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Treatment of synthetic tannery wastewater in a continuous two-phase partitioning bioreactor: Biodegradation of the organic fraction and chromium separation

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ABSTRACT

A continuous two-phase partitioning bioreactor has been tested for treating a synthetic leather tannery wastewater with the objective of achieving effective removal of the organic load and complete chromium separation. The bioreactor was operated with 5.5 m of Hytrel 8206 polymeric tubing fed with a synthetic tannery wastewater consisting of 4-chlorophenol (concentration in the range of 1000–2500 mg L^{-1}) and potassium dichromate (100 mg L^{-1} as Cr (VI)), and immersed in a 4 L bioreactor containing the microbial culture acclimatized to the compound. This configuration prevents the direct contact between the toxic wastewater and the microorganisms themselves, and provides the gradual organic substrate delivery through the tubing walls. Abiotic partition and mass transfer tests were performed to investigate the transport of dichromate and 4-chlorophenol across the tubing into the bulk phase of the bioreactor. No appreciable mass transfer of dichromate was detected. During biotic testing, the influent organic load in tubing has been varied in the range of 19–94 mg h^{-1} and the hydraulic retention time from 3 to 6 h. Achieved biological removal efficiencies were in the range of 89–95% for the highest applied loads. Process kinetics (which included consideration of both mass transfer and biological rates) were evaluated, and it was found that the increased load did not result in any decrease in 4-chlorophenol removal rate. This work has shown that the continuous two-phase partitioning bioreactor has significant potential in enhancing the biological treatment of tannery wastewater, which is a typical representative of industrial “hostile” wastewater.

1. Introduction

The tanning industry is considered to be a major source of pollution producing noxious gases, such as hydrogen sulfide, as well as wastewater and solid wastes, which negatively affect ecosystems (Thanikaivelan et al., 2004). Leather manufacturing transforms raw skins into stable and finished leather products by means of three distinct processing units: 1) beam house operations, in which the skins are processed to clean and remove unwanted materials (e.g. hair, flesh) and are prepared for the subsequent tanning process, 2) the tanning step in which the hides are permanently stabilized against putrefaction, and 3) the post-tanning process, in which the leathers are finished to provide them with the required aesthetic appeal and to improve their commercial value. In each of these operations, large amounts of water and chemical additives are used giving rise to characteristic pollutant loads. Water consumption is generally highest in the pre-tanning stages (15–22 L of water per kg of hide processed), but significant amounts of water are also consumed in the tanning and post-tanning processes, e.g. 1–2 and 2–4 L per kg of hide processed, respectively (Raghava Rao et al., 2003).

Due to the variability of the raw materials and the desired end-product characteristics, tanning processes can produce different amounts and kinds of complex and hazardous wastewaters. The effluent production generally varies over a broad range, i.e. 10–100 m^3 per ton of rawhide (Lofrano et al., 2013), whose average composition can vary significantly. Organic substances (such as proteins, carbohydrates and lipids) present in tannery wastewater

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arise from the washed and treated skins, or are introduced during the tanning and post-tanning process as solvents, additives and biocides. The skins sorb only 20% of the chemicals used in the tanning process, with the remainder consisting of vegetable and synthetic tannins, oils, aldehydes, and zirconium, aluminum, titanium, and especially chromium salts entering the processing effluent (Chowdhury et al., 2015).

In the conventional treatment of tannery wastewater, tanning effluents are segregated and treated for chromium precipitation, then a physical treatment for chloride removal and a final biological treatment step, for removal of the residual organic load (Goswami and Mazumder, 2013) are applied. Unfortunately, this conventional approach can provide effluents that still do not meet the required discharge targets (Oller et al., 2011), and the presence of residual inorganic species such as chloride, sulphide, chromium etc., which are inhibitory for microbial growth, can limit traditional downstream biological treatment. For these reasons, tannery wastewater treatment still represents an important technological challenge. Advanced Oxidation Processes (AOPs), as a single treatment or as a pre-or post-treatment combined with biological processes, are among the most studied treatment strategies (Oller et al., 2011). Membrane processes can also be applied to treat tannery leather effluents in order to remove the salt content or to separate the biomass from the effluent after chemical–physical treatments (Cassano et al., 2001). An additional advantage of membrane processes is the recovery of chromium from residual effluents of leather tanning, which provides a significant economic advantage in terms of its reuse, besides the simplification of the wastewater treatment process (Cassano et al., 2007). De Gisi et al. (2009) applied Reverse Osmosis (RO) with a plane membrane as post-treatment to remove refractory organic compounds, thus obtaining a high quality permeate reusable within the production cycle.

Alternatively, a novel technological platform, based on two-phase partitioning bioreactors (TPPBs), has been recently proposed by Tomei et al. (2016) to treat industrial wastewater containing different pollutants including organic (potentially biodegradable), and inorganic species (i.e. heavy metals, salts). A modified TPPB has been configured by means of extruded polymer tubing immersed in a bioreactor, through which organic compounds can diffuse. A TPPB operated with mixed wastewater flowing through the tubing allows in principle the selective transport of toxic organic pollutants that are present "tubing side" to microbial cells located "bioreactor side", thereby generating a residual metal concentrated stream within the tubing that could be reused in the tanning process. The biodegradable substances transferred from the wastewater, through the tubing walls, are biodegraded without any direct contact between the wastewater and the microorganisms themselves. In addition, due to the gradual substrate delivery regulated by the metabolic processes, cells are exposed to sub-inhibitory concentration levels. When required, as in the case of tannery wastewater, the biodegradation of the organic matter and the separation for recovery of the inorganic components can be achieved simultaneously in a single operation unit.

Chlorinated phenols including 4-chlorophenol (4CP) have often been found in tannery wastewater (Reemste and Jekel, 1997; Mwinyihija, 2011), associated with chromium. In the tanning operation, basic chromium sulphate $[Cr(H_2O)_5(OH)SO_4]$ is the most widely used tanning agent; in hides/skins processing, the maximum utilization of chromium is usually 60–70%, and for this reason un-reacted chromium salts are found in very high concentrations in tannery wastewater (Goswami and Mazumder, 2013). Even if chromium VI (Cr (VI)) is not used in any step of the manufacturing process, its presence in the effluent from wastewater treatment plants arises from the oxidation of the trivalent to the hexavalent state (Fuck et al., 2011). Cr (VI) is carcinogenic and is generally considered 1000 times more toxic than Cr (III) (ATSDR, 2008). Accordingly, in this study, 4CP has been chosen as the target organic contaminant to simulate a tannery wastewater containing chlorides, and a Cr (VI) salt (potassium dichromate) was added to simulate chromium content. With this strategy, a literature review was preliminarily carried out to determine a representative concentration range for 4CP and dichromate, in order to adequately simulate an industrial tannery wastewater.

The objective of this study was to demonstrate the feasibility of a continuous TPPB (C-TPPB) system for treating a leather tannery wastewater achieving effective removal of the organic load and complete chromium separation for subsequent recovery. Experiments were conducted using Hytrel 8206 polymeric tubing, because its high affinity for chlorophenols has already been demonstrated in a previous study on soil decontamination (Tomei et al., 2015). Abiotic partition and mass transfer tests were performed to investigate the transport of dichromate and 4CP from the tubing into the bulk phase of the bioreactor. Biological testing included an investigation of the effect of varying the organic and hydraulic loadings on C-TPPB performance. Overall process kinetics (including mass transfer and biological rates) were evaluated under all the applied loading conditions.

2. Materials and methods

2.1. Synthetic wastewater

The test solution was a synthetic wastewater simulating a real tannery effluent whose selected constituents were 4CP, (CAS number 106-48-9, purity >99%) as organic matter and chloride source, and potassium dichromate ($K_2Cr_2O_7$), (CAS number 7778-50-9, purity >99%) as a source of Cr (VI). The reagents used were purchased from Sigma-Aldrich (USA) and were of analytical grade.

2.2. Polymer tubing

Tubing made of Hytrel 8206 polymer was used for all experiments, according to previous results reported by Tomei et al. (2017) in the use of this material. The tubing (with internal and external diameters of 0.5 and 0.6 cm, respectively), was supplied and extruded by DuPont Canada, has a glass transition temperature of −59 °C, a specific gravity of 1.17 and a flexural modulus (ASTM D790, at room temperature) of 80 MPa (Craig and Daugulis, 2014). Before use, a multistep washing with methanol and distilled water was undertaken according a procedure described elsewhere (Tomei et al., 2016) in order to remove any residual processing residues.

2.3. Microbial culture

A microbial consortium previously adapted to chlorophenols as described in Mosca Angelucci and Tomei (2015) and already utilized for the biodegradation of 4CP (Tomei et al., 2017), was cultivated with 4CP as the sole carbon and energy source for two months, with an organic loading rate within the range of 8–13 $mg_{4CP}\ h^{-1}$. A lab-scale Sequencing Batch Reactor (SBR) was employed for growing and maintaining the biomass between each C-TPPB experiment. Additional details of SBR equipment and operation are reported in the Supplementary Material section.

2.4. C-TPPB-bioreactor

The C-TPPB reactor consisted of a glass vessel (working volume 4 L) interfaced to a dedicated control computer and equipped with magnetic stirring and temperature control (T = 27 ± 0.5 °C),