

## Organic-Metallic Interactions in Dye Industry Waste Water : A Statistical Approach

G.S. SONAWANE\* and V.S. SHRIVASTAVA†

Department of Chemistry, Kisan Arts, Commerce and Science College  
Parole-425 111, India

E-mail: drvinod\_shrivastava@yahoo.com

An attempt has been made to study the organic-metallic interactions in dye industry waste. The waste-water and soil samples were collected from Gujarat Industrial Development Corporation, Surat (Gujarat). The industrial waste samples were extracted by  $\text{CH}_2\text{Cl}_2$  and analyzed for FTIR and GC-MS for detection and identification organic compounds. ICP-AES techniques was used for detection of metals. Several organic compounds have been found which include phenol, benzonitrile, nitrobenzene, *etc.* The concentration of trace metals like As, Hg and Mn in water samples and Cd, As, Hg and Mn in soil samples was less than detection limit. The identified organic compounds and hazardous metals effect adversely the ground water and soil quality of the area.

**Key Words:** Organic-metallic interaction, FTIR, GC-MS, Dye industry.

### INTRODUCTION

The large number of textile dyeing and printing industries are located in Gujarat Industrial Development Corporation, Pandesara and Sachin at Surat (Gujarat). These industries are important sources of organic contamination and are responsible for widespread pollution of the environment particularly water. The waste water from the dyeing industry is in large volume containing various pollutants such as reactive dyes, organic acids, phenols, bases, starch<sup>1</sup>, *etc.* Recent estimates indicate that about 12 % of the synthetic textile dyes used each year are lost during manufacturing and processing operations and 20 % of these lost dyes enter the environment through effluents<sup>2</sup>. The discharged wastewater contains high concentrations of reactive dyes with carcinogenic and mutagenic characters<sup>3</sup>.

Metal contaminated soils are potentially harmful to plants, animals and human beings. Harmful effects are often related to free metal concen-

---

†Centre for P.G. Studies and Research in Chemistry, G.T.P. College, Nandurbar-425 412, India.

tration in soil<sup>4</sup>. A report from the National Academy Sciences found to be 50 % of US pregnancies result in birth defects or neurological conditions and other chronic development problems are due to toxic metals in water<sup>5</sup>. Efforts have been made for the detection and identification of organic compounds in industrial waste in the Western countries<sup>6</sup>. However, less efforts are under taken<sup>7</sup> therefore this study was undertaken to detect and identify organic and metallic interactions in dye industry.

### EXPERIMENTAL

The industrial waste water and soil samples were collected as per standard procedures from textile dyeing and printing industries<sup>8</sup> from GIDC Pandesara and GIDC Sachin, Surat (Gujarat). Organic compounds were extracted from these effluents by using dichloromethane. Extracted organic layer was concentrated into a small mass. This extracted mass was recorded for FTIR on Perkin-Elmer IR instrument and GC-MS was recorded on Hewlett-Packard made GC-MS spectrophotometer. The concentration of hazardous metals was determined by ICP-AES technique. All these instrumental facilities are availed from Sophisticated Analytical Instrument Facility (SAIF), IIT, Mumbai.

### RESULTS AND DISCUSSION

The characteristics band and IR frequencies of samples are given in Table-1. The characteristic IR bands support the presence of functional groups in the detected organic compounds by GC-MS. The GC-MS spectra of CH<sub>2</sub>Cl<sub>2</sub> extracted mass was shown in Fig. 1.

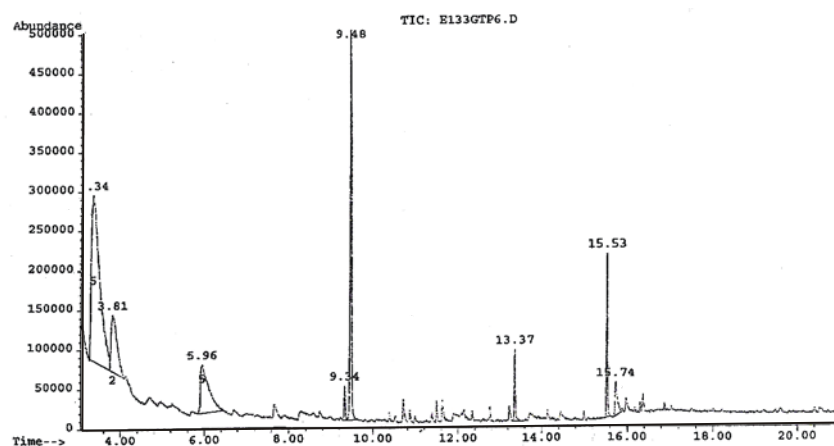
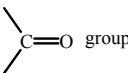
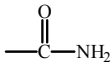
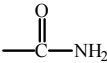


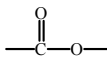


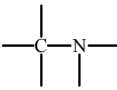

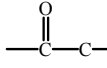


Fig. 1. GC-MS Spectrum of dichloromethane extracted mass (Sample No. 3)

TABLE-1  
IR SPECTRAL BANDS (cm<sup>-1</sup>) OF CH<sub>2</sub>Cl<sub>2</sub> EXTRACTED MASS

Sample No. 3		Sample No. 10	
Wavelength (nm)	Characterization	Wavelength (nm)	Characterization
3434	N-H stretch.	3455	Free -OH group
2961	-OH carboxylic broad band	2971	Alkyl C-H stretch.
2930	C-H stretch.	2930	Alkyl C-H stretch.
2854	C-H stretch.	2859	C-H stretch.
1744	 group	1642	
1632		1214	 alkane stretching
1499		1056	 ester linkage.
1459		598	
1387	C-H aldehydic bending vibration		
1270			
1224	 bond stretching		
1026	 linkage		
756	<i>o</i> -Disubstituted		

The detected organic compounds contain phenol, which imparts taste and odour to water and are toxic to aquatic life. Other compounds include benzene, 1-methyl 2-nitrobenzene, propyl benzene acetaldehyde, benzonitrile, 2-nitrobenzonitrile, 3-nitrobenzene, 1-isocyano-4-nitrobenzene dicarboxylic acid, *bis*(2-ethyl hexyl)phthalate. All these compounds are toxic and carcinogenic<sup>7</sup>.

The concentration of trace metals in dye industrial wastewater, ground water and soil samples are given in Tables 2 and 3. The concentration of heavy metals like As, Hg, Mn was not detected in any of the sample from

GIDC Pandesara and Sachin. Cd was not detected in soil samples in both industrial areas. Ni was not detected in ground water. The concentration of Cu in industrial wastewater was found to be in the range of 0.99-2  $\mu\text{g/mL}$  in Pandesara and 1.33-2  $\mu\text{g/mL}$  in Sachin industrial area. The ground water of Pandesara and Sachin area contains 0.62 and 0.52  $\mu\text{g/mL}$  Cu. Concentration of Cu in soil was in the range of 5.2-12  $\mu\text{g/mL}$  in Pandesara and 4-9  $\mu\text{g/mL}$  in Sachin.

The concentration of Zn was found to be in the range of 2.1-4  $\mu\text{g/mL}$  in industrial wastewater, 0.52-0.56  $\mu\text{g/mL}$  in ground water and 12-80  $\mu\text{g/mL}$  in soil samples. The concentration of Cd was found to be in the range of 0.036-0.32  $\mu\text{g/mL}$  in industrial wastewater, 0.01  $\mu\text{g/mL}$  in ground water whereas in soil Cd was not detected. The concentration of Pb was found to be in the range of 0.32-1.83  $\mu\text{g/mL}$  in industrial wastewater, 0.21-0.23  $\mu\text{g/mL}$  in ground water while 0.32-0.62  $\mu\text{g/mL}$  in soil samples. The concentration of metals like As, Hg, Mn was not detected in any of the ground water and soil sample.

The concentration of Ni was found to be in the range of 0.33-4.6  $\mu\text{g/mL}$  in industrial wastewater, 0.93-12  $\mu\text{g/mL}$  in soil but in ground water it was not detected. The concentration of Cr was found to be in the range of 0.12-1.33  $\mu\text{g/mL}$  in industrial wastewater, 0.1  $\mu\text{g/mL}$  in ground water and 0.91-12.3  $\mu\text{g/mL}$  in soil samples. The concentration of Fe was found to be in the range of 1.2-9  $\mu\text{g/mL}$  in industrial wastewater, 456-86  $\mu\text{g/mL}$  in soil and 0.66-0.67  $\mu\text{g/mL}$  in ground water.

The COD values of industrial wastewater was found to be in the range of 392-3841.3 mg/L and BOD was found in the range of 200-2340 mg/L. The COD values of soil samples was found to be in the range of 1600-6120 mg/L.

The correlation and regression analysis of the collected results are being tabulated in Tables 4 and 5. The correlation coefficient 'r' among all the detected metal was calculated, some of the metals show positive correlation which are Cu-Pb, Zn-Pb, Zn-Cr, Pb-Ni, Pb-Fe in soil samples and Cu-Zn, Cu-Cd, Cu-Cr, Zn-Fe, Cd-Cr, Ni-COD, Ni-BOD, COD-BOD in water samples. Some of the metals show negative correlation which are Cu-COD, Zn-BOD, Cd-COD, Cd-BOD, Pb-COD, Pb-BOD in water samples and Cu-Fe, Zn-Ni, Ni-Fe in soil samples. The regression studies have also been carried out on all metal-COD pairs. The values of regression coefficient interpret the regression efficiency. Some of the pairs of regression coefficient are given in Tables 5-7 for water and soil samples, respectively.

TABLE-2  
CONCENTRATION OF METALS, COD, BOD OF INDUSTRIAL WASTEWATER IN DYEING AND PRINTING INDUSTRIES AND DRINKING WATER COLLECTED FROM GIDC PANDESARA AND SACHIN (SURAT)

Sl. No.	Sampling sites near	Detected metals ( $\mu\text{g/mL}$ )											COD (mg/L)	BOD (mg/L)
		Cu	Zn	Cd	Pb	As	Hg	Ni	Cr	Fe	Mn			
1	Jaiprakash Print, Pandesara	1.18	2.57	0.042	1.83	ND	ND	4.60	0.72	8.00	ND	342.0	250	
2	Vipam Industries Ltd.	1.08	2.63	0.036	1.72	ND	ND	1.33	0.33	7.20	ND	313.6	200	
3	Premraj Industries Ltd.	1.33	2.47	0.037	0.92	ND	ND	4.20	0.72	1.20	ND	3841.6	2340	
4	Amin Industries Ltd.	0.99	3.00	0.042	0.47	ND	ND	0.33	0.66	1.46	ND	548.8	345	
5	People Dyeing & Printing	1.11	3.00	0.062	0.32	ND	ND	0.94	0.62	9.00	ND	392.0	260	
6	Geeta Dyeing & Printing	1.62	2.74	0.047	0.33	ND	ND	0.56	0.62	7.00	ND	548.8	330	
7	Astha Printing Dyeing	2.00	2.10	0.042	1.87	ND	ND	0.63	0.33	8.60	ND	470.4	315	
8	Sudha Printing & Dyeing	1.43	4.00	0.052	1.72	ND	ND	0.67	0.12	8.70	ND	548.8	380	
9	Prabhavana Industries Ltd.	1.33	2.67	0.052	1.55	ND	ND	1.36	1.00	1.34	ND	862.4	570	
10	Suprabhat Dyeing & Prints	1.67	2.92	0.062	0.94	ND	ND	1.32	1.20	7.00	ND	705.6	450	
11	Heena Processors Ltd.	2.00	3.00	0.320	0.96	ND	ND	0.96	1.33	6.30	ND	448.8	590	
12	Ground water from Sachin	0.62	0.52	0.010	0.21	ND	ND	ND	0.10	0.66	ND	-	-	
13	Ground water from Pandesara	0.53	0.56	0.010	0.23	ND	ND	ND	0.10	0.67	ND	-	-	

Note: ND means below detection limit for Cu, Zn, Cd, Fe, Ni and Cr < 0.1 ppm.

TABLE-3  
CONCENTRATION OF METALS IN SOIL SAMPLES NEAR DYEING & PRINTING INDUSTRIAL AREA OF GIDC PANDESARA AND SACHIN (SURAT)

S. No.	Sampling sites near	Detected metals ( $\mu\text{g/mL}$ )										COD (mg/L)
		Cu	Zn	Cd	Pb	As	Hg	Ni	Cr	Fe	Mn	
14	Vipan Industries Ltd.	12.0	56	<0.1	0.56	ND	ND	4.0	12.0	67	ND	2700
15	Old Bombay Dyeing	6.0	64	<0.1	0.62	ND	ND	3.9	12.3	86	ND	1600
16	Premraj Industries Ltd.	5.2	80	<0.1	<1	ND	ND	7.9	9.6	62	ND	5800
17	Geeta Printing & Dyeing	9.6	12	<0.1	<1	ND	ND	12.0	8.0	46	ND	3240
18	Gouri Printing & Dyeing	4.0	24	<0.1	0.33	ND	ND	0.96	9.2	56	ND	3320
19	Prabhavana Industries Ltd.	9.0	43	<0.1	0.42	ND	ND	0.93	0.91	52	ND	6120
20	Suprabhat Industries Ltd.	4.6	18	<0.1	<1	ND	ND	ND	0.97	53	ND	5730

Note: ND means below detection limit for Cu, Zn, Cd, Fe, Ni and Cr < 0.1 ppm, Pb < 1 ppm.

TABLE-4  
CORRELATION COEFFICIENT BETWEEN METALS AND COD & BOD FROM INDUSTRIAL WASTEWATER SAMPLES OF GIDC SACHIN AND PANDESARA (SURAT)

S. No.	Metals	Cu	Zn	Cd	Pb	Ni	Cr	Fe	COD	BOD
1	Cu	1								
2	Zn	0.5806	1							
3	Cd	0.5772	0.3360	1						
4	Pb	0.4495	0.4243	0.0448	1					
5	Ni	0.1007	0.1941	-0.0387	0.4107	1				
6	Cr	0.5663	0.4386	0.6434	0.0597	0.3062	1			
7	Fe	0.3063	0.5837	0.2228	0.4589	0.1277	0.8820	1		
8	COD	-0.0717	0.0676	-0.1571	-0.1302	0.5738	0.0841	-0.5854	1	
9	BOD	0.0087	-0.1226	-0.0111	-0.1335	0.5546	0.1673	-0.5860	0.9890	1

TABLE-5  
VALUES OF REGRESSION COEFFICIENT FOR INDUSTRIAL  
WASTEWATER SAMPLES OF SACHIN AND PANDESARA GIDC  
(SURAT)

S. No.	Parameters Pairs	A	B
1	Cu-Zn	0.8805	1.2275
2	Cu-Cd	-0.0675	0.1002
3	Cu-Pb	0.1607	0.6501
4	Cu-Cr	-0.0495	0.5028
5	Zn-Pb	0.2868	0.2903
6	Zn-Cr	0.1478	0.1842
7	Zn-Fe	-0.0318	2.0989
8	Cd-Cr	0.3976	3.2931
9	Pb-Ni	0.4147	0.8958
10	Pb-Fe	2.7387	2.4121
11	Ni-COD	212.7878	398.3214
12	Ni-BOD	193.4197	230.9102
13	Ni-Cr	0.4907	0.861
14	COD-BOD	58.9354	0.5932

TABLE-6  
CORRELATION COEFFICIENT BETWEEN METALS & COD OF SOIL  
SAMPLES OF GIDC SACHIN AND PANDESARA (SURAT)

S No.	Metals	Cu	Zn	Pb	Ni	Cr	Fe	COD
1	Cu	1						
2	Zn	0.0315	1					
4	Pb	0.4211	0.9845	1				
5	Ni	0.2019	-0.1244	0.9355	1			
6	Cr	0.1449	0.4813	0.5528	0.2255	1		
7	Fe	-0.0776	0.6872	0.8691	-0.2596	0.6451	1	
8	COD	-0.2255	-0.0262	-0.6036	-0.0547	-0.7890	-0.5892	1

TABLE-7  
VALUES OF REGRESSION COEFFICIENT FOR SOIL SAMPLES  
FROM GIDC, SACHIN AND PANDESARA (SURAT GUJARAT)

S. No.	Parameters pairs	A	B
1	Cu-Pb	0.3596	0.0158
2	Cu-Ni	2.7766	0.2845
3	Cu-Cr	5.9144	0.2297
4	Zn-Pb	0.1354	0.0074
5	Zn-Cr	3.7544	0.0898
6	Zn-Fe	45.1778	0.3561
7	Pb-Ni	-3.4984	12.3231
8	Pb-Cr	-2.1582	22.3020
9	Pb-Fe	156.8147	100.3840
10	Ni-Cr	7.5916	0.2176
11	Cr-Fe	46.7388	1.7898

### ACKNOWLEDGEMENTS

Authors are grateful to the Principal, GTP College Nandurbar for providing necessary laboratory facilities, Head RSIC (SAIF) IIT, Mumbai for providing instrumental analysis. Authors are also thankful to the Principal, Kisan College, Parola and Jai-Hind College, Dhule for their cooperation.

### REFERENCES

1. T. Nakamura, T. Tokimoto, T. Tamura, N. Kawasaki and S. Tanada, *J. Health Sci.*, **49**, 520 (2003).
2. E. Voudrias, K. Fytianos and E. Bozani, *Global Nest. The Int. J.*, **4**, 75 (2002).
3. L. Games and R. Hites, *Anal. Chem.*, **49**, 1433 (1977).
4. O. Leonard A., D. Jan, M.W. Chim and Lexmod, *Environ. Toxic. Chem.*, **20**, 1339 ().
5. M. Reinhard, J.E. Schreiner, T. Everhart and J. Graydon, *J. Environ. Pathol. Toxic. Oncol.*, **7**, 417 (1987).
6. M. Evoy and W. Giger, *Environ. Sci. Tech.*, **20**, 376 (1986).
7. S.V. Mahajan and V.S. Shrivastava, *Asian J. Chem.*, **17**, 907 (2005).
8. A.E. Greenberg, J.J. Canners and D. Jenkins, Standard Methods for Examination of Water and Wastewater, APHA, p. 512A (1989).

(Received: 26 April 2006; Accepted: 28 February 2007) AJC-5461