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ORIGINAL PAPER

Analysis of heavy metals, physicochemical parameters and effect of blending on treatability of wastewaters in Northern Ethiopia

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Abstract The present study monitored textile factory, distillery, and domestic wastewaters and investigated the effects of blending on the physicochemical properties of these wastes. Findings revealed that distillery wastewaters had the highest values of all tested parameters, including heavy metals, biodegradable organics, and nutrients. Biological and chemical oxygen demands in the textile wastewater were higher than domestic wastewater, while total phosphorus, total nitrogen, and sulfate were higher in the domestic wastewater. Likewise, while higher mean concentrations of zinc, copper, iron, and manganese were found in the domestic wastewater, the rest studied heavy metals did not show statistical differences ($p < 0.05$). This study concluded that blending improves biological treatability and effectively neutralizes the alkaline textile, acidic distillery, and domestic wastewaters at volumetric ratios of 3:1:18, respectively. This methodology will help to avoid the use of chemicals for neutralization and can be a useful entry point to establish sustainable wastewater management strategy in the developing countries. The results suggest the need for inclusion of the tested nine heavy metals in the Ethiopian standards for discharge from the distillery and domestic effluents.

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Introduction

Anthropogenic activities linked with population growth, urbanization, and industrialization have resulted in a rapid degradation and pollution of the environment (Komínková 2008). For instance, Ethiopia is one of the few African countries where fast economic growth was recorded in the past decade. As a result, over 2610 medium and low industries have been flourished (86 textile and 16 distillery industries) (CSA 2015). In addition, like the other developing countries, rapid urbanization is a recent phenomenon in Ethiopia. According to the forecast by World Bank (2012), Africa's urban population where inadequate wastewater infrastructures exist will rise to about 50% of the population by 2030. Degradation mainly related to discharging of untreated wastewaters from industrial and urban centers in these countries is more serious and a growing challenge (Patel and Kanungo 2010; Satya et al. 2011).

On the other hand, wastewater is reliable sources of nutrients and water for various purposes when it is properly treated. However, the unsustainable and environmentally unfriendly, energy and chemical intensive processes of conventional wastewater treatment systems are escalating financial and technical burden to the communities and to the industries (Mohan et al. 2010). Consequently, polluters became reluctant to implement such treatment systems, while the impacts flared. Thus, finding a sustainable and affordable treatment options that suit local condition is extremely crucial (Archana et al. 2011). In this respect, in situ or ex situ removal of contaminants from wastewater by employing ecological processes found in natural ecosystems where water, soil, plants, and microorganisms are the main components is promising options (Gupta 2013; Dipu et al. 2011). Hence, natural treatment systems such as ecologically engineered wetlands and phytoremediation are more holistic and sustainable approaches, which can be within the economic and technological capabilities of these countries (Sekomo et al. 2012; Sood et al. 2012). Nevertheless, the physicochemical characteristics of industrial wastewaters from textile and distillery are poor in supporting plant growth, microorganism activities and are difficult to treat by them (Ansari et al. 2012). In connection to this, textile and distillery wastewaters need to be diluted to create a favorable environment to support plant growth and microorganisms' activities and to enhance their treatability.

From the other side, industrial development strategies in these countries are shifting to industrial park development, rooted in the concept of industrial ecology, which seeks to optimize the total materials' cycle and to reduce net cost and environmental burdens of production and consumption processes by an integrated approach (Conticelli and Tondelli 2014; Leigh and Li 2015). This initiate the development of eco-industrial parks as a way to a more sustainable industrial development (Conticelli and Tondelli 2014). Moreover, industrial ecology is fundamentally important to the evolution of industrial ecosystems for the exchange of materials and by-products and to adopt collaborative efforts and linkages among the industries with geographic proximity (Patala et al. 2014).

The symbiotic linkage (Leigh and Li 2015) of interest in the current research considers textile factory, molasses-based distillery and public institution in relation to their wastewaters. According to Brik et al. (2006), the textile industry is a water-intensive sector, which consumes about 20–350 m^3 of water for each ton of fabric produced. The sector generates huge quantities of alkaline wastewater contaminated with colorants (dyes and pigments) and higher chemical contents, including metals, auxiliaries, total dissolved solids and others, which adversely affect the fauna and flora (Shehzadi et al. 2014; Sharma et al. 2007). Molasses-based distilleries are also among the most polluting industries generating large volumes of wastewaters (10–16 L per liter of alcohol production) with elevated organic and inorganic contaminants (Satyawali and Balakrishnan 2008; Chhaya and Kumar 2014). Distillery wastewater (spent wash) characterized by an offensive odor and dark brown in color attributed to high molecular weight organic compounds (melanoidin) are harmful to aquatic life. It is acidic in nature with pH values ranging from 3 to 5.3 (Ansari et al. 2012). Domestic wastewater is the water which returns after being used by a community for various purposes such as personal washing, flushing of toilets, food preparation and cleaning of kitchen utensils. Its characteristics and flow rates can vary depending on the economic status, living conditions of the communities and water supplies (Metcalf and Eddy 2003). Principal contaminants in domestic wastewater are suspended solids, biodegradable organics, nutrients, toxic compounds, heavy metals, and pathogens (Diaper et al. 2008; Tjandraatmadja et al. 2010).

Industrialization is a new era for the developing countries, including Ethiopia. The current industrial development strategies focus primarily on the positive side effects (Despeisse et al. 2012). However, these strategies lack connectivity with the associated environmental aspects and respective externalities. Furthermore, understandings of the current pollution status and alternative treatment options are constrained by lack of monitoring evidence. Besides, practices on the application of industrial ecology for environmental protection are low in the developing countries. In this regard, area-specific research on the material flow and possibilities for environmental protection and economic return from the wastewater streams in the face of urbanization and industrialization is fundamentally essential. The objectives of this research are to monitor textile factory, sugarcane molasses-based distillery, and domestic wastewaters and to evaluate the efficacy of blending as a preliminary treatment for neutralization and biological treatability enhancement of these waste streams. The research was conducted from May to September 2015 in Mekelle, Ethiopian.

Materials and methods

Study area description

The present study was conducted in Mekelle city, the capital of the Tigray National Regional State, located in northern Ethiopia. The city covers an area of 644.76 km^2 with a total population of 323,700 people and annual growth rate of 4.7% (CSA 2015). It is found within a region characterized by undulating topography, where more than 90% experienced arid to semi-arid conditions of highly erratic and unreliable precipitation. Its climate is generally tropical and hot with an extended dry period of nine to ten months. The mean minimum and mean maximum temperatures range between 10.2 and 12.6 °C, and 22.3 and 26.7 °C, respectively (Beyene 2015). It has a maximum effective rainy season of 50 to 67 days with mean annual precipitation of 51. 67 mm (FAO 2006). The sources of wastewaters used in this research were collected from textile factory (13°28′5″N, 39°31′56″E), sugarcane molasses-based alcohol distillery (13°29′30″N, 39°32′56″E) and domestic wastewater from higher learning institution (13°28′51″N, 39°28′58″E) located proximate to each other in the same drainage area (Fig. 1).

Sources of experimental wastewaters

Distillery wastewater was received from a distillery factory which consumes about 29.76 tons of sugarcane molasses to produce 250 L of alcohol (beverage and industrial) and liquors daily and generates 3000 L of wastewater per hour (72 m^3 per day). Textile wastewater was also obtained from a textile factory consists of spinning, dying, and garment processing to produce four tons of fabrics per day. The daily water supply of the factory is 349 m^3 out of which 238 m^3 is supplied to the production processes. On average 25–60 L of water are required to produce one kg of fabric product. The water supplied to the processes in the textile factory finally returns as a wastewater (222 m^3 per day) containing diversified contaminants. Additionally, domestic wastewater used in this study was obtained from a public higher institution with over 31,872 students enrolled. It comprises mixed gray and black waters. Wastewater generations in the institution are estimated to be 1442 m^3 per day with major contributing activities of a lavatory, manual laundry, cafeteria and beauty salon centers, and laboratory facilities. Moreover, crude sugarcane molasses samples were obtained for heavy metals analysis from the distillery factory.

Sampling, analysis, and blending of wastewaters

Triplicate grab samples of untreated wastewaters were collected manually during pumping from a homogenization tank of the textile and the distillery factories, and from the wastewater holding tank within the university's periphery subjected to daily desludging by the heavy-duty vacuum trucks. Blending was performed initially based on the estimated daily wastewater generation of 222 and 72 m^3 for textile and distillery, respectively. Accordingly, with an initial volumetric ratio of 3:1[textile/ distillery], domestic wastewater was gradually added until a constant pH value within the range of 6.5–7.5 attained. This pH range is suitable for most macrophytes' survival and growth (Hasan and Chakrabarti 2009). Blended wastewater in replicates was retained for 88 h of holding time and subjected to a repetitive pH measurement to observe the variation in pH with time.

The total concentrations of Pb, Cu, Fe, Cr, Co, Cd, Ni, Mn, and Zn in wastewater, and molasses samples were

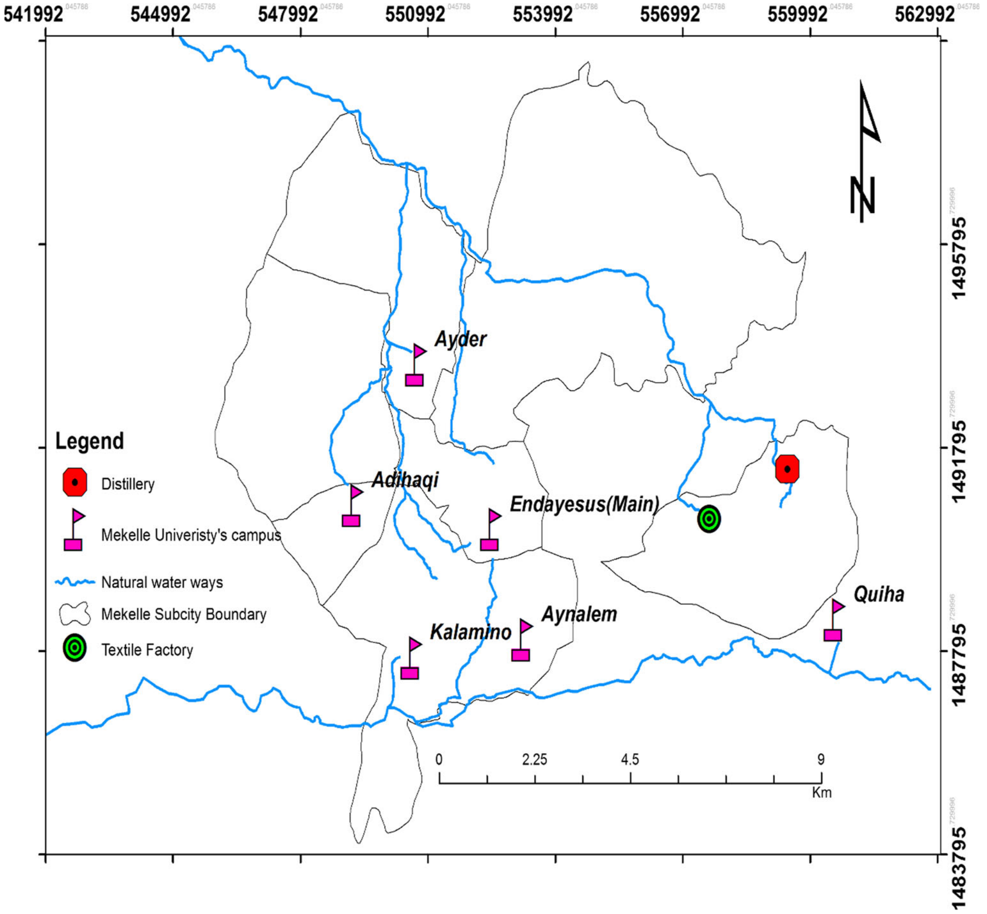

Fig. 1 Location map of wastewater sources

analyzed using an Atomic Absorption Spectrometer (Varian AA240FS). In addition, Five-day Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), and Kjeldahl nitrogen were determined using the 5-days BOD test at 20 °C, Open Reflux Method and the macro-Kjeldahl method, respectively. Concentrations of nitrate, nitrite, phosphate, and sulfate were determined using Multiparameter photometer (Palintest wagtech Photometer 7100 model). Similarly, temperature, pH, electrical conductivity (EC), and total dissolved solids (TDS) were measured on site using a calibrated portable multi-function meters (Wagtech CyberScan CON410). Furthermore, international turbidity meter (Wag-WT-3020) and Hach (HQ40d model) field kits were used to measure the turbidity and dissolved oxygen, respectively. Samples were transferred immediately to the laboratory for physicochemical and heavy metals analysis. Wastewater sample collection, handling, and analysis were performed following the procedures described in APHA (1999). Molasses sample preparation was performed in accordance with Mohamed (1999). Each equipment was calibrated before use with standard procedures. A reagent blank and duplicate samples were performed in parallel for each analysis. Besides, standard samples of known concentration were incorporated within each batch of samples analyzed for heavy metals.

Statistical analysis

Results of physicochemical and heavy metals in textile, distillery, domestic and blended wastewater samples were presented as mean indicating standard deviation. Statistical comparisons of means were examined with one-way analysis of variance (ANOVA) and Tukey's post hoc test was used to perform pairwise comparisons of means. One-way repeated measures ANOVA was also performed to evaluate the variations in pH of the blended wastewater with respect to the holding time. Results were compared with relevant standards for interpretation. Associations between the heavy metal contents of the input molasses and the distillery wastewater were evaluated using the Pearson's correlation test. For all analyses, statistical significance was set at $p < 0.05$ and performed using Origin 2015 graphing and data analysis software.

Results and discussion

Characteristics of the source wastewaters

Heavy metal concentration

As it can be seen in Table 1, while higher mean concentrations of Fe (132 mg L^{-1}), Mn (7 mg L^{-1}), and Zn (2.4 mg L^{-1}) were observed, mean concentrations of rest tested metals were ranged from 0.1 mg L^{-1} (Cd) to 0.6 mg L^{-1} (Ni) in the distillery wastewater. Analysis of variance on the mean concentration of the studied heavy metals in the distillery wastewater showed significant differences ($p < 0.05$). Variations may be attributed to the higher Fe and lower Cd, Cu, Co, Ni, Pb, and Cr concentrations. The mean concentrations of the heavy metals in distillery wastewater were in the order of Fe > Mn > Zn > Ni > Cr > Cu > Co > Pb > Cd. While the results for Cd, Co, and Zn agreed very well, values for Cu, Pb, Fe, and Mn in the present study were lower than the values reported by Sulieman et al. (2010). Higher concentration of Ni and comparable values of Cu, Cd, Cr, and Pb, but lower values of Fe and Mn were also reported by Kumar and Chandra (2004). Similarly, observations in this study were lower for Zn, Cu, and Mn and higher for Fe compared to findings reported by Chhaya and Kumar (2014). Variation in concentration with other findings could be due to the differences in inputs like molasses and water supply, and production processes. Mean concentrations of Co, Cd, Zn, Cr, Ni, Cu, Fe, and Mn in the distillery wastewater were higher than the threshold limits for agricultural reuse. Even though the Ethiopian industrial effluent discharge limits EPA (2003) does not consider heavy metal for distillery wastewater, detection of all tested heavy metal in the distillery wastewater can give a new insight to consider the heavy metals as a quality parameter to treat and monitor such wastewater in the Ethiopian context.

The major contributor of the heavy metals in the distillery wastewater may be the input sugarcane molasses. For instance, analysis of the heavy metals in the input molasses resulted in a mean concentration of Fe (302.7 mg kg^{-1} dry weight base) followed by Mn (23.9 mg kg^{-1}) and Zn (6.4 mg kg^{-1}). Mean concentrations of the rest six heavy metals were ranged from 0.3 for Pb to 2.7 for Ni (mg kg^{-1}). Correlation analysis between mean concentrations of the investigated heavy metals in the distillery wastewater and input molasses indicated strong positive associations with Pearson (r) values between 0.8 and 0.98. This association may suggest the existence of relationship attributed to the contribution of sugarcane molasses to the wastewater's heavy metals.

As it is shown in Table 1, higher concentrations of Fe (1.2 mg L^{-1}) and Zn (0.13 mg L^{-1}) were determined in textile wastewater samples. While moderate concentrations were determined for Mn (0.07 mg L^{-1}), Co (0.05 mg L^{-1}), Pb (0.05 mg^{-1}), and Cu (0.4 mg L^{-1}), lower values of Ni (0.03 mg L^{-1}), Cd (0.03 mg L^{-1}), and Cr (0.02 mg L^{-1}) were observed. The mean concentrations of the tested heavy metals in the textile wastewater were in the order of Fe > Zn > Mn > Pb > Co > Cu > Ni > Cd > Cr and

Table 1 Heavy metal concentration in wastewater samples (mg L^{-1})

	Textile ($n = 3$)		Distillery ($n = 6$)		Domestic ($n = 3$)		Blended ($n = 3$)		Limit		Detection limit
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	*	**	
Co	0.045^{a}	0.006	0.442^{b}	0.052	0.058^{a}	0.006	0.062^{a}	0.002	1	0.05	0.01
Pb	0.047^{a}	0.006	0.227^{b}	0.028	0.030^{a}	0.010	0.030^{a}	0.020	0.5	5	0.02
Cd	0.028^{a}	0.001	0.118^{b}	0.013	0.028^{a}	0.001	0.030^{a}	0.006	1	0.01	0.01
Zn	0.130^{b}	0.050	2.432^{c}	0.118	0.503^{a}	0.021	0.583^{a}	0.006	5	2	0.05
Cr	0.025^{a}	0.004	0.457^{b}	0.031	0.023^{a}	0.006	0.030^{a}	0.007	1	0.1	0.02
Ni	0.037^{a}	0.007	0.612^{b}	0.052	0.050^{a}	0.006	0.057^{a}	0.006	2	0.2	0.03
Cu	0.042^{b}	0.013	0.457^{c}	0.037	0.143^{a}	0.006	0.137^{a}	0.006	2	0.2	0.01
Fe	1.222^{b}	0.341	131.873^{c}	1.776	8.687^{a}	0.015	12.39^{d}	0.105	10	5	0.02
Mn	0.071^{b}	0.019	7.048^{c}	0.172	1.297^{a}	0.015	1.513^{a}	0.015	5	0.2	0.02

Means with different letters in a row are significantly different ($p < 0.05$)

* Discharge limits adapted from the Ethiopian Environmental Protection Authority (EPA 2003), for a textile industry and general limits

** Threshold limits for agricultural reuse adapted from USEPA (2012) and WHO (2006)

statistically different at the significant level of 0.05. Variations were due to the higher concentration of Fe. Mean concentrations of all the analyzed heavy metals in the textile wastewater were below the discharge limits. Similarly, except for Cd the mean concentrations were lower than the threshold limits for agricultural reuse. Mean concentrations of Ni, Cr, Cd, Mn, Fe, Pb, Ni, and Cu in samples from textile wastewater in the present study were lower than the findings reported by Fenta (2014) and Gitet et al. (2016). In contrast, Zn, Cu, and Cd were in agreement with values reported in Roy et al. (2010). However, mean concentrations of Cd and Pb in this research were higher than values in the literature (Momtaz et al. 2010; Gitet et al. 2016)). Variations may be due to the differences in production processes, input chemicals, and management of the water streamed from water treatment plant. For instance, the textile industry in the present study does not have the water and chemical intensive woven wet finishing process such as printing and dying. In addition, the water from the water treatment plant in the present study is discharged separately.

Similarly, Co (0.06 mg L^{-1}), Cd (0.03 mg L^{-1}), Pb (0.03 mg L^{-1}), Zn (0.5 mg L^{-1}), Ni (0.05 mg L^{-1}), Cr (0.02 mg L^{-1}), Fe (8.69 mg L^{-1}), Cu (0.14 mg L^{-1}), and Mn (1.3 mg L^{-1}) were determined in samples from domestic wastewater (Table 1). Analysis of variance on the mean concentration of the tested heavy metals in the domestic wastewater showed significant differences ($p < 0.05$). According to the Tukey's post hoc test pairwise comparisons, the variations were attributed to the elevated concentration of Fe and Mn, and low concentration of the Cd, Cr, Ni, and Pb. Generally, based on the mean concentrations the heavy metals in domestic wastewater were in the order of Fe > Mn > Zn > Cu > Co > Ni > Pb > Cd > Cr. While the mean concentrations of Co and Ni were in good agreement, lower values of Pb and higher values of Zn, Cu, Fe, and Mn were found in the present study compared to the literature values (Baawain et al. 2014). Similarly, while the value of Pb was in line with Tjandraatmadja and Diaper (2006), value for Fe was higher than values reported by Henze and Comeau (2008). The mean concentrations of Co, Cd, Fe, and Mn were found higher than the threshold limit values for agricultural reuse. The deviations of values may be attributed to the contributing activities, quantity and quality of water supply. For instance, previous investigations on the heavy metal contents of the water supply in the study area such as Mebrahtu and Zerabruk (2011) have reported the concentrations of Fe, Zn, Pb, and Cr with range values of 97–919, 80–583, 69–106 and 131–158 µg L^{-1}, respectively. Similarly, the concentrations of Fe, Cu, Cr, and Mn in the water supply during the study period were 270, 420, 50, and 320 µg L^{-1}, respectively. In addition, domestic activities and home use materials including washing detergents, laundry, personal cares, food preparation, and cleaning of kitchen utensils and installation systems have been reported to contribute heavy metals. In connection to this, an investigation conducted by Jenkins (1998) reported that cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc were contributed from household washing products. Hence, the concentrations of the heavy metals in this study are not surprising.

Analysis of variance showed that the mean concentration of the tested nine heavy metals in samples from distillery wastewaters showed statically significant differences from the concentration of the same metal species in the textile and domestic wastewaters. Similarly, while significant differences were observed between the mean concentrations of Zn, Cu, Fe, and Mn ($p < 0.05$), no statically differences ($p > 0.05$) were observed between the mean values of Ni, Co, Cd, Cr, and Pb in the textile and domestic wastewaters.

pH, EC, TDS, and turbidity

The pH value (4.02) (Table 2), of the deep-dark brown color and offensive odor distillery wastewater, was in line with the work of Chhaya and Kumar (2014). While the approximate nil dissolved oxygen content was in agreement with, the value of TDS (18.82 ± 4.76 g/L) in the present study was lower compared to the literature (Ansari et al. 2012; Chhaya and Kumar 2014) the latter was comparable with the findings of Satyawali and Balakrishnan (2008). Mean EC (41.4 ± 5.95 mS/cm) value of the samples from the distillery wastewater was in agreement with Prakash et al. (2014). The mean values of DO (0.14 mg/l), EC (5.69 ± 1.91dS/m), TDS (2.99 ± 1.22 g/L), turbidity (254 ± 14 Nephelometric Turbidity Unit (NTU)), and pH (10.2) in samples from textile wastewater were in agreement with the literature values (Roy et al. 2010; Hussein 2013). While the EC (3.78 ± 0.51 mS/cm) value determined in samples from domestic wastewater in this study was lower, TDS (1.73 ± 0.14 g/L) value was comparable with findings of Tjandraatmadja et al. (2008). Greater TDS and comparable pH (7.08) values were determined in samples from the domestic wastewater compared to the values reported by Bilgin et al. (2014). Similarly, pH, EC, and TDS values in domestic wastewater in the present study were in agreement with the findings reported by Baawain et al. (2014). Samples from the distillery and domestic wastewaters were turbid with mean values 2377 ± 45 and 267 ± 21NTU, respectively. The low values of DO in all effluents suggested that the wastewaters contained high organic substances with greater oxygen demand (Momtaz et al. 2010). The pH values of the textile and distillery raw wastewaters were not in conformity with the corresponding discharge and agricultural reuse limits. Likewise, turbidity and EC in all wastewaters and TDS in distillery wastewaters were above the threshold limits for agricultural reuse.

Nutrient and organic contaminants

As it can be seen from Table 2, distillery wastewater was found with high mean values of COD (160 g L^{-1}) and BOD_5 (46 g L^{-1}). These values were in good agreement with previous works (Nandy et al. 2002). However, COD and the ratio of COD to BOD_5 in the present study were higher than values in the literature (Satyawali and Balakrishnan 2008). Results for total nitrogen (7g L^{-1}), total phosphorus (4g L^{-1}), and sulfate (8g L^{-1}) in distillery wastewater in the present study agreed well with the finding reported by Chaudhary et al. (2013). Similarly, comparable values of nitrogen and sulfate and higher values of phosphorus were reported by Prakash et al. (2014).

Textile wastewater was variable in color (gray, pale blue, black, greenish, reddish) and odor depending on the

Table 2 Physicochemical contents of untreated wastewater samples used in this study (Values are in mg L^{-1} otherwise stated)

Parameter	Wastewater source ($n = 3$)								Limit	
	Textile		Distillery		Domestic		Blended			
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	*	**
pH	10.43^b	0.16	4.04^c	0.20	7.08^a	0.27	7.16^a	0.015	6–9	6.5–8.4
Turbidity (NTU)	266.67^a	21.13	2376.67^b	45.10	254.00^a	14.18	484.33^c	24.01	–	10
EC (dS/m) at 25 °C	5.69^a	1.91	41.40^b	5.95	3.78^a	0.51	5.58^a	0.17	–	3
TDS	2993.44^a	1217.62	$18,822.11^b$	4758.73	1729.89^a	139.81	2641.67^a	710.01	3000	2000
DO	0.14^a	0.02	0.13^a	0.02	0.17^a	0.01	0.15^a	0.02	6	–
BOD_5 (O_2)	$15,190.00^a$	10.00	$46,155.00^b$	147.56	$11,412.50^c$	78.10	$15,493.33^d$	35.12	50	10
COD (O_2)	$90,666.67^a$	9237.6	$160,000.00^b$	0.00	$74,666.67^a$	18,475.21	$34,133.33^c$	3695.04	150	–
SO_4^{-2}–S	1393.33^a	11.55	8203.33^b	15.28	1400.00^a	100.00	1618.67^c	122.99	1000	–
PO_4^{-3}–P	3310.00^b	10.00	$12,000.00^c$	20.00	3926.67^a	110.12	4615.00^d	5.00	10	–
TP (as P)	1079.39^b	3.26	3913.20^c	6.52	1280.49^a	35.92	1504.95^d	1.63	5	15
TN (as N)	389.65^a	15.97	7067.23^b	22.61	944.37^a	27.78	5133.68^c	602.51	40	30
NO_2–N	1.83^b	0.29	23.33^c	1.15	8.00^a	0.50	7.67^a	0.58	–	–
NO_3–N	226.00^a	6.00	6803.30^b	5.78	743.33^a	15.28	4768.00^c	613.18	20	–
TKN (NH_3–N)	161.81^a	13.82	240.56^b	18.17	193.04^a	18.91	358.01^c	20.65	80	25

SD standard deviation, *TP* total phosphorus, *TN* total nitrogen, *TKN* total Kjeldahl nitrogen

* Discharge limits adapted from Ethiopian Environmental Protection Authority (EPA 2003), for a textile industry and general limits

(–) value is not given; Means with different letters in a row are significantly different ($p < 0.05$)

** Threshold limits for agricultural reuse adapted from USEPA (2012) and WHO (2006) production types, mainly light, medium, and dark shades. The color was associated with the chemical reagents used in dyeing (Robinson et al. 2001). Table 2 presents the mean values of COD (91 g L^{-1}) and BOD_5 (15 g L^{-1}) which were found to be higher than the contents reported by Roy et al. (2010). TKN (0.16 g L^{-1}) and sulfate (1.39 g L^{-1}) contents were also found higher than the values reported by Hussein (2013). Variation in textile wastewater's composition from industry to industry is expected due to the variations in inputs and production process as described by Hussein (2013). As shown in Table 2, the values determined for COD (74.67 g L^{-1}), BOD_5 (11 g L^{-1}), TN (0.94 g L^{-1}) and TP (1.28 g L^{-1}) and TDS (1.7 g L^{-1}) in domestic wastewater were greater than the contents reported by Bilgin et al. (2014). However, comparable values for COD, lower values for TN and BOD_5, and higher TP were observed compared to Henze and Comeau (2008). Variations are expected because, the composition of domestic wastewaters has large and dynamic variations in terms of both place and time depending on the source, water supply, climate, the lifestyles of the contributing communities and sewage components (Henze and Comeau 2008). According to Metcalf and Eddy (2003), the domestic wastewater in the present study can be characterized as high strength. This may be attributed to the low water supply and diversified activities that contribute concentrated wastewaters mainly from the students' cafeteria where meals are prepared and served accompanied by an intensive washing activities. The mean pH value of the domestic wastewater was 7.1 ± 0.3 which likely be due to the neutralization effects of the gray and black waters such as strong base caustic soda in detergent and acidic materials like tomatoes and cooking oils (Al-Jayyousi 2003). In comparison, the distillery wastewater was found with highest concentrations of COD and BOD_5 compared to textile and domestic wastewaters. The values of COD, BOD_5, TN, TP, and TKN in the distillery, textile, and domestic wastewaters were found higher than the provisional discharge and agricultural reuse limits.

Characteristics of the blended wastewater

The pH value of the blended wastewaters was found in the range of 6.92 to 7.29 for a repeated blending trials (n = 40). This value was attained at ratios of textile/ distillery/ domestic (3:1:18v/v) which is within the recommended range (6.5–7.5) to support macrophyte and microorganism activities. Figure 2 presents the pH value of the sources and blended wastewaters at the different volumetric ratios.

From the results, it can be concluded that physical blending of the wastewaters at the determined volumetric ratio is effective in neutralizing the acidic distillery and alkaline textile wastewaters without any chemical additives. This method will help to avoid the use of sulfuric acid (H_2SO_4), hydrochloric acid (HCl), soda ash (Na_2CO_3), and calcium sulfate ($CaSO_4.2H_2O$) which are currently being used by the factories. As it is presented in Table 2, unlike the turbidity (484 ± 24 NTU) of the blended wastewater, its dissolved oxygen was not statistically different from the distillery, textile, and domestic wastewaters. Likewise, EC (5.58 ± 0.17dS/m) and TDS (2641.67 ± 710 mg L^{-1}) values of the blended were not statistically different from the textile and domestic wastewaters. In contrast, significant differences were observed between the blended and distillery wastewaters in terms of EC and TDS values. Hence, the salinity of the blended wastewater measured in terms of EC and TDS was lower than the distillery and higher than the textile and domestic wastewaters. In fact, the turbidity, EC and TDS values of the blended wastewater were beyond the discharge and agriculture reuse limits.

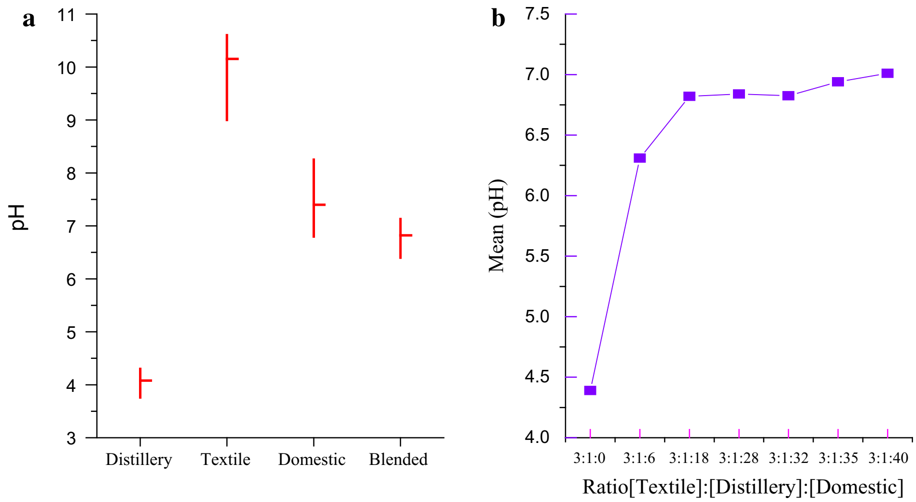

Fig. 2 (**a**-**b**). pH ranges with mean value (**a**) ($n = 4$); pH of the blended wastewater at indicated volumetric ratio

Analyzed heavy metals in the blended wastewater were found with mean concentrations of 12.4 ± 0.11 mg L^{-1}(Fe), 1.5 ± 0.02 mg L^{-1}(Mn), 0.58 ± 0.01 mg L^{-1} (Zn), 0.14 ± 0.01 mg L^{-1} (Cu), 0.06 mg L^{-1} (Co), 0.06 ± 0.01 mg L^{-1}(Ni), 0.03 ± 0.02 mg L^{-1}(Pb), 0.03 mg L^{-1}(Cr) and 0.03 ± 0.01 mg L^{-1} (Cd). Attributed to the elevated concentration of Fe and low concentration of Cd, Cr, and Pb, mean concentrations of these metals exhibit significant differences ($p < 0.05$). The tested heavy metals in blended wastewater were in the order of Fe > Mn > Zn > Cu > Co > Ni > Pb > Cd > Cr based on the mean concentrations. Distillery wastewater was with significantly higher concentrations of all tested heavy metals than the blended wastewater. In contrast, concentration in the blended wastewater was comparable with domestic except for Fe. Furthermore, while concentrations of Co, Pb, Cd, Cr, and Ni were similar, significantly higher values of Zn, Cu, Fe and Mn were observed in blended wastewater compared to textile wastewater. All analyzed heavy metals were in agreement with discharge limits set by EPA (2003). Nevertheless, Co, Cd, Fe, and Mn of the blended wastewater were beyond the threshold limit values for agricultural reuse. The mean BOD_5 content of the blended wastewater (15 g L^{-1}) was significantly different from the source wastewaters. Lower COD (34 g L^{-1}) was determined in the blended one compared to the distillery, textile, and domestic wastewaters. Moreover, its BOD_5 and COD contents were found higher than the respective discharge limits.

The ratio of BOD_5/COD has been used as an acceptable indicator to evaluate the biodegradability capacity of a wastewater with a frequent value ranged from 0.3 to 0.8 (30–80%). Accordingly, wastewater can be considered easily treatable if the ratio is greater than 0.5. On the contrary, wastewater with a value less than 0.5 requires pre-treatments prior to biological treatment. Moreover, it would be difficult to treat wastewaters biologically when the ratio falls below 0.3 (Abdalla and Hammamb 2014; Metcalf and Eddy 2003; Tran et al. 2015). The BOD_5/COD ratios for textile (0.17), distillery (0.29), and domestic (0.15) wastewater in the present study were below the limit value for effective biological treatment. However, blending has improved the ratio of BOD_5/COD to 0.45 (Table 3). Biodegradability of wastewater can also be evaluated based on the ratio of COD/ TN/ TP. In which case, while the proportions required to sustain aerobic condition is 100: 5: 1, the ratio suggested for an effective anaerobic processes range from 250: 5: 1 to 500: 5: 1 (Thompson et al. 2006; Ammary 2004) and these values have been used as benchmark for nutrient addition in nutrient limited wastewaters (Slade et al. 2011). In this regard, while samples from the textile factory were observed with low nitrogen contents followed by the domestic wastewater, samples from distillery wastewater have shown better nutrient contents due to the addition of nutrients in the yeast propagation section. In contrast, a better result was found for the blended wastewater (Table 3). The domestic wastewater in this study was observed with lower biodegradable organics and nutrient imbalance due to the presence of the gray water (Al-Jayyousi 2003).

Furthermore, according to the literature (Gajewska et al. 2015), nitrification and denitrification are widely accepted processes responsible for the removal of nitrogen compounds from wastewater in both conventional and treatment wetland plants. The ratio of BOD_5 to TN has been used as an index to understand these processes. In this context, if BOD_5/TN is less than 4; nitrification is a dominant process, but a combined process for higher values. As it can be seen in Table 3, values for all wastewaters were greater than four except for the blended wastewater. Based on the COD/TN value the wastewaters were in the order of textile (232.7), domestic (79.1), distillery (22.6), and blended (6.7). In wetland treatment systems, efficient nitrogen removal through nitrification has reported at lower BOD_5/TKN values (Gajewska et al. 2015), in this work the value was found in increasing order for blended (43) domestic (59), and textile (94), and distillery (192). From the analysis results, while the TN in blended wastewater was higher than the domestic and textile, its TKN value was higher than all wastewaters. Sulfate content of the blended wastewater was statistically different with a higher value than the textile and domestic but lower compared to the distillery wastewaters. Moreover, it was worth noting that higher proportions of the TN in textile (58%), distillery (96%), domestic (78%), and blended (93%) were from nitrate, and least nitrite proportion contributions were observed in all investigated wastewaters.

Table 3 Ratios of organic and nutrients parameters

Wastewater type	COD: BOD_5	BOD_5: COD	COD: TN	BOD_5: TN	COD: TN: TP
Domestic	6.5	0.15	79.1	12.1	100:1.3:1.7
Textile	6.0	0.17	232.7	39	100:0.4:1.2
Distillery	3.5	0.29	22.6	6.5	100: 4.4:2.5
Blended	2.2	0.45	6.7	3.0	100:15:4.4

Conclusion

Based on the investigated physicochemical properties and heavy metal concentrations distillery wastewater was found stronger than the textile and domestic wastewaters with statically differences ($p < 0.05$). Similarly, the mean concentrations of Zn, Cu, Fe, and Mn in textile and domestic wastewater were significantly different with higher values recorded in samples from domestic wastewaters. However, the rest studied heavy metals did not show significant differences ($p > 0.05$). Furthermore, while textile was found stronger in terms of EC, TDS, COD, and BOD_5, higher TN and TP were recorded in domestic wastewater. The study concluded that blending was effective to adjust the pH of the alkaline textile, acidic distillery, and domestic wastewaters to 6.92–7.29 at a volumetric ratio of 3:1:18, respectively. This methodology is a sustainable alternative to enhances the biological treatability of the wastewaters and to avoid the use of the chemicals for neutralization. The results provide further evidence on the need to consider the studied heavy metals in the Ethiopian standards for discharges as quality criteria to treat and monitor distillery and domestic wastewaters.

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Compliance with ethical standards

Conflict of interest No potential conflict of interest is reported by the authors.

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