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Electrochemical decolorization and biodegradation of tannery effluent for reduction of chemical oxygen demand and hexavalent chromium

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ABSTRACT

Tannery effluent contains enormous quantities of toxic chemicals and high level of chemical oxygen demands, which gets directly discharged into natural aqueous system, thus contaminating the water quality. Hence, it is important to develop an eco-friendly and cost effective technology to treat the tannery effluent wastewater. Our present investigation on integrated approach of electrochemical oxidation (EO) of tannery effluent (TE) using RuO_2-IrO_2-TiO_2 anode and titanium mesh electrode as cathode and followed by the biodegradation process (BP) of the treated EO effluent. Various parameters viz., sodium chloride concentration (NaCl) (1–5 g/L) and current density (10–30 mA/cm^2) are optimized. The agro waste peanut hull (PH) and rice hull (RH) are utilized as carbon source for biodegradation of tannery effluent. A maximum of 87% decolorization is observed at 5 g/L of NaCl concentration and 30 mA/cm^2 of current density after 135 min of EO treatment. The EO treated TE is further treated by BP with *Pseudomonas stutzeri* MN1, *Acinetobacter baumannii* MN3 and mixed consortia of MN1 and MN3. The 97% of chemical oxygen demand (COD) and 96% of Cr(VI) reduction was observed after 72 h of BP with mixed consortia and rice hull as carbon source. Thus, the integrated approach of EO with BP can be implied for complete a decolorization and degradation of tannery effluent.

1. Introduction

Tannery effluent (TE) from leather industry contains large quantities of toxic chemicals. On a worldwide scale, India is one of the largest producers and exporters of leather products. Tannery industry releases large quantity of wastewater of around 30 m^3 of effluent/ton of leather [1,2]. According to The United Nation Industrial Development Organization (UNIDO) report of 1997, approximately, 175 different chemicals are involved in tannery industry processes. It is estimated to contain around 300 kg of highly toxic chemicals per ton of leather in the tannery effluent. These highly toxic organic materials contribute in increasing the chemical oxygen demand (COD) level of the effluent. In addition, the untreated tannery effluent contains hexavalent chromium, Cr(VI) which was reported to cause severe environmental pollution [3,4]. Though chromium exists in a range of Cr(II) to Cr(VI) valence state, trivalent chromium, Cr (III) and Cr (VI) are predominantly found in TE [5]. Among these two, Cr (VI) is reported to possess mutagenic and carcinogenic property, unlike Cr (III) [6–9]. Therefore, the removal of Cr (VI) by reduction or absorption process can reduce the risks to human health and the environment. Meanwhile, the improper discharge of untreated tannery effluent will lead to the contamination of ground water, surface water, lakes, river and land [10–15]. The ground water system in the Palar river basin, Vellore Dist, Tamilnadu has been highly contaminated due improper discharge of untreated effluents from tannery industries. As reported earlier the concentration of total dissolved solids (TDS) in groundwater was more than 8000 mg/L in Vellore Dist [16].

Various methods like, ozonation, activated carbon adsorption, sequencing batch reactor membrane bioreactor and activated sludge processes were used to treat TE. However, these methods faced limitations for being highly expensive and operational problems. On the other hand, chemical treatments are more expensive and involves large amount of chemicals. Therefore, electrochemical treatment of wastewater is gaining interest nowadays. Treatment of wastewater containing synthetic dyes, arsenic, Cr (VI), phenols by electrochemical methods have been reported by various researchers [17–19]. In general,

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biological treatment of tannery effluent is a slow process and hence it takes longer duration for complete removal of COD [20]. Treatment of tannery wastewater by electrooxidation process has been carried out in a reactor with different type of metal oxides as anode material. This study reported on the rate of pollutant removal was significantly influenced by the type of anode material used and other electrochemical parameters [21]. Electrochemical treatment of tannery wastewater using dimensionally stable anodes (DSA) containing tin, ruthenium, titanium and iridium was reported. The results suggested that the total organic carbon (TOC) and lower absorbance in UV–vis region were observed [22]. The effect of chloride concentration towards the removal of TOC and COD during an electrochemical treatment of a synthetic tannery wastewater has also been reported [23]. Recently, few researchers have shown interest in studying the combination of electrochemical and biological process for treatment of tannery wastewater [24,25].

In this context we explore an integrated approach of electrochemical and biological method for the treating TE. In an electrochemical process, the choice of electrode material plays a vital role in oxidation [26]. Though boron doped diamond and platinum electrodes are most widely used, these electrodes are highly expensive [27,28]. Therefore, we have selected RuO_2-IrO_2-TiO_2 anode and titanium mesh cathode in the present study. This electrode possesses high corrosive resistance and electrocatalytic activity for chlorine evaluation [29–32]. In order to make the process more economical, a freely available waste product of agriculture region namely, peanut hull (PH) and rice hull (RH) are used as cheap carbon source [33]. PH consists of proteins (6–7%), fat (35–45%), cellulose (27–33%) and lignin (2–4%) [34]. RH consists of cellulose, hemicelluloses and lignin. Utilization of these wastes could solve the disposal problem and also reduce the cost of waste treatment process.

Thus, the present study of integrated approach of electrochemical and biological process is aimed with the following objectives, (i) to electrochemically decolorize the TE using RuO_2-IrO_2-TiO_2 anode and titanium mesh cathode, (ii) to study the effect of various parameters such as, sodium chloride (1–5 g/L) and current density (10, 20, 30 mA/cm^2), (iii) to perform the biodegradation process (BP) of the electrochemically decolorized TE solution using *Pseudomonas stutzeri* MN1 and *Acinetobacter baumannii* MN3, and finally (iv) to estimate the Chemical oxygen demand (COD) and Cr(VI) level at the end of electrooxidation and biodegradation process.

2. Materials and methods

2.1. Sample collection

The tannery effluent was collected from the Common Effluent Treatment Plant (CETP) located at the Sipcot Industrial Complex, Ranipet, Vellore, Tamilnadu, India (latitude 12.9320°N, longitude 79.3334°E). The geographical map of the sample collection is presented in Fig. 1. The samples were collected in sterile bottle, placed into an icebox and transported to the laboratory. Samples were stored at 4 °C until further study. The physicochemical characteristics of tannery effluent are presented in Table 1.

2.2. Microorganisms

The bacteria used in this study, *Pseudomonas stutzeri* MN1 and *Acinetobacter baumannii* MN3 were isolated and identified from crude oil sample. The nucleotide sequence has been deposited in GenBank under accession numbers KU708859 and KU708860 respectively [35].

2.3. Electrochemical decolorization of tannery effluent

The electrochemical decolorization of tannery effluent (TE) was studied in a 500 ml beaker using RuO_2-IrO_2-TiO_2 anode (10 × 5 cm^2) and Titanium (Ti) mesh cathode (10 × 5 cm^2). The effect of sodium chloride (1–5 g/L) and current density (10, 20, 30 mA cm^2) was chosen for EO. DC power supply (Aplab programmable multi output DC power supply LQ 6324P) was used to supply the desired current to the electrodes. Electrodes were arranged at distance of 1 cm. The TE was continuously stirred at 250 rpm using magnetic stirrer, to enhance the mass transfer. The decolorization of TE was monitored at every 15 min interval. The electrochemically decolorized solution was exposed to sunlight for 1 h to remove the hypochlorite. This EO treated solution was used for biodegradation studies.

Fig. 1. Geographical location of the sample collection site.

2.4. Biodegradation of electrochemically decolorized tannery effluent

For biodegradation process (BP), 1% of individual bacterial cells (2 × 10^4 CFU/mL) of MN1, MN3 and mixed consortia were added at an initial inoculum concentration of about 0.7 OD into 100 ml of electro oxidized-TE solution contained in 250 ml conical flasks. The agriculture wastes 1% peanut hull (PH) and 1% rice hull (RH) were used as carbon source for biodegradation process of tannery effluent. Three different sets of BP were set up containing EO-TE solution, EO-TE solution with 1% PH and EO-TE solution with 1% RH, with individual bacterial cells MN1, MN3 and mixed consortia respectively. The flasks were incubated at 37 °C, 120 rpm for 72 h. For every 24 h, time interval the samples were collected to measure the bacterial growth at 600 nm using UV–vis spectrophotometer (Jasco, V 730). After 72 h of incubation, the chemical oxygen demand (COD) and hexavalent chromium reduction of the TE were measured.

2.5. Analytical methods

2.5.1. Decolorization of tannery effluent

The electrochemical decolorization of TE was monitored using UV–vis spectrophotometer (Jasco V 730). at 400–800 nm. The 505 nm absorbance values were taken and percentage of decolorization was calculated using the following formula given below.

$$\%\ \text{of decolorization} = \left(\frac{\text{absorbance of control} - \text{absorbance of test}}{\text{absorbance of control}}\right) \times 100 \quad (1)$$

2.5.2. Chemical oxygen demand (COD) measurement

The chemical oxygen demand (COD) was determined after electrochemical decolorization and biodegradation was measured by digestion method using thermo reactor (Merck, Spectroquant TR 320). The COD was measured in colorimeter (Merck, Spectroquant colorimeter move