



## Performance of pilot-scale constructed wetlands for secondary treatment of chromium-bearing tannery wastewaters

Gabriela Dotro<sup>a,\*</sup>, Silvana Castro<sup>b</sup>, Ofelia Tujchneider<sup>c,d</sup>, Nancy Piovano<sup>c</sup>, Marta Paris<sup>c</sup>, Ana Faggi<sup>d,e</sup>, Paul Palazolo<sup>f</sup>, Daniel Larsen<sup>g</sup>, Mark Fitch<sup>h</sup>

<sup>a</sup> School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK

<sup>b</sup> Instituto Nacional del Agua, Centro Regional Santa Fe, Patricio Cullen 6161, 3000 Santa Fe, Argentina

<sup>c</sup> Facultad de Ingeniería y Ciencias Hídricas, Universidad Nacional del Litoral, Ciudad Universitaria CC217, 3000 Santa Fe, Argentina

<sup>d</sup> Consejo Nacional de Investigaciones Científicas y Tecnológicas, Av. Rivadavia 1917, 1033 Ciudad Autónoma de Buenos Aires, Argentina

<sup>e</sup> Facultad de Ingeniería, Universidad de Flores, Camacú 245, Ciudad Autónoma de Buenos Aires 1406, Argentina

<sup>f</sup> Department of Civil Engineering, University of Memphis, Memphis, TN 38152, USA

<sup>g</sup> Department of Earth Sciences, University of Memphis, Memphis, TN 38152, USA

<sup>h</sup> Civil, Architectural and Environmental Engineering Department, Missouri University of Science and Technology, Rolla, MO 65409, USA

### HIGHLIGHTS

- ▶ Wetlands can enhance the reliability of primary treatment of industrial effluents.
- ▶ High removal rates for Cr, COD and TSS can be achieved.
- ▶ Chromium can be retained in wetlands with non-specialized media.
- ▶ Pilot testing resulted in improved design criteria than literature values.

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### ABSTRACT

Tannery operations consist of converting raw animal skins into leather through a series of complex water- and chemically-intensive batch processes. Even when conventional primary treatment is supplemented with chemicals, the wastewater requires some form of biological treatment to enable the safe disposal to the natural environment. Thus, there is a need for the adoption of low cost, reliable, and easy-to-operate alternative secondary treatment processes. This paper reports the findings of two pilot-scale wetlands for the secondary treatment of primary effluents from a full tannery operation in terms of resilience (i.e., ability to produce consistent effluent quality in spite of variable influent loads) and reliability (i.e., ability to cope with sporadic shock loads) when treating this hazardous effluent. Areal mass removal rates of 77.1 g COD/m<sup>2</sup>/d, 11 g TSS/m<sup>2</sup>/d, and 53 mg Cr/m<sup>2</sup>/d were achieved with a simple gravity-flow horizontal subsurface flow unit operating at hydraulic loading rates of as much as 10 cm/d. Based on the findings, a full-scale wetland was sized to treat all the effluent from the tannery requiring 68% more land than would have been assumed based on literature values. Constructed wetlands can offer treatment plant resilience for minimum operational input and reliable effluent quality when biologically treating primary effluents from tannery operations.

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### 1. Introduction

Tannery operations consist of converting raw animal skins into leather through a series of complex water- and chemically-intensive batch processes. These processes can be roughly divided into four main groups: beamhouse, tannyard, post-tanning, and finishing operations; each of these can contain between 10 and 16

steps and will generate a different waste stream [1]. This wastewater is very complex and constitutes the most difficult problem among tannery wastes [2]. The amount, type and quantities of the chemicals and water used change depending on the tannery operation itself, i.e., at “full” operation all four stages are performed in one location or “wet blue” operation where only post-tanning and finishing operations are performed; the type of hide to process (e.g., bovine, game, etc.); and the individual tanneries’ methods and desired end products [1]. Conventional treatment of full tannery operation wastewaters typically involves separate chemical pre-treatment of chromium (i.e., tannyard) and sulfide bearing effluents

\* Corresponding author. Tel.: +44 (0)1234 750111x3336.

E-mail address: [g.c.dotro@cranfield.ac.uk](mailto:g.c.dotro@cranfield.ac.uk) (G. Dotro).

(i.e., beamhouse), and segregation of these from the main “general” effluent [3]. This general effluent consists of the rinses from each batch process and can therefore contain a diverse and complex chemical mixture, making them notoriously difficult to treat.

Currently available technologies for tannery wastewater treatment involve the use of a combination of primary treatment and energy-intensive processes like activated sludge and advanced oxidation processes [4–6]. It has been shown that even when conventional primary treatment is supplemented with chemicals the general wastewater still requires some form of secondary (biological) treatment process to enable the safe waste disposal into the natural environment [7]. Full tannery operations are typically located in the developing world, where hides and lower cost labor are readily available [1]. As a result, there is a real need for the adoption of low cost, reliable, and easy-to-operate alternative secondary treatment processes. Horizontal, subsurface flow constructed wetlands have the potential of addressing this challenge. In fact, wetlands have been successfully applied in trial studies to polish the effluents from conventional wastewater treatment plants [8,9], polish wet blue effluents [10,11], and treat wastewaters with high chromium contents [12–14]. However, their performance in terms of reliability and resilience when used as the sole secondary treatment process of a complete tannery operation has yet to be assessed.

This paper reports the findings of two pilot-scale wetlands for the secondary treatment of primary-treated effluents from a full tannery operation in Argentina during one year. The main challenges were the high solids content and the elevated and widely variable chemical composition when compared against current wetland applications. The technology is assessed in terms of resilience (i.e., ability to produce consistent effluent quality in spite of variable influent loads) and reliability (i.e., ability to cope with sporadic shock loads) when treating this hazardous effluent. The wetlands were also designed and tested in terms of their ability to provide treatment security in terms of effluent chromium content.

## 2. Materials and methods

This study had two parts: a lab-scale determination of chromium retention and regeneration capacity, and a pilot-scale application of the wetlands at a tannery. Both phases used primary-treated wastewaters from a local tannery (Fig. 1).

### 2.1. Laboratory determination of chromium retention and regeneration capacity

The laboratory study used small volumes of rock to treat Cr-spiked tannery wastewater in a batch system. Two types of rocks were tested in duplicate: river gravel (control) and granitic rock (selected media). Both media were sieved to a diameter of 4.75–8 mm. The surface areas and cation exchange capacities were 0.69 m<sup>2</sup>/g and 2.06 meq/100 g for the granitic rock, and 4.27 m<sup>2</sup>/g and 1.08 meq/10 g for the gravel, respectively. Surface area was determined by BET and CEC by the BaCl<sub>2</sub> compulsive exchange method [15]. The batch reactors consisted of 100 g of rocks placed in 125 mL PVC containers and allowed to react with 50 mL of fresh wastewater spiked with tanning bath solution (Cr content = 1800 mg/L, pH 4) to yield test Cr concentrations ranging between 0.1 and 32 mg/L at pH 6.8–7. After 24 h, the effluents were collected for analysis, the rocks rinsed with 50 mL of distilled water (DI), and 50 mL of 4M HCl added to each reactor to test for desorption. The selection of HCl as the de-sorbing agent was based on previous studies where it was suggested that HCl would be among the most effective chemicals to release sorbed chromium [16–18]. After 24 h, the reactors were emptied, the effluent analyzed, the

media rinsed with DI, and 50 mL of fresh solutions with the initial concentrations of chromium were added to each reactor. Total Cr determinations were made at the start and end of each treatment with Hach test kits (Hach Chemical Co, USA) using a colorimetric method [19]. Preliminary tests were conducted to ensure the 24 h reaction time was adequate for Cr sorption onto the rocks surfaces (Dotro et al., unpublished data). All experiments were run at 20 °C. Subsamples of the rock sorption media were analyzed by X-ray diffraction before and after the sorption experiments to evaluate mineralogical and chemical changes resulting from reaction. The rock samples were ground to a fine powder in a mechanical mortar prior to X-ray diffraction analysis using a Bruker D8 Discovery X-ray diffraction unit. The powdered samples were scanned from 3 to 65° 2 $\theta$  using a step of 0.030° 2 $\theta$  and count time of 2 s/step. The area under the strongest peak for each identified phase was used to quantify the mineral abundance using the reference intensity ratio relative to corundum. The precision of this method is generally within 10–15% of actual mass % and is considered semi-quantitative.

### 2.2. Treatment wetlands

The pilot systems were installed on the premises of a small tannery in Argentina that processes animal hides from small game animals into finished leather via chrome tanning. The operation produces three streams of wastewater for treatment: (a) tanning and re-tanning liquors, which contain trivalent chromium in excess of 560 mg/L, (b) beamhouse operation effluents, which contain sulfides in excess of 185 mg/L, and (c) general effluent, consisting of various wash waters from different steps along the tanning operation (Fig. 1). Two identically-sized wetlands were built after the primary treatment units with dimensions 3 m  $\times$  1.5 m  $\times$  1 m (L  $\times$  W  $\times$  D), filled with clean granitic rock (diameter 0.1–20 mm) to a depth of 0.7 m. The water level was kept at 10 cm below the rock surface. The influent distribution consisted of a metal trough which overflowed onto the beds. Both systems were planted at 4 shoots/m<sup>2</sup> with *Typha latifolia* specimens collected from a nearby natural wetland. The plants were chosen based on their proven ability to tolerate the salinity and chromium levels typically found in tannery wetlands [10,12]. The flow rate to each system was regulated before the trough through individual valves and was fed continuously five days a week. One unit was labeled “Wetland H”, the other “Wetland L”; Wetland H received a hydraulic loading rate of 0.1 m/d and Wetland L received 0.048 m/d. At a measured porosity of 0.4, the average hydraulic residence time in Wetlands H and L were 2.4 and 5 days, respectively.

### 2.3. Field sampling and testing

Wastewater was collected at the inlet and outlet of each system and taken to the laboratory within 2 h for same-day processing. Sampling and analysis were conducted once a week during the first three months of the study and biweekly thereafter. All samples were analyzed according to Standard Methods [19] for chemical oxygen demand (COD), suspended solids (TSS and VSS), total chromium (Cr), pH, dissolved oxygen (DO), conductivity, and temperature. Three random samples from both the inlet and outlet were tested for COD and 5-day biochemical oxygen demand (BOD<sub>5</sub>) to determine the COD:BOD<sub>5</sub> ratio for design interpretation purposes. Results are presented for the first 420 days of the study.

An internal sampling campaign was conducted after 6 months of starting wetland operation to determine operating conditions within the beds. Samples were collected at three locations longitudinally from inlet to outlet and two depths (0.25 and 0.4 m) from the rock surface. Each point within the bed was analyzed with portable probes to determine wetland pore water pH, DO,

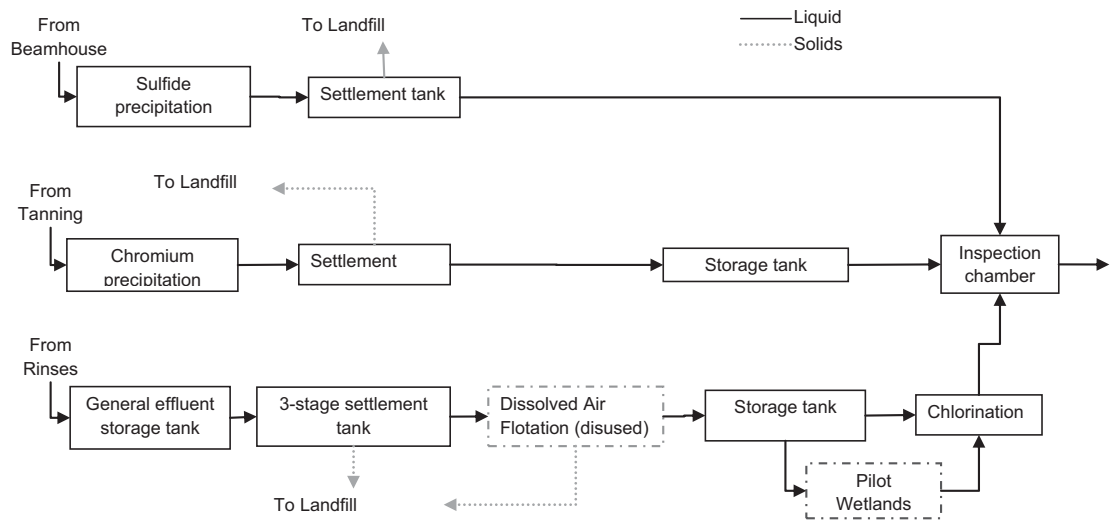


Fig. 1. Schematic of tannery operation effluent treatment units.

**Table 1**  
Parameters of Freundlich isotherms fitted to equilibrium data for the sorption and re-sorption stages of the experiments.

| Media and stage           | 1/n  | k                      | r <sup>2</sup> |
|---------------------------|------|------------------------|----------------|
| Gravel–Sorption           | 1.2  | 9.7 × 10 <sup>−4</sup> | 0.96           |
| Gravel–Re-sorption        | 0.89 | 3.3 × 10 <sup>−4</sup> | 0.96           |
| Granitic rock–Sorption    | 1.1  | 1.0 × 10 <sup>−3</sup> | 0.98           |
| Granitic rock–Re-sorption | 0.91 | 9.5 × 10 <sup>−4</sup> | 0.85           |

oxidation-reduction potential (ORP), and temperature at the time of sample collection.

All data were adjusted for evapotranspiration using the Penman method with government records for weather data for the monitoring period. The adjusted data were tested for normality and analyzed for significance with the *t*-statistic using GraphPad Prism v5.0. All tests were conducted at the 0.05 level of significance. Resilience curves were drawn based on percentile effluent concentrations. Resilience is defined here as the ability of a treatment unit to produce consistent effluent quality under varying influent characteristics. The resilience curve is generated by plotting effluent concentrations against percentile distributions of the data.

3. Results

3.1. Media chromium retention and regeneration capacity

Both rock types were efficient at retaining chromium, with 57–83% and 67–77% efficiencies in the first run for the gravel and granitic rocks, respectively (Fig. 2). Freundlich isotherm fitting was attempted for both sorption runs, with significant correlations found in most cases, except for the granitic re-sorption run (Table 1). This analysis assumes that chromium removal was only due to sorption. The exponent coefficients (1/n) were above 1 for the initial sorption in both rocks and below 1 post-treatment, indicating a small deterioration in sorption intensity.

The chromium retention ability of the granitic and gravel were significant considering their limited surface area and cation exchange capacities. For comparison, a good sorbent such as zeolite has been reported to have 29 meq/100 g for cation exchange capacity [21]. Other good sorbents have significantly higher surface areas, such as activated carbon with 638 m<sup>2</sup>/g against the 0.67 m<sup>2</sup>/g area for the rocks tested in this study. Whereas chromium retention is only expected to be a secondary goal for the treatment wetlands in

this application, it is an additional benefit that chromium could be retained.

Interferences with Cr analysis in the desorption test impeded the analysis of the first four sets of duplicates (i.e., Cr concentrations from 0.1 to 14.5 mg/L). From the samples that could be analyzed, chromium mass recoveries were variable, with higher efficiencies achieved from the gravel (50 to 73%) than the granitic rocks (18 to 53%). However, though high efficiencies were achieved for the gravel, the acid appears to have a negative effect on the granitic rock through dissolution of iron-bearing phases, hornblende and biotite (Fig. 3). This corresponded with a release of up to 300 mg/L of ferrous iron from granitic rocks as opposed to a maximum of 110 mg/L released from the gravel during this desorptive treatment.

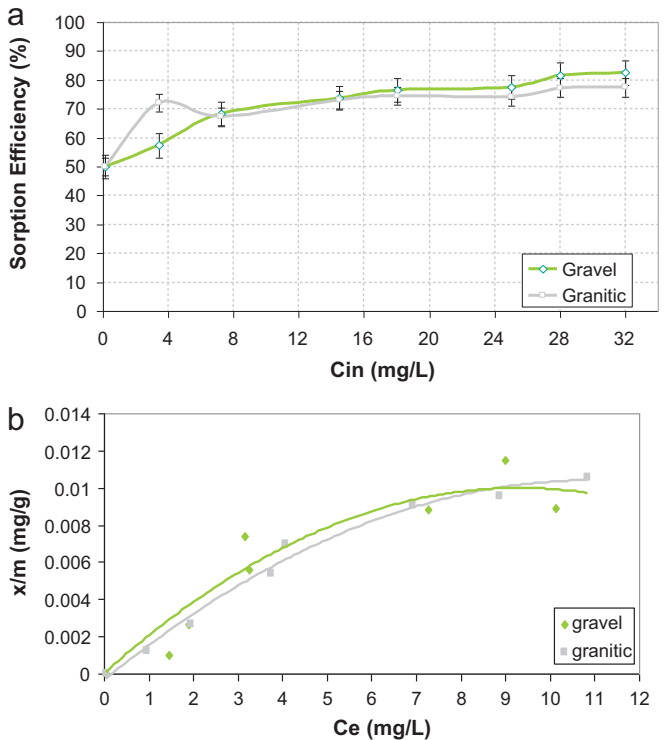
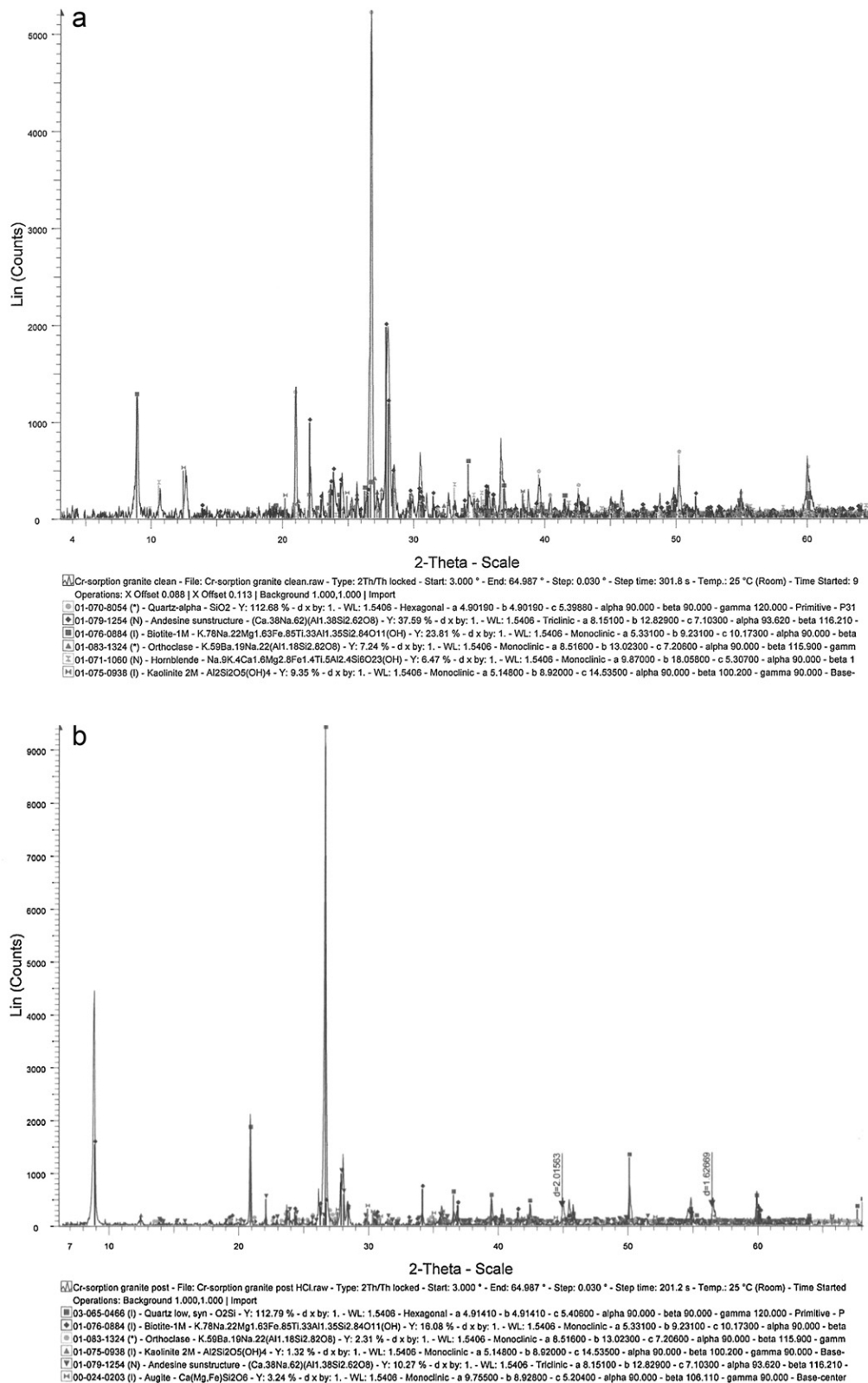


Fig. 2. Sorption results for total chromium (a) retention efficiencies, (b) Freundlich isotherm fitting.



**Fig. 3.** Effect of 4M hydrochloric acid treatment on granitic rocks, (a) rocks before acid treatment showing predominance of quartz (57%), but also significant feldspar (23%), biotite (12%), hornblende (3%) and kaolinite (5%), (b) rocks after acid treatment with predominance of quartz (79%) but lesser quantities of feldspar (9%), biotite (11%) and kaolinite (1%), and absence of hornblende.

Given that the influent iron was c. 0.5 mg/L and that hornblende and biotite is diminished in abundance in the post-reaction X-ray diffraction results, the effluent iron concentrations at the end of this treatment are most likely a result of dissolution of these

iron-rich phases. It is possible that other components from the rocks were dissolved and were responsible for the Cr assay interferences. However, as this interference was present in both types of rocks it is more likely that it was associated with other tannery effluent

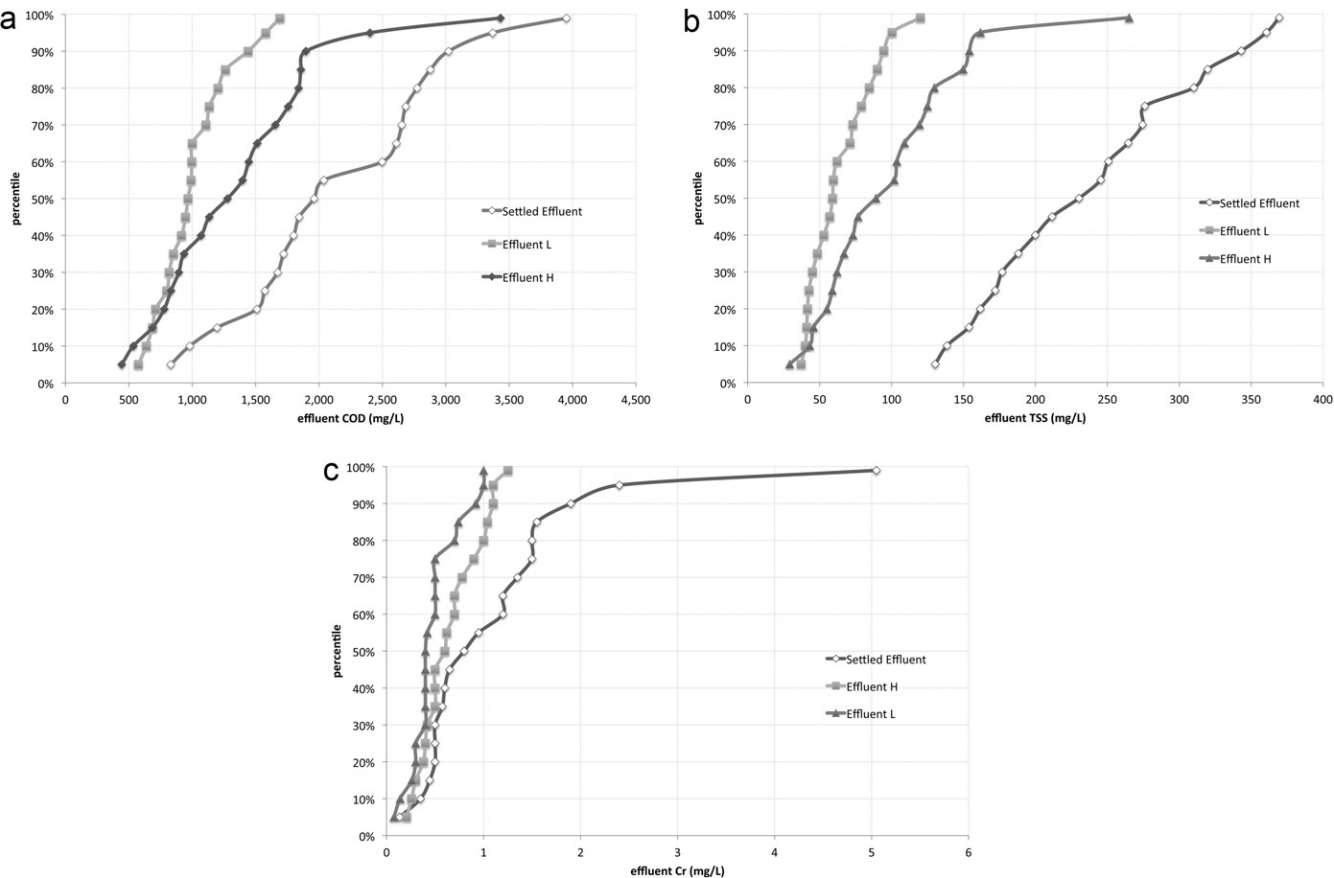


Fig. 4. Resilience curves for settled effluent (i.e., from existing settling tanks) and secondary (wetland treatment) effluents for (a) COD, (b) TSS, and (c) Cr. *n* = 28.

chemicals that were retained in the rocks and were subsequently released with the acid treatment. The loss of these phases explains the observed decline in sorption efficiency and suggests that acid washing, though efficient for desorption, has a long-term negative effect on reuse of the media.

3.2. Wetland performance

Plant establishment was remarkable in both wetlands, in spite of planting during the winter season. There was no difference in plant development in the pilot systems and, after eight months of operation, the entire surface of both wetlands was 100% covered by new plants. The plants showed no visual signs of stress.

Average concentration in and out of the wetlands were on the high end of the expected values for all parameters, except chromium were mean influent concentrations were 1.1 mg/L (Table 2). The influent to the wetlands was highly variable, with COD measurements ranging between 560 and 4134 mg O<sub>2</sub>/L, total suspended solids 101–372 mg/L, and chromium concentrations

between 0.08 and 5.9 mg/L. This variability was expected due to the batch nature of the industrial process and was successfully attenuated by the wetlands in all cases, as illustrated in the ninety-five percentile effluent concentrations and the slope of the resilience curves for Cr, TSS and COD (Fig. 4). Results show resilience was impacted by loading rate, with significantly lower 95%-ile effluent concentrations found for all parameters under lower loading rates. Although effluent concentrations were above what is typically expected of a secondary treatment wetland, the systems proved reliable and resilient under the high loading rates (and associated short residence time) and variable composition of the wastewater employed in this study.

Both systems resulted in significant improvement of the wastewater quality in terms of organic matter, solids and chromium effluent concentrations (*p* < 0.05). The performance of the wetland systems in terms of organic matter and solids removal rates were significantly higher in the highly loaded wetland than in the low loading system (*p* < 0.05). Effluent concentrations of COD were found to correlate closely with COD loading rates for both wetlands, with greater agreement found in the highly loaded systems (*r*<sup>2</sup> = 0.94 and *r*<sup>2</sup> = 0.69 for high and low loading systems, respectively; Fig. 5). This linear relationship between loading rate and effluent concentrations is important for selecting an adequate areal loading rate for any full-scale wetland if a target effluent concentration is to be reliably achieved.

Chromium content in the general effluent (influent to the systems) was consistently low and therefore a clear relationship between media sorption potential and observed efficiencies was absent (*p* > 0.05). Chromium removal rates were lower than expected based on previous studies with synthetic effluent [22] and media pre-trials. This is to be expected as sorption efficiencies

**Table 2**  
Summary of average influent and effluent concentrations in pilot wetlands.

| Parameter                  | Influent (settled effluent) | Wetland H effluent | Wetland L effluent |
|----------------------------|-----------------------------|--------------------|--------------------|
| COD (mg O <sub>2</sub> /L) | 2104                        | 1333               | 979                |
| TSS (mg/L)                 | 208                         | 98                 | 64                 |
| VSS (mg/L)                 | 176                         | 73                 | 45                 |
| Cr (mg/L)                  | 1.1                         | 0.6                | 0.5                |
| pH                         | 6.9                         | 7.5                | 7.6                |
| Conductivity (mS)          | 8.8                         | 7.5                | 7.5                |
| Temperature (°C)           | 19.1                        | 19.2               | 19.2               |

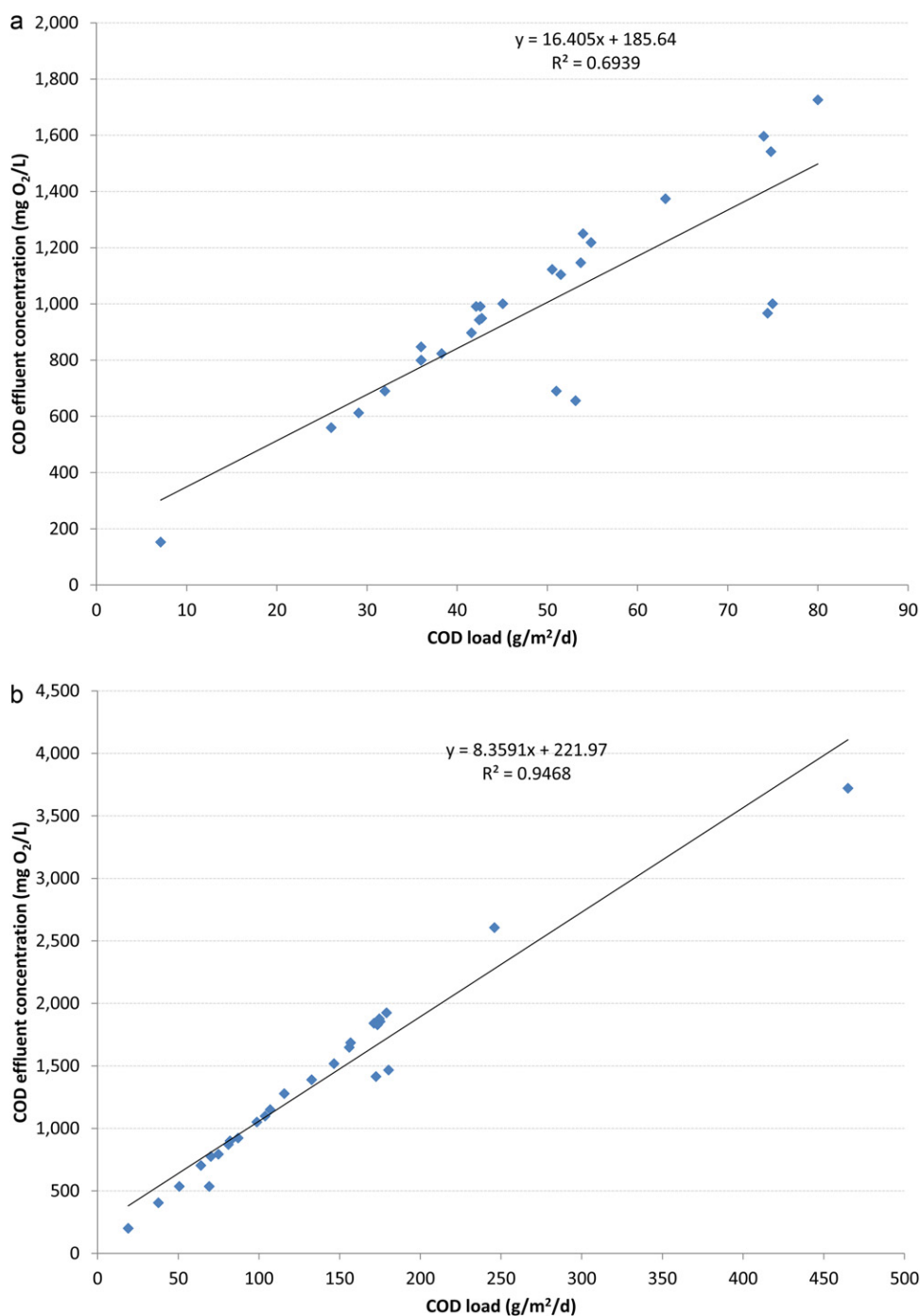


Fig. 5. Relationship between loading rates and removal rates observed in (a) Wetland H, (b) Wetland L.

are significantly affected by initial concentration values. The fact that removal rates were halved when loading rates were halved in the present study further supports this assertion.

### 3.3. Wetland operating conditions

The internal sampling campaign results suggest the wetlands were mainly operating under reducing conditions and were DO-limited, averaging 0.2 and 0.4 mg O<sub>2</sub>/L and −328 and −270 mV for DO and ORP, respectively. No direct correlation between the environmental conditions and effluent concentrations was observed ( $p > 0.05$ ). A pattern was, however, observed for liquid phase concentrations of COD and Cr concentrations throughout the wetland

bed, with decreasing values from inlet (average of depth 0.25 and 0.4 m) to outlet (average of 0.25 and 0.4 m) in both pilot wetlands (Fig. 6) [23].

Analysis of accumulated solids within the beds showed total suspended solids accumulated preferentially at the inlet of Wetland L and in the middle of Wetland H (data not shown). The average solids accumulation for the pilot systems were 460 g/m<sup>2</sup> and 544 g/m<sup>2</sup> for Wetland H and L, respectively. In the influent, between 24 and 98% of the total suspended solids were volatile solids as determined by ignition at 550 °C. This percentage of organics was significantly reduced in the accumulated solids, with a maximum of 17% VSS of the total mass recovered in Wetland L [24–26].

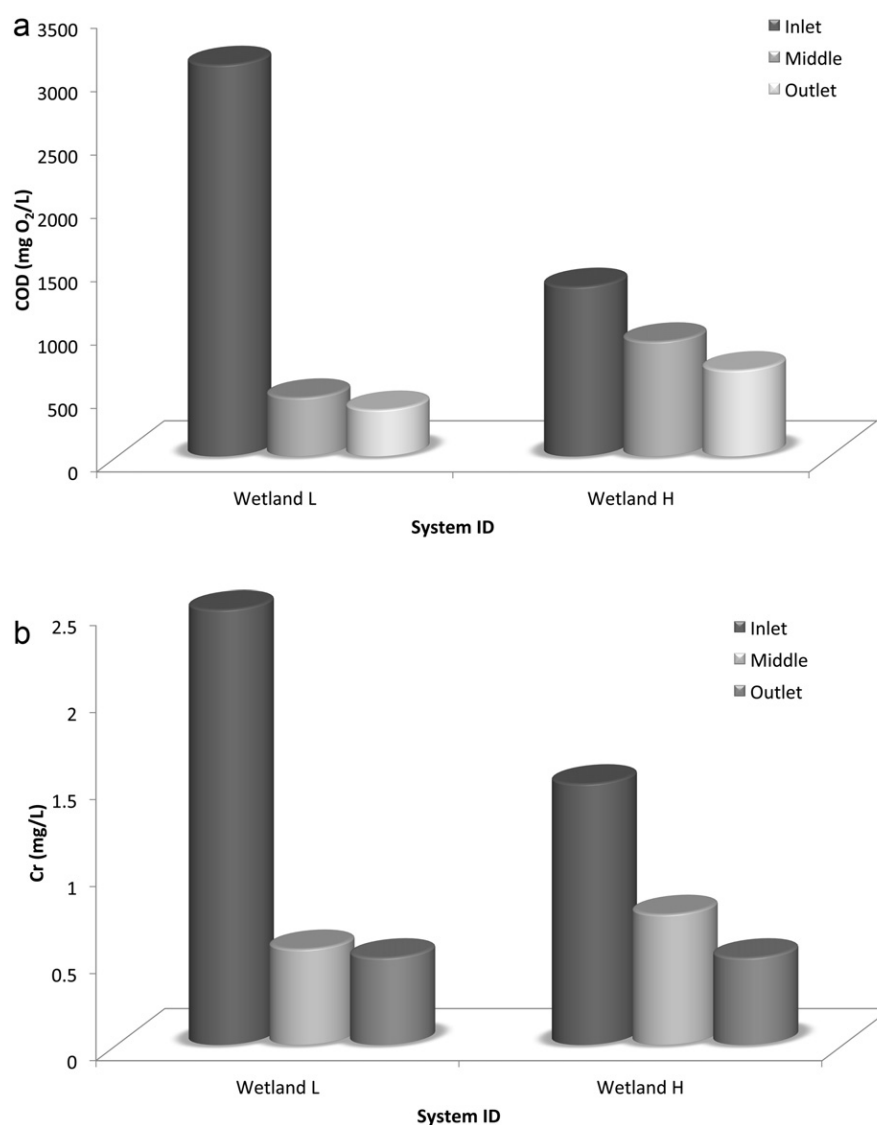


Fig. 6. Spatial profiles for (a) COD and (b) Cr in treatment wetlands.

#### 4. Discussion

Two pilot systems were built at a local tannery to assess the potential of using constructed wetlands for industrial effluent treatment. The work involved a full year of monitoring of influent and effluent quality, an internal sampling campaign and supporting laboratory-scale work to select a media that could provide additional environmental protection through chromium sorption. While it is recognized that tannery effluents contain a complex mixture of chemicals and thus, other pollutants may be of interest, this study limited the analysis to chromium as a hazardous pollutant, solids as conventional pollutant and aggregated measures of organic matter (i.e., COD) rather than focus on all chemical components (e.g., dyes, solvents, etc.). The results are interpreted in terms of the resilience, reliability and wetland design implications for this industrial wastewater treatment application.

##### 4.1. Wetland resilience and predominant removal mechanisms

To date, no study has presented results from secondary treatment of a full tannery; thus, the comparative performance of the systems has been assessed based on key similarities with other

wastewater (i.e., target parameters) and their treatment wetland systems (i.e., similar hydraulic loading rates; Table 3). The mass loading rates of this study are on the highest end of the spectrum for COD, TSS and Cr reported in tannery, domestic, and synthetic tanning wastewater for each parameter, respectively. As a result, effluent COD values are still relatively high but the removal rates are among the highest reported in the literature, with Cr removal rates being second only to systems that were fed synthetic tannery waste with lower COD loading and no suspended solids. Solids removal rates were similar to those obtained in domestic wastewater treatment systems, suggesting physical removal mechanisms were not impacted by the change in media used in this study.

The tannery wastewater is expected to have low chromium concentrations when pre-treatment is functioning correctly. In addition to secondary treatment of this effluent at all times, the wetlands were expected to provide some attenuation of the sporadic chromium pulses coming from the various washing operations and/or during catastrophic failure of the pre-treatment units. While the latter did not occur during this study, the wetlands did provide enhanced effluent quality in terms of chromium content. Enhanced quality was shown not only in terms of average and 95th percentile concentrations, but also in the overall distribution of

**Table 3**  
Mass loadings and removal rates in studied wetlands and reported rates for tanning/chromium removal in the literature.

| Reference  | System name  | Wastewater                 | Treatment stage | Hydraulic loading (cm/d) | COD              | Suspended solids              |                               | Total chromium                 |                                |       |  |
|------------|--------------|----------------------------|-----------------|--------------------------|------------------|-------------------------------|-------------------------------|--------------------------------|--------------------------------|-------|--|
|            |              |                            |                 |                          |                  | Loading (g/m <sup>2</sup> /d) | Removal (g/m <sup>2</sup> /d) | Loading (mg/m <sup>2</sup> /d) | Removal (mg/m <sup>2</sup> /d) |       |  |
| [27]       | UT 1         | Wet blue processing        | Polishing       | 8                        | 153              | 79                            | 8.6                           | 6                              | 3.4                            | 3.4   |  |
|            | UT 1         |                            |                 | 6                        | 96               | 63                            | 4.8                           | 3.4                            | 22.2                           | 12.8  |  |
|            | UT 2         |                            |                 | 6                        | 33               | 18                            | 1.4                           | 0.9                            | 9.4                            | 2.9   |  |
| [8]        | NA           | Tanning                    | Polishing       | 6                        | 12               | 1.4                           | n/d <sup>a</sup>              | n/d <sup>a</sup>               | 10.9                           | 4.9   |  |
|            | NA           |                            |                 | 4                        | 9.6              | 2.2                           | n/d <sup>a</sup>              | n/d <sup>a</sup>               | 4.7                            | 2.3   |  |
| [28]       | NA           | Domestic                   | Polishing       | 8                        | n/d <sup>a</sup> | n/d <sup>a</sup>              | n/d <sup>a</sup>              | n/d <sup>a</sup>               | 0.24                           | 0.16  |  |
| [29]       | Moina        | Domestic                   | Secondary       | 3.1                      | 21.5             | 17.5                          | 11.9                          | 11.6                           | 0.21                           | 0.15  |  |
|            | Brehov       |                            |                 | 3.2                      | 15.4             | 11.6                          | 5.6                           | 5                              | 0.36                           | 0.24  |  |
|            | Slavosovice  |                            |                 | 3.5                      | 7                | 4.7                           | 1.9                           | 1.3                            | 0.1                            | 0.03  |  |
| [12]       | Control      | Synthetic tanning effluent | Polishing       | 2.67                     | 14.2             | 13.5                          | n/d <sup>a</sup>              | n/d <sup>a</sup>               | 135                            | 132.6 |  |
|            | Intermittent |                            |                 |                          |                  |                               |                               |                                |                                |       |  |
|            | Unplanted    |                            |                 |                          |                  |                               |                               |                                |                                |       |  |
|            | Peat-based   |                            |                 |                          |                  |                               |                               |                                |                                |       |  |
| This study | Wetland H    | Tanning                    | Secondary       | 10                       | 210              | 77.1                          | 21                            | 11                             | 113                            | 53    |  |
|            | Wetland L    |                            |                 | 4.8                      | 101              | 54                            | 10                            | 6.9                            | 54.3                           | 30.2  |  |
|            |              |                            |                 |                          |                  |                               |                               |                                |                                |       |  |

<sup>a</sup> n/d not determined or not reported.

values as illustrated by the spread of values between the 50% percentile (i.e., average) and 95% percentile, and the long tail of the settled effluent versus any of the wetland pilots (Fig. 4). While the systems were not able to meet the local standards for effluent COD as designed and operated here, they were able to produce TSS and Cr compliant effluents and significantly improved the water quality exiting the existing tannery treatment plant. Thus, the wetlands fulfilled their resilience target for secondary and for hazardous pollutant removal from primarily-treated tannery effluents.

Solids quantities as well as organic contents have been shown to influence clogging development in horizontal subsurface flow wetlands for domestic wastewater treatment applications [30]. For industrial wastewaters where biodegradability of solids can be limited, this is of particular importance. The solids accumulation pattern found within the pilot systems indicate greater volatile solids quantities at the inlet of the wetland, decreasing as the flow moves towards the outlet. This is in agreement with the intended plug-flow configuration of the beds (i.e., 2:1 length to width ratio), and has been observed for organic matter in other treatment wetlands [23].

Higher organic solids quantities at the inlet of wetlands have been associated with enhanced biofilm growth due to the greater abundance of nutrients [24–26]. In this study, the combination of high loadings and narrow width may have contributed to greater inlet solids accumulation and higher organic content of the accumulated solids. While the solids removal efficiency could be explained by physical entrapment, the fact that the characteristics of the accumulated solids differ significantly from the influent solids indicates significant biological activity is taking place in the wetlands with concomitant mineralization of the pollutants, as opposed to simple storage. This is in agreement with findings from other horizontal subsurface flow wetlands for domestic wastewater treatment [31]. Based on DO and ORP measurements performed within the wetland beds, organic degradation was taking place under anaerobic conditions. This has implications in terms of kinetics (slower rates) and reactor design (minimum residence time needed).

#### 4.2. Wetland design implications

Although constructed wetland technology has been in use for wastewater treatment applications for a number of decades [32], no standard design methodology is employed. The most commonly used empirical equations are variations of the Kickuth equation (Eq. (1)) for BOD removal, with changes made for nitrogen species [33], background concentrations [34] and hydraulic conditions within the bed [35]. The simplest form of the equation is:

$$A_h = \frac{Q \times \ln(C_{in}/C_{out})}{k_{BOD}} \quad (1)$$

where  $A_h$  is the wetland surface area in m<sup>2</sup>,  $Q$  is the flow rate in m<sup>3</sup>/d,  $C_{in}$  and  $C_{out}$  are the influent and effluent concentrations in mg/L, and  $k_{BOD}$  is the areal removal rate in m/d. The  $k$  values are typically derived from a number of full-scale wetland for a particular wastewater application (e.g., domestic wastewater treatment). Where this information is not available, pilot studies become vital in providing guidance in determining the correct sizing factor.

Eq. (1) was fitted to both studied wetlands based on average influent and effluent concentrations in this study and resulted in  $k_{BOD}$  values of 0.19 m/d and 0.06 m/d for the high and low loading systems, respectively. These areal removal rates are significantly lower than values reported for secondary treatment systems, typically at 0.35 m/day [36]. This could be due to the complex nature of tannery effluent. In fact, the values found are comparable to  $k_{BOD}$  values used for tertiary treatment systems in the literature [36–38]. This is of importance when sizing a wetland, as assumptions made

from the available literature would therefore be inadequate for this particular application. To illustrate, a full-scale wetland sized to treat the full effluent from the tannery ( $80 \text{ m}^3/\text{d}$ ) based on current findings to achieve the same effluent concentrations in this study would be  $800 \text{ m}^2$  at the high loading rate, whereas a system based on typically assumed secondary treatment values would result in  $475 \text{ m}^2$  [36] or  $674 \text{ m}^2$  if tertiary treatment wetland values are employed [38]. This would inevitably result in under-sizing of the treatment system and the wetlands would fail to reliably provide the desired effluent quality. While it is recognized that the  $k$  values are derived from a pilot study, the potential risk of over-sizing is considered low when compared against the impracticalities of building several systems at full-scale to derive a more precise scaling factor. As the technology gains adoption in the industry, these  $k$  values will be refined and sizing of the systems will be more accurate.

Wetlands are invariably cited to be a low cost and low maintenance technology, especially when compared against conventional treatment technologies such as activated sludge. Recently, it has been recognized that sometimes the capital cost of so-called “conventional technologies” and secondary treatment wetlands can be similar [39,40], but wetlands continue to provide a low operational cost alternative to energy intensive processes. In regard to sustainability, the design proposed here has no external energy requirements. Thus, not only are there savings in energy use per se, but also the carbon emissions associated with energy use for driving aerobic degradation processes in conventional technologies are minimal. While the technology was primarily assessed in terms of reliability and resilience, the fact that it will be a lower carbon alternative to conventional secondary treatment must be highlighted. In addition, the lower operator skill and maintenance requirements of wetland technology make it an ideal match to small industries with difficult to treat effluents like tanneries. This is illustrated in (but not limited to) this specific case, as the tannery had installed an activated sludge plant years before this wetland trial and the technology had to be abandoned due to unsustainable operational costs and associated skilled labor required to run it. The constructed wetlands studied here present an ideal opportunity for providing secondary treatment at lower carbon emissions, cost and maintenance requirements than the failed activated sludge plant.

## 5. Conclusions

Tannery effluents are notoriously difficult to treat through biological processes due to their variable composition, batch production and associated concentrated, intermittent effluent generation, and chromium content. This study showed that mass removal rates of  $77.1 \text{ g COD}/\text{m}^2/\text{d}$ ,  $11 \text{ g TSS}/\text{m}^2/\text{d}$ , and  $53 \text{ mg Cr}/\text{m}^2/\text{d}$  can be achieved with a simple gravity-flow horizontal sub-surface flow unit operating at hydraulic loading rates of as much as  $10 \text{ cm}/\text{d}$ . The introduction of wetlands as the sole secondary treatment process resulted in a significant improvement of the effluent quality, attenuating peaks of Cr, TSS and COD. With the areal removal rates obtained in this study, a full-scale system would require a wetland 68% larger than otherwise designed based on available literature values. The passive configuration of the constructed wetlands makes them a low operational cost and lower carbon technology alternative to conventional aerobic treatment technologies.

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