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Identification of Dyes in Cloth Dyeing Industry of Jaipur (India) and its Impact on Water Quality

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Abstract: Textile industries considerably contributes to water pollution of adjoining surface water bodies which in turn remarkably alters biological, chemical and physical nature of the water bodies. The analysis of the effluent was carried out by following the standard methods of APHA, 1998. The dyes were identified with the help of Gas Chromotography Mass spectroscopy (GS-MS). The objectives of present study were to assess the major physicochemical parameters like temperature, pH, color, DO, BOD, COD, alkalinity, chloride, hardness, nitrate, phosphate, TS, TDS of the effluents. The present investigation found high level of pollution in the city of Jaipur due to the cloth dyeing industry. The experimental data suggests a need to implement common objectives, compatible policies and programs for improvement in the industrial waste water treatment methods in the city. 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.

Key words: Dye · Pollution, Physicochemical parameters · Treatment · Polices

INTRODUCTION

The textile industry is one of the rapidly growing sectors of Jaipur's economy. It has the capacity to reduce unemployment and labor demands. Its processes are based on chemical reactions in liquid medium, thereby generating large volume of toxic wastewater. Some of the major processes include: Sizing- saturation of mainly hydrophobic wraps by high viscosity macromolecular solution using sizes like starch and desizing- removal of sizes from fabric using strong chemicals such as acids, bases or oxidizing agents [1]. Other important processes include bleaching-treatment of cotton and polyester to achieve a white absorbent fabric that is suitable for dyeing, printing and finishing [1]. The bleaching process uses oxidizing agents like chlorine and hydrogen peroxides. Dyeing and printing are achieved by the use of various types and colour of dye such as azo dyes and sulphur dyes.

Textile finishing wastewater, especially dye effluents contain different classes of organic dyes, chemicals and auxiliaries thus they are colored and have extreme pH, COD and BOD values and they contain different salts, surfactants, heavy metals, mineral oils and others [2]. A composite wastewater from an integrated textile plant consist of following materials *viz.,* starches, dextrin, gums, glucose, waxes, pectin, alcohol, fatty acids, acetic acid, soap, detergents, sodium hydroxide, carbonates, sulfides, sulfites, chlorides, dyes, pigments, carboxy methyl cellulose, gelatin, peroxides, silicon's, fluorocarbons, resins etc. Textile wastewater is known to exhibit strong color, a large amount of suspended solids, high fluctuating pH, high temperature and high COD concentration. The color of reactive dyes is due to the presence of N=N azo bonds and chromophoric groups. The dyes are first absorbed on the cellulose and then on fiber. After fixation of the dyes on the fiber about 10-15% of initial loading is present in the dye bath effluent [3]. Reactive dyes in both ordinary and hydrolyzed form are not easily biodegradable and thus even after treatment;

Color may be present in the effluent. Coloured effluents from dyestuff and textile industries, the major producers and users of azo dyes, not only produce visual pollution but can also be detrimental to life, as they are

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usually resistant to biological treatment. Living organisms generally do not synthesize azo linkages and aromatic sulphonic groups and our knowledge about biodegradation of these compounds in nature is limited [4]. Dyes contain chromophores (delocalized electron systems with conjugated double bonds) and auxochromes (electron-withdrawing or electron-donating substituents that intensify the color of the chromophore by altering the overall energy of the electron system). Usual chromophores are -C=C-, -C=N-, -C=O, -N=N-, $-NO_2$ and quinoid rings, usual auxochromes are $-NH_3$, -COOH, $-SO_3H$ and –OH [5].

A large body data indicates that cloth dying effluent has greater impact on the quality of water. However, no specific work has been carried out in Jaipur district. On this aspect the impact of dye effluent on water quality may vary in this region as people have different life style and rely heavily on synthetic dyes. The aim of the present investigation is to find out the impact of different dyes on the physicochemical parameters and the variability among dyes and their potential use in Jaipur market.

MATERIALS AND METHODS

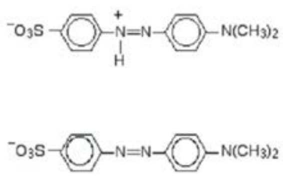
Jaipur is situated in the eastern part of Rajasthan, surrounded on three sides by the rugged Aravali hills. Jaipur is located at 26°55'N 75°49'E (26.92°N 75.82°E). Besides other products Jaipur is famous for cloth dyeing industry. Sober, low toned colors and delicate lines, creating finer designs like the poppy, rose and lotus, usually against a white background, are well known characteristic of fabrics that are printed at Jaipur. The main rivers and tributaries that are source of irrigation and drinking water and in the Jaipur district are *Banas, Banganga, Bandi, Dhund* and *Sabi* which are polluted by the cloth dyeing industries. Different types of dyes from the cloth dyeing industry found their way in this water body and change the quality and quantity of water. All the chemicals used in the study were of analytical grade and procured from Hi Media and Merck. Grab effluent samples from sites were collected in triplicates in pre cleaned plastic cans from CETP, Mandia road, Pali during 2013 and 2014 and were transported and stored at 4°C in accordance with standard procedures [6]. pH, temperature and DO were recorded at the site. Other parameters BOD, COD, hardness, chloride, alkalinity, nitrate, phosphate, TS, TDS were analyzed according to their minimum retention time. The bottles were washed with dilute acid, doubled distilled water and rinsed with effluent prior to sampling. Different cloth dyeing industries were selected for the present study based on random sampling technique and in each unit two sampling sites were studied.

Gas Chromatography-Mass Spectrophotometric (GC-MS) Analysis: Determination of dyes was 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 dyes 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 thickness). Ultra pure helium (99.999%) was used as a carrier gas at a flow rate of 1mL 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.

RESULTS AND DISCUSSION

The physical and chemical properties of Jaipur city were examined in this study and the impact caused by dyes on the properties of water. Results obtained have shown that samples collected from different areas exhibited relatively similar characteristics in terms of their physical and chemical quality. The results have revealed a general decline in the water quality of most of the parameters investigated, due to the dyes present in it.

The pH values of the samples of water ranged from 10.2±0.3 – 10.7±0.4 at sampling Unit III. All the samples in the present investigation showed higher values than the BIS and that of control. According to the [7], high and low pH levels are objectionable because of the corrosive effect on the metallic water receptacles due to low pH. Low pH could result in the metallic taste frequently associated with some packaged water. High pH levels are undesirable since they may impart a bitter taste to the water [7]. pH above 11 cause skin, eye and mucous membrane damages to the consumers. The electrical conductivity of all the samples was very high due to the presence of different ions of dyes that are being added to water by dying industry. The electrical conductivity of water measures the capacity of water to conduct electrical current and it is directly related to the concentration of salts dissolved in water. Methyl orange is an azo dye which exists in two forms depending on the pH and may change the pH of water due to following reactions:



Slightly higher temperature was recorded in all the samples. The high temperature in water may cause irreversible change in the properties of water and is not considered a healthy sign. The increase in temperature in water is due to the presence of dyes of that might have induced different types of exothermic reactions within the water. The high temperature in water effects the biological growth and influences water chemistry. High temperature decreases the solubility of gases in water which is ultimately expressed as high BOD/COD. The values of BOD and COD were within the permissible limits in the present sample in comparison to the very high values of BOD and COD in one effluent study.

The set of identified isomers belonging to different class of dyes are the priority pollutants that can't only change the physicochemical properties of water but may cause health effects to people as well. Among them 1, 2-Benzenedicarboxylic acid, mono (2-ethylhexyl) ester, dibutyl phthalate (DBP), Hexanedioic acid, bis(2-ethylhexyl) ester and Dodecanoic acid, 1,2,3- propanetriyl ester are prominent. Table 4 reveals that all of the sampling sites especially main sewerage drains are highly polluted with phthalate esters, which are due to their widespread use in a large variety of products (Table 4).

The determination of alkalinity provides an idea of the nature of salts present in it. If the alkalinity is equal to hardness, then only calcium and magnesium salts are present. If alkalinity is greater than hardness it indicates the presence of basic salts via Cu^{2+} and Mg^{2+}. When alkalinity is less than hardness, natural salts of calcium and magnesium present that are not carbonates, but sulphates [8]. In this study the alkalinity is due to presence of sulphates. The reason for the alkaline range may be due to mixing up of the alkaline chemicals, soaps and detergents as well [9].

Total dissolved solids of water samples was 3459±9.7, 4124±14.3, 3393±16, 4214±19 and 3735±13.3, 5582±13.2 at sampling site I, II at unit I, II and III, respectively (Table 1, 2 and 3). The concentration of total dissolved solids (TDS) indicated that all the samples of water contained varied concentrations of dissolved

Table 1: Physicochemical Parameters of dye effluent at cloth dyeing unit I.

Parameter	Site I	Site II	BIS Standard
pH	7.9±1	6.2±5	6.8-8.5
Electrical Conductivity (mhos/cm)	9329±3	2987±3.4	---
Temperature °C	49±4.5	40±5	25
Total Alkality (mg/l)	725±12.1	484±8.9	200
Total Hardness (mg/l)	719±8.9	684±9	200
T.D.S (mg/l)	3459±9.7	4124±14.3	500
D.O (mg/l)	3.57±0.1	1.94±0.1	---
B.O.D (mg/l)	210±9	203±10	---
C.O.D (mg/l)	4125±14	1110±10.2	---
Chloride	1556±16	1232±12.3	
Sulphate	453±12	759±12.3	200
Iron	9.32±7	5.18±9.8	0.3
Nitrate	59±12	62±7	45
Free CO_2	200±8.9	205±6.2	---

Table 2: Physicochemical Parameters of dye effluent at dyeing unit II.

Parameter	Site I	Site II	BIS Standard
pH	9.9±0.4	10.6±0.9	6.8-8.5
Electrical Conductivity (mhos)	9835±14	8232±15.3	---
Temperature °C	39±2.1	29±3.2	25
Total Alkality (mg/l)	730±13.4	615±13.2	200
Total Hardness (mg/l)	880±11	742±12.3	200
T.D.S (mg/l)	3393±16	4214±19	500
D.O (mg/l)	3.15±0.5	2.92±0.4	---
B.O.D (mg/l)	155±11	92±14.5	---
C.O.D (mg/l)	1245±13.2	1249±14.2	---
Chloride	1432±14.2	1443±18	250
Sulphate	837±16	733±	200
Iron	7.49±2	4.30±1	0.3
Nitrate	83±9	72±5	45
Free CO_2	182±13.2	182±12.5	---

Table 3: Physicochemical Parameters of dye effluent at dyeing unit III.

Parameter	Site I	Site II	BIS Standard
pH	10.2±0.3	10.7±0.4	6.8-8.5
Electrical Conductivity (mhos)	83914±???	8121±???	---
Temperature °C	58±6	62±5	25
Total Alkality (mg/l)	320±6.8	559±8.2	200
Total Hardness (mg/l)	895±21	99±11	200
T.D.S (mg/l)	3735±13.3	5582±13.2	500
D.O (mg/l)	0.2±0.4	0.7±0.4	---
B.O.D (mg/l)	210±21	208±12.3	---
C.O.D (mg/l)	2321±22.1	2392±18.3	---
Chloride	2115±14.3	2685±11	250
Sulphate	1030±13.2	985±12.2	
Iron	7.5±0.2	7.7±0.1	0.3
Nitrate	106±13.3	43±14.3	45
Free CO_2	292±11	382±11	---

mineral elements for the mineral nutrition of consumers. The source of TDS in water is attributed to natural sources, domestic wastewaters, municipal runoffs and industrial wastewaters. However, apart from that different dyes add the burdens of TDS in the water samples. Water containing TDS concentration below 1000 mg/l is usually

Table 4: Isomers of dyes identified in the dye effluent at four sampling sites.

S. No.	Dyes	S1	S2	S3	S4
1	Phenol, 2,4bis(1,1dimethyl ethyl)	0.34	0.273	ND	ND
2	Pentanoic acid, 5 hydroxy-2,4-di-t-butylphenyl esters	0.287	0.273	ND	ND
3	9,12 Octadecanoic acid,(z,z)	0.418	ND	ND	ND
4	Hexanedioic acid, bis(2-ethylhexyl)ester	0.429	ND	ND	ND
5	Heptacosane	0.124	ND	ND	ND
6	Tetracosane	0.775	ND	ND	ND
7	Pentadecane 2 – methyl	0.328	0.289	ND	ND
8	Dodecanoic acid, 1,2,3- propanetriyl ester	0.897	0.905	ND	ND
9	Docosane	0.218	0.158	ND	ND
10	Dibutyl phthalate	ND	0.368	0.274	ND
11	Octadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	ND	0.749	ND	ND
12	Octadecanoic acid, 2-3, dihydroxypropyl ester	ND	0.177	ND	ND
13	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl)ester	ND	ND	0.**451**	ND
14	1,2-Benzenedicarboxylic acid, diisooctyl ester	ND	ND	0.**345**	ND
15	Oleic acid	ND	ND	0.119	ND
16	Trans-13-ocradecenoic acid	ND	ND	0.065	
17	Trimyristin	0.112	ND	ND	ND
18	Naphthalene, 1 methoxy-4-nitro-	0.527	ND	ND	ND
19	Pyrazole, 1-methyl-3-(4-nitrophenyl)-	0.138	ND	ND	ND
20	Benzene, 1-chloro-2-phenoxy-	0.737	ND	ND	ND
21	[1,1'-biphenyl]-2-ol,3-chloro-	0.154	ND	ND	ND
22	Benzene, 1-chloro-3-phenoxy-	0.203	ND	ND	ND
23	Adipic acid, 2-ethylhexyl pentadecyl ester	0. 079	ND	ND	ND

acceptable to consumers, although acceptability may vary according to circumstances [10]. However, the presence of high levels of TDS in water may be objectionable to consumers owing to the resulting taste and to excessive scaling in water pipes, heaters, boilers and household appliances. Water with extremely low concentrations of TDS may also be unacceptable to consumers because of its flat, insipid taste [10].

Dissolved oxygen of water at sampling site I, II at unit I, II and III, respectively were 3.57±0.1, 1.94±0.1, 3.15±0.5, 2.92±0.4 and 0.2±0.4, 0.7±0.4 (Table 1, 2 and 3). The World Health Organization [11] has not set any permissible limit for dissolved oxygen concentration in drinking water. The oxidation of constituent minerals in water could also have taste and odor problems as well as decreased disinfection efficiency are to be anticipated if the water contains more than 0.2 mg/l of ammonia contributed to low concentration of dissolved oxygen. The low DO reduces water clarity and affects the pH of water body. The dye industry increases the turbidity of water that in turn reduces oxygen of water as it blows the penetration of sunlight.

The presence of chloride in water samples can be attributes to the salts depositions that are used during processing and dying of cloths. The presence of high levels of chloride in water samples may be objectionable to consumers owing to the resulting taste and to excessive scaling in water pipes, heater, boilers and household appliances. The chloride content may add TDS which also indicates that water is polluted [9].

The chloride is a conservative species that generally does not degrade in natural ground water. The amount of CO_2 present in water depends upon the temperature, pressure and mineral contents of water. However, it may be also imparted due to the presence of different dyes in water that release CO_2 when they react with as the case may be the present study.

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. The dyes are undesirable to the environment due to the presence of toxic and carcinogenic substance like benzedrine, naphthalene and other aromatic compounds [12]. Most of the dyes are azo dyes that are very highly toxic, carcinogenic and explosive due to the presence of aniliine. 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 colored 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.

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 programs 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 Jaipur.

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