Intimate coupling of electro and biooxidation of tannery wastewater

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Introduction

Globally, India is one of the major producers and exporter of finished leather products. In general, there are two major methods of tanning, vegetable tanning and chrome tanning [1]. Vegetable tanning releases less heavy metal pollutant but the leathers produced are non-stable in water, while chrome tanning has the advantage of lower production price [2]. Tanning is a water intensive industry and hence produces large amount of wastewater; around 30m3 of effluent per tone of leather and involves high amount of toxic chemicals throughout the process [1,3]. According to United Nations Industrial Development Organization (UNIDO) in 1997, around 175 types of chemicals are involved in the whole tanning process that amounts up to 300 kg chemicals per tone of hide [4,5]. Due to its highly toxic procedures and the organic nature of the hide, tannery effluent contains high level of organic materials, toxic heavy metals including chromium, chloride and other pollutants [1,6]. Thus, the tanning industry faces massive environmental problems.
especially with the surge in tanning activity in the last two decades. The release of untreated tannery effluent causes extensive damage to the ground water, land stream, surface water, and air, and there are instances where the agricultural productivity has drastically been reduced when the land is irrigated with such contaminated effluent [7–9]. The numerous techniques and stages of operation of tanning procedure create a wide and strong mixture of pollutant that poses a challenge to treat this effluent effectively [1].

Chemical and biological processes were widely applied in tannery wastewater treatment but these processes still have huge hurdle in successfully treating the complex nature of tannery wastewater. Some of the treatments of tannery wastewater are using sequencing batch reactor (SBR), ozonation, electrooxidation, activated carbon adsorption, membrane bioreactor, activated sludge process and many others [10–16]. Chemical treatment is more energy extensive and the heavy chemical usage incurs a high cost of treatment [17]. Biological processes face a few obstacle due to the high organic content and the high salinity of tannery wastewater [1,18].

To overcome the shortcomings of both processes, the recent realization is that a combined process involving both physiochemical and biological treatment is the best way to reduce and remove both the organic and inorganic pollutant from tannery effluent [1,11,14,19]. Hence, this study is to compare the effectiveness of single-approach treatment and also the combined treatment process viz. electrooxidation and biological treatment for tannery wastewater. Electrooxidation method has been successfully applied to various wastewater treatment including tannery wastewater, distillery wastewater, urban wastewater and dye while biological treatment is suitable for most organic wastewater [12,13,20–22].

2. Experimental
2.1. Wastewater characteristic

The chrome tannery wastewater was obtained from common effluent treatment plant (CETP) located in Tiruchirappalli, India and stored at 4°C. The bacteria strains were isolated from the sludge obtained from the same treatment plant. The wastewater was characterized for the following parameters such as Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), pH, Total Suspended Solids (TSS) and chloride (Cl\_). The characteristics were tabulated in Table 1.

2.2. Chemicals and reagents

Chemicals and reagents used in the study were of analytical grade. All the chemicals and reagents were purchased from Merck, India. Some of the salts used are sodium chloride (NaCl), copper (II) sulfate (CuSO\_4), zinc chloride (ZnCl\_2), iron (III) chloride (FeCl\_3) and manganese sulfate (MnSO\_4).

2.3. Microorganism and culture conditions

The microorganisms used in this study are culture of Bacillus (Strain A), Bacillus (Strain B), and Pseudomonas (Strain C) that has been isolated and enriched from the tannery effluent. The microbes were enriched by pour plate method in nutrient agar medium. Pure cultures were obtained from morphologically dissimilar, quantitatively dominant isolates that were randomly streaked on nutrient agar plates. The colonies were noted by morphological and pigmentation characteristic and stored at 4°C and periodic monthly sub culturing was done.

The characterization of bacteria up to genera level was done according to the key described in Bergey’s manual of systematic bacteriology for the differentiation and identification as per the standard method [23]. A loopful of selected stock culture was inoculated into 50mL of sterile nutrient broth. The culture tubes were kept in incubator for overnight at 37°C. From this stock, the required quantity of culture was
2.4. Batch electrochemical oxidation studies

In the electrochemical oxidation process, electrolysis was carried out under galvanostatic conditions using RuO$_2$ coated on Ti as an anode and stainless steel as cathode. The electrodes were connected to a direct current power source with an inter-electrode distance of 3 cm. Both the electrodes have surface area of 24 cm$^2$ (6cm x 4 cm). The electrode plates were cleaned manually by washing in distilled water prior to every run. The experimental setup of the electrochemical reactor operated in a batch mode operation consisted of a cylinder made of Perspex glass with a total volume of 600 mL. The working volume of the reactor was 500 mL and the effluent was agitated by magnetic stirring. The temperature of the system was maintained constantly at 27 ± 2°C. As tannery wastewater has high Cl$^-\text{content}$, no additional NaCl was added to increase the conductivity of the solution. The desired current density was applied to the electrodes submerged in the effluent. The cell voltage was read periodically and noted. Samples were collected at regular time interval and the experiments were repeated with different initial COD concentration. The COD, which was used to quantify the degradation of organics, was determined to investigate the behavior of electrochemical oxidation of tannery effluent in the batch reactor. The sample COD was determined using the dichromatic closed reflux method strictly following the APHA. The effect of current density on percentage of COD removal was done by varying the current density in the range of 0.5–1.5 Adm$^{-2}$.

2.5. Batch biodegradation studies

For biodegradation process, microorganisms isolated and selected based on their frequency of occurrence were utilized. Fifty percent of diluted tannery effluent was used. Experiments for the evaluation of three individual bacterial strains namely Bacillus (Strain A), Bacillus (Strain B), and Pseudomonas
(Strain C) were carried out in batch mode. The biodegradation systems each contained 250mL distilled water, 50mL Busnellhall’s (BH) medium broth, 5mL of bacterial culture (Strains A–C), and tannery effluent. The effect of process parameters viz., pH, nutrients and growth factors were also studied. These parameters were done in test tubes reactors containing 25mL of effluent, 5mL of BH media, and 2mL of bacteria culture. Nutrients involved in this study were glucose and peptone, while the growth factors were Cu, Zn, Mn and Fe, which were added separately into the effluent. The pH effect between 4 and 14 was studied.

2.6. Intimate coupling process

The combined electrooxidation and biological process was set-up as shown in Fig. 1. The degradation of organic matters was carried out by both electrooxidation and biodegradation methods in a recirculation mode. The electrooxidation process is set as the first stage treatment followed by biological treatment. The electrooxidation reactor has a volume of 500mL and the sample was stirred using magnetic stirrer. A fixed current density of 0.5Adm$^{-2}$ was used.
during the course of electrochemical treatment. The effluent from the electrooxidation reactor is then pumped into a vertical column of 2.5 cm diameter and 32 cm height. The column is packed with 20 cm of immobilized cell. The immobilized cell was prepared by thoroughly mixing 2% sodium alginate nickel with 4 g of acclimatized microbial activated sludge. The resulting warm jelly is then injected into a solution containing 2% calcium chloride solution using sterilized surgical syringe to form spherical beads. Separate set of sodium alginate beads was used for each strain. The circulating flow rate through the column is set at 100 mg L\(^{-1}\) with the help of peristaltic pump. Each recirculation cycle took 3 h. Samples were analyzed for COD using the spectrophotometry method every half an hour until equilibrium was reached. The COD measurement is taken to represent organic degradation.

Full text is available at:

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