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Physico-Chemical Characteristics of Different Types of Waste Waters in Thiruvananthapuram District, South India

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Abstract

Different wastewaters often exhibit very different physico-chemical characteristics accounted from variable quantities of various pollutants according to the source of generation. The characterization of wastewater is thus the foremost thing in any waste management practices as it determines the adequate methodology for treatment consideration, thereby minimizing the impacts on the receiving environment. The present study aims to assess the characteristics of effluents generated from different sources such as automobile service station, spray painting centre and sewage in Thiruvananthapuram, Kerala, South India. The results of the show that the concentration of various contaminants including heavy metals (Pb, Cd, Cr, Zn, Hg and As) are more than the standard prescribed limits by various agencies. Therefore, continuous discharge of these untreated effluents to soil or inland surface water bodies deteriorates the natural quality of soil/ water, and make it unfit for the existence of life. Thus, there is an urgent need for developing an adequate treatment methodology which can eliminate the problem of future contamination.

Keywords: Effluent; Service station; Spray paint; Sewage; Heavy metals

1. Introduction

The increasing human interferences on the environment make the air, water and soil polluted. The expanding population demands huge quantities of pure water for their needs and generate that much as wastewater. In all most all developed and developing nations of the world pure water is becoming an increasingly scarce resource and planners are forced to consider any sources of water which might be used economically and effectively to promote further development (Gross, 2005).

India Infrastructure Report (Kamyotra and Bharadwaj, 2011) shows that in India about 38,254 million litres per day (MLD) of wastewater is generated in urban centres comprising Class I cities and Class II towns having a population of more than 50,000 (accounting for more than 70 per cent of the total urban population). The municipal wastewater treatment capacity developed so far is about 11,787 MLD that is about 31 per cent of wastewater generation in these two classes of urban centres. By 2051 the projected wastewater from urban centres may cross 120,000 MLD while the rural India it will be not less than 50,000 MLD. However, the wastewater management plans do not address this increasing pace of wastewater generation and the growing scarcity. In India, in view of its developing status, the industry as well as agriculture sector are growing and require water, demand for which is also growing at the same time. The disposal of enormous quantities of untreated wastewater from various sectors leads to the depletion of surface water quality, groundwater quality, air quality and ultimately the soil in the surrounding area. Therefore, it is necessary to look at the sustainability of both environment and development simultaneously and holistically. To resolve such issues, there is a need to change the entire focus in such a way that water recycling and reuse is an integral part of our functioning so that there remains no scarcity and no damage, and the environment remains safe for living in (Ranade and Bhandari, 2014).

Wastewater treatment plays a vital role in the protection of environmental health by preventing the pollution of soil, lakes or rivers. Due to water scarcity, wastewater irrigation to edible crops is increasing. These techniques are the economically sound and good alternative for direct discharge of these effluents into streams, lakes or soil. It has obviously short-term benefits but continuous irrigation with these wastewaters creates serious environmental health impacts because those wastewaters from various sources contain a wide spectrum of pollutants including heavy metals. Buildup of these heavy metals in soil and water eventually pollutes the food chain. So, the characterization of wastewater prior to effective treatment and final disposal has invited special attention (Azizi *et al.*, 2016).

The origin of wastewater varies widely such as from industries, homes and business firms and the entry of surface water, stormwater and groundwater into the wastewater collection system widening the quantity of wastewater. The waste water source determines its characteristics and treatment methodology. Characterization of wastewater is the first step in the process of finding solutions to their treatment, recycling, reuse, and disposal (Gross, 2005).

2. Materials and Methods

2.1. Study area and Sampling stations

Thiruvananthapuram district lies in the southern part of Kerala (Fig. 1) extending between the latitudes 8° 17' 25'' to 8° 51' 46'' N and longitudes 76° 40' 25'' to 77° 17' 6'' E. The Survey of India (SOI) Toposheet 58/15/NE and 58D/

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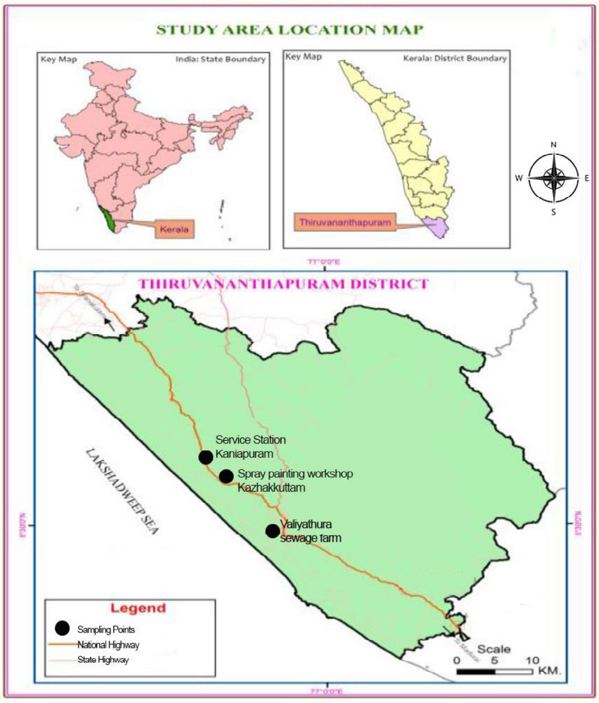

Fig. 1. Map of study area in Thiruvananthapuram, Kerala

15/SE of 1:25000 scale have been used for the preparation of location map. The wastewaters for the study were collected from the three selected stations of Thiruvananthapuram and subjected to characterisation. These include wastewater from an Automobile Service station at Kaniyapuram; Automobile spray painting workshop at Kazhakkuttom and the raw sewage from the Valiyathura sewage farm. The location map of the study area is shown in Fig. 1

a. Automobile Service Station wastewater

Like in all other developing and developed sites, there are many automobile repair centres at every nooks and corner of the Capital city, Thiruvananthapuram. The vehicle repair effluent was collected from a servicing centre located at Kaniyapuram, Thiruvananthapuram, where the wastewater was collected and stored in concrete underground tanks. The homogenous wastewater from the tank was pumped out and collected in clean dry plastic containers.

b. Automobile Spray Painting Spent wash.

With an increase in the vehicular population the servicing centres also grown up both in urban and rural sites. The painting and associated works are of great importance in contributing to the pollution of land and inland surface water bodies in urban and rural centres of the world. Automobile spray painting spent wash for the study was collected with the help of painters in a workshop at Kazhakkuttom, where the crude painting wastewater was negligibly drained out to nearby land and wetland area.

c. Sewage

Sewage is the water contaminated with human wastes or contaminated mainly due to human activities. Sewage originated in different parts of the city is collected at the collection point, sewage farm in Valiyathura, Thiruvananthapuram city, Kerala. The homogenous raw sewage from the collection point was collected using a plastic bucket.

2.2 Methodology

The physical and chemical characteristics of wastewaters were determined following the standard procedures in APHA (2012), Saxena (1994) and Trivedy and Goel (1998).

The temperature of the wastewater samples was measured at the site with an ordinary mercury thermometer. Visual comparison method (Pt-Co method) was adopted to measure the colour of water samples (Trivedy and Goel, 1998). The pH of the water samples was measured electrometrically by using a glass electrode digital pH meter (ELICO, LI 614). Electrical Conductivity of the water samples were measured using a Digital Conductivity meter (Systronics, 306). Concentration of solids (TS, TDS, TSS) in the waste water samples were determined by evaporation method described by Trivedy and Goel (1998). Total alkalinity of the samples was determined using phenolphthalein method and Acidity of the samples was determined using Methyl orange method (APHA,2012). Free carbondioxide content in the samples were determined by using phenolphthalein indicator (APHA, 2012).

Hydrogen Sulphide content in the water samples were determined by following the procedure in APHA (2012). Samples were collected in 250 mL BOD bottles and fix the hydrogen sulphide at the site using cadmium chloride. After 48 hours of incubation, cadmium sulphate precipitate was treated with 4N HCl and iodine solution. Then titrated against 0.1N sodium thiosulphate using starch as indicator. Oil and Grease contents in the samples were extracted using petroleum ether and Dissolved oxygen in the samples were determined by Winkler’s Method (APHA, 2012).

Biochemical Oxygen Demand (BOD) is one of the important water pollution indicators. BOD_3 was determined by following APHA (2012). 1L dilution water was prepared by bubbling compressed air in distilled water for about 30 minutes and treated with 1 mL of each phosphate buffer, $MgSO_4$, $CaCl_2$ and ferric chloride solutions and neutralized by 1 N NaOH. Then the contents were mixed thoroughly and then filled 2 sets of BOD bottles. For blank, filled 2 sets BOD bottles with dilution water alone. Then kept 1 set of the bottles in incubator at 27°C for 3 days, and determined the initial DO of content of another set immediately. The final DO in the water samples was determined immediately after the completion of 3 days incubation.

Chemical oxygen demand was determined by open reflux method (APHA, 2012). Nitrate –Nitrogen (NO_3 –N) content in the water samples were determined following the Brucine method (Saxena (1994) by using a UV-VIS Spectrophotometer (Model 118, Systronics, India). Total Nitrogen (TN)/ kjeldahl Nitrogen and Ammonia nitrogen were determined by kjeldahl‘s method (Saxena, 1994).

Phosphorous content in the water samples were determined following spectrophotometric method, Silicates were determined following the molybdosilicate method, Sulphates were determined by turbidimetric method by using a UV-VIS Spectrophotometer (model 118, Systronics, India) and Chloride content of water samples was estimated by Argentometric titration method of Saxena (1994).

Total hardness of the water samples were determined by EDTA titration method using Eriochrome Black-T 81 as indicator while calcium and magnesium contents were determined using murexide as indicator (Saxena, 1994). Sodium and potassium contents were determined using a Flame Photometer (ELICO Model, CL 361) by following the procedures of Trivedy and Goel (1998).

Concentration of Iron the samples were determined spectrophotometrically (Trivedy and Goel (1998). Heavy metal content in the samples were analysed by using Atomic absorption Spectrophotometer (Double beam Atomic Absorption Spectrophotometer (Shimadzu, Model: AA-7000) after acid digestion (Trivedy and Goel (1998).

3. Results and Discussion

The results of physico-chemical analysis of effluents such as service station effluent, spray painting spent wash and raw sewage are given in Table 1.

3.1. Temperature

The result showed that wastewater from various sources showed differences in their temperature (Table.1) and the comparatively higher temperature was recorded in the sewage water (31.5°C). According to EPA (2002), the effluent discharge standard for temperature is 40˚C, and thus the temperature of all the three wastewaters are within the permissible limit of discharge into surface water bodies or to land.

Temperature is considered to be an important indicator of the biochemical activity in water and every 10˚C rise in temperature doubles the biochemical activity within the temperature range of 5^{0}C - 30˚C (Dharmappa *et al*., 2011).

3.2. Colour

According to EPA (2002), the effluent discharge standard of colour is unobjectionable and the colour of the selected wastewaters was recorded as 350, 230 and 230 Hazen units for service station effluent, spray painting spent wash and raw sewage respectively (Table 1). Among the wastewater samples, service station effluent has recorded highest value (350 HU) and visually it was very dark coloured and this may be due to high concentration of organic and inorganic solids, oils, greases along with the dust which sticks on the oily surfaces. Bacterial degradation of the wastes also imparts colour to the water.

3.3. pH

The result showed that is the sewage water is highly acidic (pH 4.72) followed by the service station effluent (pH 5.61). The pH of spray painting spent wash was almost neutral (7.4). Bujang *et al*. (2012) reported that the wastewater from the automotive workshop shows pH ranging from 4.24 – 7.57. According to EPA (2002) the effluent discharge standard for pH is 5 to 9, and therefore the sewage it requires adequate treatment before its disposal as the pH value is below the permissible level. The acidity of the sewage water may be due to the presence of heavy metals, dry and wet atmospheric deposition, additives used for the storage of foods, various acidic chemicals in soap, detergents, face wash, fairness creams etc (Murtaugh and Bunch, 1965). According to Mazumder and Mukherjee (2011), the presents of oil and grease, detergents, phosphates, hydrofluoric acid, ammonium bifluoride products (ABF) etc. in car wash wastewaters contributes acidity and this may be the reason for slightly acidic wastewater from the service station.

3.4. Electrical Conductivity

Electrical conductivity (EC) denotes the capacity of a substance or solution to conduct electricity. Conductivity is mainly due to the presence of various ions present in it. Among the selected wastewaters the service station effluent shows comparatively higher electrical conductivity (212.2 µS/cm) than that of the others and the sewage water shows lower values (3.082 µS/cm). Studies by Yasin *et al*. (2012) and Fall *et al.* (2013) reported that car wash waters have a higher EC value. The high electrical conductivity of the wastewater samples may be associated with high dissolved solid content, presence of various metal ions (Na^+, K^+, Cl^- etc.), chemicals etc.

3.5. Concentration of Solids

Result (Table 1) showed that all the three types of solids were higher in service station effluent followed by spray painting spent wash and raw sewage. According to Environmental Quality Standard Regulations (1979), the effluent discharge standard for TSS and TDS are 50 and 100 mg L^{-1} and as per NEQ (2000) standards, the permissible limits are 150 and 3500 mg L^{-1}. The values were clearly explicit that the concentration of solids in all the three waste-waters were several times above than the standard permissible limit set by various agencies.

Several studies (Fall *et al.*, 2013; Yasin *et al.*, 2012) reported that the total suspended solids and total dissolved solids in waste-waters from service station effluent and painting workshop waste–water was rich in the concentration of various types of solids. Total dissolved solids are the amount of various kinds of minerals present in water and in most cases, a direct relationship exists between EC and TDS. Total suspended solids denote the suspended impurities present in the water and it represents one of the most common and visible water pollution problems in receiving water bodies (Dharmappa *et al.*, 2011).

3.6. Total Alkalinity and Acidity

The present study shows that the total alkalinity values of service station effluent were highest (850 mg L^{-1}) -followed by the spray painting spent wash (750 mg L^{-1}) and raw sewage -(176 mg L^{-1}) (Table 1). Levin and Hultman (2008) also reported high alkalinity in service station effluent. Total Alkalinity is the total amount of negatively charged ions which will react to neutralise the positively charged hydrogen ions in water and thus it is a measure of the capacity of water to neutralise the acidity and is the sum total of carbonates, bicarbonates and hydroxide ions in water (Dharmappa *et al.*, 2011).

The results (Table 1) also shows that the sewage water has the highest acidity (675 mg L^{-1}) and the spray painting spent wash has the lowest acidity (46 mg L^{-1}). The highest acidity in sewage detected may be due to chemicals from the kitchen waste, laundry wash, face creams, atmospheric depositions etc. (El-Salem and Talhouni, 1995). The acidity is the total amount of positively charged ions which

Table 1. Physico-chemical characteristics of Waste waters

Parameter	Service station effluent	Spray painting spent wash	Sewage	Levene's Test (Significance)
Temp (˚C)	31	28	31.5	0.995
Colour (Hazen unit)	350	230	230	0.000
pH	5.61	7.4	4.72	0.503
EC (μS/cm)	212.2	52.55	3.082	0.000
TS (mg L^{-1})	147620	13296	12321	0.000
TDS (mg L^{-1})	62406	4460	3669	0.000
TSS (mg L^{-1})	85214	8996	8652	0.000
TA (mg L^{-1})	850	750	176	0.000
Acidity (mg L^{-1})	76	46	675	0.000
CO_2 (mg L^{-1})	33.2	28.4	463.9	0.000
DO (mg L^{-1})	3.25	4.87	4.06	0.000
BOD (mg L^{-1})	11.62	14.82	86.75	0.077
COD (mg L^{-1})	740	963	2340	0.000
NO_3-N (mg L^{-1})	0.68	0.82	1.57	0.000
NO_2-N (mg L^{-1})	0.02	0.07	0.48	0.000
NH_3-N (mg L^{-1})	6.4	9.3	31.41	0.000
TN (mg L^{-1})	14.6	16.7	44.06	0.000
ON (mg L^{-1})	3.23	4.27	9.67	0.000
IP (mg L^{-1})	2.47	2.13	4.27	0.000
OP (mg L^{-1})	1.92	1.04	2.07	0.000
TP (mg L^{-1})	4.44	3.27	7.48	0.000
Silicates (mg L^{-1})	25.8	16.4	21.7	0.000
SO_4^{2-} (mg L^{-1})	172.6	72.3	134.6	0.001
Cl^- (mg L^{-1})	184.9	1235.4	142.6	0.000
Hardness(mgL^{-1} as $CaCO_3$)	197.1	1160.1	310.9	0.000
Ca(mg L^{-1}as $CaCO_3$)	121.6	1082.16	214.7	0.000
Mg(mg L^{-1}as $CaCO_3$)	75.5	77.94	95.3	0.000
Na (mg L^{-1})	437.5	115.6	125.44	0.001
K (mg L^{-1})	79.8	85.4	95.6	0.000
TOG (mg L^{-1})	527.16	137.6	261.7	0.000
H_2S (mg L^{-1})	2.19	0.92	14.6	0.000
Iron (mg L^{-1})	10.6	1.2	3.7	0.000

will react to neutralise the negatively charged hydroxyl ions in water and thus it is a measure of the capacity of water to neutralise the alkalinity.

3.7. Carbon dioxide

In the present study highest value of CO2 content was recorded in sewage (463.9 mg L-1) followed by service station effluent (33.2 mg L^{-1}) and spray painting spent wash (28.4 mg L^{-1}) and this is an indication of high biological organic pollutant load and its active degradation in sewage. Studies by Zhou *et al.* (2006) points out that the aerobic bacterium in the sewage consumes O_2 for degradation and respiration and produce carbon dioxide (CO_2) as a by-product, and thus sewage is a very good source of CO_2 production. It was again confirmed by El-Savaf (2005) that the sewage water has a high concentration of biological activity than many other industrial waste-waters and degradation of these biological organic wastes contributed the high CO_2 content in the sewage water.

3.8. Hydrogen Sulphide

The results of the study (Table 1) showed that highest concentration of H_2S was reported in sewage water (14.6 mg/L) and it denotes active degradation of biological organic wastes in sewage than that of the others. According to Environmental Quality Standard Regulations (1979), the maximum permissible limit of H_2S in waste–waters for safe disposal is 0.5 mg/L, and in the present study, the H_2S content in the selected waste-waters were above the standard permissible limit. Previous studies reported that sewage is a mixture of all such wastes and majority of which are easily biodegradable hence the presence of a high concentration of H_2S is an indication of microbial degradation of such wastes. The less oxygen concentration and appropriate substrates in the waste–water streams favour the growth of sulphate reducing bacteria which generate H_2S in the waste–waters (Anonymous, 2009; Domingos, 2011).

3.9. Total Oil and Grease

The highest value of total oil and grease (TOG) content was recorded in service station effluent (527.16 mg/L) and lowest was in spray painting spent wash (137.6 mg/L). Because oil and grease are the major components of car wash waste–water. Studies by Fall *et al.* (2013) and Yasin *et al.* (2012) reported that high levels (1070- 2876 mg/L) of TOG in automobile service station effluents. Results of the present study showed that the concentration of TOG content in all the three selected waste-waters were above the standard permissible limit (10 mg/L) set by Indian Environmental Standards (2006).

3.10. Dissolved Oxygen

The results showed that among the selected waste-waters higher DO was reported in spray painting spent wash (4.87 mg/L) and lesser in service station effluent (3.25 mg/L). This indicates that all the different types of waste-waters were with less amounts of dissolved oxygen. The temperature plays an important role in the solubility of oxygen in the water and it reflects the physical and biological processes prevailing in water and it affects the solubility and availability of nutrients (Harrison, 1994). An average of 0.15 – 9.42 mg/L of DO was reported in service station effluent in many studies (Bujang *et al.*, 2012; Fall *et al.*, 2007).

3.11. Biochemical Oxygen Demand

Result (Table 1) showed that all three waste-waters contain appreciable amounts of biological organic pollutants and organic pollution was high in sewage water (86.75 mg/L). As per EPA (2002). the maximum permissible level of BOD for safe discharge into land or surface water is 40 mg/L. In the present study, BOD of the sewage waters was above the permissible limit, and in the case of the other two waste-waters BOD was within the permissible levels set by various agencies. The highest BOD in sewage water is an indication of high organic pollution (CPCB, 2005). Many studies (Lau *et al.* (2013); Yasin *et al.*, 2012; Bujang *et al.*, 2012) also reported that the car wash effluent is rich in BOD, and the high BOD may due to the high heavy metal load in these waters. The presence of metals in water accelerates the growth of algae in standing waters and it reduces the DO and enhances the BOD content (Ogundiran *et al.*, 2012).

3.12. Chemical Oxygen Demand

The results showed that (Table 1) all three waste-waters contain appreciably higher concentrations of COD. According to Indian Environmental Standards (2006), the maximum permissible concentration of COD in industrial waste-water is 250 mg/L, and as per EPA (2002), it is 120 mg/L. High COD indicates a high degree of pollution in water and the results showed that all the three waste-waters were rich in COD and are above the permissible limits for safe disposal. It was also found that comparatively high COD values in the sewage water (2340 mg/L), and may–be due to high oxygen demanding wastes in the sewage (Laws, 2000). Earlier studies (Yasin *et al.*, 2012; Fall *et al*., 2013; Bujang *et al.*, 2012) also reported that the painting and car wash water also contains high oxygen demanding chemicals and thus the COD will be very high.

3.13. Concentration of Nutrients

According to Indian Environmental standards (2006), the maximum allowable concentration of NO_3 – N is 18 mg/L and NO_2-N in the waste-water is 10 mg/L for disposal into inland water bodies or to land. The results (Table 1) showed that both the NO_3 – N and NO_2-N concentrations in service station effluent, spray painting spent wash and raw sewage were within the permissible limit for safe disposal into inland surface water bodies.

According to Indian Environmental Standards (2006) and EPA (2002) the maximum permissible level of total nitrogen (TN) in waste–waters, which can be disposed safely into inland surface water is 25mg/L. Results (Table 1**)** showed that the concentration of TN content in the sewage water is above the standard permissible limits for effluent disposal (44.6 mg/L), and all the other waste waters were falling within the standard permissible limits. According to WHO (2006) wastewater typically contains between 20 to 85 mg/L total nitrogen. Excessive nutrient discharge in–to the water bodies eventually leads to eutrophication and algal blooms.

It indicates the amount of biodegradable materials in the waste–waters. As per Indian Environmental standards (2006) and EPA (2002), the maximum permissible level of ammonia nitrogen in industrial waste-water for disposal into inland surface water is 1mg/L. From the recorded results (Table 1) it is clear that all the waste waters analysed contain appreciably higher amounts of ammonia nitrogen than the permissible concentration for safe disposal and the highest concentration was found in sewage. It was also noted that comparatively high organic nitrogen (ON) content was also recorded in the sewage, indicates high pollution load.

Results showed that among the selected waste–waters, sewage water contains comparatively higher concentrations of all the three forms (inorganic, organic and total phosphorous) of phosphorous and it may be due to the degradable organic wastes, pigments, salts, soaps, detergents, dyes, pigments etc present in it.

Lau *et al.* (2013) various chemicals used for cleaning, washing, lubricating etc. of vehicles contribute major portion of nitrogen and phosphorus to car wash effluent. The chemicals present in the paints of vehicles will also discharge nutrient--rich waste-water and therefore high levels of phosphates, nitrates, polycyclic aromatic hydrocarbons (PAH), Zn, Cu, Pb, TSS, Fe etc. are common in service station waste-water (Anonymous, 2011).

3.14. Silicates and Sulphates

The result showed that silicate content in the selected waste waters was within the standard -permissible standard limit. Vasantha *et al*. (2012) reported that silicate in sewage may be contributed by nail polishes, creams, dish washings, food items, faeces and urine.

It was also noted that appreciable amounts of sulphates are present in all the three waste-waters and service station effluent contains higher concentrations of sulphate followed by sewage and spent wash from spray painting industry. Yasin *et al.* (2012) reported a concentration of 112 mg/L of SO_4^{2-} in car wash effluent and the sulphate content in the sewage may be from shampoo, soap, creams, drugs, urine and faeces etc (Rudolfs, 1997). As per Indian Environmental Standards (2006) the maximum permissible level of sulphates in the waste–water for disposal into an inland water body is 250 - 400 mg/L. In the present study, the concentrations were within the permissible standard limits for disposal.

3.15. Chlorides

As per Indian Environmental standards (2006), maximum permissible level of chloride in waste–water for land disposal is 1500 mg/L and according to EPA (2002), permissible level for disposal is 750 mg/L. The result showed that chloride content in spray painting waste water exceeds the permissible level and needs adequate treatment before the discharge to inland water bodies or lands. Friedler (2004) reported approximately 166-450 mg/l of Cl^- ions in waste-water from bath-room or laundry and this may be the reason for Cl^- ions in sewage.

3.16. Total Hardness

As per Indian Environmental standards (2006), the maximum allowable concentration of total hardness in the waste-water is 300 - 400 mg/L. From the results (Table 1), it was clear that the total hardness content in the service station effluent and sewage were within the standard permissible limit, while in spray painting spent washes the value was above the permissible levels for disposal. Therefore the spray painting spent wash is not suitable for safe disposal before adequate treatment. Studies by Ntwampe *et al*. (2013) also reported a high concentration of total hardness in spray painting spent wash.

3.18. Micronutrients

Ca^{2+}, Mg^{2+}, Na^+, K^+ and Fe^{2+} are considered essentially as micro–nutrients and are found naturally in water, contribute hardness to the water.

Calcium and Magnesium

The major cations imparting hardness are calcium and magnesium (Sawyer *et al*., 1994). According to Indian Environmental standards (2006), the desirable limit of calcium and magnesium in the waste-water which can be disposed into an inland water body or land is 75 mg/L. The results (Table 1) showed that the concentration of Ca^{2+} and Mg^{2+} ions in the selected waste-waters exceeds the standard permissible limits and thus these waters cannot be disposed directly to land or water bodies.

Sodium and Potassium

The present investigation showed that appreciable concentrations of sodium and potassium are found in the selected waste–waters and sodium was higher than the potassium content. The results (Table 1) showed that higher concentration of both sodium and potassium ions were present in sewage, and it may be contributed by the nutrient-rich waste-water from industrial establishments and other institutions (Dissanayake *et al.*, 2008). It was also reported that waste–water from service stations was also very rich in both sodium and potassium (Anonymous, 2008).

Iron

According to NEQS (2000), the maximum permissible concentration of iron in industrial waste-water which can be disposed directly into an inland surface water body is 2.0 mg/L. The result (Table 1) showed that higher concentrations of iron in service station effluent and sewage. Many studies revealed that service station effluent contains an average of 4.14 mg/L of iron content (Yasin *et al.*, 2012; Anonymous, 2008) and many others reported that sewage water is act as a major pool of Fe and other pollutants including heavy metals and it may come from various sources food items, cooking dishes, drugs, cosmetics, detergents and soaps, metal parts etc. (Fall *et al.*, 2007; Dissanayake *et al.*, 2008)**.**

3.19. Heavy metals

The result of the analysis of heavy metals such as lead, cadmium, chromium, zinc, mercury and arsenic are given in Fig. 2.

Lead is one of the important toxic heavy metal found in the earth crust (Yusuf *et al.*, 2002). The result (Fig. 2) showed that the lead content in all the three types of waste waters exceeded the maximum permissible limits set by various agencies. As per Indian Environmental Standards (2006) the maximum permissible range of Pb in industrial waste-water which can be disposed directly into an inland surface water body is 0.1mg/L, and as per NEQS (2000), it is 0.5 mg/L. The high concentration of Pb is reported in spray painting spent was followed by service station effluent and sewage. The sources of Pb in waste–water may include the usage of gasoline additives in automobiles, petrol, diesel, dyes, paint, old plumbing, pottery, insecticides, tobacco smoke, textiles, scrap metal, automobile exhaust, canned fruit juices, car batteries, crayons, hair colouring, air pollution, mascara, and smelting of lead (Walker *et al.*, 2001) -and irrigation with heavy metals containing waste-waters resulting into build -up of these metals in soil and there–by enters into the food chain and ultimately affects the human beings (Wolfyang *et al.*, 1995).

Cadmium is another toxic heavy metal due to its wide range of organ toxicity and long elimination half-life of 10-30 years; poisoning result in *itai-itai* or *ouch-ouch* disease in man and it is phyto-toxic to plants (Jarup *et al.*, 1996). As per Indian Environmental Standards (2006), the maximum permissible limit of Cd in industrial effluent for safe disposal into an inland surface water body is 2.0 mg/L, while according to NEQS (2000) it is only 0.1 mg/L. From the results (Fig. 2) it was observed that a high concentration of Cd was in sewage followed by service station effluent and spray painting spent wash. According to Indian Environmental Standards (2006) the service station effluent and spray painting spent wash was within the permissible limit while according to NEQS (2000) the Cd content in all the selected waste–waters were exceeded the safe limit of discharge.

The main sources of Cd in sewage may be contributed through cigarette smoke, tobacco, coffee, gasoline, steel cooking pans, metal pipes, tap water, rubber, fertilizers, dental alloys, batteries, candy, refined cereals, colas, copper refineries, fungicides, refined grains, plastics, marijuana, evaporated milk, motor oil, oysters, paint, pesticides, processed foods, soft drinks, pharmaceutical and recreational drugs (Jarup *et al*., 1998). All these wastes are coming together in sewage and resulted in high concentrations of heavy metals.

Chromium is a very toxic heavy metal on the earth and it is naturally found in the soil, volcanic emissions, rocks etc. and there–by in plants and other living organisms (EPA, 1996). According to Indian Environmental Standards (2006), the maximum permissible range of Cr in industrial waste-water which can be disposed directly into an inland surface water body is 0.3 mg/L. The result showed that (Fig. 2) high concentration of Cr was in sewage followed by spray painting spent wash and service station effluent. It is clear from the result that, all the three waste–waters were rich in Cr and these values are extremely higher than the permissible levels of discharge. According to Rinin and Andrews (2012), one of the main sources of Cr is vehicle service station effluent. Adriano (1984) reported that domestic waste water contains 50 - 30,000 ppm of Cr. According to Tjandraatmadja *et al*. (2010), Cr in sewage may be coming from toilet wastes, bath-rooms, laundry etc. Icon (2001) reported that sewage water contains 20-40% of Cr as a major heavy metal pollutant.

Zinc is an important micronutrient and it is present naturally low amounts in soil and water. According to Indian Environmental Standards (2006) and NEQS (2000) maximum permissible limit of Zn in the industrial waste water for safe disposal into an inland water body is 5.0 mg/L and as per EPA (2002), it is 2 mg/L. The result showed that (Fig. 2) as per the permissible limits, Zn content in all the selected waste–waters were above the permissible concentration, and the highest concentration was reported in sewage water followed by service station effluent and spray painting spent wash. -Munasinghe and Athapattu (2013) reported that effluent from automobile workshops and painting workshops contains approximately 100 mg/L of Zn and domestic waste-waters were also highly polluted with Zn.

Mercury is one of another highly toxic heavy metal found naturally in very small amounts in soil and water. According to Indian Environmental Standards (2006) and NEQS (2000) the maximum permissible limit of Hg in the industrial waste–water for safe disposal into a water body is 0.01 mg/L. The analysis showed that the highest amount of Hg was present in the service station effluent followed by spray painting spent wash and least concentration was in sewage. As per Indian Environmental Standards (2006), the Hg content in the waste-waters was above the standard permissible limit. The Hg used for making batteries, lamps and thermometers and in dentistry Hg used as an amalgam for fillings and by the

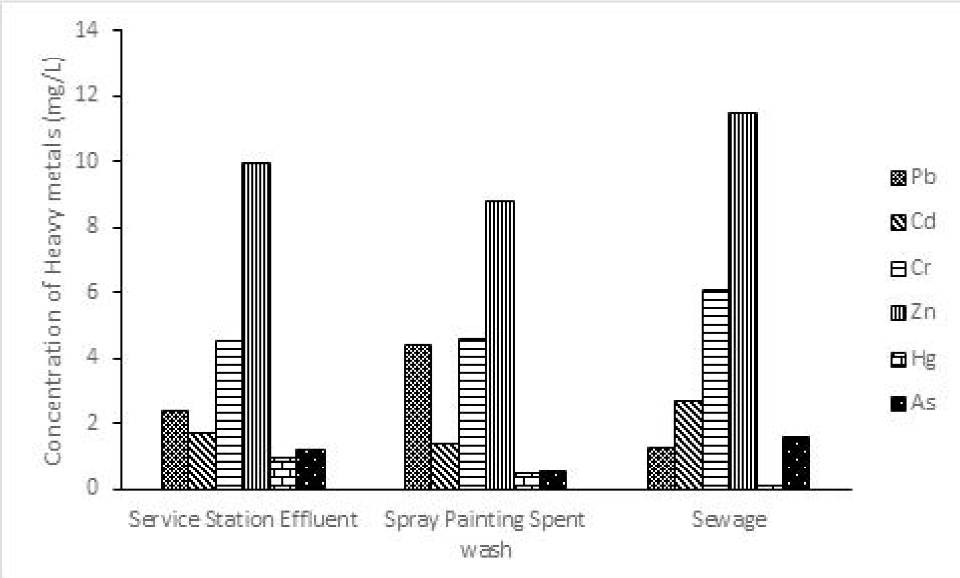

Fig. 2. Concentration of Heavy metals in various types of waste waters

pharmaceutical industry (Iqbal and Asmat, 2012) and these contribute a higher level of Hg in sewage.

Arsenic is also an important highly toxic heavy metal element found in the earth crust. According to Indian Environmental Standards (2006) and NEQS (2000), the maximum permissible limit of As in the industrial waste water for safe disposal into an inland water body or soil is 0.2 mg/L. It could be understood that is a highest amount of As was reported in the sewage water followed by the service station effluent and spray painting spent wash. As per the Standards, the As content in the selected waste waters were above the permissible limit. High levels of As was reported from sewage and it may have resulted from different types of fertilizers (EPA, 2002).

A plethora of studies suggests that the waste-water from various sources such as sewage water, painting waste water, service station effluent etc. contains remarkably high concentrations of heavy metals, where washing, painting servicing etc. are common (Luter *et al*., 2011; Achi *et al.*, 2011; Ilemobayo and Kolade, 2008). Abagale *et al*. (2013) reported that the critical pollutants in the car wash water includes petroleum hydrocarbons, gasoline, diesel and motor oil, nutrients such as nitrogen and phosphorus, surfactants, suspended and dissolved solids and heavy metals such as Cu, Pb, Zn etc. and the urban waste-waters such as sewage, motor vehicle body repair and painting waste–waters from various industries, commercial establishments etc. are very rich in solids, salinity, temperature, pH, BOD, COD, oil and grease and various heavy metals (Dissanayake *et al*., 2008).

The sewage and sewage sludge were rich in heavy metals such as Zn, Cu, Cd, Pb and Cr and these may be contributed from run-off, rain, roofs and building surfaces, vehicles, tires, lamp posts and street furniture (Vasanthi *et al*., 2012). Atmospheric wet deposition as rain may wash out the gaseous metal pollutants from the various above said sources in the air get precipitated and enters into the sewage water. Pb, Zn, Cr, Cd, Ni etc. are found in good quantities in the air and get deposited through the rain (Comber and Gunn, 1996). As per the reports of Palm and Ostund (1996) and CPPI (2004) the petroleum and associated products contain moderate concentrations of heavy metals and mean total metal concentrations of 180.8 µg/L of Cu, 308.5 µg/L of Zn and 46.4 µg/L of Pb were present in the car washing and service station effluent and these values were greatly exceeded the recommended guidelines (Sullivan *et al*., 2011).

Indiscriminate disposal of waste–waters rich in both essential and toxic heavy metals on a long term basis will result in the build-up of these heavy metals in soil, water and eventually it contaminates the food chain and biomagnifies in the living tissues and ultimately in man (Salt and Rauser (1995); Wolfyang *et al.*, 1995).

The analysis of the three selected waste-waters such as service station effluent, spray painting spent wash and raw sewage revealed that all the three waste-waters were highly polluted. Majority of the water quality characteristics were above than the permissible limit of effluent discharge set by various agencies such as EPA (2002), NEQS (2000) and Indian Environmental Standards (2006). It was also noted that all three selected waste–waters showed undesirable colour and odour. So the waste-waters should be treated to remove undesirable amounts of pollutants before it is disposed into the inland surface waters or soil.

In order to assess and prove the difference between the selected waste water (service station effluent, spray painting spent wash and sewage), multivariate analysis was done using SPSS-17 version. The results of statistical analysis (Levene‘s Test of Equality of Error Variances) of the physico-chemical characteristics and heavy metal concentrations of the selected waste waters are given in Table 1.

The multivariate tests for different types waste water showed statistically highly significant variation (P=0.000) from one another. The Levene‘s Test of Equality of Error Variances also showed that there is highly significant difference (P=0.000) between majority of the physico-chemical parameters (colour, EC, TS, TDS, TSS, total alkalinity, acidity, CO_2, BOD, COD, NO_3-N, NO_2-N, NH_3-

N, TN, ON, IP, OP, TP, silicates, sulphates, chloride, hardness, Ca, Mg, Na, K, TOG, H_2S, Fe, Pb, Cd, Cr, Zn, Hg and Pb) analysed in the present study. Results also showed that there is no significant variation (P>0.1) between the parameters such as temperature, pH and DO content in the selected waste water samples. The multiple comparison tests such as Bonferroni, Dunnett t (2-sided) and Tukey HSD also showed that highly significant variation (P=0.000) exists between different types of waste water with respect to different physico-chemical parameters.

4. Conclusion

The characterisation of the waste-waters realised that these are highly polluted with various pollutants including toxic heavy metals and direct discharge of these waste-waters to the surface waters or soil damages the natural quality of them and make it unfit for the organisms depends them for life. The continuous discharge of these untreated effluents deteriorates the physico-chemical properties of the receiving water body or soil and causes the build-up of these toxic chemicals in the eco-system there–by threatens the food-chain through bio-magnification. Therefore, developing an adequate treatment mechanism for the treatment of these effluents before the disposal takes the greatest importance.

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5. References

Abagale, F.K., Sarpong, D.A., Ojediran, J.O., Osei-Agyemang, R., Shaibu, A.G. and Birteeb, P.T. 2013. Heavy Metal concentration in Wastewater from Car Washing Bays used for Agriculture in the Tamale Metropolis, Ghana, Int. J. Curr. Res., 5(6): 1571-1576.

Achi, M.M., Uzairu1, A., Gimba1, C.E. and Okunola, O.J. 2011. Chemical fractionation of heavy metals in soils around the vicinity of automobile mechanic workshops in Kaduna Metropolis, Nigeria, J. Environ. Chem. Ecotoxicol., 3(7): 184-194.

Adriano, D.C.1984. Trace Elements in the Environment Springer Verlag, New York.

Anonymous. 2008. Environmental Guidelines from water discharge from Petroleum Industry sites in New Zealand, Ministry for Environment, Wellington, Newzealand, 1-38.

Anonymous. 2009. Hydrogen Sulphide and Public Health, Environmental Health Guide, Government of Western Australia, Department of Health, 1-12.

Anonymous. 2011. Technical Guidelines No. 9, Guidelines for Service Station Waste water Management/Disposal, Environmental Control Section (ECS), Environment Department, Dubai Municipality, Government of Dubai.

APHA. 2012. Standard Methods for the Examination of Water and Wastewater. 22nd ed., APHA- AWWA- WEF, Washington, DC.

Azizi, S., Kamika, I and Tekere, M. 2016.Evaluation of Heavy Metal Removal from wastewater in a Modified Packed Bed Biofilm Reactor. PLoS One, 11(5): e0155462.

Bujang, M., Ibrahimand, N.A. and Eh Rak, A 2012. Physicochemical Quality of Oily Wastewater from Automotive Workshop in Kota Bharu, Kelantan Malaysia, Aust. J. Basic Appl. Sci., 6(9): 748-752.

Comber, S.D.W. and Gunn, A.M. 1996. Heavy metals entering sewage treatment works from domestic sources, J.CIWEM, 10: 137-142.

CPCB. 2005. Central Pollution Control Board Report, Status of Sewage Treatment in India, Central Pollution Control Board, Ministry of Environment & Forests, Parivesh Bhawan, East Arjun Nagar, Delhi.

CPPI. 2004. Canadian Petroleum Products Institute, Best management practices- Vehicle wash operations.

Dharmappa, H.B., Sivakumar, M. and Singh, R.N. 2011. Waste water characteristics, Management and Reuse in Mining and Mineral Processing Industries in Waste water Recycle, Reuse and Reclamation, Encyclopedia of Life Support Systems.

Dissanayake, P., Tennakoon, M. and Burmeister, J. 2008. Guide to On-site waste water Management for Industrial and Commercial Establishments and other Institutions, International Waste Management Institute, Srilanka.

Domingos. 2011. Vertical flow constructed wetlands for the treatment of inorganic industrial wastewater, Ph. D. Thesis, Faculty of Science and Engineering, Murdoch University WA, Australia.

El-Salem, S.M. and Talhouni, M. 1995. Planning and Strategy of Wastewater and Wastewater re-use in Jordan, Doc. No. 17, FAO, Regional Seminar on the Treatment and Use of Sewage Effluent for lrrigation, Nicosia, Cyprus.

El-Sawaf, N. 2005.Response of Sorghum spp. to Sewage Waste-water Irrigation, Int. J. Agric. Biol., 7(6): 869-874.

Environmental Quality Standards Regulations. 1999. National Environment Management Act, 1994, Establishment of Environmental Quality Standards Board.

EPA. 2002. The Environment Protection Act- 2002, Standards for Effluent Discharge Regulations, General Notice. No. 44 of 2003.

Fall, C., López-Vázquez, C.M., Jiménez-Moleon, M.C., Bâ, K.M., Díaz-Delgado, C., García-Pulido, D. and Lucero-Chavez, M. 2007. Carwash wastewaters: characteristics, volumes, and treatability by gravity oil separation, REV. MEX. ING. QUIM., 6(2):175-184.

Friedler, E., Quality of individual Domestic Grey water streams and its implication for onsite treatment and reuse possibilities, Exp. Technol., 25: 997-1008.

Gross, M.A. 2005. Wastewater Characterization Text. in (M.A. Gross and N.E. Deal, eds.) University Curriculum Development for Decentralized Wastewater Management. National Decentralized Water Resources Capacity Development Project. University of Arkansas, Fayetteville, AR.

Harrison, R, M. 1994. Understanding Our Environment- An Introduction to Environmental Chemistry and Pollution, 3rd edition, the Royal Society of Chemistry, Cambridge, U.K.

Icon. 2001. Pollutants in Urban Waste and Sewage Sludge, Official Publications of European Communities, IC Consultants Ltd.

Ilemobayo, O. and Kolade, I. 2008. Profile of Heavy metals from Automobile workshop in Akure, Nigeria, J. Environ. Sci. Technol., 1 (1): 19-26.

Indian Environmental Standards. 2006. Raman, N.S. and Devotte, S., (Eds.), Hand book of Indian Environmental Standards. National Environmental Engineering Research Institute, Nagpur.

Iqbal, K. and Asma,t M. 2012. Uses and effects of Mercury in Medicine and Dentistry. J. Ayub. Med.. Coll Abbottabad, 24: 3-4.

Jarup, L., Bergluud, M. and Elinder, C.G. 1998. Health effects of cadmium exposure—a review of the literature and a risk estimate, Scand. J. Work. Environ. Health., 24: 1-51.

Kamyotra, J.S. and Bhardwaj, R.M. 2011. Municipal wastewater management in India, India Infrastructure Report, Chapter 20; Water: Policy and Performance for Sustainable Development, Infrastructure Development Finance Corporation, New Delhi, Oxford University Press.

Lau, W.J., Ismail, A.F. and Firdaus, S. 2013. Car wash industry in Malaysia: Treatment of car wash effluent using ultrafiltration and nanofiltration membranes, Sep. Purif. Technol., 104: 26–31.

Laws, A.E. 2000. Aquatic Pollution: An Introductory Text, John Wiley & Sons, Inc., New York.

Levlin, E. and Hultman, B.2008. Conductivity measurements as measure and control at municipal wastewater facilities, Swedish Water Development Report No. 2008-04, Stockholm.

Luter, L., Terngu, A.J. and Attah, S. 2011. Heavy Metals in Soils of auto- mechanic shops and refuse dumpsites in Makurdi Nigeria, J. Appl.Sci. Environ. Manage., 15(1): 207 – 210.

Mazumder, D. and Mukherjee, S. 2011. Treatment of Automobile Service Station Wastewater by Coagulation and Activated Sludge Process, Int. J. Environ. Sci. Devel., 2 (1): 64-69.

Munasinghe, K.A. and Athapattu, B.C.L. 2013. Economical Wastewater Treatment System for Automobile Service Stations in Sri Lanka. Proceedings of the International Forestry and Environment Symposium 2013 of the Department of Forestry and Environmental Science, University of Sri Jayewardenepura, Sri Lanka.

Murtaugh, J.J. and Bunch, R.L. 1965. Acidic Components of Sewage Effluents and River Water, J. Water Poll. Cont. Fed., 37(3):, 410-415.

NEQS. 2000. National Environmental Quality Standards for municipal and liquid industrial effluents.

Ntwampe, I.O., Jewell, L.L., Hildebrandt, D. and Glasser, D. 2013. The effect of water hardness on paint wastewater treatment by coagulation-flocculation, J. Environ. Chem. Ecotoxicol., 5(3): 47-56.

Ogundiran, M.B., Ogundele, D.T., Afolayan, P.G. and Osibanjo, O. 2012. Heavy Metals Levels in Forage Grasses, Leachate and Lactating Cows Reared around Lead Slag Dumpsites in Nigeria, Int. J. Environ. Res., 6 (3): 695-702.

Palm, V. and Östlund, C. 1996. Lead and zinc flows from technosphere to biosphere in a city region, Sci. Total. Environ., 192, 95-109.

Ranade, V. V and Bhandari, V. M. 2014.Industrial wastewater Treatment, Recycling, and Reuse.B. H-Elsevier Publications, ISBN: 978-0-08-099968-5, 543p.

Rinin, J. and Andrews, E. 2012. Disposing of hazardous Waste from the Home: Waste Oil and Other Automotive products, Co-operative Extension Publishing.

Rudolfs, W. 1997. Industrial Wastes and their disposal and treatment, Allied Scientific Publishers (1997)

Salt, D.E., Rauser, W.E. 1995. Mg ATP – dependent transport of phytochelatins across the tonoplast of oat roots, J. Plant Physiol., 107:1293-1301.

Sawyer, C.N., McCarty, P.L. and Parkin, G.F. 1994. Chemistry for Environmental Engineering. New York, USA, McGraw-Hill.

Saxena, M.M. 1998. Environmental Analysis – Water, Soil and Air, Agro Botanica Publications (1998)

Sullivan, O.A., Smalley, D. and Good, J. 2011. Quantifying the impact of car washing on water quality and assessing simple treatment strategies, Environment Canterbury Report, Environment Canterbury, File Reference: NO2C/00383, 1-23.

Tjandraatmadja, G., Pollard, C., Sheedy, C. and Gozukara, Y. 2010. Sources of contaminants in domestic wastewater: Nutrients and additional elements from household products, CSIRO, Water for a Healthy Country National Research Flagship, 1-104.

Trivedy, P.K. and Goel, P.K., Practical methods in Ecology and Environmental Science, Environmedia Publications, India.

Vasanthi, N., Saleena, L.M. and Raj, S.A. 2012. Silicon in Day Today Life, World Appl. Sci. J., 17(11):1425-1440.

Walker, W.M., Miller, J.E. and Hassett, I.I. 2001. Effect of lead and Cadmium on the Mg, K and P concentration in plants, Soil Sci., 124: 145 -151.

WHO. 2006. The World Health Report-2006, Working together for Health, WHO Press, World Health Organization, Geneva.

Wolfyang, W. and Dohler, H. 1995. Heavy metals in Agriculture, Soil Sci.Plant Nutr , 17, 195-198.

Yasin, S., Iqbal, T., Arshad, Z., Rustam, M. and Zafar, M. 2012. Environmental Pollution from Automobile Vehicle Service Stations, J. Qual. Technol. Manage., 1: 61-70.

Yusuf, A.A., Arowolo, T. and Bamgbose, O. 2002. Cd, Cu and Ni levels in vegetables from Industrial and Residential Areas of Lagos City, Nigeria, Glob. J. Environ. Sci., 1: 1- 3.

Zeid, I.M. and Ghate, H.M.A.E. 2007. Effect of Sewage water on Growth, Metabolism and yield of Bean, J. Biol. Sci., 7 (1): 34-40.

Zhou, Y., Jiang, H. and Niu, K. 2006. Carbon dioxide emission on the process of Sewage treatment during the “11th Five year Plan” Period.