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# Treatability study of liming waste water in tannery by electro coagulation

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The liming waste water from tannery industry creates more pollution problem with the environment. Liming waste water contains higher amount of COD (Chemical Oxygen Demand), sulfate, free ammonia and nitrate ion concentration. Lots of treatment methods have been tried by different authors, but the small industries could not give importance to install the treatment methods. So the drawback of liming waste water and the optimum treatment condition for the maximum above 90% removal of COD, TDS (Total Dissolved Solids), sulfate, nitrate, chloride and free ammonia by electro coagulation process with different *p*H, different electrolysis time and electrode distance with varying current density have been analyzed. Finally, the results discuss about the challenges of liming waste water by electro coagulation method.

**Keywords:** Liming water, Electro coagulation, Electrolysis time, Electrode distance, Energy consumption

The highest leather manufacturing units were located in Tamil Nadu, India. It is the third largest leather producer in the world. The Indian leather industries play an important role for weak section peoples to give the employers' opportunity. The conversion of hides and skins into leather produce huge amount of pollution waste by directly or indirectly in air, water and land. Blacksmith Institute's reported only 20% of chemicals used for leather processing, remaining 80% released as waste to the environment[1]. It is possible to divide the released leather industry effluent load in four main stages such as, initial beam house processing, tanning, post-tanning and finishing process. The biggest part and problematic waste water in tannery were released from beam house process.

The initial beam house process, the raw material introduced in various cleaning and conditioning process with variety of chemicals. Conserved hides are soaked in clean water to remove the impurities such as, dirt, blood and conservation salt. The waste water generated from the soaking operation i.e., soak liquor, contains high amount of salt and suspended matters[2]. In Tamil Nadu, according to pollution control regulations, the tanneries are required to segregate the salt laden soak liquor and discharge into solar evaporation pan (SEP). After this soaking, the liming process takes place, used to remove natural oils and proteins, in the hide. By adding lime and sodium sulfide, *p*H-value of liming waste water shifted to around 11 and produces an obnoxious smell in that area. By doing so, hair is chemically removed from the surface of the hide. Since, these highest COD value effluents are toxic to the aquatic environment, it is essential to neutralize them in below the toxic limit[3]. Deliming process used to remove the excessive lime by ammonium salts. Major parts of the ammonium load in the effluents were released in this process. Pickling is used to reduce hide *p*H, which favors tanning. Authors were reported, tannery waste water contains different types of pollutants with huge amount of concentration[4]. The main pollutants are chloride, ammonium ions, nitrate and Sulfide ions originated from liming process of tannery and most of the pollutants are insoluble and only few are colloidal[5]. The amount of COD and sulfide ion concentration reaches several thousand of mg/L of oxygen[6-10.]

Treatment of waste water is becoming more important due to the diminishing water resources, increasing waste water disposal costs and stricter discharge regulations that have lowered permissible contaminant levels in waste streams. Various physical or chemical[11-20] or biological methods[21-25] or combined treatments[26-28] were carried out by different authors in tannery waste water. Especially, direct discharge of liming waste water from tanneries into water streams creates detrimental effect on the environment. Based on the economic aspect, liming waste water was treated with alum by chemical coagulation used in maximum tannery industries in India. The use of Coagulation method is reduces the chemical cost and produce higher sludge volumes and it removes reasonable percentage of COD, colour and odour. But at the same time, produced sludge was toxic and hazardous to the environment and disposal of sludge cause land depletion[29].

Based on literature, few advantages are observed in electro coagulation process[30-32]. The result showed the survey, the removal effect of different pollution with mild steel electrodes are superior with respect to aluminum as sacrificial anode during the treatment of liming waste water produce better result than aluminum[33,34]. Nitrate and ammonia removal by electro coagulation method produced better results in various field[35-40]. The big challenge of tannery liming water was the complete removal of pollutants which is not possible at same operating condition such as electrode distance, electrolysis time and *p*H. In liming drum, waste water contains a mixture of soaking and liming effluent, the removal efficiency of COD, sulfide and oil-grease reached 82, 90 and 96% in current density 35 mA/cm$^2$ at 10 min electrolysis time and *p*H 3 (Ref.33). Authors can explain only two or three parameters influenced in liming waste water. So, the treatment method cannot install successfully in all tannery industries. Leather Associations and Councils in India has been reported, most of the Indian tanneries faced some challenges such as, low level of technology in small tanneries and no specific dedicated industrial areas for leather sector, poor capacity utilization in most tanneries leading to higher financial cost, pollution problem and poor database[41].

In the present study, the feasibility and efficiency of electro coagulation and the determination of the optimum treatment conditions for maximum removal of chemical oxygen demand (COD), Total dissolved solids (TDS), sulfate, ammonia, nitrate and chloride with *p*H, different current densities, different electrolysis time with soluble electrodes (mild steel electrode and aluminum electrode) were studied in detail with liming waste water.

## Experimental Section

For the present investigation, the liming waste water was collected at processing industrial effluent discharged from the industry located at Erode, Tamil Nadu in India. Soaking liquor discharged in solar evaporation pans, after that process liming waste water was collected and all the pollutant parameters include COD, *p*H, total dissolved solids, nitrate, sulfate, free ammonia and chlorine concentration were analyzed as per the Standards Methods (APHA-AWWA-WPCF) for the examination of water and waste water and methods are reported in literature[42] and the observed values are tabulated in Table 1. Liming waste water were treated by using mild steel and aluminum electrodes (10.4cm×3.5cm×0.6cm) in electro chemical cell for Electro Coagulation (EC) treatment. This is due to fact that they are cheap and production is very simple. The electrodes are connected to a DC power supply (0-40V, 15Watts, 0-3A) and the temperature maintained 30°C throughout the process.

## Results and Discussion

The removal efficiency of impurities from liming water by EC process depends on several operating parameters, such as the type of electrode material, initial *p*H, current density and electrolysis time. The investigation concentrate to determine the optimum operating conditions for liming waste water under initial *p*H, current density and electrolysis time on COD, TDS, sulfate, chloride, nitrate removal, electrodes and energy consumption.

### Effect of *p*H

In the electro coagulation process the *p*H of the solution is known to play an important role in the removal of pollutants[32,33]. The liming water *p*H was adjusted with using diluted sodium hydroxide or hydrochloric acid. The experiments were conducted for *p*H ranges from 3 to 10 by keeping the electrode distance 4 cm current density constant at 25V for electro coagulation time of 40 min. Table 2 shows concentration of COD drops down from 20,052 to 1050 mg/L with a removal of 94.7% at *p*H 4-5. It was observed that the TDS and chloride also decrease in acidic medium with a removal of 91.4 and 86.9% at the *p*H range 4-5. At the same time, the sulfate and nitrate ion concentration can be decreased slowly and reach maximum removal of 86% and 89% at *p*H 8 indicated in Fig. 1. After the analysis, the *p*H of

Table 1 — Characteristics of liming waste water before treatment

| Parameters | TDS | COD | BOD | Electrical conductivity | *p*H | Free ammonia | Nitrate ($NO_3$) | Chloride | Sulfate |
|---|---|---|---|---|---|---|---|---|---|
| Unit in (mg/L) | 20052 | 30600 | 10780 | 286.4 | 12.9 | 889.41 | 1306 | 3000 | 1457 |

Table 2 — Percentage of removal efficiency of different parameters at different *p*H

Electrolysis time: 40 min ; Voltage: 25V ; Electrode distance: 4 cm

| *p*H | TDS | COD | Free ammonia | Sulfate | Nitrate | Chloride | *p*H after analysis |
|---|---|---|---|---|---|---|---|
| 2 | 47 | 52 | 36 | 19 | 26 | 27 | 3.2 |
| 3 | 64 | 78.2 | 62 | 27.7 | 33 | 44 | 4.3 |
| 4 | 84.3 | 91.4 | 90.5 | 44.2 | 48 | 68 | 5.3 |
| 4.5 | 90.7 | 94.7 | 89.5 | 59.7 | 53.5 | 86.9 | 6.1 |
| 5 | 91.4 | 87.4 | 72.5 | 73.5 | 58.5 | 86 | 33.5 |
| 6 | 72 | 81.6 | 62.7 | 78.3 | 62 | 65 | 7.1 |
| 7 | 53 | 68 | 46.4 | 83 | 76 | 42 | 8.5 |
| 8 | 46 | 43 | 32 | 86 | 89 | 38 | 9.4 |
| 9 | 34 | 35 | 29 | 78 | 85 | 27.6 | 10.4 |
| 10 | 23 | 25 | 22 | 70 | 83 | 19.3 | 11.1 |

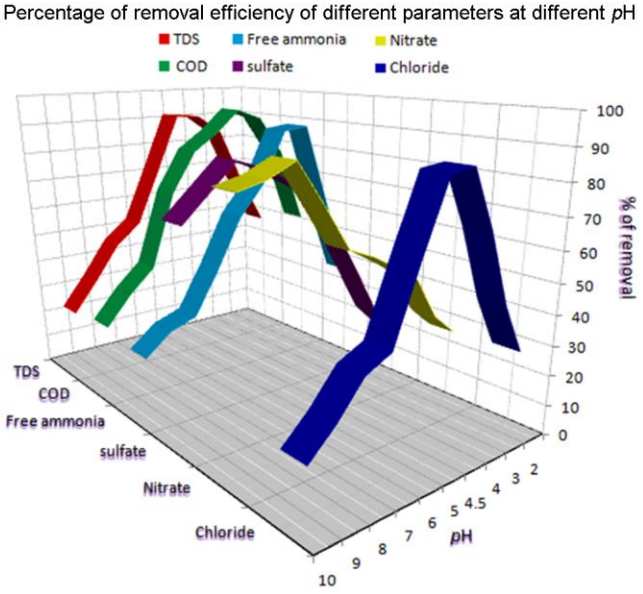

Fig. 1 — Removal efficiency of liming water pollutants at different *p*H by electro coagulation (Electrode distance 4 cm, current density 25V and 40 min electrolysis time)

the waste water can increase at least one unit (Table 2). During the analysis, the coagulation developed to remove COD, TDS, sulfate, chloride and nitrate by cathode reactions and it slowly increases the *p*H of the waste water. From the results, it is seen that the optimum *p*H for the coagulation of tannery liming waste water is 4-5 for COD, TDS, chloride removal and 8 for sulfate and nitrate removal. In alkaline medium, the sulfate and nitrate were settled, at the same time the sludge formation increase COD, TDS concentration in waste water at higher *p*H. The optimum *p*H can identified both acidic and alkaline condition for the removal of different parameters for liming waste water. Increase of *p*H after analysis in waste water; produce more electrode consumption and operating cost. Treatment of waste water with alteration of *p*H is only useful for the removal of two or three pollutants and not suitable for all parameters. A small disadvantage was observed that after coagulation, tannery effluents were very alkaline and electrodes consumption was also high for liming waste water. Therefore, the *p*H of the treated tannery liming waste water should be adjusted to be neutral before they are discharged into water steams, otherwise combined or biological treatment will be required to meet safe environmental standards.

### Effect on COD

Initially, the experiment was carried out with raw waste water (*p*H 4.5 adjusted) with varying voltages 10, 15, 20, 25, 30 and 35V in different electrode distance 2-4.5 cm intervals of 0.5 cm. Figure 2 clearly indicate that the percentage of COD removal increased with increasing electrode distance. Results shows, when the electrode distance increased from 2-4.5 cm, the percentage of COD removal varied from 68.5-96.8% at 35 min of electrolysis time at 25V. Less interaction of pollutant ions with hydroxide ions could decrease the removal percentage COD beyond 4 cm. The formation of solid particles and bubbles at anodes and cathodes produce electrical distance, for this reason, the removal efficiency is lower for electrode distance from 2 to 3.5 cm compared to 4 cm. The removal efficiency increased with increasing electrolysis time up to 30 min, this depends on the concentration of hydroxyl and metal ions produced on the electrodes. Thus, the optimum electrolysis time for this study is chosen as 35 min at 25V with 4 cm electrode distance for the maximum removal of COD.

### Effect on TDS

The removal efficiency of TDS at 25V shows 4 cm electrode distance in 15,30,35 min, the

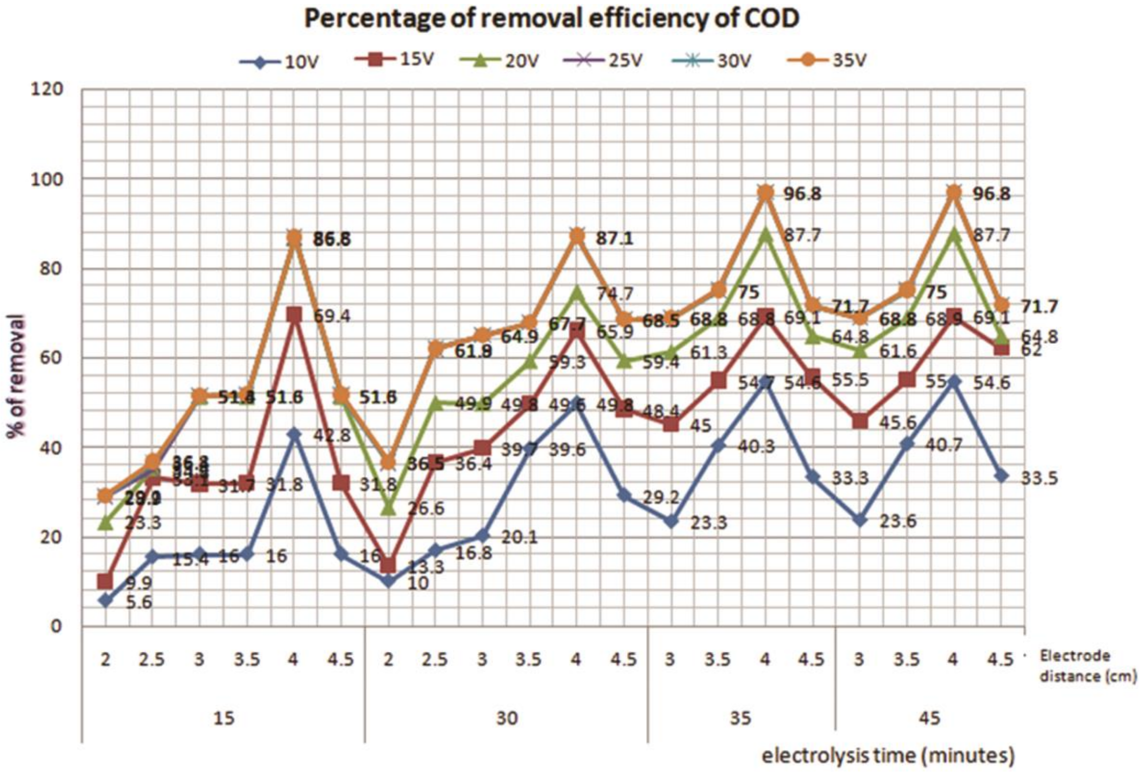

Fig. 2 — Removal of COD in different electrode distance and electrolysis time at 10, 15, 20, 25, 30 and 35V.

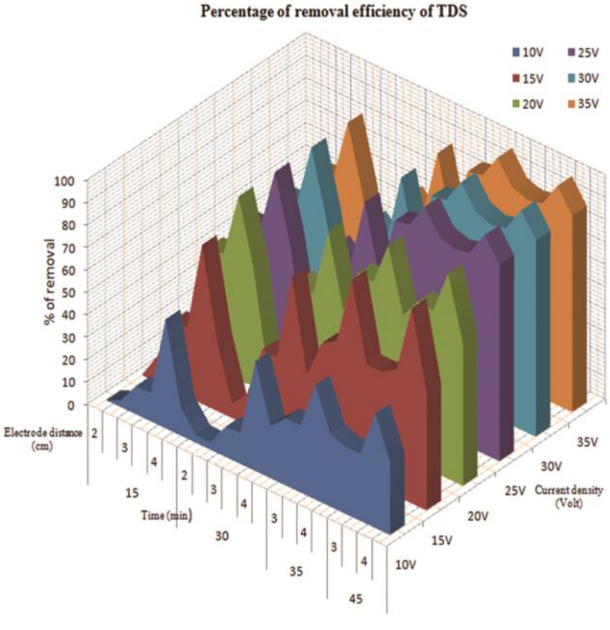

Fig. 3 — Removal percentage of TDS in various electrode distance at different electrolysis time with different current density by electro coagulation method.

concentration of TDS fall down 20052 mg/L to 9442, 2567 and 433 mg/L, considerable amount of removal was not obtained by increase of electrode distance (Fig. 3). The reason mentioned above for COD was accepted for increasing electrode distance for TDS. During electro coagulation process, in 35 min a remarkable change of 97.8% TDS removal (Fig. 3) at 25V was produced, but on increase in electrolysis time nearly above 120 min, TDS removed nearly 99.5% in liming waste water and also increase in electrolysis time can increase the energy consumption cost.

### Effect on sulfate

The results found for sulfate was quite interesting to analyze, the removal of ions started after 25 min of electrolysis time (Fig. 4). In 25 min at 30V, the removal efficiency was 68.6% in 3 cm electrode distance, 78.5% for 3.5 cm electrode distance and 87.2% for 4 cm respectively. In 30V of current density at 4 cm electrode distance, 88.4% of sulfate ions were removed, but the same percentage was obtained in 70 min at 25V and 100 min at 20V. The electrolysis time, i.e. 150 min onwards, 93% of removal efficiency was obtained for sulfate ions at 20V of current density (Fig. 4). During the analysis, concentration of ions and hydroxide ions were produced in the anodes and cathode were found to increase with increasing electrolysis time and also the bad smell produce from the waste water indicated conversion of sulfate ion into sufide ion during the process. For this reason, removal efficiency of sulfate

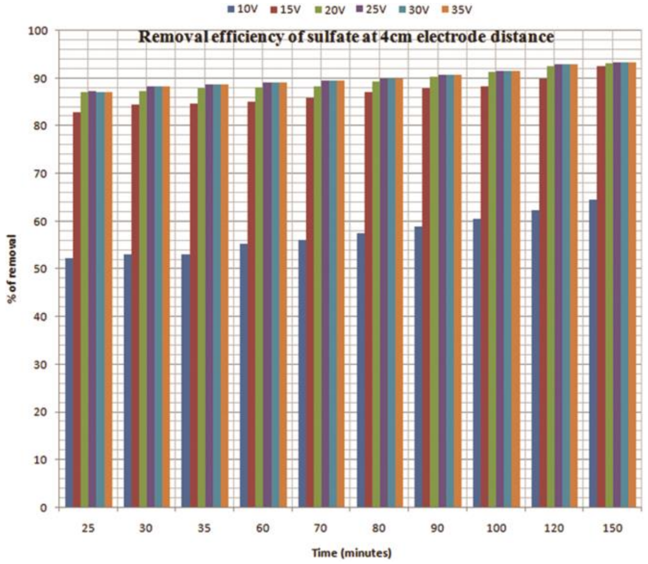

Fig. 4 — Removal percentage of sulfate in various electrode distances at different electrolysis time with different current density.

was increased with increasing electrolysis time. In 30 min, the rate of removal was 82.9% at 20V, which is acceptable when compared with other parameters. On increasing electrolysis time, the concentration of sulfate ion can decreased, meanwhile sludge formation slowly increased the COD and TDS concentration in liming waste water.

### Effect on free ammonia and nitrate ions

It is noted that the concentration of free ammonia decreases from 889 mg/L to 92 mg/L very quickly, and reach 90% of the removal in 15 min, 20V (Fig. 5). Further increase of electrolysis time and electrode distance does not produce more difference in units. So the optimum condition was chosen for free ammonia, later the analysis indicates the nitrate ion concentration was decreased very slowly even after the change of operating conditions. Compared to other parameters, the removal efficiency increases with increase in electrolysis time or electrode distance or current density, but not in the case of nitrate. Nitrate removal efficiency is maximum 85.0% at 25 V in 30 min **(**Fig. 6**)**, to improve the results, higher electrolysis time was given but 85.1% at 45 min and 85.14% at 60 min were obtained. The reason can be noted that during the analysis, ammonium ions were converted into nitrate ions based on electrode reactions. The results clearly indicate that the removal efficiency depends on electrode reactions in electro coagulation process[34].

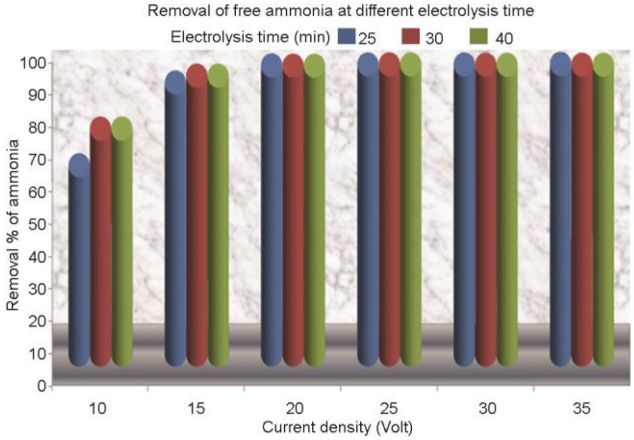

Fig. 5 — Removal percentage of free ammonia in various electrode distance at different current density in 25, 30 and 40 min.

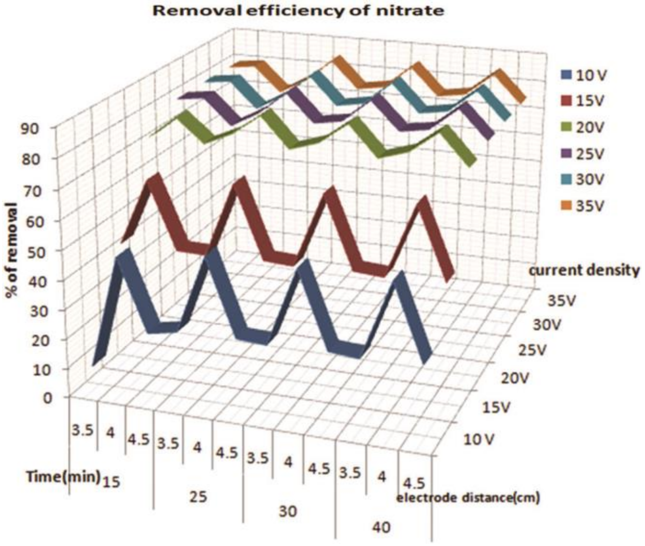

Fig. 6 — Removal percentage of nitrate in various electrode distances with different electrolysis time.

### Effect on chloride ion

The percentage of chloride ion removal varied from 68 to 95% in 30 min at different current density and with varying electrode distance, 64 to 95% results obtained at 25V. The maximum removal efficiency of chloride ion at 25V in 30 min of electrolysis time reaches 95.1% in 4 cm electrode distance (Fig. 7). Changes in electrode distance or electrolysis time or current density did not increase the removal efficiency of chloride. The chloride ion could be removed along with COD, TDS at same conditions.

### Energy consumption

The energy consumption can be calculated during electro coagulation process in terms of kWh/m$^3$ of treated effluent by using Faraday's Law. Electrical

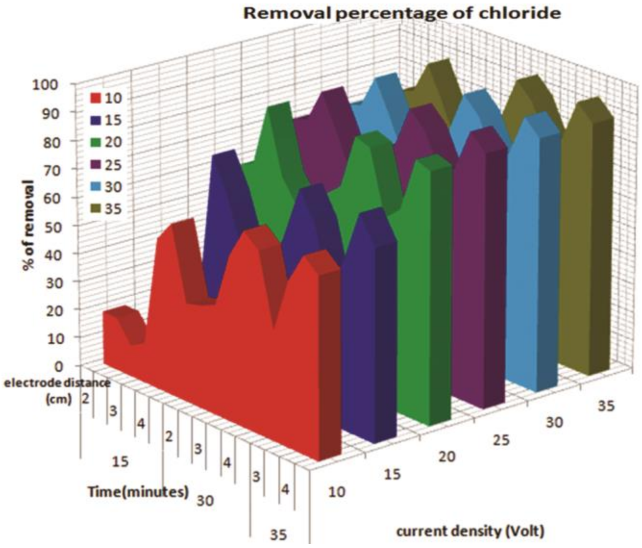

Fig. 7 — Removal efficiency of chlorine in different operating condition.

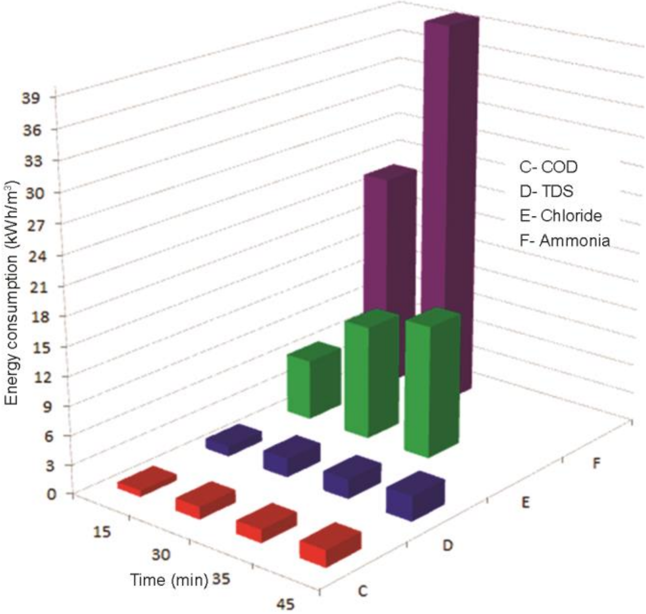

Fig. 8 — Electrical consumptions for COD, TDS, chloride, free ammonia at 4 cm electrode distance in terms of kWh/m$^{3.}$

consumptions for COD, TDS, Chloride, free ammonia removals were found to be 0.63, 1.03, 6.28 and 22.58 kWh/m$^3$ in 15 min of electrolysis time (Fig. 8). When the energy consumption is considered for COD, TDS, the removal efficiency was higher in 35 min of electrolysis time at 25 V. Highest removal were obtained for COD and TDS in 35 min with 1.33, 2 kWh/m$^3$ electrical consumption. The lower electrolysis time of chloride and free ammonia produce 89% of removal with higher energy consumption of 11.81 and 45.16 kWh/m$^3$. In 15 min, 33.2 kWh/m$^3$ of energy was consumed for 93.4% of nitrate removal. Then the amount of 21.79kg /m$^3$ sulfate was removed for 88.8% in 35 min, compared to other parameters, the removal percentage should be low (Fig. 9). However, it was observed that more electrolysis time require for removing high percentage of sulfate ion, this leads to increase in the energy consumption cost for sulfate removal. For a given time, the removal efficiency increased with the increasing of cell current. At higher electrolysis time, it produces higher removal of pollutants, because hydroxide flocs formed by metal oxidation and also the bubble size decrease with increasing density. Analysis of the results show that the removal percentage increased with time. This is due to the oxidation and reduction reactions. Similar results were obtained regarding the effect of treatment time [43-46].

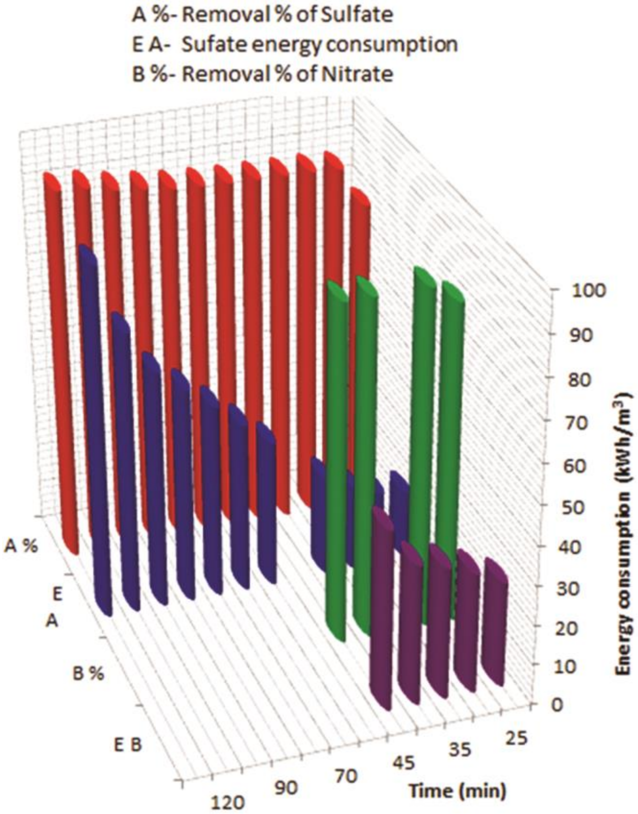

Fig. 9 — Electrical consumptions (kWh/m$^3$) of sulfate and nitrate in different electrolysis time at 4 cm electrode distance.

## Conclusion

The concentration of the pollutants was decreased maximum in 4 cm electrode distance by electrocoagulation process with liming waste water.

The removal efficiency of COD for 96.8% and 97.8% of TDS is found at 25V with 35 min of electrolysis time. The same current density nitrate and chloride ion are removed at 85% and 95.1% in 30 min of electrolysis time. In 15 min, a 20V ammonium ion shows 90% of the removal and decrease of ammonium ion concentration increases the nitrate ion in waste water. In case of sulfate ion, the removal efficiency increases with increasing electrolysis time and decreases the current density, but more of electrolysis time can cause more energy consumption in the treatment. Electro coagulation process is suitable for the removal of important two or three parameters influenced in waste water. From the reported results, some disadvantages are to be noted that the removal of sulfate ion increases the treatment cost of liming waste water and after the analysis, treated effluent produces a bad smell due to the conversion of sulfide ion. Sacrificial anodes are replaced frequently at higher *p*H and the usage stainless steel electrode creates brown color to the treated effluent. The pollutant present in the liming waste water with higher concentration requires higher energy in electro coagulation process or combined treatment with EC process to produce best results with low energy consumption.

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