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Electrochemical oxidation and reuse of tannery saline wastewater

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ABSTRACT

In this present work, electrochemical treatment of saline wastewater with organic (protein) load was studied. The influence of the critical parameters of electro-oxidation such as pH, period, salt concentration and current density on the reduction of organic load was studied using graphite electrodes. It was found that current density of 0.024 A/cm^2 for a period of 2 h at pH 9.0 rendered best results in terms of reduction in COD and TKN. The energy requirement for the reduction of 1 kg of TKN and 1 kg of COD are 22.45 kWh and 0.80 kWh respectively at pH 9 and 0.024 A/cm^2. Reuse experiments were conducted at commercial scale. One of the saline waste streams in leather manufacturing process, pickling was treated and reused continuously thrice. The characteristics of the waste stream and the quality of the leathers indicate that the reuse of saline streams with intermittent electrochemical treatment is feasible.

1. Introduction

Wastewater with high level of total dissolved solids (TDS) is generated from many industrial processes. Biological treatment of saline wastewater by biological methods particularly by activated-sludge process typically results in poor removal of chemical oxygen demand (COD) as a result of plasmolysis of cells caused by high salt content (>1%) [1]. Results of biological treatment of saline wastewater indicate that large concentrations of inorganic salts adversely affect the microbiological system and organic removal efficiency was affected mainly due to cations of salt [1–4]. Salt removal is an essential prerequisite for the biological treatment of saline wastewater. With the customary wastewater treatment systems, it is seldom possible to remove salt from the wastewater. Advanced methods such as ultra-filtration [5], nano-filtration [6] reverse osmosis [7], electro-Fenton process [8] and photochemical-electrodialysis [9] had been studied for the treatment of waste streams with high TDS. Desalination techniques particularly membrane systems demand near zero removal of organic load [10].

With high salt content, the wastewater has high conductivity due to the presence of anions and cations. Therefore, electro-assisted method of treatment of saline waste streams might be a good proposition [11]. Many studies have been carried out on the electro-oxidation of organic compounds and several anode materials have been tested. Electro-oxidation method has been successfully applied for the treatment of wastewater from textile industry [12,13], tannery [14–16], distillery [17], domestic sewage [18] and also for landfill leachate [19]. Various types of anodes are used for the treatment of organic wastes from different industries [20,21]. Recently graphite electrodes have been widely used for the organic removal because of the low cost. It has large surface area and may result better in the attenuation of pollution through the combination of adsorption and electrochemical degradation. It has high current efficiency compared to other electrodes [13]. In graphite electrodes, oxidation is dominated mainly by physisorbed active oxygen hydroxyl radicals. These hydroxyl radicals cause the complete destruction of organic matters. However, the relatively poor service life due to surface corrosion especially when the electro-oxidation is conducted at high potential is the notable short-coming of graphite electrode. Detoxification of composite tannery wastewater by electrolysis using Ti/Pt anodes and SS304 cathode were studied. It was reported that the electrolytic oxidation brought about reduction in COD by 52% [22]. In another study, tannery wastewater after secondary clarification was treated by electro-oxidation technique using Ti/Pt, Ti/PbO_2 and Ti/MnO_2 anodes and Ti cathode. It was found that Ti/Pt electrode brought about higher COD reduction. Efficiency of Ti/Pt electrode was 0.802 kg COD h^{-1} A^{-1} m^{-2} and 0.27 kg NH_4^+ h^{-1} A^{-1} m^{-2}. The energy requirement for the reduction of 1 kg COD was 5.77 kWh and for the reduction of 1 kg NH_4^+ was 16.63 kWh [16]. It was reported that the rate of pollutant removal was significantly influenced by the type of anode material and electrochemical parameters. It was opined that the electrochemical oxidation could be applied as a post-treatment after the conventional biological process in order to remove the residual ammonia with low energy consumption [20].

Significant volume of saline wastewater is generated from tanneries. About 15% (w/w) to 40% (w/w) of common salt is used for

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Table 1
Pollution load of soaking and pickling streams in tannery.

Pollution	Load in soaking wastewater (mg/L)	Load in pickling wastewater (mg/L)
TS	25,000–40,000	30,000–70,000
TDS	22,000–33,000	29,000–67,000
BOD	11,000–25,000	4000–7000
COD	3000–6000	1000–3000
Cl^-	15,000–30,000	20,000–30,000

preserving animal skins and it is removed during the first operation, soaking. The waste stream of soaking contains mainly high organic load, high salinity and high suspended solids. Pickling is one of the unit processes of leather manufacturing where 10% (w/w) of common salt is used. The general characteristics of this wastewater are shown in Table 1 [23]. Because of high salt content, waste streams from soaking and pickling are segregated from other waste streams and subjected to open solar evaporation pan in tanneries in India [24]. The presence of high dissolved organic matter and suspended solids retards the rate of evaporation in solar evaporation pan. The salt recovered is contaminated with protein and halophilic bacteria. Therefore it is unsuitable for reuse. Pickling wastewater can be reused directly [25]. However, the presence of organic load in pickling wastewater hampers the continuous reuse of pickling wastewater. Elimination of organic pollutants in soaking wastewater would render the recovered salt reusable. Similarly the pickling wastewater if treated for the removal of organic load then it can be reused continuously [26].

In the electrochemical oxidation, organic pollutants are removed by electro-generated oxidizing agents like chlorine and hypochlorite [27]. In general, the following reaction takes place during electro-oxidation using graphite electrodes in the presence of sodium chloride.

At the anode:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad (2)$$

At the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (3)$$

In the undivided cell, chlorine formed at the anode and hydroxides formed at the cathode react to form chloride and hypochlorites. Both the hypochlorite and free chlorine are chemically reactive and oxidize the organic pollutants in the effluent to carbon dioxide and water [17].

HOCl is then formed.

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \quad (4)$$

The HOCl further dissociates into OCl^- and H^+ ions.

$$HOCl \rightleftharpoons H^+ + OCl^- \quad (5)$$

This hypochlorite ions act as a main oxidizing agent in the organic degradation.

The overall desired reaction of electrolysis is:

$$\text{Organicmatter} + OCl^- \rightarrow \text{intermediates} \rightarrow CO_2 + Cl^- + H_2O \quad (6)$$

The objective of the present work is to study the electro-oxidation of tannery saline (synthetic and real) wastewater using graphite electrode. The parameters of electrochemical oxidation such as pH, period of oxidation, concentration of sodium chloride and current density were varied. Scope of the present work also includes the study of reusability of treated wastewater.

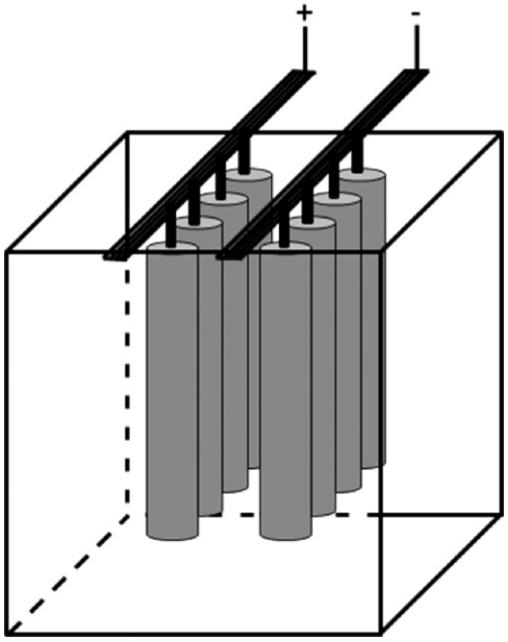


Fig. 1. Schematic diagram of electro-oxidation cell.

2. Materials and methods

2.1. Electro-oxidation cell

A cylindrical vessel of 2 L working volume was used as the electro-oxidation cell (Fig. 1). Cylindrical graphite electrodes with a diameter of 2.54 cm and a length of 13 cm were used both as a cathode and as an anode. Total surface area of the electrodes was 427.84 cm^2. The electrodes were arranged parallel to each other with a constant electrode gap of 1 cm to minimize the ohmic potential drops. Ohmic potential drop is potential drop due to solution resistance i.e. the difference in potential required to move ions through the solution. The electric power supply was provided by laboratory D.C. power source equipped with current–voltage monitoring and of maximum output of 60 A. Commercial scale electro-oxidation was carried out using electro-oxidation cell of 1 m^3 working volume. Total surface area of the electrodes was 62,500 cm^2 and the distance between the cathodes and anodes was 1 cm.

2.2. Synthetic wastewater

To prepare synthetic wastewater, 2.5 g of bovine serum albumin (Hi-Media) was added to double distilled water to make up a volume of 1 L. The amount of bovine serum albumin was arrived on the basis of Total Kjeldahl Nitrogen (TKN) level in the tannery saline wastewater [28]. Sodium chloride to the required quantity for each experiment has been added. The pH of the synthetic wastewater was altered using HCl or NaOH.

2.3. Analysis of wastewater

Pollution parameters such as chemical oxygen demand (COD) and Total Kjeldahl Nitrogen (TKN), chlorides (Cl^-) were analysed following the standard procedure as reported by American Public Health Association [29]. The results were ensured using standards as well as duplicates. Mercuric sulphate was added to overcome the likely interference of Cl in the COD estimation. The pH of the solution was measured using pH meter of HACH model HQ40d. The precision is 0.01 either way.

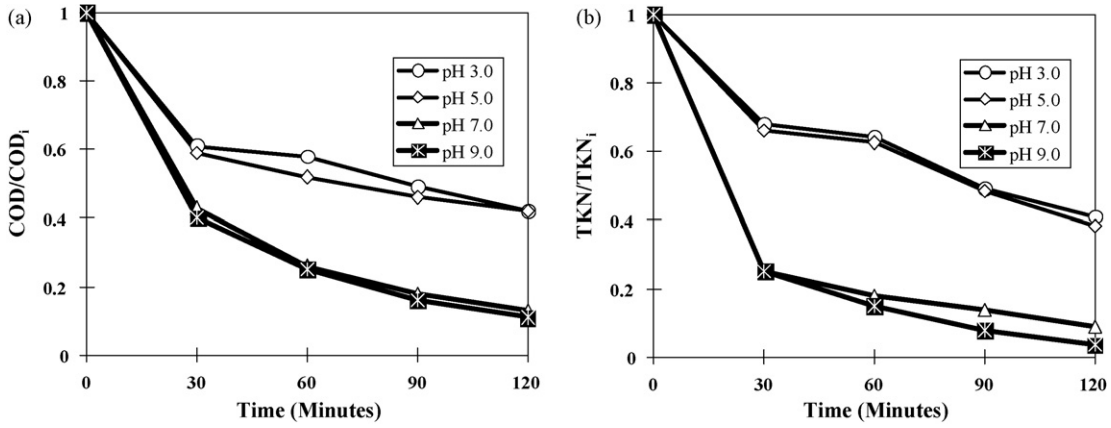


Fig. 2. (a) Effect of current density on COD reduction rate with electrolysis time at 0.012 A/cm^2 and 40 g of NaCl/L. (b) Effect of current density on TKN reduction rate with electrolysis time at 0.012 A/cm^2 and 40 g of NaCl/L.

2.4. Total current efficiency (TCE)

Total current efficiency (TCE) was calculated using the formula given below [30]:

$$\text{TCE} = \frac{[\text{COD}_t - \text{COD}_{t+\Delta t}]\ FV}{8I\Delta t} \quad (7)$$

where COD_t and $\text{COD}_{t+\Delta t}$ are chemical oxygen demands at times t and $t+\Delta t$ in gram of O_2 per dm^3 at times $t=0$ (initial) and t respectively; F is Faraday's constant (96,487 C mol^{-1}); V is the volume of electrolyte in litres and I is the current in Ampere and 8 is the oxygen equivalent mass (g/equiv.$^{-1}$).

2.5. Anode efficiency

Anode efficiency was calculated as per the formula given below [31]:

$$\text{Anode efficiency} = \frac{\text{COD removed (kg)}}{\text{Time (h)} \times \text{Current (A)} \times \text{Surface area of anodes (m}^2\text{)}} \quad (8)$$

2.6. Energy consumption

Energy consumption was also calculated on the basis of COD reduction [31]:

$$\text{Energy consumption} = \frac{tVA/S_V/1 \times 10^3}{\Delta\text{COD}/1 \times 10^6}\ \text{kWh/kg COD} \quad (9)$$

where t is the time of electrolysis in hours, V is the average cell voltage, A is Ampere, S_V is sample volume in litres and ΔCOD is the difference in COD in time t in mg/L.

2.7. Reuse study

For reuse study, the wastewater generated during pickling process had been collected and treated electrochemically. Treated wastewater had been reused for pickling process. Pickling process was carried out as per the following procedure. Delimed pelts of Indian cowhides were treated with 100% water (on the weight of skin) and 10% of sodium chloride for 10 min in drums of 9 rpm. Then 1% sulphuric acid diluted with 10% water was given in three instalments. After first and second instalments the drum was run for 15 min and after third instalment the drum was run for 30 min. Half of the volume of the pickling wastewater was retained for carrying out chrome tanning and the remaining is collected for treatment. Chromium tanning was carried out with 8% basic chromium sulphate of 33% basicity and 22.4% (w/w) of Cr_2O_3. Finally the pH of the leather was adjusted to 4 using sodium formate and sodium bicarbonate. This procedure had been repeated thrice.

2.8. Leather analysis

Chromic oxide content of leather and shrinkage of chrome tanned leathers were determined following the procedures of SLC 9 and SLP 20 as per the SLTC test methods [32].

3. Results and discussion

3.1. Effect of pH on pollution reduction

The process standardization of electro-oxidation of tannery saline wastewater was carried out by studying the effects of pH, current density, salt concentration and electrolysis time. For these studies, the synthetic saline tannery wastewater was used. Initial COD and TKN of the prepared synthetic wastewater are 10,175 mg/L and 352 mg/L respectively.

For first set of experiments, pH had been varied from 3 to 9 with an increment of 2. Current density and NaCl concentration were kept constant at 0.012 A/cm^2 and 40 g/L of NaCl. COD was reduced by 57.57% and 59.73% at pH 3.0 and pH 5.0 respectively. The rate of COD reduction and TKN reduction with respect to time is shown in Fig. 2(a) and (b). TKN was reduced by 58.24% and 61.65% at pH 3 and pH 5 respectively. It is evident that the rate of COD reduction was found to be insignificant at pH 3 and pH 5. But increase in pH resulted in the increase in the degree of reduction of COD. At pH 9.0, COD was reduced by 89.11% and TKN was reduced by 96.31%. This can be explained by Eqs. (5) and (6). In acidic conditions, the OCl^- ions are instable. The OCl^- and H^+ ions in acidic conditions undergo the reverse reaction of combining with each other to produce HOCl (Eq. (10)). In alkaline conditions the reverse reaction is not favoured and OCl^- ions may oxidize the organic matters.

$$HOCl \rightleftharpoons [H^+ + OCl^-] \quad (10)$$

Anode efficiency and energy consumption were also estimated using formulas (7) and (8) respectively. The influence of pH on anode efficiency and energy consumption is presented in Fig. 3. The highest value of anode efficiency 6.07 was obtained at pH 9.0. There is not much difference between the anode efficiencies at pH 7.0 and pH 9.0. Energy consumption was also found to decrease with the increase in pH. Total energy consumption (TCE) was 0.94 kWh/kg COD at pH 9 and found to be lowest. Depending on the pH, the TCE values were observed to vary from 4.0% to 6.07% (Fig. 4). TCE

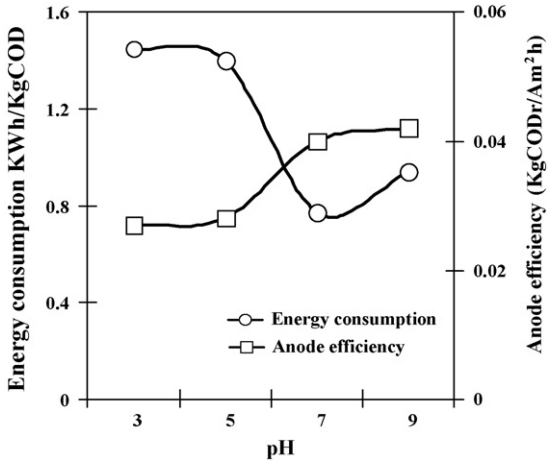


Fig. 3. Anode efficiency and power consumption with pH; electrolysis time: 120 min; current density: 0.012 A/cm^2.

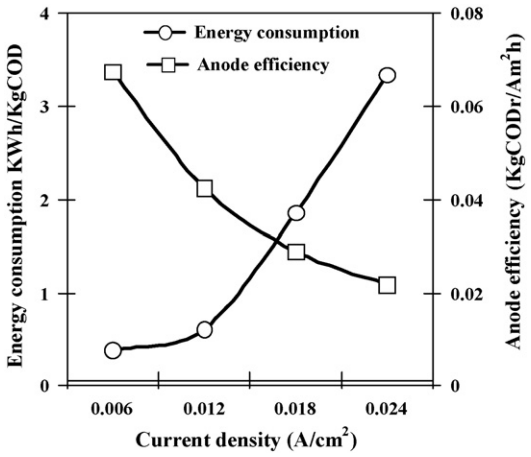


Fig. 6. Anode efficiency and power consumption with current density; electrolysis time: 120 min; pH: 9.0.

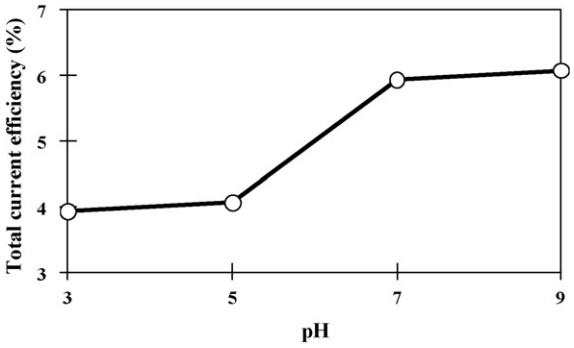


Fig. 4. Total current efficiency with pH.

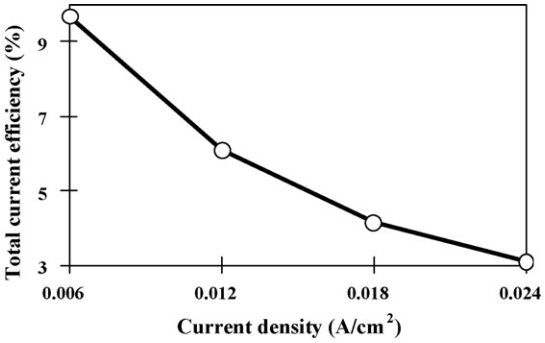


Fig. 7. Total current efficiency with current density.

was found to increase with increase in pH. The increase in TCE from pH 5.0 to pH 7.0 was found to be relatively significant. Therefore neutral and alkaline conditions are favourable for pollution reduction.

3.2. Effect of current density

The next set of experiments was carried out varying the current density from 0.006 A/cm^2 to 0.024 A/cm^2 with an increment of 0.006 A/cm^2. In these experiments, the pH was kept constant at 9.0 and salt concentration was 40 g of NaCl/L. The rate of COD reduction and TKN reduction with respect to time is shown in Fig. 5(a) and (b). COD attenuation was increased significantly when the current density increased. COD attenuation rate was not significant beyond 0.012 A/cm^2 (Fig. 5). That is, COD was reduced by 71.06%, 89.11%, 91.12% and 91.02% at 0.006, 0.012, 0.018 and 0.024 respectively. The increased rate of generation of hypochlorite ion with increase in current density may be attributed to the above results. Anode efficiency and energy consumption were also calculated (Fig. 6). Increase in current density decreased the total current efficiency (TCE) and increased the energy consumption (Fig. 7). It is concluded that the electro-oxidation at lower current density is advantageous

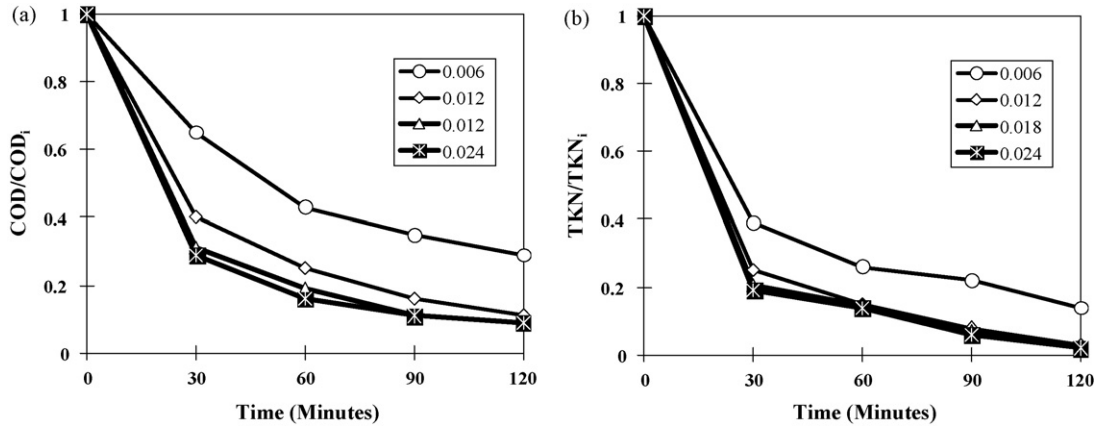


Fig. 5. (a) Effect of current density on COD reduction rate with electrolysis time at pH 9.0 and 40 g of NaCl/L. (b) Effect of current density on TKN reduction rate with electrolysis time at pH 9.0 and 40 g of NaCl/L.

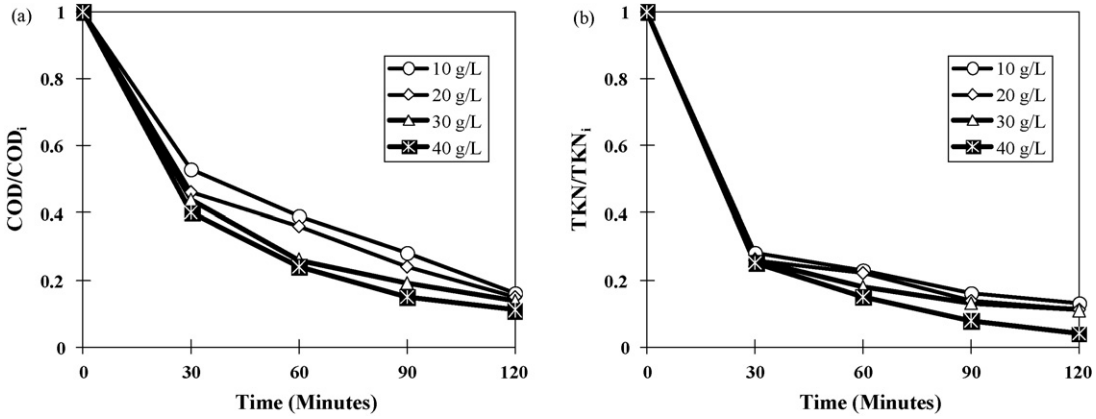


Fig. 8. (a) Effect of salt concentration on COD reduction rate with electrolysis time at pH 9.0 and 0.012 A/cm^2. (b) Effect of salt concentration on TKN reduction rate with electrolysis time at pH 9.0 and 0.012 A/cm^2.

due to less power consumption and current efficiency. Increases in current density decreased the anode efficiency and increased the energy consumption. At 0.012 A/cm^2, 0.018 A/cm^2 and 0.024 A/cm^2 the energy consumed in 120 min for the reduction of 1 kg COD were 0.61 kWh, 1.86 kWh and 3.34 kWh respectively. In other words, for an equivalent reduction of COD more energy was consumed when the current density was more than 0.012 A/cm^2. This may be due to the competing water electrolysis reaction that becomes dominant at higher current densities [33]. Therefore 0.012 A/cm^2 is the optimum current density for the treatment of saline wastewater.

3.3. Effect of salt concentration

In the third set of experiments, the concentration of sodium chloride was varied from 10 g to 40 g of NaCl per L with an increment of 10 g/L keeping the pH and current density constants at 9.0 and 0.012 A/cm^2 respectively. Rate of COD and TKN reduction was found to be directly proportional to the salt concentration (Fig. 8a and b). Attenuation of COD and TKN was increased with increase in salt concentration. However the increase in the attenuation of COD and TKN with respect to ascending salt concentration was not significant. Maximum reduction in COD and TKN were 89.11% and 96.31% at 40 g of NaCl/L. The observed results are in congruence with the reported literature [19]. This trend probably could be attributed to the increased level of generation of chlorine and hypochlorite when the salt concentration is increased [19]. The

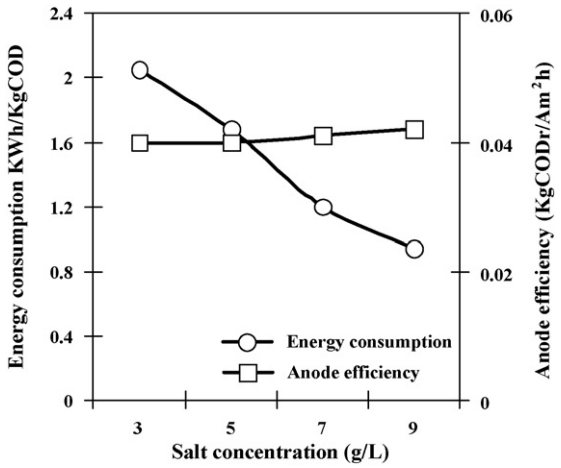


Fig. 9. Anode efficiency and power consumption with salt concentration; electrolysis time: 120 min; current density: 0.012 A/cm^2.

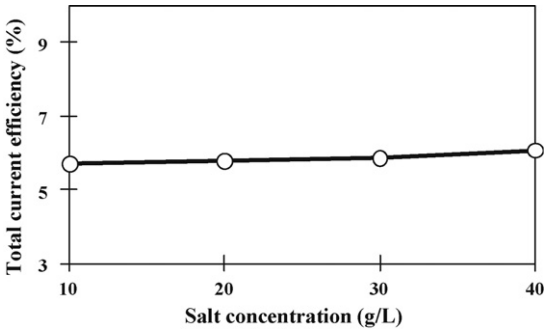
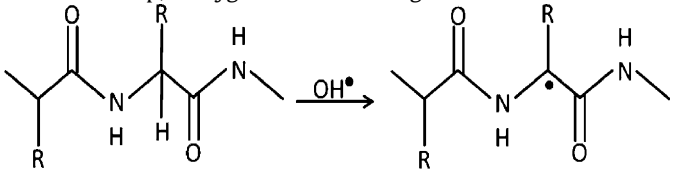


Fig. 10. Total current efficiency with salt concentration.

variation of anode efficiency and energy consumption with salt concentration is presented in Fig. 7 and also total current efficiency is shown in Fig. 10. Anode efficiency and total current efficiency were found to be independent of salt concentration (Figs. 9 and 10). The energy consumption was reduced by 54% i.e. from 2.05 kWh/kg COD to 0.94 kWh/kg COD when the salt concentration is increased from 10 g/L to 40 g/L (Fig. 9). This may be due to the decrease of cell potential brought about by the increase in conductivity of the wastewater.

The mechanism associated with electrochemical attenuation of organic matter is complicated and not unravelled completely. The important products of electrolysis include Cl_2, ClO_2, O_3, $OH^\bullet$, $O^\bullet$, $ClOH^\bullet$, H_2O_2, O_2, H_2 and CO_2. Since the radicals $OH^\bullet$, $O^\bullet$ and $ClOH^\bullet$ are short lived due to their high oxidation potential, they may undergo decomposition to produce other oxidants which may oxidize the organic compounds. This process is called as direct oxidation. On the other hand, the primary (Cl_2 and O_2) and secondary (ClO_2, O_3 and H_2O_2) oxidants have quite long life. They are capable of diffusing into the areas away from the electrodes and continue to oxidize the pollutants [22]. In the oxidation of proteins, as the first step organic radicals are formed by hydrogen abstraction. In the second step, dioxygen reacts with organic radical.



$$R^\bullet + O_2 \longrightarrow ROO^\bullet$$

$$ROO^\bullet + R'H \longrightarrow RCOOH + R'^\bullet$$

Table 2
Characteristics of pickling wastewater and reuse details.

Parameter	TKN (mg/L)		COD (mg/L)		NaCl (mg/L)	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
Batch 1 (control)	390	52	9520	1970	30,145	29,234
Batch 2 (reuse 1)	352	49	9370	1784	30,228	29,400
Batch 3 (reuse 2)	385	44	9463	1820	32,283	31,301
Batch 4 (reuse 3)	398	56	9472	1796	30,346	29,500

Further abstraction of a hydrogen atom leads to the formation of organic hydroperoxide (ROOH) and another organic radical. The organic hydroperoxides are relatively unstable. They may undergo decomposition to cause molecular breakdown [17]. In the present study, the protein present in the saline waste streams might have undergone oxidation to produce peptides initially and amino acids later. Further, electro-oxidation may lead to the production of H_2O, CO_2 and N_2 during eventual mineralization. However the presence of minimum residual COD indicates that substantial level of degradation had taken place but not complete mineralization. The initial step of conversion of proteins into peptides and further into amino acids would result in the reduction of COD. The final conversion of amino acids into H_2O, CO_2 and N_2 would result in the reduction of both COD and TKN.

The electrical energy required for the treatment of 1 m^3 of saline wastewater is 9.3 kWh considering 0.012 A/cm^2 of current density and 120 min of treatment. Energy cost is the main and principal cost component in electro-oxidation. Therefore the cost of treatment of 1 m^3 of wastewater is US$ 1.13 (assuming the cost per unit of energy is US$ 0.12). The cost of energy and the total cost of treatment would diminish significantly as the treatment is carried out at commercial scale. It can be seen from the above that the cost of treatment is relatively lower. Cost of other similar treatment systems such as advanced oxidation process, membrane process, ultra-filtration and nano-filtration) is very high [34].

3.4. Reuse experiments

Saline wastewater of batch 1 of volume 310 L was collected and treated. Prior to treatment the pH of the collected wastewater was increased to 9.0 using NaOH. Electro-oxidation was carried out for 120 min at pH 9.0 and 0.012 A/cm^2. The treated wastewater was reused for pickling of batch 2. Likewise reuse was carried out three times. Wastewater prior to and after treatment was characterised for every reuse. The removal of organic load was assessed by estimating TKN and COD. From the results (Table 2), it is evident that the reuse did not result in the accumulation of pollutants as the recycling progresses. The chromium content and shrinkage temperature of the tanned leathers are the important parameters for indicating the quality. There is not much variation in the quality of the tanned leathers on the reuse of the treated pickling wastewater (Table 2).

4. Conclusions

For the treatment of tannery saline wastewater to remove the organic pollution current density of 0.012 A/cm^2, salt concentration equal or more than 30 g/L and at neutral and alkaline pH conditions are found to be better with respect to pollution reduction and energy requirement. Saline streams from tannery can be treated effectively and adequately rendering the wastewater suitable for reuse. Characteristics of the saline wastewater after electro-oxidation indicate that the no accumulation of organic load is effected due to reuse.

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