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

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Research

Keywords: total Cr, Chemical oxygen demand, Constructed wetland unit, Tannery wastewater, local plants, Vesicular Basalt

Posted Date: May 5th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-437057/v1

Abstract

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 5th unit was left unvegetated (control). The constructed wetland units in horizontal subsurface flow systems were effective in removing total Cr, COD, and 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 the 6 days of HRT. The removal efficiency of TSS, TP, and NO_3^- obtained a maximum of 70.59 %, 62.32 %, and 71.23 % respectively. This integrated system was effective for removing tannery wastewater, which is below the Ethiopian surface water standard discharge limit set to BOD (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}).

Introduction

The tanning industry uses 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. (1).The various chemicals in the tannery effluent pollute water bodies, soil, and the air and seriously affect human health and other biological organisms. 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 (2, 3) mutagenic (4), and teratogenic (5) effects on humans and other animals.

Tannery wastewater is treated conventionally by using chemical coagulants and aerobic treating microorganisms (6). It has been shown that HSSF constructed wetland system showed efficient removal of total suspended solids (TSS), organic matter, and heavy metals from tannery wastewater. This is the combined effect of physical, chemical, and biological processes (7, 8). Tannery wastewaters with high, BOD, COD, and salt content are potentially treated in HSSF constructed wetland systems (9, 10). Despite many research efforts to understand the removal of pollutants in CWS, interaction with each other and interferences in the existing environment are still incomplete. This may be due to the interaction of different components in the constructed wetland system, such as substrate, sediment, vegetation, and water column (11). Biogeochemical processes can take part in the treatment of trace metals from the liquid waste in CWSs. The design largely determines how wastewater treatment occurs and which mechanisms are effectively operating in that specific physical condition (12).

The selection of plants is an important issue in CWS, as they must survive the potentially toxic effects of

es australis (common Red), *Typha latifolia*, bulrushes (*Scipus* spp.), and *Phalaris arundinacea* wetland plants have been used for both domestic and industrial wastewater treatment in a CWS (13, 14). Recent studies have shown that some wetland plant species such as *Typha domingensis*, *Phragmites karka* (Reeds), *Phragmites australis*, *Arundo donax*, *Sarcocornia fruticosa* have the potential to withstand the saline chrome containing tannery effluent and phytoremediate chromium after secondary treatment in a constructed wetland system at a pilot-scale (15–17).

This study has been designed to investigate the combined effect vesicular basalt and local plant species (*P.purpureum*, *T. domingensis*, *C. latifolius, and E. pyramidalis)* in constructed wetland system via HSSF for the remediation of 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-constructed wetland units were established in the premise of Bahir Dar Tannery PLC, Bahir Dar, Ethiopia (Fig. 1). The area is a semi-arid region that can reach a maximum temperature of 30°C during the day and a minimum temperature of 6°C during the night (18). It has high rainfall and low temperature in the summer and high temperature and little rainfall in the winter.

Reagents and Standard Solutions

The reagents potassium dichromate, $K_2Cr_20_7$ (≥ 99 % purity); sulfuric acid, H_2SO_4 (assay ≥ 95%); ferrous ammonium sulphate hexahydrate, Fe $NH_4SO_4)_2.6H_2O$ (≥ 98.5 % purity);mercury (II) sulphate, Hg_2SO_4 (≥ 99 % purity); silver sulfate, Ag_2SO_4 (≥ 99 % purity); diphenylcarbazide solution (prepared by dissolving 250 mg 1, 5-diphenylcarbazide (98 %) in 50 mL acetone) (assay ≥ 99.5 %)) based on the standard procedures in APHA [19]. 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 μs cm^{-1}), was obtained from the Evoqua Water Technologies. All the reagents were of analytical grades. The Stock solution of Cr metal (1000μg mL^{-1}, Buck Scientific Puro-Graphic tm, USA), prepared as nitrates in 2% HNO_3, was used to prepare calibration standards for determination Cr using ICP-OES (Optima 8000 ICP-OES, Perkin Elmer).

Pilot-Scale Tannery Wastewater Treatment Using HSSF 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 2000 L was installed to store the wastewater from the equalization tank and to feed the constructed wetland units (Fig. 2 **(a)**). Each unit had a length of 2.8 m, a width of 0.80 m, and a height of 0.62m (volume of 1.39 m^3) as shown in Fig. 2 **(b)**. The aspect ratio of each bed was 3.5:1 and bed slope 1% (20). 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 40–80 mm diameter rock to prevent clogging. The reactor zone 0.59 m depth 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 left 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 HDPE pipe with a control valve. The HRT in the bed was 6 days. Studies indicated that optimal 6–7 HRT for the treatment of primary and secondary wastewater for temperatures above 15 ^{o}C (21, 22). The level of wastewater was 3 cm below the surface of the bed.

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 measuring cylinder. The hydraulic retention time (HRT) was determined using Darcy's law Eq. 1 (20).

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

The removal efficiency (% R) of wastewater parameters on each constructed wetland unit were calculated using Eq. 2 below.

$$\%R = \frac{C_i - C_e}{C_e} \times 100(2)$$

Where, C_i influent concentration and C_e effluent concentration of the tannery wastewater parameters

Plants Selection and Adaptation to Wastewater

Four plant species *Pennisetum purpureum*, *Typha domingensis*, *Cyprus latifolius*, and *Echinochloa pyramidalis* were selected from the nearby wetland of Abay 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 0.3–0.6 m spacing by hand according to US EPA (20). 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 (23). At 1:1 mixing proportion of the tap water to wastewater, the shock

ually. Applying beyond this proportion (100% of the wastewater) might damage most of the plants and difficult to reinstate. Therefore, throughout the experiment, a mixture of 1:1proportion 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 in a month during three consecutive months during the study period. The samples were collected using cleaned plastic bottles. Temperature (T^{o}) and pH were analyzed at the sampling sites. The preservation and measurement for each parameter were performed using the standard procedures in APHA (19): Cr total (digestion using concentrated HNO_3 followed by inductively coupled plasma optical emission spectroscopy), pH using 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 8000 photometer), and total phosphorus (Digestion followed by 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, dried in an oven at 105 ^{o}C. The dried roots, stems, and leaves of each plant were ground using a cleaned mortar and pistil. 1g 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 ^{o}C in a flask on a hot plate. The digestion process continued until the formation of a clear solution. Then, it was taken off, cooled, and filtered with whatman filter paper (grade 42). Finally, it was diluted up to 50 mL volumetric flask with deionized water (24). The Cr total 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 analysis were performed using Microsoft Excel and Origin lab software. One-way ANOVA ($p < 0.05$) was used to investigate a statistically significant 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 an HDPE plastic tank with a volume of 2000 liters to feed the CWUs. The average compositions of the inflow and outflow (after treatment) in a constructed wetland in the three months of sampling were characterized as shown in **Table 1** below.

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
Cr total (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})	1185.5± 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 -	(2.3-12.48)	(4.92-12.04)	(3.10-13.36)	(2.30-20.18)	(2.78-17.86)

T^0 (°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)

The constructed wetland units worked with an average hydraulic loading rate of 0.0357 m d^{-1} (3.57 cm d^{-1}), increased by 0.57 cm d^{-1} to the HLR used by Calheiros *et al.*(9). 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 to 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 1976 mg L^{-1} with an average concentration of 1185.5 ± 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 inflow wastewater was also possessed of an average TSS of 427.83 ± 305.90 mg L^{-1} in the range of 36 to 859 mg L^{-1}.

The pH of an average feed wastewater from the equalization tank was 7.2 ± 0.27, which was in the range of 6.92 to7.71 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 between 2.17-6.85 ms cm^{-1}.

The wastewater composition of tanning industries varied in their physicochemical properties. Tadese & Seyoum (16) reported the average concentrations of Mojo tannery effluent as Cr 40 ± 27 mg L^{-1}, COD 4434 ± 1846 mg L^{-1}, BOD_5 1054 ± 448 mg L^{-1} and Aregu *et al*. (25) reported the concentrations of Dire Tannery effluent as pH 9.1 ± 3.1, total Cr 35.7 ± 8.6 mg L^{-1}, COD 12913 ± 6874.7 mg L^{-1}, BOD_5 1081 ± 159.55 mg L^{-1} and TSS 2426 ± 515.2 mg L^{-1}. Mandal *et al.*(26) also reported the wastewater generated from tanneries in the area Tiljala, Tangra, and Topsia of Kolkata, India as total Cr 258 mg L^{-1}, COD 2533 mg L^{-1} , BOD_5 977 mg L^{-1}, TSS 1244 mg L^{-1} and, EC 20.042 ms cm^{-1}. All the above three studies indicated wide differences in their compositions of tannery wastewater. The variations might be due to the type of hides used, differences in the unit processes, and capacity of producing finished leather, and amount /type of chemicals used.

Plants 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 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. 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 tape water. Based on observation of biomass production and propagation, *P. purpureum* > *T. domingensis* > *C. latifolius* > *E. pyramidalis* (**Fig. 3**).

The root structures of the plants after treatment are shown in **Fig. 4** below. *P. purpureum* has dense, fine compacted roots 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 contains extremely dense propagated roots and fibrous in nature that helps to hold components of 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 with attached root nodules.

Percent of removal of Cr in the Pilot 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 (16), 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 vesicular basalt rock (27), microbial treatment (28), biosorption of Cr by plants (24), and precipitation of Cr with hydroxides, sulfides, sulphates and, carbonates obtained during the chemicals used in the leather processing (29).

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 (11). Plants can also provide optimal conditions for microbial growth; give an impact on metal mobility and toxicity through root exudates release, entrapment, and accumulation of Cr in the parts of plants such as root, shoot, and leaf (30). 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 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 (31).

The accumulation of Cr in the plant parts is indicated in **Table 2**. 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 Cr in the plant parts (32, 33).

Table 2 Average total chromium concentration (mg g^{-1}) 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

Removal Efficiency of COD, BOD, and TSS

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, BOD5, and TSS is shown in **Fig. 5** 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. 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 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%) compared to all wetland units. No significant differences were seen in BOD_5 removal among each wetland units and the control.

According to Calheiros *et al.*[9], HSSF constructed wetland units vegetated with different plants, an average inflow COD of 1966 - 2093 mg L^{-1}, the removal efficiency of the pilot units varied between 41- 67 % for HLR of 3 cm d^{-1} and 54-73% for HLR 6 cm d^{-1}, respectively. Moreover, the pilot units with an average inflow BOD5 concentrations in the range 875- 898 mg/L removed 41-55% for HLR of 3 cm d^{-1}, and 41-58 % for an HLR of 6 cm/d respectively. Calheiros *et al.* (17) also reported maximum 80 % COD and 90 % BOD_5 removal efficiencies for a conventionally treated tannery wastewater of inlet concentration of 68-425 mg L^{-1} COD and 16-220 mg L^{-1} BOD_5 respectively using three horizontal subsurface flow wetland units in series. The system was operated on a HLR of 60 mm d^{-1} and a hydraulic retention time (HRT) of 2 days). Alemu *et al.* (8) also reported 90 % COD and 91.4 % BOD_5 removal efficiencies with an average inflow concentration of 1,134 ± 269 mg L^{-1} and 523 ± 219 mg L^{-1} respectively. This was obtained after an integrated two phase anaerobic and aerobic SBR followed by a horizontal subsurface flow 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 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 (9, 34).

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 gravel 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 (35, 36). Colloidal solids might be removed by bacterial growth that could decay & settle it. Moreover, collisions of colloids with solids (gravel, plant roots, suspended solids, etc.) could favour adsorption (37). This study was supported by Calheiros *et al.* (9) that TSS removal efficiencies varied between 48-92% for 3 cm d^{-1} and 62-77% for 6 cm d^{-1} HLRs for horizontal subsurface flow wetland system vegetated with different plants with an inflow concentration ranged between 33 -125 mg L^{-1} TSS. In another study, Calheiros *et al.* (17) reported the removal efficiency of TSS did not differ significantly between the Arundo and the Sarcocornia-planted beds. Billore *et al.* (38) also reported 78 % removal of TSS for the treatment of domestic wastewater based on a sub-surface 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 TP and NO_3^-

The TP concentration in the inlet varied between 2.99 - 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.* (39) 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 (40). Plants uptake a low concentration of phosphorus, unless high sorption media are used in the constructed wetland unit (41, 42). 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 (35, 43, 27). Calhereious *et al.* (17) reported 40-93 % removal of TP in 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 range between 63.28 and 71.23 %. NO_3^--

N concentrations in the outflow decreased on 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 unvegetated unit (CWU5) reduced the inflow NO_3^--N concentration by 63.28 % in the outflow of the HSF 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 (44). 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 (45). Denitrification is the most important process in which nitrate is converted into free nitrogen (N_2) through intermediates NO_2^-, NO and N_2O [46, 40].

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 [47, 48]. Studies indicated that the optimum pH for removal of NO_3^--N ranged between pH 6 and 8 and an increase in temperature with lower bound 5 ^{o} C and upper bound 70 ^{o} C [49, 50]. Belmont *et al.* [51] reported 76.7 % NO_3^--N removal in a HSSF constructed wetland vegetated with Cattail and an average inflow concentration of 28.4 ± 7.3 mg L^{-1}. Alemu *et a*l. [8] also reported 66.3% removal of NO_3^--N with an influent concentration of 87.2 ± 26 mg L^{-1} in a HSSF constructed wetland system.

Both TP and NO_3^- removal in the HSSF constructed wetland units were lower when compared with that of the provisional maximum discharge limit set by EEPA [31] for the tannery industry, which are 10 mg L^{-1} 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. *P. purpureum* indicated better propagation and growth overcoming the toxic tannery wastewater in the constructed wetland units. The constructed wetland units were effective in removing Cr, COD and BOD_5 from the inflow tannery wastewater. Its removal efficiency reached up to 99.38 %, 84.03 % and 80.32% for Cr, COD, and BOD_5, respectively. It can fulfill the interim discharge limit of tanneries set by EEPA (2003). The removal efficiency of TSS in the constructed wetland units indicated in the range of 67.75 - 70.59 %. This was due to the role of gravel in the filtration of suspended matter and the long hydraulic residence time (6 days) for sedimentation of suspended materials during operation. The maximum removal efficiency of TP (62.32 %), and NO_3^- (71.23 %) was observed at CWU 3 (C*. latifolius)*, and CWU 2 (*T. domingensis)*, respectively. This study helps to reduce the risk of pollution from the expanding tanning industries in Ethiopia with safe, low cost and environmentally friendly way. This method may be preferred to the existing conventional methods that require high investment for the treatment of wastewater and can produce other extra burdens on the environment.

Declarations

Acknowledgments

The authors 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.

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.

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Ethics declarations

Competing interests

The authors declare that they have no competing interests

Availability of data and materials

The data sets used and/or analysed during the current study are available from the corresponding author on reasonable request.

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Figures

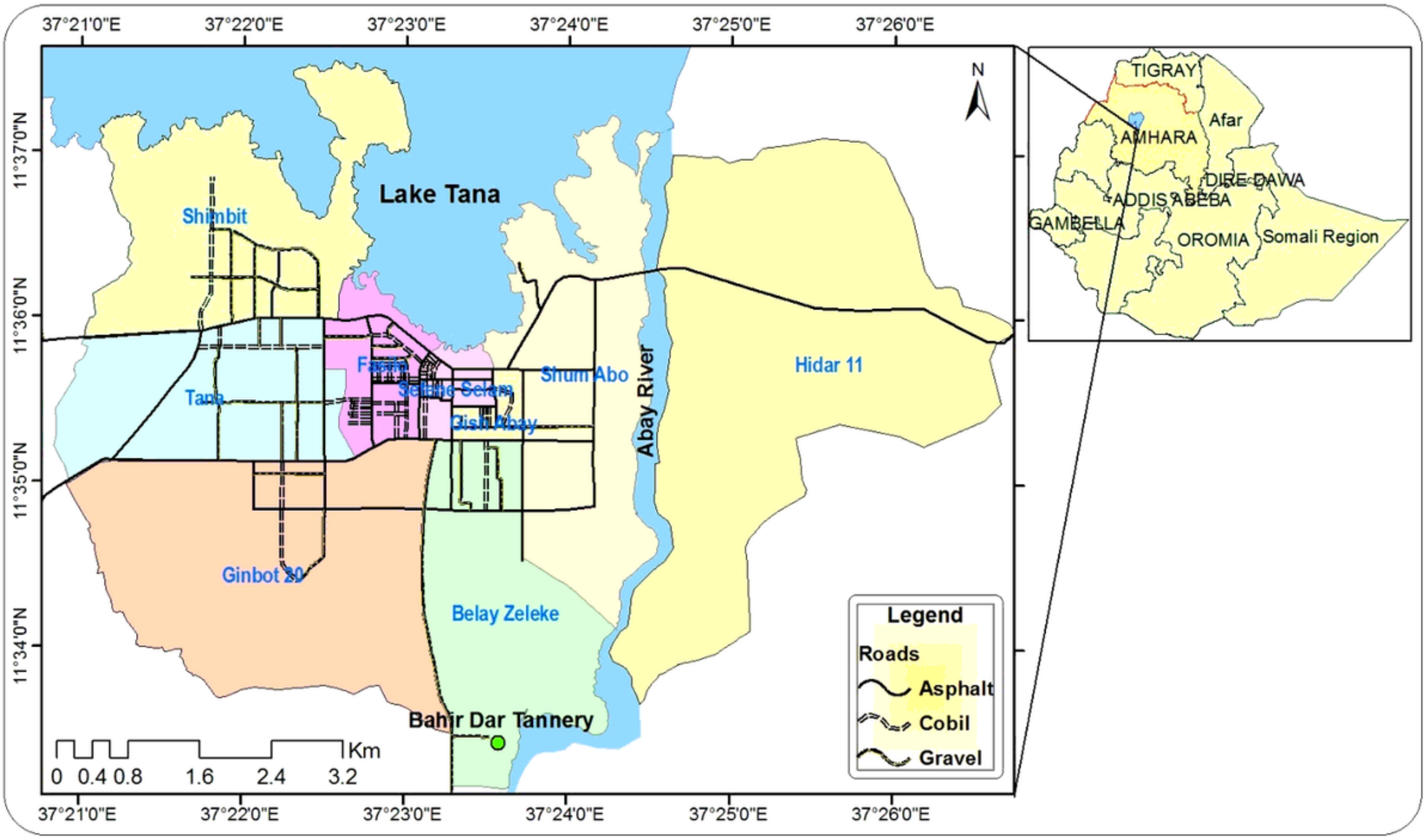

Figure 1

Map of the study site

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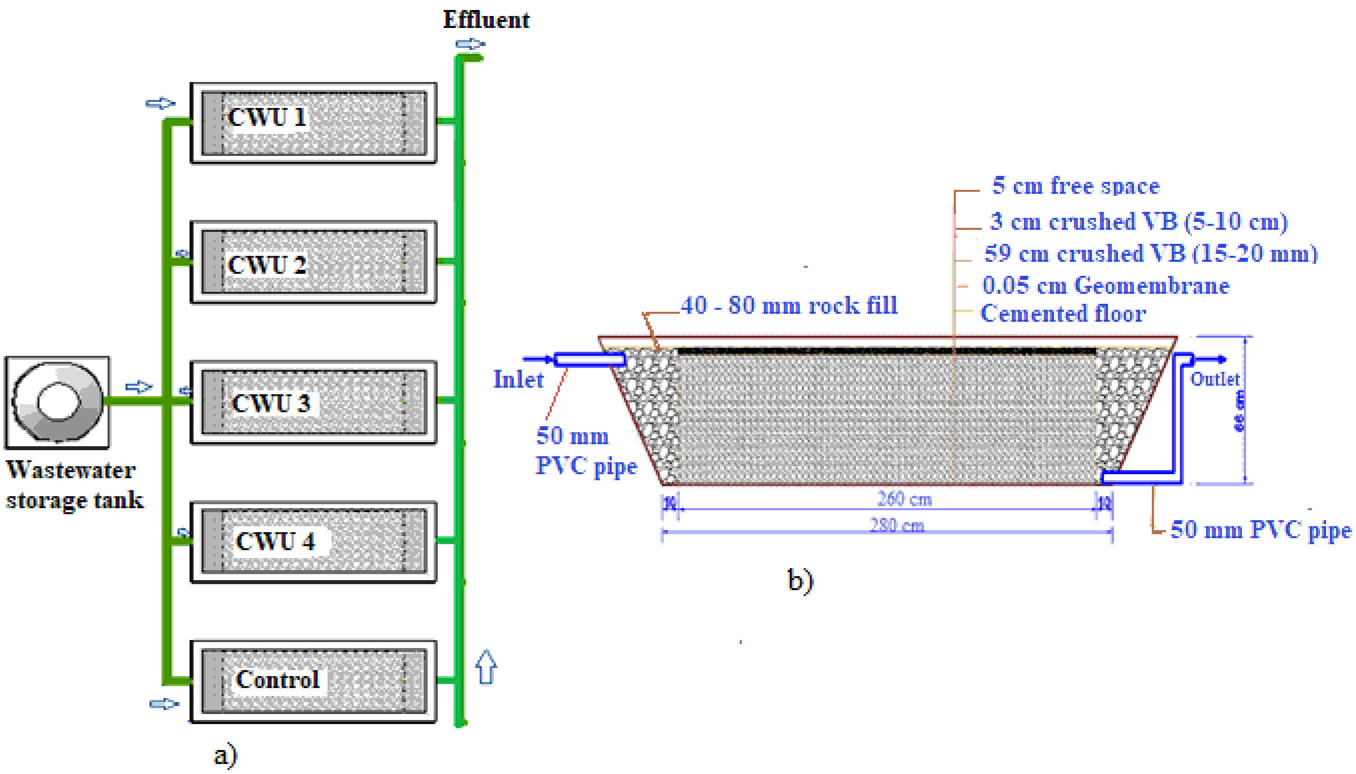

Figure 2

Design of the experimental CWUs layout plan (a), each bed unit component of the CWUs (b).

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Figure 3

The pilot CWUs established for the treatment of tannery wastewater.

Figure 4

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

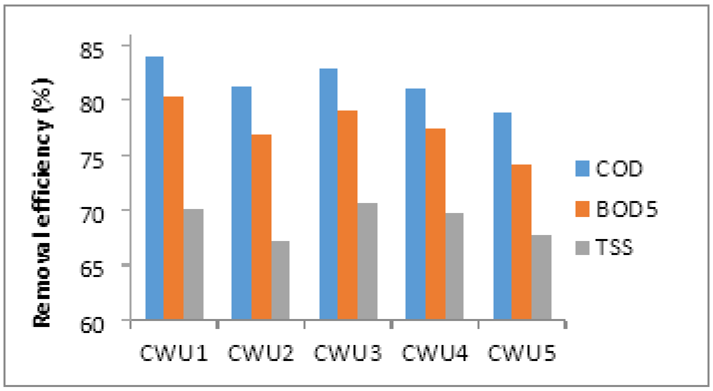

Figure 5

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).

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