Constructed wetland systems vegetated with different plants applied to the treatment of tannery wastewater

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Phytoremediation
Tannery wastewater
Horizontal subsurface flow
Phragmites australis
Typha latifolia

Abstract

Wastewaters from leather processing are very complex and lead to water pollution if discharged untreated, especially due to its high organic loading. In this study the survival of different plant species in subsurface horizontal flow constructed wetlands receiving tannery wastewater was investigated. Five pilot units were vegetated with Canna indica, Typha latifolia, Phragmites australis, Stenotaphrum secundatum and Iris pseudacorus, and a sixth unit was left as an unvegetated control. The treatment performance of the systems under two different hydraulic loading rates, 3 and 6 cm d⁻¹, was assessed. COD was reduced by 41–73% for an inlet organic loading varying between 332 and 1602 kg ha⁻¹ d⁻¹ and BOD₅ was reduced by 41–58% for an inlet organic loading varying between 218 and 780 kg ha⁻¹ d⁻¹. Nutrient removal occurred to lower extents. Phragmites australis and Typha latifolia were the only plants that were able to establish successfully. Despite the high removal of organic content from the influent wastewater, during 17 months of operation, no significant differences in performance were observed between units.

Introduction

Constructed wetlands (CWs) can be used for primary, secondary and tertiary treatment of municipal or domestic wastewaters, stormwater, agricultural and industrial wastewaters such as landfill leachate, petrochemicals, food wastes, pulp and paper and mining, usually combined with an adequate pre-treatment (Kadlec et al., 2000). Although they are widely used for municipal wastewater, the application to industrial wastewater has to be carefully analyzed since its composition is frequently highly variable and the treatment needs are not the same. However, the use of CWs for the treatment of industrial wastewaters has increased over the past ten years (Korkusuz, 2005).

The discharge of tannery wastewaters can cause severe environmental problems due to its high chemical oxygen demand (COD) level and, sometimes, high chromium concentration and deep color content (Song et al., 2000). The effluent treatment systems for the tannery industry experience frequent problems due to the fact that they are often working over the capacity due to poor design, or to increases in production. In these situations, a CW can be potentially used to enhance the overall biological performance (Daniels, 2001b), or can be an alternative to the conventional biological treatment (Daniels, 2001a; Kucuk et al., 2003). However, no detailed studies on the treatment of tannery wastewater using CWs are known in the literature.

The choice of plants is an important issue in CWs, as they must survive the potential toxic effects of the wastewater and its variability. The most widely used CWs design in Europe is the horizontal subsurface flow system vegetated with the common reed (Phragmites australis) (Vymazal, 2005), although other plant species, such as cattails (Typha spp.) bulrushes (Scirpus spp.) and reed canarygrass (Phalaris arundinacea) have
been used for both domestic and industrial wastewater treatment (Mbuligwe, 2005; Vymazal, 2005; Vymazal and Kröpfelová, 2005; Shepherd et al., 2001). In Portugal, the main macrophyte species used in CWs are P. australis, Iris pseudacorus (yellow iris) and Cyperus spp. In some systems, Juncus effusus (soft rush), other Juncus spp., and Scirpus spp. (bulrushes) are also found to establish spontaneously (Korkusz, 2005).

The present study aimed at assessing the use of different plant species in CWs receiving wastewater from a tannery production plant. Six pilot units, with horizontal subsurface flow, were evaluated for a period of 17 months in terms of treatment performance and plant survival when subject to two different hydraulic loadings rates (HLRs).

Methods

Wetland site

The experimental pilot units were located at a leather company in the north of Portugal, and placed after a primary treatment of the effluent. This company has only the post-tanning and finishing operations, although in a complete productive cycle other operations are included, such as hide and skin storage, beamhouse, deliming, bating, pickling and tanning.

Wastewater sampling and analysis

The tannery wastewater to be applied to the pilot units was characterized over a one-year period. The following parameters were determined, based on standard methods (APHA, 1998): pH (Potentiometric Method), chemical oxygen demand (COD; Closed Reflux, Colorimetric Method), biochemical oxygen demand (BOD₃; 5-Day BOD Test), total suspended solids (TSS; Total Solids Dried at 103–105 °C Method), Kjeldahl nitrogen (TKN; Kjeldahl Method), nitrate (NO₃⁻; Nitrate Electrode Method), ammonia (NH₃; Phenate Method), total phosphorus (Total P; Manual Digestion and Flow Injection Electrode Method), biochemical oxygen demand (BOD₅; COD, TSS, TKN, NH₃, NO₃ and Total P. To average depth of liquid in the bed, h₅ = 0.55 m. Near the wastewater inflow and outflow of the beds a layer of coarse rock was put in place in order to facilitate the distribution of the effluent. Feeding of wastewater to the six pilot units was made through a perforated polyvinylchloride (PVC) rigid pipe with flow control.

The units were filled with water and after three weeks the wastewater was applied. The systems then operated for 17 months under different hydraulic conditions. During the first two months, no monitoring of the efficiency of the system was carried out, apart from measuring the pH of the inflow and outflow. After that, for 11 months (corresponding to days 60–391), the systems were monitored under a HLR of 3 cm d⁻¹, with a nominal wetland detention time of 6.8 days. By the 8th month (between days 214 and 242), the systems were not fed continuously due to the shutdown of the tannery production plant, although during that period the level of the liquid in the units was kept at approximately 5 cm below the surface by adding of stored tannery wastewater as required. A second period of operation occurred subsequently during 4 months (corresponding to days 392–511) under a HLR of 6 cm d⁻¹, with a nominal wetland detention time of 3.4 days. Samples were periodically taken at the inlet and outlet of the CWs.

Plant material

The plant material used in the pilot units was chosen based on the plant species established in the surroundings of a wastewater discharge tank of the leather company: cattail (T. latifolia), yellow flag (I. pseudacorus), canna (C. indica) and St. Augustine grass (S. secundatum). These plants were transplanted from this site to the pilot units. The common reed (P. australis) was also used because it is very abundant in Portugal and it is frequently applied in CWs. It was transplanted from an industrial polluted site in Estarreja, Portugal (Oliveira et al., 2001). All the plants used for transplantation to the pilot units were apparently well established in their place of origin. The vegetation was planted by hand with a range of plants of 10 m⁻². The plant material was placed in the substrate at a depth equal to the operational water level of the units. The number of plants was monitored throughout operation.

Maintenance

The systems were inspected on, at least, a weekly basis concerning the overall functioning. Major attention was given to the inlet flow, which was checked twice a week, as obstruction of the pipes due to suspended solids in the effluent could occur. A general cleaning of the pipes was usually undertaken twice a month.

Data analysis

Statistical analysis was performed using the SPSS program (SPSS Inc., Chicago, IL, USA; Version 12.0). The data was analyzed through one-way analysis of variance (ANOVA) to compare the performance of each bed concerning the removal of BOD₅, COD, TSS, TKN, NH₃, NO₃ and Total P. To
detect the statistical significance of differences \( (p < 0.05) \) between means of treatments, the Tukey test was performed.

**Results**

**Tannery wastewater characterization**

The characteristics of the tannery wastewater are presented in Table 1, demonstrating its variability during the year. The variations also occur through each working day. The variation of COD and pH, determined hourly, was analyzed during two different days—the average COD and pH were 2010 mg O\(_2\) L\(^{-1}\) (±516) and 6.98 (±0.05), respectively, in one day, and 2068 mg O\(_2\) L\(^{-1}\) (±446) and 7.93 (±0.08), respectively, in another day.

**Table 1 – Mean composition of the tannery wastewater for 1 year. Average, minimum and maximum values (±SD) are shown**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average ± SD</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.14 ± 1.10</td>
<td>4.62</td>
<td>8.13</td>
</tr>
<tr>
<td>COD(^a) (mg O(_2) L(^{-1}))</td>
<td>2250 ± 565</td>
<td>1100</td>
<td>3000</td>
</tr>
<tr>
<td>BOD(^b) (mg L(^{-1}))</td>
<td>1000 ± 88</td>
<td>900</td>
<td>1200</td>
</tr>
<tr>
<td>TSS(^b) (mg total solids L(^{-1}))</td>
<td>92 ± 36</td>
<td>58</td>
<td>200</td>
</tr>
<tr>
<td>TKN(^b) (mg TKN- N(_L) L(^{-1}))</td>
<td>188 ± 17</td>
<td>150</td>
<td>220</td>
</tr>
<tr>
<td>NH(_3)(^b) (mg NH(_3)- N(_L) L(^{-1}))</td>
<td>100 ± 14</td>
<td>75</td>
<td>135</td>
</tr>
<tr>
<td>NO(_3)(^b) (mg NO(_3)- N(_L) L(^{-1}))</td>
<td>44 ± 9</td>
<td>36</td>
<td>67</td>
</tr>
<tr>
<td>Total P(^b) (mg PL(^{-1}))</td>
<td>1.0 ± 0.7</td>
<td>0.1</td>
<td>2.0</td>
</tr>
<tr>
<td>Total Cr(^b) (mg Cr L(^{-1}))</td>
<td>0.027 ± 0.075</td>
<td>&lt;0.001</td>
<td>0.360</td>
</tr>
<tr>
<td>Cr VI(^b) (mg Cr L(^{-1}))</td>
<td>0.004 ± 0.006</td>
<td>&lt;0.001</td>
<td>0.020</td>
</tr>
</tbody>
</table>

\(^a\) \(n = 44\).

\(^b\) \(n = 24\).

**Development of plant material in the pilot units**

The growth of the plants was monitored during the operation of the pilot units. A limited natural colonization by some plants occurred in all units, except on the control unit, namely by Aster squamatus, Picris echioides, Polypogon viridis, Dactylis glomerata, Paspalum paspalodes, Vicia sativa, Sonchus oleraceus and Rumex crispus. No intervention was made to control their growth. The development of the plants in terms of total number of shoots is shown in Fig. 1. By the end of the first period (corresponding to day 391) of operation at an HLR of 3 cm d\(^{-1}\), the counting of the existing number of plants was 7 for Canna indica, 10 for T. latifolia, 200 for P. australis, 5 for I. pseudacorus, while S. secundatum did not show any development. After the feed interruption period (between days 214 and 242), there was a 14% decrease for C. indica, a 17% decrease for I. pseudacorus, while there was an increase of 4% for T. latifolia and of 35% for P. australis. After the second period of operation, corresponding to four months (corresponding to days 392–511) at a higher HLR of 6 cm d\(^{-1}\), the counting of the existing number of plants was 3 for C. indica, 25 for T. latifolia, 400 for P. australis and 9 for I. pseudacorus. S. secundatum almost disappeared.

**Removal efficiency of the pilot units**

The efficiency of the pilot units subject to the different hydraulic conditions was monitored through their operation, and the characteristics of the wastewater collected from the inflow and outflow of each pilot unit are shown in Tables 2 and 3.

In the first 2 months of wastewater application, the outflow pH of the units was more alkaline than in the following periods of operation, varying between 8.69 and 10.39 (data not shown). A decrease of the pH at the outflow of all pilot units occurred with time, but the pH was higher at the outflow than that observed at the inflow at all times. When operating at an HLR of 3 cm d\(^{-1}\), the average pH at the inflow was 7.45, while the pH at the outflow, for the different units, varied between 7.95 and 9.88. When operating at an HLR of 6 cm d\(^{-1}\) the
Table 2 – Mean composition of the inflow and outflow of the pilot units for a HLR of 3 cm d⁻¹. Minimum and maximum values are indicated in brackets

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Average results (min.-max.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inflow</td>
</tr>
<tr>
<td>pH</td>
<td>7.45 (4.64–8.75)</td>
</tr>
<tr>
<td>COD₅ (mg O₂ L⁻¹)</td>
<td>1966 (1108–3141)</td>
</tr>
<tr>
<td>BOD₅ (mg L⁻¹)</td>
<td>875 (727–1080)</td>
</tr>
<tr>
<td>TSS (mg total solids L⁻¹)</td>
<td>75 (33–125)</td>
</tr>
<tr>
<td>NH₃ (mg NH₃-NL⁻¹)</td>
<td>74 (45–100)</td>
</tr>
<tr>
<td>NO₃ (mg NO₃-NL⁻¹)</td>
<td>36 (20–60)</td>
</tr>
<tr>
<td>Total P (mg PL⁻¹)</td>
<td>0.30 (0.08–0.45)</td>
</tr>
<tr>
<td>Total Cr³ (mg Cr L⁻¹)</td>
<td>0.017 (&lt;0.001–0.025)</td>
</tr>
<tr>
<td>Cr VI⁴ (mg Cr L⁻¹)</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

⁻ n = 27.
⁺⁺ n = 10.
⁻⁻ n = 19.
⁻⁻⁻ n = 13.

Table 3 – Mean composition of the inflow and outflow of the pilot units for a HLR of 6 cm d⁻¹. Minimum and maximum values are indicated in brackets

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Average results (min.-max.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inflow</td>
</tr>
<tr>
<td>pH</td>
<td>6.55 (5.84–7.13)</td>
</tr>
<tr>
<td>COD₅ (mg O₂ L⁻¹)</td>
<td>2093 (1755–2669)</td>
</tr>
<tr>
<td>TSS (mg total solids L⁻¹)</td>
<td>79 (66–100)</td>
</tr>
<tr>
<td>TKN² (mg TKN-NL⁻¹)</td>
<td>126 (90–162)</td>
</tr>
<tr>
<td>NH₃ (mg NH₃-NL⁻¹)</td>
<td>88 (75–100)</td>
</tr>
<tr>
<td>NO₃ (mg NO₃-NL⁻¹)</td>
<td>30 (20–40)</td>
</tr>
<tr>
<td>Total P (mg PL⁻¹)</td>
<td>0.25 (0.20–0.38)</td>
</tr>
<tr>
<td>Total Cr³ (mg Cr L⁻¹)</td>
<td>0.010 (0.001–0.0027)</td>
</tr>
<tr>
<td>Cr VI⁴ (mg Cr L⁻¹)</td>
<td>0.005 (&lt;0.001–0.001)</td>
</tr>
</tbody>
</table>

⁻⁻ n = 12.
⁻⁻⁻ n = 6.
average pH of the inflow was 6.55, while the outflow values varied between 8.01 and 8.78. The performance of the units concerning organic matter and nutrients removal was measured thereafter.

In terms of organic matter removal (COD and BOD$_5$) no significant differences were found between the different pilot units. For an HLR of 3 and 6 cm d$^{-1}$ the average COD inflow concentration was 1966 and 2093 mg O$_2$ L$^{-1}$, respectively. The removal efficiencies of the pilot units varied from 41% to 67% for an HLR of 3 cm d$^{-1}$, and from 54% to 73% for an HLR of 6 cm d$^{-1}$. The average BOD$_5$ inflow concentration was 875 and 898 mg L$^{-1}$ for an HLR of 3 and 6 cm d$^{-1}$, respectively. At the outflow of the pilot units the removal efficiency varied between 41 and 55% for an HLR of 3 cm d$^{-1}$, and between 41% and 58% for an HLR of 6 cm d$^{-1}$.

The TSS inflow concentration ranged between 33 and 125 mg total solids L$^{-1}$ and the removal efficiencies varied between 48% and 92% for 3 cm d$^{-1}$ and between 62% and 77% for 6 cm d$^{-1}$. There were no significant differences between the units for the two HLRs.

Nutrients removal was in general low for the two hydraulic conditions. The TKN and NH$_3$ inflow concentrations ranged between 90–230 mg TKN-N L$^{-1}$ and 45–100 mg NH$_3$-N L$^{-1}$. For the HLR of 3 cm d$^{-1}$, the removal efficiencies varied from 18% to 42% for TKN and 11–27% for NH$_3$. For an HLR of 6 cm d$^{-1}$ the average removal efficiencies for TKN and NH$_3$ were in the range of 16–30% and 2–16%, respectively. There were no significant differences between the units for the two HLRs. The NO$_3$ inflow concentration ranged between 20 and 60 mg NO$_3$-N L$^{-1}$; at the outlet concentration varied between 17 and 52 mg NO$_3$-N L$^{-1}$.

Phosphorus and chromium (total and hexavalent) were only detected at low concentrations at the inflow and outflow of the units. For phosphorous removal, there were no significant statistical differences between the pilot units. The chromium concentration at the outflow of the units was below the detection limit, being the average inflow concentration of 0.010 mg Cr L$^{-1}$. These low levels are due to the fact that the leather production plant does not use chromium in high amounts.

The removal of COD, BOD$_5$ and TSS was proportional to the influent load. The linear relationship between mass removal and mass loading is illustrated in Figs. 3–5. For an HLR of 3 cm d$^{-1}$, the organic loading (COD) inflow of the units varied between 332 and 942 kg ha$^{-1}$ d$^{-1}$, being the mass removal between 152 and 582 kg ha$^{-1}$ d$^{-1}$. For an HLR of 6 cm d$^{-1}$, the organic loading (COD) varied between 1053 and 1602 kg ha$^{-1}$ d$^{-1}$, being the mass removal between 573 and 1092 kg ha$^{-1}$ d$^{-1}$.

In terms of BOD$_5$, the loading varied from 218 to 324 kg ha$^{-1}$ d$^{-1}$, for a 3 cm d$^{-1}$, being the mass removal between 92 and 168 kg ha$^{-1}$ d$^{-1}$, while for an HLR of 6 cm d$^{-1}$ it varied between 444 and 780 kg ha$^{-1}$ d$^{-1}$, and the mass removal was between 198 and 456 kg ha$^{-1}$ d$^{-1}$. The maximum and minimum TSS loading was, respectively, 10 and 38 kg ha$^{-1}$ d$^{-1}$ for 3 cm d$^{-1}$ and 40 and 60 kg ha$^{-1}$ d$^{-1}$ for 6 cm d$^{-1}$, being the correspondent mass removals variations of 6–33 and 25–45 kg ha$^{-1}$ d$^{-1}$.

**Discussion**

In this study, six constructed wetland pilot unit systems receiving tannery wastewater operated for 17 months using horizontal subsurface flow under two different HLRs, 3 and 6 cm d$^{-1}$. The performance of the units varied between 8.01 and 8.78. The efficiency of COD removal was not affected by the feed interruption period, corresponding to the tannery plant shutdown at day 214. When the feed was restarted, after one month, the efficiency was resumed. The COD removal efficiency was not significantly affected by the time of the year, varying between 41% and 67% in Spring/Summer (April–September) and between 41% and 65% in Autumn/Winter (October–March).

**Relationship between removal efficiency and organic load**

Fig. 2 shows, as an example, the pattern of COD removal during the system operation at the two HLRs for the Phragmites australis unit. The outflow values of COD, for all units, gradually decreased at the beginning of operation but remained fairly constant thereafter. The efficiency of COD removal was not affected by the feed interruption period, corresponding to the tannery plant shutdown at day 214. When the feed was restarted, after one month, the efficiency was resumed. The COD removal efficiency was not significantly affected by the time of the year, varying between 41% and 67% in Spring/Summer (April–September) and between 41% and 65% in Autumn/Winter (October–March).
Fig. 3 – COD loading vs. COD removal. Unit 1: Canna indica, Unit 2: Typha latifolia, Unit 3: Phragmites australis, Unit 4: Stenotaphrum secundatum, Unit 5: Iris pseudacorus and Unit 6: control. The coefficients of the linear correlation are represented all with $p < 0.05$.

Fig. 4 – BOD$_5$ loading vs. BOD$_5$ removal. Unit 1: Canna indica, Unit 2: Typha latifolia, Unit 3: Phragmites australis, Unit 4: Stenotaphrum secundatum, Unit 5: Iris pseudacorus and Unit 6: control. The coefficients of the linear correlation are represented all with $p < 0.05$.

Fig. 5 – TSS loading vs. TSS removal. Unit 1: Canna indica, Unit 2: Typha latifolia, Unit 3: Phragmites australis, Unit 4: Stenotaphrum secundatum, Unit 5: Iris pseudacorus and Unit 6: control. The coefficients of the linear correlation are represented all with $p < 0.05$. 
6 cm d\(^{-1}\). In the leather manufacturing, different operations and processes result in effluents with different compositions (Song et al., 2000), and wastewater treatment systems should withstand such variability. The type of wastewater may influence crucially the survival of plants in a CW. In the present study, the patterns of the tannery wastewater produced were characterized. Prior to the operation of the pilot units, the one year assessment of the chemical characteristic of the wastewater has revealed that the composition was variable, with the COD ranging from 1100 to 3000 mg O\(_2\) L\(^{-1}\) and the BOD\(_5\) from 900 to 1200 mg L\(^{-1}\). The inflow to the pilot units varied thereafter in a similar manner.

The choice of different plant species should take into account some factors such as the rooting depth, plant productivity and tolerance to high loads of wastewater (Brix, 1994). The main emergent macrophyte species used in CWs in the Mediterranean countries are *Canna* spp., *Iris* spp., *Cyperus* spp., *Phragmites* spp., *Juncus* spp., *Poa* spp. and *Paspalum* spp. (Korkusuz, 2005). In this study, plant distribution and propagation varied according to the species planted in the pilot units. *P. australis*, which is considered as highly invasive, and *T. latifolia* were the species that were better established in the units, while the propagation and development of *Iris* spp. and *Canna* spp. was reduced. The former plants supported different hydraulic conditions. The potential of using *P. australis* and *T. latifolia* in CWs is found in literature in several studies dealing with domestic and industrial—tannery, dye-rich wastewater, food processing and high-strength winery—wastewater treatment (Vymazal, 2005; Vymazal and Kröpfelová, 2005; Mbuligwe, 2005; Kucuk et al., 2003; Shepherd et al., 2001; Vrhovšek et al., 1996). Vymazal (2005) also reported the successful use of *Iris* spp. (*pseudacorus* and *sibirica*) in CWs for urban wastewater treatment. In a similar manner to *Iris* spp. and *Canna* spp., the *S. secundatum* used in the present study was also clearly not suitable for tannery wastewater treatment as it was not able to survive. Less frequently used plants have also been tested in CWs for wastewater treatment. Klamkøj and Nitsoravut (2005) evaluated the feasibility of using CWs to remove pollutants from saline wastewater using eight emergent plants. They reported that among *Typha angustifolia*, *Digestaria bicornis*, *Cyperus corymbosus*, *Brachiaria mutica*, *Vetiveria zizaniodes*, *Spartina patens*, *Leptochloa fusca* and *Echinodorus cordifolius*, the first two, *T. angustifolia* and *D. bicornis*, were clearly superior for nitrogen uptake and BOD\(_5\) removal. Maine et al. (2006), in a free water surface CW, tested several locally available macrophytes (*Eichhornia crassipes*, *Typha domingensis* and *Pontederia cordata*) in order to treat wastewater from a metallurgic industry, aiming at nutrient and metal removal. The *E. crassipes* became dominant and covered about 80% of the water surface, and *T. domingensis* and *Panicum elephantipes* developed as accompanying species, with 14% and 4% cover, respectively. The tannery wastewater applied to the CWs, in the present study, may have a negative effect upon the growth of wetland species due to the complexity of its composition. There are several possible causes for the inhibition of plant growth, such as the presence of toxic levels of contaminants and deficiency of nutrients for plant development. The pH of the substrate may have also influenced plant growth. In the first weeks of application of the wastewater to the plant units, the inflow was slightly alkaline and the outflow wastewater was strongly alkaline, as the pH of the substrate was strongly alkaline (9.75). With time, the outflow pH stabilized to moderately alkaline. The optimum pH for plant development is considered to be between 3.0 and 8.5 for *T. latifolia*, 3.7 to 8.0 for *P. australis*, 6.0 to 7.5 for *I. pseudacorus* (USEPA, 2000a), 5.3 to 7.5 for *C. indica* (Jett, 2005) and 6.0 to 8.5 for *S. secundatum* (Smith and Valenzuela, 2002). It is possible that the plants could have had some difficulty in developing and propagating considering that the pH of the matrix, particularly at the beginning of operation, was out of their optimum range.

CWs with subsurface horizontal flow usually provide high removal of organic matter (BOD\(_5\) and COD) and suspended solids but lower nutrient removal (Vymazal, 2005; Kadlec et al., 2000). In this study, for the HLR of 3 cm d\(^{-1}\), the maximum removal efficiency in terms of COD was 67% for an average inflow of 1966 mg O\(_2\) L\(^{-1}\) (590 kg ha\(^{-1}\) d\(^{-1}\)), 55% for BOD\(_5\) for an average inflow of 875 mg L\(^{-1}\) (263 kg ha\(^{-1}\) d\(^{-1}\)) and 92% for TSS for an average inflow of 75 mg L\(^{-1}\) (23 kg ha\(^{-1}\) d\(^{-1}\)). Concerning the HLR of 6 cm d\(^{-1}\), the maximum removal efficiency in terms of COD was 73% for an average inflow of 2093 mg O\(_2\) L\(^{-1}\) (1256 kg ha\(^{-1}\) d\(^{-1}\)), for BOD\(_5\) was 58% for an average inflow of 898 mg L\(^{-1}\) (539 kg ha\(^{-1}\) d\(^{-1}\)) and for TSS was 77% for an average inflow of 79 mg L\(^{-1}\) (47 kg ha\(^{-1}\) d\(^{-1}\)). The COD at the outlet of the CWs was in average 850 (±191) mg O\(_2\) L\(^{-1}\) despite the different HLRs applied, which may indicate that a part of the COD from the tannery wastewater is not readily biodegradable in the system under the different hydraulic retention times tested. Daniels (2001a) reported that in the first year of operation of a five-day retention time pilot root–zone treatment with reeds, 80–85% of the COD of a tannery effluent was removed, for an inlet COD level ranging from 1000 to 2000 mg L\(^{-1}\). In another study reported by the same author, carried out with effluent of the manufacture of finished shoe upper leather from multisource wet blue with a typical COD inflow of 1160 mg L\(^{-1}\), reductions of 85%, 82% and 70% COD were obtained, for an average inflow of 1160 mg L\(^{-1}\), 2200 mg L\(^{-1}\), 3300 mg L\(^{-1}\), respectively. The removal of organic matter and nutrient removal efficiencies, Kucuk et al. (2003) reported a maximum COD removal of 58% for an average inflow of 79 mg L\(^{-1}\). Despite the different HLRs applied, which may indicated that a part of the COD from the tannery wastewater is not readily biodegradable in the system under the different hydraulic retention times tested. Daniels (2001a) reported that in the first year of operation of a five-day retention time pilot root–zone treatment with reeds, 80–85% of the COD of a tannery effluent was removed, for an inlet COD level ranging from 1000 to 2000 mg L\(^{-1}\). In another study reported by the same author, carried out with effluent of the manufacture of finished shoe upper leather from multisource wet blue with a typical COD inflow of 1160 mg L\(^{-1}\), reductions of 85%, 82% and 70% COD were obtained, for CWs planted with two subspecies of *Glyceria maxima* and *Phragmites*, respectively, in a five day root–zone system. Both species proved to be extremely robust and survived shock dosing, long periods of drying out, total immersion and cold (Daniels, 1998). However, no detailed information is provided on the hydraulic loadings applied to the systems. In contrast with these high removal efficiencies, Kucuk et al. (2003) reported a maximum COD removal of 30% for a tannery wastewater with an inlet concentration of 300 mg L\(^{-1}\), using a hydraulic retention time of 8 days. It is thus clear that the specificity of the different tannery wastewaters affect their biodegradability in a CW.

Nutrients removal occurred to lower extents, but was found to be within the range reported by other authors for subsurface horizontal flow CWs (Mantovi et al., 2003; García et al., 2005), although for different types of wastewater. Wetland plants are known to take up nutrients but this amount may be insignificant compared to the wastewater inflow loading (Brix, 1994, 1997). According to Vymazal (2005) the removal of nutrients (nitrogen and phosphorus) is usually low in CWs and does not exceed 50% when dealing with municipal sewage. Also, according to Tanner (2001), on an annual basis, the net accumulation of nutrients in plant tissues in mature wetlands is reduced. However, factors such as climate,
nutrient regime and type of plant can play a significant role in this mechanism (Vymazal, 2005; Tanner, 2001). The phosphorus uptake capacity of macrophytes is reported to be lower than the nitrogen uptake capacity (Brix, 1994). In the present study, due to the low inflow levels of phosphorus, we cannot infer about the capacity of the different plants to remove it from the wastewater. The removal of chromium was also negligible in the present study, but it is possible that differences in chromium removal would have been achieved between the units if the concentration of the metal in the effluent was higher, as different plants have different capacities to remove heavy metals (Maine et al., 2006; Kadlec et al., 2000).

In the present study the ability of treating wastewater at high organic loading—typical of tannery wastewater—was evaluated. The organic loading removal achieved in the pilot units was high, up to 1092 kg COD ha\(^{-1}\) d\(^{-1}\), 456 kg BOD\(_5\) ha\(^{-1}\) d\(^{-1}\), and 45 kg TSS ha\(^{-1}\) d\(^{-1}\), increasing with the influent load in a linear correlation. This behavior corresponds to a first-order kinetics, showing that the removal rate was proportional to the inflow amount. In Tanner (2001) monotonic relationships between BOD and COD mass loading and removal rates are also presented, with little difference between planted and unplanted beds. Shepherd et al. (2001) used a CW for winery wastewater treatment with similar average organic loadings, varying between 345 and 1640 kg COD ha\(^{-1}\) d\(^{-1}\), and reported removal efficiencies of ca. 99%, while in the present study a maximum removal efficiency of 73% was achieved. For horizontal subsurface beds, some authors do not recommend the application of organic loadings higher than 67 kg BOD\(_5\) ha\(^{-1}\) d\(^{-1}\) (Metcalff and Eddy Inc., 1991) or out of the range of 67–157 kg BOD ha\(^{-1}\) d\(^{-1}\), and for TSS 45–168 kg TSS ha\(^{-1}\) d\(^{-1}\) (USEPA, 2000b). García et al. (2004) have reported that in order to obtain a BOD\(_5\) removal of 90%, for urban wastewater, an organic surface loading of 200 kg ha\(^{-1}\) d\(^{-1}\) should not be exceeded (based on the first year of operation system). For the treatment of tannery wastewater, there is a need for appropriate design parameters.

No significant differences were found between the planted and unplanted systems during the 17 months of operation of the systems. Plants can contribute to wastewater treatment processes in a number of ways, such as settlement of suspended solids, providing surface area for microorganisms, increasing uptake of nutrients and trace elements and providing oxygen release (Kadlec et al., 2000; USEPA, 2000a; Brix, 1994, 1997). The beneficial role of plants in CWs is not always evident, and that seems to depend on several parameters, such as the time length of operation, type of vegetation and characteristics of the wastewater. Huang et al. (2000) found no difference in the removal of ammonium and TKN from domestic wastewater as a result of the presence of plants in a CW. Baptista et al. (2003) also reported similar performances in a CW planted with Phragmites and in unplanted units, when treating filtered beer with an average BOD\(_5\) concentration of 104 mg L\(^{-1}\) (91% and 92% removal, respectively). The similar performance of the planted and unplanted beds obtained in the present study may be explained by the fact that the units had not reached maturity. A complete root–rhizome development for a newly CW may require 3–5 years (Kadlec et al., 2000). For Phragmites, three to four growing seasons are usually needed to reach maximum standing crop but in some systems it may take even longer (Vymazal and Kröpfelová, 2005). Vrhovšek et al. (1996) studied the application of CWs with Carex gracillis and P. australis to the secondary treatment of wastewaters from a food processing plant, showing that depuration improved with bed maturity, and after several years a continuous efficiency of more than 90% was obtained regarding the removal of BOD\(_s\), COD and orthophosphate. Other studies show improvements in performance in planted beds. Mbuligwe (2005) reported for the treatment of a dye-rich wastewater, with an organic loading of 106 kg COD ha\(^{-1}\) d\(^{-1}\), cattail and coco yam units outperformed an unplanted unit in terms of organic removal efficiency by 17.5–21.7%, being the organic removals of 86.8, 92.1 and 64.4 kg COD ha\(^{-1}\) d\(^{-1}\), respectively. However, there are authors who suggest that the primary benefits of vegetation in these systems may be mainly insulation and esthetics (Mæhlum and Sta˚lnacke, 1999).

The findings from this study show that the application of CWs systems to the treatment of tannery effluents may be an attractive approach for integrated secondary treatment, but longer term operation of such units is important to ascertain for the role and benefits of the plants in such systems.

**Conclusions**

The aim of this study was to investigate the application of different plant species in CWs receiving wastewater from a tannery production plant. The conclusions are as follows:

1. The plants T. latifolia and P. australis were the plant species better adapted to tannery wastewater in terms of survival and propagation.
2. CWs with horizontal subsurface flow seem to be a viable alternative for reducing the organic matter content from tannery wastewater, being able to tolerate inflow fluctuations, including interruptions in the feed.
3. Nutrient removal is low when compared with the removal efficiencies achieved for COD and BOD\(_s\).
4. The fact that the plant beds may have not reached maturity may contribute to the similar performance obtained for vegetated and unvegetated units.

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