Journal of Advanced Chemical Sciences 2(3) (2016) 327–330

ISSN: 2394-5311

Contents List available at JACS Directory

Journal of Advanced Chemical Sciences

journal homepage: www.jacsdirectory.com/jacs

Study of Detection of Heavy Metals and Organic Compounds in Water Sample of Some Rivers in Maharashtra

P.R. Patil[1,*], V.S.Shrivastava[2]

[1]*Department of Chemistry, S.S.V.P.'s Arts Commerce and Science College, Shindkheda – 425 406, Maharashtra, India.*
[2]*Nano Chemistry Research Laboratory, G.T.P. College, Nandurbar – 425 412, Maharashtra, India.*

ARTICLE DETAILS

Article history:
Received 28 May 2016
Accepted 13 June 2016
Available online 10 July 2016

Keywords:
Heavy Metals
Godavari River
Krishna River

ABSTRACT

In present study the water samples were collected from various sites of Godavari and Krishna River. The water samples were extracted by HNO_3-HCL mixture and extracted mass was analyzed for Heavy metals concentration by using ICP-AES technique. The water samples were extracted by using CH_2Cl_2 Solvent and extracted mass was analyzed for different functional group by FTIR and organic compounds by GC-MS technique. The heavy metals and organic compounds in river water adversely affect the water quality and human health.

1. Introduction

River plays an important role in the development of nation and sustenance of life which are being polluted due to rapid industrialization urbanization and other developmental activities. However, rapid industrial development, economic growth and population growth have intensified the requirement for a vast number of materials and products, leading to increase in number of factories in various places across the world. Consequently, available water resources have been reduced. Due to unplanned industrialization and modernization, over exploitation natural resources, lack of ecological education and population explosion have all resulted degradation of aquatic ecosystem. There has been a steady deterioration in quality of river water. The rivers received million liters of sewage, industrial and agricultural wastes which changes physical and chemical characteristics of river water which causes great damage to the riverine biota. The water quality of the Indian rivers is deteriorating continuously, so its quality is likely to change day by day and from source to source. Any change in the natural quality may disturb the equilibrium system and would become unfit for designated uses. However, recently, social concerns and the requirement of environmental conservation are attracting more attention towards river water pollution and recently has been the subject of much research [1-3].

A tremendous increase in the use of heavy metals over a past few decades has resulted in an increased flux of metallic substances in the environment. The metals are of special concern because of their non-biodegradable and persistence in the environment. These heavy metals are very toxic and carcinogenic in nature. Some metal ions are accumulative poisons, capable of being assimilated and stored in the tissues of organisms causing noticeable adverse physiological effects [4, 5]. The industrial effluent from dye, pigments, paper and pulp, pharmaceutical, food processing and leather etc. industries contain variety of organic compounds. The organic compounds are carcinogenic and mutagenic affect quality of river water and human health [6-9]. On the basis of the current information India's 14 major 55 minor and several hundred small river are being polluted due to receiving million liters of sewage, industrial and agricultural wastes. Most of these rivers have been rendered to sewage flowing drains [10].

Godavari and Krishna are the most significant rivers in Maharashtra. Godavari River rises at Brahmagiri in Tryambakeshwar of Sahyadri and flowing from west to east in Maharashtra. While Krishna river rises at Mahabaleshwar and flowing in southern-western region of Maharashtra. In view of above we would like to communicate the organic and metallic pollution status of Godavari and Krishna river water. The ICP-AES technique is most effective and advance technique used for determination of concentrations of heavy metals [11, 12]. While GC-MS technique is advanced and commonly used for determination of organic compounds in water samples [13-15].

2. Experimental Methods

For present investigation the water samples were collected from various sampling sites of Godavari and Krishna River covering bathing Ghats, confluences of tributaries, main sewers and drain, cremation Ghats and dumping of industrial wastes. The water samples were digested in 3:1 ratio of concentrated nitric acid and hydrochloric acid. The total metal concentration was determined by inductively coupled plasma atomic emission spectrophotometer (ICP-AES) at Sophisticated Analytical Instrument facility (SAIF), Indian Institute of Technology (IIT), Powai, Mumbai. While for detection of organic compounds, the water sample was extracted by using CH_2Cl_2 solvent and extracted mass was analyzed for different functional group by FTIR and organic compound by GC-MS technique at SICCART, Vaillabh Vidya Nager, Gujarat.

3. Result and Discussion

3.1 Detection of Metals

The results obtained during the course of present study are discussed under the individual headings. The concentration of heavy metals in Godavari and Krishna river water samples are given in Tables 1 and 2.

3.1.1 Copper (Cu)

During the course of present investigation copper was found in all water samples of Godavari and Krishna River. The concentration of copper in Godavari and Krishna river water samples at different sites was found to be in the range 0.09 - 0.94 and 0.077 - 0.96 ppm. Copper is the essential nutrient for plants for the synthesis of chlorophyll and functioning of certain enzymes. While at high concentration it is toxic to inhibit growth of plant. The surrounding population use river water for the various purposes like drinking bathing and irrigation. However Cu has been found

*Corresponding Author
Email Address: patilpiran@gmail.com (P.R. Patil)

toxic for human health. Large quantities of Cu in drinking water irritate stomach causes neurological complaints, liver and kidney dysfunction, hyper tension, uremia and also produces pathological changes in brain tissues [16].

Table 1 Concentration of heavy metals (ppm) by ICP-AES in Godavari River Water Samples

S.No.	Sites of sample collection	Metals Concentration in (ppm)							
		Cu	Zn	Cd	Pb	Fe	Cr	As	Hg
1	Tryambakeshwar	0.11	1.26	ND	0.03	8.61	0.018	ND	ND
2	Showmeshwar	0.13	1.16	ND	0.02	6.62	ND	ND	ND
3	Nashik	0.14	1.33	ND	0.02	6.18	ND	ND	ND
4	Kopergaon	0.09	1.12	ND	ND	5.72	ND	ND	ND
5	Pravara Sangam	0.08	1.11	ND	ND	5.78	ND	ND	ND
6	Paithan	0.13	1.33	ND	0.02	6.13	0.09	ND	ND
7	Gangakhed	0.94	1.10	ND	0.03	5.78	ND	ND	ND
8	Nanded	0.12	1.25	ND	ND	5.79	ND	ND	ND

where, ND means less than 0.01 ppm

Table 2 Concentration of heavy metals (ppm) by ICP-AES in Krishna river Water Samples

S.No.	Sites of sample collection	Metals Concentration in (ppm)							
		Cu	Zn	Cd	Pb	Fe	Cr	As	Hg
1	Wai	0.08	1.30	ND	ND	5.72	ND	ND	ND
2	Mahuli	0.077	1.34	ND	ND	5.66	ND	ND	ND
3	Karad	0.12	1.28	ND	0.03	6.0	ND	ND	ND
4	Sangli	0.96	1.36	ND	ND	5.86	ND	ND	ND
5	Narshobawadi	0.12	1.28	ND	ND	6.0	ND	ND	ND
6	Miraj	0.13	1.42	ND	0.02	5.77	ND	ND	ND
7	Bhilvadi	0.99	1.28	ND	ND	5.62	ND	ND	ND
8	Audumbar	0.12	1.36	ND	ND	5.74	ND	ND	ND

where, ND means less than 0.01 ppm

3.1.2 Zinc (Zn)

The concentration of Zn in Godavari and Krishna river water samples at different sites was found to be in the range of 1.10-1.33 and 1.30 - 1.42 ppm. The presence of Zinc in river water samples is due to the discharge of industrial effluents from pharmaceuticals, galvanizing, paint, pigment, several insecticides, and cosmetics industries. Zinc is very essential micronutrient in human beings and only at very high concentration it may causes some side effects. The high concentration of zinc in drinking water causes gastrointestinal complaints. The high concentration of zinc in water causes disagreeable taste [17].

3.1.3 Cadmium (Cd)

The concentration of Cd in Godavari and Krishna River water samples at all sites it was not detected (< 0.01 ppm). The presence of Cd in river water is due to the discharge of effluent from electroplating, pigment and chemical industry.

Cadmium is usually mined and extracted from zinc ores, especially zinc sulphide. Industrially cadmium is used as an antifriction agent as a rust proffer and in alloys. It is also used in semiconductors, control rods for nuclear reactors, electroplating bases, PVC manufacture and batteries. In the environment Cd is dangerous because many plants and animals absorb it efficiently and concentrate it within their tissues. Once absorbed cadmium associates with the low molecular weight protein, metallothionein and accumulates in the kidney, liver and reproductive organs cause kidney problems, anemia and bone marrow disorders. The major portion of Cd ingested into our body is trapped in the kidney and eliminated [18-19]. Its intake of more than 0.01 µg/mL in drinking water damages our kidneys causes 'Itai-Itai' in which bones become fragile and muscles contracted with deformation and pain [17].

3.1.4 Lead (Pb)

The concentration of Pb in Godavari river water samples at different sites was found to be in the range of 0.02-0.03 ppm and at sites 4, 5 and 8 it was not detectable. While in Krishna river water samples it was found to be 0.03 ppm at site-3 and 0.02 ppm at site-6 and it was not detecteable at sites 1, 2, 4, 5, 7 and 8. It is thrown in the atmosphere by vehicles due to antiknock compounds [$Pb(CH_3)_4$] and [$Pb(C_2H_5)_4$] added to the automobile fuel with the scavengers 1,2 dichloro ethane and 1,2 dibromo ethane that reaches the drainage system with rain water and ultimately reaches in river water. According to rough estimation about 2,10,000 tons of lead are released annually into the environment in variety of ways like in fumes dusts, from industrial effluents, Pb pipes, paints pigments, varnishes, printing inks etc. Lead arsenate is used as a pesticide and borate finds use in plastic industries. The presence of Pb in river water is also due to industrial waste from printing, dyeing, and oil refineries etc. Inorganic lead acts as an agent to cause a variety of effects on human health including liver and kidney damage, gastrointestinal damage, mental health effects in children and abnormalities in fertility and pregnancy. Lead is toxic element and it accumulates in the bone marrow, where red blood corpuscle formation (heamatopoiesis) occurs. Pb affects at least five stages in the formation of heam part of heamoglobin, but in enzymes most affected are S amino laevulinic dehyratase (ALAD) and ferrochetalase [20].

3.1.5 Iron (Fe)

During the course of present investigation Iron was found in all water samples of Godavari and Krishna river. The concentration of iron in Godavari and Krishna river water samples at different sites was found to be in the range 5.78 - 8.61 and 5.62 - 6.0 ppm. Iron is an essential micronutrient required in the trace quantities for the normal metabolism of plant and animals. It is a constituent of cytochromes and non-haeme iron proteins involved in photosynthesis, nitrogen fixation and respiratory linked dehydrogenase [21]. The present of Iron in river water is due to Discharge of effluents from dye industry in which complex salt of Fe and Cr are used [16]. Higher amount of ferrous sulphate and ferric chloride are used for the precipitation of direct dye in treatment process. In addition, corrosion of pipes and pumps due to acidic effluents from the industry can increase the concentration of Fe in soil and sediment samples. It is reported that dissolved Iron in water is difficult to remove. When drinking water containing high concentration of Fe can lead to liver diseases [19].

3.1.6 Chromium (Cr)

In present study the concentration of Cr in Godavari river water samples at site-1 was found 0.018 ppm and at site-6 0.09 ppm and it was not detectable at sites 2, 3, 4, 5, 7 and 8. While in Krishna river water samples it was not detectable at all sites.

3.1.7 Arsenic (As)

In present study the concentration of As in Godavari and Krishna river water at all different sites it was not detectable (< 0.01 ppm).

The presence of Arsenic in river water is due to discharge of industrial effluents of ceremics, tannaries, chemical, metal preparation and pesticide industry [17]. Arsenic is a toxic, non-essential element and widely occurs in nature. It is used in alloys, pesticides, wood preservatives and some medicinal preparations. Industrial wastes are main source of arsenic pollution in the environment. It occurs in river water as a result of mineral dissolution, industrial discharges or the application of insecticides, herbicides and fungicides [22]. Further the arsenic compounds in industrial effluents have led to the microbial methylation of arsine resulting in the formation of the toxic trimethyl arsine [23]. Arsenic is accumulative poison, accumulated in body tissues to cause arsenosis and causing vomiting and abdominal pains prior to death. The drinking water containing higher concentration of arsenic it is readily absorbed by the digestion tract abdominal cavity and muscle tissues. It is a human and animal carcinogenic producing tumor of the skin and believed to produce liver cancer and hemangiothelioma [23, 24].

3.1.8 Mercury (Hg)

In present study the concentration of Hg in Godavari and Krishna river water at all different sites it was not detectable (< 0.01 ppm).

Mercury is a highly toxic metal. It is used in the production of electrical apparatus, in the chloro-alkali industry, which produces chlorine and caustic soda, in fungicides. Its compounds like mercuric sulphate are used as a catalyst in the production of acetaldehyde in industry. Hence it is thrown into the environment due to the industrial use. When it enters into the environment, various transformations can take place, the most serious of these is the transformation of metallic mercury to methyl and dimethyl derivatives by anaerobic micro-organism [24]. Hg in its inorganic forms attacks mainly liver and kidney whereas organomercurial transverse through the biological membranes and concentrates especially in the brain [17-19].

3.2 FTIR and GC-MS Studies

The FTIR spectra of Godavari and Krishna river water is shown in Figs. 1 and 2. The characteristic bands and IR frequencies are given in Tables 3 and 4. While the GC-MS spectra of CH_2Cl_2 extracted sample of Godavari and Krishna river water sample are shown in Fig. 3-6. The organic compound detected in sample was identified by comparison with library search.

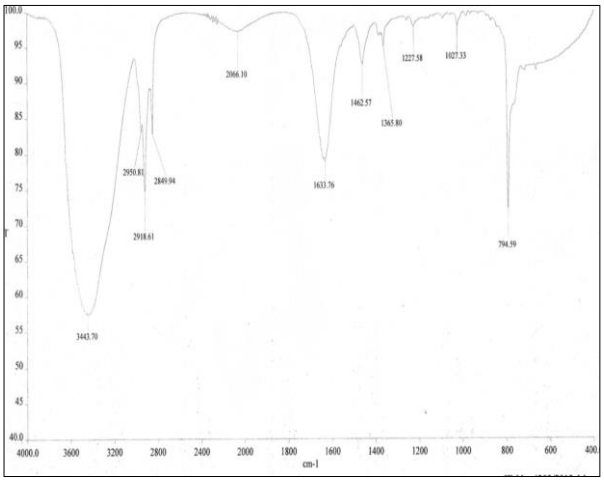

Fig. 1 FTIR Spectra of CH_2Cl_2 extracted sample of Godavari river water

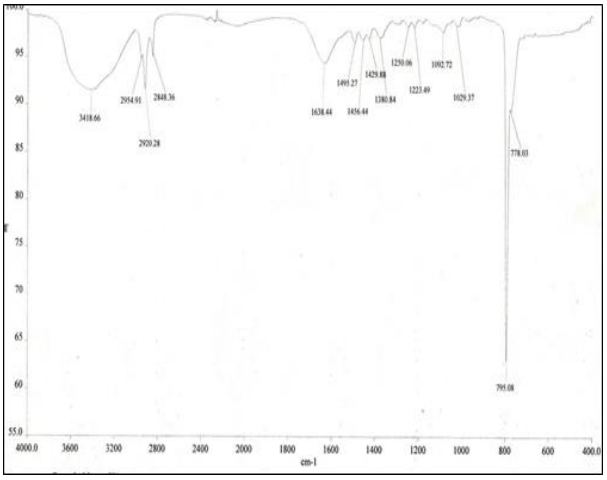

Fig. 2 FTIR Spectra of CH_2Cl_2 extracted sample of Krishna river water

Table 3 IR frequencies and characteristic bands of Godavari River water sample

S. No	Frequency (cm^{-1})	Characteristics bands
1)	3443.70	-O-H Stretching (Carboxylic acid free –OH group)
2)	2950.81	-C-H Stretching (-CH_3groups)
3)	2918.81	-C-H Stretching (-CH_2groups)
4)	2849.94	-C-H Stretching (alicyclic -CH_2groups)
5)	2066.10	>C=O Stretching (Ketonic group)
6)	1633.76	-C-N Stretching
7)	1462.57	-C-H bending (Asymmetric) –CH_2 group
8)	1365.80	-C-H bending (symmetric) –CH_2 group
9)	1227.58	-C-H bending (asymmetric) –CH_2 group
10)	1027.33	-C-O Stretching (alcoholic)
11)	794.59	=C-H bending (P- disubstituted alkenes)

Table 4 IR frequencies and characteristic bands of Krishna River water sample

S. No	Frequency (cm^{-1})	Characteristics bands
1)	3418.66	-O-H Stretching (alcoholic free –OH group)
2)	2954.91	-C-H Stretching (-CH_3groups)
3)	2920.28	-C-H Stretching (-CH_2groups)
4)	2848.36	-C-H Stretching (alicyclic -CH_2groups)
5)	1638.44	>C=O Stretching (Ketonic group)
6)	1495.27	-C=C- Stretching
7)	1456.44	-C-H bending (Asymmetric) –CH_3 group
8)	1429.88	-C-H bending (Asymmetric) –CH_3 group
9)	1380.84	-C-H bending (symmetric) –CH_2 group
10)	1250.06	-C-O-C- Stretching (aryl)
11)	1223.49	-C-O- Stretching (acidic C-O)
12)	1092.72	-C-OH Stretching (primary alcohol)
13)	1029.37	-C-O Stretching (alcoholic)
14)	795.08	=C-H bending (P- disubstituted alkenes)
15)	778.03	-C-H bending vibration (Rocking)

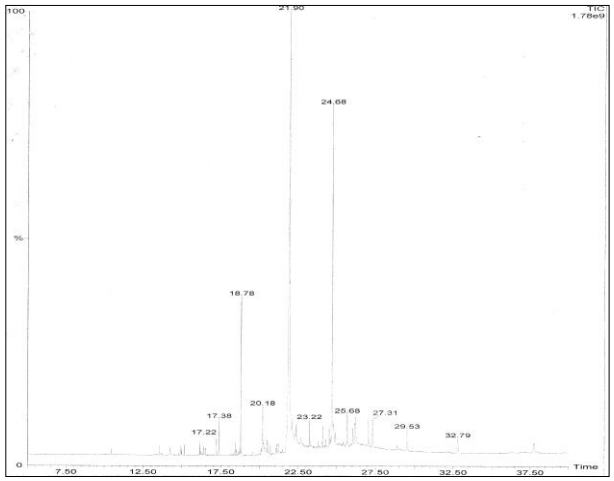

Fig. 3 GC analysis of CH_2Cl_2 extracted sample of Godavari river water

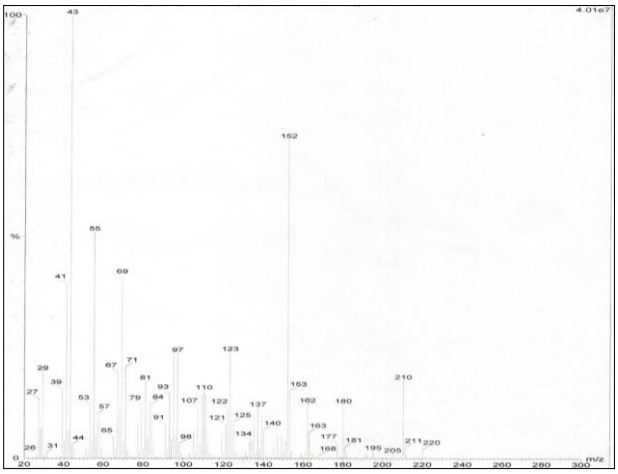

Fig. 4 Mass Spectra of CH_2Cl_2 extracted sample of Godavari river water

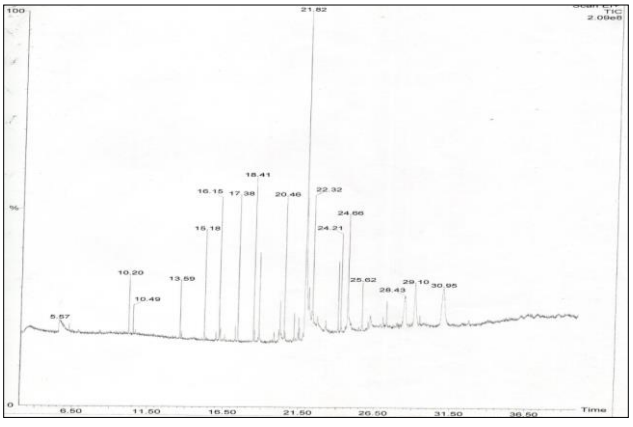

Fig. 5 GC analysis of CH_2Cl_2 extracted sample of Krishna river water

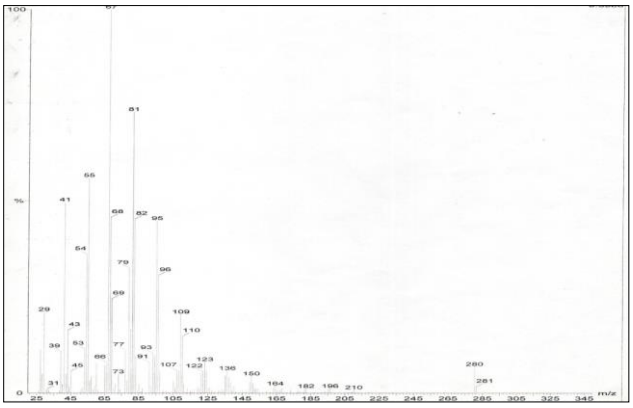

Fig. 6 Mass Spectra of CH_2Cl_2 extracted sample of Krishna river water

The organic compound detected in sample was identified by comparison with library search. The GC-MS spectra shows the Godavari and Krishna river water sample contain following organic compounds as shown in Tables 5 and 6.

Table 5 Some organic compounds found in CH_2Cl_2 extracted mass of Godavari river water sample

S. No	Name of organic compound	Molecular formula	Molecular weight
1)	11,12-Dibromo-tetradecan-1-ol acetate	$C_{16}H_{30}O_2Br_2$	412
2)	N-hexadecanoic acid	$C_{16}H_{32}O_2$	256
3)	L-(+)-Ascorbic acid 2,6-dihexadecanoate	$C_{38}H_{68}O_8$	652
4)	9,12-Octadecadienoic acid, methyl ester	$C_{19}H_{34}O_2$	294
5)	9,12-Octadecadienoic acid, ethyl ester	$C_{20}H_{36}O_2$	308
6)	Methyl 9,12-heptadecadienoate	$C_{18}H_{32}O_2$	280
7)	Pentadecanoic acid, 15-bromo-	$C_{15}H_{29}O_2Br$	320
8)	L-Ascorbic acid, 6-octadecanoate	$C_{24}H_{42}O_7$	442

Table 6 Some organic compounds found in CH_2Cl_2 extracted mass of Krishna river water sample

Sr. No	Name of organic compound	Molecular formula	Molecular weight
1)	9,12-Octadecadienoic acid (Z,Z)-	$C_{18}H_{32}O_2$	280
2)	9,12-Octadecadienoic acid, methyl ester	$C_{19}H_{34}O_2$	294
3)	2-chloroethyl linoleate	$C_{20}H_{35}O_2Cl$	342
4)	Z,Z-2,15-octadecadiene-1-ol Acetate	$C_{20}H_{36}O_2$	308
5)	9-octadecen-1-ol, (E)-	$C_{18}H_{36}O$	268
6)	9,12-octadecadienoyl chloride, (Z,Z)-	$C_{18}H_{31}OCl$	298
7)	Z-5, 17-octadecadien-1-ol acetate	$C_{20}H_{36}O_2$	308
8)	5,8-Octadecadienoic acid, methyl ester	$C_{19}H_{34}O_2$	294

4. Conclusion

The result achieved in the present investigation using ICP-AES gives the concentrations of heavy metals and GC-MS study of sample confirms the presence of organics in river water. Also the heavy metals enter in the human body by different pathways and causes harmful effects. Some of the metals and organic compounds detected are toxic to the environment. Day by day as the discharge of wastewater in river water continues from these industries, due to non-biodegradability of heavy metals their concentration in environment continuously increases. It affects the quality of river water.

Acknowledgments

Authors are gratefully acknowledged to the Indian Institute of Technology (IIT), Powai, Mumbai, for ICP-AES and SICART, Vallabh Vidyanagar for FTIR and GC-MS studies. Authors are also thankful to the Principal, G.T.P. College, Nandurbar for providing necessary laboratory facilities. I am also thankful to the Principal, S.S.V.P.'s Arts Commerce And Science College, Shindkheda for promoting for research work.

References

[1] R. Kumar Gangwar, P. Khare, J. Singh, A.P. Singh, Assessment of physico-chemical properties of water: River Ramgangaat Barilly, U.P, J. Chem. Pharm. Res. 4(9) (2012) 4231-4234.
[2] J. Sirajudeen, M.M. Mohamed Mubashir, Statistical approach and assessment of physico- chemical status of ground water in near proximity of south bank canal, Tamil Nadu, India, Arch. Appl. Sci. Res. 5(2) (2013) 25-32.
[3] S.R. Barai, S. Kumar, Evaluation of the physico-chemical characteristics of river Varuna at Varanasi, Ind. J. Environ. Bio. 34 (2013) 259-265.
[4] A. Singh, S. Pandey, Study of trace element in ground water Bhopal city, Ultrachem. 1(2) (2005) 59-62.
[5] A.R. Nisha, S.N. Pandey, Heavy metals and health, Env. Engg. 65(1) (1999) 1-6.
[6] C.H. Sujata, S.M. Nair, J. Chocko, Determination and distribution of endosulfan and melathion in an Indian estuary, Wat. Res. 33(1) (1999) 109-114.
[7] R.P. Chavan, R.S. Lokhande, S.I. Rajput, Seasonal variations of organic pollutant in the Thane creek water Maharashtra, Poll. Res. 25(1) (2006) 201-206.
[8] R.P. Chavan, R.S. Lokhande, S.I. Rajput, Monitoring of organic pollutants in the Thane creek water Maharashtra, Poll. Res. 25(4) (2006) 877-880.
[9] A.W. Garrison, J.D. Pope, F.R. Allen, Identification and analysis of organic pollutants in water, Keith L.H. Ed., Ann. Arborsci. 30 (1990) 517-556.
[10] R.K. Trivedi, Pollution and biomonitoring of Indian rivers, 1st Ed., ABD Publishers, Jaipur, India, 2000.
[11] S.V. Mahajan, S. Khare, V.S. Shrivastava, Hazardous metals by ICP-AES and their bioaccumulation, correlation and regression study, Asian J. Chem. Environ. Res. 5(1-2) (2012) 51-58.
[12] A.K. Patil, V.S. Shrivastava, Analysis of metals and organic in river water by ICP-AES and GC/MS Techniques, Asian J. Chem. 19(5) (2007) 3645-3651.
[13] V. Sing, A. Jain, K.K. Verma, Solid phase micro extraction of residues of organophosphorous pesticide from aqueous samples for their determination by gas chromatography - mass spectroscopy, Ind. J. Chem. 42 (2003) 2993-2999.
[14] C.V. Nandre, V.S. Shrivastava, Solvent extraction, detection and identification of organics in industrial waste water by FTIR and GC/MS techniques, Asian Jour. Chem. Environ. Res. 4(2) (2011) 67-72.
[15] A. Muller, P. Duchting Elemer, W. Weiler, A multiplex GC/MS technique for sensitive and quantitative single run analysis of acidic phytohormones and related compounds and its application to Arabidopsis planta, Thaliana Planta 216 (2002) 44-56.
[16] A.K. Singh, Concentration of copper in surface and surface water of Rawanwara colliery area of Pench valley coal field and its environmental impact on human health, Ind. J. Env. Prot. 23(3) (2003) 313-316.
[17] R.K. Trivedy, P.K. Goel, Chemical and biological methods for water pollution studies, Environmental Publication, Karad, India, 2004.
[18] L. Campanella, M.E. Conti, F. Cubadela, C. Sucapane, Trace metal in sea grass algae and moluscus from an incontaminated area in the mediterranean, Env.Poll. 11 (2001) 117-126.
[19] A.K. De, Environmental chemistry, 2nd Ed., Wiley Eastern Ltd., New Delhi, 1992.
[20] Y. Mido, M. Satake, Chemical in environment, 2nd Ed., Discovery Publishing house, New Delhi, 2003.
[21] F.T. Noggle, G.J. Fritz, Introductory plant physiology prentice-Ha, India Pvt. Ltd., New Delhi, 1986.
[22] P.L. Palaniappan, R.M. Karthikeyen, S. Subhhayakam, By mercury containing wastewater from acetaldehyde production, Toxic impact of waste water on aquatic Environment, J.E. Tapp, RSC, UK, 1996, pp. 287-288.
[23] C.B. Dissanayake, Metal organic interaction in environmental pollution, Int. J. Env. Studies (22) (1993) 25-42.
[24] S. Krishnamurthy, Bio methylation and environmental transport of metals, J. Chem. Edu. 69(5) (1992) 347-350.