Journal of Hazardous Materials 239–240 (2012) 142–151

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

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

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

[a] School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK
[b] Instituto Nacional del Agua, Centro Regional Santa Fe, Patricio Cullen 6161, 3000 Santa Fe, Argentina
[c] Facultad de Ingeniería y Ciencias Hídricas, Universidad Nacional del Litoral, Ciudad Universitaria CC217, 3000 Santa Fe, Argentina
[d] Consejo Nacional de Investigaciones Científicas y Tecnológicas, Av. Rivadavia 1917, 1033 Ciudad Autónoma de Buenos Aires, Argentina
[e] Facultad de Ingeniería, Universidad de Flores, Camacuá 245, Ciudad Autónoma de Buenos Aires 1406, Argentina
[f] Department of Civil Engineering, University of Memphis, Memphis, TN 38152, USA
[g] Department of Earth Sciences, University of Memphis, Memphis, TN 38152, USA
[h] 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.

ARTICLE INFO

Article history:
Received 15 March 2012
Received in revised form 20 August 2012
Accepted 21 August 2012
Available online 28 August 2012

Keywords:
Horizontal flow constructed wetlands
Chromium
Anaerobic
Solids
Sizing

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^2/d, 11 g TSS/m^2/d, and 53 mg Cr/m^2/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.

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 (G. Dotro).

0304-3894/$ – see front matter
http://dx.doi.org/10.1016/j.jhazmat.2012.08.050

(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^2/g and 2.06 meq/100 g for the granitic rock, and 4.27 m^2/g and 1.08 meq/10 g for the gravel, respectively. Surface area was determined by BET and CEC by the $BaCl_2$ 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° 2θ using a step of 0.030° 2θ 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 × 1.5 m × 1 m (LxWxD), 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^2 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_5) to determine the COD:BOD_5 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,