ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Characterization, correlation studies and electrocoagulation treatment of printing industrial effluent with adsorbent (CAC, MWCNTS or GR)

T. Sugumaran[1*], A. Ramu[2] and N. Kannan[3]

1. Center for Research and Post-Graduate Studies in Chemistry, Ayya Nadar Janaki Ammal College, Sivakasi-626 124, Tamil Nadu, India.

2. Department of Inorganic Chemistry, Madurai Kamaraj University, Madurai- 625 021, Tamil Nadu, India

3. Center for Research and Post-Graduate Studies in Chemistry, Ayya Nadar Janaki Ammal College, Sivakasi-626 124, Tamil Nadu, India

Manuscript Info

Manuscript History:

Received: 11 January 2014
Final Accepted: 23 February 2014
Published Online: March 2014

Key words:
Printing effluents
Water Quality Parameters
Electrocoagulation
Adsorbents

Corresponding Author

T. Sugumaran

Abstract

In the present study, characterization, correlation analysis and treatment by Electrocoagulation (EC) process were carried out for the printing effluent samples which were collected from the industry located at south of Madurai near Sivakasi, Tamil Nadu, India. Most of the water quality parameters (WQPs) of printing effluent were found to be higher than the tolerance limit prescribed by Bureau of Indian Standards (BIS) for the discharge of industrial effluent. EC technique is employed for the treatment of printing effluent with and without adsorbent using iron and aluminium electrodes. The decrease in values of Total Dissolved Solids (TDS) was higher in the case of EC with Graphene (GR) and EC with Multi Walled Carbon Nanotubes (MWCNTs) than EC with Commercial Activated Carbon (CAC) and EC without adsorbent. The decrease in concentration of both anions and cations are relatively higher in EC with GR and EC with MWCNTs than EC with CAC and without adsorbent. It was observed that the percentage removal of cations is relatively lower than the other WQPs. The result of present investigation on printing industrial effluent revealed that generally the EC process with adsorbent is an effective tool for the treatment of industrial effluent.

1. Introduction

Inks and paper are the primary raw materials used in printing. Other input materials include photo-processing and plate making materials, fountain solutions, cleaning solvents and solutions, and lubricating oils. Solvents and some waste inks represent hazardous materials. Because of the variety of processes and printing substrates used and differences in the final product desired, many different inks are used. Some inks may contain flammable and toxic solvents and/or toxic heavy metals [1-3]. The solvents and ink oils used in the printing inks are common volatile organic compound include isopropyl alcohol (from fountain solutions), toluene, kerosene, methanol and some chlorinated solvents (found in type washes, roller, blanket, and press washes). Cleaning solvents used to clean the presses are including methanol, toluene, naphtha, trichlomethane and methylene chloride [4-6].

All the above facts disclose the magnitude of environmental pollution that may be caused by untreated printing effluent when mixed with natural water bodies [7-9]. Hence a detail study of printing industrial effluent (*viz.*, characterization and cost effective treatment) is required to minimize the pollution. This paper deals with the discussion of the results obtained from the studies on the characterization, water quality index, correlation, linear regression, assessment of irrigation quality and electrocoagulation treatment of industrial effluent discharged from the printing industry located at south of Madurai near Sivakasi, Tamil Nadu, 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 Printing Effluent Sampling Procedure

The printing industrial effluent samples for this study were collected from industry located at south of Madurai near Sivakasi, Tamil Nadu, 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 reported in literatures [10,11]. The values of physico-chemical characteristics of printing industrial effluent are shown in Table 1.

2.3 Electrocoagulation (EC) Treatment Studies of Printing Effluent

The electrochemical cell consisted of two mono polar electrodes, one cathode (mechanically polished) 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 20min. 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

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

3 Results and Discussion

3.1 Characterization of printing industrial effluent

The physico-chemical characteristic of the printing 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.

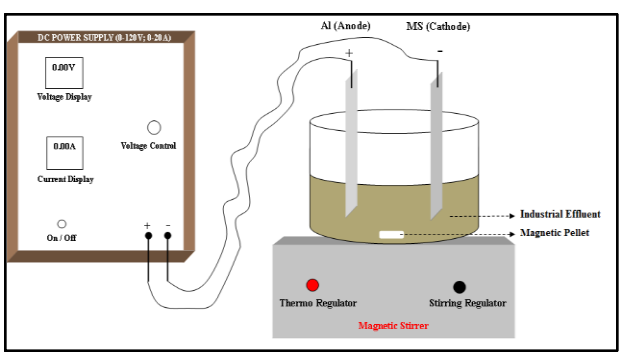


Figure 1. Schematic diagram of experimental set-up for EC process

Table 1 Water Quality Parameters of printing industrial effluent

T	pH	K	TDS	TSS	THA	HAT	HAP	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	BOD	COD	Fe^{2+}	Cr^{6+}
27.9	8.2	3382	2214	1086	979	605	374	540	138	540	11	301	104	212	1245	19	9
27.3	8	2934	1965	783	704	459	245	467	110	452	9	212	78	188	1065	25	5
28.1	7.9	3136	2044	924	1062	662	400	556	126	490	12	172	62	262	1314	20	8
27.6	9.7	2876	1558	985	852	537	315	483	107	334	10	250	73	194	1068	15	7
28.6	8.2	2460	1771	822	762	461	301	468	102	431	14	196	68	190	1242	9	12
28.9	8.1	2164	2059	945	784	492	292	456	134	442	13	162	42	231	1369	13	8
27.8	7.7	2798	1914	1006	1036	661	375	522	105	456	11	254	96	252	1296	24	13
28.2	7.6	2862	1716	721	774	488	286	465	98	406	8	192	82	216	1359	22	9
29.1	7.9	2362	1769	868	796	498	298	442	122	431	15	174	77	229	1110	30	6
28.6	8.1	2426	1928	972	887	561	326	483	118	396	12	212	96	175	1085	27	13
28.7	7.8	2672	1482	859	769	486	273	462	101	415	16	185	70	218	1220	24	15
28.1	8.3	2983	1851	881	967	608	359	435	142	394	12	228	82	195	1188	18	13
29.2	7.8	3016	2092	1110	820	502	318	480	130	429	10	192	84	178	1011	21	12
28.9	7.9	2724	1868	953	810	504	306	465	108	435	18	182	75	191	992	17	9
28.6	8.1	2916	1441	706	874	551	323	492	96	392	14	209	80	215	1145	25	7
29.1	7.5	1931	1826	942	717	448	369	432	90	428	19	168	94	190	1265	16	14
28.3	7.9	2558	1906	878	784	491	293	416	112	411	22	182	58	208	992	22	10
27.9	8	3247	1781	822	937	588	349	523	124	372	17	198	45	204	1090	31	15
28.6	7.8	2368	2010	829	810	508	302	484	84	377	10	176	49	356	1238	17	11
28.9	7.9	2981	2261	967	772	511	261	428	98	532	14	202	53	242	1412	18	8
27.9	8.2	2202	1827	802	597	366	231	376	116	298	18	134	71	186	1019	12	10
28.5	7.6	2667	1578	794	567	352	215	336	74	387	24	104	56	242	981	8	13
29.4	7.4	1903	1915	899	648	401	247	298	70	291	10	137	46	197	1001	17	11
28.4	8	2368	1862	1012	734	456	278	332	88	368	20	168	38	208	1242	9	16

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

Table 2 Statistical Data of printing industrial effluent

WQPs	N	Range	Minimum	Maximum	Sum	Mean
T	24	2.10	27.30	29.40	682.60	28.4417
pH	24	2.30	7.40	9.70	191.60	7.9833
K	24	1479.00	1903.00	3382.00	63936.00	2664.0000
TDS	24	820.00	1441.00	2261.00	44638.00	1859.9167
TSS	24	404.00	706.00	1110.00	21566.00	898.5833
THA	24	495.00	567.00	1062.00	19442.00	810.0833
HAT	24	310.00	352.00	662.00	12196.00	508.1667
HAP	24	185.00	215.00	400.00	7336.00	305.6667
Cl^-	24	258.00	298.00	556.00	10841.00	451.7083
SO_4^{2-}	24	72.00	70.00	142.00	2593.00	108.0417
Na^+	24	249.00	291.00	540.00	9907.00	412.7917
K^+	24	16.00	8.00	24.00	339.00	14.1250
Ca^{2+}	24	197.00	104.00	301.00	4590.00	191.2500
Mg^{2+}	24	66.00	38.00	104.00	1679.00	69.9583
BOD	24	181.00	175.00	356.00	5179.00	215.7917

COD	24	431.00	981.00	1412.00	27949.00	1164.5417
Cr^{6+}	24	11.00	5.00	16.00	254.00	10.5833

3.2 Comparison of WQPs of printing industrial effluent with BIS Limit

The value of mean temperature of printing industrial effluent is 28.44°C. The range (min - max) of temperature of printing industrial effluent is 27.30 – 29.40°C. The average temperature of the sample is found to be ambient. Hence, the effluent is not polluted thermally. The pH of printing industrial effluent is 7.9. The min-max range of pH of printing industrial effluent is 7.4 – 9.7. The pH value of the effluent is within the tolerance limit prescribed by BIS [10-17].

The average value of specific conductance of printing industrial effluent is 2664 µmhocm^{-1}. The range of specific conductance value of printing industrial effluent is 1903-3382 as against the tolerance level of 3000 µmho/cm prescribed by BIS. The average value of TDS of printing industrial effluent is 1860 mg/L. The min – max range for TDS in printing industrial effluent are 820-2261. Based on the mean values of specific conductance as well as TDS the effluent is moderately polluted. Hence, proper effluent treatment is required in order to bring down the values of TDS and specific conductance to BIS standards. The mean value of TSS of printing industrial effluent is 899mg/L. Further, the min – max range of TSS in mg/L of printing industrial effluent are 706-1110. Based on the mean value of TSS the effluent is severely polluted. The average value of THA of printing industrial effluent is 810mg/L. The min – max range of THA values of printing industrial effluent are 567-1062. The printing industrial effluent has very high value of THA and indicates that the effluent sample is hard and highly polluted. Hence the effluent requires pretreatment before discharge in to natural water bodies.

The average value of temporary hardness of printing industrial effluent is 508 mg/L and the values of range of carbonate hardness are found to be 352-622 mg/L. The percentage of average values of temporary hardness relative to that of total hardness is 63 for the effluent. This indicates that the permanent hardness is less compared to the temporary hardness in printing effluent [10-17]. The average value of permanent hardness of printing industrial effluent is 306mg/L. The range of min-max of printing industrial effluent is 215-400mg/L. The percentage values of permanent hardness relative to that of total hardness is 37. Although the permanent hardness in the effluent is moderate still it can be removed using water softening techniques like ion exchange, lime soda process *etc*., or by electrocoagulation technique which successfully removes the dissolved ions.

The average value and the range of chloride in printing industrial effluent are 452mg/L and 298-556mg/L. The amount of chlorides present in printing industrial effluent is within the discharge limit prescribed by BIS. The average value of sulphate in mg/L of printing industrial effluent is 108 and the range of min-max is 70-142. The amount of sulphate present in printing industrial effluent is within the tolerance limit prescribed by BIS, hence primary treatment is not mandatory for the effluent before it is discharged into natural water bodies. The average value of sodium ions in mg/L in printing industrial effluent is 413. The range of Na^+ ions in the effluent is 291-540. The amount of sodium present in printing effluent is above the discharge limit prescribed by BIS and hence they may be discharged only after proper effluent treatment. The average value of K^+ ions in printing industrial effluent is 14mg/L. The min - max range of potassium ions in printing industrial effluent are 8-24mg/L. The amount of potassium present in printing industrial effluent is within the tolerance limit prescribed by BIS. 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 printing industrial effluent are 191 and 70mg/L respectively and found to be within the limit prescribed by BIS and hence the effluent do not require any specific treatment for their removal.

The BOD and COD of the printing effluent sample exceed 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 samples. Hence, the effluents are to be discharged only after proper treatment to reduce the values of BOD and COD.

The mean values and min - max ranges of total Fe^{2+} and Cr^{6+} ion concentration in printing effluent samples are 19 and 13.8 mg/L and 8-31 and 5-16mg/L respectively and they are above the prescribed limit of BIS indicating the need for the treatment to reduce its level before discharge.

Figure 2 gives a judicious comparison of the WQPs of printing industrial effluent sample (TDS, TSS, THA, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, BOD and COD) with BIS tolerance limits of major pollutants of industrial effluent discharged on land for irrigation[8-17].

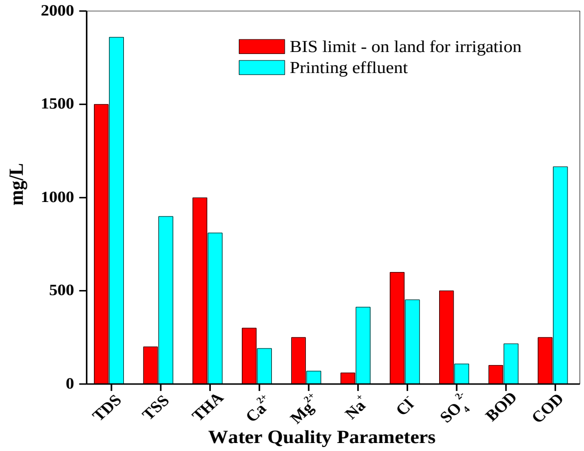


Figure 2. Comparison of WQPs of printing industrial effluent with BIS limit

3.3 Water Quality Index (WQI)

The procedure for calculating WQI of printing effluent is adopted from the literature as reported by Tiwari *et al* [18]. The mean WQI value indicates that the effluent is contaminated approximately six times above the tolerance limit prescribed BIS which indicates that the effluent is highly polluted with a heavy load of various pollutants. Hence, the treatment becomes significant.

3.4 Correlation analysis of WQPs of printing 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.

The minimum and maximum values for both positive and negative correlations as well as for total correlations for printing effluent are given in Table 4 and Figure 3. The minimum and maximum values of correlation co-efficients for the printing effluent are -0.525 (between K - T) and 0.994 (between HAT - THA), respectively. The studies show that a few WQPs are positively correlated with high 'r' values such as such as 0.994 (between HAT - THA), 0.884 (between HAP -THA), 0.855 (between HAP - HAT), 0.802 (between Cl^- - HAT), 0.805 (between Cl^- - THA) and 0.729 (between Cl^- - HAP) while some water quality parameters are positively correlated with low 'r' value (<0.5) and some are negatively correlated which are highly insignificant [10,11,14-17].

3.5 Linear Regression (LR) studies of printing industrial effluent

A few statistically significant LR equations for the printing effluent is calculated using Table 5 and WQPs calculated using LR equations for the effluent is given in Table 6.

THA = 1.556HAT + 19 (HAT = 508 ; r = 0.994)
THA = 2.291HAP + 110 (HAP = 0.306 ; r = 0.884)

3.6 Assessing printing 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}) for printing effluent[19-23] were calculated using equations 3.1 to 3.4 and the relevant data are given in Table 7.

$$SAR = Na^{+} / [(Ca^{2+} + Mg^{2+}) /2]^{1/2} \quad \text{----} \quad (3.1)$$
$$PS = 100 [(Na^{+} + K^{+}) / (Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})] \quad \text{----} \quad (3.2)$$
$$KR = [Na^{+} / (Ca^{2+} + Mg^{2+})] \quad \text{----} \quad (3.3)$$
$$MR = 100 [Mg^{2+} / (Ca^{2+} + Mg^{2+})] \quad \text{----} \quad (3.4)$$

Based on the SAR, PS and KR results the printing 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.

Table 3 Correlation Coefficient Matrix of printing industrial effluent

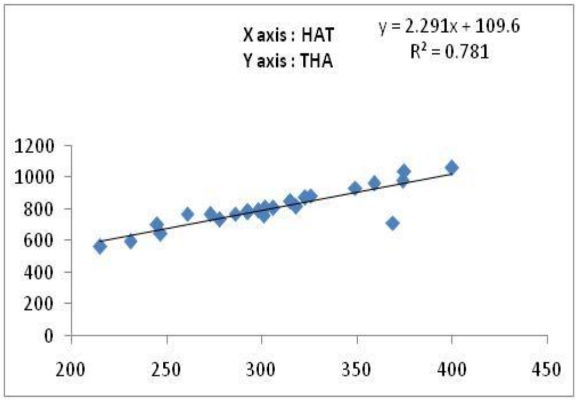
WQPs	T	pH	K	TDS	TSS	THA	HAT	HAP	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	BOD	COD	Fe^{2+}	Cr^{6+}
T	1																	
pH	-0.485	1																
EC	-0.525	0.270	1															
TDS	0.078	-0.194	0.113	1														
TSS	0.160	0.159	0.104	0.574	1													
THA	-0.311	0.231	0.613	0.231	0.343	1												
HAT	-0.332	0.227	0.626	0.241	0.326	0.994	1											
HAP	-0.152	0 .126	0.386	0.201	0.392	0.884	0.855	1										
Cl	-0.362	0.257	0.635	0.157	0.143	0.805	0.803	0.729	1									
SO_4^{2-}	-0.282	0.349	0.469	0.352	0.329	0.587	0.565	0.505	0.572	1								
Na	-0.028	-0.148	0.502	0.532	0.349	0.455	0.482	0.406	0.551	0.383	1							
K	0.165	-0.190	-0.258	-0.287	-0.114	-0.409	-0.424	-0.261	-0.458	-0.239	-0.140	1						
Ca^{2+}	-0.471	0.467	0.614	0.202	0.383	0.712	0.726	0.595	0.675	0.482	0.462	-0.517	1					
Mg^{2+}	-0.190	0.083	0.261	-0.022	0.202	0.353	0.347	0.457	0.458	0.335	0.322	-0.306	0.591	1				
BOD	0.022	-0.215	0.011	0.167	-0.140	0.171	0.190	0.067	0.179	-0.255	0.172	-0.107	-0.105	-0.333	1			
COD	-0.001	-0.100	0.097	0.294	0.086	0 .354	0.383	0.346	0.334	0.084	0.542	-0.302	0.264	-0.010	0.409	1		
Fe^{2+}	-0.107	-0.118	0.365	-0.035	-0.108	0.474	0.508	0.336	0.518	0.336	0.185	-0.303	0.366	0.332	-0.040	-0.072	1	
Cr^{6+}	0.155	-0.295	-0.178	-0.151	0.181	-0.026	-0.056	0.113	-0.233	-0.201	-0.263	0.385	-0.166	-0.110	-0.073	-0.004	-0.169	1

Table 4 Correlation co-efficient range of WQPs of printing industrial effluent

Sample	For total correlation		For positive correlation		For negative correlation	
	Min	Max	Min	Max	Min	Max
Printing industrial effluent	– 0.525 (K – T)	0.994 (HAT – THA)	0.22 (BOD – T)	0.994 (HAT – THA)	– 0.525 (K – T)	– 0.001 (COD – T)

Table 5 Linear Regression Values of printing industrial effluent

X	Y	r	m	c
HAT	THA	0.99358	1.5564	19.196
HAP	THA	0.88397	2.2914	109.67
HAP	HAT	0.85539	1.4156	75.47
Chloride	THA	0.80474	1.5693	101.21
Chloride	HAT	0.80262	0.9992	56.805
Chloride	HAP	0.7287	0.5482	58.035



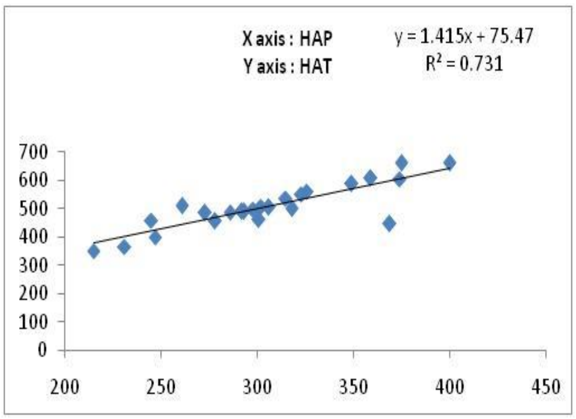


Figure 3. Correlation between HAP vs THA and HAP vs HAT of printing effluent

3.7 Electrocoagulation treatment studies of printing industrial effluent

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

3.7.1 Optimization of adsorbents for EC processes

The optimization of dose of adsorbents (CAC, MWCNTs and GR) for EC studies of printing 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.

Table 6 Linear Regression Study of printing industrial effluent: HAT vs THA

$y = 1.5564x + 19.196; R^2 = 0.9872$

S. No.	THA	HAT	THAcal
1	979	605	960.818
2	704	459	733.5836
3	1062	662	1049.533
4	852	537	854.9828
5	762	461	736.6964
6	784	492	784.9448
7	1036	661	1047.976
8	774	488	778.7192
9	796	498	794.2832
10	887	561	892.3364
11	769	486	775.6064
12	967	608	965.4872
13	820	502	800.5088
14	810	504	803.6216
15	874	551	876.7724
16	717	448	716.4632
17	784	491	783.3884
18	937	588	934.3592
19	810	508	809.8472
20	772	511	814.5164
21	597	366	588.8384
22	567	352	567.0488
23	648	401	643.3124
24	734	456	728.9144

Table 7 Quality of printing industrial effluent for irrigation

*Parameter/ ratio	Printing industrial effluent			
	Min	max	mean	Status for irrigation
Na^+	291	540	413	---
K^+	8	24	14	---
Ca^{2+}	104	301	191	---
Mg^{2+}	38	104	70	---
SAR	---	---	36	Poor
PS	---	---	62.1	Poor
KR	---	---	1.60	Poor
MR	---	---	26.80	Fair

*unit mg/L

3.7.2 Removal of WQPs of printing effluents before and after EC processes

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

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

WQPs	WQP Values				
	Before EC	After EC			
		Without adsorbent	With CAC	With MWCNTs	With GR
Colour	Black	Light black	Almost colorless	Almost colorless	Almost colorless
pH	8.0	7.4 (8)	7.5 (6)	7.6 (5)	7.4 (8)
K	2363	688 (71)	545 (77)	468 (80)	460 (81)
TDS	1862	464 (75)	394 (79)	318 (83)	346 (81)
TSS	1012	513 (49)	312 (69)	220 (78)	285 (72)
Na^+	368	167 (55)	126 (66)	102 (72)	112 (70)
K^+	20	13 (35)	10 (50)	10 (50)	9 (55)
Ca^{2+}	168	110 (35)	102 (39)	82 (51)	94 (44)
Mg^{2+}	38	22 (42)	18 (53)	16 (58)	17 (55)
Cl^-	332	219 (34)	186 (44)	190 (43)	168 (49)
SO_4^{2-}	88	64 (27)	50 (43)	43 (51)	56 (43)

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

3.7.2.1 Measurement of pH before and after EC processes

The initial pH of the raw printing industrial effluent is 8.0. It is observed from the Table 8, the pH of the effluent is reduced after EC with and without adsorbents. The result indicates that decrease in pH is due to decline in the concentration of H^+ ions present in the printing 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.

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

3.9.2 Removal of 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 printing industrial effluent after electrocoagulation with MWCNTs and electrocoagulation with GR are relatively higher than electrocoagulation with CAC and electrocoagulation 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 gases evolved at the electrodes may impinge on and cause flotation of the coagulated materials. The EC process is intrinsically 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 [24-26].

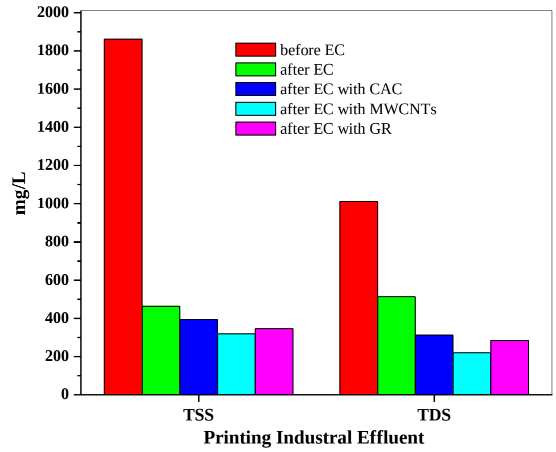


Figure 4. Removal of TDS and TSS in printing effluent by EC with and without adsorbents

3.9.3 Removal of anions and cations before and after EC processes

The reduction in the concentration of anions such as Cl^- and SO_4^{2-} during EC of printing effluent with and without absorbent 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.

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

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 [27-30].

$$2Cl^- \leftrightarrow Cl_2 + 2e^-$$
$$Cl_2 + H_2O \leftrightarrow HClO + H^+ + Cl^-$$
$$HClO \leftrightarrow ClO^- + H^+$$

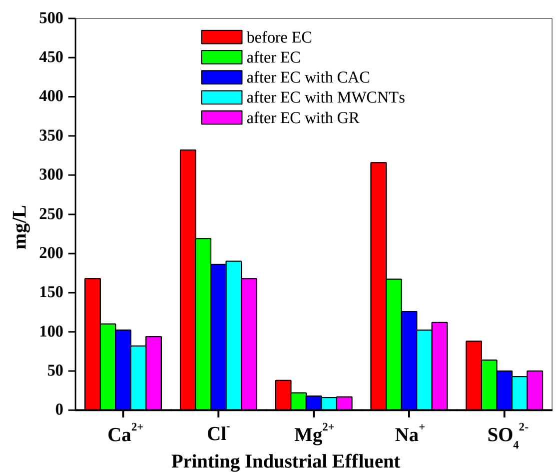


Figure 5. Removal of cations and anions in printing effluent by EC with and without adsorbents

The removal of cations in printing 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 adsorbent. 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 [24-28].

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

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

3.9.5 Surface morphological studies of adsorbents before and after EC process

The typical SEM photographs of adsorbents, before and after EC of printing 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 [31,32].

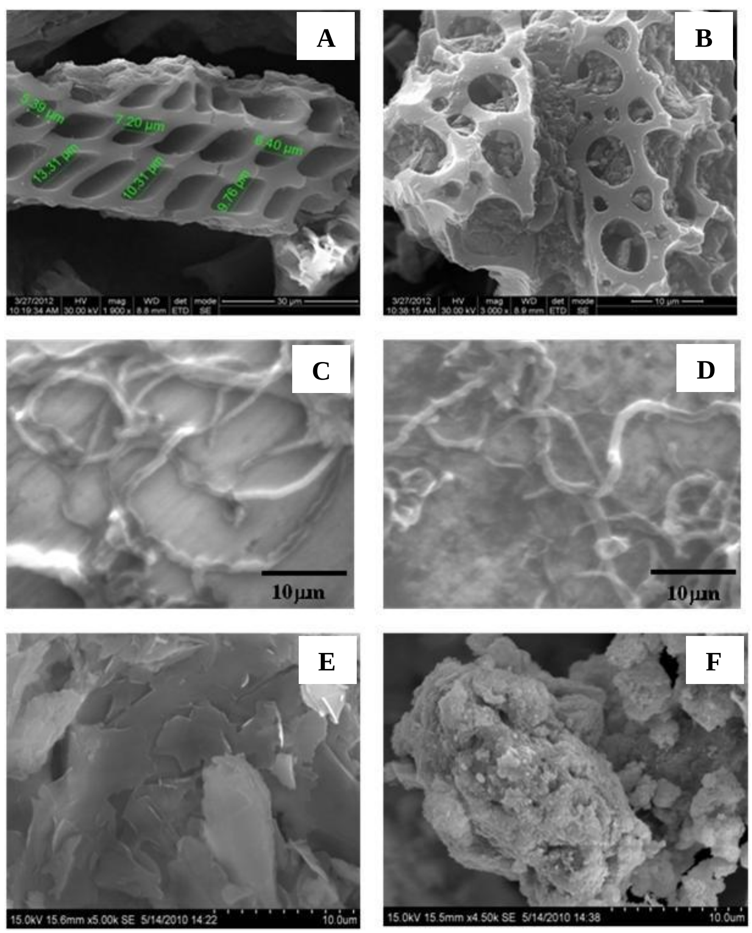


Figure 6. SEM images of A, C and E represent CAC, MWCNTs and GR respectively before EC processes: B, D and F represent CAC, MWCNTs and GR respectively after EC processes of printing effluent

4 Conclusions

The printing effluent samples were collected from industry located at south of Madurai near Sivakasi, Tamil Nadu, India. Characterization, correlation analysis and treatment by EC process were carried out. The following conclusions were made from the results of present study:

- ✓ Most of the WQPs of printing effluents were found to be higher than the limit prescribed by BIS for the discharge of industrial effluent.
- ✓ The WQI value of printing 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 suitable for irrigation purposes only after proper treatment.
- ✓ EC technique is employed for the treatment of printing effluent with and without adsorbents using iron and aluminium electrodes.
- ✓ 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 and without 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. It was observed that the percentage removal of cations is relatively lower than the other WQPs and
- ✓ The SEM studies show adsorbed effluents molecules are either engulfed or surrounded by the porous adsorbent particles.
- ✓ The result of present investigation on printing industrial effluent revealed that generally the EC process with adsorbent is an effective tool for the treatment of industrial effluent.

References

1. Mondal, B., Chandra Srivastava, V., Prakash Kushwaha, J., Bhatnagar, R., Singh, S., and Deo Mall I., *Sep. Purif. Tech.*, 109 (2013) 135.
2. Guedez, A.A., and Püttmann, W., *Sci. Total Environ.*, 468–469 (2014) 671.
3. Capar, G., Yetis,U., and Yilmaz, L., *J. Membr. Sci.*, 277 (2006) 120.
4. Flick, E.W., Printing Ink and Overprint Varnish Formulations, 2nd Edition, Elsevier Inc. 1999.
5. Husain, I., and Hussain, J., *Inter. J. Environ. Bioener.*, 2 (2012) 100.
6. Rigoni-Stern, S., Szpyrkowicz, L., and Zilio-Grandi, F., *Water Sci. Technol.*, 33 (1996) 95.
7. Rosin, K.G., Kaur, R., Singhb, S.D., Singh, P., and Dubey, D.S., *Procedia Environ. Sci.*, 18 (2013) 200.
8. Matkar, L.S., and Gangotri, M.S., *J. Ind. Poll. Cont.*, 18 (2002) 139.
9. Gupta, R.K., Singh, G. and Bandopadhyay, P., *Indian J. Env. Prot.*, 19 (1999).
10. Kannan, N., Karthikeyan, G., Vallinayagam, P., and Tamilselvan, N., *Indian J. Env. Prot.*, 26 (2006) 438.
11. Kannan, N., Karthieyan, G., Vallinayagam, P., and Tamilselvan, N., *Indian J. Env. Prot.*, 24 (2004) 856.
12. Venkateswara Rao, A., Singanan, M., and Somasekhara Rao, K., *J. Ind. Poll. Cont.*, 12 (1996) 61.
13. Nemade, P.N., and Shrivastava, V.S., *Poll. Res.*, 15 (1996) 245.
14. Nemade, P.N. and Srivastava, V.S., *Indian J. Env. Prot.*, 17 (1997) 133.
15. Rezacc, A., Ansari, M., Khavanin, A., Sabzali, A., Aryan, M.M., *Am. J. Env. Sci.*, 1 (2005) 259.
16. Pathak, V., Shrivastava, R.S., and Karla, P.D., *Indian J. Env. Prot.*, 17 (1997) 685.
17. Prasad, N.V.V.S., Sarat Babu, M., and Somasekhara Rao, K., *Indian J. Env. Prot.*, 16 (1996) 481.
18. Tiwari, T.N., and Ali, M., *Indian J. Env. Prot.*, 7 (1987) 1149.
19. Matcalf and Eddy., 'Wastewater Engineering, Treatment, Disposal and Reuse', IV edition, Tata McGraw Hill, New Delhi (2003).
20. Kelley, W.P., "Alkali Soils – Their Properties and Reclamation', Rein Hold Publ. Corpn., New York, 1951.
21. Richards, L.A., "Diagnosis and improvement of saline and alkali soils", US Salinity Laboratory, U.S. Department of Agriculture Hand Book – 60, Washington, D.C. (1954).
22. Venkateswara Rao, A., Singanan, M. and Kaza Somasekhara Rao, Indian J. Env. Prot., 12 (1996) 61.
23. Wilcox, D.V., "The quality of water for irrigation use", U.S. Agriculture Technology Bulletin, Washington, D.C. (1948).
24. Akbal, F., and Camci, S., *Environ. Prog. Sust. Energy* 31 (2011) 340.
25. Bellebia, S., Kacha, S., Bouyakoub, A.Z., and Derriche, Z., *Environ. Prog. Sust. Energy* 31 (2012) 361.

26. Chang, S.H., Wang, K.S., Liang, H.H., Chen, H.Y., Li, H.C., Peng, T.H., Su, Y.C., and Chang, C.Y., *J. Hazard. Mater.*, 175 (2010) 850.
27. Linares-Hernandez, I., Barrera-Diaz, C., Roa-Morales, G., Bilyeu, B., and Urena-Nunez, F., *J. Hazard. Mater.*, 144 (2007) 240.
28. Narayanan, N.V., and Ganesan, M., *J. Hazard. Mater.*, 161 (2009) 575.
29. Secula, M.S., Cagnon, B., De Oliveira, T.F., Chedeville, O., and Fauduet, H., *J. Taiwan Inst. Chem. Eng.*, 43 (2012) 767.
30. Verma, S.K., Khandegar, V., and Saroha, A.K., *J. Hazard. Toxic. Radio. Waste* 17 (2013) 146.
31. Pradeep, T., Nano: The Essentials, Tata McGraw-Hill Publishers, New Delhi, 2007.
32. Kohler, M., and Fritzsch, W., Nanotechnology, Wiley-VCH Publishers, Weinheim, 2004.