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CHARECTERISATION OF SPENTWASH AND PIEZOMETER SAMPLES BY GC-MS

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Abstract–Postmethanated Distillery Spentwash (PMDSW) contains a large amount of salts and plant nutrients. Therefore monitoring and charecterisation of spentwash and piezometer leachates are necessay to prevent groundwater contamination. The PMDSW and piezometer leachates were analysed in GC-MS to check the contamination of organic compounds present in spentwash on ground water. On GCMS analysis different compounds like 7-Oxabicyclo-dec-4-en-8-one, 1,2-Dimethyl-4-heptylcyclohexane, Tert-Hexadecanethiol, Hexadecanoic acid 1,2-Bis(1-butyn-3-onyl)benzene, 7,9-di-tert-butyl-1-oxaspiro-decadienedione, 1,2-Benzenedicarboxylic acid, Squalene were present in the spent wash. Comparing both PMDSW the piezometer leachates compounds like Tert-Hexadecanethiol, Hexadecanoic acid, 7,9-di-tert-butyl-1-oxaspiro-decadienedione were present in both spentwash and leachate sample. The spentwash leachate from piezometer contains only a limited number of compounds present in the spentwash. This suggests that there is limited chance for contamination of organic compounds from spentwash on groundwater.

INTRODUCTION

The effluent from the distillation process, called spentwash, contains high concentration of decomposable organic matter and dissolved salts and has a persistent dark brown colour, which is one of the most recalcitrant and unutilized waste in nature . Hence, the molasses based distillery industry for the production of rectified spirit for use as industrial alcohol and for human consumption, is considered as one of the most polluting industries and included in the group of 17 categories of industries identified in the country for priority action for control of pollution..

For every liter of alcohol produced, about 15 liters of spent wash is released as wastewater. At present there are about 315 distilleries in India producing 50 to 60 billion liters of effluent annually. As per the Ministry of Environment and Forests (MoEF), Government of India, alcohol distilleries are listed at the top of the ¯Red category industries having high polluting potentials.

Spent wash is a non-toxic, highly biodegradable liquid which is purely of plant origin and contains large quantity of soluble organic matter and plant nutrients which the sugarcane plant has absorbed from the soil. Chemically, raw spent wash is highly acidic (pH 3.7- 4.1) wastewater released from distilleries which has high EC (22-29 dS m^{-1}), BOD (40000-52000 mg L^{-1}), COD (86000-105000 mg L^{-1}), organic carbon (12.1-16.4 per cent), and appreciable amounts of soluble N, P, K and micronutrient (Kumari *et al.*, 2010).

Central Pollution Control Boards have laid down the standards for treatment of effluent before disposal. According to the prescribed standards, waste waters should have a BOD less than 30 mg l^{-1} before disposal into natural water bodies and less than 100 mg l^{-1} for disposal on land. In 2003, Central Pollution Control Board, India stipulated that, distilleries should achieve zero discharge in inland surface water courses by the end of 2005. Hence, the present study is aimed to charecterise the distillery spentwash and piezometer leachate by GC-MS and also to monitor, whether spentwash is contaminating the ground water through piezometer study.

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MATERIALS AND METHODS

Characterization of Distillery Spentwash

Collection and preservation of samples

The Postmethanated Distillery Spentwash (PMDSW) sample was collected from the distillery unit of M/s. Bannari Amman Sugars Ltd., located at Sathyamangalam Taluk, Erode district. The samples was collected in polycarboryl containers, properly sealed and stored at 4°C for further analysis. The physico-chemical properties of distillery spentwash was assessed as per the methods outlined in Table 1

After measuring pH and EC, a portion of the sample was taken for the immediate measurement of Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD).

Piezometer Study : Farmers' Holdings

In Erode district, Postmethanated Distillery Spentwash (PMDSW) was applied to farmers' field, particularly in dry land, as a source of irrigation and nutrients. The piezometers were installed at a depth of 0.5 m in both spentwash applied and control plots. Leachate samples were collected at 30th day, 60th day, 90th day and 120th day and samples were analyzed for various water quality indices.

Structure of Piezometers

The PVC pipe of 50 mm diameter with a total length of 1.95m was taken. The bottom of PVC pipe was sealed with end cap without any leakage of the water from the pipe. Leaving the 0.15 m length from the bottom of the pipe for the collection of the leachate, perforation i.e., circular holes or longitudinal slits in a zig zag fashion to the length of 0.5m were made just above the collection tank. Then, the pipe was marked with marker to the height of 0.5m, from the top of the perforated portion in order to maintain the soil column of 0.5m depth from the soil surface to the perforated portion. About 0.30m length pipe was left above the surface layer of the field and the top end of the PVC pipe was fitted with screw cap for easy operation during the collection of the leachate and also to avoid entry of

Table 1. Analytical methods followed for the analysis of PMDSW and leachate

S.No	Properties	Methodology	Reference
1	Colour	Assessed by visual comparison with distilled water	APHA (1989)
2	Moisture	Oven temp. 105º C	A.O.A.C (1962)
3	Ph	pH meter	Jackson (1973)
4	EC	Conductivity meter	Jackson (1973)
5	Biochemical Oxygen Demand	5 days at 20º C, Dissolved Oxygen method	APHA (1965)
6	Chemical Oxygen Demand	Chromic acid-Reflux method	APHA (1965)
7	Total Solids	Oven temp. 105º C	Ramteke and Moghe (1988)
8	Total Dissolved Solids	Oven temp. 105º C	Ramteke and Moghe (1988)
9	Total Suspended Solids	Oven temp. 105º C	Ramteke and Moghe (1988)
10	Organic Carbon	Chromic acid - Wet Digestion method	Walkley and Black (1934)
11	Nitrogen	Bremner method	Jackson (1973)
12	Phosphorus	Vanadomolybdate Colorimetric Method	APHA (1989)
13	Potassium	Flame photometric method	Jackson (1973)
14	Calcium	Versenate titration method	Jackson (1973)
15	Magnesium	Versenate titration method	Jackson (1973)
16	Chloride	Mohr's method	Jackson (1973)
17	Carbonates and Bicarbonates	Titrimetric method	Jackson (1973)
18	Sulphate	Turbidometric method	Jackson (1973)
19	Sodium	Flame photometric method	Jackson (1973)
20	Sodium Adsorption Ratio (SAR)	$Na / [\frac{1}{2}(Ca + Mg)]^{0.5}$	USDA (1954)
21	Residual Sodium Carbonate (RSC)	$(CO_3 + HCO_3) - (Ca + Mg)$	Eaton (1950)

external water sources. The perforated portion of 0.5m length in the pipe was completely covered with 2 mm nylon net and sealed at both end of perforated portion by cello tape. This arrangement of structures facilitated the easy movement of water through the soil column of 1m depth and easy operation during collection.

Installation of Piezometers

Piezometers were installed in the farmer's field at about 0.5m depth to measure the shallow and deep ground water to confirm the nutrient distribution. . A hand operated piling was used to dig holes for each piezometer installation. The piezometers were made from slotted PVC pipes that were covered with mesh at the base, and then inserted into the holes. The space around the tubes was backfilled with sand till the level of holes and then with white cement and followed by clay to prevent preferential flow pathways developing outsides of the PVC tubes. A PVC tube extended above the soil surface for 0.5m to avoid the surface water flow entering into the piezometers. Finally they were end capped to avoid rain filling the tubes. The design of the piezometers are prepared on the models of nested piezometers. After completing this process of piezometer installation in the individual plot, the treatments were imposed as per the method prescribed.

Leachate collection

Piezowater samples were collected at four different intervals *viz*., 30, 60, 90 and 120 days after the application of spentwash as pre-sown respectively and analysed for pH and EC, immediately after collection.

Charecterisation of Distillery Spentwash and piezometer leachate by GC-MS

The dry residue obtained from liquid–liquid extraction method using ethyl acetate was derivatised with trimethylsilyl (TMS). In this method, 100 µl dioxane and 10 µl pyridine was added to samples followed by silylation with 50 µl trimethyl silyl [BSTFA (N, O-bis (trimethylsilyl) trifluoroacetamide) and TMCS (trimethyl chlorosilane)]. The mixture was heated at 60°C for 15 min with periodic shaking to dissolve residues. An aliquot (2 µl) of silylated samples were injected in GC–MS (PerkinElmer, UK) equipped with a PE auto system XL gas chromatograph interfaced with a Turbomass mass spectrometric mass selective detector. The analytical column connected to system was a PE-5MS capillary column (length 20 m 9 0.18 mm i.d, 0.18 ìm film thickness). Helium gas was used as carrier gas with flow rate of 1 ml min^{-1}. The column temperature was programmed as 50 °C (5 min); 50–300 °C (10 °C min^{-1}, hold time: 5 min). The transfer line and ion source temperatures were maintained at 200 and 250 °C, respectively. A solvent delay of 3.0 min was selected. The chromatographic run time was maintained up to 33.84 min. In full-scan mode, the electron ionization mass spectra were recorded in range of 30–550 (m/z) at 70 eV. The organic pollutants and metabolic products were identified by comparing their mass spectra with that of National Institute of Standards and Technology (NIST) library available with instrument and by comparing the retention time with those of available authentic organic compounds (Chandra and Abhishek, 2011).

Statistical Analysis

The experimental results were statistically scrutinized as suggested by Panse and Sukhatme (1985). The critical difference was worked out at 5 per cent (0.05) probability levels

RESULTS AND DISCUSSION

Characteristics of Post Biomethanated Distillery Spentwash (PMDSW)

The important physical, chemical and biological characteristics of PMDSW samples collected from M/s. Bannari Amman Sugars Ltd, Ealur, Sathyamangalam taluk, Erode district, Tamil Nadu, are presented in Table 2**.** The PMDSW was dark brown in colour with an unpleasent odour of burnt sugar. It carries large amount of Total Suspended Solids (9259 mg l^{-1}), Total Dissolved Solids (39160 mg l^{-1}), Total Solids (45638 mg l^{-1}), BOD (7217 mg l^{-1}) and COD (36519 mg l^{-1}). The PMDSW was slightly alkaline in pH (7.42) with an EC of 32.5 dSm^{-1} and organic carbon 13.7 per cent. Among the major plant nutrients, potassium was found in higher amounts (10513 mg l^{-1}) followed by nitrogen (1760 mg l^{-1}) and phosphorus (149 mg l^{-1}).

The PMDSW was dark brown in colour with an unpleasent odour of burnt sugar. The brown colour could be ascribed to the presence of melanoidin, the reaction products of sugar amine condensation (Baskar *et al.*, 2003). The presence of melanoidin with high similarity to synthetic melanoidin and humic acid might be the reason for dark brown

Table 2. Characteristics of Post Biomethanated Distillery Spentwash (PMDSW)

Parameters	Value
Colour	Dark brown
Odour	Unpleasant
Moisture (per cent)	87.1
Specific gravity (g cc^{-1})	1.14
pH	7.42
EC (dS m^{-1})	32.5
Total Suspended Solids (mg l^{-1})	9259
Total Dissolved Solids (mg l^{-1})	39160
Total Solids (mg l^{-1})	45638
Organic Carbon (per cent)	13.7
BOD (mg l^{-1})	7217
COD (mg l^{-1})	36519
Nitrogen (mg l^{-1})	1760
Phosphorous (mg l^{-1})	149
Potassium (mg l^{-1})	10513
Calcium (mg l^{-1})	2161
Magnesium (mg l^{-1})	1422
Sodium (mg l^{-1})	657
Chloride (mg l^{-1})	9400
Carbonate (mg l^{-1})	Nil
Bicarbonate (mg l^{-1})	126.675
Sulphate (mg l^{-1})	72.135
Iron (mg l^{-1})	84.91
Manganese (mg l^{-1})	8.965
Zinc (mg l^{-1})	13.56
Copper (mg l^{-1})	4.865

colour of distillery effluent. The unpleasant odour is due to the presence of skatole, indole and other sulphur compounds (H_2S) which are not effectively decomposed by yeast or methanogenic bacteria (Thiyagarajan, 2001).

The spentwash carries large amount of suspended solids, dissolved solids, total solids, BOD and COD. The PMDSW was slightly alkaline in pH with an EC of 32.5 dSm^{-1} and organic carbon 13.7 per cent. Among the major plant nutrients, potassium was found in higher amounts followed by nitrogen and phosphorus. Similarly, the contents of calcium, magnesium, chloride and sulphate were also relatively high.

The BOD and COD of distillery spentwash were very high and exceeded the permissible limit of 30 and 250 mg l^{-1}, respectively as prescribed by the Central Pollution Control Board. The high BOD and COD content in distillery spentwash might be due to presence of soluble form of organic matter and the inorganic compounds. Similar results were reported by Nandy *et al*. (2002).

In general, among the plant nutrients, K was present in larger amounts compared to N and P. The Ca content was higher than Mg content. The presence of Ca was considered as a potential amendment in reclaiming the sodic soils. Similar results were reported by Pathak *et al.* (1999).

Piezometer Study

The results on the characteristics of leachate collected at 30,60,90 and 120 days after application from the piezometers installed at a depth of 0.5 m in soil are given in this section.

Characteristics of leachate samples

The piezometer leachates were collected from field near Modur after 30,60,90 and 120 days of application and analysed for pH, EC, Na, K, Ca, Mg, SO_4, CO_3, HCO_3 and Cl.

pH

The effect of spentwash on pH was given in the Table 3. The mean pH ranged between 8.75 and 8.97. The pH was high in field which received PMDSW compared to the control field. The pH of the leachates were alkaline and varied from 8.66 in 30th day, 8.75 in 60th day, 8.78 in 90th day and 8.84 in 120th day in control field and in treated field it was 8.78 in 30th day, 8.98 in 60th day, 9.00 in 90th day and 9.14 in 120th day. The pH of the leachate increased over the days after planting and the highest pH (9.14) was observed in spentwash treated field at 120 days. The pH of the leachate increased over the days after planting and the highest pH was observed in spentwash treated field at 120 days. The sodium bicarbonate among the four sodium salts (carbonate, bicarbonate, chloride and sulphate) was the most marked in increasing the pH and the degree of alkalization. Similarly, bicarbonate also present in high quantity in the spentwash that might have dominated in influencing pH over chloride and sulphate ions which along with sodium leads to neutral reaction. As there were sufficient other salts added through the Spentwash, there was not much increase in pH.

Saliha (2003) also reported an increase in pH of the leachate with leaching events in the sodic soil treated with distillery spentwash. The increase in the pH might be due to addition of salts by spentwash which favours alkalinity and continuous release of exchangeable bases *viz.,* Ca, Mg, Na and K in the soil solution (Sridharan, 2007).

EC

The mean EC of the leachate was 0.98 dS m^{-1} in control and 1.41 dS m^{-1} in treated fields respectively (Table 3). The EC of the leachate increased with spentwash application and it decreased over the period of collection. The EC was 1.03 dS m^{-1} in 30th day, 0.99 dS m^{-1} in 60th day 0.96 dS m^{-1} in 90th day and 0.94 dS m^{-1} in 120th day. Whereas in treated it was 1.62 dS m^{-1} in 30th day, 1.48 dS m^{-1} in 60th day 1.31 dS m^{-1} in 90th day and 1.26 dS m^{-1} in 120th day. The highest EC (1. 26 dS m^{-1}) was recorded in treated field in 30th day whereas the lowest EC (0.94 dS m^{-1}) was observed in control field at 120th day.

The highest EC was recorded in treated field in 30th day whereas the lowest EC was observed in control field at 120th day. Since the salts present such as chlorides and sulphates in the spentwash are highly soluble in nature, so they might have been leached down along the movement of water, thereby resulting in high EC in the Spentwash applied field compared to control.

The salt accumulation in soil depends on many factors. One of the major factors is seasonal effect. When there is heavy rainfall, there may be chance of more leaching from surface layer which may increase the salts. The amount of rainfall recorded during the experimental period of piezometer study was given in appendix 1. The high EC in Spentwash plots compared to control may be that the salt loading was very high due to spentwash containing high TDS.

Ashok Kumar *et al.* (2011) reported that the increase in EC was very well correlated with the increase in the levels of spentwash application and application of spentwash at higher rates might lead to build up of salts in the soil and ground water.

Calcium

The mean Ca content of the leachate was 3.18 meq L^{-1} in control and 4.28 meq l^{-1} in treated fields respectively (Table 3). The Calcium content of the leachate increased with spentwash application and it decreased over the period of collection. The Ca content was 3.56 meq l^{-1} in 30th day, 3.40 meq l^{-1} in 60th day 3.09 meq l^{-1} in 90th day and 2.69 meq l^{-1} in 120th day. Whereas in treated it was 6.02 meq l^{-1} in 30th day, 3.83 meq l^{-1} in 60th day 3.72 meq l^{-1} in 90th day and 3.58 meq l^{-1} in 120th day. The highest Ca content (6.02 meq l^{-1}) was recorded in treated field in 30th day whereas the lowest Ca content (2.69 meq l^{-1}) was observed in control field at 120th day.

Magnesium

The mean Mg content of the leachate was 2.73 meq l^{-1} in control and 2.97 meq l^{-1} in treated fields respectively (Table 3). The Mg content of the leachate decreased over the period of collection and increased with spentwash application. The Mg content was 2.90 meq l^{-1} in 30th day, 2.79 meq l^{-1} in 60th day 2.67 meq l^{-1} in 90th day and 2.57 meq l^{-1} in 120th day. Whereas in treated it was 3.19 meq l^{-1} in 30th day, 3.01 meq l^{-1} in 60th day 2.88 meq l^{-1} in 90th day and 2.83 meq l^{-1} in 120th day. The highest Mg content (3.19 meq l^{-1}) was recorded in treated field in 30th day whereas the lowest Mg content (2.59 meq l^{-1}) was observed in control field at 120th day.

Potassium

The mean K content of the leachate was 0.87 meq l^{-1} in control and 2.61 meq l^{-1} in treated fields respectively (Table 3). The K content of the leachate decreased over the period of collection and increased with spentwash application. The K content was 0.93 meq l^{-1} in 30th day, 0.87 meq l^{-1} in 60th day 0.85 meq l^{-1} in 90th day and 0.83 meq l^{-1} in

Table 3. Charecteristics of the leachate collected in piezometer at different intervals.

Sl. No.		Parameters					Control Treated				
		30 days	60 days	90 days	120 days	Mean	30 days	60 days	90 days	120 days	Mean
1	pH	8.66	8.75	8.78	8.84	8.75	8.78	8.98	9.00	9.14	8.97
2	EC (dS m^{-1})	1.03	0.99	0.96	0.94	0.98	1.62	1.48	1.31	1.26	1.41
3	Ca (meq l^{-1})	3.56	3.40	3.09	2.69	3.18	6.02	3.83	3.72	3.58	4.28
4	Mg (meq l^{-1})	2.90	2.79	2.67	2.57	2.73	3.19	3.01	2.88	2.83	2.97
5	Na (meq l^{-1})	1.95	1.90	1.68	1.46	1.74	2.45	2.21	2.09	1.96	2.17
6	K (meq l^{-1})	0.93	0.87	0.85	0.83	0.87	4.10	2.53	1.95	1.87	2.61
7	Cl (meq l^{-1})	3.44	3.30	3.13	2.78	3.16	6.16	5.44	4.04	3.11	4.68
8	SO_4^{2-} (meq l^{-1})	3.21	3.09	2.95	2.71	2.99	6.43	5.61	4.23	3.49	4.94
9	HCO_3^- (meq l^{-1})	1.95	1.92	1.82	1.76	1.86	3.88	3.73	3.56	3.32	3.62
10	SAR	0.65	0.63	0.52	0.41	0.55	0.77	0.77	0.72	0.65	0.72
11	RSC (meq l^{-1})	-5.51	-5.27	-4.94	-4.50	-5.05	-6.33	-4.11	-4.04	-4.09	-4.63

120^{th} day. Whereas in treated it was 4.1 meq l^{-1} in 30^{th} day, 2.53 meq l^{-1} in 60^{th} day 1.95 meq l^{-1} in 90^{th} day and 1.87 meq l^{-1} in 120^{th} day. The highest K content (4.1 meq l^{-1}) was recorded in treated field in 30^{th} day whereas the lowest K content (0.83 meq l^{-1}) was observed in control field at 120^{th} day.

Sodium

The mean Na content of the leachate was 1.74 meq l^{-1} in control and 2.17 meq l^{-1} in treated fields respectively (Table 3.). The Na content of the leachate decreased over the period of collection and increased with spentwash application. The Na content was 1.95 meq l^{-1} in 30^{th} day, 1.90 meq l^{-1} in 60^{th} day 1.68 meq l^{-1} in 90^{th} day and 1.46 meq l^{-1} in 120^{th} day. Whereas in treated it was 2.45 meq l^{-1} in 30^{th} day, 2.21 meq l^{-1} in 60^{th} day 2.09 meq l^{-1} in 90^{th} day and 1.96 meq l^{-1} in 120^{th} day. The highest Na content (2.45 meq l^{-1}) was recorded in treated field in 30^{th} day whereas the lowest Na content (1.96 meq l^{-1}) was observed in control field at 120^{th} day.

Chloride

The mean Cl^- content of the leachate was 3.16 meq l^{-1} in control and 4.68 meq l^{-1} in treated fields respectively (Table 3). The Cl^- content of the leachate decreased over the period of collection and increased with spentwash application. The Cl^- content was 3.44 meq l^{-1} in 30^{th} day, 3.30 meq l^{-1} in 60^{th} day 3.13 meq l^{-1} in 90^{th} day and 2.78 meq l^{-1} in 120^{th} day. Whereas in treated it was 6.16 meq l^{-1} in 30^{th} day, 5.44 meq l^{-1} in 60^{th} day 4.04 meq l^{-1} in 90^{th} day and 3.11 meq l^{-1} in 120^{th} day. The highest Cl^- content (6.16 meq l^{-1}) was recorded in treated field in 30^{th} day whereas the lowest Cl^- content (3.44 meq l^{-1}) was observed in control field at 120^{th} day.

Sulphate

The mean SO_4^{2-} content of the leachate was 2.99 meq l^{-1} in control and 4.94 meq l^{-1} in treated fields respectively (Table 3.). The SO_4^{2-} content of the leachate decreased over the period of collection and increased with spentwash application. The SO_4^{2-} content was 3.21 meq l^{-1} in 30^{th} day, 3.09 meq l^{-1} in 60^{th} day 2.95 meq l^{-1} in 90^{th} day and 2.71 meq l^{-1} in 120^{th} day. Whereas in treated it was 6.43meq l^{-1} in 30^{th} day, 5.61 meq l^{-1} in 60^{th} day 4.23 meq l^{-1} in 90^{th} day and 3.49 meq l^{-1} in 120^{th} day. The highest SO_4^{2-} content (6.43 meq l^{-1}) was recorded in treated field in 30^{th} day whereas the lowest SO_4^{2-} content (3.21 meq l^{-1}) was observed in control field at 120^{th} day.

Bicarbonates

The mean HCO_3^- content of the leachate was 1.86 meq l^{-1} in control and 3.62 meq l^{-1} in treated fields respectively (Table 3). The HCO_3^- content of the leachate decreased over the period of collection and increased with spentwash application. The HCO_3^- content was 1.95 meq l^{-1} in 30^{th} day, 1.92 meq l^{-1} in 60^{th} day 1.82 meq l^{-1} in 90^{th} day and 1.76 meq l^{-1} in 120^{th} day. Whereas in treated it was 3.88 meq l^{-1} in 30^{th} day, 3.73 meq l^{-1} in 60^{th} day 3.56 meq l^{-1} in 90^{th} day and 3.32 meq l^{-1} in 120^{th} day. The highest HCO_3^- content (3.88 meq l^{-1}) was recorded in treated field in 30^{th} day whereas the lowest HCO_3^- content (1.95 meq l^{-1}) was observed in control field at 120^{th} day.

Sodium AR

The mean SAR content in the leachate are 0.55 in control field and 0.72 in treated field (Table 3). The SAR content of the leachate increased over the increasing dose of spentwash application and it decreased over the days after planting. The highest SAR content was 0.77 recorded in 30^{th} in treated field and the lowest SAR content was 0.41 recorded in 120^{th} day in control field.

RSC

The mean RSC content in the leachate are -0.05 in control field and -4.63 in treated field (Table 3). The SAR content of the leachate increased over the increasing dose of spentwash application and it decreased over the days after planting. The highest RSC content was -6.33 recorded in 30^{th} in treated field and the lowest RSC content was -4.5 recorded in 120^{th} day in control field.

Among the cations, Ca dominated and they were in the order of Ca > Mg > Na > K. Among the anions, Cl dominated and they were in the order of Cl > SO_4 > HCO_3. The salt content was decreased in 60^{th} day compared to 30^{th} day. As the total soluble salts increases there will be more conductivity.

Shenbagavalli *et al.* (2011), reported that the ground water samples from spentwash applied field contained large amount of salts, particularly K^+ and Cl suggesting that the water contamination is mainly due to the application of distillery spentwash.

Latha *et al.* (2013) reported that there was an increase in pH, EC, anions and cations content due to the application of spentwash over the recommended dose and were within the critical limits and have not influenced the ground water and there is no possibility of pollution by BDS application.

As the spentwash contained high concentration of Cl which might have enriched the soil solution with soluble Cl resulted in greater concentration of this ion in the leachate (Latha *et al.*, 2010). In most of the soil amended with spentwash, large accumulation of salts followed by greater amount of leaching were reported by Rajukkannu *et al.* (1996).

Although leaching of salts has the potential to affect the quality of groundwater, the actual impact will depend on the rate of recharge of groundwater, initial status of groundwater quality and agro-management practices followed in the area. Therefore, Spentwash must be applied judiciously according to crop requirements and soil fertility status to prevent contamination of shallow groundwater with nitrate and other toxic ions.

GCMS characterization of spentwash and leachate

The spentwash sample and leachates collected from piezometer was analyzed by GC-MS to find transport of the compounds present in the effluent to groundwater. The chromatograph corresponding to the compounds extracted with ethyl acetate from the acidified supernatants obtained from spentwash and leachate samples are shown in Figure 1 and 2 respectively and the compounds identified in the spentwash and leachate samples were presented in the Table 4 and 5 respectively.

Various acid and aromatic type of compounds were identified in spentwash. Complex polymers had produced due to the reaction between amino carboxyl groups that are recalcitrant in nature and exist in molasses and other agri-based industrial waste liquid.

Some of the major compounds identified in GCMS analysis of spentwash are:

- 7-Oxabicyclo-dec-4-en-8-one also called as 4-Ethylguaiacol, a phenolic compound with molecular formula $C_9H_{12}O_2$ which produced produced along with 4- ethylphenol in wine and beer by yeast.
- 1,2-Dimethyl-4-heptylcyclohexane also called as Drimane with a a molecular formula $C_{15}H_{28,}$ which is a bicyclic sesquiterpene found in several plants.
- Tert-Hexadecanethiol with a molecular formula $C_{16}H_{34}S$, which is dopaminergic agent.
- Hexadecanoic acid also called as margaric acid with a molecular formula of $C_{17}H_{34}O_{2,}$ which is a saturated fatty acid found in trace amount in some vegetable fats.
- 1,2-Bis(1-butyn-3-onyl)benzene also called as 9, 10 Dihydroxyanthracene with a molecular formula $C_{14}H_{10}O_{2,}$ which is formed when a compound named Anthraquinone is used a redox catalyst in industrial process.
- 1,2-Benzenedicarboxylic acid also with an molecular formula $C_{24}H_{38}O_4$, which is a is the most common member of the class of phthalates.
- Squalene with an molecular formular $C_{30}H_{50,}$

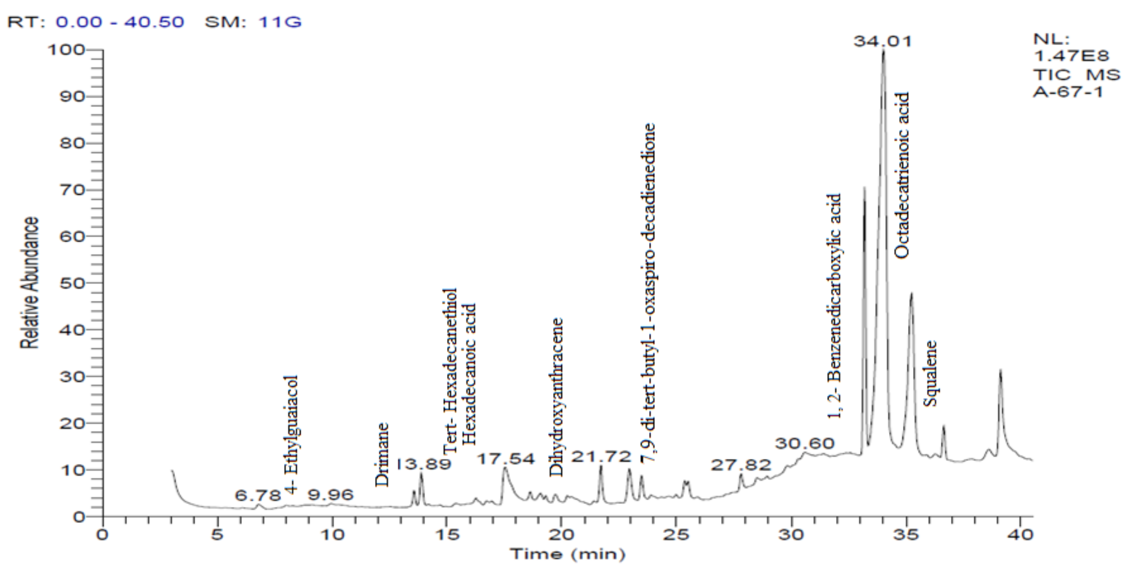

Fig. 1. Chromatogram of organic compounds present in Spentwash

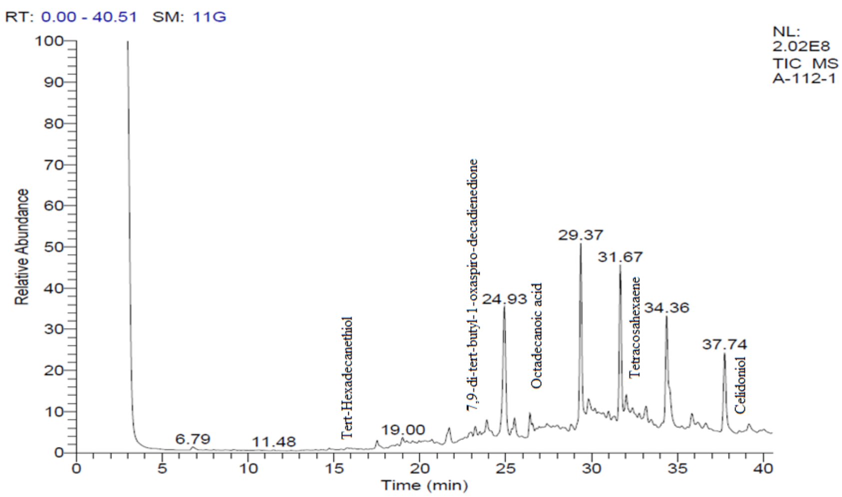

Fig. 2. Chromatogram of organic compounds present in leachate collected from piezometer

Table 4. Analysis of organic compounds present in spentwash through GC-MS

Sl. No.	Compound Name	Retention Time	Molecular Formula	Molecular Weight	Area
1	N-Methyl-N-propargyl-2 oxocyclopentane-1-carboxamide	6.78	$C_{12}H_{17}NO_2$	207	0.43
2	7-Oxabicyclo-dec-4-en-8-one	9.96	$C_9H_{12}O_2$	152	0.40
3	2Pentamethyl-cis-hexahydro-gamma chromene	13.56	$C_{14}H_{24}O$	208	0.81
4	1,2-Dimethyl-4-heptylcyclohexane	13.89	$C_{15}H_{28}$	208	1.89
5	Tert-Hexadecanethiol	16.27	$C_{16}H_{34}S$	258	0.55
6	Hexadecanoic acid	16.74	$C_{19}H_{33}BrO_2$	372	0.44
7	Exo-Tricyclododecan-2-ol	17.52	$C_{12}H_{20}O$	180	3.61
8	4-(2-Ethoxycarbonylpyrrol-4-yl)butyric acid	18.62	$C_{11}H_{15}NO_4$	225	0.41
9	4-endo-methoxy-tetramethyl-benzobicyc lo-octa-triene	19.07	$C_{17}H_{20}O$	240	0.83
10	Thiophene, 2-ethyl-5-heptyl	19.73	$C_{13}H_{22}S$	210	0.60
11	2-(t-Butyl)-3-methylthiophene	20.24	$C_9H_{14}S$	154	0.89
12	Hexadecanoic acid	21.72	$C_{17}H_{34}O_2$	270	2.43
13	1,2-Bis(1-butyn-3-onyl)benzene	22.94	$C_{14}H_{10}O_2$	210	2.46
14	6-Acetyl-3-methyl-3,4-dihydrothieno-pyrazin-2-one	23.47	$C_9H_{10}N_2O_2S$	210	1.35
15	7,9-di-tert-butyl-1-oxaspiro-decadienedione	23.90	$C_{17}H_{24}O_3$	276	0.41
16	9-Octadecenoic acid	25.35	$C_{19}H_{36}O_2$	296	1.76
17	1-Acetyl carboline	27.82	$C_{13}H_{10}N_2O$	210	0.94
18	Methylsulfinatoindium	28.51	$C_{37}H_{47}InN_4O_2S$	726	0.44
19	Diapo-20-methoxycarotene-8-dial	28.93	$C_{21}H_{26}O_3$	326	0.30
20	Cyclohexane –dodecylidenebis -methyl	29.82	$C_{26}H_50$	362	0.29
21	Trihydro-oxo-5-(3,4,5-trimethoxyphenyl) furonaphtho-1,3-dioxol-6-one	30.58	$C_{22}H_{20}O_8$	412	1.30
22	Docosanoic acid, methyl ester	31.41	$C_{23}H_{46}O_2$	354	0.29
23	Diethyl 4-hydroxy-4-methyl-6-oxo-2-phenyl-1,3-cyclohexane dicarboxylate tms	32.56	$C_{22}H_{32}O_6Si$	420	0.56
24	1,2-Benzenedicarboxylic acid	33.19	$C_{24}H_{38}O_4$	390	11.41
25	Octadecatrienoic acid	34.04	$C_{19}H_{32}O_2$	292	42.01
26	Methano-cyclopropa di Oxolo cyclopenta cyclodecadioxin-15-one,-octahydro-1-(hydroxymethyl)-heptamethyl-	35.24	$C_{26}H_{36}O_6$	444	14.54
27	Dibromoschizandrin	36.28	$C_{24}H_{30}Br_2O_7$	588	0.41
28	Squalene	36.65	$C_{30}H_{50}$	410	1.65
29	1H-Cyclopropa-benzazulenetetrol, 3-[(acetyloxy)methyl]-octahydro-tetramethyl-triacetate	38.60	$C_{28}H_{38}O_9$	518	0.85
30	13-Docosenamide	39.12	$C_{22}H_{43}NO$	337	5.75

which is a hydrocarbon and a triterpene, and is a natural and vital part of the synthesis of all plant and animal sterols.

Some of the major compounds identified in GCMS analysis of piezometer water samples are Docosane, 11-decyl- (CAS) also called as Higher alkanes with a an molecular formula of $C_{32}H_{66}$, which is an alkane compound having nine or more carbon atoms.

- Octadecanoic acid, methyl ester (CAS) also called Nonadecyclic acid with an molecular formula $C_{19}H_{38}O_2$ is a 19 carbon long chain saturated fatty acid, which is found in fats and vegetable oils.
- Celidoniol also called as Nonacosane with a molecular formula of $C_{29}H_{60}$ which is an insect pheromone which is also found in many eddential oils.
- Tetracosahexaene also called as squalene, a plant sterol which is also found in the spentwash sample.

Comparing with the piezometer leachates compounds like Tert-Hexadecanethiol, 7,9-di-tert-butyl-1-oxaspiro-decadienedione were present in both spentwash and leachate sample. The water leachate from piezometer contains only a limited number of compounds present in spentwash. This may due to degradation of the compounds present in spentwash by microorganisms before reaching the groundwater or adsorption of the organic compounds with soil surface or due to enzymatic activity in soil. This suggest that there is limited chance for contamination of organic compounds from spentwash on groundwater.

CONCLUSION

GCMS analysis different compounds like 7-

Table 5. Analysis of organic compounds present in piezometer leachate through GC-MS

Sl. No.	Compound Name	Retention Time	Molecular Formula	Molecular Weight	Area
1	Tert-Hexadecanethiol	3.05	$C_5H_8Br_2O_2$	258	0.54
2	Heptacosane (CAS)	15.78	$C_{27}H_{56}$	380	0.48
3	Octadecane (CAS)	17.52	$C_{18}H_{38}$	254	0.97
4	Docosane, 11-decyl- (CAS)	19.00	$C_{32}H_{66}$	450	1.15
5	7-(Methylthio)-5,6-dihydronaphtha[b]carbalzole	20.71	$C_{21}H_{17}NS$	315	0.55
6	Pentadecanoic acid, 14-methyl	21.71	$C_{17}H_{34}O_2$	270	2.35
7	Trans-6,7-Dihydroxy-6,7-dihydro-4H-cyclopenta chrysene	23.23	$C_{19}H_{14}O_2$	274	1.47
8	7,9-di-tert-butyl-1-oxaspiro-decadienedione	23.90	$C_{17}H_{24}O_3$	276	2.23
9	Octacosane (CAS)	24.93	$C_{28}H_{58}$	394	15.99
10	Octadecanoic acid, methyl ester (CAS)	25.51	$C_{19}H_{38}O_2$	298	2.22
11	Ethylene brassylate	26.41	$C_{15}H_{26}O_4$	270	2.86
12	Tricosane (CAS)	26.95	$C_{23}H_{48}$	324	1.68
13	1,7-Dipyrrolidinylperylene-3,4:9,10-tetracarboxylicacid bisanhydride	27.40	$C_{32}H_{22}N_2O_6$	530	0.67
14	2.8-Dichloro-decamethyl-5,11-dicarba-cyclohexasiloxane	28.00	$C_{12}H_{34}C_{l2}O_4Si_6$	480	0.54
15	Docosane (CAS)	28.80	$C_{22}H_{46}$	310	0.70
16	Octacosane	29.37	$C_{28}H_{58}$	394	15.66
17	H-Purin-6-amine, [(2-fluorophenyl)methyl]	29.82	$C_{12}H_{10}FN_5$	243	1.97
18	Docosane (CAS)	30.98	Docosane (CAS)	310	0.65
19	8,12-Diethyl-1,9-dioxo-hexamethyl- tetrahydro-21H-bilin	31.33	$C_{29}H_{34}N_4O_2$	470	0.52
20	Nonacosane	31.67	$C_{29}H_{60}$	408	14.17
21	Tetracosahexaene	32.02	$C_{30}H_{50}$	410	3.22
22	1H-Purin-6-amine, [(2fluorophenyl)methyl]-	32.39	$C_{12}H_{10}FN_5$	243	1.45
23	Di-(2-ethylhexyl)phthalate	33.18	$C_{24}H_{38}O_4$	390	1.76
24	Triacontane	34.36	$C_{30}H_{62}$	422	12.48
25	1-[Bis(trimethylsilyl)amino]-1-fluoro-3,3,3-trimethy l-1-[(trimethylsilyl)amino]disiloxane	35.85	$C_{12}H_{37}FN_2OSi_5$	384	1.72
26	Tridecanol (CAS)	36.18	$C_{13}H_{28}O$	200	0.84
27	3,7,11-Trimethyl-2,6,10-Dodecatrien-1-ol	36.64	$C_{15}H_{25}DO$	222	0.81
28	Celidoniol, Deoxy	37.74	$C_{29}H_{60}$	408	8.42
29	3-Hydroxy-1,2-dimethoxy-9,10-(methylenedioxy)-nor-aporphine	39.17	$C_{19}H_{19}NO_5$	341	1.28

Oxabicyclo-dec-4-en-8-one, 1,2-Dimethyl-4-heptylcyclohexane, Tert-Hexadecanethiol, Hexadecanoic acid 1,2-Bis(1-butyn-3-onyl)benzene, 7,9-di-tert-butyl-1-oxaspiro-decadienedione, 1,2-Benzenedicarboxylic acid, Squalene were present in spent wash. Comparing both PMDSW the piezometer leachates compounds like Tert-Hexadecanethiol, Hexadecanoic acid, 7,9-di-tert-butyl-1-oxaspiro-decadienedione were present in both spentwash and leachate sample. The water leachate from piezometer contains only a limited number of compounds present in spentwash. This suggest that there is limited chance for contamination of organic compounds from spentwash on groundwater. The pH and ECof the leachates increased at 30th day and decreased at 60th day Among the cations in leachate, Ca dominated and they were in the order of Ca > Mg > Na > K. Among the anions, Cl dominated and they were in the order of Cl > SO_4 > HCO_3. The salt content gradually decreased from 120th day compared to 30th day. Therefore, Spentwash must be applied judiciously according to crop requirements and soil fertility status to prevent contamination of shallow groundwater with nitrate and other toxic ions.

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