frontiers in Environmental Science

ORIGINAL RESEARCH
published: 15 October 2021
doi: 10.3389/fenvs.2021.721014

Evaluation of Tannery Wastewater Treatment by Integrating Vesicular Basalt With Local Plant Species in a Constructed Wetland System

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Specialty section:
This article was submitted to Water and Wastewater Management, a section of the journal Frontiers in Environmental Science

Received: 05 June 2021
Accepted: 06 September 2021
Published: 15 October 2021

Citation:
Alemu A, Gabbiye N and Lemma B (2021) Evaluation of Tannery Wastewater Treatment by Integrating Vesicular Basalt With Local Plant Species in a Constructed Wetland System. Front. Environ. Sci. 9:721014. doi: 10.3389/fenvs.2021.721014

Tannery wastewater is composed of a complex mixture of organic and inorganic components from various processes that can critically pollute the environment, especially water bodies if discharged without treatment. In this study, integrated vesicular basalt rock and local plant species were used to establish a horizontal subsurface flow constructed wetland system and to investigate the treatment efficiency of tannery wastewater. Four pilot units were vegetated with *P. purpureum*, *T. domingensis*, *C. latifolius*, and *E. pyramidalis*, and a fifth unit was left unvegetated (control). The constructed wetland units in horizontal subsurface flow systems were effective in removing total chromium (Cr), chemical oxygen demand (COD), and 5-day biological oxygen demand (BOD_5) from the inflow tannery wastewater. The removal efficiency reached up to 99.38, 84.03, and 80.32% for total Cr, COD, and BOD_5, respectively, in 6 days of hydraulic retention time (HRT). The removal efficiency of total suspended solid (TSS), total phosphorus (TP), and nitrate (NO_3^-) of the constructed wetland units reached a maximum of 70.59, 62.32, and 71.23%, respectively. This integrated system was effective for treating tannery wastewater, which is below the Ethiopian surface water standard discharge limit set to BOD_5 (200 mg L^{-1}), COD (500 mg L^{-1}), total Cr (2 mg L^{-1}), NO_3^- (20 mg L^{-1}), TSS (50 mg L^{-1}), and TP (10 mg L^{-1}).

Keywords: total Cr, constructed wetland unit, tannery wastewater, local plants, vesicular basalt

INTRODUCTION

Tanning industries use several types of chemicals at different unit processes starting from preservation to the finished leather products. The tannery wastewater is characterized by complex mixtures of organic and inorganic chemicals with high concentrations of Cr, BOD, COD, TDS, strong color, and pH (Buljan et al., 2011). The various chemicals in the tannery effluents pollute water bodies, soil, and air, and seriously affect human health and other biological organisms (Sivaram and Barik, 2019). Cr is one of the chemical components in the tannery wastewater which can be oxidized from +III to +VI oxidation states. Cr (VI) is more toxic than Cr (III). It can cause carcinogenic (IARC, 1990; Rowbotham et al., 2000), mutagenic (McCarroll et al., 2010), and teratogenic (Elsaieed and Nada, 2002) effects on humans and other animals.

Tannery wastewater is treated conventionally by using chemical coagulants and aerobic treatment using microorganisms (EIPPCB, 2013). Currently, the constructed wetland system (CWS) attracts the public attention, due to lower construction and operation costs, and environmental and esthetic benefits. It has been shown that the horizontal subsurface flow (HSSF) constructed wetland system showed efficient removal of TSS, organic matter, and heavy metals from tannery wastewater (Calheiros et al., 2007; Alemu et al., 2016; Alemu et al., 2018). This is the combined effect of physical, chemical, and biological processes (Inc and Inc, 2006). The removal of pollutants in a CWS is a complex process, where the substrate, vegetation, and pollutants in the wastewater interact with each other and the surrounding environment (Stottmeister et al., 2003). The design largely determines how wastewater treatment occurs and which mechanisms are effectively operating in that specific physical condition (Kosolapov et al., 2004). The HSSF–CWS is advantageous because of the potential health and safety concerns. It isolates the wastewater from vectors (malaria mosquitoes), pathogens, and odor from animals and humans.

Substrates used in the CWS, which have a high adsorption capacity, can increase the removal efficiency heavy metal ions and nutrients from wastewater. According to Aregu et al. (2021), a constructed wetland using pumice and gravel substrates for the treatment of tannery wastewater indicated that the former has better Cr and nutrient treatment efficiency than the later. Vesicular basalt (VB) rocks provide high adsorption of Cr in a solution (Alemu et al., 2019). The vesicular nature of the rock increases the surface area of contact with the contaminants and becomes a good harbor for microorganisms to degrade the organic matter in the wastewater.

The selection of plants is an important issue in a CWS as they must survive the potentially toxic effects of the wastewater and its variability. *Phragmites australis* (common Red), *Typha latifolia*, bulrushes (*Scipus* spp.), and *Phalaris arundinacea* wetland plants have been used for both domestic and industrial wastewater treatments in a CWS (Bastviken et al., 2005; Vymazal and Kröpfelová, 2008; Afzal et al., 2019). Studies indicated that some wetland plant species such as *Typha domingensis*, *Phragmites karka* (Reeds), *Phragmites australis*, *Arundo donax*, and *Sarcocornia fruticosa* had the potential to withstand the saline chrome containing tannery effluent and phytoremediate chromium after secondary treatment in a CWS at a pilot-scale (Calheiros et al., 2012; Saeed et al., 2012; Tadese and Seyoum, 2015; Zapana et al., 2020).

Tanneries are one of the top pollutants in Ethiopia. This is also a common problem in many developing countries in the world. In this study, a constructed wetland with a HSSF system was developed by integrating VB with different locally available plant species (*P. purpureum*, *T. domingensis*, *C. latifolius*, and *E. pyramidalis*) to evaluate the treatment performance of contaminants from the tannery wastewater in a pilot-scale.

MATERIALS AND METHODS

Description of the Study Site

Vesicular basalt rocks used for the construction of bed units were collected around the gorge of Abbay River at about 11°36′00″ N latitude and 37°24′00″ E longitude at an elevation of 1,800 m, where volcanic rocks are abundantly available. The pilot CWUs were established in the premise of Bahir Dar Tannery PLC, Bahir Dar, Ethiopia. The area is a semiarid region that can reach a maximum temperature of 30°C during the day and a minimum temperature of 6°C during the night (Vijverberg et al., 2009). It has high rainfall and low temperature in the summer and high temperature and little rainfall in the winter.

Reagents and Standard Solutions

Reagents such as potassium dichromate, $K_2Cr_20_7$ (≥99% purity); sulfuric acid, H_2SO_4 (assay ≥95%); ferrous ammonium sulphate hexahydrate, Fe $(NH_{4)2}SO_4).6H_2O$ (≥98.5% purity);mercury (II) sulphate, Hg_2SO_4 (≥99% purity); silver sulfate, Ag_2SO_4 (≥99% purity); and diphenylcarbazide solution (prepared by dissolving 250 mg 1, 5-diphenylcarbazide (98%) in 50 ml acetone) (assay ≥99.5%)) are based on the standard procedures in APHA (1998). All the reagents were obtained from Fisher Scientific. Hydrochloric acid (36.5–38%), nitric acid (assay 68–70%), and chromium chloride hexahydrate ($CrCl_3.6H_2O$) (≥99% purity) were supplied from BDH laboratory. Deionized water (conductivity = 0.05 $\mu s\ cm^{-1}$) was obtained from the Evoqua Water Technologies. All the reagents were of analytical grades. The stock solution of Cr metal (1,000 $\mu g\ ml^{-1}$, Buck Scientific Puro-Graphic^{TM}, United States), prepared as nitrates in 2% HNO_3, was used to prepare calibration standards for determining Cr using inductively coupled plasma optical emission spectroscopy (Optima 8000 ICP-OES, Perkin Elmer).

Pilot-Scale Tannery Wastewater Treatment Using a Horizontal Subsurface Flow Constructed Wetland System

Constructed Wetland Pilot Units

Five parallel bed units were constructed close to the stabilization pond of Bahir Dar Tannery. The four units were used for experimental purposes and one unit as a control. A plastic tank of 2,000 L was installed to store the wastewater from the equalization tank and to feed the constructed wetland units (**Figure 1A**). Each unit had a length (L) of 2.8 m, a width (W) of 0.80 m, and a height of 0.62 m (volume of 1.39 m^3) as shown in **Figure 1B**. The aspect ratio of each bed was 3.5:1 and the bed slope 1% (USEPA, 1993). The floors and internal walls of the constructed bed units were cemented and covered with 0.5 mm thickness geomembrane to prevent leakage and interaction of wastewater with the bed. The constructed bed units inlet and outlet ends were filled with a 40- to 80-mm-diameter rock to prevent clogging. The reactor zone with 0.59 m depth (D) was filled with 15–20 mm VB followed by 0.03 m depth with 5–10 mm of VB. Above the bed, 0.05 m depth was left as a space to control overflowing of the wastewater. The porosity of the VB filled in bed was 38%. The wastewater was feed to the wetland units through a HDPE pipe with a control valve. The HRT in the bed was 6 days. Studies indicated optimal 6–7 HRT for the treatment of primary and secondary wastewater for temperatures above 15°C (Crites, 1988; Akratos and Tsihrintzis, 2007; Aregu et al., 2021). The level of wastewater was 3 cm below the surface of the bed.

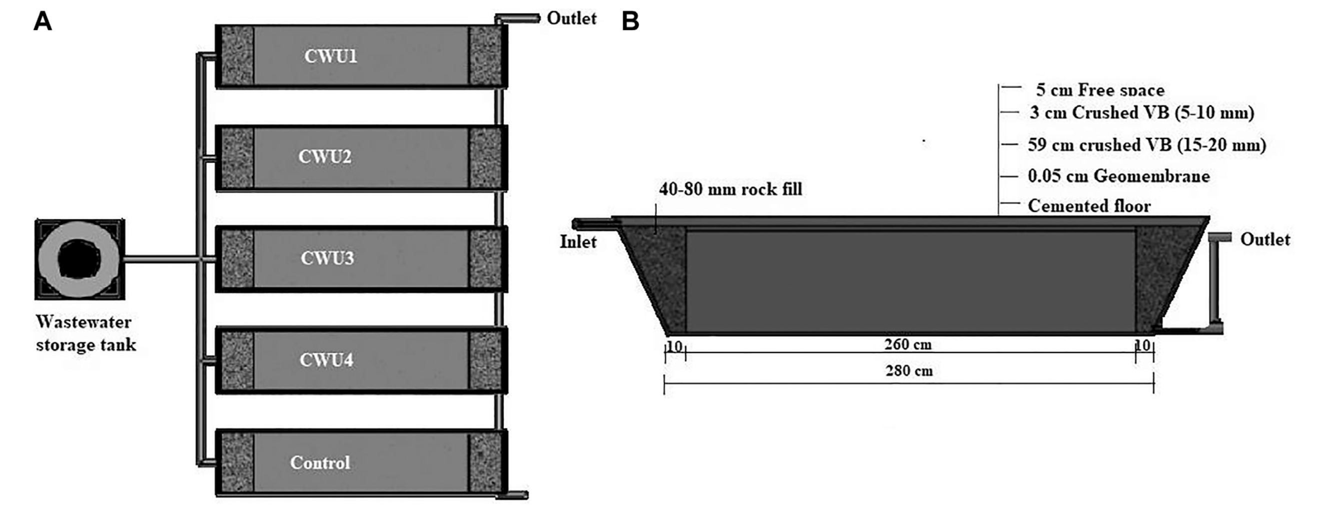

FIGURE 1 | Design of the experimental CWU layout plan **(A)** and each bed unit component of the CWUs **(B)**.

The wastewater flows from the equalization tank to constructed wetland units by the force of gravity. The volumes of inflow and outflow rates of the wastewater were regulated by using a stopwatch and a measuring cylinder. The HRT was determined using Darcy's law (**Eq. 1**) (USEPA, 1993).

$$HRT = \frac{L.W.D.n}{Q}, \tag{1}$$

where n is the porosity and Q is the volumetric flow rate.

Plants Selection and Adaptation to Wastewater

Four plant species, namely, *Pennisetum purpureum*, *Typha domingensis*, *Cyprus latifolius*, and *Echinochloa pyramidalis*, were selected from the nearby wetland of Abbay River. The selected plant species were found well adapted in the effluent discharge site and indicated an ability to withstand high saline conditions and being an emergent type of plant species. The selected plants were collected upstream of Abbay River (above wastewater discharge area) to transplant on the constructed beds. The plants with an individual root/rhizome material with a growing shoot of 0.2 m length were vegetated between 0.3 and 0.6 m spacing by hand according to USEPA (1993). The vegetated plants were first fed with tap water followed by different proportions of mixtures of tap water and tannery wastewater from low to high concentrations. This was done to minimize the shock produced by toxic tannery wastewater and provide time for adaptation for the plants vegetated on the bed units (Davis, 1995). At an equal mixing proportion of tap water with wastewater (1:1), the shock was severe to the plants but propagated gradually. Applying beyond this proportion (100% of the wastewater) might damage most of the plants and difficult to be reinstated. Therefore, throughout the experiment, this mixing proportion was supplied to the pilot-scale constructed wetland units, though the nature of the waste was variable throughout the study.

Wastewater Sampling and Analysis

Wastewater samples feed into the CWUs and outflow after treatment were collected twice a month during three consecutive months of the study period. The samples were collected using cleaned plastic bottles. Temperature (T°) and pH were analyzed at the sampling sites. The preservation and measurement for each parameter were performed using the standard procedures in APHA (1998): Cr total (digestion using concentrated HNO_3 followed by inductively coupled plasma optical emission spectroscopy), pH using a pH meter, COD (closed reflux, titrimetric method), BOD (5-day BOD test), total suspended solids (TSS), electrical conductivity (EC) and T° (conductivity meter), NO_3^- (Palintest Nitratest method, using a 8000 photometer), and total phosphorus (digestion followed by the ascorbic acid method).

Analysis of Plant Tissue

The plant tissues were cleaned with distilled water to remove strange materials attached to them. The samples were cut into small pieces and dried in an oven at 105°C. The dried roots, stems, and leaves of each plant were ground using a cleaned mortar and pestle. One gram of the ground plant parts was digested with a mixture of 69% HNO_3 and 30% H_2O_2 in the ratio of 6:2 by volume at the temperature of 95–100°C in a flask on a hot plate. The digestion process was continued until the formation of a clear solution. Then, it was taken off, cooled, and filtered with a Whatman filter paper (grade 42). Finally, it was diluted up to 50 ml volumetric flask with deionized water (Kassaye et al., 2017). The total Cr in the plant samples was determined using ICP-OES. The wavelength selected for Cr analysis was 267.716 nm.

Statistical Data Analysis

The statistical data analyses were performed using Microsoft Excel and Origin lab software. One-way analysis of variance ($p < 0.05$) was used to investigate a statistically significant

TABLE 1 | The mean composition of the inflow and outflow concentration (minimum-maximum) ranges of the pilot CWUs (n = 6).

Parameters	Influent conc. (mg L^{-1})	Effluent concentration (mg L^{-1}) for each wetland unit				
		CWU1	CWU2	CWU3	CWU4	CWU5
Total Cr I (mg L^{-1})	11.73 ± 7.00	0.07 ± 0.07	0.12 ± 0.13	0.09 ± 0.11	0.19 ± 0.14	0.32 ± 0.24
Range	4.27–20.48	0.01–0.15	0.01–0.27	0.05–0.25	0.03–0.32	0.05–0.59
BOD_5 (mg L^{-1})	163.90 ± 94.26	32.25 ± 22.40	38.05 ± 25.34	34.40 ± 20.97	37.04 ± 19.87	42.29 ± 23.43
Range	53.75–299.20	11.00–62.2	15.00–75.20	12.50–60.20	20.40–68.00	20.61–72.94
COD (mg L^{-1})	1,185.5 ± 596.08	189.36 ± 111.09	222.84 ± 148.6	203.2 ± 144.53	225.28 ± 121.33	251.55 ± 123.27
Range	297.024–1976	106.2–400.39	70.8–456.74	65.1–451.17	70.80–441.17	139.50–425.61
TP (mg L^{-1})	3.74 ± 0.50	1.478 ± 0.384	1.54 ± 0.389	1.41 ± 0.483	1.572 ± 0.680	1.597 ± 0.575
Range	2.99–4.77	0.945–1.935	0.745–1.981	0.773–1.994	0.538–2.216	0.58–2.203
TSS (mg L^{-1})	427.83 ± 305.90	128.00 ± 80.90	140.5 ± 85.64	125.83 ± 77.42	129.33 ± 80.58	138.00 ± 85.32
Range	36–859	15–207	25–230	24–211	22–235	8–354
EC (ms cm^{-1})	4.933 ± 1.788	4.134 ± 1.281	4.328 ± 1.617	3.881 ± 1.517	4.174 ± 1.843	3.235 ± 1.08
Range	2.17–6.85	1.893–5.481	1.987–6.29	1.78–5.71	1.739–6.35	1.3–4.25
pH	7.2 ± 0.269	7.457 ± 0.403	7.287 ± 0.402	7.255 ± 0.434	7.215 ± 0.384	7.675 ± 0.257
Range	6.92–7.71	6.9–8.06	6.82–7.91	6.84–7.97	6.73–7.82	7.4–8.06
NO_3^--N (mg L^{-1})	29.61 ± 7.91	8.87 ± 6.94	8.52 ± 3.72	8.92 ± 3.91	10.33 ± 7.33	10.87 ± 6.25
Range	19.48–42.52	2.3–12.48	4.92–12.04	3.10–13.36	2.30–20.18	2.78–17.86
Temperature (°C)	22.21 ± 0.86	20.45 ± 1.04	20.55 ± 1.07	20.48 ± 0.90	20.52 ± 0.98	20.2 ± 0.55

Data Collected From October to December 2017 (n = 6)

difference in the mean removal efficiencies of pollutants between the CWUs. Multiple comparisons were done using Tukey's HSD tests. Statistical analyses were done using SPSS Statistics 24.0.

RESULTS AND DISCUSSION

Tannery Wastewater Characterization

Bahir Dar Tannery produces hides and skins in the form of crust and finished leather for export and local markets. The wastewater generated from the industry was collected in a large equalization pond having a volume of 486 m^3. The diluted wastewater from this pond was collected in a high-density polyethylene (HDPE) plastic tank with a volume of 2,000 L to feed the CWUs. The average compositions of the inflow and outflow (after treatment) in a constructed wetland in 3 months of sampling are characterized as shown in **Table 1** below.

The constructed wetland units worked with an average hydraulic loading rate (HLR) of 0.0357 m d^{-1} (3.57 cm d^{-1}). This was increased by 0.57 cm d^{-1} to the HLR used by Calheiros et al. (2007). The feed inflow wastewater compositions into the pilot CWUs indicated variability during the study time. This would be due to numerous types of chemicals used in the tanning processes. The concentration of total Cr in the wastewater was found in the range of 4.27–20.48 mg L^{-1} with an average value of 11.73 ± 7.00 mg L^{-1}. The variation of inflow COD concentration ranged from 297.02 to 1,976 mg L^{-1}, with an average concentration of 1,185.5 ± 596.08 mg L^{-1}. The average influent loading rate of COD was 423.39 kg d^{-1} ha^{-1}. The influent concentration of BOD_5 ranged from 53.75 to 299.2 mg L^{-1}, with an average loading rate of 58.53 kg d^{-1} ha^{-1}. The BOD_5/COD ratio was about 0.138. This indicates low biodegradable organic waste in the tannery effluent. This might be the degradation of the organic waste in the equalization tank before it was fed to the CWUs. Studies on the BOD_5/COD of tannery wastewater effluent indicated 0.3 (Durai and Rajasimman, 2011) and 0.2 (Elabed et al., 2019). The inflow wastewater also possessed an average TSS of 427.83 ± 305.90 mg L^{-1} in the range of 36–859 mg L^{-1}. The pH value of an average feed wastewater from the equalization tank was 7.2 ± 0.27, which was in the range of 6.92–7.71 during the operation period. This was a good pH range for the plants to grow well and microorganisms to degrade the input wastewater to it. The average temperature of the inflow tannery wastewater was 22.21 ± 0.86°C. The inflow wastewater was also composed of high salinity with electrical conductivity (EC) between 2.17 and 6.85 ms cm^{-1}.

The wastewater composition of tanning industries varied in their physicochemical properties (Mandal et al., 2010; Tadese and Seyoum, 2015; Aregu et al., 2018). These variations might be due to the type of hides used, differences in the unit processes, capacity of producing finished leather, and amount/type of chemicals used

Plant Growth and Adaptations of Tannery Wastewater in the CWUs

The vegetated plants on the bed units were adapted to the toxic tannery wastewater by irrigating it progressively with increasing concentrations. The plants indicated some observable changes with an increasing concentration of the tannery wastewater such as turning off the plant leaves to yellow, drying, dropping of leaves, and dying of a few plants (Hussain et al., 2019). Despite these observable phenomena, there were good growth and propagations. The effect was severe in all the plants at the concentration reaching 1:1 proportion of mixing tannery wastewater with tap water. Based on the observation of biomass production and propagation, *P. purpureum* > *T. domingensis* > *C. latifolius* > *E. pyramidalis* in a review (**Figure 2**).

The root structures of the plants after treatment are shown in **Figure 3** below. Plant root structures have an impact in the treatment of wastewater. According to Majumder et al. (2016), plants with hairy roots have a high potential to remove both

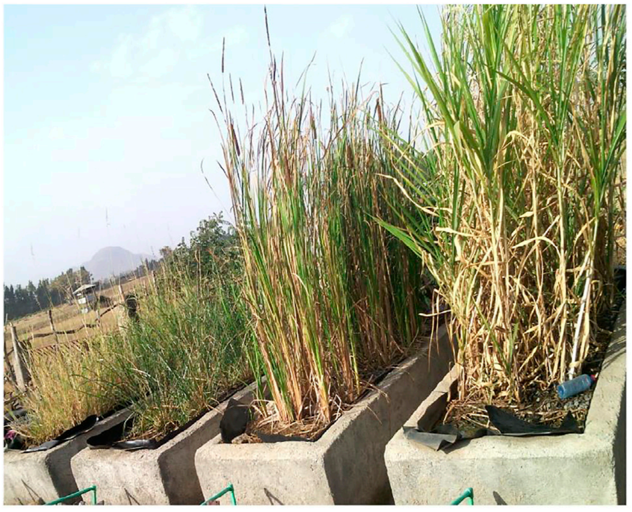

FIGURE 2 | The pilot CWUs established for the treatment of tannery wastewater.

organic and inorganic contaminants in the environment. *P. purpureum* has dense, fine, compacted, and full of root nodules. Its length is about 32 cm. The fine and dense nature of the root holds rocks tightly and filters the wastewater strongly. The roots of *T. domingensis* are relatively short about 28 cm and thick in size. The root of *C. latifolius* plant is about 48 cm long, contains extremely dense propagated roots, and fibrous in nature that helps to hold contaminants in the wastewater in it. The roots of *E. pyramidalis* plants are relatively short with a maximum length of about 37 cm, which are thinner, and fibrous structures are with attached root nodules. The root structures of the plants used in this study indicated that *P. purpureum*, *C. latifolius*, and *E. pyramidalis* showed a better structure for the treatment of wastewater than *T. domingensis*.

Removal of Cr in the CWUs

The influent from the equalization tank and effluent from the CWUs of concentrations total Cr are shown in **Table 1**. The maximum removal efficiency of Cr (99.38%) was observed at CWU 1 vegetated with *P. purpureum*, and relatively the lowest removal efficiency (97.32%) was observed at CWU 5 (control). This study was in agreement with the research reports of Tadese and Seyoum (2015), which is about the removal of Cr by some selected wetland plants, a CWS using tannery wastewater. All the pilot treatment units were efficient for removing Cr from tannery wastewater. This might be from the adsorption potential of the VB rock (Alemu et al., 2019), microbial treatment (Dotro et al., 2011), biosorption of Cr by plants (Kassaye et al., 2017), and precipitation of Cr with hydroxides, sulfides, sulfates, and carbonates obtained from the chemicals used in the leather processing.

The pilot-scale CWUs indicated better Cr removal efficiencies than the control bed unit. This might be due to the plants' integrated effect in the treatment process. Plants play a great role in the distribution of oxygen to the root, stem, and leaves; nutrient uptake; and degradation of pollutants (Stottmeister et al., 2003). Plants can also provide optimal conditions for microbial growth and give an impact on metal mobility and toxicity through root exudating release, entrapment, and accumulation of Cr in the parts of plants such as root, shoot, and leaf (Zhang et al., 2010).

There was no statistically significant difference in the mean removal efficiencies of Cr between the vegetated and the control constructed units. This might be due to the precipitation in the alkaline condition and long retention time (6 days). The maximum concentrations of Cr after treatment were below the permitted guideline limit (2 mg L^{-1}) for tanneries (EEPA, 2003).

The accumulation of Cr in the plant parts is indicated in **Table 2**. The maximum accumulation of Cr was observed in the roots compared with other parts. *P. purpureum* accumulated a higher concentration (0.194 ± 35.10 mg g^{-1}) of Cr in its root, and the lowest (0.026 ± 9.20 mg g^{-1}) was accumulated in the root of *E. pyramidalis*. The concentration of Cr was lowest in the stem of all the plants in this study compared with other parts. This is in agreement with other studies of accumulation of Cr in the plant parts (Sultana et al., 2015; Papaevangelou et al., 2017).

Removal Efficiency of Chemical Oxygen Demand, Biological Oxygen Demand, and Total Suspended Solid

The removal efficiency of the CWUs was determined from the characteristics of the wastewater collected from the inlet and outlet of each unit shown in **Table 1**. The organic matter removal efficiency of COD, BOD_5, and TSS is shown in **Figure 4** below.

COD removal efficiencies of the pilot constructed wetland units varied in the range of 78.78–84.03% during the experimental period. The maximum removal efficiency of COD (84.03%) was observed for the HSSF bed unit planted with *P. purpureum* (CWU1). It was followed by *C. latifolius* planted wetland unit (CWU3) with an average COD removal efficiency of 82.86%. Wetland units planted with *T. domingensis* (CWU2) and *E. pyramidalis* (CWU4) showed 81.02 and 80.99% COD removal efficiencies, respectively. The control (unvegetated) removed 78.78% of COD, which was relatively low as compared to vegetated units. The ANOVA analysis illustrated that there were no statistically significant differences ($p > 0.05$) between the constructed wetland units in the removal efficiency of COD.

The average removal efficiencies of BOD_5 in the outlet of constructed wetland units varied in the range of 74.20–80.32% during treatment operations. The maximum removal efficiency (80.32%) was observed by *P. purpureum* vegetated wetland unit (CWU1). *C. latifolius* (CWU3) also showed a high removal efficiency (79.01%) of BOD_5 close to pilot CWU1, while E. *pyramidalis* (CWU4) and *T. domingensis* (CWU2) showed a removal efficiency of (77.4%) and (76.78%), respectively. The lower removal efficiency of BOD_5 was observed in the control (74.2%) than in all wetland units. No significant differences were seen in BOD_5 removal among each wetland units and the control.

According to Calheiros et al. (2007), HSSF constructed wetland units vegetated with different plants, an average

FIGURE 3 | The nature of plant roots used in the treatment of tannery wastewater in a CWUs.

inflow COD of 1,966–2,093 mg L^{-1}, the removal efficiency of the pilot units varied between 41 and 67% for an HLR of 3 cm d^{-1} and 54–73% for HLR 6 cm d^{-1}, respectively. Moreover, the pilot units with average inflow BOD5 concentrations in the range 875–898 mg L^{-1} removed 41–55% for an HLR of 3 cm d^{-1} and 41–58% for an HLR of 6 cm d^{-1}, respectively. Calheiros et al. (2012) also reported maximum 80% COD and 90% BOD_5 removal efficiencies for a conventionally treated tannery

TABLE 2 | Average total Cr concentration (mg g^{-1}) dry weight (DW) plant parts of the CWUs (n = 3).

Wetland plant species	Root	Stem	Leave
P. purpureum	0.194 ± 35.10	0.012.25 ± 1.81	0.020 ± 1.90
T. domingensis	0.083 ± 14.40	—	0.01 ± 1.60
C. latifolius	0.124 ± 23.10	0.008.80 ± 0.60	0.024 ± 1.80
E. pyramidalis	0.026 ± 9.20	0.007 ± 0.90	0.017 ± 1.40

wastewater of inlet concentration of 68–425 mg L^{-1} COD and 16–220 mg L^{-1} BOD_5, respectively, using three HSSF wetland units in series. The system was operated on an HLR of 60 mm d^{-1} and a hydraulic retention time (HRT) of 2 days. Alemu et al. (2016) also reported 90% COD and 91.4% BOD_5 removal efficiencies with an average inflow concentration of 1,134 ± 269 and 523 ± 219 mg L^{-1}, respectively. This was obtained after an integrated two-phase anaerobic and aerobic sequencing batch reactor (SBR) followed by an HSSF wetland system on a 5-day HRT. In this study, the observed treatment efficiencies for organic matter were inspiring compared with the above integrated multistage studies. This might be due to the optimum conditions produced by dilution, such as increased dissolved oxygen (DO), reduced organic and inorganic loadings, and inlet pH in the range of 7–8, which produced an optimum condition for microbial degradation of the waste, nutrient transformation, and plant uptake. Moreover, the long period of HRT (6 days) would facilitate sedimentation, filtration, precipitation, and adsorption (Calheiros et al., 2007; Vymazal, 2011).

The removal efficiency of TSS in the pilot wetland units with an average inflow concentration in the range of 36–859 mg L^{-1} was determined. It was observed that a maximum of 70.59% TSS was removed in a wetland bed vegetated with *C. latifolius* (CWU3). The removal efficiency of *P. Purpureum* containing bed (CWU1) showed 70.08% TSS, which was comparable to *C. latifolius* vegetated bed (CWU3). The control showed a removal efficiency of 67.75% TSS. TSS removal did not differ significantly ($p > 0.05$) between the vegetated and the control (unvegetated) units. This indicates the role of VB in the filtration of suspended matter and the long hydraulic residence time (6 days) for sedimentation of suspended materials during operation. Moreover, the colloidal particles that are not removed by pretreatment are removed by settlement and filtration in the first few meters away from the inlet zone (Vymazal 2005; Kadlec and Wallace, 2008). Colloidal solids might be removed by bacterial growth that could decay and settle it. Moreover, collisions of colloids with solids (gravel, plant roots, suspended solids, *etc.*) could favor adsorption (Stowell et al., 1981). This study was supported by Calheiros et al. (2007) that TSS removal efficiencies varied between 48 and 92% for 3 cm d^{-1} and 62–77% for 6 cm d^{-1} HLRs for a horizontal subsurface flow wetland system vegetated with different plants with an inflow concentration ranged between 33 and 125 mg L^{-1} TSS. In another study, Calheiros et al. (2012) reported the removal efficiency of TSS did not differ significantly between the Arundo and the Sarcocornia-planted beds. Mburu et al. (2013) also reported 74.9% removal of TSS for the treatment of domestic wastewater based on a subsurface horizontal flow CW vegetated with indigenous *P. karka*.

The accumulation of suspended solids in the porous beds is a major threat to the good performance of HSSF systems as the solids may clog the bed. Therefore, effective pretreatment is necessary for HSSF treatment systems.

Removal Efficiency of Total Phosphorus and Nitrate

The TP concentration in the inlet varied between 2.99 and 4.50 mg L^{-1} (**Table 1**). The outlet concentration in the pilot HSSF constructed wetland units varied in the range of 0.58–2.22 mg L^{-1}. CWU3 vegetated with *C. latifolius* indicated 62.32% removal of TP as compared to the other units. It was followed by CWU1 (*P. purpureum*) with a removal efficiency of 60.48%. The unvegetated unit removed 57.32%. The one-way ANOVA indicated that there was no significant difference in the removing of TP between the vegetated and unvegetated units. This was supported by Keizer-Vlek et al. (2014) that there was no significant difference in the removal of TP for vegetated and unvegetated units. Studies indicated that the major phosphorus removal processes include sorption, precipitation, and plant uptake (Vymazal, 2007). Plants uptake a low concentration of phosphorus, unless high sorption media are used in the constructed wetland unit (Arias and Brix, 2005; Akratos and Tsihrintzis, 2007). The vesicular basalt rock used in this study, characterized for its composition of Fe and Al on the surfaces, might promote both the adsorption and precipitation of phosphates in the pilot-constructed wetland units (Cooper et al., 1996; Arias et al., 2001; Alemu et al., 2019). Calheiros et al. (2012) reported 40–93% removal of TP in an HSSF-constructed wetland system planted with *A. donax* and *S. fruticosa*.

The NO_3^--N inflow wastewater concentration varied between 19.48 and 42.52 mg L^{-1}. The average removal efficiency in the constructed wetland units varied in the

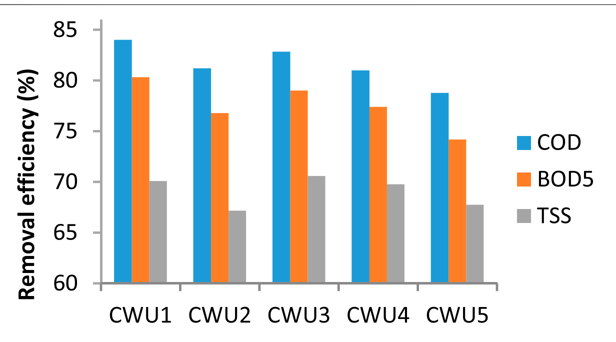

FIGURE 4 | Removal efficiency of COD, BOD5, and TSS (%) on the average inlet and outlet concentrations of tannery wastewater in the pilot HSSF-constructed wetland units. n = 6, CWU1, *P. purpureum*; CWU2, *T. domingensis*; CWU3, *C. latifolius*; CWU4, *E. pyramidalis*; and CWU5, control (unvegetated).

range between 63.28 and 71.23%. NO_3^--N concentrations in the outflow decreased on an average up to 71.23% high in CWU2 (*T. domingensis*). CWU1 (*P. purpureum*) decreased NO_3^--N in the outflow as high as 70.05% from the inflow concentration, while the unvegetated unit (CWU5) reduced the inflow NO_3^--N concentration by 63.28% in the outflow of the HSSF constructed system. No significant differences have been observed in the vegetated and unvegetated units in the removal of NO_3^--N from the wastewater. The main nitrogen removing mechanisms in constructed wetlands include microbial interactions with nitrogen, sedimentation, chemical adsorption, and plant uptake (Lee et al., 2009). A study on the fate of 15N-nitrate in the riparian of wetland soil microcosms indicated 24–26% immobilized in the soil, 11–15% assimilated in the plant, and 61–63% was lost through denitrification (Matheson et al., 2002). Denitrification is the most important process in which nitrate is converted into free nitrogen (N_2) through intermediates NO_2^-, NO, and N_2O (Martens, 2004; Vymazal, 2007).

Different environmental factors influence denitrification such as pH value, temperature, the absence of O_2, redox potential, substrate type, and presence of denitrifiers, organic matter, and nitrate concentration (Vymazal, 1995; Bowles et al., 2012). Studies indicated that the optimum pH for the removal of NO_3^--N ranged between pH 6 and 8 and an increase in temperature with a lower bound of 5 °C and an upper bound of 70 °C (Akpor et al., 2008). Beutel et al., 2009 reported 76.7% NO_3^--N removal in an HSSF-constructed wetland vegetated with Cattail and an average inflow concentration of 28.4 ± 7.3 mg L^{-1}. Alemu et al. (2016) also reported 66.3% removal of NO_3^--N with an influent concentration of 87.2 ± 26 mg L^{-1} in an HSSF-constructed wetland system.

Both TP and NO_3^- removal in the HSSF-constructed wetland units were lower than that of the provisional maximum discharge limit set by the Ethiopian EPA (2003) for the tannery industry, which are 10 and 20 mg L^{-1} or >80% removal for TP and NO_3^-, respectively. This indicates that the dilution of tannery wastewater can help to reach the effluent discharge limit in areas where there is sufficient water.

CONCLUSION

In this study, VB rock and local plant species integrated to establish a HSSF constructed wetland system to evaluate the treatment potential of tannery wastewater. The constructed wetland units were effective in removing Cr, COD, and BOD_5 from the inflow tannery wastewater. But the removal efficiency of TP, NO_3^-, and TSS was relatively low. On the other hand, the treatment performance of vegetated and unvegetated bed units indicated a marginal difference for the feed tannery wastewater. This might be the variable nature of the tannery wastewater that produce intermittent shocks on the plants and not work with their full potentials. The overall performance of the integrated CWS gives confidence for its ultimate application of tannery wastewater treatment with a high discharge volume. Nevertheless, further experimentation is required for a wide range of volumetric flow rate (HRT) to elucidate the hydrodynamic and flow characteristics of the CWS.

DATA AVAILABILITY STATEMENT

The data generated from this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

AA conceptualized and designed the study, performed field and lab works, interpreted, analyzed, and finally contributed in writing up the manuscript. BL and NG contributed in data interpretation and analysis, supervision, and manuscript writing. The author(s) read and approved the final manuscript.

FUNDING

The authors are grateful to Biotechnology Research Institute, Bihar Dar University, for financial support. Addis Ababa University and Connecticut University from the US are also acknowledged for additional funds for lab analysis during the study.

ACKNOWLEDGMENTS

We are grateful to Bahir Dar Tannery, for their kind cooperation to provide land for the construction of the pilot-scale constructed wetland units in the premise of industry and to produce the desired size of vesicular basalt rock by their milling machine. We are also thankful to the University of Connecticut from the US for allowing us to use their online library

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