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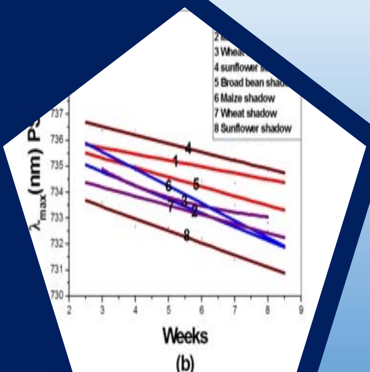

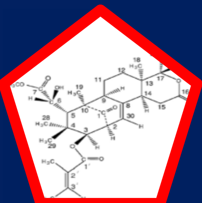

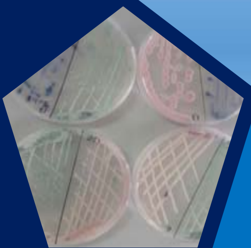

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Characterization of Sugarcane Vinasse

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ABSTRACT

The characterization of waste water is the most important issue in wastewater treatment plant, to select suitable and effective treatments method. Vinasse is a byproduct of ethanol and poseda real environmental harms. Sudan produces ethanol from sugarcane and significant amounts of vinasse were generated. In this work the characterization of two vinasse samples were carried out with reference to COD, BOD, TS, TSS, TDS and pH values. Both samples have high BOD, COD and TOC with low pH. The high concentration of K and Na were observed in the two samples. GC-MS was used to analyze the organic compounds. In general most compounds detected by GCMS were phenolic and carboxylic acids.

Keywords: Sugarcane Vinasse, Wastewaters, COD, BOD, TSS, GCMS

1. INTRODUCTION

The World progressively developing especially in industries sectors. Releasing of industries wastes into the environment causes an excessive hazards to the environment. Among these industries, ethanol manufacturing has negative effects on the ecosystem. During recent decades, ethanol production has increased significantly all over the World, due to its application as alternative fuel (Pejin et al., 2015). Ethanol can be produced from many feed stocks such as sugar crops, starch crops and/or cellulosic crops (Satyawali and Balakrishnan, 2008), the by-products of ethanol production is called vinasse. Vinasse also has been known as a spent wash distillery, distillery wastewater or stillage (Dowd et al., 1994). It is produced in large quantities, normally a ratio of 9-14 litters of vinasse are produced per litter of ethanol. The characteristics of vinasse are variable depending on soil quality, raw materials and distillery processes used for producing ethanol (España-Gamboa et al., 2011). In general, vinasse is acidic (pH 4.5–4.8) dark brown liquid with high BOD (45,000–100,000mg/l) and COD (90,000–210,000mg/l), and it emits an unpleasant odor (Jyoti et al 2006). Disposal of vinasse into the environment is hazardous and has high pollution potential. High COD, total nitrogen and total phosphate content of the effluent may result in eutrophication of natural water bodies (Kumar et al., 1997). Direct disposal of vinasse into the aquatic environments tend to increase the organic content of water and consequently causes the proliferation of bacteria that depleted the dissolved oxygen and water quality (Mohana et al., 2009). Further, dark color hinders photosynthesis by blocking sunlight and is therefore damaging of the aquatic life (Fitz Gibbon et al., 1998). Leaching down of vinasse has an effect on the groundwater quality by altering its physicochemical properties such as color, pH, electrical conductivity (EC) (Jain et al., 2005). Moreover constant disposal/irrigation of the soil with the effluent led to deleterious effect on the soil properties (Dhembare and Amin 2002).

Hence alcohol distilleries are ratedas one of the 17 most polluting industries (Satyawali and Balakrishnan, 2008) and the characteristics of vinasse are highly variable, consequently the study of vinasse characterization is very important to meet the challenging of vinasse pollution. Sudan have been producing ethanol from sugar cane since 2009 in White Nile state namely in Kenana sugar company, and no any effective treatment or alternative utilization methods are applied for vinasses. Thus the aim of the present investigation is to study some biological, physical and chemical properties of vinasse as well as to pave suitable method for vinasse treatment.

2. MARTIALS AND METHODS

2.1 Chemicals and Reagents

Potassium bromide, Hexane, Sodium sulfate and sulfuric acid (98%) were purchased from (Merck, Germany), Dichloromethane (DCM) was obtained from (Suprasolv, Germany), N,O-bis trimethylsiyl trifluoroacetamide (BSTFA), Trimethylchlorosilane (TMCS) were obtained from (Supelco, USA). Sodium hydroxide was purchased from (Fluka-Germany). Ultrapure water (Elga, USA) was used for the preparation of all aqueous solutions.

2.2 Instrumentations

Total organic carbon (TOC) Shimadzu TOC analyzer (model TOC-L CPN, Japan).Gas chromatography mass spectrometer GCMS Shimadzu (model GC-MS QP2010-Plus, Kyoto, Japan).IR (Model Perkin Elmer USA). pH meter (model Mettler Toledo FE 20, Switzerland).Filtration system (model VE-11, Korea).Atomic absorption spectrometer, AAS, model 210 (GP-Puck Scientific, USA).

2.3 Experiments

All glassware was washed with detergent. The glassware was rinsed four times in tap water and once in distilled water. Ultrapure water (Elga, USA) was used for the preparation all aqueous solutions. All stock solutions were kept in a 4°C refrigerator until use. The physico-chemical parameters i.e. pH, BOD, COD, TDS, TSS, TS and metal were determined according to standard method for examination of water and wastewater (Clesceri et al., 1998). The TOC, TC,IC and TN were determined by using TOC instrument.

2.4 Collection of Samples

The vinasse used in this work was obtained from an ethanol distillery located at White Nile state, Sudan. Two Samples were collected from distillery column after the distillation. Vinasse (1) was collected at 8 Am while vinasse (2) collected at 8pm on the same day.

2.5 Sample Preparation

250 ml of vinasse was dried, 2-3 mg of dried vinasse were mixed with approximately 0.5- 1 g of KBr. and then mixture was grinded to fine powder for IR analysis. While the solvent extraction method were used for GCMS, raw vinasse were placed in two separation funnels. Hexane and dichloromethane (DCM) were added in ratio 1:4 for each and shook manually for approximately 5 min. The solvent were removed from organic layer by rotary evaporation (37 °C). Organic layer extracted was reduced under a

gentle nitrogen stream (approximately 50 min). TMCS were added to DCM extracted, heated to 70°C for 4 hr. and dried under nitrogen stream stored in fridge until GCMS analysis.

2.6 GC-MS Analysis

The analyses of the extract were performed by Gas Chromatography mass spectrometry. These analyses were carried out on a Hewlett- Packard Model 6890 gas chromatograph with splitless injector and a VB-5 5% phenylmethyle polysiloxane column (30 m Length, 0.25 mm I.D., 0.25 µm film thickness) equipped with a Hewlett- Packard Model 6890 mass selective detector provide with a HP ChemStation data acquisition system. Helium (purity 99.999%) was used as a carrier gas. The chromatographic condition are present in Table 1. The data for analysis was acquired from electron impact (EI) mode 70 (eV), scanning from 50-550 amu at 1.5 sec/scan.

Table 1. GCMS conditions

Oven Temperature program	Ini al oven temperature 60°C, hold for 2 minutes; then up to 280°C at 6°C/min, then held at 280°C for 20 min
Gas flow rates	1.2 ml/min
Injection port temperature	290°C
Injection mode	Splitless (1 min) (1.0-1.4 µl; hot needle technique)
Column inlet pressure	10.4 pis

Average Velocity	40cm/s
Temperature of transfer line	300°C
Solvent delay	4 min

3. RESULTS AND DISCUSSION

3.1 Vinasse characterization

The chemical characteristics of the two vinasse sampels were showed in Table 2. According to obtained results most of vinasse characteristics is agree with (Satyawali and Balakrishnan, 2008) and (España-Gamboa et al., 2011).

Table 2. Vinasse characteristics.

Parameters	Units	Vinasse 1	Vinasse 2
pH	-	3.5	4.85
BOD	mg/l	68.978	65.000
COD	mg/l	125.777	200.000
TOC	mg/l	489.60	480.4
TC	mg/l	490.00	484.5
IC	mg/l	0.40	4.077
TN	mg/l	6.669	8.309
TS	mg/l	111.46	119.57

TDS	mg/l	63.8	97.47
TSS	mg/l	13.0	17.1
K	mg/l	121.3	92.3
Na	mg/l	120.55	87.9
Ca	mg/l	73.75	22.65

The results showed that the vinasse 1 and 2 have acidity nature with pH values of 3.5 and 4.85,respectively. Thus the disposal of vinasse to the land without treatment will cause casing and soil salinization. (Mohana et al, 2009).The dark brown colour of vinasse is due to the presence of coloured organic compounds such as melanoidins (Mohana et al., 2009). Adsorption and coagulation–flocculation treatment methods were often used for removal of colour from vinasse (Satyawali and Balakrishnan, 2008). On the other hand, combined coagulation–flocculation with polyelectrolyte followed by adsorption resulted in almost complete de decolourization (Sekar and Murthy, 1998).

High levels of pollutants (mainly organic matter) in water cause an increase in BOD, COD, TDS and TSS, they make the water unsuitable for drinking, irrigation or any other use (Shrivastava et al 2012). The results showed high BOD (68.978 mg/L, and 65.000 mg/L)for vinasse (1) and (2) respectively, while COD was 125.777 mg/L and 200.000 mg/L for vinasse

(1) and (2) respectively. The obtained results indicate that vinasse has high pollution effects.

So far biological treatment has been used for decreasing COD (Satyawali and Balakrishnan, 2008; Mohana et al., 2009). Although the biological treatment of vinasse has drawbacks such as producing sludge (Chopra et al., 2011),moreover, vinasse has recalcitrant nature due to presence of the melanoidins, These compounds have antioxidant properties, which render them toxic to many microorganisms such as those typically present in wastewater treatment processes (Mohana et al., 2009).Therefore, removal of melanoidins by conventional biological treatment is not operative.

The importance of measuring total organic carbon (TOC) which is a measure of the concentration of organically bound carbon. Also it can provides the information on the amount of organic compounds that containing in vinasse. Up to now COD has been used for monitoring of vinasse degradation (Sreethawong and Chavadej, 2008; Yang et al., 2008; Campos et al., 2014), but the natures of oxidants, sometime can effects of COD precisely, and therefore, it cannot reflect the degree of organic content. Also the acidity of reaction solution and catalyst have effects on COD measurement accuracy as well(Hua et al., 2011). The major drawbacks of using COD is production of hazardous wastes and the cost of COD disposal. Thus, recently TOC has been used to evaluate the performance of water treatment (EPA). Moreover, comparing with COD, TOC measurement is relatively simple and fast (Dubber et al 2010).

The physical characteristics such as total solids (TS), total dissolved solids (TDS) and total suspended solids (TSS) are important to select the suitable method for wastewaters treatment (Punmia 1998).TS, TDS and TSS contents of wastewater are used in the design and process control of wastewater treatment facilities. Moreover, TSS was commonly monitored to evaluate the degree of pollution in natural waters and serves as a key process to control parameters for wastewater treatment operations.

As showed in table (2) the concentration of Kwere121.3 and 92.3 mg/l for vinasse (1) and (2) respectively, while the Na and Ca were 120.55, and 73.75 for vinasse (1), 87.9 and22.65 mg/l for vinasse (2). According to the obtained results vinasse can used in irrigationas Fertirrigation. When used vinasse as Fertirrigation it can fertilizes the crop, lowering the costs with chemical fertilizers (Laime et al., 2011). Such technology started in Brazil since 1950s and were conducted by the Luiz de Queiroz College of Agriculture (ESALQ) (Camargo et al., 2009).

3.1.1 IR analysis

Infrared (IR) spectroscopy is a technique used to identify the structure of chemicals based on the interaction of atoms with infrared radiation. Molecular vibration and rotation can be excited by the absorption of radiation in an infrared region. Such molecular vibrations and rotation scan be directly measured as absorbance in the infrared spectrum(Yuen et al., 2005).

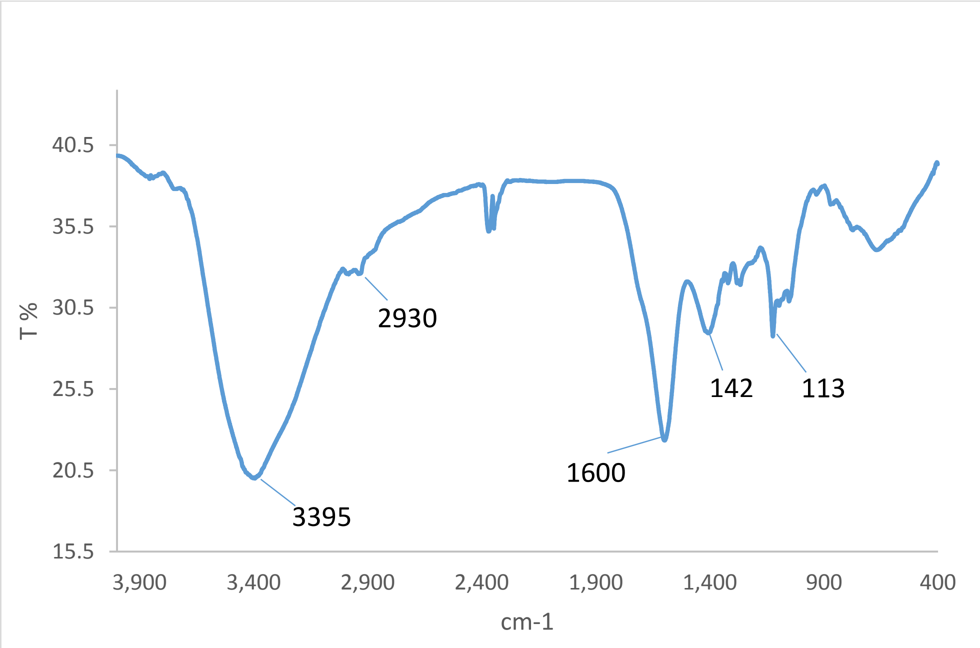


Fig 1 .IR Spectra for vinasse 1

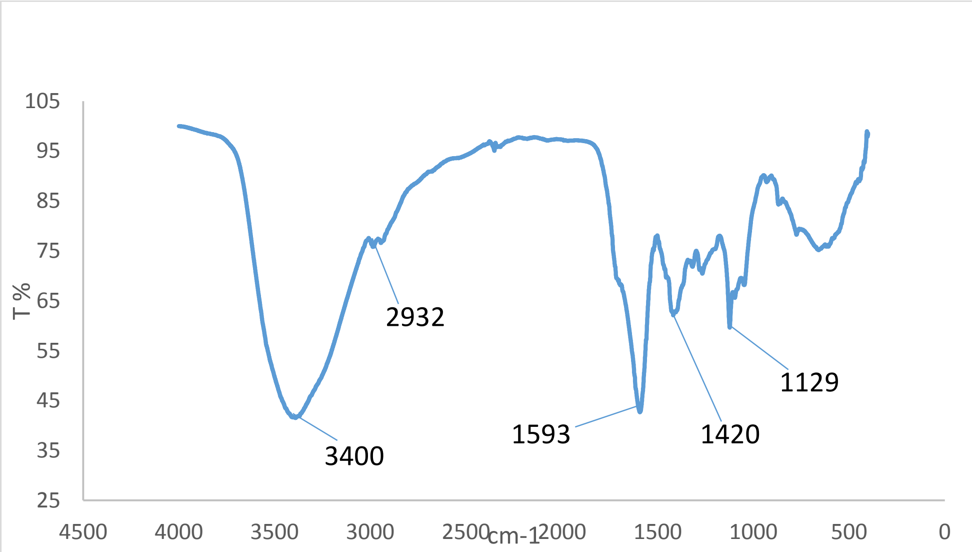


Fig 2. IR Spectra for vinasse 2

The IR spectrum of vinasse (1) and vinasse (2) were given in fig. (1) and fig. (2) respectively. A decent spectrum with sharp peaks was observed in (OH) region in tow samples. Displayed characteristics absorption band at (Ʋ) (KBr) 3395 cm-1 (OH), 2930 cm-1 (CH- stretching), 1600 cm-1 (C=O), 1420 cm-1 (CH- bending) and 1130 cm-1 (C-O Ester) for vinasse (1). And 3400 cm-1 (OH), 2932 cm-1(CH- stretching), 1593 cm -1 (C=O), 1420 cm-1 (CH- bending) and 1129 cm-1 (C-O Ester) for vinasse (2).as observed in fig (1) and fig (2) there is no actual different in absorption band between vinasse (1) and vinasse (2).

3.1.2 GCMS analysis

The identification of unknown compounds was initially accomplished by comparison with the MS library (NIST) and comforted by using Chemo bio draw program version ultra 11.0. The comparison of the mass spectrums with the data base on MS library gave about 75% - 95% matchas well as confirmatory compound structure match.

GCMS analysis of Vinasse (1)

Figure 1 shows thetotal ion chromatogram of hexane extracted compounds while Figure 2 shows total ion chromatogram of DCM extracted compounds. Tables 3 and4 summarize the identified compounds which were extracted by hexane and DCM, respectively.

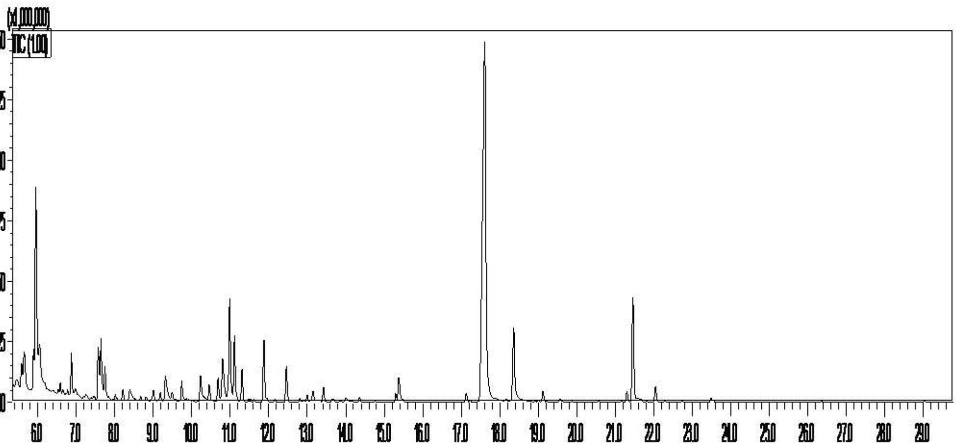
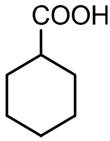
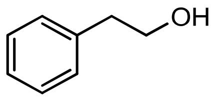
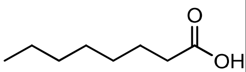
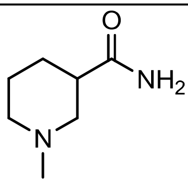
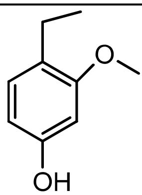
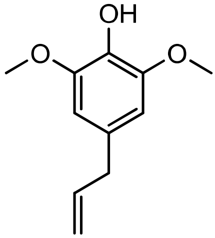
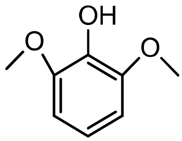
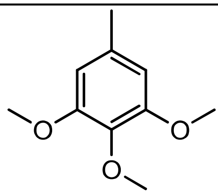
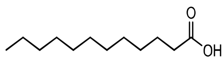
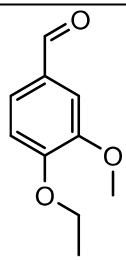
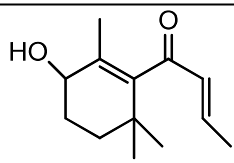
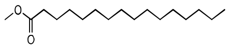
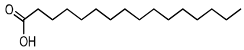
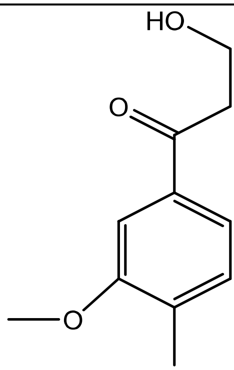
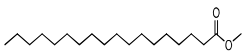
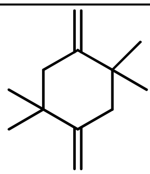


Fig 3. Total ion chromatogram of vinasse (1) extracted by hexane

Table 3.Identification of compounds extracted by hexane from vinasse (1)

No	Name	Structure	MW		Class
1	Cyclohexane carboxylic acid		128	$C_7H_{12}O_2$	Carboxylic acid
2	2-phenyl ethanol		122	$C_8H_{10}O$	alcohol
3	Octanoic acid		144	$C_8H_{16}O_2$	Carboxylic acid
4	1-methyl piperidine-3-Carboxamide.		142	$C_7H_{14}N_2O$	Amide
5	4-ethyl-3-methoxy phenol.		152	$C_9H_{12}O_2$	Phenol

6	4-allyl-2,6-dimethoxy phenol		194	$C_{11}H_{14}O_3$	phenol
7	2,6- dimethoxy phenol.		154	$C_8H_{10}O_3$	phenol
8	1,2,3- trimethoxy-5-methyl benzene		182	$C_{10}H_{14}O_3$	Aromatic (benzene ring)
9	Dodecanoic acid.		200	$C_{12}H_{24}O_2$	Carboxylic acid
10	4-ethoxy-3-methoxy benzaldhyde.		180	$C_{10}H_{12}O_3$	Aldehyde
11	1-(3-hydroxy-2,6,6-trimethylcyclohex-1-enyl)but-2-en-1-one		208	$C_{13}H_{20}O_2$	Ketone

12	Methyl palmitate		270	$C_{17}H_{34}O_2$	Esters
13	Palmitic acid		256	$C_{16}H_{32}O_2$	Carboxylic acid
14	3-hydroxy-1-(3-methoxy-4-methylphenyl)propan-1-one.		194	$C_{11}H_{14}O_3$	Ketone
15	Methyl stearate		298	$C_{19}H_{38}O_2$	Esters
16	1,1,4,4-tetramethyl-2,5-dimethylenecyclohexane		164	$C_{12}H_{20}$	Cycloalkane

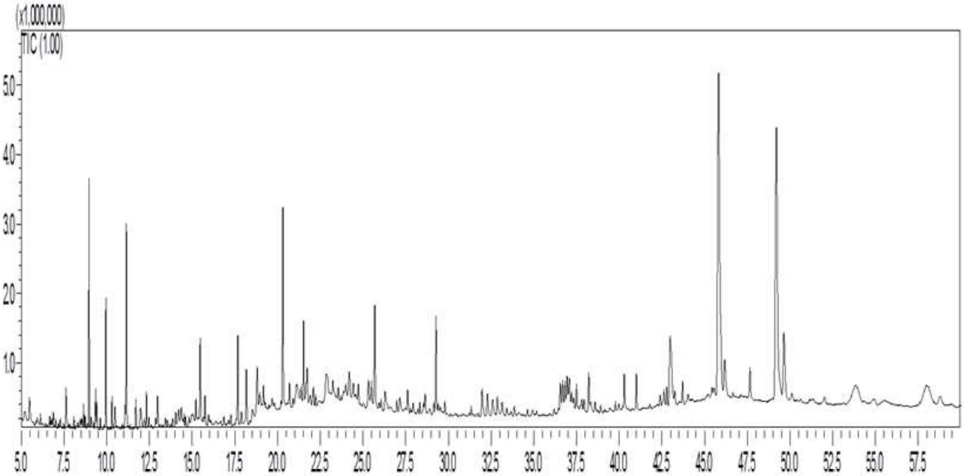
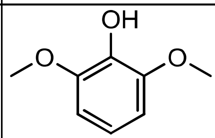
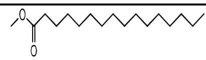
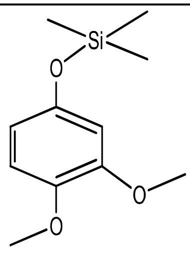


Fig.4. Total ion chromatogram of vinasse (1) extracted by DCM

Table 4.Identification of compounds extracted by DCM from vinasse (1)

No	Name	Structure	M.W		Classe
1	2,6 dimethoxyphenol		154	C8H10O3	Phenol
2	Methyl palmitate		270	C17H34O2	Esters
3	(3,4-dimethoxy phenoxy)trimethylsilane		226	C11H18O3Si	Phenol

About 19 compounds of vinasse (1) were identified,16 extracted by hexaneand only three by DCM. The results showed that the majority of compounds were phenolic,as showed in table (4) the existence of Si in (3,4-dimethoxy phenoxy)trimethylsilanecompound it might be due to the silylation.

GCMS analysis of Vinasse (2)

Total ion chromatogram of vinasse (2) extracted by hexane and DCM were shown in fig 5 and 6. While table (5) and (6) summarize the identified compounds.

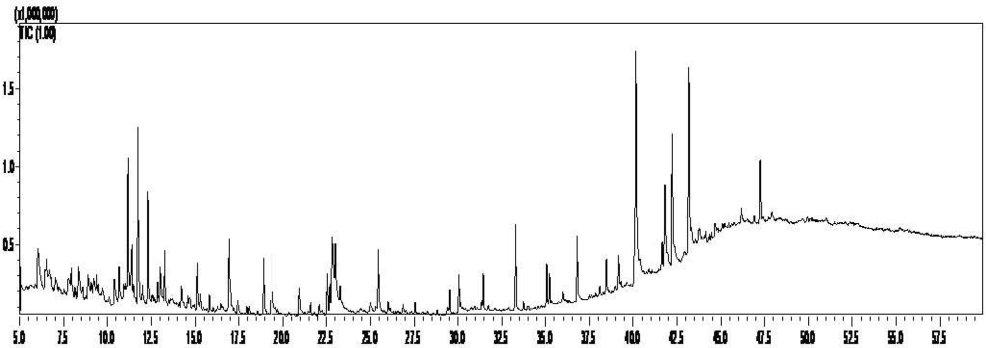
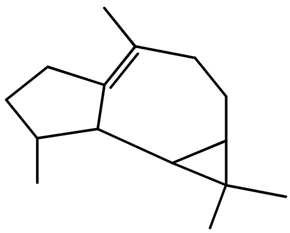
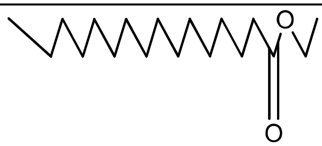
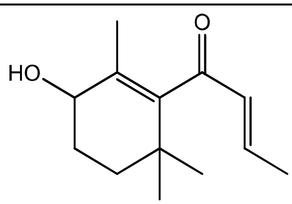
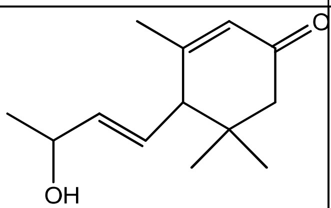
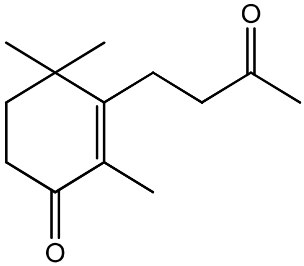
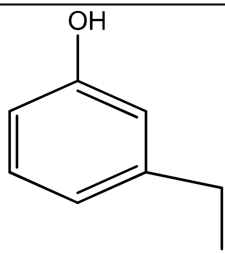


Fig 5. Total ion chromatogram of vinasse (2) extracted by hexane

Table 5. Identification of compounds extracted by hexane from vinasse (2)

No	**Name**	**Structure**	**M. W**	**Formula**	**Class**
1	1,1,4,7-tetramethyl-1a,2,3,5,6,7,7a,7b-octahydro-1 H-cyclopropa[e]azulene		204	$C_{15}H_{24}$	alkene
2	Ethyle palmitate		284	$C_{18}H_{36}O_2$	Carboxylic acid
3	1-(3-hydroxy-2,6,6-trimethylcyclohex-1-enyl)but-2-en-1-one		208	$C_{13}H_{20}O_2$	Ketone
4	4-(3-hydroxybut-1-enyl)3,5,5-trimethylcyclohex-2-en		208.	$C_{13}H_{20}O_2$	Ketone

5	2,4,4 Trimethyl-3-(3- oxobutyl)cyclohex-2-enone		208	$C_{13}H_{20}O_2$	Ketone
6	3-ethylphenol		122	$C_8H_{10}O$	Phenol

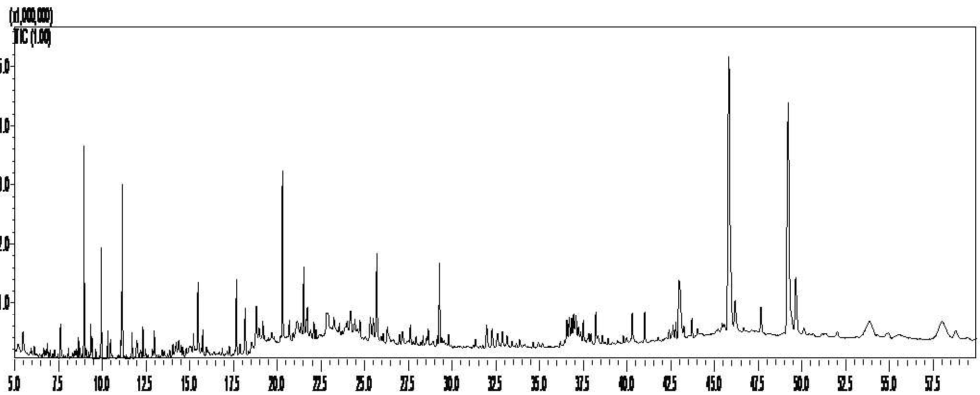
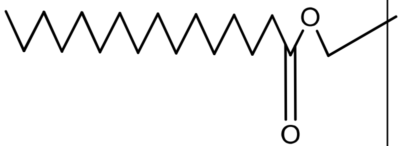
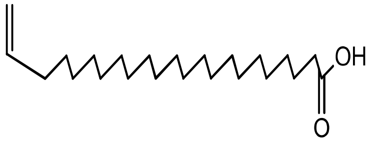
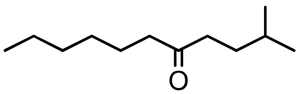
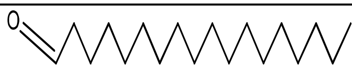


Fig 6. Total ion chromatogram of vinasse (2) extracted by DCM

Table 6. Identification of compounds extracted by DCM from vinasse (2)

No	Name	Structure	M.W		Class
1	Ethyle palmitate		284	$C_{18}H_{36}O_2$	Esters
2	Tricosenoic acid		352	$C_{23}H_{44}O_2$	Carboxylic acid
3	2-methylundecan-5-one		184	$C_{12}H_{24}O$	Ketone
4	Stearaldehyde		268	$C_{18}H_{36}O$	Aldehyde

The GCMS analysis showed that the most compound detected in the two vinasse samples were phenolic compounds. These results were illustrated by the IR analysis which displayed strong broad peaks in (OH) region in both vinasse samples.

Phenols compounds were considered the most hazardous compounds that may have serious effects on human and natural environment (Urszula et al., 2012).Thus effective treatment techniques should be used for vinasse treatment.

4. CONCLUSION

Both vinasse samples have high BOD, CODand TOC with acidity nature.They arehighly rich in coloured compounds which rendersvinasse as pollutant materials. Most compounds detected were phenolic and carboxylic, thus primary and secondary treatment of vinasse treatment plants is strongly recommended to ensure effective treatment. Vinasse can be used as frirrigation due to the high concentration of potassium it contains.

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