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Detection and identification of organics and trace metals by FTIR, GC/MS and ICP-AES and their organic-metallic statistics

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ABSTRACT

The organic compounds were identified in pulp and paper mill effluent samples which were taken from Ukai, Songhad and Padamji, Pune paper mills. These effluent samples were extracted with CH_2Cl_2 (Dichloromethane), liquid-liquid extract. These samples were then identified and by gas chromatography mass spectrometry (GC/MS). The obtained mass has also been recorded for different functional groups by FTIR. They found organic compounds are saturated and unsaturated hydrocarbons, aromatic alcohols, phenols and dicarboxylic acids which affect adversely to the soil and ground water quality of the area. The concentrations of the metals in HNO_3-HCL extract were detected by ICP-AES. Beside the above spectroscopic the organic and metallic statistics analyses have also been evaluated.

Keywords: Pulp and paper mills effluents, organic compounds, FTIR, GC-MS, ICP-AES, statistical evaluations.

INTRODUCTION

The industrial pollutants in wastewater can be categorized into organic, inorganic compounds [1]. The inorganic pollutants cannot be destroyed by biological processes and hence cannot be successfully applied for their treatment [2]. The common methods for water and other oxidation products are by biological or thermal treatment. Pulp and paper mill effluents contains many organic compounds as byproducts due to the part of wood pulping process, which releases compounds called wood extractives. Also the effluent from paper industry contains variety of toxic heavy metals [3] and manufacturing process adopted. The pollutants in the pulp and paper mills effluents are mostly organic in nature and contain lignin and its

derivatives in addition to other color imparting phenolic and resinous compounds [4]. The discharges of these effluents are very harmful to agricultural crops, aquatic life and human beings. Numerous methods for analysis of cationic surfactants have been developed for water quality investigations in water treatment industries. Cationic surfactants are commonly treated with anionic dyes to form ion-pair complexes, which can be extracted by solvents and followed by Spectrophotometry[5,6]. Gas chromatography(GC) or gas chromatography/mass spectrometry (GC/MS) is not only more readily available in many environmental laboratories, but it does provide a higher chromatographic resolutions with a capillary column than do the LC/MS methods.

Statistics in environmental science provides more attractive attention through it deviates from real situation [7,8]. In view of the above, it has been considered worthwhile to identify the presence of organics and trace metals in pulp and paper mill effluents by using GC-MS and ICP-AES techniques. The statistical analysis has also been carried out for organic and metallic status.

MATERIALS AND METHODS

Pulp and paper mill effluent samples were collected form Ukai, Songad and Padmji, Pune paper mills. Effluent samples were extracted with dichloromethane [9] Liquid- Liquid extraction. This extracted organic layer was collected in evaporating dish and heated up to dryness to form a small mass. The obtained small mass, FTIR was recorded on Perkin-Elmer make IR instrument and GC-MS was recorded on Hewlett-Packered made GC-MS spectrophotometer and trace metals by ICP-AES technique at Sophisticated Analytical Instrument Facility (SAIF). IIT, Mumbai. The statistical parameter i.e. COD estimated and correlation coefficient was calculated using standard methods[10].

RESULTS AND DISCUSSION

FTIR Spectrum is based on the absorption of infrared radiation at frequencies that match those of the normal modes of vibration within the macromolecule. These absorption features are characteristics of the molecular configuration, sequencing and conformation. The intensity of an absorption band is related to the dipole moment change associated with the molecular vibration. Infrared spectroscopy is highly specific and the frequencies of all the sharp bands are accurate to $\pm 1 cm^{-1}$ [11]. The observed IR frequencies are given in Table.1. The characterization and interpretation of various functional groups also discussed in table.

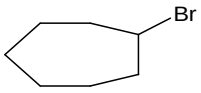
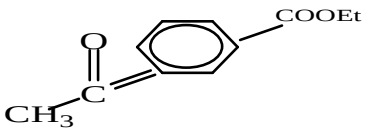
Table No. 1 Results of FTIR Spectra

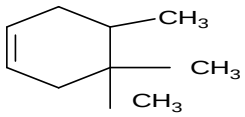
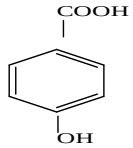
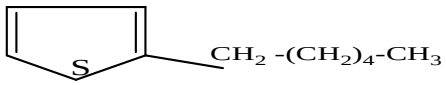
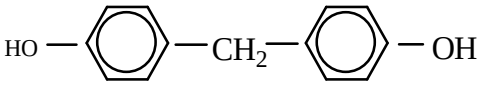
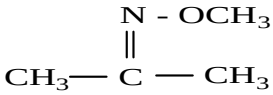
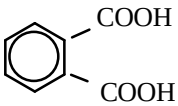
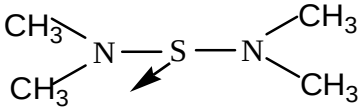
Sr. No.	Wave number cm-1	Characterization (Interpretation)
1.	3404.2	C=N-H, N-H stretching, Indole N-H.
2.	2961.2	CH_2 , - CH_3 Saturated C – H.
3.	2920.5	Saturated C – H.
4.	2854.3	N – CH_3, C – H Stretch.
5.	1749.4	α,β – Unsaturated, γ - lactone, C= O Stretch
6.	1459.1	aromatic, C = C stretching
7.	1280.9	C – O stretching

8.	1087.4	C – O stretching, C – N stretching
9.	1041.6	C – OH, C – O stretching
10.	756.4	A r – (Monosub-)
11.	3419.5	-OH alcoholic
12.	2935.8	C-H stretching vib
13.	2869.6	alkyl, C-H stretching vib
14.	1632.2	C = O, amides, C = C stretching
15.	1510.0	N --- O stretching vib nitro compounds
16.	1464.2	C – H stretching
17.	1382.7	C – H bending vib, gemdimethly gr.

The detected organic compounds present in the collected Paper Mill effluents by GC/MS method are presented in Table.2 along with structure of compounds, molecular formula and molecular weight. Heavier hydrocarbons were identified in waste water samples.

Table no. 2. List of detected and Identified Organic Compounds by GC/MS

Sr. No.	Name of Compound	Structure of Compound	Molecular formula	Molecular Weight
1.	Tetradecane	$CH_3-(CH_2)_{12}-CH_3$	$C_{14}H_{30}$	198
2.	Hexdecane	$CH_3-(CH_2)_{14}-CH_3$	$C_{16}H_{34}$	226
3.	Octadecane	$CH_3-(CH_2)_{16}-CH_3$	$C_{18}H_{38}$	254
4.	Heptadecane	$CH_3-(CH_2)_{15}-CH_3$	$C_{17}H_{36}$	240
5.	Nonadecane	$CH_3-(CH_2)_{17}-CH_3$	$C_{19}H_{40}$	280
6.	Cycloheptane Bromo		$C_7H_{14}B_r$	180
7.	Ethyl 4-acety Benzoate		$C_{11}H_{12}O_3$	192

8.	2,3,3Trim ethyl Cyclohexene		$C_9 H_{16}$	124
9.	Benzoic acid4-hydroxy		$C_7 H_6 O_3$	138
10.	Thiophene,2 hexyl		$C_{10} H_{16} S$	168
11.	Sulpher	S	S	32
12.	2-Nonanone, O-methyloxime		$C_9 H_{18} O$	142
13.	Phenol2, 2methylene bis [6-(1,1-d)]		$C_{13} H_{12} O_2$	200
14.	2,Propanone O-Methyloxime		$C_4 H_9 ON$	87
15.	1,2, benzene dicarboxylic acid		$C_8 H_6 O_4$	166
16.	Tetramethyl thiuram monosulphide		$C_4 H_{12} N_2 S$	120

The trace elements present in the collected effluent samples determined are presented in Table.3.In most of the samples As, B and Mn are not detected. In samples iron present was in high value in comparison to Cu, Zn, Cd, Pb and Hg. Ni content is also high next to iron.

Table No. 3. Trace Elements present in effluents

Sample Collection	Cu	Zn	Cd	Pb	Hg	As	Ni	B	Mn	Fe
Ukai Songad	0.24	0.36	0.24	1.32	0.26	ND	1.64	ND	ND	20
Pulp and	0.38	0.54	0.52	1.62	0.30	ND	1.96	ND	ND	24
Paper Mill	0.32	0.44	0.36	1.41	0.29	ND	1.69	ND	ND	22

	0.18	0.28	0.43	1.22	ND	ND	1.22	ND	ND	ND
	0.38	0.49	0.39	1.42	ND	ND	1.06	ND	ND	ND
	0.29	0.39	0.14	1.38	0.22	0.20	1.72	ND	0.38	ND
	0.32	0.52	0.32	0.98	ND	ND	1.08	ND	ND	ND
	0.21	0.26	0.27	0.98	ND	ND	0.96	ND	0.11	22.2
	0.38	0.46	0.45	1.40	0.18	0.21	2.00	ND	0.29	40
	0.36	0.38	0.41	1.46	ND	0.18	1.22	ND	0.22	32
	0.25	0.38	0.28	1.36	ND	ND	1.68	ND	ND	21
	0.41	0.68	0.66	1.94	0.24	0.01	2.48	ND	ND	24
	0.04	0.48	0.34	1.49	0.21	ND	1.80	ND	ND	22
Padmji	0.22	0.26	0.22	0.87	ND	ND	ND	ND	ND	ND
Pulp and	0.42	0.67	0.46	0.92	0.26	0.21	1.91	ND	0.21	ND
Paper Mill Pune	0.37	1.27	1.00	2.60	ND	ND	1.28	ND	ND	ND
	0.24	0.28	0.20	0.41	ND	ND	ND	ND	ND	5.72
	0.44	0.70	0.46	0.96	0.27	0.21	2.1	ND	ND	6.92
	0.38	1.82	1.00	2.80	ND	ND	2.1	ND	ND	12.6
	0.23	0.22	0.18	0.87	ND	ND	0.62	ND	0.22	28.7
	0.48	0.77	0.57	1.0	0.27	0.22	1.96	ND	0.82	88
	0.42	1.21	1.1	1.67	ND	ND	1.42	ND	0.73	50
	0.24	0.28	3.6	0.92	ND	ND	ND	ND	ND	24
	0.29	0.92	7.9	0.97	ND	ND	0.4	ND	ND	30
	0.42	1.92	1.0	2.7	0.01	1.41	1.4	ND	ND	24

The Chemical oxygen demand was determined for the effluents because they contain both organic and inorganic compounds and the results were presented in Table.4. High COD was observed in Pune effluents.

Table No. 4 Chemical oxygen demand (COD).

Ukai Songarh	ND	ND	ND	254.8	205.8	215.6	39.2	180	160	80	247.3	2.37	10.3
Padmji Pune	8928	53.5	19.6	10400	1480	10	199.9	399.8	19	33007.2	16503.6	6.0	ND

The statistical analysis results are presented in Table.5

Table No. 5: Correlation coefficient (r) between various metals of both mills & Chemical oxygen demand (COD)

Sr. No.	M/M	r	Sr. No.	M/M	r

1.	Cu/Hg	10.57	14.	Hg/Fe	3.98
2.	Cu/As	21.85	15.	Hg/As	9.30
3.	Cu/Mn	15.35	16.	Hg/Mn	7.90
4.	Zn/Hg	13.60	17.	Ni/As	24.86
5.	Zn/As	32.12	18.	Ni/Mn	21.68
6.	Zn/Mn	22.96	19.	Fe/As	9.88
7.	Cd/Hg	10.37	20.	Fe/Mn	6.48
8.	Cd/As	22.91	21.	As/Mn	1.82
9.	Cd/Mn	16.46	22.	Cu/Ni	0.92
10.	Pb/Hg	19.74	23.	Zn/Pb	0.90
11.	Pb/As	46.02	24.	Mn/Fe	0.84
12.	Pb/Mn	32.10	25.	Cd/COD	0.60
13.	Hg/Ni	11.77			

The FTIR spectra obtained for two Mills effluents were shown in Figures 1-3. The GC/MS spectra were shown in Figures 4-6.

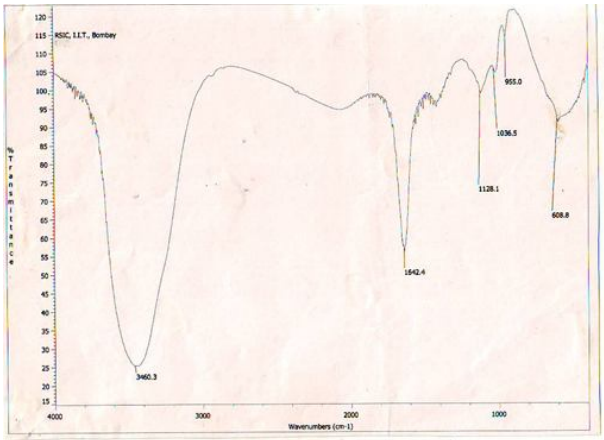


Fig 1 : FTIR spectra of CH_2Cl_2 extracted mass of paper mill Wastewater (Ukai-Songarh) sample no.1.

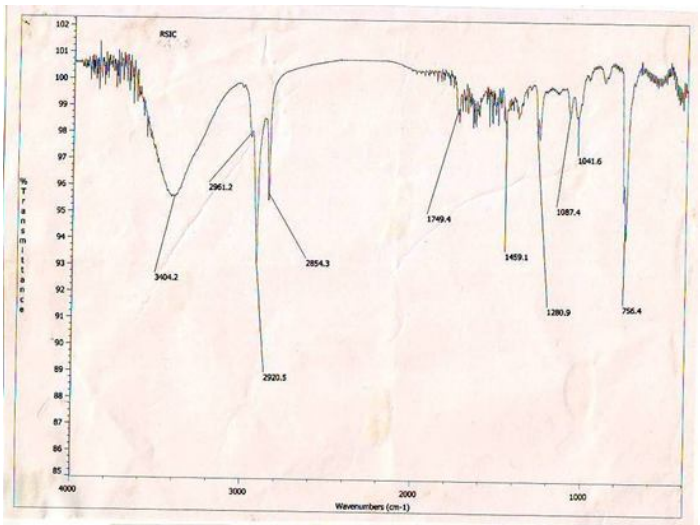


Fig 3 : FTIR spectra of CH_2Cl_2 extracted mass of paper mill Wastewater (Padmji, Pune) sample no.3.

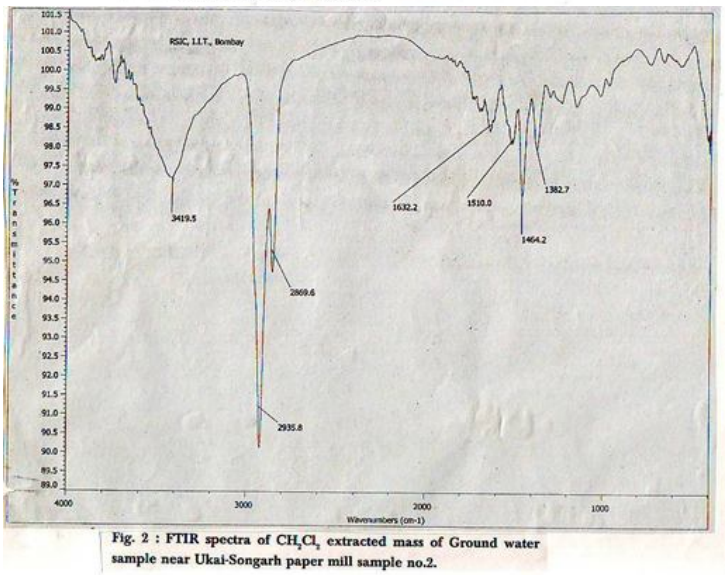


Fig. 2 : FTIR spectra of CH_2Cl_2 extracted mass of Ground water sample near Ukai-Songarh paper mill sample no.2.

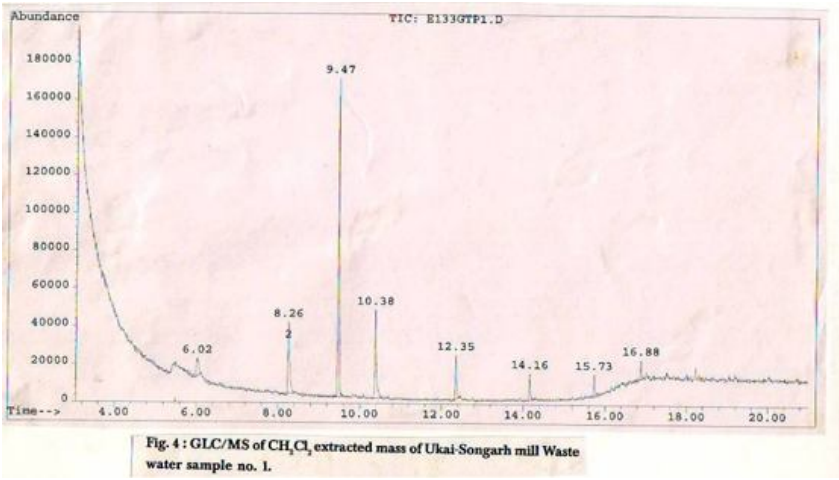


Fig. 4 : GLC/MS of CH_2Cl_2 extracted mass of Ukai-Songarh mill Waste water sample no. 1.

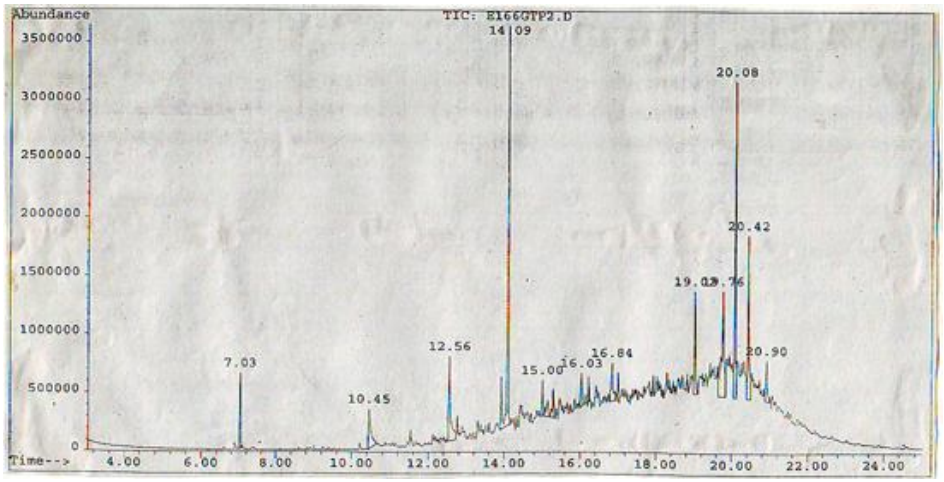


Fig. 5: GLC/MS of CH_2Cl_2 extracted mass of ground water sample near Ukai-Songarh paper mill (Sample No.2)

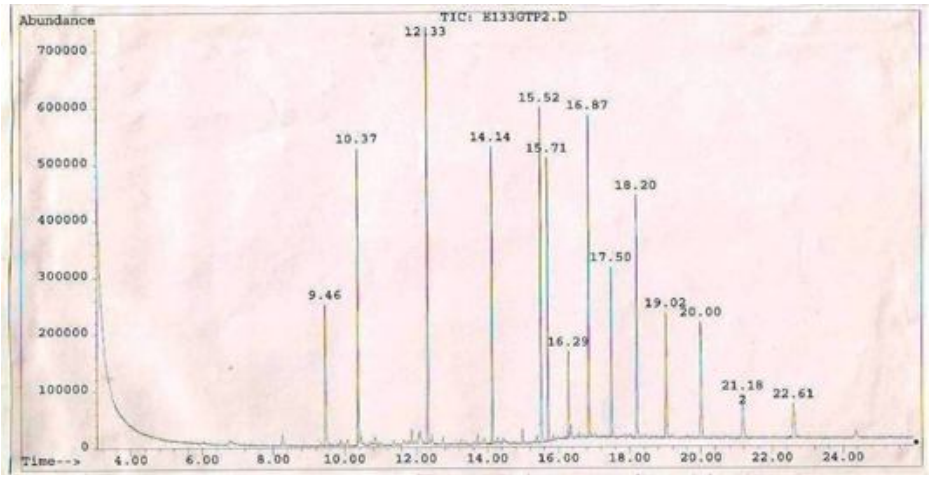


Fig. 6 : GLC/MS of CH_2Cl_2 extracted mass of Padmji, Pune paper mill waste water sample no. 3

APPLICATIONS

These studies help to know the effect of effluents on the Environment and useful to suggest the concerned Industries

CONCLUSIONS

Saturated hydrocarbons present in effluents upto octane, can produce anesthesia and narcosis in many lower animals. Low boiling point aromatic hydrocarbons are even more toxic and their greater water solubility tends to enhance their distribution and uptake by aquatic organisms. Benzene characteristically inhibits blood cell formation in bone marrow. All cause local irritation of the respiratory system and excitation or depression of the central nervous system. Polycyclic aromatic hydrocarbons are specially dangerous in this respects.

All the above compounds in pulp and paper mill wastewater will be a complex mixture of contaminants with the predominance of any type depend on effluents hydrology, discharge sources and general wastewater may cause of worry for the ecosystem, aquatic life, soils, flora and fauna as well as for the peoples living in the surrounding area.

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