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RESEARCH ARTICLE

A comprehensive study on electroplating effluent: Characterization, correlation analysis and electrocoagulation treatment in presence of adsorbent

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Abstract

A wide variety of industries make use of metal finishing processes. Some of the principal industries that use metal finishing processes are the motor car industry, aircraft industry, kitchen, domestic ware industry etc. Electroplating effluents will generally be acid, usually with up to 200 or 300 mg/L of suspended solids, copper nickel and zinc in varying amounts, perhaps up to 300 to 600 mg/L, occasionally with chromium or cadmium or lead and frequently with cyanide present. The cyanide content will sometimes reach several hundreds of mg/L. Processes like blacking give rise to much solid matter in suspension and small concentrations of metals in solution. The wide variety of the processes used in metal finishing leads to effluents that may not be very complex in chemical composition from a single process but which are extremely complicated chemically when they are all present in a sewerage system. In the present study, characterization, correlation analysis and treatment by Electrocoagulation (EC) process were carried out for the electroplating industrial effluent collected from industry located at Thirumangalam near Madurai, Tamilnadu, India. Most of the water quality parameters (WQPs) of printing effluent were found to be higher than the limit prescribed by Bureau of Indian Standards (BIS) for the discharge of industrial effluent. EC technique is employed for the treatment of electroplating effluent with and without adsorbents using iron and aluminium electrodes. The decrease in values of Total Dissolved Solids (TDS) was higher in the case of EC with and without Graphene (GR) and Multi Walled Carbon Nanotubes (MWCNTs) than Commercial Activated Carbon (CAC). The decrease in concentration of both anions and cations are relatively higher in EC with and without GR and MWCNTs than CAC. It was observed that the percentage removal of cations is relatively lower than the other WQPs. The result of present investigation on electroplating industrial effluent revealed that generally the EC process with adsorbent is an effective tool for the treatment of industrial effluent.

1 Introduction

A wide variety of industries make use of metal finishing processes. Some of the principal industries that use metal finishing processes are the motor car industry, aircraft industry, kitchen and domestic ware industry, heavy electrical industry for the manufacture of electrical components, non-ferrous and ferrous parts for the building industry, ornaments and fancy goods and industries concerned with the treatment of steels such as stainless steel, tubes or steels meant to withstand very high temperatures [1,2].

The term metal finishing includes: Pretreatment, using solvents for degreasing and cleaning, chemical cleaning, pickling with acids, phosphating by dipping steel or zinc base alloys in a solution of acid phosphates, chromating, sodium hydride descaling, abrasive cleaning, shot blasting, ultrasonic cleaning, barrelling and polishing etc. Anodising in sulphuric or chromic acid, Metal coating by galvanizing, sherardizing, Peen plating, calorizing, chromating, zinc or aluminium spraying or hot dip aluminizing; Paint coating by brush, spray or electrostatic or airless processes, dipping, curtain coating, flow coating, rumbling, hot spraying or electropainting; Chemical colouring by blackening, blueing or chromating, Plastic coatings, applied by spray, dipping, fluidized bed, powder spraying [3-5].

The wide variety of the processes used in metal finishing leads to effluents that may not be very complex in chemical composition from a single process but which are extremely complicated chemically when they are all present in a sewerage system. For instance, copper may be plated from a bath containing the cyanides of copper, sodium, besides Rochelle salt and sodium carbonate; lead may be plated on iron from a bath containing lead oxide, fluosilicate and glue; one process of nickel plating uses nickel sulphate and chloride, with boric acid and organic additives; while in tin plating tin fluoborate, fluoboric acid and boric acid are used [6-10]. Electroplating effluents will generally be acid, usually with up to 200 or 300 mg/L of suspended solids, copper nickel and zinc in varying amounts, perhaps up to 300 to 600 mg/L, occasionally with chromium or cadmium or lead and frequently with cyanide present. The cyanide content will sometimes reach several hundreds of mg/L. Processes like blacking give rise to much solid matter in suspension and small concentrations of metals in solution [11-14]. Organic matter is also a constituent of a number of metal finishing effluents, which could be objected to in the case of a direct discharge to a river. The sources of some of the organic matter are the organic additives used in some processes. The water from paint spray booths may have a high content of organic matter. Spent oil suds are not only a source of waste oil but also of soluble organic, bactericidal Substances which can raise the organic content of an effluent to high level. Fluorine generally present as hydrofluoric acid though presumably also as fluoborates is derived from several sources such as the etching of glass and the preparatory cleaning of glass tubes. Fluoride has been found in effluents from the treatment of aluminium and its alloys. The most important process giving rise to the fluorides in effluents is the pickling of stainless steel which may give rise to waste liquors containing 13000 mgF per litre.

All these facts reveal that the magnitude of environmental pollution that can be caused by untreated electroplating effluent. Hence a comprehensive study of electroplating industrial effluent (*viz.*, characterization and cost effective treatment) is required to minimize the pollution [15,16]. A few works have been reported in literature regarding the treatment of electroplating effluent by other methods, but treatment of electroplating effluent by electrocoagulation in the presence of adsorbents is very limited. The present study focused on characterization, water quality index, correlation and linear regression analysis, irrigation quality evaluation and electrocoagulation treatment using three different adsorbents (CAC, MWCNTs and GR) for effluent discharged from the electroplating industry located at Thirumangalam near Madurai, Tamilnadu, India.

2. Experimental Methods

2.1 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.

2.2 Electroplating Industrial Effluent Sampling Procedure

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

2.3 Electrocoagulation (EC) Treatment Studies of Electroplating Industrial 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 90Am^{-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 or 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.

2.4 Characterization studies

Thermogravimetry (TGA) analysis results were recorded using a Perkin Elmer Thermal Analyzer over a temperature range of 0 to 700°C in an inert atmosphere at a heating rate of 10°C min^{-1}. The surface morphology of the adsorbents was investigated by scanning electron microscope (model: LEO 440 I).

3 Results and Discussion

3.1 Characterization of electroplating industrial effluent

The physico-chemical characteristics of (WQPs) electroplating industrial effluent are presented in Table 1. The statistical values such as minimum (min) and maximum (max), and average (mean) for all the WQPs of electroplating effluent are given in Table 2. The WQPs determined for electroplating industrial effluent are compared with the same for tolerance limit of drinking water and industrial effluent discharged on land for irrigation prescribed by BIS [17-29].

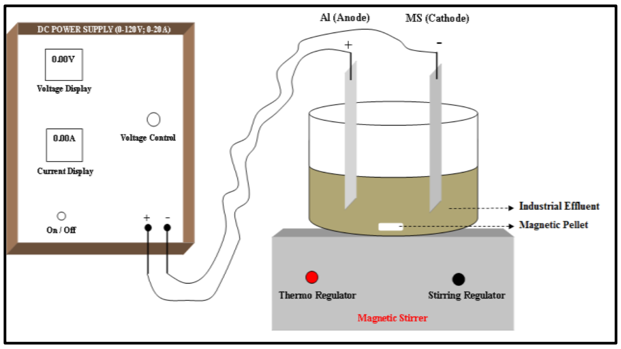

Figure 1. Schematic diagram of experimental set-up for EC process

Table 1 Water quality parameters of electroplating industrial effluent

T	pH	K	TDS	TSS	THA	HAT	HAP	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	BOD	COD	Zn^{2+}	Cr^{6+}	Cu^{2+}
25.4	4.3	2930	855	570	550	360	190	750	680	220	55	265	290	140	210	1.25	7.6	0.07
25.6	4.2	2647	765	460	600	415	185	685	555	150	65	295	315	120	170	1.35	6.5	0.04
25.9	5.5	3560	910	515	515	310	205	565	720	195	47	235	285	85	150	1.2	8.4	0.01
29.5	5	4170	867	415	590	335	255	644	480	210	40	285	310	104	180	1.4	7.2	0.02
29.3	4.8	4550	752	580	485	265	220	592	570	145	50	275	250	92	240	1.5	6	0.01
29.4	5.3	4680	814	485	560	340	220	683	523	195	70	280	295	84	100	1.45	8.5	0.04
27.4	4.9	3760	895	405	528	324	204	595	547	175	54	265	275	76	160	1.35	7.2	0.08
28.2	5.1	2785	880	655	595	364	231	624	588	204	48	290	305	93	205	1.28	7.8	0.16
29.3	5.6	3150	790	585	615	390	225	686	610	230	42	280	325	112	155	1.35	6.6	0.02
28.5	5.9	3459	825	559	505	325	180	647	490	173	48	245	265	108	194	1.4	9.2	0.08
26.4	4.7	4068	855	515	590	385	205	654	550	194	63	280	310	97	160	1.1	6.4	0.11
25.5	4.9	2776	878	565	550	370	180	670	510	205	57	285	270	88	195	1.5	7.1	0.1
27	5.1	4118	815	575	585	386	199	591	525	175	48	265	265	78	115	1.25	7.5	0.03
29.5	5.3	4515	875	480	565	356	209	654	548	180	64	290	295	96	190	1.3	6.4	0.07
29.8	4.6	2789	680	450	595	365	230	640	550	200	44	285	285	90	205	1.35	7.8	0.08
30.4	4.9	3641	758	445	604	370	234	674	505	155	56	280	316	106	200	1.4	8.6	0.03
27.9	5.2	3072	875	495	516	310	206	635	598	173	63	275	332	103	185	1.35	8.1	0.06
27.5	5.3	2984	715	510	498	290	208	680	565	188	68	255	275	83	164	1.25	7.1	0.09
25.8	5.1	3865	795	525	558	355	203	598	515	198	56	225	286	92	198	1.3	9.2	0.13
25.7	5.8	2895	815	480	596	385	211	641	600	176	48	268	290	89	210	1.19	8.2	0.02
25.1	4.9	4002	840	535	568	370	198	625	583	192	62	283	315	97	165	1.25	8.8	0.07
25	4.5	3458	790	610	525	330	195	639	532	168	57	270	298	102	202	1.3	7.4	0.08
26.5	5.7	4010	865	526	535	345	190	681	568	188	46	255	280	107	175	1.4	6.6	0.05
27.8	4.8	4365	825	585	585	355	230	706	618	165	52	290	264	116	190	1.35	7.1	0.03

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

Table 2 Statistical Data of electroplating industrial effluent

WQPs	N	Range	Minimum	Maximum	Sum	Mean
T	24	5.40	25.00	30.40	658.40	27.4333
pH	24	1.70	4.20	5.90	121.40	5.0583
K	24	2033.00	2647.00	4680.00	86249.00	3593.7083
TDS	24	230.00	680.00	910.00	19734.00	822.2500
TSS	24	250.00	405.00	655.00	12525.00	521.8750
THA	24	130.00	485.00	615.00	13413.00	558.8750
HAT	24	160.00	255.00	415.00	8300.00	345.8333
HAP	24	75.00	180.00	255.00	5013.00	208.8750
Cl^-	24	185.00	565.00	750.00	15559.00	648.2917
SO_4^{2-}	24	240.00	480.00	720.00	13530.00	563.7500
Na^+	24	85.00	145.00	230.00	4454.00	185.5833
K^+	24	30.00	40.00	70.00	1303.00	54.2917
Ca^{2+}	24	70.00	225.00	295.00	6521.00	271.7083
Mg^{2+}	24	82.00	250.00	332.00	6996.00	291.5000
BOD	24	64.00	76.00	140.00	2358.00	98.2500
COD	24	140.00	100.00	240.00	4318.00	179.9167
Zn^{2+}	24	0.40	1.10	1.50	31.82	1.3258
Cr^{6+}	24	3.20	6.00	9.20	181.30	7.5542
Cu^{2+}	24	0.15	0.01	0.16	1.48	0.0617

3.2 Comparison of WQPs of electroplating industrial effluent with BIS tolerance limit of drinking water and industrial effluent

The value of mean temperature (T in ^oC) of electroplating effluent is 27.43. The range (min - max) of temperature of electroplating effluent is 25.00 – 30.40^{o}C. The average temperature of the electroplating effluent was found to be ambient and almost equal to the room temperature observed on the day of collection of the sample. Hence, the effluent is not polluted thermally. The pH of electroplating effluent is acidic and the mean pH value of electroplating effluent was found to be 5.1. The min-max ranges of pH of the electroplating effluent are 4.2 – 5.9. The pH value of the effluent exceeded the permissible limit prescribed by BIS. Therefore, the effluent must be treated before discharge into natural water bodies or on land as alterations in the pH are detrimental to the living systems.

The average value of specific conductance, in µmhocm^{-1}, of the electroplating effluent is 3593. The ranges of specific conductance value of electroplating effluent are 2647-4680 as against the tolerance level of 3000 µmho/cm. The high value of specific conductance in electroplating effluent is due to usage of salts, acids etc., during the preparation of electroplating bath. The average value of TDS in electroplating effluent is 822 mg/L. Another important observation is the min – max range for TDS in electroplating effluent is 680 – 910 mg/L (≅ 1.5 times). Hence, proper effluent treatment is required in order to bring down the values of TDS and specific conductance, before discharge [17-29]. Total Suspended Solids (TSS) value of electroplating effluent was found to be very high. The mean value of TSS of electroplating effluent is 522 mg/L. Further, the min – max range of TSS in mg/L of electroplating effluent are 405-655 (≅ 1.5 times).

The average value of THA of electroplating effluent is 559 mg/L. The min – max range of THA value of electroplating effluent are 485-615 (≅1.5 times). The value of THA indicates that the effluent sample is hard and highly polluted. The effluent is severely contaminated with the salts of calcium and magnesium and hence requires pretreatment before discharge.

The average values of temporary hardness, as mg of $CaCO_3$ per litre (HAT, in mg/L) of electroplating effluent is 346 and the values of range of carbonate hardness are found to be 255-415. The percentage of average value of temporary hardness relative to that of total hardness is 62. The average value of permanent hardness (HAP, in mg/L of $CaCO_3$) of electroplating effluent is 209. The percentage value of permanent hardness relative to that of total hardness is 38.

The average value and the range of chloride of electroplating effluent are 648 and 565-702 respectively. The amount of chlorides present in electroplating effluent is above the discharge limit prescribed by BIS and hence they may be discharged only after proper effluent treatment. The average value of sulphate in mg/L of electroplating effluent is 564. The range of sulphate ions of electroplating effluent is 480-720. The average value indicates that the sulphate ion concentration in the effluent is within the permissible limit prescribed by BIS for effluent standard.

The average value of sodium ions in electroplating effluent is 186 mg/L. The range of Na^+ ions in electroplating effluent is 145-230mg/L. Sodium salts which are used as raw materials for preparing electroplating bath are mainly responsible for its high presence in the effluent sample. The average value of K^+ ions in the electroplating effluent is 54mg/L. The min - max range of potassium ions in electroplating effluent are 6.5-110. The contaminated effluent, when let out untreated, will affect the soil quality.

The range of permissible limits 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 concentration of Ca^{2+} and Mg^{2+} ions in the electroplating effluent are 272 and 292mg/L respectively. The values are found to be above the permissible limit prescribed by BIS, and hence the effluent may be treated before letting them out from the industry.

Bio-chemical Oxygen Demand is a measure of biologically degradable organic matter and COD is a measure of chemically oxidisable organic as well as inorganic matter. The average values of BOD and COD of electroplating effluent are 98 and 180mg/L respectively. The min-max ranges of BOD and COD in dyeing effluent are 76-140 and 100-240mg/L respectively. The experimental results indicate that the BOD and COD values of effluent are within the permissible limit prescribed by BIS for discharge of industrial effluent for irrigation [17-29].

The mean value and min - max ranges of total ion as Cr^{6+} of the electroplating effluent are 7.5 mg/L and 6-9.2mg/L. The Cr^{6+} ion in effluent is above the prescribed limit by BIS (2.0 mg/L) for discharge of industrial effluent for irrigation, indicating the need for the treatment to reduce its level before discharge. Apart from Cr^{6+} ions, the trace metals such as copper and zinc ions were determined for electroplating effluent and found to be lower than the prescribed limit. Figure 2 gives a judicious comparison of the major WQPs of electroplating 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.

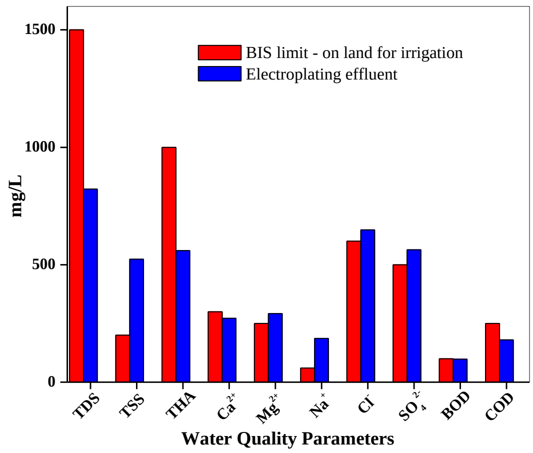

Fig. 2 Comparison of WQPs of electroplating industrial effluent with BIS limit

3.3 Calculation of Water Quality Index (WQI) of electroplating effluent 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 very much important [30].

3.4 Correlation analysis of WQPs of electroplating effluent industrial effluent

The water quality data (24 in numbers for the electroplatin effluent, which were collected fortnightly for a period of one year; *i.e.,* 24 observations) is pre+sented 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) [17-23]. 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 electroplating industrial effluent

WQPs	**T**	**pH**	**K**	**TDS**	**TSS**	**THA**	**HAT**	**HAP**	**Cl^-**	**SO_4^{2-}**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**BOD**	**COD**	**Zn^{2+}**	**Cr^{6+}**	**Cu^{2+}**
T	1																		
pH	0.205	1																	
EC	0.290	0.119	1																
TDS	-0.281	0.228	0.176	1															
TSS	-0.260	0.024	-0.085	0.068	1														
THA	0.151	-0.175	-0.123	-0.100	-0.126	1													
HAT	-0.210	-0.106	-0.366	-0.011	-0.126	0.683	1												
HAP	0.698	0.005	0.246	-0.189	-0.219	0.416	-0.200	1											
Cl^-	0.038	-0.205	-0.203	-0.153	0.056	0.269	0.130	-0.048	1										
SO_4^{2-}	-0.312	0.009	-0.222	0.249	0.263	-0.106	-0.177	-0.064	0.066	1									
Na^+	-0.051	0.157	-0.220	0.255	0.139	0.257	0.292	0.127	0.215	0.212	1								
K^+	-0.198	-0.276	0.089	-0.060	-0.142	-0.191	0.006	-0.336	0.238	-0.101	-0.257	1							
Ca^{2+}	0.313	-0.433	-0.023	-0.074	-0.050	0.531	0.225	0.362	0.372	-0.143	-0.083	0.148	1						
Mg^{2+}	0.048	-0.109	-0.246	0.105	-0.223	0.480	0.492	0.229	0.192	0.057	0.248	0.201	0.352	1					
BOD	-0.088	-0.315	-0.199	-0.004	0.185	0.200	0.101	-0.091	0.712	0.255	0.082	-0.063	0.201	0.308	1				
COD	0.012	-0.207	-0.287	-0.177	0.181	-0.139	-0.199	0.063	0.056	0.037	-0.202	-0.255	0.059	-0.138	0.339	1			
Zn^{2+}	0.452	0.004	0.148	-0.148	-0.059	-0.204	-0.272	0.104	0.131	-0.435	-0.192	-0.104	0.209	-0.239	0.049	0.170	1		
Cr^{6+}	-0.084	0.283	-0.105	0.026	-0.057	-0.036	0.045	-0.053	-0.220	-0.057	0.088	0.009	-0.461	0.101	-0.123	-0.076	-0.094	1	
Cu^{2+}	-0.228	-0.161	-0.297	0.103	0.267	-0.037	0.165	-0.236	-0.028	-0.220	0.280	0.263	-0.081	0.040	-0.128	0.185	-0.209	0.166	1

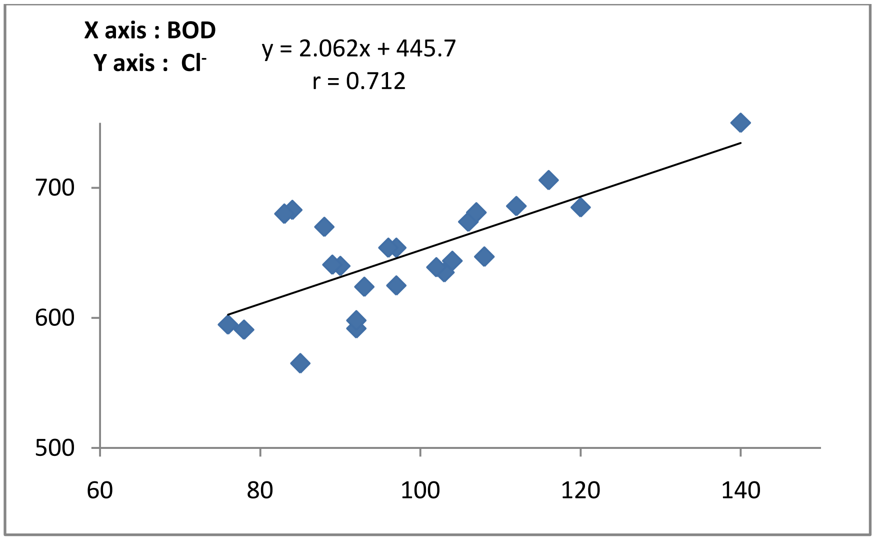

Figure. 3 Correlation between BOD and Cl^- of electroplating industrial effluent

The minimum and maximum values of correlation co-efficients for electroplating effluent are -0.461 (between Cr^{6+} - T) and 0.712 (between BOD - Cl^-), respectively. Some WQPs may be positively correlated with high 'r' values (>0.6) such as 0.712 (between BOD-Cl^-), 0.698 (between T - HAP) and 0.683 (between HAT - THA) while most of the water quality parameters are positively correlated with low 'r' value and some are 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 electroplating effluent

Sample	For total correlation		For positive correlation		For negative correlation	
	Min	Max	Min	Max	Min	Max
Electroplating effluent	– 0.461 (Cr^{6+} – Ca^{2+})	0.712 (BOD – Cl^-)	0.004 (pH – Zn^{2+})	0.712 (BOD – Cl^-)	– 0.461 (Cr^{6+} – Ca^{2+})	– 0.004 (BOD – TDS)

3.5 Linear Regression (LR) studies of electroplating industrial effluent

The statistically significant LR equation for the electroplating effluent is given below and a graph is given in Figure 3. The WQP calculated using LR equation for the electrplating effluent is given in Table 4.

HAP = 7.585T + 0.806 (r =0.698)

Table 5 Linear Regression Study of electroplating effluent: T vs HAP
$y = 7.5845x + 0.806$; $r = 0.698$

T	HAP	HAPcal
25.4	190	193.4523
25.6	185	194.9692
25.9	205	197.2446
29.5	255	224.5488
29.3	220	223.0319
29.4	220	223.7903
27.4	204	208.6213
28.2	231	214.6889
29.3	225	223.0319
28.5	180	216.9643
26.4	205	201.0368
25.5	180	194.2108
27	199	205.5875
29.5	209	224.5488
29.8	230	226.8241
30.4	234	231.3748
27.9	206	212.4136
27.5	208	209.3798
25.8	203	196.4861
25.7	211	195.7277
25.1	198	191.177
25	195	190.4185
26.5	190	201.7953
27.8	230	211.6551

3.6 Evaluation of quality of electroplating effluent 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}) [31-34] for electroplating effluent are calculated using equations 1 to 4. The status of any industrial effluents for irrigation is given in Table 6. The quality of electroplating effluent for irrigation is given in Table 7.

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

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 electroplating industrial effluent for irrigation

*Parameter/ ratio	Electroplating effluent			
	min	max	mean	Status for irrigation
Na^+	145	230	186	---
K^+	40	70	54	---
Ca^{2+}	225	295	272	---
Mg^{2+}	250	332	292	---
SAR	---	---	11.08	Good
PS	---	---	29.85	Fair
KR	---	---	0.32	Fair
MR	---	---	51.77	Poor

*unit mg/L

Based on the SAR, PS and KR results the electroplating effluent is not suitable for irrigation as such. However, after the removal of Na^+, K^+, Ca^{2+} and Mg^{2+} ions from electroplating effluent through proper treatment the effluent can be used for irrigation purpose.

3.7 Electrocoagulation treatment studies of electroplating industrial effluent

The physico-chemical characteristics of electroplating industrial effluent were found to be higher than the tolerance limit prescribed by BIS for the discharge of industrial effluents. This indicates that the electroplating industrial effluent should be discharged only after proper effluent treatment. Hence, treatment by EC processes have been carryout on electroplating industrial effluent and the percentage removal of various WQPs with and without adsorbent namely CAC, MWCNTs or GR was determined.

3.7.1 Optimization of adsorbents for EC processes

The optimization of dose of adsorbents (CAC, MWCNTs and GR) for EC studies of electroplating industrial effluent was determined by measuring TDS and results indicated that the optimum dose for CAC was found to be 1g, for both MWCNTs and GR were 175mg.

3.7.2 Removal of WQPs of electroplating industrial effluent before and after EC processes

The physico-chemical WQPs of dyeing industrial effluent before and after EC with and without adsorbent in presence of iron cathode (MS) and aluminium anode electrodes are given in Table 8.

Table 8 Characteristics of electroplating industrial effluent before and after EC with and without adsorbent

Water Quality Parameters	Water Quality Parameters Values				
	Before EC	After EC			
		Without adsorbent	With CAC	With MWCNTs	With Graphene
Colour	Dark brown	Light brown	Almost colourless	Almost colourless	Almost colourless
Ph	4.8	5.6 (17)	6.2 (29)	6.4 (33)	6.1 (27)
K	4365	1065 (76)	768 (82)	365 (92)	410 (91)
TDS	825	364 (56)	290 (68)	195 (76)	220 (73)
TSS	585	265 (55)	212 (64)	204 (65)	395 (67)
Na^+	165	96 (42)	68 (59)	62 (62)	70 (58)
K^+	52	32 (38)	22 (58)	19 (63)	28 (46)
Ca^{2+}	290	155 (47)	134 (54)	124 (57)	110 (62)
Mg^{2+}	264	142 (46)	98 (63)	85 (68)	90 (63)
Cl^-	706	324 (54)	220 (69)	194 (73)	174 (75)
SO_4^{2-}	618	302 (52)	252 (59)	189 (69)	216 (65)

Units: K in μmho/cm and remaining parameters except pH are in mg/L

3.7.3 Measurement of pH before and after EC processes

Initial pH is an important operating parameter in EC process. Generally, the pH of the electroplating effluent is changed during the EC. This variation in initial pH of the solution depends upon the electrode material, adsorbent material and on the initial pH of the effluent. At high pH, the Al^{3+} ions as $Al(OH)_3$ act as a coagulant. The wastage of Al^{3+} ion occurs at pH less than 4.5 and greater than 10. Hence, the pH of the effluent is adjusted by adding 0.1M NaOH solution to maintain the pH between 4.5 and 10.

The initial pH of the raw electroplating effluent is 4.8. It is observed from the Table 8. The pH the effluent is considerably increased after EC with and without adsorbent. The result indicates that increase in pH is due to decline in the concentration of H^+ ions present in the electroplating effluent. The H^+ ions present in the electroplating effluent undergone electronation at cathode resulting in evolution of H_2 gas and also adsorb over the surface of adsorbent materials [35-41].

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

Evolution of hydrogen bubbles at cathode and subsequent reaction with anions such as Cl^-, SO_4^{2-}, HCO_3^-, NO_3^- *etc.*, caused an increase in pH. Moreover, these anions replace some of the OH^- ions from $Al(OH)_3$ and cause giant leap in the increase of pH. As a result, the pH of the electroplating effluent is increased to 5.6 of EC without adsorbents. However, due to the addition of adsorbent, this value is further increased.

3.7.4 Effect on TDS and TSS before and after EC processes

TDS is a measure of the total ions present water systems. From the Table 8 and Figure 4, the decrease in the values of TDS in electroplating industrial effluent after electrocoagulation with MWCNTs or GR is relatively higher than CAC and without adsorbent. 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 heavy coagulants get settled at bottom while light ones undergo electroflocculation and the hydrogen bobbles produce in the electrolytic cell uplift the later particles to the surface, from where in can be easily removed.

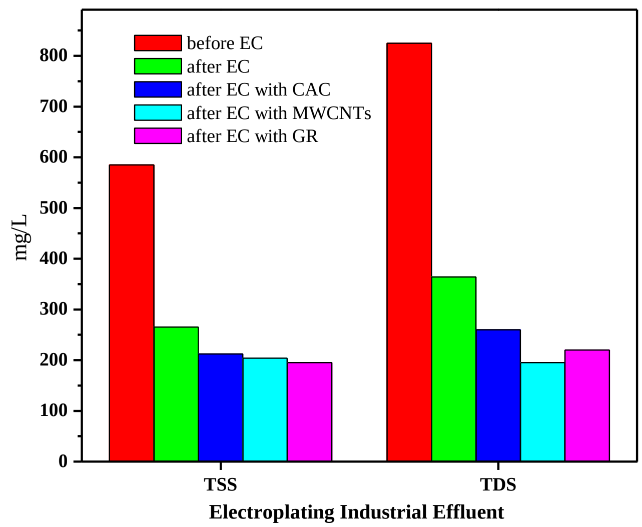

Figure. 4. Removal of TDS and TSS in electroplating industrial effluent by EC with and without adsorbents

3.7.5 Effect on anions before and after EC processes

The reduction in the concentration of anions such as Cl^- and SO_4^{2-} during with EC of electroplating effluent with and without absorbents is given in the Table 8 and Figure 5. It may be due to (i) electrochemical oxidation of anions at anode, (ii) reaction of anions Al^{3+}, $Al(OH)_3$ resulting in corresponding chloride and sulphate precipitates and (iii) the anions undergo adsorption on the surface of CAC, MWCNTs and GR during electrocoagulation [35-41].

$$Cl^- \rightarrow e^- + 1/2Cl_2\uparrow \quad \text{(at anode)}$$
$$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_{3(s)} + 3H^+$$
$$Al^{3+} + 3Cl^- \rightarrow AlCl_3\downarrow$$

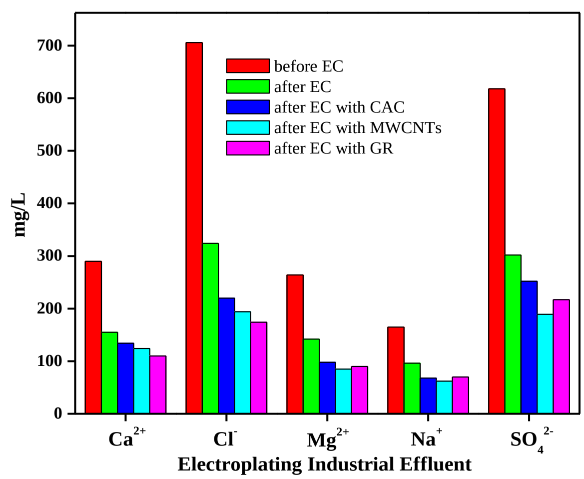

Figure. 5. Removal of cations and anions in electroplating industrial effluent by EC with and without adsorbents

3.7.6 Effect on cations before and after EC processes

The decrease in the concentration of cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} in electroplating effluent after EC with and without adsorbents is shown in Table 3.5 and Figure 5. It may be due to electrochemical reduction of these cations at cathode and also adsorption of cations on the surface of CAC, MWCNTs and GR during electrocoagulation.

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

The percentage removal of pollutants in electroplating effluent is higher in the case of EC processes in presence of GR or MWCNTs than CAC and without adsorbent and it can be attributed to good adsorption and their conducting behavior. Since EC process is common in all four treatment studies of electroplating effluent, the efficiency of treatment lies on the adsorbing capacity of the adsorbent materials used during EC processes [35-41].

3.7.7 Surface morphological studies of adsorbents before and after EC process

The surface morphology of adsorbents (CAC, MWCNTs and GR) was carried out using scanning electron microscope (SEM) and studies provide useful information regarding the textural morphological characteristics of the surface of the adsorbents. The typical SEM photographs of adsorbents, before and after EC of electroplating 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.

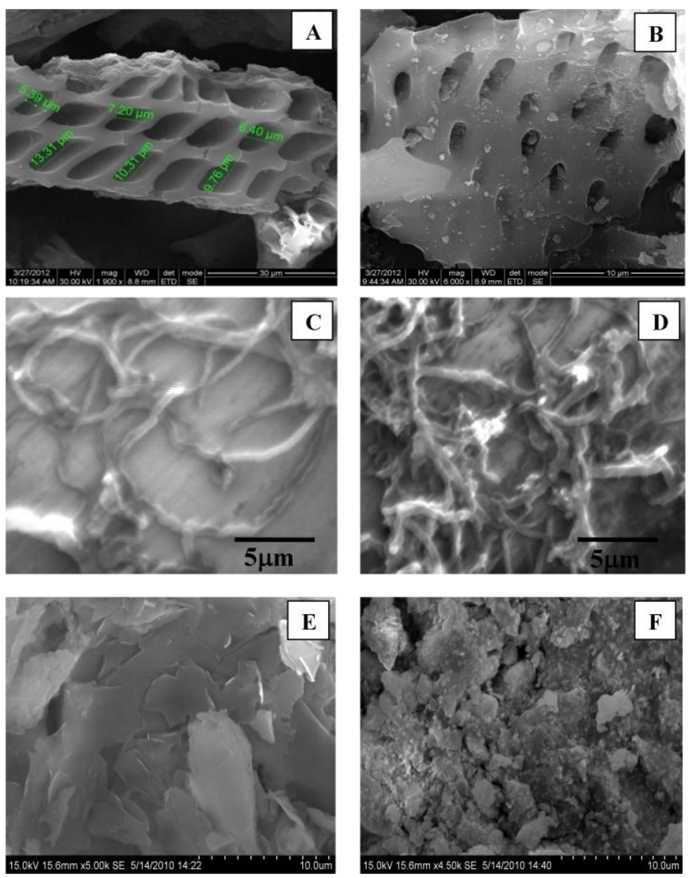

Figure 6. SEM images of A, C and E represent CAC, MWCNTs and GR respectively before EC processes: B, D and F represent CAC, MWCNTs and GR respectively after EC processes electroplating effluent

3.7.8 Thermogravimetric studies (TGA) of adsorbents before and after EC process

The TGA studies were carried out to study the thermal stability of adsorbent materials before and after EC processes of electroplating industrial effluent is given in Figure 7. It was observed that all the three adsorbents *viz.*, CAC, MWCNTs and GR undergo two step decomposition patterns. In the first step of degradation (~0-200 ◦C), a small fraction of weight loss occurred, which is due to the removal of water molecules/moisture that might be present in adsorbents. The second step of weight loss occurs in the temperature range of 200-700 ◦C is due to the removal of the removal of labile oxygenated surface groups and carbon skeleton corresponding to the release of COx, H_2O and carbon combustion. It is seen that from the TGA curve all adsorbent materials have almost comparable thermal stability before and after EC processes [42-44].

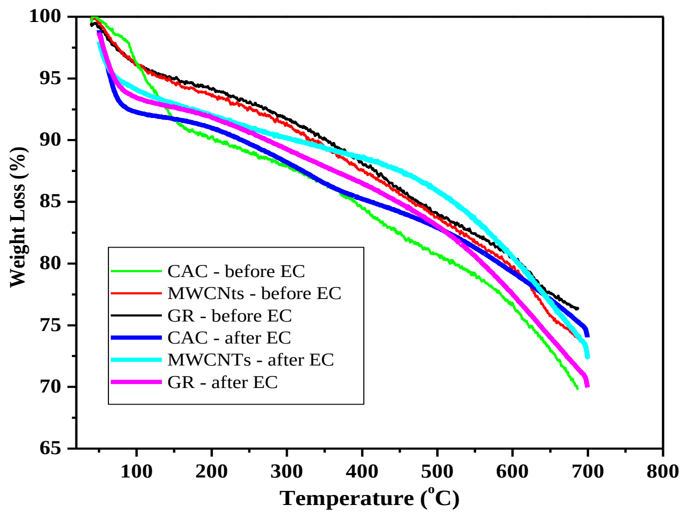

Figure7. Thermogravimetric curves of adsorbents before and after EC process of electroplating effluent

4. Conclusions

Characterization, correlation analysis and treatment by EC processes with and without CAC, MWCNTs or GR were carried out for the electroplating industrial effluent collected from industry located at Thirumangalam near Madurai, Tamilnadu, India. The following conclusions were made from the results of present study:

- ✓ Most of the WQPs electroplating industrial effluent were found to be higher than the limit prescribed by BIS for drinking water and industrial effluent.
- ✓ The WQI value of electroplating industrial effluent showed that it was contaminated six times higher than the limit prescribed by BIS.
- ✓ The rapid monitoring of water pollution was verified using correlation and linear regression analysis
- ✓ The studies on quality of effluent for irrigation showed that to certain extent it is suitable for irrigation purposes.
- ✓ pH of the effluent is considerably reduced after EC with and without adsorbents.
- ✓ The decrease in values of TDS was higher in the case of EC with GR/MWCNTs than CAC and without adsorbent.
- ✓ The decrease in concentration of both anions and cations are relatively higher in EC with GR/MWCNTs than CAC and without adsorbent.
- ✓ TGA studies were made for adsorbents before and after EC processes and
- ✓ The SEM studies show adsorbed effluents molecules are either engulfed or surrounded by the porous adsorbent particles.

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