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Tanning facility wastewater treatment: Analysis of physical–chemical and reverse osmosis methods

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ABSTRACT

The process of leather tanning produces harmful chemical and organic pollutants. This study explored physical and chemical treatment methods to efficiently treat the wastewater. Multiple wastewater streams representative of various stages in the tanning and wastewater treatment processes were initially characterized and subsequently treated through means of chemical coagulation and flocculation, adsorption, filtration and reverse osmosis. Through a series of jar test experiments, use of multiple industry-grade polymers as chemical coagulants greatly reduced chromium concentrations and turbidity levels. All samples had chromium levels below 5 mg/L (below USEPA standards). A combination of the polyamine resins was the most effective at reducing chromium concentrations within a short settling period of less than 20 min. Adsorption experiments utilizing titanium dioxide nanoparticles and activated carbon were conducted on the wastewater streams to determine chromium and nitrogen removal efficiency over a 24 h period. Poor adsorption of chromium occurred for both the nanoparticles and activated carbon, the activated carbon was successful in reducing nitrogen levels to about 40%. Additionally, reverse osmosis was used to determine the effectiveness of removing pollutants of concern and to determine its ability to recycle and reuse the wastewater in the tannery processes. Results showed that RO treatment could be used to treat the wastewater to conditions similar to the potable water used. Having tested four different methods for wastewater treatment, the use of polymers as coagulants was the most successful at removal of chromium and improvement in clarity as a conventional method. However, as an alternative method, the reverse osmosis system proved the most successful due to the pristine quality of water produced, especially as a potential for reuse within the tanning facility and potentially a cost effective, sustainable option.

Introduction

The existing methodologies of leather tanning produce a great amount of chemical and organic waste. The improvement of treatment technologies is of great importance for this age-old practice as it transitions into the 21st century. Local and federal environmental regulatory agencies across the globe are determined to control the detrimental environmental impact of tannery waste discharge. When tannery by-products are discharged into the sewage systems, proper disposal is of highest concern to the tanning facility as well as the local regulatory agency and treatment plants. Thus proper pre-treatment and discharge techniques are essential to limit any problems from tanning facilities [1]. According to the United States Environmental Protection Agency [2], there are a number of toxic air, liquid and solid waste pollutants produced directly or indirectly by tanning facilities. The most common pollutants include: chromium (III), copper, lead, zinc, chlorine, toluene, methyl ethyl ketone, glycol ether, acetone and sulfuric and phosphoric acids. Chromium discharges are often criticized because it is carcinogenic and thus have harmful effects on human health [3]. As chromium(III) is the key binding agent used throughout the tanning process, the prevalence in discharge is sought to be as low as possible through the implementation of appropriate, effective and innovative treatment techniques. Outside of basic physical treatment, treatment of tannery wastewater includes biological treatment, chemical treatment, ion exchange, adsorption, electrochemical and combinations of the aforementioned treatment processes [4]. Though other unique treatments have surfaced such as simulated wetlands [5] and reverse osmosis membrane technology [6], the traditional combination of physical–chemical treatments prevails. Specifically, according to the USEPA, additions of lime, soda ash and coagulating agents have been deemed most effective alongside gravity settling, screenings, filters and filter presses. If appropriate

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in-house treatment of wastewater is accomplished through these physical–chemical methods, the effluent can then enter municipal sewage systems if proper pre-treatment is conducted.

The following study attempts to determine the optimum physical–chemical wastewater treatment processes using wastewater from a leather tanning facility located in San Antonio, TX. This tanning facility both tans and finishes animal hides on-site at their facility. The tanning process follows the conventional protocol of chrome tanning. Chrome tanning, when done correctly, allows skins to preserve natural properties, retain a balanced chemical configuration and deter breakdown. The traditional treatment method of coagulation–flocculation is a critical step in deterring harmful chromium concentrations from entering the natural environment [7]. This treatment method is the most established method for most industrial wastewater treatment due to its ability to destabilize suspended solids [8]. Most tanning waters contain colloids with very little capability of division. This causes the colloids to take large amounts of time to settle, thus costing the tanning facility valuable treatment space and time [9]. Emerging technology focuses on streamlined methods and enhanced coagulants in order to optimize these methods for efficiency [10]. In this study, the physical and chemical treatment methods that were investigated included the use of polymers as coagulants, adsorption, filtration and reverse osmosis (RO).

In this study, we investigated the utilization of simpler and more-cost effective treatment methods, although some methods may be considered less traditional for wastewater treatment within the tanning industry [11]. Polymers typically allow for higher floc strength due to strong polymer chain bonds [12,13]. Adsorption has been used to remove heavy metals from tannery wastewaters with traditional and innovative techniques [14]. Filtration is not a typical treatment method within the tanning facility yet has been used in other wastewater treatment facilities [14]. As simple and cost-effective methods, these less traditional treatment methods offer innovative alternatives to lower harmful concentrations in discharge. Reverse osmosis has been studied to improve heavy metal concentrations as well as total dissolved solids [6]. Several studies have been conducted on the industrial applications of reverse osmosis, including the cost effectiveness [15,16]. In this particular study, a simple prototype was utilized in order to look into the viability of the use of such a technology on pretreated wastewater.

In order to thoroughly evaluate the current tanning wastewater treatment practices, this study took a holistic approach in examining each treatment method. In order to determine the most effective treatment process that could be utilized by the tanning facility, characterization of all wastewaters from the tanning process was conducted. Additionally, treatment experiments such as jar tests, filtration, adsorption, reverse osmosis were designed to determine which treatment would be most appropriate for the tanning facility both economically and environmentally. This study provides fundamental understanding of treatment processes used by tanneries and non-traditional methods for treatment of its wastewater.

Materials and methods

Tanning and wastewater treatment processes

Wastewater from a tannery with full production has been used; that is one producing full chrome tanning from an input of predominantly dry salted hides. The general tannery process was the following (1) wash–soak: surfactant and ground water were added to pre-salted skins; (2) pickling: sodium chloride, sulfuric acid and formic acid were added to washed skins; (3) tanning: sodium chloride, chromium, sodium bicarbonate and synthetic liquors were added to pickled skins; (4) dyeing: chromium, sodium acetate, synthetic tanneries, ammonia, dye powders, fat liquors and formic acid were added to tanned skins; and (5) rinse: groundwater was added to rinse the skins before dry cleaning and distribution.

All the wastewater from the different processing stages were collected and mixed in holding tanks throughout the tanning process and then treated. For consistency, roughly 8000 Gal of wastewater is treated at 100–140 °F at a pH of 7–8. In Step 1, alum was added to begin the coagulation process and the pH is lowered to 5.0 based on the alum addition. In Step 2, caustic soda and lime were added and the pH was then lowered to 8.5 with sulfuric acid if higher than 8.5 then Superfloc and Bufloc polymers were added and allowed to sufficiently mix. In Step 3, the wastewater was then sent to dissolved air floatation (DAF), which used air to separate solids instead of gravity; additional Bufloc polymer was added to ensure separation of solids. The treated liquid was sent to municipal wastewater treatment plant and the collected sludge from the DAF was treated on-site. Step 4 was the treatment of the DAF sludge. The sludge was held in a holding tank for further separation by gravity. Then iron chloride and lime were mixed with the sludge and sent to the filter press to form cakes. The liquid was returned to the holding tanks for further treatment and the cakes were disposed of.

Sampling of wastewater

About 5 Gal wastewater samples were collected from a tanning facility in San Antonio, TX from August 2011 to July 2013 and were representative of various stages of the tanning process and the wastewater treatment process. Samples were stored at 4 °C after collection unless analyzed immediately.

Analytical methods for characterization of wastewater samples

In order to characterize respective samples, a wide range of water quality parameters were analyzed based on the methods described in Table S1. All samples were characterized based on typical testing parameters in accordance with the United States Environmental Protection Agency approved Hach methods displayed in Table S1. The methods used for the testing parameters are in accordance with the standard methods [17]. These parameters include pH, TDS, conductivity, salinity, turbidity, COD, BOD_5, nitrogen, total suspended solids (TSS) and oil and grease. Chromium was determined via PerkinElmer dynamic reaction cell-e inductively coupled plasma mass spectrometer (ICP-MS) or a PerkinElmer inductively coupled plasma optical spectrometry (ICP-OES). All concentrations of calcium and silica were determined on the ICP-OES.

Lower concentrations (typically less than 1 mg/L) were measured on the ICP-MS (PerkinElmer, Waltham, MA, USA) having a quadruple mass spectrometer. The plasma was argon gas with a nebulizer gas flow of 0.83 L/min, a lens voltage of 6.5 V, and RF power of 1200 W. Operating conditions were determined after optimization of each parameter. Metal standards were prepared from 100 μg/mL standard stock solutions (VHG Labs), and diluted to meet the desired calibration standard concentrations of 1, 10 and 100 μg/L. Each calibration standard was acidified with 1% HNO_3 by volume. Higher concentrations were measured on the ICP-OES (PerkinElmer Optima 2000 DV, Atlanta, GA, USA) with Yttrium at 5 mg/L and 371.029 nm was used as an internal standard for calibration. Standards were prepared from 100 μg/mL standard stock solutions (VHG Labs), and diluted to meet the desired calibration standard concentrations of 1, 5 and 50 mg/L. Each calibration standard was acidified with 2% HNO_3 by volume. Coefficients of determination (r^2) were greater than 0.999 in most cases with a relative standard deviation less than 5%.