 m (Other side of effluent drainage)
8	W_7	N 07° 46' 22.1'', E 004° 34' 43.2''	336 m	7.03 m	13.0 m (Same side as effluent drainage)

TJHME = Herbal Mixture Effluent
W_1 - W_7 = Well 1 to Well 7

Sampling

Herbal mixture industry began production in Surulere area not earlier than 2007, ever since the industry started production; there have been no functioning wastewater treatment facilities within its premises. Waste waters are discharged at every stage of production including wash water into open drainage of a single lane road in the community. The untreated herbal mixture effluents were collected in October and December, 2013 and seven well water samples were collected in July, August and December, 2013 and January, 2014. The parameters determined were: temperature, pH, turbidity, conductivity, total suspended solids (TSS), total dissolved solids (TDS), total acidity, total alkalinity, chloride, sulphate, nitrate, phosphate, chemical oxygen demand (COD), biological oxygen demand (BOD) and dissolved oxygen (DO). Sodium, calcium, potassium, magnesium and heavy metals such as Cd, Cr, Cu, Fe, Mn, Pb and Zn were also determined. Water temperature and dissolved oxygen fixation were done *in-situ*; other parameters were determined in the Hyrobiology Laboratory, Zoology Department of Obafemi Awolowo University, Ile-Ife. Metals were determined at Centre for Energy Research and Development of the same institution.

Experimental

Temperature was determined using graduated mercury in-bulb thermometer, apparent colour was determined on unfiltered samples colorimetrically using Potassium Chloroplatinate-cobalt (Pt-Co.) solutions standards, while turbidity was determined nephelometrically by comparison with turbidity (NTU) standards (APHA, *et. al.*, 1998). The pH and conductivity were determined using pH-meter and conductivity meter respectively. Dissolved oxygen (DO) was determined using Winkler methods while biochemical oxygen demand (BOD) was determined by dilution method (Golterman, *et. al*., 1978). Chemical oxygen demand (COD) was determined by dichromate digestion method, chloride by mercuric nitrate method (APHA, *et. al.,* 1998). The nitrate ion was analysed using brucine-sulphanlinic acid method (Golterman, *et. al*., 1978), the phosphate by the vanadomolybdo-phosphoric acid colorimetric method and the sulphate by turbidimetric method (Ademoroti, 1996).

The total solids (TS) as well as total dissolved solids (TDS) of samples were determined gravimetrically after oven drying them to constant weight at 105 ± 2°C (USEPA, 1998).Total suspended solids (TSS) were calculated as the difference between TS and TDS. Total acidity, Total alkalinity were determined by titrimetric methods (Golterman, *et. al*., 1978). Sodium, K, Ca, Mg, Cd, Cr, Cu, Fe, Mn, Pb and Zn were determined using Atomic Absorption Spectrophotometry (AAS) after the samples had been digested, (APHA *et. al,* 1998). Sample collection, preparation and treatment were carried out according to the standards (APHA *et. al,* 1998). All the chemicals used were of analytical reagent grade and all the equipment were checked and calibrated according to the manufacturer's specifications. Duplicate analyses of the samples were run. Data obtained from the analyses were run using Microsoft Excel and SPSS.

RESULTS

In Table 1, effluent mean temperature measured was 27.51±0.085 ºC and 28.40±0.283 ºC. The mean values of apparent colour measured were 1579.35±0.071 Pt.-Co. and 1643.32±0.821 Pt.-Co., while turbidity ranged between 140.84±0.057 NTU and 144.11±0.157 NTU, respectively. A range of 6.11±0.165 and 6.21±0.127 was recorded for pH. Total acidity of the effluent ranged from 170.0±7.071 mg$CaCO_3$/L to 180.0±11.31 mg$CaCO_3$/L, while the total alkalinity ranged between 200.0±2.828 mg$CaCO_3$/L and 220.0±7.071 mg$CaCO_3$/L, respectively. The DO obtained values ranged between 4.09±0.011 mg/L and 4.13±0.00 mg/L while the mean BOD_5 concentrations ranged from 20.05±1.655 mg/L and 24.40±0.566 mg/L A range of 297.87±0.431 mg/L and 301.01±0.014 mg/L was obtained for COD. The TSS, TDS and conductivity values were ranged between 639.0±12.73 mg/L and 643.0±1.414 mg/L; 293.0±0.000 mg/L and 348.6±0.283 mg/L and 488.0±11.31 µS/cm and 498.0±11.31 µS/cm, respectively. The concentrations of anions range of values were : SO_4^{2-} (91.06±0.078 – 92.08±0.042 mg/L), NO_3^- (9.156±0.007 – 9.733±0.004 mg/L), Cl^- (23.18±0.014 – 23.35±0.071 mg/L) and PO_4^{3-} (6.571±0.071 – 6.793±0.004 mg/L). Also in the effluent, potassium (3.991±0.001 mg/L) had the highest concentration while sodium (1.009±0.012) had the least concentration. Heavy metal such as Cd, Cr and Cu had their mean values between 0.006±0.001 mg/L and 0.281±0.005 mg/L while Fe, Mn, Pb and Zn ranged between 0.008±0.007 mg/L and 0.188±0.001 mg/L.

In Table 2, the mean values of well water temperature ranged from 23.38 ºC to 26.25 ºC. The mean values of well water apparent colour ranged from 56.97 Pt.-Co to 1280.3 Pt.-Co. while the mean turbidity values of well water ranged from 5.99 NTU to

104.93 NTU. Total suspended solid of the well water during the study ranged from 61.85 mg/L to 288.50 mg/L, while TDS ranged from 59.40 mg/L to 721.50 mg/L. The conductivity mean values of well water varied from 98.93 µS/cm to 1204.5 µS/cm. The mean pH of the well water during the study varied from 6.40 to 10.18. The mean DO values ranged from 0.30 mg/L to 4.40 mg/L; BOD_5 had its mean concentration between 43.17 mg/L and 53.02 mg/L. Chemical oxygen demand mean concentrations ranged between 23.47 mg/L and 32.28 mg/L.

In the table 2 also, sulphate concentrations ranged from 13.00 mg/L to 78.03 mg/L, nitrate concentrations ranged from 0.492 mg/L to 1.1.326 mg/L, phosphate from 3.966 mg/L to 6.791 mg/L and chloride from 31.70 mg/L to 270.20 mg/L, respectively. Between calcium, sodium, potassium and magnesium in the well water, Ca (37.19 mg/L) had highest concentration while Mg (1.316 mg/L). The ranges of mean values obtained in the entire wells for Cd (0.052 – 0.122 mg/L) and Cr (0.113 – 0.161 mg/L), Fe (0.036 – 0.119 mg/L), Mn (0.039 – 0.077 mg/L), Cu (0.088 – 0.119 mg/L) and Zn (0.091 – 0.176 mg/L) were respectively.

Table 1: Mean Values of Physico-chemical Parameters of Herbal Mixture Effluent

Parameters	October (Mean ±SD)	December (Mean ± SD)	NESREA
Water temperature °C	27.51±0.085	28.40±0.283	40.0
Apparent colour Pt.-Co.	1579.35±0.071	1643.32±0.821	Colourless
Turbidity (NTU)	140.84±0.057	144.11±0.157	5.0
Ph	6.11±0.165	6.21±0.127	6.0-9.0
Acidity (mg$CaCO_3$/L)	170.0±7.071	180.0±11.31	NA
Alkalinity(mg$CaCO_3$/L)	200.0±2.828	220.0±7.543	NA
DO (mg/L)	4.132±0.009	4.088±0.011	3.0
BOD (mg/L)	20.05±1.655	24.40±0.566	20.0
COD (mg/L)	301.01±0.041	297.87±0.431	40.0
TSS (mg/L)	639.0±12.73	643.0±1.414	10.0
TDS (mg/L)	293.0±0.009	348.6±0.283	500.0
Conductivity (µS/cm)	488.0±11.31	498.0±13.01	1000.0
Sulphate (mg/L)	91.06±0.078	92.08±0.042	100.0
Nitrate (mg/L)	9.733±0.004	9.156±0.007	10.0
Chloride (mg/L)	23.18±0.014	23.35±0.071	100.0
Phosphate (mg/L)	6.793±0.004	6.571±0.071	2.0
Na (mg/L)	1.009±0.012	2.998±0.003	NA
K (mg/L)	3.991±0.001	3.189±0.001	NA
Ca (mg/L)	1.872±0.002	3.199±0.001	NA
Mg (mg/L)	3.711±0.002	2.019±0.001	NA
Cd (mg/L)	0.122±0.001	0.119±0.003	0.1
Cr (mg/L)	0.010±0.008	0.006±0.001	0.01
Cu (mg/L)	0.281±0.005	0.281±0.001	1.0
Fe (mg/L)	0.122±0.002	0.188±0.001	2.0
Mn (mg/L)	0.099±0.001	0.051±0.006	1.0
Pb (mg/L)	0.010±0.003	0.008±0.007	0.1
Zn (mg/L)	0.119±0.002	0.131±0.002	5.0

S.D= Standard Deviation

NA = Not Available

NESREA= National Environmental Standards and Regulations Enforcement Agency

Table 2: Physicochemical parameters of well water samples

Parameters	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6	Well 7	WHO	P value
Water temperature °C	23.50	25.63	23.38	26.25	25.35	26.25	25.13	40.0	0.108
Apparent colour Pt.-Co.	59.97	56.97	224.90	595.75	1280.3	435.82	219.91	Colourless	0.510
Turbidity (NTU)	7.72	5.99	10.17	59.17	104.93	22.42	11.71	5.0	0.944
pH	8.28	6.78	7.89	10.18	9.18	9.25	6.40	6.5-8.5	0.284
Acidity (mg$CaCO_3$/L)	25.50	44.25	35.00	41.88	66.75	67.5	69.65	-	0.011
Alkalinity(mg$CaCO_3$/L)	77.05	33.07	62.75	614.25	246.77	269.75	41.65	-	0.742
DO (mg/L)	3.98	3.33	4.40	1.50	1.30	0.30	3.49	3.0	0.033
BOD (mg/L)	43.49	43.17	49.28	50.00	49.65	53.02	52.13	50.0	0.003
COD (mg/L)	24.23	23.47	26.31	25.88	29.72	30.60	32.28	-	0.972
TSS (mg/L)	81.85	61.85	70.08	288.50	210.50	88.90	92.40	150	0.554
TDS (mg/L)	74.65	59.40	78.43	721.50	327.75	334.60	59.43	500.0	0.878
EC (µS/cm)	117.4	98.83	131.03	1204.5	544.75	556.75	100.64	1000.0	0.869
Sulphate (mg/L)	33.01	13.00	13.720	52.90	73.49	78.03	66.19	250.0	0.164
Nitrate (mg/L)	0.492	0.566	0.744	1.301	1.326	0.834	0.541	50.0	0.151
Chloride (mg/L)	85.79	31.70	79.14	270.20	190.30	217.83	131.74	250.0	0.051
Phosphate (mg/L)	3.966	4.220	4.210	4.281	5.509	6.791	5.069	5.0	0.203
Na (mg/L)	12.52	8.718	10.838	4.308	17.00	14.68	18.09	200.0	0.001
K (mg/L)	2.958	3.637	2.445	5.869	2.697	4.025	3.748	10.0	0.000
Ca (mg/L)	20.41	12.67	21.13	22.92	37.19	13.35	34.23	75.0	0.056
Mg (mg/L)	3.353	2.776	2.707	3.227	4.065	1.316	4.132	50.0	0.000
Cd (mg/L)	0.071	0.077	0.060	0.058	0.052	0.065	0.122	0.003	0.017
Cr (mg/L)	0.161	0.143	0.133	0.149	0.139	0.119	0.113	0.05	0.000
Cu (mg/L)	0.097	0.103	0.088	0.097	0.119	0.109	0.107	2.0	0.045
Fe (mg/L)	0.039	0.046	0.036	0.045	0.119	0.057	0.091	0.3	0.057
Mn (mg/L)	0.059	0.062	0.048	0.046	0.070	0.039	0.056	0.1	0.000
Pb (mg/L)	0.041	0.017	0.055	0.077	0.016	0.004	0.052	0.01	0.001
Zn (mg/L)	0.097	0.176	0.091	0.135	0.119	0.112	0.123	3.0	0.000

*$P<0.05$ significant.

W.H.O. =World Health Organisation

DISCUSSION

In Table 1, the mean values obtained for apparent colour, turbidity, total suspended solid, phosphate and chromium were above NESREA limit value. High suspended solid, apparent colour and turbidity in the effluent could be associated with materials used in herbal mixture production. The presence of such waste material in the environment could lead to increased organic matter in receiving water bodies, hence inimical. The high TSS values could be attributed to remains of flowers, stem, bark, nuts, fruits, resins, seeds, roots, and leaves in herbal effluent. The effect of presence of total suspended solids is the turbidity due to silt and organic matter (Mahananda, *et. al.,* 2011). High phosphate values in the effluent could be attributed to detergent that is used in cleaning pots and other materials for herbal productions. Water used in the production could also be the source of phosphate. Phosphate leads to eutophication process in water body. Chromium is an important industrial metal, where it is used in alloys such as stainless steel, protective coatings on other metals, and pigments for paints, rubber, and floor coverings. Sources of high concentration of chromium in the herbal mixture effluent could be from dissolution of chromium metal from chromium coated/plated machine/herbal cooking pot and water being used in the industry.

Dissolved oxygen, biological oxygen demand, chemical oxygen demand were also higher than the permissible limits (NESREA), Table 1. This is attributed to the presence of a high content of biodegradable organic pollutants in the plant materials. Changes in pH can be indicative of an industrial pollutant, the slightly acidic pH values obtained were within NESREA limits of 6 to 9 for chemicals, soap and detergent effluent discharge into the environment. Temperature, alkalinity, acidity total dissolved solids and conductivity values were lower than NESREA permissible limits for wastewater discharged into the environment. Other parameters including heavy metals were lower than nation limit.

In table 2, the temperature values obtained in this study is similar to the findings of Ojo, *et. al.,* (2014) on groundwater studies in Osogbo. The temperature values were within the permissible limits (40 ^oC) of W.H.O. (2008) standards. The apparent colour and turbidity values of well water were higher in well 5 than other wells. High apparent colour and turbidity values in the wells could be attributed to the combined effects of characteristic coloured effluent from herbal mixture industry infiltrating into the wells, the release of colouring substances from basement rocks of the wells due to their locations. Both the apparent colour and turbidity values are higher than WHO permissible limits in all the wells. Though high turbidity is often a sign of poor water quality and land management, crystal clear water does not always guarantee healthy water. Meanwhile, TSS mean values obtained for the well 4 and well 5 are much higher than the recommended 150 mg/L limit of W.H.O; higher values of TSS can also lead to increased turbidity. The TDS and conductivity mean values are within the recommended W.H.O., 2008 limits except for well 4, hence attributed to catchments' geology, or herbal mixture effluent impacts. The mean pH of well 4, well 5 and well 6 are more than permissible range (6.5 – 8.5) of W.H.O. The report is in line with the studies of Ojo, *et. al.,* (2014) and Edet, *et. al.,* (2011) on groundwater quality.The high mean pH values obtained from samples from those wells might be connected with groundwater recharges via infiltration from effluent runoff from herbal mixture. It might be due to the presence of dissolved substances coming from bedrocks, soils and other materials in the soil because basic rocks such as limestone contribute to higher pH values, Brown and Caldwell, 2004. Human activity such as water guard treatment chemicals which were used by the residents could also be responsible for high pH values recorded. According to Mosley *et. al*., (2004), water with a pH > 8.5 indicates hard water.

Also in Table 2, W.H.O limits (3.0 mg/L, DO) are exceeded in wells 1, 2, 3 and 7. The low DO could be attributed to the fact that groundwater has no natural re-aeration process available, so once depleted; groundwater DO will remain very low. The BOD_5 values were probably due to the increased input of decomposable organic matter into the wells through effluent discharges aided by high precipitation. However, the BOD_5 studied exceeded the safe limit for drinking water quality (W.H.O., 2008) in wells 4, 6 and 7. Chemical oxygen demand mean concentrations were above the permissible limits- 10 mg/L, (W.H.O., 2008) in the entire wells. Phosphate concentrations exceeded safe limits (W.H.O) meant for domestic uses in wells 5, 6 and 7, while mean values of chloride also exceeded the permissible limit (250 mg/L) in well 4. This is an attestation of the use of chlorine in treatment methods of the wells in the study area, and effluent impacts.

Sodium, potassium, calcium and magnesium mean concentrations are lower than safe limits of (W.H.O). The range of mean values obtained in the entire wells for Cd and Cr are above W.H.O. standard while Fe, Mn, Cu and Zn are below W.H.O. standard. The mean concentrations of Pb are higher than W.H.O standard limits in the entire wells except well 5 (Table 2). Cadmium is accumulated at higher rate than many of the other heavy metals and its danger is particularly higher in man by the fact that it is only eliminated in very small amount through faecal losses mainly by the kidney. Chromium causes cancer, nephritis, gastrointestinal ulceration, perforation in partition of nose. It penetrates cell membrane and badly affects central nervous system. It causes respiratory trouble, lung tumours when inhaled and may cause complications during pregnancy and has as adverse effects on aquatic life. Leads to high rate of miscarriages, affects skin, and respiratory system, damages kidney, liver and brain cells. Disturbs endocrine system, causes anaemia, and long term exposure may cause even death, Ian, *et al.,* 2006.

CONCLUSION

Herbal mixture industry discharges organic pollution load, high TSS, apparent colour, turbidity, phosphate and cadmium. The effect of untreated effluent from herbal industry has accumulated over years resulting into pollution of groundwater located around the effluent's drainage. This is a situation that should alert the National Environmental Standards and Regulations Enforcement Agency (NESREA) to continuously monitor industrial effluents and enforce Nigeria's Environmental Laws. The study concluded that the level of pollution of herbal effluents had exceeded the permissible levels and the well water in the study area were negatively impacted.

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