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Characterization, correlation and electrocoagulation studies of leather processing industrial effluent

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ABSTRACT

This study was performed to investigate the characterization, water quality index, correlation, linear regression analysis and assessment of irrigation quality of leather processing industrial effluent discharged from the industry located at west of Madurai near Dindigul, Tamilnadu, India. Further the treatment study by electrocoagulation was carried out with and without adsorbents viz., Commercial Activated Carbon (CAC), Multi Walled Carbon Nanotubes (MWCNTs) and Graphene (GR). Most of the water quality parameters (WQPs) of effluent were found to be higher than the limit prescribed by Bureau of Indian Standards (BIS) for the discharge of industrial effluent. The decrease in values of Total Dissolved Solids (TDS), both anions and cations were higher in the case of EC with GR and MWCNTs than CAC.

Keywords: Leather Processing Effluent, Correlation analysis, Electrocoagulation, Adsorbents

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INTRODUCTION

The use of leather goes back to the pre-historic times. The principal raw material is the hide or skin of animals including that of reptiles, fish and birds. The tannery operation involves converting the raw skin, a highly putrescible material, into leather, a stable material, which can be used in the manufacture of a wide range of products. The whole process involves a sequence of complex chemical reactions and mechanical processes. Performing various steps of pre- and post-treatment, generates a final product with specific properties: stability, appearance, water resistance, temperature resistance, elasticity and permeability for perspiration and air, *etc* [1-4].

Leather is an intermediate industrial product, with numerous applications in down-stream sectors of the consumer products industry. For the latter, leather is often the major material input and is cut and assembled into shoes, clothing, leather goods, furniture and many other items of daily use. The tanning of hides and skins also generates other by-products, which find outlets in several industrial sectors such as-dog biscuits and other animal food production, fine chemicals including photography and cosmetics, soil conditioning and fertilizers. The process of making leather has always been associated with odour and water pollution [5].

A considerable potential impact of tanning and associated activities on air, surface and ground water, soil and other natural resources arises from the chemicals applied, the raw materials used, the effluents, wastes and off-gases release generated in the process. Therefore, provisions for pollution control, waste generation and disposal, chemical safety, accidents, raw material/ water/ energy consumption are essential [6-9].

Volume of wastewater (effluent) and its characteristics vary from tannery to tannery. They may also vary within the same tannery from time to time. The wastewater from beam house process *viz.* soaking, liming, deliming, *etc*., are highly alkaline, containing decomposing organic matter, hair, lime, sulphide and organic nitrogen with high BOD and COD. The wastewater from tan yard process *viz.*, pickling, chrome tanning are acidic and coloured. Effluent from vegetable tanning contains high organic matter. The chrome tanning wastes contain high amounts of chromium mostly in the trivalent form [10,11]. The colored wastewaters released into the ecosystem from leather processing industries are toxic and even mutagenic towards living organisms in aquatic environment. Although there are many treatments techniques are available to reduce the level of pollutants in tannery effluents among them EC is one of the best method. The detailed survey of literature shows that only few works have been carried out using EC process [12-15].

In this connection the present study focused on the characterization, water quality index, correlation, linear regression analysis, assessment of irrigation quality and treatment by EC using adsorbents of leather processing industrial effluent discharged from the industry located at west of Madurai near Dindigul, Tamilnadu, India.

EXPERIMENTAL SECTION

Chemicals and Regents

The adsorbent materials CAC and MWCNTs were purchased from Sigma-Aldrich Chemicals used without any further purification. GR was synthesized by the modified Hummer's method. All the other chemicals and reagents used in the studies are analytical grade and used as received.

Leather Processing Industrial Effluent Sampling Procedure

The leather processing industrial effluent samples for this study were collected from industry located at west of Madurai near Dindigul, Tamilnadu, India. The samples have been collected bimonthly over a period of one year in a 2L polythene can. The sampling of effluents and its characterisation were carried out as per the method recommended by BIS and APHA and methods are reported in literature [10,11]. The values of physico-chemical characteristics of leather processing industrial effluent are shown in Table 1.

Electrocoagulation (EC) Treatment Studies of Leather Processing Effluent

The electrochemical cell consisted of two mono polar electrodes, one mechanically polished cathode (to avoid ohmic over potential) and another anode *viz.*, *iron* (mild steel-MS) and aluminium, respectively. Both the electrodes are purchased from the local market (purity: Al = 99.5%, Fe = 99%). The dimension of iron electrode and aluminium (anode) electrode is 10.4cm×2.5cm×0.6cm each. The spacing between the electrodes was maintained at 2.8cm. The electrodes are connected to a DC power supply (120V, 20A). About 100mL of well-mixed, screened, homogeneous industrial effluent was taken in the borosilicate electrochemical cell. The temperature of the effluent before EC was noted to be 30 °C. The temperature was maintained throughout EC (deviation ±1 ◦C). For efficient electrochemical coagulation, 30V DC was passed through the electrodes throughout the EC process by getting a constant current density of $125Am^{-2}$. The experimental set-up with laboratory prototype reactor is schematically shown in Figure 1. The whole set-up was placed on a magnetic stirrer and the sample under study was subjected to constant stirring in order to avoid concentration over potential. The WQPs of effluent have been analyzed after 15minutes. Similar EC experiments were carried out in the presence of CAC, MWCNTs and GR with constant, slow stirring to facilitate effective electrocoagulation. After each EC process the effluent was filtered through Whatman 42 filter paper and analyzed for various water quality parameters.

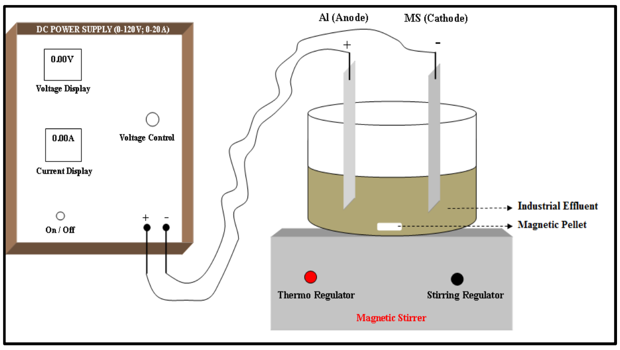

Figure 1. Schematic diagram of experimental set-up for EC process

Characterization studies

The surface morphology of the adsorbents was investigated by scanning electron microscope (model: LEO 440 I).

RESULTS AND DISCUSSION

Characterization of leather processing industrial effluent

The physico-chemical characteristics of the leather processing effluent is presented in Tables 1. The statistical values such as minimum (min) and maximum and average (mean) for the effluent is given in Table 2. The WQPs determined for leather processing effluent are compared with tolerance limits of BIS for both drinking water and industrial effluent discharge on land for irrigation [16-21].

Table 1 Water Quality Parameters of leather processing industrial effluent

T	pH	K	TDS	TSS	THA	HAT	HAP	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2-}	Mg^{2+}	BOD	COD	Cr^{6+}
27.6	11.1	4435	7430	842	786	485	301	2876	1420	325	190	550	455	238	1418	12.01
28.3	11.9	4963	6655	726	1152	696	456	2259	1245	361	181	602	384	296	1247	14.26
29.1	12.1	6115	8428	668	1007	599	408	2662	1362	387	165	518	506	220	1568	13.24
28.4	12.3	7064	7226	794	886	474	412	3068	1168	422	198	480	493	208	1019	16.25
29.3	12.6	6012	7048	565	1259	696	563	2969	1056	403	222	465	418	261	1622	12.56
29.9	12	8021	7817	614	1451	829	622	2204	1496	410	156	488	524	286	1784	13.5
30.1	11.8	4750	6913	714	1317	775	542	2213	1520	368	169	614	507	193	1017	14.75
30.3	12.5	6627	7005	793	1001	554	447	2455	1462	343	172	469	525	214	992	14.15
28.7	10.9	6945	7118	701	1224	673	551	2688	1487	400	185	583	494	188	1066	13.85
28.3	11.6	5003	7655	771	947	536	411	2002	1367	417	198	500	456	261	1602	11.05
29.4	12.1	6512	8135	838	874	446	428	1998	1114	378	139	562	487	221	1372	15.5
29.7	10.6	5796	7324	871	1442	829	613	3367	1176	336	188	488	519	203	1022	14.65
28.6	10.9	5542	6560	812	1130	568	562	2456	1209	391	169	462	529	269	1267	13.9
27.9	10.7	5852	6016	742	943	442	501	2551	1358	312	182	492	481	251	1658	12.85
27.7	11.8	7967	8000	688	868	470	398	2868	1622	302	163	518	397	213	1091	13.55
28.8	10.1	6565	6858	715	1359	874	485	2383	1456	319	208	502	466	201	1885	13.05
29.3	10.9	7114	7445	748	1245	802	443	2262	1372	298	219	533	419	217	1465	13.65
29.4	12.1	5205	7056	655	1295	880	415	1988	1241	415	248	511	508	209	1352	12.8
29.9	11.2	6116	7815	815	1013	629	384	2204	1330	385	202	542	507	242	1728	13.15
30.1	11	4801	8318	603	1333	631	702	2692	1224	404	180	503	459	200	1342	14
28.6	10.7	4226	6966	724	1402	834	568	2268	1555	369	192	472	429	194	1118	14.05
29.4	11.3	5416	8254	808	1348	854	494	2687	1429	348	154	448	487	213	1009	14.85
28.3	11.8	6613	8009	829	1423	839	584	3003	1059	312	172	498	429	238	1332	15.65
29.1	10.9	6022	7857	656	1098	596	502	2568	1274	408	168	518	501	219	1502	13.95

Units: T in ^oC, K in μmho/cm. and remaining parameters except pH are in mg/L.

Table 2 Statistical Data of leather processing industrial effluent

WQPs	N	Range	Minimum	Maximum	Sum	Mean
T	24	2.70	27.60	30.30	696.20	29.0083
pH	24	2.50	10.10	12.60	274.90	11.4542
K	24	3795.00	4226.00	8021.00	143682.00	5986.7500
TDS	24	2412.00	6016.00	8428.00	177908.00	7412.8333
TSS	24	306.00	565.00	871.00	17692.00	737.1667
THA	24	665.00	786.00	1451.00	27803.00	1158.4583
HAT	24	438.00	442.00	880.00	16011.00	667.1250
HAP	24	401.00	301.00	702.00	11792.00	491.3333
Cl^-	24	1379.00	1988.00	3367.00	60691.00	2528.7917
SO_4^{2-}	24	566.00	1056.00	1622.00	32002.00	1333.4167
Na^+	24	124.00	298.00	422.00	8813.00	367.2083
K^+	24	109.00	139.00	248.00	4420.00	184.1667
Ca^{2+}	24	166.00	448.00	614.00	12318.00	513.2500
Mg^{2+}	24	145.00	384.00	529.00	11380.00	474.1667
BOD	24	108.00	188.00	296.00	5455.00	227.2917
COD	24	893.00	992.00	1885.00	32478.00	1353.2500
Cr^{6+}	24	5.20	11.05	16.25	331.22	13.8008

Comparison of WQPs of leather processing effluent with BIS tolerance limit

The value of mean temperature of leather processing industrial effluent is 29.01^{o}C. The range (min - max) of temperature of the effluent is 27.60 – 30.30^{o}C. The average temperature of the effluent is found to be ambient and almost equal to the room temperature observed on the day of collection of the samples. Hence, the effluent is not polluted thermally. The mean pH value of leather processing industrial effluent is 11.4. The min-max range of pH of the effluent are 10.1 – 12.6. The pH values, by and large, exceeded the permissible limit prescribed by BIS. Therefore, the effluent must be treated before discharge into natural water bodies or on land. The average value of specific conductance of leather processing industrial effluent is 5987µmhocm^{-1}. The range of specific conductance value of the effluent is 4226-8021 µmhocm^{-1} as against the tolerance level of 3000 µmhocm^{-1}. The extremely high values of specific conductance were found in the effluent. The average value of TDS and TSS in leather processing industrial effluent are 7413 and 737mg/L respectively. The min – max range for TDS and TSS in leather processing industrial effluent are 1441 – 2261 mg/L (≅ 2 times) and 565-871 (≅1.5 times) respectively. It is concluded that the effluent is highly polluted form specific conductance, TDS and TSS studies. Therefore, proper effluent treatment is required in order to bring down the values of specific conductance, TDS and TSS before discharge.

The average values of THA, HAT and HAP of leather processing industrial effluent are 1158, 667 and 491mg/L, respectively. The min – max range of THA, HAT and HAP values of effluent are 786-1451 (≅ 2 times), 442-880 and 301-702 respectively. The percentage of average values of temporary hardness and permanent hardness respectively to that of total hardness are 58 and 42. From the hardness studies of leather processing industry it is found that the effluent is highly polluted. Hence treatment becomes mandatory before the discharge of the same in the nearby water systems.

The average value and range of chloride and sulphate present in leather processing industrial effluent are 2529 and 1333mg/L and 1988-3367 and 1056-1622mg/L respectively. The mean values of chloride and sulphate in effluent indicate that they are above the discharge limit prescribed by BIS and hence they may be discharged only after proper effluent treatment. The average values of sodium and potassium ions in the leather processing industrial effluent are 367 and 184mg/L respectively. The range of sodium and potassium ions in the same are 298-422 and 139-248 mg/L respectively. The values obtained for sodium and potassium ions of effluent are found to be above the tolerance limit of effluent discharge prescribed by BIS. The range of permissible limits by BIS for the presence of Ca^{2+} and Mg^{2+} ions in drinking water are 75 - 200 mg/L and 30 - 150 mg/L, respectively. The average values of Ca^{2+} and Mg^{2+} ions of leather processing industrial effluent are 513 and 474mg/L respectively. The min-max range of Ca^{2+} and Mg^{2+} ions in the effluent are 448-614 and 384-529mg/L respectively. The average values of Ca^{2+} and Mg^{2+} ions of the leather effluents are exceeded the tolerance limit prescribed by BIS and hence it must be treated before letting out from the industries.

The average values of BOD and COD of leather processing industrial effluent are 227 and 1352mg/L respectively. The min-max ranges of BOD and COD in the effluent are 188-296 and 992-1885mg/L respectively. The BOD and COD of the leather effluent exceeded the tolerance limit prescribed by BIS and indicate a high load of organic as well as some inorganic substances and highly polluted nature of the effluent sample. Hence, the effluent is to be discharged only after proper treatment to reduce the values of BOD and COD.

The mean values and min - max range of Cr^{6+} ion in leather processing effluent 14mg/L and 11-16.25mg/L. The sample contain Cr^{6+} ion above the prescribed limit of BIS (2.0 mg/L) and hence treatment of effluent becomes essential in order to reduce the level of Cr^{6+} ion before its discharge [16-21].

Figure 2 gives a judicious comparison of the major WQPs of leather processing industrial effluent (TDS, TSS, THA, Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, BOD and COD) with BIS tolerance limits for industrial effluent discharged on land for irrigation [16-21].

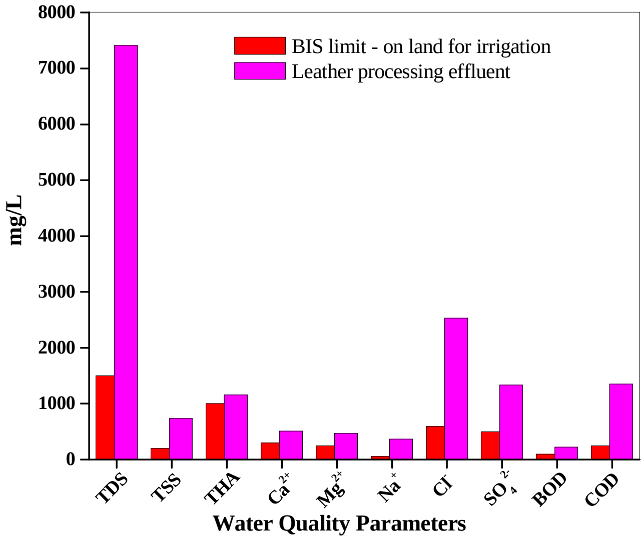

Fig. 4.13 Comparison of WQPs of leather processing industrial effluent with BIS Limit

Calculation of Water Quality Index (WQI) of leather processing industrial effluent

The mean WQI value indicates that the effluent is contaminated approximately six times above the prescribed limit which indicates that the effluent is highly polluted with a heavy load of various pollutants. Therefore, the treatment becomes vital [18-21].

Correlation analysis of WQPs of leather processing industrial effluent

The water quality data (24 in numbers for the printing effluent, which were collected fortnightly for a period of one year; i.e., 24 observations) is presented in Table 1 was used for correlation analysis. One of the parameters i.e., 'i' is chosen as x (independent variable) and other one 'j' as y (dependent variable) [9-15]. The correlation co-efficients (r values) between each pair of the 24 WQPs are calculated and are presented in the form of correlation co-efficient matrix in Table 3.

Table 3 Correlation Coefficient Matrix of leather processing industrial effluent

	T	pH	K	TDS	TSS	THA	HAT	HAP	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	BOD	COD	Cr^{6+}
T	1																
pH	0.182	1															
EC	0.030	0.219	1														
TDS	0.235	0.204	0.211	1													
TSS	-0.193	-0.194	-0.097	-0.044	1												
THA	0.442	-0.248	-0.078	-0.020	-0.273	1											
HAT	0.375	-0.205	-0.089	-0.007	-0.172	0.917	1										
HAP	0.387	-0.226	-0.030	-0.033	-0.335	0.763	0.442	1									
Cl^-	-0.224	-0.056	0.163	0.108	0.133	0.036	-0.079	0.210	1								
SO_4^{2-}	-0.063	-0.244	0.082	-0.059	-0.129	-0.036	0.058	-0.175	-0.258	1							
Na^+	0.308	0.337	-0.149	0.130	-0.392	0.011	-0.080	0.156	-0.243	-0.254	1						
K^+	-0.040	-0.083	-0.182	-0.381	-0.211	0.147	0.308	-0.169	-.066	-0.158	0.092	1					
Ca^{2+}	-0.033	0.019	-0.105	-0.038	0.001	-0.179	-0.094	-0.250	-0.306	0.147	-0.036	-0.075	1				
Mg^{2+}	0.517	-0.018	0.068	0.000	0.172	0.030	-0.020	0.100	-0.087	0.009	0.392	-0.193	-0.163	1			
BOD	-0.228	0.261	0.029	-0.172	-0.048	-0.144	-0.167	-0.054	-0.191	-0.265	0.118	-0.080	-0.051	-0.174	1		
COD	-0.041	-0.159	0.134	0.039	-0.322	-0.033	0.010	-0.091	-0.324	-0.102	0.072	0.236	-0.049	-0.031	0.455	1	
Cr^{6+}	0.211	0.160	0.229	0.150	0.310	0.205	0.107	0.288	0.282	-0.281	-0.058	-0.434	0.029	0.117	-0.310	-0.584	1

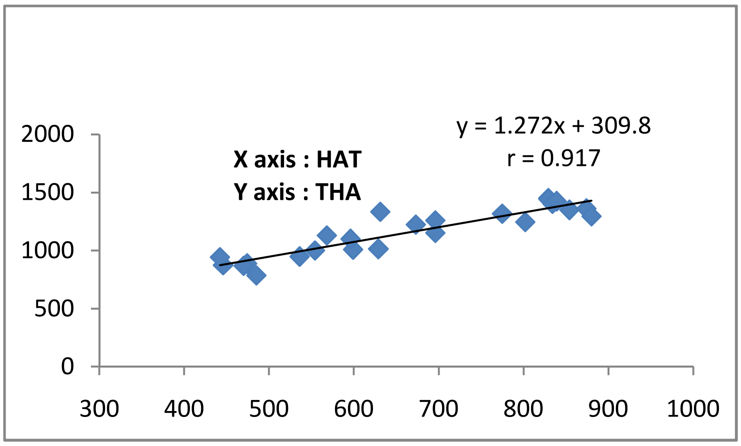

Figure 3. Correlation between HAT and THA

The minimum and maximum values for both positive and negative correlations as well as for total correlations for leather processing effluent are given in Table 4. The minimum and maximum values of correlation co-efficients for leather processing effluent are -0.392 (between Na^+ - TSS) and 0.917 (between HAT - THA), respectively. The studies shows that only a few WQPs 0.763 (between HAP –THA) and 0.517 (between Mg^{2+} - T) are positively correlated with 'r' value (>0.5), while most of the WQPs are either correlated positively with low 'r' value (<0.5) or negatively correlated, which are highly insignificant and only the positive correlations were found to be statistically significant.

Table 4 Correlation co-efficient range of WQPs of leather processing effluent

Sample	For total correlation		For positive correlation		For negative correlation	
	Min	**Max**	**Min**	**Max**	**Min**	**Max**
Leather processing effluent	– 0.392 (Na^+ – TSS)	0.917 (HAT – THA)	0.010 (COD – HAT)	0.917 (HAT – THA)	– 0.392 (Na^+ – TSS	– 0.007 (HAT – TDS)

Linear Regression (LR) studies of leather processing effluent

A few statistically significant LR equations for the leather processing effluent are given below and the corresponding graph is given in Figure 3. The WQP calculated using LR equations for the leather processing effluent are given in Table 4 and Table 5.

Table 4. Linear Regression Values of leather processing effluent

X	Y	r^2	R	M	C
HAT	THA	0.8418	0.917497	1.2721	309.8
HAP	THA	0.5817	0.762693	1.7195	313.63

THA = 1.272HAT + 310 (r = 0.9175); HAP = 0.0095THA + 25(r = 0.7627)

Table 5. Linear Regression Study of leather processing effluent (HAT vs THA)

y = 1.2721x + 309.8; r = 0.9175

S. No	THA	HAT	THAcal
1.	786	485	926.7685
2.	1152	696	1195.182
3.	1007	599	1071.788
4.	886	474	912.7754
5.	1259	696	1195.182
6.	1451	829	1364.371
7.	1317	775	1295.678
8.	1001	554	1014.543
9.	1224	673	1165.923
10.	947	536	991.6456
11.	874	446	877.1566
12.	1442	829	1364.371
13.	1130	568	1032.353
14.	943	442	872.0682
15.	868	470	907.687
16.	1359	874	1421.615
17.	1245	802	1330.024
18.	1295	880	1429.248
19.	1013	629	1109.951
20.	1333	631	1112.495
21.	1402	834	1370.731
22.	1348	854	1396.173
23.	1423	839	1377.092
24.	1098	596	1067.972

Assessing leather processing industrial effluent quality for irrigation needs

The minimum, maximum and average values of sodium absorption ratio (SAR_{min}, SAR_{max} and SAR_{av}), percent sodium (PS_{min}, PS_{max} and PS_{av}), Kelly's ratio (KR_{min}, KR_{max} and KR_{av}) and magnesium ratio (MR_{min}, MR_{max} and MR_{av}) [23-27] for leather processing effluent are calculated using equations 1 to 4. The status of any industrial effluents for irrigation is given in Table 6. The quality of leather processing effluent for irrigation is given in Table 7.

$$SAR = Na^+ / [(Ca^{2+} + Mg^{2+}) /2]^{½} \quad (1)$$
$$PS = 100 [(Na^+ + K^+) / (Ca^{2+} + Mg^{2+} + Na^+ + K^+)] \quad (2)$$
$$KR = [Na^+ / (Ca^{2+} + Mg^{2+})] \quad (3)$$
$$MR = 100 [Mg^{2+} / (Ca^{2+} + Mg^{2+})] \quad (4)$$

Table 6. Values of SAR, PS, KR and MR of industrial effluents and its status for irrigation

Ratio	Status for irrigation
SAR	0 to 10 = Excellent
	10 to 18 = Good
	18 to 28 = Fair
	Above 28 = Poor
PS	Less than 50
KR	Less than 1
MR	Less than 50

Table 7. Quality of leather processing industrial effluent for irrigation

Parameter/ ratio (mg/L)	Leather processing industrial effluent (mg/L)			
	Min	max	Mean	Status for irrigation
Na^+	298	422	367	---
K^+	139	248	184	---
Ca^{2+}	448	614	513	---
Mg^{2+}	384	529	474	---
SAR	---	---	16.5	Good
PS	---	---	35.8	Fair
KR	---	---	0.37	Fair
MR	---	---	48.02	Fair

Based on the SAR, PS, KR and MR results the leather processing industrial effluent is suitable for irrigation. However, the higher values of other WQPs of effluent indicate that it may be useful for irrigation only after proper treatment.

Electrocoagulation treatment studies of leather processing industrial effluent

The physico-chemical characteristics of leather processing industrial effluent were found to be higher than the tolerance limit for the discharge of industrial effluent prescribed by BIS. This indicates that the leather processing industrial effluent could be discharged only after proper effluent treatment. Hence, treatment by EC processes has been carryout on leather processing industrial effluent to evaluate the percentage removal of various WQPs with and without adsorbents namely CAC, MWCNTs and GR.

Optimization of adsorbents for EC processes

The optimization of dose of adsorbents (CAC, MWCNTs and GR) for EC studies of leather processing effluent was determined by measuring TDS (in mgL^{-1}) and the results indicate that the optimum dose for CAC, MWCNTs and GR are 2g, 150mg and 150mg respectively.

Removal of WQPs of leather processing effluent before and after EC processes

The physico-chemical WQPs of leather processing industrial effluent before and after EC with and without adsorbents in presence of iron cathode (MS) and aluminium anode is given in Table 8.

Table 8. Characteristics of leather processing industrial effluent before and after EC with and without adsorbents in presence of iron and aluminium electrodes

S. No	WQPs	Water Quality Parameters Values				
		Before EC	After EC			
			Without adsorbent	With CAC	With MWCNTs	With GR
1	Colour	Black	Light black	Almost colourless	Almost colourless	Almost colourless
2	pH	11.8	8.7 (26)	8.2 (31)	7.8 (34)	7.9 (33)
3	K	6613	1652 (75)	556 (92)	432 (93)	385 (94)
4	TDS	8009	945 (88)	768 (90)	535 (93)	535 (93)
5	TSS	829	410 (51)	365 (56)	320 (61)	305 (63)
6	Na^+	312	168 (46)	134 (57)	117 (63)	105 (66)
7	K^+	172	52 (70)	32 (81)	28 (84)	22 (87)
8	Ca^{2+}	498	225 (55)	175 (65)	143 (71)	162 (67)
9	Mg^{2+}	429	189 (56)	135 (69)	105 (76)	112 (74)
10	Cl^-	3003	750 (75)	460 (85)	362 (88)	382 (87)
11	SO_4^{2-}	1059	424 (60)	320 (70)	310 (71)	305 (71)

Units: *K in μmho/cm and remaining parameters except pH are in mg/L.*
The values given in bracket refer percentage (%) removal

Measurement of pH before and after EC processes

The initial pH of the raw leather processing industrial effluent is 8. The pH of the effluent was adjusted to below 10 by adding 0.1M H_2SO_4. It is observed from the Table 8 and Figure 4, the pH of the effluent is reduced after EC with and without adsorbents. The result shows the decrease in pH is due to reduction in the concentration of H^+ ions present in the leather processing effluent. The H^+ ions present in the printing effluent may undergo electronation at cathode and adsorption on adsorbent materials resulting in evolution of H_2 gas.

$$H^+ + e^- \longrightarrow \frac{1}{2} H_2\uparrow$$

Effect on TDS and TSS before and after EC processes

TDS is a measure of the total ions present water systems. From the Table 9 and Figure 5, the decrease in the values of TDS in leather processing industrial effluent after electrocoagulation with MWCNTs and GR are relatively higher than CAC. The high percentage removal of TDS and TSS is due to the formation of coagulants and flocculants by electrolytically added Al^{3+} generated from aluminium anode. The dissolved and suspended particles undergo coagulation with Al^{3+}. The gases evolved at the electrodes may impinge on and cause flotation of the coagulated materials. The EC process is basically associated with electroflotation since bubbles of hydrogen and oxygen are produced at the cathode and anode, respectively. The success of an EC process and for that matter electroflocculation (EF) process is determined by the size of the bubbles as well as by the proper mixing of the bubbles with wastewater. It is generally believed that the smaller bubbles provide more surface area for attachment of the particles in aqueous stream, resulting in better separation efficiency of the EF process [28-35].

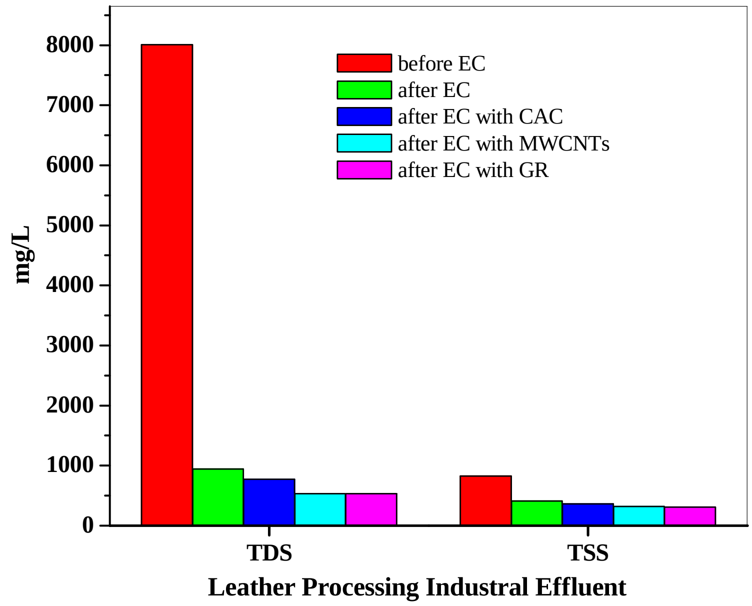

Figure 4. Removal of TDS and TSS in leather processing effluent by EC with and without adsorbents

Effect on anions and cations before and after EC processes

The details of reduction in the concentration of anions such as Cl^- and SO_4^{2-} during EC of leather processing effluent with and without absorbents is given in the Table 8 and Figure 5. It may be due to de-electronation of these anions at anode resulting in electrochemical oxidation, they also undergo reaction with Al^{3+}, $Al(OH)_3$ to produce corresponding chloride and sulphate precipitates and further the anions undergo adsorption on the surface of CAC, MWCNTs and GR during electrocoagulation.

Cl^- $\rightarrow$ $e^- + 1/2Cl_2\uparrow$(at anode)

$Al^{3+} + 3H_2O$ $\leftrightarrow$ $Al(OH)_{3(s)} + 3H^+$

$Al^{3+} + 3Cl^-$ $\rightarrow$ $AlCl_3\downarrow$

In addition, chlorine produced at anode as a result of oxidation is a strong oxidant that can oxidize some organic compounds and promote electrode reactions [36-43].

$2Cl^-$ $\leftrightarrow$ $Cl_2 + 2e^-$

$Cl_2 + H_2O$ $\leftrightarrow$ $HClO + H^+ + Cl^-$

$HClO$ $\leftrightarrow$ $ClO^- + H^+$

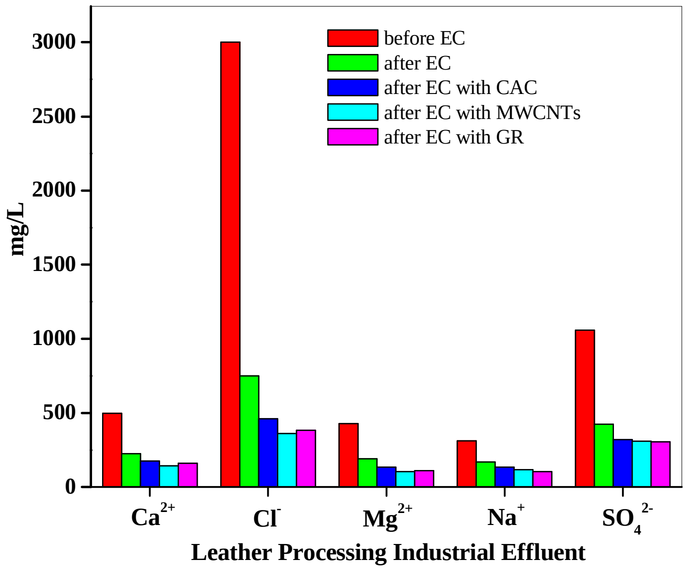

Figure 5. Removal of cations and anions in leather processing effluent by EC with and without adsorbents

The removal of cations in leather processing effluent before and after EC process in presence and absence of adsorbents is shown in Table 8 and Figure 5. From the result it is observed that there is decrease in concentration of cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} in effluent after EC with and without adsorbents. This may be due to the electronation of cations at cathode and also adsorption of cations on the surface of CAC, MWCNTs and GR during electrocoagulation. Form the results, it is also observed that the percentage removal of cations is relatively lower than the percentage removal of other WQPs this may be due the lower hydrogen over potential on iron cathode [44].

$Ca^{2+}_{(aq)}$ + 2e- → $Ca_{(s)}$
$Mg^{2+}_{(aq)}$ + 2e- → $Mg_{(s)}$
$Na^{+}_{(aq)}$ + e^- → $Na_{(s)}$
$K^{+}_{(aq)}$ + e- → $K_{(s)}$

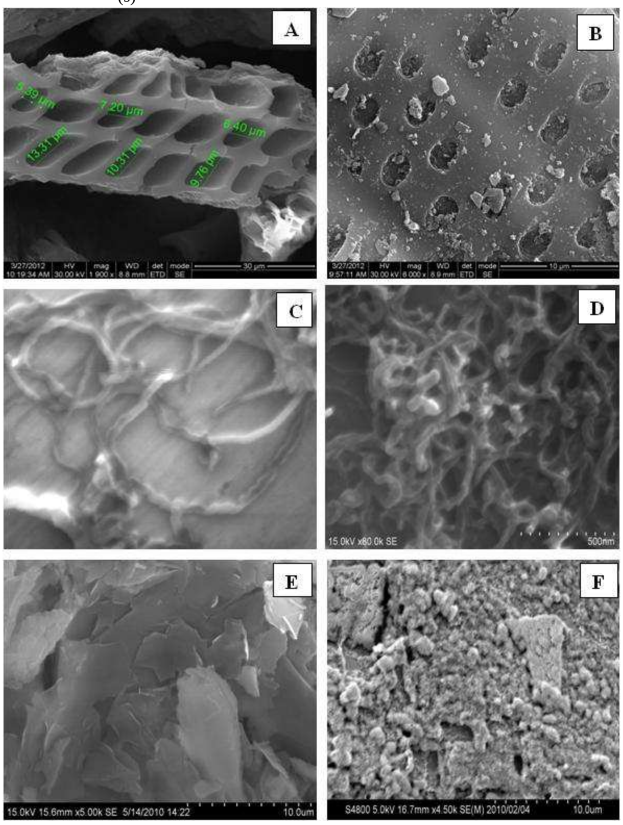

Figure 6. SEM images of A, C and E represent CAC, MWCNTs and GR respectively before EC processes: B, D and F represent CAC, MWCNTs and GR respectively after EC processes of leather processing effluent

The percentage removal of pollutants in leather processing effluent is higher in the case of GR and MWCNTs than CAC during EC processes can be attributed to their good adsorption as well as conducting properties. Since EC process is common in all the four treatment studies of leather processing effluent the efficiency of treatment lies on the adsorbing capacity of the adsorbent materials used during EC processes.

Surface morphological studies of adsorbents before and after EC process

The typical SEM photographs of adsorbents, before and after EC of leather processing effluent are shown in Figure 6. SEM photographs of adsorbents before EC process clearly reveal the surface texture and porosity of the adsorbents (Fig. 6A, C, E). SEM photographs also show that the particles can be roughly approximate as spheres or globules, if the roughness factor is included to account for their regularities. SEM photographs of adsorbents after EC processes depict the porosity nature of the adsorbents and also presence of grains in it (Fig. 6B, D, F). Furthermore, the adsorbed effluents molecules are either engulfed or surrounded on the surface of porous CAC, MWCNTs and GR adsorbents [45,46].

CONCLUSION

The leather processing industrial effluent samples for this study were collected from industry located at west of Madurai near Dindigul. Characterization, correlation analysis and treatment by EC process were carried out. Most of the WQPs of leather processing effluents were found to be higher than the limit prescribed by BIS for the discharge of industrial effluent. The average WQI value of leather processing industrial effluent showed that it was contaminated six times higher than the prescribed limit. Correlation and linear regression were carried out in order to study the rapid monitoring of water pollution. The studies of quality of effluent for irrigation showed that, it is not suitable for irrigation purposes as such. The decrease in values of TDS was higher in the case of EC with GR and MWCNTs than CAC. The decrease in concentration of both anions and cations are relatively higher in EC with and without GR and MWCNTs than CAC and the SEM studies show adsorbed effluents molecules are either engulfed or surrounded by the porous adsorbent particles.

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