Ethiop. J. Biol. Sci. **18(1): 77–94, 2019**

ISSN: 1819-8678

RESEARCH ARTICLE

ASSESSMENT OF THE PHYSICO-CHEMICAL CHARACTERISTICS OF A TANNERY WASTEWATER AND ITS POLLUTION IMPACT ON THE WATER QUALITY OF LITTLE AKAKI RIVER

Tesfaye Admassu[1,*], Adey Desta[2] and Fassil Assefa[2]

ABSTRACT: Tannery wastewater is one of the most hazardous industrial pollutants containing organic and inorganic substances. For this reason, tanneries are required to treat their wastewater before discharging into the environment. The objective of this study was to evaluate efficiency of Batu tannery wastewater treatment plant and the impact of the tannery affluent on the quality of the Little Akaki River. The physico-chemical characteristics of tannery wastewater before and after treatment were determined based on triplicate measurements for each sample. The data showed that raw tannery wastewater has high loads of pollutants. The highest COD, TDS, ammonia-N, sulfate, total nitrogen, sulfide and total chromium observed in the raw tannery wastewater was 7213 mg/l, 6236 mg/l, 228 mg/l, 352 mg/l, 310 mg/l, 294 mg/l and 26 mg/l, respectively. Average removal efficiency of the treatment system for the COD, sulfide, ammonia-N, TDS, total nitrogen was 51%, 62.6%, 48%, 47%, 59.5% and 52.7%, respectively. The pH, temperature and electrical conductivity was reduced by less than 10% in treated tannery effluent, but COD, TN, sulfide, total chromium, sulfate and TDS exceeded the national discharge limit for the tannery effluent. Analysis of similar parameters in the Little Akaki River showed that insufficiently treated tannery effluent caused an increase in the river water physico-chemical characteristics except for temperature and pH. However, one-way analysis of variance showed that only the COD, total chromium and sulfate of downstream LAR water were significantly ($p<0.05$) different from upstream similar parameters. This showed that impact of the tannery effluent on the river water quality is insignificant for most of the studied parameters. Nevertheless, the physico-chemical data of upstream LAR water showed that the river is severely polluted by other upstream sources and the river water is beyond the recommended water quality values for human, animal and agricultural uses.

Key words/phrases: Leather, Little Akaki River, Physico-chemical characteristics, Tannery, Wastewater.

[1] Institute of Biotechnology, Addis Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia. E-mail: tesadsanka@gmail.com

[2] Department of Microbial, Cellular and Molecular Biology, Addis Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia. E-mail:adey.desta@gmail.com; asefafasil2013@gmail.com

* Author to whom all correspondence should be addressed.

INTRODUCTION

Leather tanning is one of the important industries which produce finished and semi-finished leather in Ethiopia. The second Ethiopian growth and transformation plan (2015–2020) projected that the tanning industry would play an important role in the economic transformation of the country. Currently, there are more than 27 operational tanning industries in Ethiopia (Mekonnen Birhanie *et al*., 2017) with a capacity of processing about 9,000 hides and 153,650 skins each day (UNIDO, 2012). Hu *et al*. (2011) estimated that a tanning process of 1000 kg of raw hides produce approximately 250 kg leather, 450–730 kg solid waste and about 50,000 m^3 wastewater after using large volume of water and several chemicals. The wastewater then contain 100–400 mg/l chromium, 200–800 mg/l sulfide, high levels of fat and other solid wastes per ton of hide processed (El-Bestawy *et al*., 2013). Thus, tannery wastewater is one of the serious environmental pollutants containing organic and inorganic substances that are detrimental to human and animal health. The pollutant load of tannery wastewater is determined by analyzing wastewater quality parameters such as the total nitrogen (TN), ammonia-N, nitrate, chemical oxygen demand (COD), total dissolved solid (TDS), sulfides, sulfates, total chromium, pH, temperature and electrical conductivity (Haydar and Aziz, 2009).

Over the years, rivers in and around Addis Ababa are increasingly polluted due to increase in population and industrialization. The population in the city is projected to reach 4.7 million by the in the next ten years with an annual growth rate of 3.8% (UNHSP, 2017). Apart from that, 65% of the country’s industries are located along the river basins in and around the city. Little Akaki River (LAR) is one of the rivers in Addis Ababa which receive raw and treated wastewater from domestic and industrial wastewaters. Among the industries located on the periphery of LAR in Addis Ababa is the Batu tannery which discharges its treated tannery wastewater to the river. Few studies were conducted on the LAR showed that there is high pollution pressure on the river water (Samuel Melaku *et al*., 2007; Ferezer Eshetu, 2012). Despite the high pollution pressure, the downstream suburban communities use Akaki River water for different activities including for irrigation to produce different vegetables that contribute to about 60% to the Addis Ababa city’s market (van Rooijen *et al*., 2010). The objective of this study was therefore, to assess the strength of tannery wastewater before and after treatment and evaluate the impact of tannery effluent on the physico-chemical quality characteristics of LAR water. We assume the physico-chemical characteristics of LAR water before and after the treatment either remain the same or differ significantly after receiving tannery effluent. In order to test this assumption (hypothesis), we use statistical test.

MATERIALS AND METHODS

Description of the study site

This study was carried out at Batu tannery wastewater treatment plant located in Akaki Kality Sub city, Addis Ababa. Batu tannery is a medium size factory producing finished leather using cattle hide and shoat (goat and sheep) skin. Batu tannery wastewater treatment plant apply combined biological and chemical enhanced coagulation processes in a series of pond systems. The tannery wastewater treatment facility consists of sulfur oxidation, aeration and sedimentation ponds as well as separate chromium recovery system.

Raw tannery influent enters to the treatment plant through three channels. The largest volume of raw influent come from the beam house operations and all the three channels finally mixed in the sulfur oxidation (equalization) pond which is called the raw general (G) wastewater by the treatment plant operators. The deep blue coloured chrome wastewater come from tanyard operation and detained in the separate pond from which it is channeled into chromium recovery facility. After chromium recovery stage the chrome influent piped out to the equalization tank. The general wastewater is then drawn into aeration tank passing through small dye containing influent detention pond. From the aeration pond, mixed liquor is pumped into a coagulation chamber where the coagulants (aluminum sulfate and ionic polymers) are added. The wastewater is then piped out into the sedimentation pond where flocculated biomass is separated from the effluents by gravitational force. Finally, treated tannery effluent is released out into the LAR (Fig. 1).

Sample collection

Wastewater samples were collected from the general (equalization-sulfur oxidation) pond, aeration tank and at the discharge point of tannery effluent from sedimentation pond respectively using sterile plastic polyethylene bottles. LAR water samples were collected upstream (8°55′56.37″ N, 38°45′26.52″ E) before the tannery effluent enter the river and about 250 metres downstream (8°55′48.01″ N, 38°45′23.00″ E) from the tannery effluent discharge point (Fig. 2). Tannery wastewater and LAR water samples were collected at the same time in November, February and April in the year 2016/17, and all the months were dry during the sampling time. From each sample stations, three grab samples were collected at different points of the Batu tannery wastewater treatment plant (8°55′54.35″ N, 38°45′29.78″ E, Elev. 7094 ft) and the grab samples were mixed into composite sample for each sample site. The tannery wastewater and LAR river water samples were transported under freezing condition and stored in the laboratories of Institute of Biotechnology and bioinstrumentation laboratory of Microbial and Cellular Microbial Biology. Physico-chemical analysis was carried out within 12 hours of sampling and samples were stored at 4°C until analysis was completed.

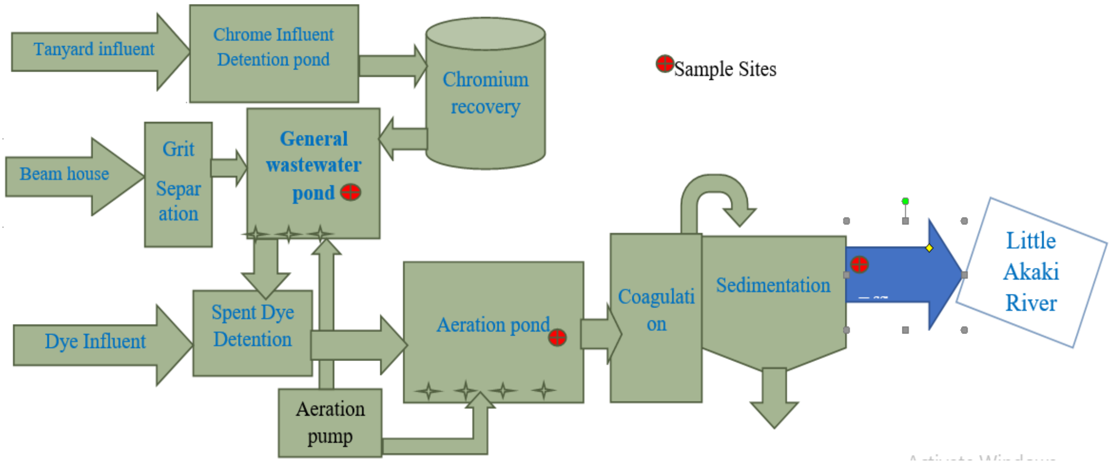

Fig. 1. Schematic tannery wastewater treatment plant of Batu tannery showing the sampling points and different pond systems. The yellow and red circles denote the sampling sites.

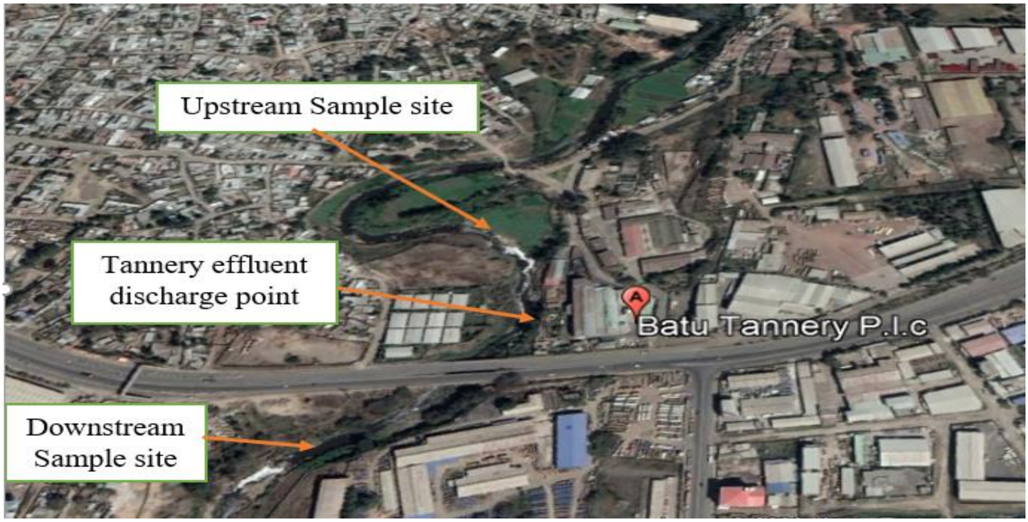

Fig. 2. A satellite map of Batu tannery and nearby Little Akaki River.

Physico-chemical analysis

Physico-chemical characteristics of the tannery wastewater and LAR samples were determined in order to evaluate the extent of removals of pollutants using the major wastewater parameters before and after treatment by the tannery wastewater treatment plant. The same parameters were determined for the LAR water before (upstream) and after receiving (downstream) the tannery effluent. The tested parameters were pH, temperature, electrical conductivity (EC), chemical oxygen demand (COD), Total Nitrogen (TN), sulfide, sulfate, total dissolved solids (TDS), ammonia as N (NH_3-N), nitrate and total chromium (TotCr).

The pH, EC and temperature were measured on-site during sampling by using portable multi-probe pH meter (Thermo AP85 meter, Fisher scientific, Singapore) with separate probes for pH and EC. Analysis of physico-chemical characteristics was carried out after triplicate measurement of each samples following the standard methods prescribed in American Public Health Association for the determination of water and wastewater (APHA, 1999). Accordingly, TDS was determined by thermogravimetric method (#2540C) and COD was determined by titrimetric closed reflux method (#5220). Ammonia-N of tannery wastewater and LAR river water samples was determined by Nessler method (#4500-NH_3 B & C); Nitrate by cadmium reaction method (#4500-NO_3-N) and Total Nitrogen by persulfate methods (#4500 N). Sulfate was determined by the turbidimetric method (#4500-SO_4^{2}-E) and sulfide was measured using Methylene blue method

(#4500 S_2-D). Total chromium was determined by atomic absorption spectrometer (AAS). Distilled water was used as blank with similar volume to the experimental samples (Aniyikaiye *et al*., 2019).

Data analysis

Statistical analysis of means, standard deviations, range, minimum and maximum values of each parameter were computed using statistical package for social studies (IBM SPSS, version 23). One-way analysis of variance (ANOVA) was analysed to test the mean difference between the upstream and downstream LAR water parameters before and after receiving tannery effluent at alpha level of $p<0.05$. Pearson correlation coefficient (r) was calculated to evaluate the relationship between the test parameters in the raw and treated tannery wastewater. The extent of correlation was considered very 'strong' when $r > 0.9$, 'strong' when $0.7 < r < 0.9$, medium when $0.4 < r < 0.6$ and weak when $r < 0.3$.

RESULTS AND DISCUSSION

The mean physico-chemical characteristics of raw tannery wastewater (G), treated tannery effluent (E) and the LAR water is presented in Table 1 and Table 3. Physico-chemical analysis of raw tannery wastewater showed that there is high load of pollutants that it is dangerous to human and environmental health if released without sufficient treatment. In the treated tannery effluent, there was considerable reduction in the amount of those pollutants by 51%, 48.8%, 59.5%, 62.6%, 52.7% and 49% for COD, ammonia-N, TN, sulfide, total chromium and TDS, respectively. This showed that most of the pollutants exceed the permissible environmental discharge limit for tannery effluent (EPA, 2003).

The physico-chemical characteristics of the raw tannery wastewater was 'strong' (high mean value) and has wider ranges for almost all parameter except nitrates and pH (Table 1). In some parameters, the strength of raw tannery wastewater in this study was similar to previous reports in Ethiopia, but significantly differ in many of the remaining parameters (Assefa Wosnie and Ayalew Wondie, 2014; Mekonnen Birhanie *et al*., 2017). Jahan *et al.* (2014) reported that the strength of tannery wastewater varied from tannery to tannery and the variability is likely to result from the type of raw material (skin or hide), amount and type of chemicals used in the tanning processes as well as types of final product. The release of insufficiently treated tannery wastewater to rivers can affect the quality of river water which is used by the downstream inhabitants for different purposes.

Table 1. The physico-chemical characteristics of tannery wastewater before and after treatment.

Parameters	Tannery wastewater	Mean±Stdev (n=9)	Minimum	Maximum	Difference	Discharge limit (EPA)
pH	Raw	8.7±0.287a	8.2	9.2	8.5	9-Jun
	Treated	7.96±0.578b	7	8.6		
Temp (°C)	Raw	25.4±2.32a	22	28	2.4	40
	Treated	24.8±2.15a	22	28		
EC (mS/cm)	Raw	26.6±8.37a	16.1	36.9	8.6	-
	Treated	24.3±5.32a	18.7	31.6		
COD (mg/l)	Raw	6755.4±567.9a	5674	7213	51	500
	Treated	3308.7±191.3b	3032	3542		
NO_3 (mg/l)	Raw	2.5±4.02a	0	12	-47	45
	Treated	4.7±3.33b	0.4	9		
NH_3-N(mg/l)	Raw	174.3±46.9a	102	228	48.8	30
	Treated	91.2±10.25b	79	112		
TN (mg/l)	Raw	301±19.5a	245	310	59.5	60
	Treated	122±16.4b	100	144		
S_2- (mg/l)	Raw	218.7±45.4a	168	294	62.6	1
	Treated	81.9±23.9b	46	118		
SO_4^{2-} (mg/l)	Raw	240.4±89.4a	122	352	-10.3	
	Treated	268.1±41.3a	205	318		2
TotCr(mg/l)	Raw	20.7±3.7a	14	26	52.7	
	Treated	9.8±3.4b	4	14		
TDS (mg/l)	Raw	4827.4±726.3a	4315	6236	49	-
	Treated	2463.6±446.3b	2118	3144		

*Samples with same letters (a-a, b-b) do not differ significantly, samples with different letters (a-b) differ significantly from each other. EPA = Environmental Protection Authority; EC = Electrical Conductivity; COD = Chemical Oxygen Demand; TN = Total Nitrogen; TDS = Total Dissolved Solid; Removal (%) refers to the difference in the physicochemical values between the raw and treated wastewater.

The average pH of raw tannery wastewater was slightly alkaline but reduced to almost neutral pH in the treated effluent (Table 1). The data also showed that the pH in the treated effluent was within the discharge limit for pH of the tannery effluent (pH 6.0–9.0). Similar pH to this study was reported in combined tannery wastewater treatment plant (Shegani, 2014), composite raw tannery wastewater (Goswami and Mazumder, 2016) and in post tanning treatment of tannery wastewater (pH 8.11±1.1) treated by lime/bittern coagulation (Ayoub *et al*., 2011). The mean temperature value of the raw tannery wastewater reduced by an average of 2.4% in the tannery effluent at the point of discharging to the river (Table 1). Like the pH, temperature in the treated effluent was within the range of discharge limit of tannery effluent to the river water (EPA, 2003).

Similarly, the mean EC of treated tannery wastewater reduced by an average of 8.6% showing the treated effluent still had high conductivity, and there was no significant difference in the EC of the raw tannery wastewater and treated tannery effluent (Table 1). The EC content of the tannery wastewater can be attributed with the presence of chemicals mainly the cations and anions (Sugasini and Rajagopal, 2015) such as the sulfate ions which are unlikely to be eliminated by the current treatment set up which lacks anaerobic stage. The TDS in the raw tannery wastewater was also high, but 49% of the TDS was removed by the treatment process. Low TDS removal by the treatment plant can be credited with the slight alkalinity of raw tannery wastewater since alkaline pH can affect the TDS removal in the wastewater treatment process (Hashem *et al*., 2016).

The relationship between water quality parameters of the tannery wastewater was indicated by the Pearson correlation coefficient (r). The correlation coefficient (r) was calculated to determine the association of wastewater quality parameters in the raw and treated tannery wastewater (Table 2). According to the Pearson coefficient matrix data, the relation of water quality parameters ranged from very high (> 0.9) to weak (< 0.3). Unpredictably, high negative correlation was observed between temperature and EC (r = -790), and this relationship was observed to be significant (p< 0.01). The COD showed high positive correlation with NH_3-N, TN, sulfide, total chromium and TDS, but has weak relation with sulfate. The pH has strong relation with TN, and sulfide, but the pH relates negatively with the nitrate (Table 2).

The COD value in the raw tannery wastewater showed wider ranges and variation in the COD concentration may be linked with a difference in the tanning operations and resulting wastewater concentration. In the final effluent, the COD concentration was reduced by average of 51% showing the COD surpass the permissible discharge limit for tannery effluent (EPA, 2003; Haile Reda, 2016). The COD removed from tannery effluent was lower than the theoretical total biodegradable COD (57.4%) from raw wastewater (Pire-Sierra *et al*., 2016). A similar low COD removal in the range of 40 to 70% from similar tannery influent strength (7,255 mg/l) was reported in Egypt (El-Sheikh *et al*., 2011). But compared to the tannery wastewater treated by using yeast (Stanley *et al*., 2017), and UASB reactor (El-Sheikh *et al*., 2011), the COD and TDS removed by the tannery wastewater treatment plant in this study was lower.

Table 2. Pearson correlation matrix among the physico-chemical parameters of tannery wastewater.

		pH	**Temp**	**EC**	**COD**	**NO_3**	**NH_3-N**	**TN**	**Sulfide**	**Sulfate**	**TotCr**	**TDS**
pH	Pearson correlation	1	0.522*	-0.101	0.654**	-0.546*	0.563*	0.752**	0.638**	0.213	0.762**	0.311
	Sig. (2-tailed)		0.026	0.691	0.003	0.019	0.015	0	0.004	0.396	0	0.208
Temp	Pearson correlation		1	-0.790**	0.156	0.119	-0.136	0.272	-0.124	-0.339	0.132	0.147
(°C)	Sig. (2-tailed)			0	0.538	0.637	0.591	0.275	0.623	0.169	0.601	0.561
EC	Pearson correlation			1	0.101	-0.284	0.327	0.035	0.465	0.388	0.236	0.12
(mS/cm)	Sig. (2-tailed)				0.69	0.253	0.186	0.89	0.052	0.111	0.347	0.636
COD	Pearson correlation				1	-0.384	0.872**	0.983**	0.899**	-0.032	0.883**	0.778**
(mg/l)	Sig. (2-tailed)					0.116	0	0	0	0.899	0	0
NO_3 (mg/l)	Pearson correlation					1	-0.643**	-0.43	-0.516*	-0.697**	-0.646**	0.079
	Sig. (2-tailed)						0.004	0.075	0.028	0.001	0.004	0.757
NH_3-N	Pearson correlation						1	0.826**	0.886**	0.414	0.867**	0.458
(mg/l)	Sig. (2-tailed)							0	0	0.088	0	0.056
TN (mg/l)	Pearson correlation							1	0.875**	-0.055	0.899**	0.768**
	Sig. (2-tailed)								0	0.827	0	0
Sulfide	Pearson correlation								1	0.21	.895**	0.646**
(mg/l)	Sig. (2-tailed)									0.404	0	0.004
Sulfate	Pearson correlation									1	0.268	-0.564*
(mg/l)	Sig. (2-tailed)										0.282	0.015
TotCr	Pearson correlation										1	0.547*
(mg/l)	Sig. (2-tailed)											0.019
TDS	Pearson correlation											1
(mg/l)	Sig. (2-tailed)											

*Denote correlation is significant at $p<0.05$ level (2-tailed). ** Denote correlation is significant at $p<0.01$ level (2-tailed).
COD = Chemical Oxygen Demand, TDS = Total Dissolved Solid, EC = Electrical Conductivity, TN =Total Nitrogen, TotCr = Total Chromium

TDS is the measure of total inorganic salt and other dissolved substances in water (Parveen *et al*., 2017). Like COD, the TDS of raw tannery influent showed large variation as presented in the range of values in Table 1. High concentration of TDS in the raw tannery influent is attributable with the presence of soluble substances such as nitrates, carbonates, bicarbonates, chlorides and sulfates (Sugasini and Rajagopal, 2015). The TDS recorded in the current study was 6 to 8 times lower than previous research reports in India (influent 34,200 mg/l and effluent 28,600 mg/l) (Mangal *et al*., 2013).

Ammonia-N and total-N was eliminated by 48.8% and 59.5% leaving 91.2±10.25 mg/l NH_3-N and 122±16.4 mg/l TN in the treated effluent, respectively. This amount is still above the permitted discharge limit of HN_3-N and TN for tannery effluent. The studied chemical enhanced tannery wastewater treatment process showed lower HN_3-N removal performance compared to previous report of moving-bed biofilm reactor (MBBR) which had 97% HN_3-N removal efficiency (Ding *et al*., 2016). Unlike the other nitrogen families, the amount of nitrate in the raw tannery wastewater was very low, but it increased by 47% in the tannery effluent after aeration step (Table 1). The increase in the amount of nitrate in the final effluent is likely due to nitrification carried out by nitrifying bacteria in the presence of oxygen (Ju and Zhang, 2014).

Sulfide and sulfate are the other major pollutants in the tannery wastewater. As presented in the Table 1, the average concentration of sulfide in the raw tannery wastewater was significantly different from the sulfide in the treated effluent. There was 62.6% sulfide removal after sulfide oxidation process in the equalization and aeration basins. The elimination of sulfide is likely to be carried out by the air stripping mechanism assisted by an aeration pump (Midha and Dey, 2008). The neutral and slightly alkaline pH of raw tannery wastewater could enhance the generation and elimination of sulfide, but at pH greater than 9.0 sulfide can remain in the dissolved state (Santos and Camacho, 2014). There was an increase in the amount of sulfate by 10.3% in the effluent samples. Higher mean sulfate (1,240 mg/l) but comparable sulfide (156 mg/l) content of raw tannery wastewater to this study was reported in chemically enhanced primary tannery wastewater treatment (Haydar and Aziz, 2009). However, the mean sulfate and sulfide contents of raw tannery wastewater in this study was lower than the amount of sulfide reported at Dire tannery (Mekonnen Birhanie *et al*., 2017) and Mojo tanneries (Tadesse Alemu and Seyoum Leta, 2015).

Chromium is another serious environmental pollutant produced in tanneries. The average total chromium (mg/l) in the raw tannery wastewater was 20.7±3.7 from which 52.7% was removed by the treatment operation. The amount of chromium was higher than the total chromium reported at a complete leather production wastewater (9±0.11 mg/l) in Bangladesh (Chowdhury *et al*., 2013), but lower than the total chromium from common effluent treatment plant in India (Bhatnagar *et al*., 2013). The total chromium in the raw tannery wastewater in this study was also lower by 25% from previously reported data at Modjo tannery (Adey Feleke *et al*., 2014), and by 42.3% from Dire tannery (Mekonnen Birhanie *et al*., 2017). Despite an encouraging removal by the treatment process, the total chromium in the treated tannery effluent still exceed the discharge limit for tanneries (EPA, 2003). The presence of chromium more than the permissible discharge limit is a serious human health concern since chromium is a carcinogen and mutagen to humans. Overall, the amount of COD, sulfide, total N, Ammonia-N and total chromium in the treated tannery effluent surpass the discharge limit for tannery wastewater by up to 7.1 times for COD, 3.5 times for NH_3-N, 2.5 times for TN, 104 times for sulfide and 6 times in total chromium.

The physico-chemical characteristics of LAR water

The physic-chemical characteristics of LAR water was analysed before (upstream) and after mixed (downstream) with the tannery effluent to evaluate the impact of the tannery effluent on the water quality parameters of the river. As presented in Table 3, the water quality data showed that sulfide, NH_3-N, TDS, sulfate, COD, EC and total chromium in the LAR water exceeded the recommended surface water quality, but temperature and pH were in acceptable ranges according to the WHO guidelines (Rickwood *et al*., 2007). Up on receiving the tannery effluent, the pH and EC of the river water increased by 8.1% and 9% on average, respectively, but downstream temperature of the river water remains very close to the upstream water temperature. This shows that there is no thermal pollution to LAR water associated with the discharge of tannery effluent from the Batu tannery wastewater treatment plant. Although it was not significant, the TDS, NH_3-N, TN and sulfide increased by average values of 10%, 14.7%, 17% and 19.7% and in the downstream river water, respectively.

Table 3. Little Akaki River water quality (mean and standard deviation calculated from nine samples).

Parameters	***Upstream**		****Downstream**		**WHO standard**
	Mean±Stdev	**Range**	**Mean±Stdev**	**Range**	
pH	7.9±0.6	7.2–8.8	8.6±0.6	8–9.3	9-Jun
Temp	25.3±0.83	24–26.2	25.4±1.0	24.2–26.8	-
EC (mS/cm)	44.8±9.6	32–59	49.2±8.5	41–62	-
COD (mg/l)	1111.9±77	1022–212	1202.5±90.9	1126–1332	250
TN (mg/l)	127.8±31.7	94–182	153.9±47.4	105–224	-
NH_3-N (mg/l)	89.0±38.3	42–142	105.1±43.8	49–165	1.5
NO_3 (mg/l)	39.6±19.2	Nov-62	41.5±18.3	17–63	-
TDS (mg/l)	8496±1039	7356–9882	9487±1274	8123–11214	500
S_2- (mg/l)	57.2±21.5	29–87	66.1±22	41–97	0.1
SO_4^{2-} (mg/l)	411.4±49.7	342–468	512.6±46.3	440–562	250
TotCr (mg/l)	10.7±1.9	14-Aug	22.1±6.7	14–32	0.1

*Upstream = before receiving tannery effluent, **Downstream = after receiving tannery effluent.

The total nitrogen, ammonia-N, pH, and temperature were very close to the water quality reports of Modjo river contaminated by tannery discharges (Haile Reda, 2016), but the TDS, COD and sulfides were higher in the LAR water. The nitrate concentration in the LAR water was lower than the report in previous study (189±319 mg/l) conducted in the similar dry months (Ferezer Eshetu, 2012), but higher than the physico-chemical characteristics of LAR water reported in 2007 (Samuel Melaku *et al*., 2007). It is observed that physico-chemical data of LAR has an increasing trend when compared to the previous reports. This suggested the deterioration of LAR water quality which results from the rapid addition of industrial and domestic wastes to the river.

One-way ANOVA analysis was done to determine the relationship or differences of water quality parameters between the upstream and downstream sampling stations of the LAR water at 95% significance level ($\alpha = 0.05$). The analysis revealed that there is significant difference in the mean LAR water parameters of COD, total chromium and sulfate ($p<0.05$) between the upstream and downstream samples (Table 4). The ANOVA result does not show significant difference in the water quality parameters of pH, temperature, EC, sulfides, NH_3-N, Nitrate, TN and TDS ($p>0.05$) between the upstream and downstream samples.

Table 4. One-way Analysis of Variance of water quality parameters between upstream and downstream sample sites of LAR.

		Sum of squares	df	Mean square	F	Sig.
pH	Between groups	1.45	1	1.45	3.675	0.073
	Within groups	6.3	16	0.39		
	Total	7.74	17			
Temp	Between groups	0.067	1	0.067	0.07	0.794
	Within groups	15.3	16	0.957		
	Total	15.4	17			
EC	Between groups	86.2	1	86.24	0.94	0.347
	Within groups	1467.618	16	91.73		
	Total	1553.9	17			
COD	Between groups	36964.8	1	36964.81	4.632	0.047
	Within groups	127689.9	16	7980.62		
	Total	164654.7	17			
TDS	Between groups	4421346.7	1	4421346.72	2.907	0.108
	Within groups	24337347.8	16	1521084.24		
	Total	28758694.5	17			
TN	Between groups	3068.1	1	3068.06	1.679	0.213
	Within groups	29240.4	16	1827.53		
	Total	32308.5	17			
NH_3	Between groups	1168.1	1	1168.06	0.613	0.445
	Within groups	30482.9	16	1905.18		
	Total	31650.9	17			
NO_3	Between groups	17.21	1	17.21	0.043	0.838
	Within groups	6337.8	16	396.11		
	Total	6355	17			
Sulfide	Between groups	355.6	1	355.56	0.678	0.422
	Within groups	8390.4	16	524.4		
	Total	8746	17			
Sulfate	Between groups	46005.6	1	46005.56	17.746	0.001
	Within groups	41478.4	16	2592.4		
	Total	87484	17			
TotCr	Between groups	589.4	1	589.39	21.784	0
	Within groups	432.9	16	27.06		
	Total	1022.3	17			

df = degree of freedom, Sign. = significance, F = F-statistics (ratio of mean squares)

Although the one-way ANOVA revealed significance difference in three parameters only, there is still increase in the percentage of the other parameters in the downstream of LAR water after receiving tannery effluent. The pH of LAR water slightly increased after receiving tannery effluent as presented in Table 3. This was likely to result from the presence of free ammonia-N in the tannery effluent (Prabu *et al*., 2011), and from upstream unlawful streams of different sources which contain nitrogen and sulfide contaminants. The TDS in the upstream LAR water was high, and it has agricultural concern since the amount of TDS in river water is an important parameter for evaluating the suitability of the river water for irrigation. By virtue of this assumption, the current condition of TDS in the LAR water was very high that it is unfit to be used for irrigation. Besides, the high concentration of TDS in the river water worsen the aesthetic value of the river water that its physical appearance become unpleasant as it is darker in colour (Fig. 3). Aesthetic displeasure of the river water comes from several residential and industrial discharges of upstream sources including the breweries, wineries, pharmaceuticals, distillers and alcohol liquor industries which are located on the peripheries of the LAR (Yared Worku and Giweta, 2018).

Fig. 3. The discharge point of Batu tannery effluent to LAR (Left) and downstream condition of the river after receiving tannery effluent (Right). The picture was taken in January 2017.

In the upstream LAR water, unexpected high amount of nitrate was observed, and there was no significant increase of nitrate in the downstream river water after tannery effluent is released. This is likely due to the low nitrate profile of the tannery effluent that is too low to cause difference in the amount of the nitrate in the LAR water. A more concerning observation was the presence of relatively high concentration of total chromium in the LAR water which increased by up to 51% after tannery effluent is released to the river. This data supports the one-way ANOVA analysis which revealed significant difference ($p<0.05$) between the men values of total chromium in the upstream and downstream LAR water (Table 4). The increase in the amount of chromium could be pronounced by the decreasing volume of the river water in the dry months when there is a reduction in the flow rate and volume of the river water (Tadesse Animaw, 2011). For most of the studied parameters the impact of tannery effluent to the physicochemical condition of the river water was not statistically significant ($p>0.05$). However, the physical and chemical conditions of LAR water is below the recommended standard quality of surface water to use for human, animal and agricultural purposes.

CONCLUSION

This study was carried out on the tannery wastewater treatment plant to assess the differences in the raw and treated tannery wastewater in terms of physico-chemical parameters. The assessment included estimation of the removal efficiency of the tannery wastewater treatment plant and possible impact of the tannery effluent on the physicochemical water quality characteristics of LAR. The data revealed that COD, TDS, ammonia-N, total N, sulfide and total chromium exceeded the permissible discharge limit of effluent to inland waters according to the Ethiopian EPA guidelines. One-way NOVA analysis indicated that there was significant difference ($p < 0.05$) in the mean values of COD, total chromium and sulfate between the upstream and downstream LAR water, and the difference was incurred by the tannery effluent. This asserts that the tannery effluent has impact on the downstream LAR water in terms of the COD, chromium and sulfide concentrations exacerbating the pollution problem that the river suffers upstream. Although the impact of tannery effluent was not statistically significant for most parameters during the study time on the LAR water, continuous release of the tannery effluent to the LAR in the long term can affect the river ecology and aggravate the pollution problem of the river. Therefore, we recommend the enforcement of stringent treatment using the existing EPA guidelines.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Addis Ababa University for the financial support through adaptive research grant. We also thank the Batu tannery owners for allowing us to collect samples from the tannery wastewater treatment plant. We also highly appreciate the staff members and treatment plant operators of the factory for their assistance during sample collection. We acknowledge the administrative support of Institute of Biotechnology, and the office of Associate Dean for Graduate Research, College of Natural and Computational Sciences, Addis Ababa University.

REFERENCES

Adey Feleke, Fassil Assefa, Seyoum Leta, Stomeo, F., Wamalwa, M., Njahira, M. and Djikeng, A. (2014). Microbial community structure and diversity in an integrated system of anaerobic-aerobic reactors and a constructed wetland for the treatment of tannery wastewater in Modjo, Ethiopia. *PLoS ONE* **9**(12): 1–22.

Aniyikaiye, T., Oluseyi, E., Temilola, J.O. and Edokpayi, J.N. (2019). Physico-chemical analysis of wastewater discharge from selected paint industries in Lagos, Nigeria. *Int. J. Environ. Res. Public Health* **16**(1235): 1–17.

APHA (1999). **Standard Methods for the Examination of Water and Wastewater**.

American Public Health Association, Washington, D.C.

Assefa Wosnie and Ayalew Wondie (2014). Assessment of downstream impact of Bahir Dar tannery effluent on the head of Blue Nile River using macroinvertebrates as bioindicators. *Int. J. Biodiv. Conserv.* **6**(4): 342–350.

Ayoub, G.M., Hamzeh, A. and Semerjian, L. (2011). Post treatment of tannery wastewater using lime/bittern coagulation and activated carbon adsorption. *Desalination*. **273**(2–3): 359–365.

Bhatnagar, M.K., Raviraj, S., Sanjay, G. and Prachi, B. (2013). Study of tannery effluents and its effects on sediments of River Ganga in special reference to heavy metals at Jajmau, Kanpur, India. *J. Environ. Res. Develop.* **8**(1): 56–59.

Chowdhury, M., Mostafa, M.G., Biswas, K.T. and Saha, A.K. (2013). Treatment of leather industrial effluents by filtration and coagulation processes. *Water Resour. Ind.* **3**: 11–22.

Ding, Y., Qian, Y., Li, L., Ren, H. and W.Q. (2016). Total nitrogen removal of synthetic leather wastewater treated by MBBR. In: **2nd International Conference on Machinery, Materials Engineering, Chemical Engineering and Biotechnology**, pp. 565–569, Atlantis Publishers.

El-Bestawy, E., Ranya, F.A. and Reham, A. (2013). Biological treatment of leather-tanning industrial wastewater using free-living bacteria. *Adv. Life Sci. Technol*. **12**: 46–65.

El-Sheikh, M.A., Saleh, H.I., Flora, J.R. and Abdel-Ghany, M. (2011). Biological tannery wastewater treatment using two stage UASB reactors. *Desalination* **276**: 253–259.

EPA (Ethiopian Environmental Protection Authority) (2003). Provisional standards for industrial pollution control in Ethiopia, Addis Ababa.

Ferezer Eshetu (2012). **Physico-chemical Pollution Pattern in Akaki River basin, Addis Ababa, Ethiopia**. Masters Thesis, Stockholm University, Sweden.

Goswami, S. and Mazumder, D. (2016). Comparative study between activated sludge process (ASP) and moving bed bioreactor (MBBR) for treating composite chrome tannery wastewater. In: **Materials Today**, International Conference on Advances in Bioprocess Engineering and Technology, pp. 3337–3342 (Ramkrishna, D. and Sengupta, S., eds.). Vol. 3(10) Part A, Proceedings. Elsevier Ltd.

Haile Reda (2016). Physico-chemical characterization of tannery effluent and its impact on the nearby river. *Open Access Library J.* **3**(3): 1–8.

Hashem, M.A., Nur-A-Tomal, M.S. and Bushra, S.A. (2016). Oxidation-coagulation-filtration processes for the reduction of sulfide from the hair burning liming wastewater in tannery. *J. Clean. Prod.* **127**: 339–342.

Haydar, S. and Aziz, J.A. (2009). Coagulation - flocculation studies of tannery wastewater using combination of alum with cationic and anionic polymers. *J. Hazard. Mater.* **168**: 1035–1040.

Hu, J.X., Zuobing, Z., Jahan, M.A.A., Akhtar, N., Khan, N.M.S., Roy, C.K. and Islam, R. (2011). Ecological utilization of leather tannery waste with circular economy model. *J. Clean. Prod*. **19**(2–3): 221–228.

Jahan, M.A.A., Akhtar, N., Khan, N.M.S., Roy, C.K. and Islam, R. (2014). Characterization of tannery wastewater and its treatment by aquatic macrophytes and algae. *Bangladesh J. Sci. Ind. Res*. **49**(4): 233–242.

Ju, F. and Zhang, T. (2014). Bacterial assembly and temporal dynamics in activated sludge of a full-scale municipal wastewater treatment plant. *ISME J.* **9**(3): 683–695.

Mangal, M., Agarwal, M. and Bhargava, D. (2013). A case study of impacts of tannery effluent of leather industry of Manpura Machedi on ground water quality of that area. *J. Pharmacogn. Phytochem*. **2**(2): 229–233.

Mekonnen Birhanie, Seyoum Leta, and Mazharuddin, M.K. (2017). Removal of hazardous pollutants from tannery wastewater by naval filter medium (pumice) through adsorption and filtration method. *IOSR J. Environ. Sci. Toxicol. Food Technol.* **11**(9): 38–45.

Midha, V. and and Dey, A. (2008). Biological treatment of tannery wastewater for sulfide removal. *Int. J. Chem. Sci.* **6**(2): 472–486.

Parveen, S., Bharose, R. and Singh, D. (2017). Assessment of physico-chemical properties of tannery wastewater and its impact on fresh water quality. *Int. J. Curr. Microbiol. Appl. Sci*. **6**(4): 1879–1887.

Pire-Sierra, M.C., Cegarra-Badell, D.D., Carrasquero-Ferrer, S.J., Diaz-Montiel, N.E.A and Rosa, A. (2016). Nitrogen and COD removal from tannery wastewater using biological and physico-chemical treatments. *Rev. Fac. Ing.* **80**: 63–73.

Prabu, P.C., Wondimu, L. and Tesso, M. (2011). Assessment of water quality of Huluka and Alaltu Rivers of Ambo, Ethiopia. *J. Agric. Sci. Technol.* **13**(1): 131–138.

Rickwood, C., Geneviève, M. and Carr, K.H. (2007). **Global Drinking Water Quality Index Development and Sensitivity Analysis**. United Nations Environment Programme Global Environment Monitoring System (GEMS)/Water Programme, Ontario.

Samuel Melaku, Taddese Wondimu, Dams, R. and Moens, L. (2007). Pollution status of Tinishu Akaki River and its tributaries (Ethiopia) evaluated using physico-chemical parameters, major ions, and nutrients. *Bull. Chem. Soc. Ethiop.* **21**(1): 13–22.

Santos, T.F.S. and Camacho, L.A. (2014). Water quality modelling of tannery effluent (Cr, Sulfur, Cl) in Upper Bogota River Basin (Colombia). In: **Eleventh International Conference on Hydroinformatics**, pp. 1–9, CUNY Academic Works, New York.

Shegani, G. (2014). Treatment of tannery effluents by the process of coagulation. *Int. J. Environ. Ecol. Eng.* **8**(4): 240–244.

Stanley, I.R.O, Igiri, B., Udeh, C., Edenta, C. and Gauje, B. (2017). Tannery effluent treatment by yeast species isolates from watermelon. *Toxics* **5**(6): 1–10.

Sugasini, A. and Rajagopal, K. (2015). Characterization of physicochemical parameters and heavy metal analysis of tannery effluent. *Int. J. Curr. Microbiol. Appl. Sci.* **4**(9): 349–359.

Tadesse Alemu and Seyoum Leta (2015). Evaluation of selected wetland plants for removal of chromium from tannery wastewater in constructed wetlands, Ethiopia. *Afr. J. Environ. Sci. Technol.* **9**(5): 420–427.

Tadesse Animaw (2011). **Understanding the Situation of Wastewater Irrigation in Community-Based Irrigation Schemes: The Case of Akaki Catchment, Ethiopia**. Wageningen University, Wageningen.

UNHSP (United Nations Human Settlements Programme) (2017). The State of Addis Ababa 2017. United Nations Human Settlements Programme, Nairobi.

UNIDO (United Nations Industrial Development Organization) (2012). Technical assistance project for the upgrading of the Ethiopian leather and leather products industry. Independent evaluation report, UNIDO project number: TE/ETH/08/008.

van Rooijen, D.J., Biggs, T.W., Smout, I. and Drechsel, P. (2010). Urban growth, wastewater production and use in irrigated agriculture: A comparative study of Accra, Addis Ababa and Hyderabad. *Irrig. Drain. Syst.* **24**(1–2): 53–64.

Yared Worku and Giweta, M. (2018). Can we imagine pollution-free rivers around Addis

Ababa city, Ethiopia ? What were the wrong-doings ? What action should be taken to correct them ? *J. Pollut. Effects Control* **6**(3): 1–9.