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Investigation of Dyes and Certain Chemical Parameters in Water Samples around Cloth Dyeing Industry during different Seasons

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ABSTRACT: Water from cloth dyeing industry was collected at the vicinity of dyeing industries to study the impact of dyeing industry effluent on water quality. Chemical parameters, namely sodium, potassium, nitrate nitrogen, nitrate nitrogen and phosphate were analyzed by following standard methodologies. The different dyes present in the water were identified as well with the help of GC – Ms. The results indicated the presence of these chemicals in appreciable quantities in the water which is a cause of concern. Hence it is recommended that treatment plants and organic dyes can be incorporated to minimize the pollution.

Keywords: water quality, chemicals, dyes, treatment, organic dyes.

I. INTRODUCTION

Chemicals are vital to modern society, certain chemicals may harm our health and environment severely. There is an increase in health problems may result due to the use of chemicals. Some synthetic chemicals are found in the most remote places in the environment and become part of our body as well. Dyes have wide range of uses in various industries like: textile dyeing, paper printing, colour photography, pharmaceutical, food, cosmetics, inks, paints etc. All dyes are made from natural sources till the middle of 19th century, most of them were vegetable extracts and some were animal products.

Environmental pollution is an inevitable consequence of economic development and people's desire to improve their quality of life. With the increasing demand of textile industries in India discharge colored effluents is also increased. These colored effluents give undesirable perspective to the water streams where as some dyes and their metabolites pose toxic, carcinogenic and mutagenic effects Adamu, (2008) [1]. Of various pollutants contained in industrial waste waters, dye is considered to be very important from the aesthetic point of view and is stated as visible pollutant. Dyes usually have a synthetic origin and complex aromatic molecular structures, which make them more stable and more difficult to biodegrade and are widely used in textiles, paper, plastic, leather, cosmetics and food industries to color their products. The extensive use of dyes often caused pollution problems in the form of colored waste water discharged in to environmental water bodies (Aseel and Aljebori, 2010) [5]. The synthetic dyes are cheap and offer a very wide vast range of new colors (Liu *et al.,* 1995) [8].

The synthetic dyes are used in many spheres of life and their applications are continuously growing in various industries like textile, leather, cosmetics, paper, paint and food. Approximately 10,000 different dyes and pigments are used industrially, and over 0.7 million tones of synthetic dyes are produced annually. About 3×10^5 ton of different dyestuffs are used per year thus making this industry as a major consumer of synthetic dyes and consequently are the major cause of water pollution. The dyes may cause disruption of biogeochemical cycles and irreversible damage to the aquatic environment. Dyes cause aesthetic problems and strongly absorb sunlight thus inhibiting the photosynthetic activity of aquatic plants and severely damage the whole ecosystem. Demand and necessity of synthetic dyes are continuously growing for dye manufacturing and dye utilizing companies all over the world. However, the major consumers of dyes are textile industries.

The largest class of dyes identified so far is azo dyes are largest colourants both in number and also in production volume and constitute 70% of organic synthetic dyes produced in the world Knat, (2012) [7]. Azo dyes are successful as they are produced by simple properties, good structural properties, moderately higher fastness properties and higher molar extinction coefficient. However, these dyes when present in water may cause the changes in certain parameters (Viz., Sodium, Potassium, Nitrate, Nitrite and Phosphates) of the water. The aim of the present study is to determine the concentration of textile dyes both qualitatively and quantitatively in the real samples of drinking water and effluent. The textile dye industry is widespread and is fundamental and essential as these provide employment to large population [13].

II. MATERIALS AND METHODS

A. Study area

There are 268 dyeing industries in Ludhiana, of which 10 industries are in large scale and 258 are in medium and small scale sector. Out of 258 medium and small scale dyeing industries, 200 dyeing units are located in 5 clusters namely Tajpur Road (73 industries, discharge-40 MLD), Industrial Area-A (37 industries, discharge-20 MLD), Focal Point (53 industries, discharge-40 MLD), Rahon Road (19 industries, discharge-15 MLD) and Bahadurke Road (18 industries, discharge-15 MLD). The remaining 58 small and medium dyeing industries are scattered in various parts of the Ludhiana city. The textile dyeing industries are generating 150 MLD of wastewater from their process which is having organic as well as chemical pollutants. The level of B.O.D. concentration varies in the range of 500-700 mg/l. All the 268 dyeing units have installed effluent treatment plant to treat their wastewater, out of which 36 no. of units are required to carry out major up-gradation of their existing effluent treatment plants so as to achieve the standards laid down by the Board and the remaining 10 units are required only minor up-gradation in their existing treatment facilities. The effluent from dye units enter into river Sutlej from Budha Nalla.

III. EXPERIMENTAL

A. Chemical parameters

Sodium and Potassium was estimated with the help of flame photometric method. Nitrite nitrogen was estimated in mg/L by Diazotization method (APHA, 2005) [3]. Nitrate nitrogen was determined by Phenol disulphonic acid method by following, Trivedy and Goel (1984) [11]. Phosphorous was estimated as phosphate following APHA (2005) [3].

B. Identification

The dyes were identified by comparison of the retention time in real samples with those of standard solutions under the same conditions (mobile phase, flow rate, temperature, pH and wave length).

C. Gas Chromatography –Mass Spectrophotometric (GC-MS) Analysis

Determination of dye residues were carried out mainly at the SAIF Indian Institute of Technology (IIT) Mumbai, Maharashtra, India. The concentrated extract was analysed using splitless injection gas chromatography–mass spectrometer (GC–MS) in the MS mode. The analysis of all pesticides was performed using a gas chromatograph (Agilent 7890) interfaced to a Joel Accu TOF GCV ion trap mass detector with data system-software required for the calibration, collection of GC–MS spectra and data processing for qualitative and quantitative analysis with library program. Separation was achieved on a high resolution DB-5 MS capillary column (30 m × 0.25 mm id×0.25 µm film thicknesses). Ultra pure helium (99.999%) was used as a carrier gas at a flow rate of 1-mL min^{-1} (68,947 Pa). The MS was taken at 70eV. The identification of compounds was done by comparing the spectrum of unknown dyes with the spectrum of known dyes.

IV. RESULTS AND DISCUSSIONS

A. Sodium and Phosphate

The maximum Na of 121.40±30.95 was recorded at S II in winter, the amount of Na at SI, SII, SIII and SIV was 121.6±10.25, 121.40±30.95, 118.08±23.85 and 117.6±.0.35, respectively during winter (Table 1).

Dyers of textile related industries mostly use sodium chloride (common salt) for colouring and bleaching purposes. In Ludhiana belt that has more than a hundreds of dyeing and bleaching units around 800 tonnes of sodium chloride is being dumped and washed off in an estimated seven lakh litres of water that mostly finds its way to the water sources and bodies including Sutlej. Textile cloth dyeing units of Ludhiana produce large amounts of liquid wastes that is concentrated with organic and inorganic compounds (Ghaly *et al.,* 2014) [6]. The effluents generated from the textile industry of Ludhiana are of utmost concern because of their high volume and pollution potential. The release of colored wastewater from this industry may present eco-toxic hazard and may eventually affect human life through food chain if accumulated (Nese *et al.,* 2007)[9].

Table 1: Monthly variation of samples during 2015-17 at four sampling sites in winter.

Sites	Na (mg/1)	K (mg/1)	Nitrate nitrogen (mg/1)	Nitrite nitrogen (mg/1)	PO_4(mg/1)
Site I	121.6±10.25	91.76±13.3	31.83±5.3	0.33±0.32	23.66±2.50
Site II	121.40±30.95	90.8±11.8	31.83±4.3	0.23±0.34	24.41±2.60
Site III	118.08±23.85	91.1±9.8	30.25±5.3	0.3±0.4	20.91±1.25
Site IV	117.6±.0.35	91.61±8.2	32.33±3.4	0.24±0.42	28.75±1.10

B. Potassium

The amount of Potassium at SI, SII, SIII and SIV was 91.022±10.50, 92.822±20.50, 93.311±19.50 and 90.077±2.45 respectively during summer (Table 2).

C. Nitrate and Nitrite

The amount of Nitrate nitrogen at SI, SII, SIII and SIV was 39.77±10.20, 34.55±5.0, 35.55±12.0 and 34.55±13.0 respectively during summer (Table 2). 0.28±0.50, 0.3±0.55, 0.275±0.30 and 0.4±0.60 Nitrite nitrogen was found at SI, SII, SIII and SIV during monsoon (Table 3). Nitrite and nitrate are chemical species in water that need monitoring, due to their known toxicity to animal and human metabolism. When nitrite is present in water, it can react with secondary amines to form carcinogenic N-nitrosamines which are harmful to human health. Traces of nitrite in drinking water may lead to methemoglobinalmia in infants, and with long term exposure is a possible cancer risk (McMullan *et al.,* 1995) [9]. Nitrite and nitrate are intimately involved in the over all nitrogen cycle in soil and plants. Nitrite and nitrate levels in our natural waters are important indicators of water quality. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the textile effluent highly toxic. Nitrite is an active form of nitrogen cycle, resulting from incomplete oxidation of ammonium ions or reduction of nitrate in the environment by denitrification bacteria. Therefore, to develop a sensitive reliable and cost effective analytical methodology for the determination of nitrite ion at nano and microgram levels is extremely important in environmental studies.

D. Phosphates

The amount of phosphate at SI, SII, SIII and SIV was 31.88±2.50, 30.66±5.60, 32.77±1.25 and 29.44±1.10, respectively during Post Monsoon (Table 4). A phosphate is a natural substance present in all potable water and it is usually present in sewage as a metallic salt. Its concentration in fresh water is quite low and generally less than that of Sulphate and bicarbonates. However, its concentration in water contaminated with dyes may increase. During the present investigations efforts.

Table 2: Monthly variation of samples during 2015-17 at four sampling sites in Summer.

Sites	Na (mg/1)	K (mg/1)	Nitrate nitrogen (mg/1)	Nitrite nitrogen (mg/1)	PO_4(mg/1)
Site I	113.588±10.50	91.022±10.50	39.77±10.20	0.355±0.50	28.22±2.50
Site II	110.44±20.50	92.822±20.50	34.55±5.0	0.388±0.55	25.33±2.60
Site III	110.35±19.50	93.311±19.50	35.55±12.0	0.455±0.30	24.55±1.25
Site IV	107.97±2.45	90.077±2.45	34.55±13.0	0.411±0.60	23.77±1.10

Table 3: Monthly variation of samples during 2015-17 at four sampling sites in Monsoon.

Sites	Na (mg/1)	K (mg/1)	Nitrate nitrogen (mg/1)	Nitrite nitrogen (mg/1)	PO_4(mg/1)
Site I	115.716±0.50	90.56±10.50	35.83±10.20	0.28±0.50	29.83±2.50
Site II	112.566±0.55	94.9±20.50	37.5±5.0	0.3±0.55	31.16±2.60
Site III	114±0.30	89.583±19.50	35.33±12.0	0.275±0.30	36.5±1.25
Site IV	115.05±0.60	91.583±2.45	35.16±13.0	0.4±0.60	33.5±1.10

Table 4: Monthly variation of samples during 2015-17 at four sampling sites in post monsoon.

Sites	Na (mg/1)	K (mg/1)	Nitrate nitrogen (mg/1)	Nitrite nitrogen (mg/1)	PO_4(mg/1)
Site I	115.311±10.20	93.5±10.50	36.66±10.20	0.401±0.50	31.88±2.50
Site II	112.788±5.0	93.32±20.50	36.44±5.0	0.316±0.55	30.66±5.60
Site III	111.41±12.0	94.31±19.50	37±12.0	0.322±0.30	32.77±1.25
Site IV	110.51±13.0	96.17±2.45	38.22±13.0	0.214±0.60	29.44±1.10

E. Dyes in water

The nature has been affected by numerous ways by new synthetic compounds that have been introduced by human activities and that are causing health problems by altering physiological functions (Vera *et al.,* 2005). For the citizens of Ludhiana and environmental authorities, one of the most important environmental concerns is water pollution by dyes (Vera *et al.,* 2005) [12]. However, in developing countries like India where treatment of wastewater is not practiced often and where industrial and municipal sewerage is directly spilled into the water resources, no concerns are shown to assessment of water contamination and its sources. Water pollution by dyes is one of the most crucial environmental concerns that should be given utmost importance in India.

Presence of enormous number of inorganic dyes in the environment poses potentially dangerous consequences and there is great need for the urgent establishment of information that reveals the presence, amount, possible bioaccumulation path way, and conduct of these toxins in the human body. Due to this reason many researchers have published screening reports for environmental waters (Alaton *et al.,* 2002; Arslan & Balcioglu 1999) [2,4]. However, these studies and most of other monitoring programs are limited to the targeted screening of preselected groups of dominantly priority pollutants because of need to eliminate intrusion from co-eluting peaks. To assure sensitivity, tandem mass spectrometry (MS/MS) or selective ion monitoring (SIM) mode are commonly used for analysis of trace organic contaminants. This new class of contaminants in the form of dyes is mostly not considered in monitoring network programs due to scarce knowledge about its occurrence in environment. The textile dye industry is considered to be one of the fast growing industries and has a share in GDP of the country. However, this industry produces tones of effluents concentrated with dyes and there are only few industries in our country that are treating dye effluent before discharging the same in aquatic environment. Although it is recommended that waste water from dye industries should be recycled due high level of contamination in dyeing and finishing process. Most of the dyes are azo dyes that are very highly toxic, carcinogenic and explosive due to the presence of aniline. The azo dyes are considered to be deadly poisons. Sometimes due to the presence of copper and zinc these dyes turn out to be carcinogenic in nature and with formaldehyde they become carcinogenic in nature. The dyes whose structure containing free aromatic amine groups become highly toxic on reduction and cleavage due to the presence of bacterial degradation. These strongly coloured azo compounds are frequently used as dyes known as azo dyes. The one made from phenylamine (aniline) is known as "aniline yellow" may change the properties of water due to following reactions. The exposure to n-Dodecane ($CH_3(CH_2)_{10}CH_3$) any chemical may cause skin and eye irritation. It is suspected that it may be a tumorogenic in mouse (dermal) and other similar tested animals. However, Dodecane (C_{12}-H_{26}) may be toxic to lungs, central nervous system (CNS). Repeated or prolonged exposure to Dodecane can damage target organs. Bis (2-ethylhexyl)phthalate and its isomers has been classified as carcinogen, reproductively hazardous and teratogen by OSHA and effects mainly to gastrointestinal tract, kidney, liver. Ether, m-chlorophenyl p-nitrophenyl is a posinous chemical and has been reported to cause mutation in microorganisms. Exposure to di(2ethylhexyl) adipate may cause dermatitis n humans, damage to rats liver and kidneys

The different dyes that were identified in the samples are shown in Table 5. The dyes having phenolic moiety, containing hydroxyl group as an auxochrome group.

Table 5: Isomers of dyes identified in the dye effluent at four sampling sites.

Dyes	S1 (mg/l)	SII (mg/l)	SIII(mg/l)	SIV(mg/l)
Phenol, 2,4bis(1,1dimethyl ethyl)	0.34	0.273	ND	ND
Pentanoic acid, 5 hydroxy-2,4-di-t-butylphenyl esters	0.287	0.273	ND	ND
9,12 Octadecanoic acid,(z,z)	0.418	ND	ND	ND
Hexanedioic acid, bis(2-ethylhexyl)ester	0.429	ND	ND	ND
Heptacosane	0.124	ND	ND	ND
Tetracosane	0.775	ND	ND	ND
Pentadecane 2 – methyl	0.328	0.289	ND	ND
Dodecanoic acid, 1,2,3- propanetriyl ester	0.897	0.905	ND	ND
Docosane	0.218	0.158	ND	ND
Dibutyl phthalate	ND	0.368	0.274	ND
Octadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	ND	0.749	ND	ND
Octadecanoic acid, 2-3, dihydroxypropyl ester	ND	0.177	ND	ND
1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl)ester	ND	ND	0.451	ND
1,2-Benzenedicarboxylic acid, diisooctyl ester	ND	ND	0.345	ND
Oleic acid	ND	ND	0.119	ND
Trans-13-ocradecenoic acid	ND	ND	0.065	ND
Trimyristin	0.112	ND	ND	ND
Naphthalene, 1 methoxy-4-nitro-	0.527	ND	ND	ND
Pyrazole, 1-methyl-3-(4-nitrophenyl)-	0.138	ND	ND	ND
Benzene, 1-chloro-2-phenoxy-	0.737	ND	ND	ND
[1,1'-biphenyl]-2-ol,3-chloro-	0.154	ND	ND	ND
Benzene, 1-chloro-3-phenoxy-	0.203	ND	ND	ND
Adipic acid, 2-ethylhexyl pentadecyl ester	0. 079	ND	ND	ND

Such auxochromic (-OH) and chromophoric (C=O) group containing compound i.e. 1, 2-Benzenedicarboxylic acid, mono (2-ethylhexyl) ester, dibutyl phthalate (DBP), Naphthalene, 1 methoxy-4-nitro-, Benzene, 1-chloro-3-phenoxy-, Hexanedioic acid, bis(2-ethylhexyl) ester and Dodecanoic acid, 1,2,3- propanetriyl ester has shown wide applications as a polymer additives. It is an excellent UV absorber, which prevents the photo degradability of most of vinyl polymers. The area in which the acid azo dyes and mordent azo dyes formation based on this compound has not been developed except of few patents. The peaks of the dyes were observed at 3745, 346.1, 2923.3, 2854.4, 1583.4, 1445.8, 1227.2, 1178.6 for O-H, O-H, C-H, O=C-H, C=C, C-H, C-O and aromatic stretching. The experimental data suggests a need to implement common objectives, compatible policies and programmes for improvement in the industrial waste water treatment methods. It also suggests a need of consistent, internationally recognized data driven strategy to assess the quality of waste water effluent and generation of international standards for evaluation of contamination levels. The existing situation if mishandled can cause irreparable ecological harm in the long-term well masked by short term economic prosperity in India with special reference to the city of Ludhiana.

It is concluded that around the world as countries are struggling to arrive at an effective regulatory regime to control the discharge of industrial effluents into their ecosystems, Indian economy holds a double edged sword of economic growth and eco-system collapse. The experimental data suggests a need to implement common objectives, compatible policies and programmes for improvement in the industrial waste water treatment methods. The existing situation if mishandled can cause irreparable ecological harm in the long-term well masked by short term economic prosperity in India with special reference to the city of Ludhiana

SUGGESTIONS

To improve the water quality the following mitigative measures may be taken into account.

1. Water conservation technique should be promoted at the workplace. The most important is to monitor the water use by installing water meters throughout the operation.
2. Effluent dilution may help in reducing the water pollution problems to the greater extent. However, it will be better to treat the effluent before it will enter into the Nalla.
3. The promotion of cheap organic dyes obtained from living things can be promoted that will not only reduce water related problems but will decrease the impact on the health of workers and subsequently on the consumers.
4. The production of cheap end products like paints, textiles, printing inks, paper, plastics and food will push dye houses to simply react to local regulations by moving operations to another city.
5. The workers of the textile industry must ensure that the production area is away from the dining area to avoid the exposure of chemicals through air.
6. The assessment of heavy metals in dye effluent, alternative green dyes and bio techniques may improve the water quality and the workers health is needed further in-depth study.

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