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Intimate coupling of electro and biooxidation of tannery wastewater

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ABSTRACT

Tannery wastewater contains high organic loadings and other pollutants, making it challenging to be treated efficiently. A combined process involving both advance oxidation process and biological treatment seems to be the best solution to achieve the regulatory standard for discharge. This investigation reports on the degradation of tannery wastewater which was represented by the removal Chemical Oxygen Demand (COD) using electrochemical process, biological degradation and finally, the combination of both processes. Electrolysis was carried out in batch reactor under different current density and dilution. Biological degradation was carried out with three isolated microbial strain and optimization of pH, nutrients, and growth factors were analyzed. The combined process involved an electrooxidation reactor connected to a column packed with immobilized biomass. Electrooxidation technique was found to obtain maximum percentage COD reduction in 73.1% at 1.5 $A\,dm^{-2}$ using raw effluent. *Bacillus* Strain B proved to be superior in terms of COD reduction capabilities with a high 91.5% reduction with diluted wastewater. Biodegradation process was found to be most effective at pH 6. Intimate coupling of electro and biooxidation recorded good degradation for both raw and diluted samples, achieving 66.2 and 76.6% degradation, respectively.

Keywords: Tannery wastewater; Electrochemical; Biodegradation; Combined process; COD

1. 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 30 m^3 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

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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 50 mL 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 extracted for further studies.

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

Table 1
Characteristics of tannery wastewater obtained from CETP

Parameters	Values
COD	4,600–6,000 $mg\,L^{-1}$
BOD	1,600–2,000 $mg\,L^{-1}$
TSS	3,000–3,500 $mg\,L^{-1}$
pH	8.2–8.6
Cl^-	3,500–4,000 $mg\,L^{-1}$
Conductivity	17,633–20,152 μS/m

direct current power source with an inter-electrode distance of 3 cm. Both the electrodes have surface area of 24 cm^2 (6 cm × 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^- 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 A dm^{-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 250 mL distilled water, 50 mL Busnellhall's (BH) medium broth, 5 mL 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 25 mL of effluent, 5 mL of BH media, and 2 mL 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

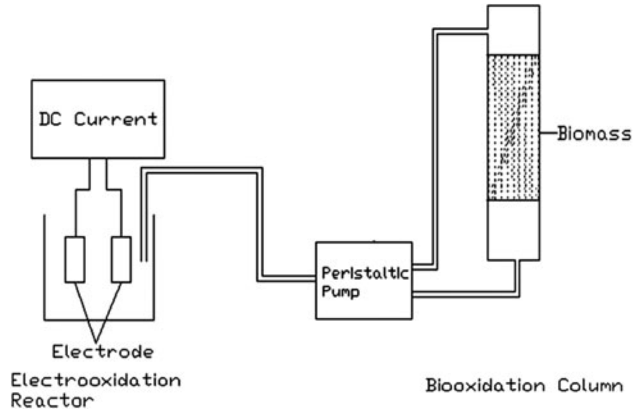

Fig. 1. Schematic diagram of the intimate coupling experimental set-up.

electrooxidation and biodegradation methods in a recirculation mode. The electrooxidation process is set as the first stage treatment followed by biological treatment. The electrooxidation rector has a volume of 500 mL and the sample was stirred using magnetic stirrer. A fixed current density of 0.5 A dm^{-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.

3. Results and discussion

3.1. Electrooxidation process

The effect of current density and concentration of COD (raw, 50% dilution) on percentage COD reduction by electrooxidation process were studied. The current densities varied at 0.5, 1.0, and 1.5 A dm^{-2} for raw and 50% diluted effluent. From Fig. 2, it can be observed that the maximum percentage COD reduction for raw effluent was 57.0, 63.8 and 73.1% for the current density of 0.5, 1.0 and 1.5 A dm^{-2} respectively.

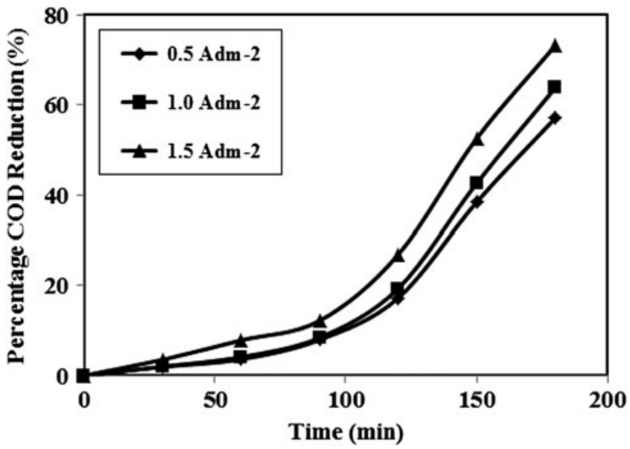

Fig. 2. Effect of current density on the percentage COD reduction for raw effluent with respect to electrolysis time.

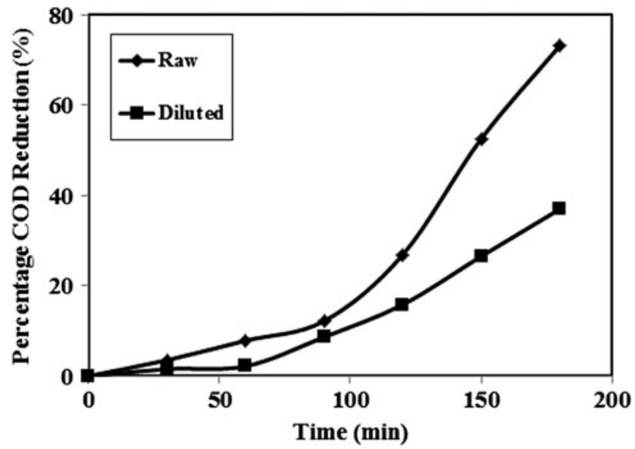

Fig. 3. Effect of effluent dilution on the percentage COD reduction at current density 1.5 A dm^{-2}.

In the case of 50% diluted effluent, the percentage COD reduction was found to be 28.6, 31.5 and 37.0% (data not shown). The percentage COD reduction increased with the increase in current density. This is consistent with Faraday's law of electrolysis which states that the mass of the substance or element altered is directly proportional to the quantity of electricity transferred at that electrode and also to the element's equivalent weight [24]. Similar trends were also observed in distillery industry wastewater, synthetic tannery wastewater and organic dye [13,22,25]. The average cell voltage was observed 2.3, 2.7 and 2.9 V at current densities of 0.5, 1.0 and 1.5 A dm^{-2} respectively. The energy consumption of the system varied from 2.76 to 1.96 kW/kg of COD when current density changed from 0.5 to 1.5 A dm^{-2}.

Fig. 3 shows the effect of effluent dilution on the percentage COD reduction at current density of 1.5 A dm^{-2}. The COD reduction increases with the increase in initial COD from 37 to 73.1%. This may be due the mass transfer limitation when oxidation depends on the rate of which the organic molecules are carried from the bulk liquid to the electrode surface [26]. Previous studies have shown that higher COD concentration will contribute to higher instantaneous current efficiency up to a COD mass transfer limit, assuming a direct oxidation model [27]. At higher COD concentration, more organic compound was oxidized at the electrode surface, hence contributing to better COD reduction.

3.2. Biodegradation study

Diluted tannery effluent was used in this process because it has been found that lower COD concentration results in better degradation in biological treatment of tannery wastewater [17]. Experiments for the evaluation of individual bacterial strain were carried out in batch mode. From the three strains isolated, Strain B showed the most promising results, recording 91.5% of COD removal as seen in Fig. 4. Microbial Strains A and C managed to reduce 62.1 and 66.3% of COD respectively.

3.3. Effect of nutrient (glucose and peptone) and growth factors

The effect of glucose and peptone as additional nutrient on the efficiency of organic matter degradation is shown Fig. 5 below. The changes in the degradation of COD are related to the growth of the bacteria strains. Increase in biomass will increase the degradation of organic matter [14]. Overall, peptone

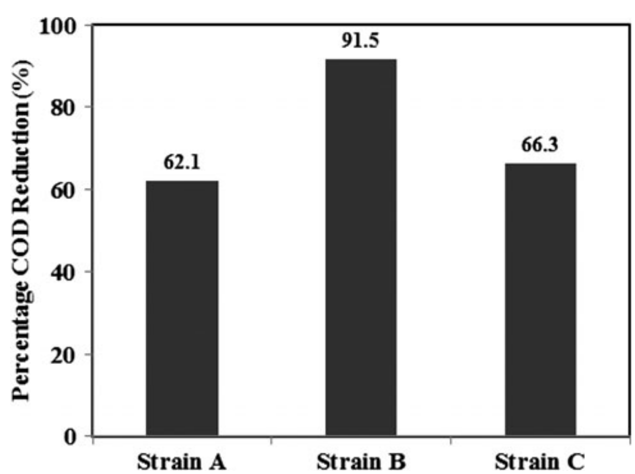

Fig. 4. Influence of strain on the percentage COD reduction.

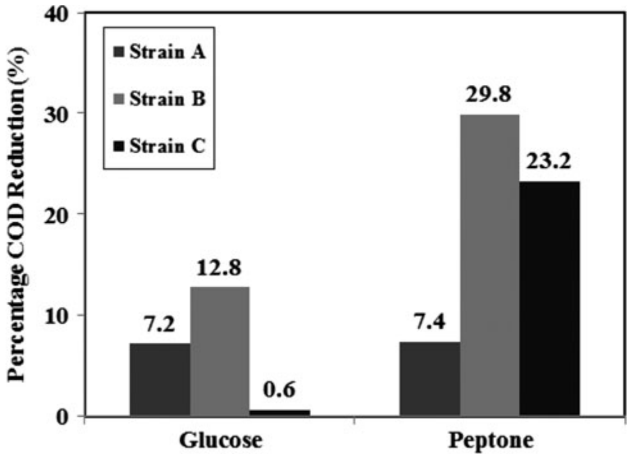

Fig. 5. Influence of additional nutrient on the percentage COD reduction.

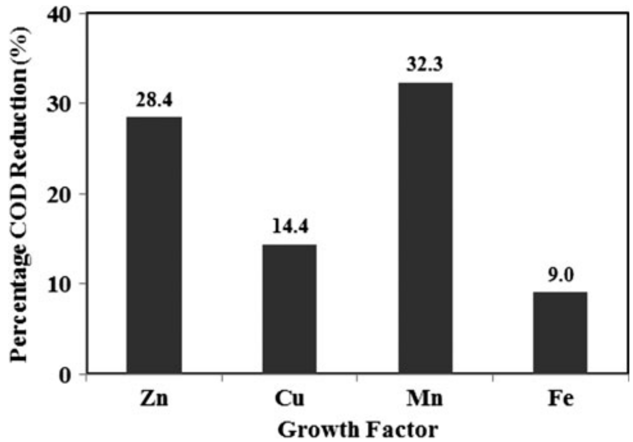

Fig. 6. Influence of growth factors on the percentage COD reduction.

had more influence compared to glucose in increasing the effectiveness of biodegradation. Strain B and C responded well with peptone and showed much lower efficiency during the addition of glucose. The COD removal increased 39 times when peptone was added for Strain C and two times for Strain B. Strain A registered little changes in both additional nutrient (7.2 and 7.4%). The maximum degradation of organic matter was obtained when Strain B was used for both additional nutrients. Comparatively, the addition of peptone to protozoan isolates also recorded a better nitrate and phosphorus removal in the long term compared to glucose [28]. The low performance of glucose addition can be rectified with the combination of glucose and organic acid mixture as reported by Kargi et al. where combined glucose-organic acid showed increment in phosphorus uptake in SBR [29].

Growth factors, Zn, Cu, Mn, and Fe were added to observe their effect on the percentage of COD reduction. The effect of Mn was the greatest (32.3%) followed by Zn and Cu while Fe recorded the lowest COD reduction (9%) as projected in Fig. 6.

3.4. Influence of pH

pH is an important factor in biological degradation of wastewater especially for bioremoval of heavy metals [9,17]. The optimum pH was found to be pH 6 which recorded a 75.5% COD removal as seen in Fig. 7. The may be due to the neutrophile (optimum growth range of pH 6–9) nature of the strain, causing optimum growth rate of biomass at pH 6, hence increasing COD reduction. Mixed culture obtained from CETP from tannery wastewater reported by Durai et al. was also optimum in neutral condition [17].

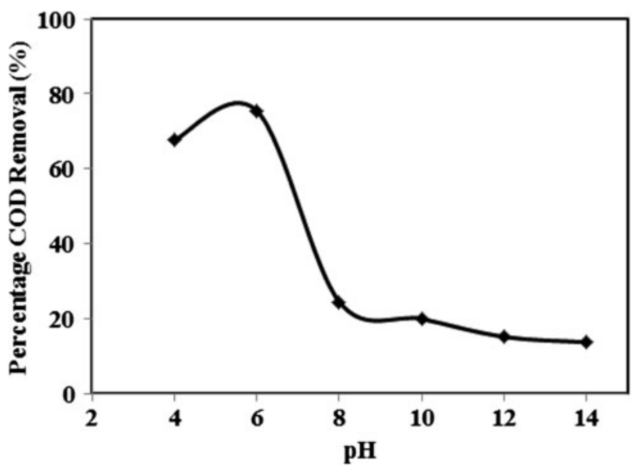

Fig. 7. Influence of pH on the percentage COD reduction.

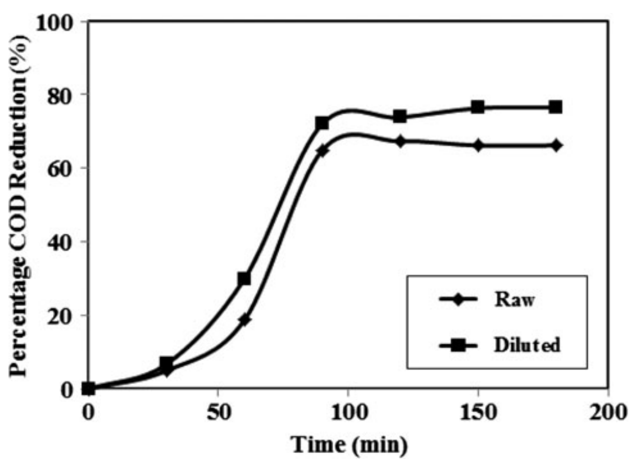

Fig. 8. Effect of effluent dilution on the percentage COD reduction in the intimate coupling process.

3.5. Intimate coupling process

In the combined process (Fig. 8), the diluted effluent sample was found to be more effective compared to raw effluent. The COD removal was 76.1% for diluted sample and 63.7% for the raw sample at equilibrium. However, both of the samples achieved equilibrium at 90 min. Both the samples showed increase in removal percentage with the increase in contact time until equilibrium was reached. The high rate of COD removal was due to the electrochemical oxidation, while the high COD removal of diluted sample was attributed to the biological treatment process. Temperature was measure throughout the recirculation cycle showed that the temperature increase was around 3˚C.

4. Conclusion

The experimental results showed that the intimate coupling process of electrooxidation and biodegradation is a conceivable method to degrade organic matter in the tannery wastewater. The electrochemical treatment was able to treat raw effluent (73.1%) effectively but reduced its efficiency by almost half when treating the diluted effluent (37.0%). The biological process was used to treat diluted samples with the maximum removal of 91.5% by Strain B bacteria. The addition of peptone as nutrient and Mn as growth factor caused a major improvement on the performance of the strains for COD removal. The optimum pH of this system is found to be pH 6. The time taken for the combined process to reach equilibrium is also reduced to 90 min compared with the stand alone biological systems which took seven days. This is attributable to the combined effect of electrochemical and biological process. Combined process proved to be the most applicable treatment system with good efficiency and acceptable retention time for both high- and low-organic loading.

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