

Treatment of Tannery Wastewater with Nano-Electrocoagulation Process

Abubaker Tajelsir Osman^{1*}, Mohamed Rahmtalla Elamin² and Mohammed Hassan Almalki³

¹Industrial Research and Consultancy Center, IRCC, Sudan

²Al Imam Mohammad Ibn Saud Islamic University (IMSIU) and IRCC, Sudan

³Advanced Materials and Nano Research, Najran University, Najran, KSA

Abstract

This work, aims to treat tannery wastewater sample to remove or reduce the pollutants load by using electrocoagulation technique using an electrode of aluminum nanoparticles. The aluminum nanoparticles were synthesized using sol-gel method and characterized with XRD, TEM, SEM, EDX and FTIR. All the results show that these materials were in nano range. XRD pattern showed that the diameter of aluminum particles was around 14 nm and a peak at 2 theta 18 of aluminum hydroxide. TEM and SEM images of aluminum nanoparticles confirmed the XRD results. The EDX and FTIR indicate the presence of oxygen and hydroxyl ions accompanying the preparation of aluminum nanoparticles. The investigation of the tannery waste water showed high signs of pollution. The pH, turbidity, COD, TDS, chromium, sulphide, chloride and sulphate were 7, 13900 NTU, 10155 ppm, 462 ppm, 28950 ppm, 412 ppm, 6471.5 ppm and 5995 ppm respectively. All these values exceed the limits of the industrial effluent standards, except for the PH. In electrocoagulation treatment at 80 mA, 3 h and pH 7, succeeded to remove best 98.98%,90.6%,70.40%,99.9% and 88.3% of Turbidity, COD, TDS, Chromium and Sulphide respectively.

Keywords: Electrocoagulation; Tannery waste water; Aluminum nanoparticles electrode; Turbidity; Chromium

Introduction

The water consumption and effluent disposal in the leather industry is considered as a serious environmental threat. About 85% of fresh water used in leather processing, is disposed off as wastewater, carrying dissolved and suspended chemicals and other substances used in the process, creating serious pollution problems [1]. There are four operating processes applied to leather until it becomes a final product, these are; pretanning operation (Beam House Operation), tanning operation, wet- finishing operation and finishing operation. Every tanning step, with exception of the crust finishing operations, produces wastewater. An average of 35 m³ of wastewater is produced per ton of raw hide [2].

This wastewater contains: salts (NaCl), fat, protein, preservatives from soaking; lime, ammonium salts, ammonia, protein (hair), and sulphides from fleshing, trimming, bating steps; chromium (salts) and poly phenolic compounds from tanning; and dye and solvent chemicals from wet-finishing step. Toxic effects of tannery waste were caused by the presence of toxic chemicals such as sulphides, chromates and other tanning agents that may interfere biological waste treatment. Toxic discharges retard the process of self-purification and sometimes may cause the death of aquatic life [3]. It is important to determine the principal impurities in the effluent and to pretreat these impurities as necessary step before being released to the sewer, river or lakes. Many industrial effluent contaminants can be eliminated by mechanical, biological or chemical methods [4-10] nanotechnology has been extensively studied by researchers as it offers potential advantages like low cost, reuse and high efficiency in removing and recovering the pollutants of industrial wastewater [11,12].

Electrochemical preparation methods are one of the possible and powerful options for the fabrication of a new class of nanomaterials. It is useful to develop methods which are less expensive and lead to similar quality of final products. Electrocoagulation (EC) is a process that does not require the addition of any external coagulants; the coagulation-flocculation process is very similar to chemical coagulation, except that

the coagulant is generated *in-situ* through the dissolution of sacrificial anodes that are connected to an electric current [13].

The process involves connecting metal electrodes to a direct current generator. The chosen metal should be suitable for use as sacrificial anodes; that is, it should produce metal cations in the solution. Aluminum and iron are the materials of choice because they produce a higher valence. Hydroxyl ions and hydrogen gas formed at the cathode, and metal ions are released at the anode by electrolytic oxidation of the metal electrode [14]. The main objectives of this work are to: prepare and characterize aluminum nanoparticles and use them as anode in an electrocoagulation cell to treatment tanneries waste water.

Experimental Work

10 mmol of aluminum carbonate(AR) and 30 mmol of lithium aluminum hydride(AR) were added to 110 ml of dipropylene glycol(AR). The mixture was refluxed at 140°C for 90 minutes and stirred with magnetic stirrer on a hot plate. The nitrogen gas was inserted to isolate the solution from the oxidation. The product was collected by centrifugation at 16000 rpm for 15 min. The solution was decanted and the product was washed with anhydrous ethanol several times, filtered and dried in an oven at 105°C for 2 hours [15]. Characterization of aluminum phases nanoparticles was carried using XRD, (XRD; PANalytical X'Pert PRO) and Scanning Electron Microscopy (FESEM; JEOL-JSM- 7600F) and Transmission Electron Microscopy (TEM; JEOL-JEM-2100) and in Figures 1-3 explains the pattern and the images of aluminum phases.

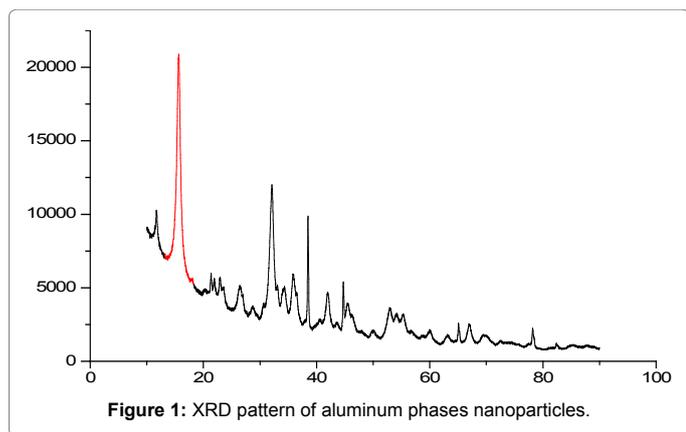
*Corresponding author: Abubaker Tajelsir Osman, Industrial Research and Consultancy Center, IRCC, Sudan, Tel: +966175428888; E-mail: bakry114@gmail.com

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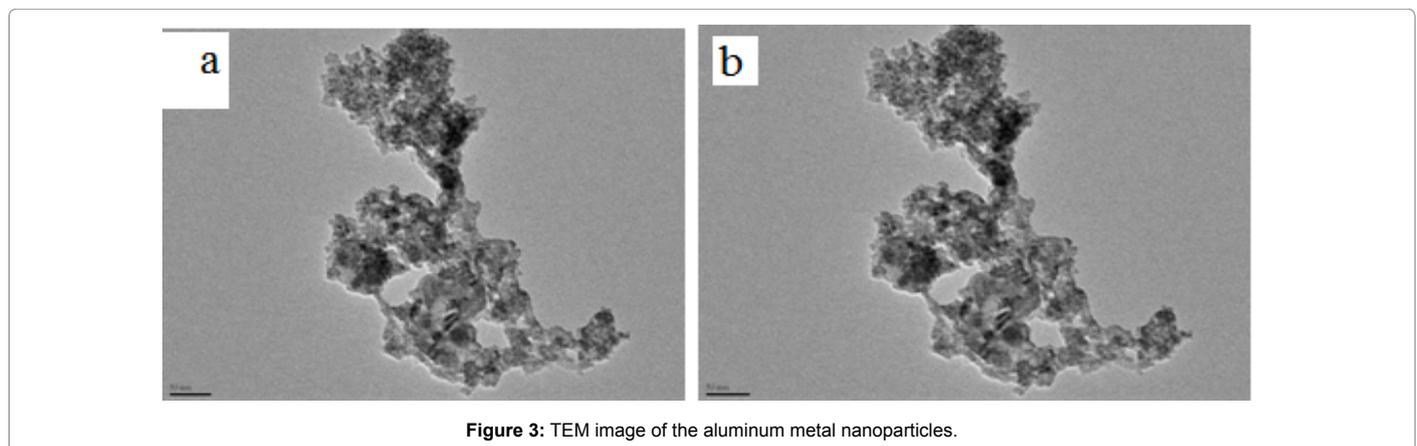
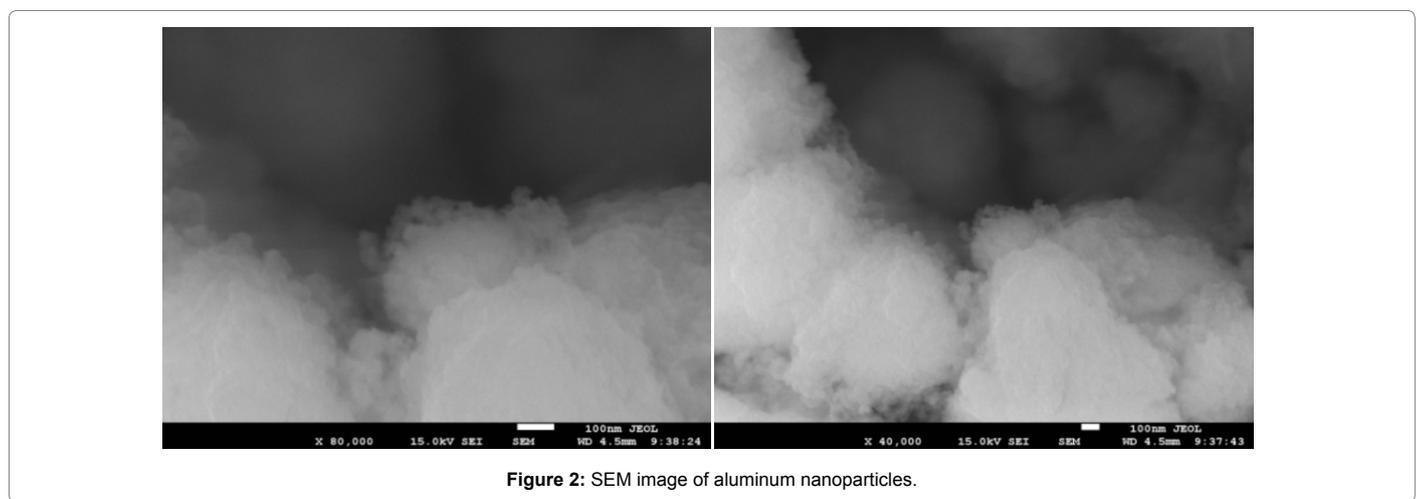
A composite sample of the tannery wastewater was collected in a plastic container from the White Nile tannery, Sudan. The sample was analyzed for Chemical Oxygen Demand (COD), pH, chromium content, turbidity, Total Dissolved Solid (TDS) and sulphide before and after the treatment according to Standard Methods for the Examination of Water and Wastewater (SMWW4000 - 6000) [16] and compared with the Sudanese wastewater treatment standards [17]. Electrocoagulation treatment trials were conducted in 600 ml glass beakers. During the treatment, waste water was stirred with magnetic stirrer.



The Aluminum nanopowder was pressed in the compressor using 5 ton in a mold and tested until it gave solid mould and good conductivity for electric current. A copper wire was inserted in the pressed aluminum powder electrode. The aluminum electrode dimensions are 50 mm, 30 mm, 3 mm. The anode was a carbon column obtained from a dry battery for the electrochemical cell. The distance between the electrode plates was 40 mm. Standard laboratory power supplies were used in the experiments. 300 ml of wastewater samples at certain pH values were poured into the reactor. The samples were filtered on 0.45 micron filter paper and analyzed for different parameters. The efficiency of treatment at electrical potentials of 20, 40, 60 and 80 mA and different pH values of 3, 7 and 10, and time intervals of 1, 2 and 3 hours were determined.

Results and Discussion

The particle size of the of aluminum nanoparticles was characterized by X-ray diffraction (XRD; PAN alyticalX'Pert PRO) using Sherrer's equation $D = k\lambda / \beta \cos\phi$ and found to be 14 nm. When comparing the obtained spectrum with the standard patterns of aluminum phases [18], we can conclude to that, the intense peak at 2 theta 18 may be due to aluminum hydroxide phase $Al(OH)_3$ [19]. The other peaks represent the characteristic peaks of aluminum metal resulting as the pattern explained in Figure 1. SEM images of the aluminum nanoparticles exhibit cloudy cotton like morphology as in Figures 2a and 2b, showed particle size was 100 nm.



TEM images confirmed the approximate particle size calculated from the XRD pattern, where Figures 3a and 3b, showed particle size less than 20 nm. The EDX chart of aluminum nanoparticles showed the presence of oxygen peak indicating the expected oxidation of outer surface aluminum nanoparticles when react with air oxygen, this confirmed the presence of aluminum oxide peaks in the XRD pattern.

The FTIR (FTIR; Perkin Elmer-FTIR Spectrum-10) spectrum of aluminum nanoparticles was shown in Figures 4 and 5. The spectrum showed absorption peak in the range 1200-1300 cm^{-1} , due to the bending mode of aluminum-oxygen bonds [20]. The broad and weak peak around 2750 cm^{-1} may indicate the hydroxyl absorption of the aluminum hydroxide appeared in the XRD pattern. The investigations of the tannery waste water showed highly polluted effluent. All the examined parameters, except pH, exceed the Sudanese industrial discharge limits [15], as shown in Table 1.

When electrocoagulation treatment was applied to the tannery waste water at pH 3, 7 and 10, at variable currents for different time periods, the pollutants decreased appreciably with variable proportions for all currents and in all time periods as shown below. Before treatment the turbidity value was found to be 13900 NTU which is higher than the Sudanese industrial wastewater limit (40 NTU). The Figures 6-8 blow illustrates the effect of pH on the removal of turbidity during the 1, 2 and 3 hours of the contact time at current densities of 20, 40, 60, 80 mA/cm^2 . The best removal efficiency at pH 7, was obtained at 3 hour contact time and 80 mA, where 99.6% of the turbidity was removed. In pH 10 at 3 hours reaction period and 80 mA/cm^2 current density the removal of suspended materials was 100%. In pH 3, in 3 hours reaction period at 80 mA/cm^2 current density the removal of suspended materials was also 100% [16-23].

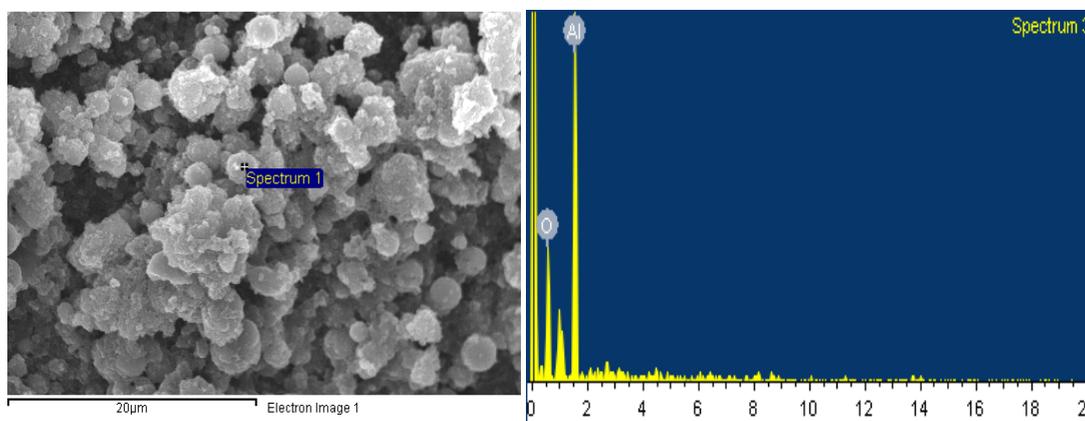


Figure 4: SEM-EDX image of aluminium metal nanoparticles.

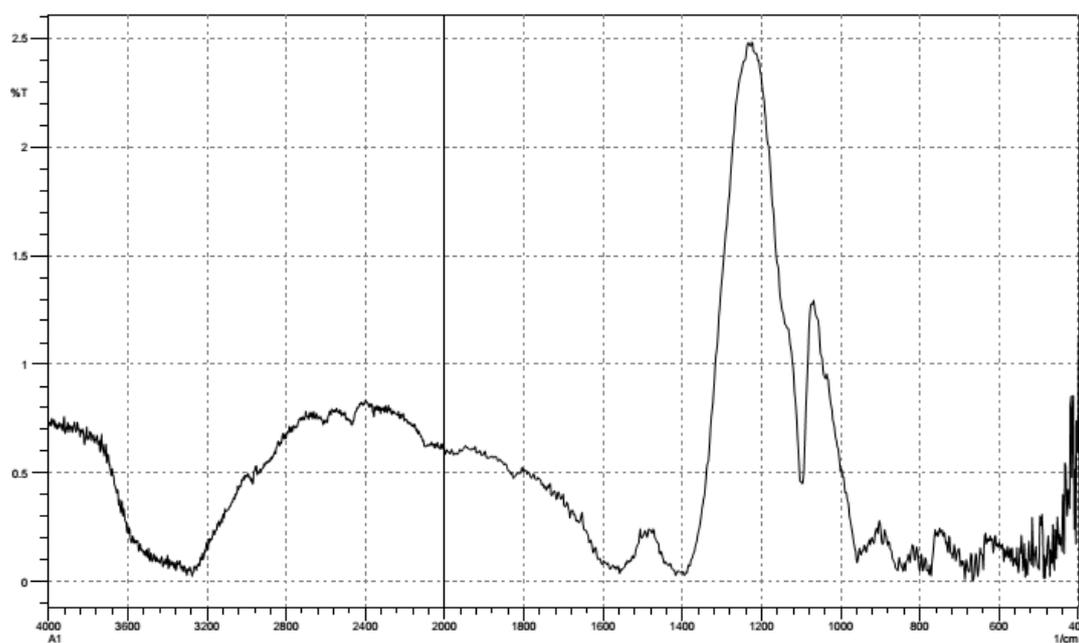


Figure 5: FTIR spectrum of aluminium nanoparticles.

No	Parameters	Concentration	STD limit
1	pH	7	6-9
2	Turbidity	13900 NTU	40 NTU
3	COD	10155 pp	1000 ppm
4	Chromium	462 ppm	1.5 ppm
5	TDS	28950 ppm	2500 ppm
6	Sulphide	412 ppm	2 ppm
7	Sulphate	5995 ppm	300 ppm
8	Chloride	6471.5 ppm	1000 ppm

Table 1: Initial characterization of the tannery waste water and standard limits [17].

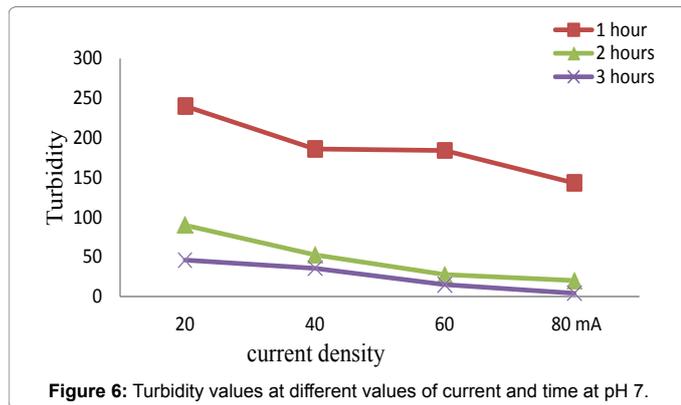


Figure 6: Turbidity values at different values of current and time at pH 7.

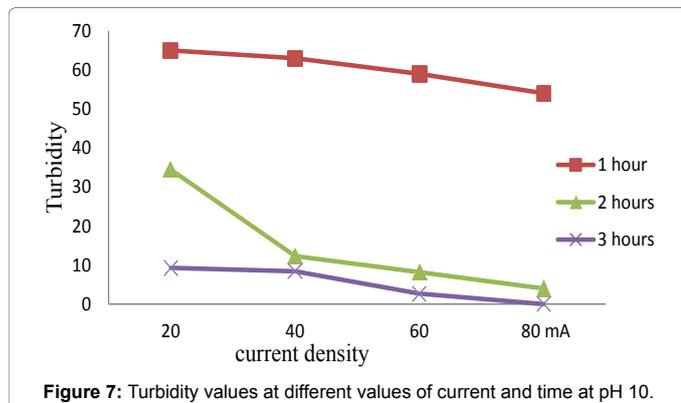


Figure 7: Turbidity values at different values of current and time at pH 10.

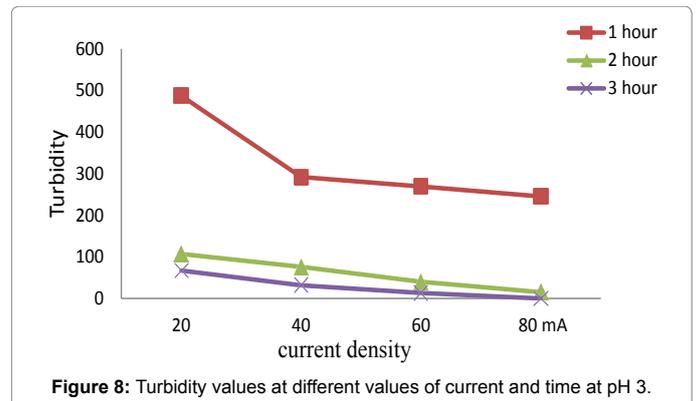


Figure 8: Turbidity values at different values of current and time at pH 3.

The chemical oxygen demand, COD in tannery wastewater, was reduced to variable extents at the different parameters of the treatment, but it is still higher the allowed limits, except when the current density was 80 mA for 3 hours period where 955 ppm value was obtained. Although, the COD was decreased by, 76.57 5%, 90.60% and 79.84% at PH 3, 7 and 10 respectively at 80 mA and 3 hours period. Figures 9-11 showed the trends. 28950 ppm of Total dissolved solids (TDS), indicates the presence of high levels of soluble pollutants in the tannery wastewater, while the allowed limit is 2500 ppm. The best removal percentages, 70.40%, was achieved at pH 7, current density 80 mA and for 3 hours period. The highest removal percent of TDS was 66.2% and 64.5% at pH 10 and 3 respectively at 80 mA current density and for 3 hours period. The chromium level was found to be 462 ppm in TWW (Tables 1-6), this level exceeds the permissible chromium levels (1.5 ppm) of effluent discharged into inland surface waters. The best removal efficiency was 99.9% in 3 hours reaction period and 80 mA current density at pH 7, also at 2 hours reaction period at 40,60 and the amount of chromium were in range of the permissible levels. At pH 10 in 3 hour's reaction period the removal efficiency reached 99.8%. At pH 3, removal, up to 87.3%, was obtained at 80 mA and three hours contact time Figures 12-20. The sulfide, S²⁻, content was found to be 412 ppm in TWW, as a result of liming and unhairing process. 88.35%, 88.35% and 81.07% of the sulphide was removed at PH 3,7 and 10 respectively at current density 80 mA/cm² and 3 hours contact time [24-29].

TWW pH	pH=3				pH=7				pH=10			
Current mA/ time	20	40	60	80	20	40	60	80	20	40	60	80
1 hour	487	292	269	245	240	186	184	143	65	63	59	54
2 hours	107	76	40	15	90	52.6	27.7	20.2	34.5	12.3	8.2	4.0
3 hours	67	31.5	13.1	00	46	35.5	15.1	4.2	9.3	8.4	2.7	00

Table 2: Turbidity in TWW at different pH values, currents density and reaction time.

TWW pH	pH=3				pH=7				pH=10			
Current mA/ time	20	40	60	80	20	40	60	80	20	40	60	80
1 hour	6912	5804	4592	2944	5712	4680	3738	2500	6496	4680	3338	2640
2 hours	6178	4903	3865	2734	4490	3638	2433.6	1288	4299	3764	3038	2352
3 hours	5511	3744	3266	2380	3364	3061	2014	955	3677	3325	2856	2048

Table 3: COD of TWW at different pH values, current density and reaction time.

TWW pH	pH=3				pH=7				pH=10			
	20	40	60	80	20	40	60	80	20	40	60	80
Current mA/ time												
1 hour	23270	19355	16462	14105	24443	19050	16790	13920	22567	18900	14810	12965
2 hours	18900	16748	14870	12450	18835	16438	14299	10695	19902	16562	12768	10665
3 hours	15642	13864	11980	10282	16650	13960	11165	8570	16095	14897	11031	9790

Table 4: TDS in TWW at different pH values, current density and reaction time.

TWW pH	pH=3				pH=7				pH=10			
	20	40	60	80	20	40	60	80	20	40	60	80
Current mA/ time												
1 hour	112.9	109	106.4	104.6	3.456	2.218	1.863	1.676	2.280	2.004	1.811	1.406
2 hours	99.8	91.8	90.2	89.4	2.293	1.142	0.721	0.493	1.403	1.312	1.252	1.134
3 hours	87.7	81.3	67.2	58.6	1.223	0.896	0.614	0.416	1.331	1.307	1.143	0.509

Table 5: Chromium in TWW at different pH values, current density and reaction time.

TWW pH	pH=3				pH=7				pH=10			
	20	40	60	80	20	40	60	80	20	40	60	80
Current mA/time												
1 hour	80	72	64	56	112	88	80	72	178	168	160	152
2 hours	64	56	56	56	94	72	64	56	164	160	152	114
3 hours	64	56	56	48	88	62	54	48	156	136	120	78

Table 6: Sulphide in TWW at different pH values, current density and reaction time.

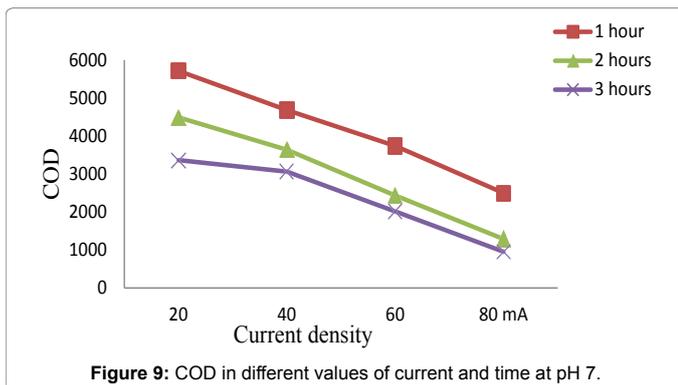


Figure 9: COD in different values of current and time at pH 7.

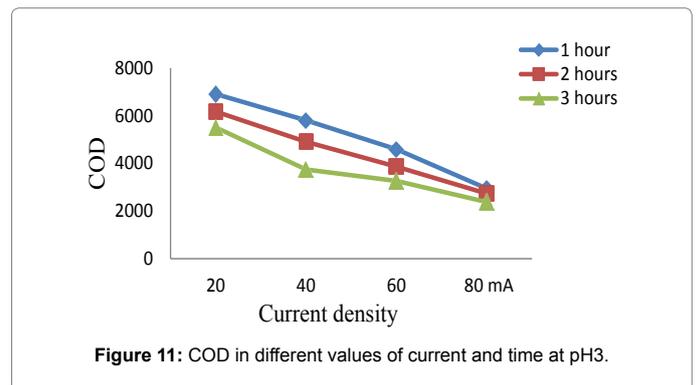


Figure 11: COD in different values of current and time at pH3.

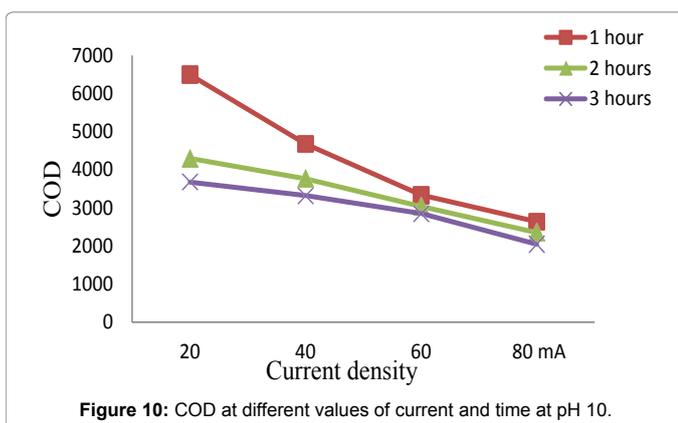


Figure 10: COD at different values of current and time at pH 10.

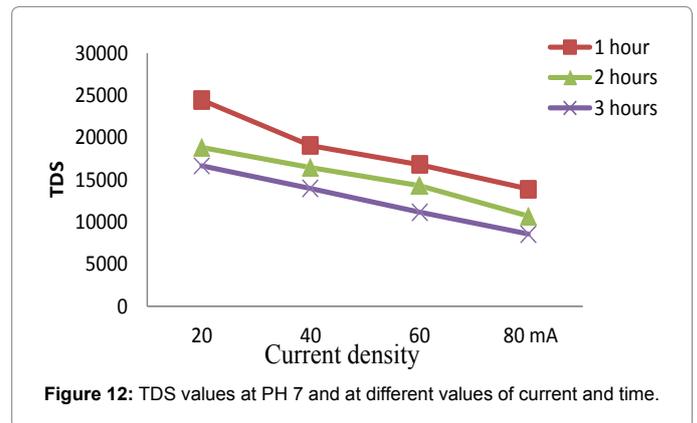
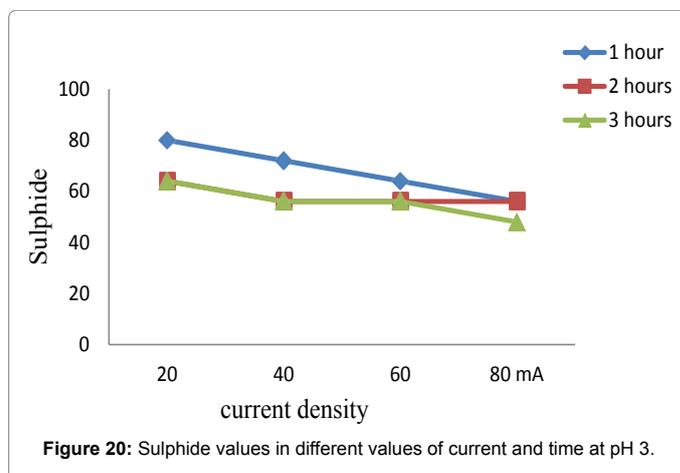
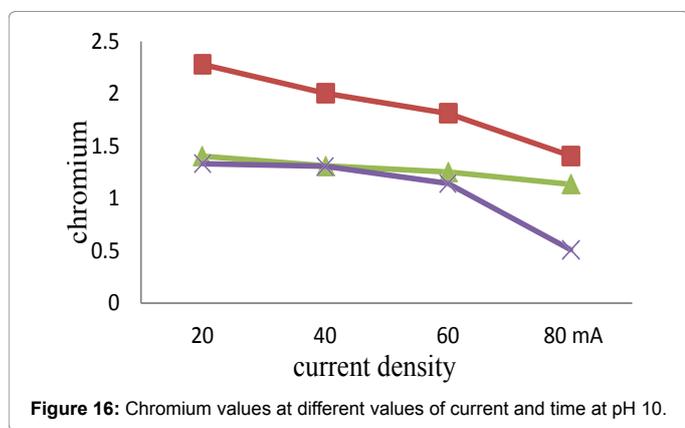
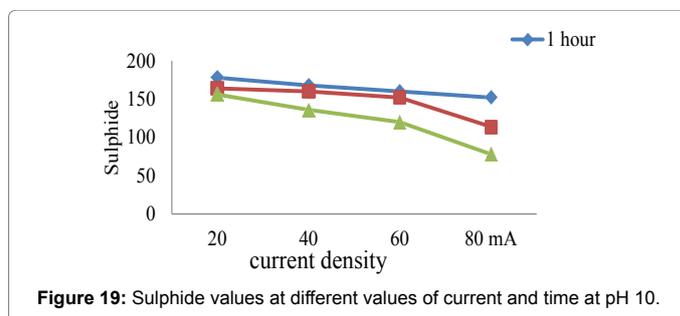
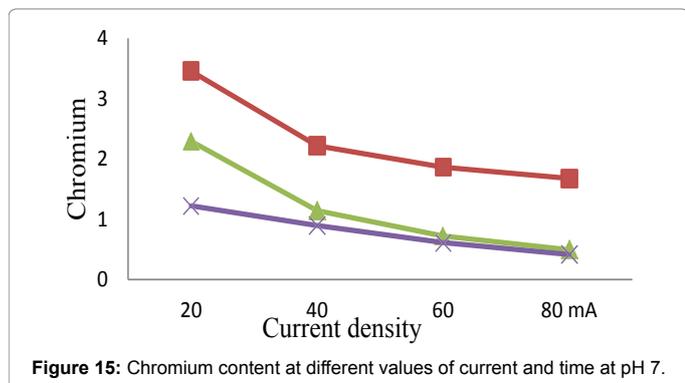
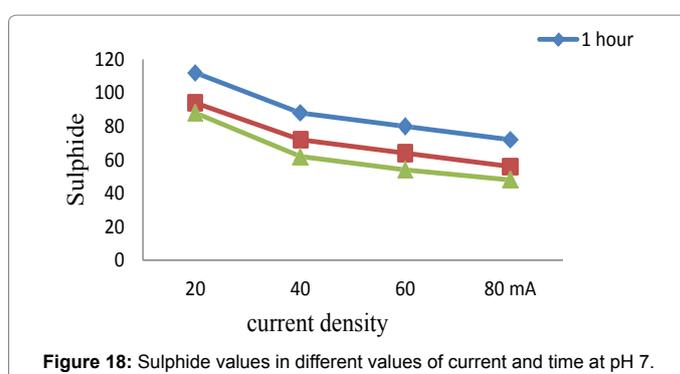
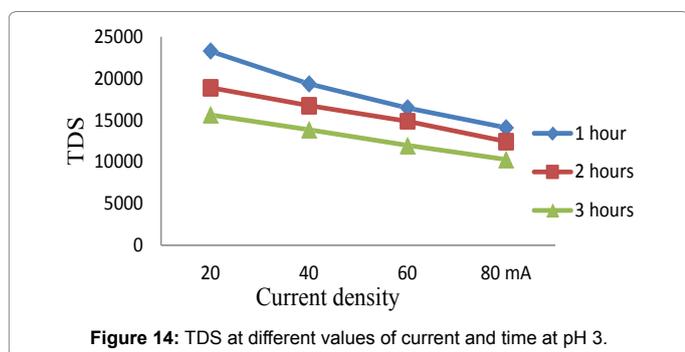
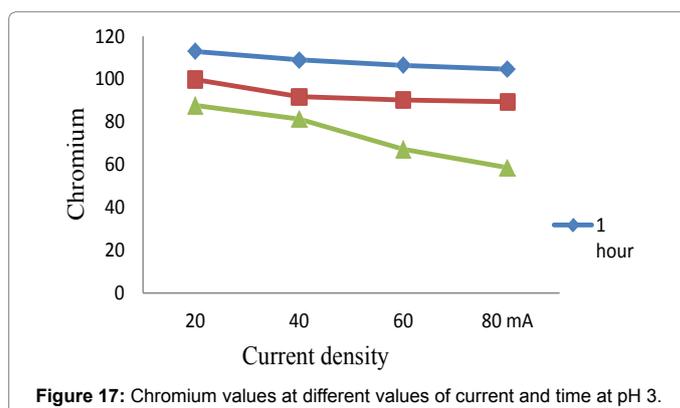
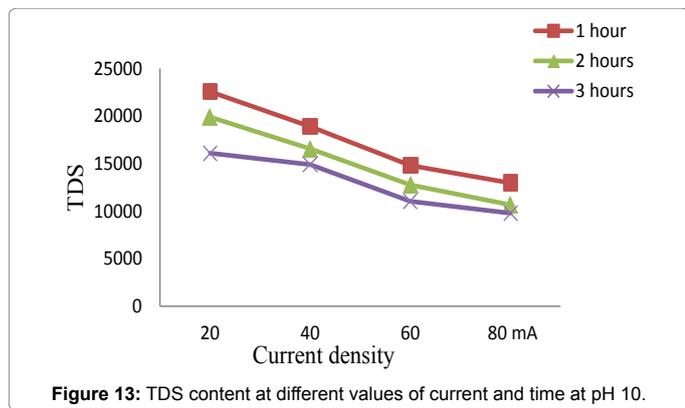


Figure 12: TDS values at PH 7 and at different values of current and time.



Conclusion

The results of the analysis indicate that the White Nile tannery discharge is highly polluted liquid waste. In this study it was found that the electrocoagulation technique using aluminum nanoparticles electrode reduced turbidity, COD, sulphide and chromium to satisfactory levels. This technique could be used successfully as a pretreatment step for highly polluted tannery waste water.

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