Reuse of Treated Tannery Wastewater for Irrigation by a Combined Electrocoagulation/ Electrodialysis Process

Abdalhadi   Deghles
Department of Scientific Research, Alistiqlal University, 10 Jericho, Palestine

Abstract
Most of countries have plentiful water resources and they all provide priority to the protection of water quality. In this work, a laboratory scale a combined electrocoagulation (EC)/ Electrodialysis (ED) process was applied to treat the tannery wastewater in order to bring the quality up to the international wastewater reuse standards. The effects of operational variables on performance were examined. The electrocoagulation current density, operating time and pH are the most important variables. In wide ranges, conductivity has no remarkable effects on pollutant removal but constitutes a good way for minimizing operating costs. Thus, it was found that that removing of 1 Kg of COD produces 0.35 Kg of organic sludge. In contrast, we concluded that 1 Kg of chromium produces regarding 6.5 Kg of inorganic sludge. However, combined process was sufficient to reuse treated tannery wastewater for irrigation. The quality of treated tannery wastewater was compared with various international standards/guidelines for wastewater reuse. It was found that the studied parameters such as, pH, COD, NH_3-N, Cr and color were within allowable limits. In addition, electrical conductivity and TDS are important to determine the suitability of wastewater for safe irrigation. Their values are within safe range. Ultimately, it can be confirmed that the study may help to conserve tannery wastewater and alleviate the water shortage problem in the study area.
Keywords: Combined process; irrigation; guidelines; tannery; reuse
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1. Introduction
A few decades ago, water and energy sources were classified as the top two challenges for the twenty-first century. These challenges force the mangers, planners, and researchers to look for additional water and energy supply without compromising the environmental, public health and sustainability dimensions (Deghles and Kurt 2015). Problems are compounded as an Increasing pollution from point and non-point sources such as industry and agriculture, respectively, the ever-increasing population, urbanization and climatic changes, all of these are being leaded to decline water quality and quantity (Bagastyo et al.2011; Deghles and Kurt 2016) To circumvent this problem, an alternative water resource plan is being advocated.

However, the present and future severe water supply in agricultural sector is being the limiting factor in securing products and food to the community. In this context, Wastewater treatment is considered as an efficient tool to mange water resources which can be reused safely. However, wastewater loads an extensive spectrum of pathogenic organisms, which pose risk to agricultural workers, crop handlers and consumers. Thus, high levels of nitrogen in wastewater may result in nitrate pollution of groundwater resources. As well as, accumulation of heavy metals in soils and its uptake by plants is another risk associated with wastewater irrigation (Saleem 2009)

Absolutely, the environmental impact of the RWW reuse needs to take into consideration the direct effects of RWW in irrigation reuse (effect on soil, on crops and on the landscape vegetation) or in environmental reuse (ecosystem), and also the hydrological indirect effects of water bodies. From this point, the WHO and FAO guidelines continue to be the benchmark target for decision makers in developing the wastewater recycling sector. Here, it should be referred that WHO guidelines that focus mainly on the protection of human and public health, the FAO has developed a field guide for evaluating the suitability of water for irrigation (Ayers and Westcot 1985).

As well known, tannery industry is recognized widely as higher consumer of water as well leading economic sector in many countries. Tanneries, ultimately, generate wastewater in the range of 30–35 L Kg-1 skin/hides process with high concentrations of organic and inorganic pollutants (Sundarapandiyan et al. 2011). Tannery, in the one hand, is characterized as an influential pollutant that can cause strict environmental problem associated to its high chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TSS), total kjeldahl nitrogen (TKN), sulfides, chromium, deep color content together with variable pH and low biodegradability (Durai et al. 2011). It should be, absolutely, searched a cleaner technology, economically as well as environmentally sustainable tannery wastewater treatment methods.

Electrochemical technologies have investigated in recent year in environmental applications especially for treating water/wastewater. One of these processes electro-coagulation (EC) which has achieved much attention due to have attractive advantages like; simple, reliable and cost effective operation for the treatment of wastewater. However, it engrosses dissolution of metal from the anode with simultaneous formation of Hydroxyl ions and hydrogen gas is generated at the cathode and it can be recovered for use as an energy source or a reactant for other industrial applications (Calheiros et al. 2009). Therefore, EC is considered as a low sludge production technology,

flocs are relatively large, contains less bound water, are more stable, amenable to filtration , and therefore are not required to chemical aids (Song and Williams 2004). On the other hand, membrane technology has been applied in wastewater treatment and recycling. One of the most important of the membrane technology or electrochemical separation process is electro-dialysis (ED). Generally, the most importance different of ED compared to other membrane processes is the use of an electrical current with low levels, rather than pressure; which helps to reduce the cost of ED (Huang et al.2007). Thus, it has been successfully applied in recycling systems, drinking water and wastewater treatment, to reduce pollution and water reuse, recycling valuable components from the waste streams. One of these applications of electrodialysis in wastewater treatment systems is processing rinse water from the electroplating industry (Suthanthararajan et al. 2004). Sometimes it becomes necessary to use two or more methods of treatment, i.e. hybrid processes, to ensure efficient treatment of wastewater (Mollah at al. 2004).

Present study is carried out first to characterize the wastewater quality generated at OTIR and then to treat it by integrated electrocoagulation (EC) / electrodialysis (ED) technologies to bring the pollutants within the guidelines of national and international environmental protection agencies. As well as, the study fits into a growing body of research in the field of water reuse strategies and provides data on the quality of tannery wastewater. It is one of the first focused investigations into the reuse of tannery wastewater for food crop irrigation, which may become a vital survival strategy for residents of water-scarce regions in years to come.

2. Materials and methods
2.1. Chemicals and analytical techniques
Experiments were carried out using a tannery wastewater, it issued from different outflow wastewaters of the Organized Tannery Industrial Region (OTIR) which is located in the Tuzla quarter of Istanbul, Turkey. This tannery wastewater was already used in previous investigations (Deghles and Kurt 2016). The physicochemical features of the tannery wastewater to be treated are reported in Table 1. The wastewater analyses were carried out in accordance with the Standard Methods for Examination of Water and Wastewater (APHA, 1985). "pH, conductivity, COD, total chrome, and color were determined with (A Jenway 3040 brand, HACH HQ40d, closed reflux titrimetric method 5220C, A-Analyst 400, atomic absorption spectrometer, and HACH LANGE GmbH DR 5000 (spectrophotometer), respectively)". Merck analytical quality chemicals were used in the preparation of reagents.

Table 1

Characteristics of raw tannery wastewater used in this study

Parameter	Value
PH	4.10 at 6.5 ^{0}C
Conductivity (mS cm^{-1})	11.71
COD	2200-3000
Soluble COD	1436- 1959
Suspended solids	912
Chloride	1691
Total chromium	570
Color	824
NH3-N	180

Note: Color ADMI (10) Pt-Co, all other parameters as mgL^{-1}.

2.2 Experimental set-up and the procedure
The effluent tannery wastewater was passed through electrocoagulation process and afterwards was treated by the integrated EC-ED system. The electrochemical reactor was constructed with Plexiglas having a dimension of 5.0 × 10.0 ×20 cm. It contained a set of 5 pairs of electrodes made of iron or aluminum, which reduced the working volume to 2.5 L. The electrodes were connected vertically with a gap distance of 7 mm. The con figuration resulted in a total electrode working area of 45 cm^2. The electrodes were connected in monopolar parallel mode to a DC power supply and the electrochemical reactor was operated in continuous mode. The operating parameters and conditions are summarized in Table 2. In this context, EC treatment process is proposed that not enough efficiently for reuse tannery wastewater safety for irrigation. So, the ED technique was linked with EC technique. In this study; bipolar membrane electrodialysis (BMED) process was stratified. A PCCell ED 64-4 unit and BMED 1-3 bench ED pump unit obtained from PCCell GmbH were utilized. Electrodialysis experiments were performed in a pilot scale ED system, using platinized titanium (Titane/Pt-Ir coated) electrode as anode and cathode with effective membrane area of 64 mm2 per membrane, the distance between two membranes was 0.5 mm. The number of membrane pairs in the cell was one Hydrogen chloride at a concentration of 0.01 M was used as electrode rinsing solution in all experiments. The effluent was fed into the concentrate and dilutes chambers in the

ED cell. A constant potential of 24 V was applied. At the start of each test one sample was taken for analysis.

Table 2

Conditions and operating parameters

Operating parameter	Value
Current density, mA/cm^2	7 and 14
Electrode number, pair	5 for Al or Fe
Electrode gap, cm	0.7
Wastewater volume	2.5 L
Inlet flow rate, ml/min	17, 20, 25, 33, 50 and100
Electrocoagulation time (min)	25, 50, 75, 100, 125, and 150
Initial pH	6 for Al and 7 for Fe electrodes

3. Results and discussion

3.1 Sludge production

Clearly, EC has characterized as less sludge formation which is readily settable and easy to dewater as it is chiefly composed of metallic oxides and hydroxides. Flocs formed by EC are similar to chemical flocs except that EC flocs are larger, contain less bound water and are more stable. Hence, they can be separated faster by settling and filtration (Kumar and Goel 2010). EC sludge production is proportional to characteristics of raw wastewater, settable solids and matter destabilized by coagulation and concentration flocculent (Kobya et al. 2006). It can be observed from table 3 that the amounts of organic sludge were 0.43 – 0.72 Kg/m^3 in the case of aluminum electrodes while they were 0.38- 0.67 Kg/m^3 in the case of iron electrodes. The amount of sludge produced is related to the amount of pollutants removed. Based on our results in two cases (Al &Fe) we approximately found that removing of 1 Kg of COD produces 0.35 Kg of organic sludge. In contrast, we concluded that 1 Kg of chromium produces regarding 6.5 Kg of inorganic sludge.

Table 3

Sludge production by Electrocoagulation process (kg/m^3)

COD removed	Chromium removed	Organic sludge	Inorganic sludge
			For aluminum electrodes
1.26	0.524	0.43	1.10
1.48	0.566	0.50	1.50
1.74	0.568	0.57	2.60
1.93	0.569	0.65	2.95
2.00	0.569	0.70	3.5
2.00	0.569	0.72	3.9
			For iron electrode
1.18	0.564	0.38	1.45
1.40	0.567	0.47	1.75
1.60	0.568	0.58	2.60
1.80	0.569	0.63	3.0
1.88	0.569	0.65	3.70
1.88	0.569	0.67	5.40

3.2 Changes of pH values

It has already been established that pH is a vital operating factor influencing the performance of electrocoagulation process (Deghles and Kurt 2016). Typically, pH of the medium is changing during the process, as observed also by other investigators (Chen, et al. 2000). This change depends on the type of electrode and the initial pH. The pH is continuously observed during the study.

The results are presented in Figure 1.a and b. In the case of A1 electrodes, it can be seen from Figure. 1. a, when current density and initial pH were 7 mA/cm^2 and 4.1 respectively, pH changed from 4.1 to 6.2. And also, when current density and initial pH were 14 mA/cm^2 and 4.1 respectively, pH changed from 4.1 to 7.4. However, when current density and initial pH were 7 mA/cm^2 and 6 respectively, pH changed from 6 to 7.5. And also, when current density and initial pH were 14 mA/cm^2 and 6 respectively, pH changed from 6 to 9.48. It could be explained by the excess of hydroxyl ions produced at the cathode and by the liberation of OH$^-$ due to the occurrence of a partial exchange of Cl$^-$ with OH$^-$ in Al (OH)$_3$ (Feng 2006).

In the case of Fe electrodes, it can be noticed from Figure 1.b, when current density and initial pH were 7 mA/cm^2 and 4.1 respectively, pH changed from 4.1 to 6.35. And also, when current density and initial pH were 14 mA/cm^2 and 4.1 respectively, pH changed from 4.1 to 6.5. However, when current density and initial pH were 7 mA/cm^2 and 7 respectively, pH changed from 7 to 8.1. And also, when current density and initial pH were 14

mA/cm^2 and 7 respectively, pH changed from 7 to 9.1. The pH of water is anticipated to be high after EC; this is may be due to ammonia stripping process.
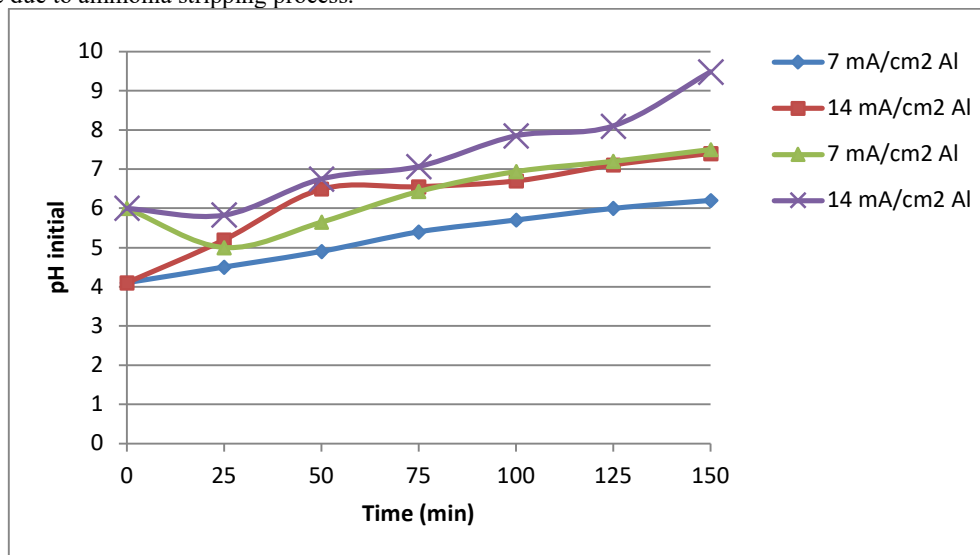

Fig. 1. (a) Change of pH values during electrocoagulation process using aluminum electrodes
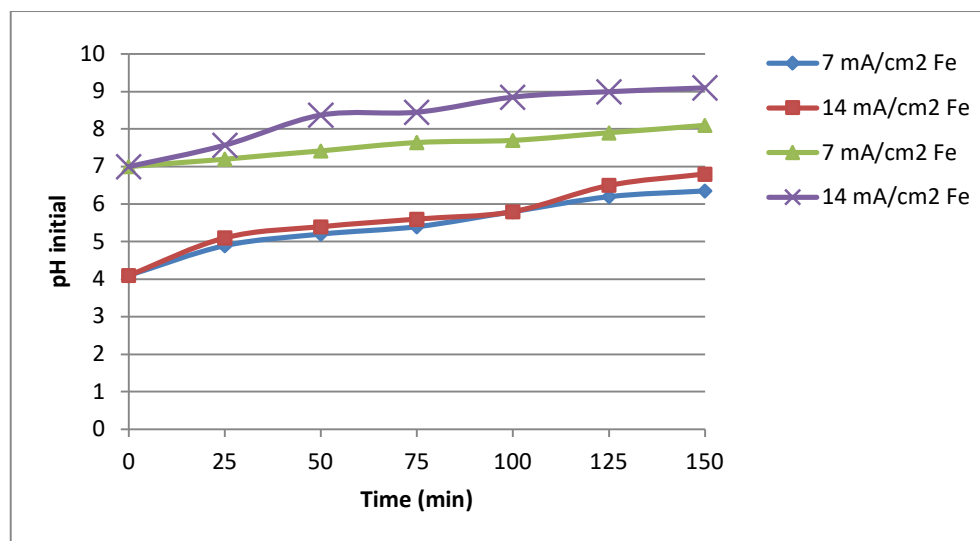

Fig. 1. (b) Change of pH values during electrocoagulation process using iron electrodes

3.3 Effect of wastewater conductivity on the specific energy consumption
Usually, sodium chloride is employed to increase the electrical conductivity of the wastewater to a suitable level. Wastewater conductivity affects faradic yield, cell voltage and thus energy consumption in EC cells. Sodium chloride was chosen because of its low toxicity at moderate levels, its reasonable cost, and because the chloride species avoids inhibition phenomena at the surface of sacrificial anodes (Kim et al. 2002). However, an excessive concentration of sodium chloride was proved to be detrimental to process efficiency (Merzouk, 2009). According to our results, already, it has established that increasing the conductivity of wastewaters had not a considerable effect on pollutants removal efficiency. Figure 2.a and b show the Variation of tannery wastewater conductivity vs. electrocoagulatiom time.
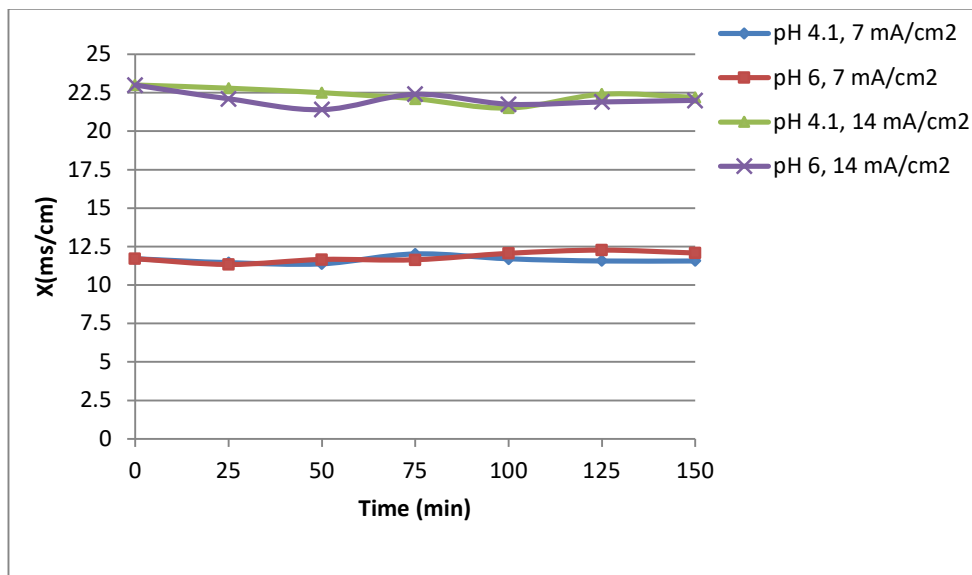
Fig. 2. (a) Variation of wastewater conductivity vs. electrocoagulatiom time (min) using aluminum electrodes
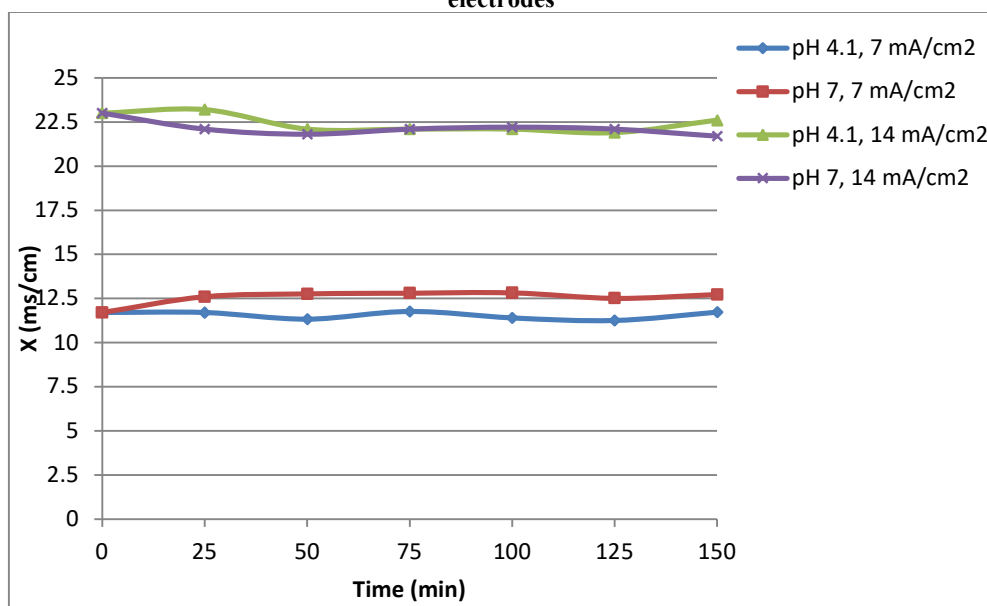

Fig. 2. (b) Variation of wastewater conductivity vs. electrocoagulatiom time (min) using iron electrodes

However, it must be pointed out that the absence of supporting electrolyte is never the optimum situation from an energetic point of view. In this work, the conductivity of wastewater was adjusted using 4 g NaCl/L for the current density 14 mA/cm^2. This is illustrated by Figure 3.a and b that report the evolution of specific energy consumption as a function of NaCl addition in terms of Y_{COD}. The electrical energy consumed, expressed as kWh/m^3 of the tannery wastewater treated. Energy consumption in kWh/m^3 of wastewater has been obtained from the data generated at cell current 6 A. figures 5.8 a indicated that at optimum condition of COD_f (125 min), COD_f of 0.756 Kg was noted at the energy consumption of 3.7 kWh/m^3 in the case of aluminum electrodes. The corresponding COD removal efficiency was 73%. However, in the case of iron electrodes figure 5.8 b indicated that the energy consumption of COD_f of 4.0 kWh/m^3, when the COD_f of 0.924 Kg and the corresponding removal efficiency was 67%. On the other wards, it is obvious from that electrolyte addition was beneficial for the continuous EC process and constitutes a good way for minimizing operating costs.
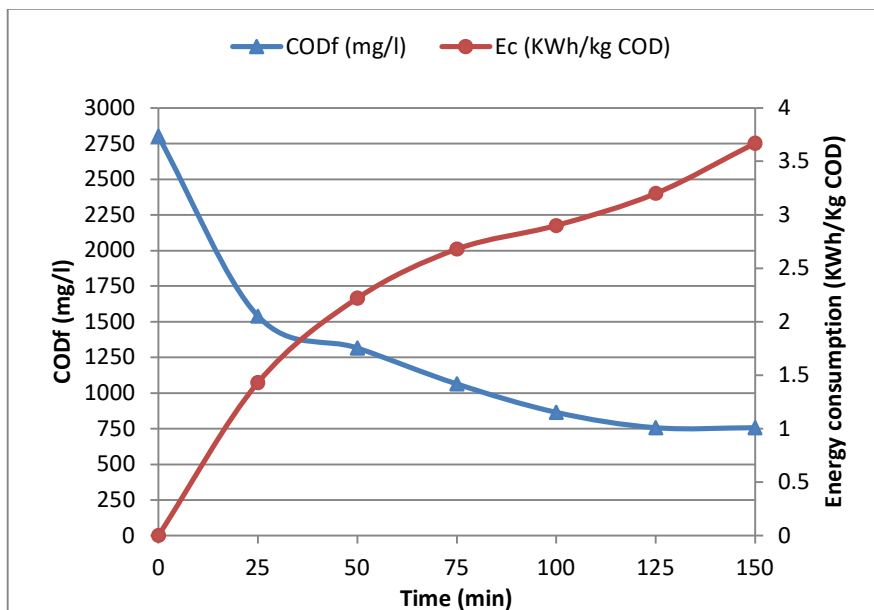
Fig. 3. (a) Effect of NaCl addition on energy consumption Y COD for current density j = 14 mA/cm2, COD_i = 2800 mg/l, pH 6, and five pairs of aluminum electrodes.
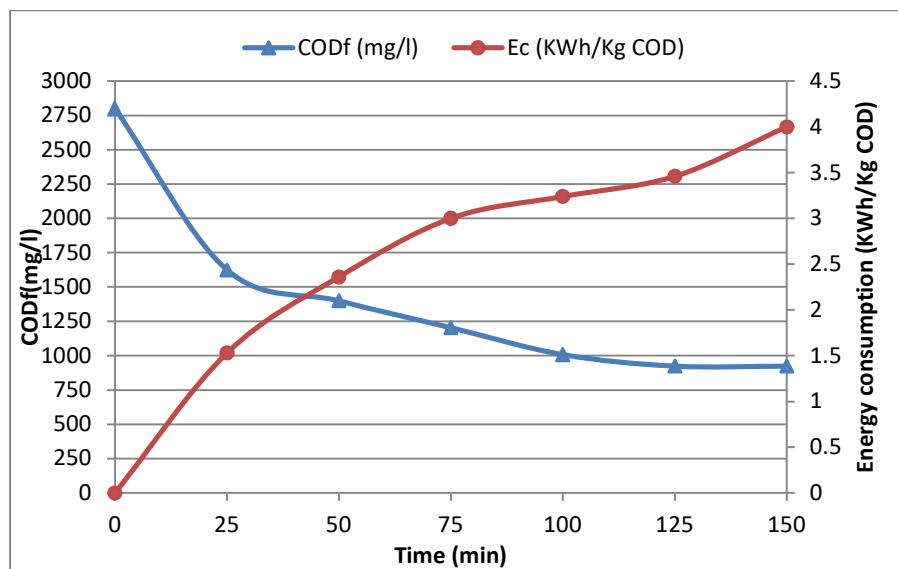

Fig..3. (b) Effect of NaCl addition on energy consumption Y COD for current density j = 14 mA/cm2, CODi = 2800 mg/L, pH 7, and five pairs of iron electrodes

3.4 Applicability of reuse treated tannery wastewater in irrigation
At optimum conditions of EC process has determined. Then, the integrated process EC/ED EC is investigated to achieve the quality standard for wastewater irrigation. Anyway, the environmental impact of the RWW reuse needs to take into consideration the direct effects of RWW in irrigation reuse (effect on soil, on crops and on the landscape vegetation) or in environmental reuse (ecosystem), and also the hydrological indirect effects of water bodies. Based on reviews, WHO, FAO and EPA have guidelines quality for reuse treated wastewater, as well as, the states of Palestine, turkey, Jordan and united states of America. But, for a long time Palestine did not have any specific wastewater regulation, references were usually made to the WHO recommendations or to the neighbored countries standard (Egypt, Jordan). Recently, the Environment Quality Authority with coordination of Palestinian ministries and universities has established specific wastewater reuse regulations (Ayers and Westcot 1985; Fig 2012].

However, after determining the optimum values of aforementioned operating parameters, the treated tannery wastewater quality was compared with various international wastewater reuse quality standards (Table 4). Comparison allows judging the effectiveness of EC-ED process for the treatment of wastewater to be utilized for landscape irrigation and plantation. The analysis shows that Electrical conductivity, TDS, color and COD are within the allowable limits of various countries. However, COD slightly exceed the limits of Palestinian standards, since these standards are relatively stringent compared to other countries. These standards are specific for unrestricted (uncooked eaten crops) irrigation.

The final pH value of treated tannery wastewater is basic (8.1 ± 0.3) which is within the allowable limits (6-9). Similarly NH_3-N and chromium (Cr) are below allowable limits.

It should be pointed out that the electrical conductivity and TDS has great importance in irrigation business. Higher EC and TDS may damage the soil and become a potential irrigation problem. The conductivity and TDS values of studied wastewater are coming under 'Good' class (Class 2) of irrigation water (Fipps 2004).

Table 4.

Comparison of studied treated tannery wastewater quality with various wastewater reuse standards

Parameter	Effluent treated (EC_{Al}-ED)	Effluent treated (EC_{Fe}-ED)	WHO	FAO	Palestine	Jordan	Turkey	USA
pH	8.1 ± 0.3	7.9 ± 0.5	6-9	6.5-8.4	6-9	6-9	6.5-8	6-9
Conductivity mS/cm	1.5	1.5	*	< 0.7-3.0	*	2.5	*	*
TDS	985	1020	*	< 450-2000	*	1500	*	*
Color	< 1	< 1	*	*	free	free	*	*
COD	224	364	500	500	150-250	500	400	*
NH3-N	< 1	< 1	25	91.5-518.5	50	45	50	*
Cr	< 0.1	< 0.1	< 0.1	0.1	0.1	0.1	0.1	1.0

4. Conclusion

Most of countries have plentiful water resources and they all provide priority to the protection of water quality. In these countries, a require for extra supply through the reuse of treated wastewater is not considered as a key issue, but on the other hand, the protection of the receiving environment is considered important. However, industry is generally encouraged to reuse recycled wastewater.

Firstly, at optimum conditions, a laboratory scale EC process was utilized to evaluate of sludge production, change of pH and effect of the conductivity on energy consumption. In two cases with aluminum and iron electrodes, it was found that that removing of 1 Kg of COD produces 0.35 Kg of organic sludge. In contrast, we concluded that 1 Kg of chromium produces regarding 6.5 Kg of inorganic sludge. Further, Change in pH value during EC treatment was also noted and maximum value of 9.48 in the case of aluminum electrode was observed and maximum value of 9.10 in the case of iron electrodes was reported at the end of treatment. Here, it is pointed out that two values are without allowable limits. At optimum condition, in the case of aluminum electrodes, the energy consumption of 3.7 kWh/m^3 corresponding COD_f of 0.756 Kg was recorded, While, in the case of iron electrodes indicated that the energy consumption of COD_f of 4.0 kWh/m^3, when the COD_f of 0.924 Kg. Ultimately, it is obvious from that electrolyte addition was beneficial for the continuous EC process and constitutes a good way for minimizing operating costs.

Secondary, A laboratory scale integrated (EC/ED) process was utilized to treat the tannery wastewater in order to bring the quality up to the required level. After EC/ED treatment, the wastewater quality was compared with various international wastewater quality standards.

It was established that the studied parameters were within the allowable limits except COD slightly exceed the limits of Palestinian and Jordanian standards, since these standards are relatively stringent compared to other countries. These standards are specific for unrestricted (uncooked eaten crops) irrigation. Electrical conductivity and TDS are important to determine the suitability of wastewater for safe irrigation. Their values are within safe range.

Finally, this study shows that the tannery wastewater generated at ORT after integrated process (EC/ED) treatment is safe for landscape irrigation and plantation. It can be confirmed that the study may help to conserve tannery wastewater and alleviate the water shortage problem in the study area.

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