Post-treatment of tannery wastewater using pilot scale horizontal subsurface flow constructed wetlands (polishing)

Tadesse Alemu, Andualem Mekonnen and Seyoum Leta

ABSTRACT

In the present study, a pilot scale horizontal subsurface flow constructed wetland (CW) system planted with *Phragmites karka*; longitudinal profile was studied. The wetland was fed with tannery wastewater, pretreated in a two-stage anaerobic digester followed by a sequence batch reactor. Samples from each CW were taken and analyzed using standard methods. The removal efficiency of the CW system in terms of biological oxygen demand (BOD), chemical oxygen demand (COD), Cr and total coliforms were 91.3%, 90%, 97.3% and 99%, respectively. The removal efficiency for TN, NO3⁻/CO3²⁻ and NH4⁺-N were 77.7%, 66.3% and 67.7%, respectively. Similarly, the removal efficiency of SO4²⁻/CO3²⁻, S²⁻ and total suspended solids (TSS) were 71.8%, 88.7% and 81.2%, respectively. The concentration of COD, BOD, TN, NO3⁻/CO3²⁻, NH4⁺-N, SO4²⁻, S²⁻ and TSS in the final treated effluent were 113.2 ± 52, 56 ± 18, 49.3 ± 13, 22.75 ± 20, 17.1 ± 6.75, 88 ± 120 and 0.4 ± 0.44 mg/L, respectively. Pollutants removal was decreased in the first 12 m and increased along the CW cells. *P. karka* development in the first cell of CW was poor, small in size and experiencing chlorosis, but clogging was higher in this area due to high organic matter settling, causing a partial surface flow. The performance of the pilot CW as a tertiary treatment showed that the effluent meets the permissible discharge standards.

Key words | horizontal profile, *Phragmites karka*, subsurface flow constructed wetland, tannery wastewater, tertiary treatment

INTRODUCTION

Constructed wetlands (CWs) are engineered systems that have been designed and constructed to employ the natural process involving use of substrate (soil or gravel), wetland vegetation and microbial assemblages to assist in treating wastewater (Vymazal 2010). CW can be free (surface) flow or subsurface flow (vertical or horizontal). The most common CW systems are designed with horizontal subsurface flow (HSSF) and can provide a reliable secondary and/or tertiary level of treatment with regard to organic matter, total suspended solids (TSS) and heavy metals (Kivaisi 2001; Vymazal & Kropfelova 2009). However, many CWs are less effective for nitrogen removal, unless a longer hydraulic retention time (HRT) and enough oxygenation are provided (Liu et al. 2005). In HSSF, CWs organic compounds are degraded aerobically as well as anaerobically by biofilms attached to the roots, rhizomes and media surface. The oxygen transport capacity of some plants, such as reeds, is sufficient to ensure aerobic decomposition in the rhizospheres and anoxic and anaerobic decomposition plays an important role in pollutant removal in HSSF CWs (Vymazal & Kropfelova 2009).

HSSF CWs are used to remove a variety of pollutants from domestic, industrial, agricultural wastewaters, runoff and landfill leachate (Vymazal 2009). Treating tannery wastewater in a single stage (level) treatment system was difficult, and hence integrating biological treatments system integrated with CW, connected in a series (as polishing) have been introduced (Alemu et al. 2016). Most priority pollutants in the biologically treated effluent exceeded the Ethiopian Environmental Protection Agency (EEPA) permissible effluent discharge limits (MPDL) for most residual parameters (Wang 1991; Rittiruk et al. 2011; El-Bestawy et al. 2013), which requires post-treatments. Integrating CWs as a...
secondary or tertiary treatment can meet industrial wastewater discharge standards with negligible use of fossil-based energy and chemicals.

Horizontal subsurface CWs are very effective not only for the removal of organic matter and TSS but also efficient in the removal of heavy metal and pathogens (total coliforms and fecal coliforms) (Vymazal 2005; Alemu et al. 2016). Industrial wastewater with high chemical oxygen demand (COD), biological oxygen demand (BOD), nutrients and high salt content are now possibly treated by HSSF CWs (Vymazal 2009; Calheiros et al. 2010; Alemu et al. 2016). A variety of removal mechanisms, including physical, chemical, and biological processes are employed in HSSF CWs (Kadlec & Knight 1996; Faulwetter et al. 2009; Vymazal 2011). The removal of most organic pollutants in CW is mainly due to microbial activity (Kadlec & Knight 1996; Stottmeister et al. 2003; Faulwetter et al. 2009). For example, organic matter and the majority of total nitrogen (TN) removal is basically through microbial transformations, while the uptake of nutrients by plants is minor process (Kadlec & Knight 1996). High microbiological productivity, aided by soil, substrate or sludge biofilm and vegetation, wetlands can transform a variety of pollutants into less harmful by- or life-supporting products such as vegetation, wetlands can transform a variety of pollutants into less harmful by- or life-supporting products such as products such as nutrients. CW plant root morphology and development and substrates are important factors that affect treated wastewater quality partially results from their effect on bacterial assemblages (Vymazal et al. 2001; Stottmeister et al. 2003) and through its influencing microbial-plant interaction (Gagnon et al. 2007).

Nutrient removal efficiency also influenced by climatic conditions due to its influence on abiotic factors such as temperatures, which stimulate faster year-round vegetation growth (Kantawanichkul et al. 2001; Kyambadde et al. 2004; Kadlec & Wallace 2009; Bodin 2013) and microbiological activity. Thus, tropical CWs have higher nutrient uptake and organic carbon biodegradation (Kivaisi 2007; Diemont 2006; Katsenovich et al. 2009; Bodin 2013). Hence, plant harvesting contributes to significantly higher removals of nutrients (Kantawanichkul et al. 2001; Kyambadde et al. 2004). However, tropical CWs treatment performance can be affected by high evapotranspiration (ET), which may reduce outflow effluent rates resulting in higher HRTs and through condensation increase outflow pollutant concentrations (Kadlec & Knight 1996; Bodin 2013).

CWs performance is also affected by extreme rain and drought, pH, pollutant load, wetland vegetation, substrate, hydraulics, aspect ratio (length, width ratio), climate and season (Trepel & Palmeri 2002; Garcia et al. 2010; Bodin 2013). An optimum temperature (25–35 °C) and optimum pH (6.5–8.5) is important for pollutant removal (Reed et al. 1995). High or low values inhibit activity of microorganisms, whereby the treatment efficiency (removal of pollutants) might reduce. A large aspect ratio helps to utilize the entire wetland area and minimize the effect of jet short-circuiting and corner dead zones, which tends to improve HRT (Kadlec & Wallace 2009). The removal efficiency might also further be enhanced by using in series connected CWs. Therefore, the objective of this paper is to evaluate the removal efficiency and nutrient dynamics along the horizontal profile of one HSSF CWs, separated into three cells for the treatment of pretreated high strength tannery wastewater.

**MATERIAL AND METHODS**

**Pilot-scale CW systems**

The pilot scale integrated treatment technology (two-stage anaerobic reactors and sequence batch reactor (SBR)) integrated with the CW system, for the treatment of tannery wastewater, was established at Modjo Tannery Share Company premises found in Modjo town, 75 km south of Addis Ababa.

The pilot-scale CW was fed an effluent pretreated with biological treatment system; which consisting of two-stage anaerobic reactors: a hydrolysis anaerobic reactor and a SBR (Figure 1(a)). The biologically treated effluent was collected in a sedimentation tank (50 m³). The sedimentation tank was connected to a HSSF CW with a L.W of 15 m × 30 m equipped with two baffle walls every 5 m and a total hydraulic path length of 90 m (Figure 1(b)). The depth of the substrate was 0.6 m (15 m clay at the bed and 45 m gravel). The CW was filled with medium-sized gravel, (6–20 mm) with a porosity of 35% (US EPA 1993) and vegetated with Phragmites karka. The flow rate into the CW was 23,625 m³/day and total area of CW was 450 m². The HRT used in the present study was 3 days. P. karka growth rate was recorded after harvesting the matured plant (every 5–6 months) on the months of October and April 2015. The performance of pilot CW treatment system has been recorded for 3 years.

**Sampling techniques**

In the present study, the biologically pretreated tannery effluent was then further treated by HSSF CW. Triplicate composite samples from four sites along each CW cell...
were collected from perforated polyvinyl chloride (PVC) tubes, installed within the CW cells, using a sterilized plastic bottle, for 3 years (May 2012 to June 2015). Effluent samples were collected 1 month after operated HRT. To avoid reduction of $\text{SO}_4^{2-}$ and $\text{NO}_3^- / \text{CO}_3^-$ by microorganisms, samples were store at 4°C. Samples of shoots, leaves and root of the $P.$ karka, from a CW, were collected in triplicates at maturity stage from each CW cell and oven dried at 100°C for 24 h.

**Wastewater analysis**

Triplicate samples from the influent, supernatant at the end of SBR treatment system and final effluent of CW was collected. Detailed influent, effluent wastewater and longitudinal profiles characterization was performed using standard methods (APHA) for the following selected parameters: COD, TN, ammonium nitrogen (NH$_4^+$/N), nitrate (NO$_3^-$) sulfides ($\text{S}_2^-$) and sulfate ($\text{SO}_4^{2-}$). All these were measured using a spectrophotometer (DR/2010 HACH, Loveland, USA) according to HACH instructions and APHA (1998). BOD was analyzed using titration (Winkler) method.

Total Cr, TSS, total dissolved solids (TDS) and total coliform (TC) were also measured according to standard methods (APHA 1998). The pH was measured using a pH-meter (HI 9024 HANNA). TDS and conductivity were measured using a conductivity meter (CC-401, ELMETRON). Cr containing wastewater samples were digested using mixed nitric acid digestion (5 mL) and hydrogen peroxide (2 mL) and were analyzed using flame atomic absorption spectrophotometer (Analytic Jena Nova AA 400P, Germany). The percent of pollutant removal rates were calculated according to the following equation:

$$R = \frac{C_i - C_f}{C_i} \times 100$$
where: \( R \) is the removal rate (\%); \( C_i \) is the influent concentration (mg/L); and \( C_f \) is the effluent concentration (mg/L).

**Plant sample analysis**

1 g DW (dried weight) of Phragmites root, stem and leaf samples were transferred to the hot plate and heated at 200 °C for 40 min and then calcinated at 450 °C for 2 h (ash method). The extraction of chromium was performed by adding 5 mL, 6 M HNO₃ (nitric acid), 2 mL H₂O₂ and digested by gently boiling until 1 mL remained. Then 5 mL, 3 M HNO₃ was added and reheated for further 30 min. The warm solution was filtered into 50 mL volumetric flask. The extract was recovered through filtration. Deionized water was added to dilute the recovered sample to 50 mL. The concentration of chromium in the extract was determined by atomic absorption spectrophotometer (AAS) (flame method, 0.01 mg/L detection limit). A blank was prepared to subtract the Cr contained in the reagent from the plant extract.

Total carbon (c) and nitrogen (N) content (% dry weight) were determined on dried and homogenized leaf sample. Nitrogen use efficiency (NUE) of leaf was determined by using the formula:

\[
\text{NUE} = \frac{\text{Total plant dry weight}}{\text{Leaf N content}}
\]

**Table 1** | Characteristics of influent and effluent wastewater (mean ± STDEV)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Influent conc.</th>
<th>Range</th>
<th>Effluents</th>
<th>Range</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8 ± 0.4</td>
<td>6-4-8</td>
<td>6.53 ± 0.2</td>
<td>6.3-6.7</td>
<td>–</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>22.4 ± 1.5</td>
<td>21-23</td>
<td>20 ± 2</td>
<td>19-22</td>
<td>–</td>
</tr>
<tr>
<td>DO (mg/l)</td>
<td>0.9</td>
<td>0.6-1.5</td>
<td>3.18 ± 1</td>
<td>1.5-5.7</td>
<td>–</td>
</tr>
<tr>
<td>BOD (mg/l)</td>
<td>525 ± 219</td>
<td>330-900</td>
<td>45 ± 18</td>
<td>30-100</td>
<td>91.4</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>1,134 ± 269</td>
<td>789-1,410</td>
<td>113 ± 76</td>
<td>65-261</td>
<td>90</td>
</tr>
<tr>
<td>TN (mg/l)</td>
<td>221 ± 99</td>
<td>122-365</td>
<td>49.4 ± 17</td>
<td>20-70</td>
<td>77.7</td>
</tr>
<tr>
<td>NH₄-N (mg/l)</td>
<td>96 ± 31</td>
<td>65-150</td>
<td>17.2 ± 14</td>
<td>11-45</td>
<td>67.7</td>
</tr>
<tr>
<td>NO₃ (mg/l)</td>
<td>87.2 ± 26</td>
<td>48-121</td>
<td>29.2 ± 12</td>
<td>13-68</td>
<td>66.3</td>
</tr>
<tr>
<td>S²⁻ (mg/l)</td>
<td>6.7 ± 4</td>
<td>2.05-10.2</td>
<td>0.76 ± 5</td>
<td>0.15-1.88</td>
<td>88.7</td>
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<tr>
<td>SO₄²⁻ (mg/l)</td>
<td>435 ± 147</td>
<td>100-470</td>
<td>86 ± 33</td>
<td>10-139</td>
<td>71.8</td>
</tr>
<tr>
<td>TSS (mg/l)</td>
<td>325 ± 80</td>
<td>207-382</td>
<td>61.2 ± 27</td>
<td>23-91</td>
<td>81.2</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>760 ± 122</td>
<td>600-950</td>
<td>447.4 ± 33</td>
<td>432-480</td>
<td>41.2</td>
</tr>
<tr>
<td>TC</td>
<td>101 ± 2</td>
<td>98-103</td>
<td>1 ± 0</td>
<td>0-2</td>
<td>99</td>
</tr>
<tr>
<td>FC</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>–</td>
</tr>
<tr>
<td>Total Cr (mg/l)</td>
<td>18.7 ± 7</td>
<td>10-35</td>
<td>0.5</td>
<td>0.3-0.85</td>
<td>97.3</td>
</tr>
<tr>
<td>ORD (mV)</td>
<td>–82 ± 4.5</td>
<td>78-91</td>
<td>–61 ± 7</td>
<td>–65-71</td>
<td>–</td>
</tr>
</tbody>
</table>

**Statistical data analysis**

Data analysis was performed using IBM SPSS statistics 20, Origin Lab17 software and Microsoft Excel XP version 2010.

**RESULT AND DISCUSSION**

**Removal efficiency of the constructed wetland**

The average removal efficiency of the CW system in terms of BOD was 91.3%, COD was 90% and total coliforms were 99%. The efficiency of HSSF CW systems for TN, NO₃⁻-N and NH₄⁻-N were 77.7%, 66.3% and 67.7%, respectively. Similarly, the final effluent concentration of S²⁻ and SO₄²⁻ were 0.76 and 86 mg/L with a removal efficiency of 88.7% and 71.8%, respectively (Table 1). Nutrient removal in the present study was found to be above the range reported by Rangel et al. (2007) and Vymazal (2005) for tannery and domestic wastewater, respectively, due to the use of biologically pretreated wastewater and connected to the CW. The inlet concentrations showed high variability due to variation in the HRT of the SBR effluents (Figure 2).

The composition of inlet wastewater to the CW varied over time and the mean inlet concentration differed significantly (\( P < 0.05 \)). The mean inlet pH values was 8 ± 0.4
and slightly decreased to 6.53 ± 0.2 in the outlet (Figure 2). The inlet concentration of DO was low (0.6 to 0.9) and increased (1.5 to 2.7 mg/L) in the outlet (Table 1). Organic pollutants are degraded relatively fast as a consequence of the high temperature.

**Pollutant longitudinal profiles**

Longitudinal assessment of organic matter and nutrient in the CW showed that there is an increase in concentration in the inlet (1st cell) and then decrease in the flow direction through the two CW cells.

**Organic matter profile**

BOD, COD and TSS concentrations along HSSF CW showed that the highest removal efficiency occurred in the first few meters of CW where the highest level of biological interactions might occur. The mean inlet concentration of BOD were high (330 to 900 mg/L) and decreased to 30 to 100 mg/L in the outlet. Mean inlet concentration of COD was varied from 789 to 1,410 mg/L and decreased to 65 to 261 mg/L in the outlet (Figure 3(a)).

A greater amount of BOD and COD, in the form of suspended matter, were settled and removed faster than soluble BOD and COD (Figure 3(a)). This might be due to the lower porosity of the media, which enhances clogging and filtration by subsurface wetland. There was a decrease in inlet to outlet BOD/COD ratio from 0.46 to 0.39 showing that organic matter liable to biological degradation was removed. The first cell of the CW system absorbs the highest nutrient and organic load. The mean influent and effluent TSS values were 325 ± 80 and 61.2 ± 27 mg/L, respectively. TSS at the inlet varied between 207–382 mg/L (Table 1) and the outlet ranges between 23 to 61.2 mg/L. The TSS average removal efficiency was 81.2%. Plant residues and organic matter settling in the first cell of the CW might increase the value of TSS. Suspended matter might be removed primarily through the mechanisms of interception and settling in the first 5 to 16 m of the first cell of the CW.

BOD and COD removal mainly occurred in the anaerobic bed zone and aerobic degradation in the upper zone as oxygen levels constantly rose in the planted bed during passage through bed media. Old and decaying roots probably decomposed throughout the bed and may have contributed to the relatively high additional values of BOD and COD. The results showed that there were decreases in BOD and COD concentrations along the flow path from inlet to

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*Figure 2* | Inlet variation of BOD, COD and nitrogen species at different sampling times ($N = 6$).

*Figure 3* | The progressive distance of (a) BOD and COD concentrations with distance through a wetland operated in continuous flow mode. (b) Aspect ratio versus COD, BOD removal ($N = 6$). Each data point represents the average of sample collected.
outlet of the HSSF CW system. Due to the greatest reduction in hydraulic conductivity (low velocities that occur within the inlet of HSSF CW beds) the organic matter in the effluent might be settled and deposited within the first few meters (5%) of the inlet region of the CW which was supported by Fisher (1990), Sanford et al. (1995) and Kadlec & Wallace (2009). In the inlet cell of the CW bed, there might be highest microbial populations associated with organic matter degradation and nutrient cycling due to the elevated contaminant concentrations.

**HSSE bed clogging in the inlet region**

Longitudinal organic matter profile result showed that the first part of the CW was increasingly clogged by both the wastewater and plant residues, causing a partial surface flow. Inlet bed clogging was primarily due to the development of plant root networks and microbial biomass formation in the inlet region of the CW. Organic matter settling and microorganism associated biofilms, deposition of suspended solids, accumulation of refractory organic materials and formation of insoluble precipitates are also reducing the pore space (pore volume) in the inlet region of the CW beds (Kadlec & Wallace 2009). Suspended solids are mainly removed by physical mechanisms, such as sedimentation and filtration processes, and most solids were removed in the first cell of the CW. Kadlec & Watson (1993) also reported a 10% pore space blockage by volatile and inorganic solids. This, in turn, reduces the hydraulic conductivity in the inlet region and resulting over-flow and non-uniform hydraulic gradient throughout the CW systems (Fisher 1990; Watson & Choate 2001).

**Aspect ratio and organic matter removal**

In this study the samples were taken from every 6 meters with variable aspect ratio from CW1, S1 of cell 1 (L:W = 1.2) to CW3, S4 (L: W = 16.8). As illustrated by the Figure 3(b) BOD removal was highest at CW cell 1 for an aspect ratio is 7.2: 1, thereafter removal did not show significant improvement. This showed that higher aspect ratio (greater than 5:1) has no significant effect on BOD percent removal. However, COD removal was highly dependent on the aspect ratio up to 14:4. The result was supported by Melton (2005) report, which states that an aspect ratio of 4:1 achieved a 10% grater removal of organic matter than a 1:1 ratio. A large aspect ratio helps to utilize the entire wetland area and minimize the effect of jet flow short-circuiting and corner dead zones, which tends to improve the HRT for settling (Kadlec & Wallace 2009). This might increase COD removal efficiency as aspect ratio increase.

The BOD and COD removal values can be approximated by a first order plug flow relationship. The plug flow was assumed, because the system compared three CW cells, each with aspect ratio of 5:1. The BOD and COD removal after 3 days of HRT was limited and believed to be influenced by the production of residual BOD and COD in the system and evapotranspiration (Alemu et al. 2016). This is compatible with the previous idea that BOD and COD are removed rapidly in the first part of CW system. Lower and higher aspect ratio showed a decreased of mass removal rates, due to insufficient time for removal processes to occur or/and short circuiting and high evapotranspiration which concentrate pollutants at higher HRT, respectively. As long as the flow is distributed effectively, a CW with a high aspect ratio (18:1) did not have significant removal efficiency than one with a lower aspect ratio (5:1) for COD removal, which is supported by Kadlec & Wallace (2009).

**Nitrogen profile along CW**

Mean inlet concentrations of TN were high, 122 to 365 mg/L and decreased to 20 to 70 mg/L in the outlet (Table 1). Mean inlet concentration of NH4-N was high (65 to 150 mg/L) and decreased (11 to 45 mg/L) in the outlet (Table 1). According to Vymazal (2007) Nitrogen removal in CW occurs through adsorption, assimilation into microbial and plant biomass, ammonium volatilization and coupled nitrification-denitrification. In this study, the major removal mechanisms of N in CW are adsorption, nitrification and denitrification processes. Nitrification is a chemoautotrophic process in which ammonium is oxidized to nitrate by nitrifying bacteria (Nitrosomonas and Nitrobacter) in the aerobic zone of CW bed. Nitrifying bacteria are inhibited by high concentration of NH4-N, pH (7.5–8.6) and oxygen concentration below 1 mg/L (Vasudevan et al. 2011). The CW bed was dominated by anaerobic conditions (−81.86 ± 4.4 to −42.8 ± 1.6 mV), which favor denitrification. In this study ammonium volatilization was probably very low, as the pH, within the CW cells, was in the range of 6.3 to 7.2. The plant uptake of N might also have contributed to the nutrient removals (Kyambadde et al. 2004; Konnerup et al. 2009).

The use of higher aspect ratio (18:1) in the present study was reducing pollutants such as nitrogen to the level below permissible limits. Kadlec & Wallace (2009) reported that nitrogen represents a principal concern due to algal bloom.
in lakes, oxygen demanding in the receiving water bodies and ammonia toxicity to aquatic species. The result showed that, integrating connected CW cells, with higher aspect ratio, enhance the nitrogen removal efficiency and protect the receiving water bodies. As illustrated by the Figure 4(a) the TN and NH$_4^+$N concentration in the inlet region increased which results in lower removal (even negative) for the first parts of the CW (aspect ratio up to 7.2:1). Thereafter, removal was improved as the aspect ratio increases. The increase in concentration of TN and ammonium nitrogen in the inlet part of the CW was due to the accumulation of sludge which favors an anaerobic environment. However, nitrate removal is increasing as aspect ratio increases, due to denitrification processes, plant uptake and adsorption in CW substrate.

**Sulfur transformation along CW**

The inlet concentrations of SO$_4^{2-}$ were in the range between 100 to 470 mg/L and decreased to 10 to 139 mg/L in the outlet. The range inlet concentration of S$^{2-}$ were high (1.39 to 33 mg/L) and decreased (0.1 to 2.8) mg/L in the outlet (Figure 5). Sulfate removal from tannery wastewater and its profile in CWs is still considered to be secondary importance compared to the removal of chromium, BOD and nitrogen compounds. As a result, it is comparatively less understood and few case studies exist for evaluation. Unlike other nutrients, wetland sulfur cycles are very complex, and the control over removal processes is often very complex, making it a challenge to design systems to process sulfur in wetlands efficiently. Since the majority of sulfur removal was largely by sedimentation, higher aspect ratio may contribute to the higher removal of sulfide and sulfate in this study.

Sulfur removal in CW systems includes H$_2$S and dimethyl sulfur loss, metal precipitation and plant uptake. Although microbial routes provide for gaseous loss of H$_2$S and dimethyl sulfur ((CH$_3$)$_2$S), it requires very low redox potentials and usually occurs in deeper wetland sediments (Kadlec & Wallace 2009). Metal sulfide precipitation often blocks H$_2$S loss by immobilizing sulfur in the sediment. Plant sulfur uptake is minimal. Kadlec & Wallace 2009 reported only 1% take up by plants in HSSF treatment wetlands. They reported that majority of sulfur was largely stored in the wetland soil as elemental sulfur (31%) and organic sulfur (25%), and that only a small fraction was released by volatilization to the atmosphere. Sulfur reduction may be improved by anaerobic mode of operation in HSSF CW bed zones. Sulfate reduction was strongly dependent on BOD, for carbon source. The presence of higher BOD, in the present study (>200 mg/L (Kadlec & Wallace 2009)), led to a higher removal of sulfur. The mean inlet concentrations of chlorides (Cl$^-$) were 760 ± 122 mg/L and decreased to 432–480 mg/L in the outlet. Cl$^-$ showed a decreased in concentration in moving from the 1st to the 2nd cell and increased 3rd...
cell CW; this might be due to the concentration of pollutants resulting from high evapotranspiration rate.

**Plant growth profile along CW**

Wastewater treatment capability of *P. Karka* was tested in many CW studies. *Phragmites karka* plant tolerated high Cr concentration ranging from 10 to 35 mg/L, and therefore proves their potential for phytoremediation. As the wetland became older (3–4 years), *P. karka* in the first CW cell was unhealthy due to lower redox potential (−81.86 ± 4.4 mV) in the root zone, sulfide (H₂S) and Cr toxicity. The growth rate of *P. karka* was increased as the Cr and organic matter concentration decreases along the CW (Figure 6). This might be due to inhibition of alcohol dehydrogenase activity by H₂S, thereby limiting the ability of plants to use alternative anoxic energy sources (Kadlec & Wallace 2003).

Plant growth rate analysis showed that, after harvesting the CW plant, growth rate increases in moving from Cell 1 to Cell 3 of the CW. The plant growth rate results, between 2 and 5 weeks, showed that there is a statistically significant growth difference between the three CW cells at P < 0.05. However, within the same CW cell significances difference in growth rate was not observed. In 3 years of operation, clogging was increased, particularly the first part of the CW cell due to wastewater and plant residue accumulation, causing a partial surface flow.

**Plant carbon to nitrogen ratio**

Root C/N ratios in *P. karka* were increased from Cell 1 to Cell 3 (Figure 7(b)). The increasing salinity leads to a slight increase in root C content while N content decreased, causing consistently higher C/N ratio along CW. Nitrogen use efficiency of leaf (NUE) decreases moving Cell 1 to Cell 2, nevertheless, higher growth was observed as carbon content increases. NUE was affected by N translocation from root to shoot. Similarly, the leaf C/N ratio in *P. karka* correlated positively with salinity. Increase in salinity along CWs, as a result of high evapotranspiration, leads to a slight increase in C content while N content decrease causing constantly higher C/N ratio (Figure 7(b)).

**Chromium accumulation in Phragmites karka**

*Phragmites* root accumulates highest Cr than leaves (Figure 7(a)). No detectable Cr concentration was observed in the stem. *P. karka* development in the first cell of CW was poor, with the majority of plants experiencing chlorosis and stunted growth due to high shock. These were due to the toxic effects cause by high Cr, S²⁻, organic matter accumulation and more reduced anaerobic zone (−81.86 ± 4.4 mV). The first cell of CW has highest Cr bio-accumulation factor which is in agreement with the results reported by Tadesse & Seyoum (2015). Tolerance to metals by the plants could be achieved by sequestering them in tissues or cellular compartments (e.g. central vacuoles) that are insensitive to metals and adsorbed at the extracellular negatively charged sites (COO⁻) of the root cell walls (Weisa & Weisb 2003; Tadesse & Seyoum 2015). The translocation of excessive metals into leaves and harvesting it before shedding can also be considered as tolerance mechanisms.

**CW plant management**

*Phragmites* plant was selected for this study considering its performance, Cr uptake capability, shock resistance and management criteria (Tadesse & Seyoum 2015). *P. karka* matures in a 5–6 month interval and is harvested every 6 months. The plant stem was used for roofing and fencing.
by the local community. Leaves and shoots were used as a feedstock for biogas production (as co-digestion) (Andualem & Seyoum 2013). Harvesting aboveground plant biomass was done to enhance nutrient uptake and removal efficiency (by 40–50% as reported by Meuleman et al. (2002)). Periodical harvesting prevents the release of nutrients into the CW via biomass decomposition, which causes lower net removal compared to those in colder regions (DeBusk & Ryther 1987; Reddy et al. 1999; IWA 2000; Kadlec 2005). Proper monitoring and management of CW therefore improves the potential of plant nutrient uptake and phytoremediation.

CONCLUSION

The effluent quality of the biological treatment systems (anaerobic-SBR) alone did not meet the acceptable discharge limit for most pollutants. The use of CW as a tertiary treatment (polishing) for high strength tannery wastewater enables high effluent quality. The tertiary treated effluent greatly reduces the pollution burden released into the receiving river. In the present study, it was clearly observed that post-treatment of tannery effluent, using HSSF CW, achieved the highest removal efficiencies (ranges between 66.3–99%) for BOD, COD, TSS, pathogens, heavy metal (Cr), and nutrients. The inflow fluctuation tolerance by the P. karka, including interruptions in the feeding, was found to be high. The highest pollutant load was removed in the first cell of the CW system, which results in clogging of the first CW cell. Anaerobic condition as a result of clogging and high shock due to Cr and S$^{2-}$ toxicity in the first cell of CW results in poor growth of P. karka. However, the use of series connected CW cells further enhances the removal efficiency of the integrated system. The study proved that the use of CW as a post-treatment can turn industrial wastes into clean water for use for domestic purposes and agriculture.

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