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Eco-parameter analysis of printed textiles produced in small scale printing units

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Abstract
In the present study printed fabric samples collected from various small scale printing units were tested for some Eco parameters like formaldehyde, heavy metals, pH, and pentachlorophenol and banned amines. Results obtained showed that these fabric samples were not detected for banned amines, pentachlorophenol and some of the heavy metals like Cd, Hg and Ni whereas the level of Ph, formaldehyde and heavy metals like zinc and chromium in all tested printed fabric samples were also within the permissible limit. However the concentration of copper and lead were found higher than the permissible limits as per Oeko-Tex standard.

Keywords: Ecoparameters, textile, banned amines, pentachlorophenol, formaldehyde, heavy metals

Introduction
In line with the changing trends of green consumerism ecological issues are becoming important factors in marketing of consumer goods, including textiles, all over the world. In the recent years, the environmental sensitivity and efforts for the protection of health against environmental hazards have increased significantly.

Textile industry is a very diverse sector in terms of raw materials, processes, products and equipment and has very complex chain. Textile wet processing is an important step in textile production as it adds maximum value to the textiles by improving its aesthetics, comfort and functional properties [1]. The beauty of textile is enhanced by surface ornamentation in fabric. It can be achieved by various methods, of which dyeing and printing are most popular and extensively used.

The processing sector, i.e. dyeing, finishing and printing is dominated by large number of independent, small-scale enterprises [2]. Gujarat, Rajasthan and some areas of Uttar Pradesh, are important centres of ethnic textile printing, having greater demand in the national and international market.

Printing on textiles has started with the use of bio degradable products originated from nature as natural dyes. With the passage of time dyers and printers has given space to brilliant tints created by synthetic dyes, found their use less expensive, mainly due to the ease of process of application, fastness of colour and yield of the desired colour shade even on bulk fabrics[3].

Apart from many synthetic dyes, Indigo sol, Rapid fast and Aniline dyes are the most common dyes that are use by majority of small scale printing units of different printing clusters of India. Yearly tonnes of fabric in vibrant shades and prints are produced by these small scale units which cater Indian mass market for utility products such as bedspreads and casual wear dress materials.

The Rapid Fast colours are stabilized azoic dyestuffs specially prepared for printing. They are applied to the fiber in one operation. When developed under acidic condition, full bright shades are obtained which possess very good fastness properties. Dyestuffs of others groups may be used to supplement the colour range, particularly for greens and blues of indigo sols [4]. Indigosol dyes produce excellent wash and light fastness properties particularly in pale shade [5]. In textile printing, aniline black is used almost exclusively, since in addition to its economical price it also gives a fully bloomy black and possesses good light fastness and wash resistance. Majority of the small scale printing units use the black colour developed bydirect style of printing using aniline hydrochloride, sodium chlorate and copper sulphate is known as (*Syahi*) by the local printers of Pilkhuwa [6]. Whereas it is known as *Chuna Patri* process in Sanganer and Bagru (Rajasthan) when used along with lime *(chuna)* for white and colour resist printing process [7, 8].

Some of the chemicals, acquired through the skin can cause allergic reactions. Prolonged exposure to these chemicals and auxiliaries may cause health problems [9]. Textile materials can be carcinogenic and mutagenic.

Toxicity and mutagenicity cover a wide range of properties and constituents. Heavy metals, formaldehyde, banned amines of them. Considering the interaction of textiles with the human skin, the past decade has been marked by a growing interest on the characteristic of textile products**.** Determination of eco parameters of textile materials is very important not only for the safety of the workers exposed during the production and finishing process of these textiles but also for the end consumers.

So the present study was plan to analyse the printed fabrics with commonly used dyes in small scale printing clusters for eco-parameters.

Methods and materials

In the present work 12 printed samples were collected from different small scales printing units around Pilkhuwa (U.P.). These samples were printed with rapid fast, Indigo sol, Aniline hydrochloride (*Syahi* or *Patri)* and Pigment dyes.

Fabric

All the samples were printed on bleached and mercerized casement fabric (plain weave) on same types of fabric with following properties

Fabric count (warp x weft) 27x30
Fabric weight, GSM 150
Fabric thickness (mm) 0.62

Table 1: Different types of dyes used for printing

Printed sample	Dye used
1.	Rapid fast colour and aniline black
2.	Rapid fast green
3.	Pigment blue
4.	Indigo sol colour and aniline black
5.	Indigo sol and rapid fast
6.	Aniline black (*Syahi)*
7.	Rapid fast red
8.	Rapid fast green
9.	Pigment orange
10.	Indigo sol purple
11.	Indigo sol sea green *(Firozi)*
12.	Indigo sol blue

Fig 1: Different printed samples for Eco analysis

Data analyses

The values were expressed as means of the measurements. Comparisons of the printed samples were made by employing one way ANOVA using Window SAS version 12.0.

Results

Printed samples were tested for eco logical parameters in order to get a clear picture about the particular recepie of printing responsible for deviation in the tested ecological properties i.e. analysis banned amines, pH content, free formaldehyde, released formaldehyde, concentration of PCP (Pentachlorophenol) and heavy metals.

Table 2: Permissible limits in textiles for different Eco parameters [10, 11]

S.No	Parameters	Baby cloth	In direct contact with skin	Not in direct contact with skin	Decorative Materials
1.	pH	4.0-7.5	4.0-7.5	4.0-9.0	4.0-9.0
2.	Free /Release Formaldehyde(mg/kg)	20	75	250	300
3.	Pentachlorophenol(mg/kg)	0.05	0.5	0.5	0.5
4.	**Heavy metals**				
	Cd	0.1	0.1	0.1	.1
	Cr	1.0	2.0	2.0	2.0
	Co	1.0	4.0	4.0	4.0
	Cu	25.0	50	50	50
	Hg	.02	.02	.02	.02
	Ni	1	4.0	4.0	4.0
	Pb	0.2	1.0	1.0	1.0
	Zn	5.0	-	-	-

Analysis of banned amines

In the present study, presence of harmful amines in printed fabrics were also analysed which are carcinogenic and banned in India. As per the Indian regulations, since 1993 the manufacturing, processing, storage, consumption and sale of Benzidine based dyes are banned and a corresponding ban was also enforced in 1997 on the use of Azodyes, which are carcinogenic when used in textile fabrics [12]. German test method-35 LMBG was used for detection of banned amines in the printed samples and permissible limit is 5 mg/kg. HPTLC (High Performance Thin Layer Liquid Chromatography) was used for taking the reading. The amines tested includes,4-Aminodiphenyl, Benzidine, 4-Chloro-o-toluidine, 2-Naphthylamine, O-Amino azotoluene**,** 2-Amino-4-nitrotoluene**,** p-chloroaniline**,** 2, 4-Diaminoanisole**,** 4, 4'-Diamino diphenylmethane**,** 3, 3'-

Dichloro Benzidine**,** 3, 3'-Dimethoxy Benzidine**,** 3, 3'-Dimethyl-4,4'-diamino-diphenyl methane**,** p-cresidine**,** 4, 4'-Methylene-bis (2-chloro-aniline)**,** 4, 4'-Oxydianiline**,** 4, 4'-Thiodianiline**,** O-Toluidine**,** 2, 4-Diamino toluene**,** 2, 4, 5-Trimethlaniline. All printed samples, were not detected for aromatic amines. The results shows that all printed samples are safe with respect to this parameter.

Analysis of pH content

Test method which was used for detection of pH level in the printed samples was AATCC 81-1974 and permissible limit is 4.0-9.0pH meter was used for taking the values. The results depicting pH content of the printed samples are given in Table 3.

Table 3: pH of various printed samples

S. No	pH
Sample 1.	4.11±.073
Sample 2.	5.91±.314
Sample 3.	6.03±.414
Sample 4.	6.38±.048
Sample 5.	5.82±.489
Sample 6.	3.89±.074
Sample 7.	8.84±.071
Sample 8.	8.73±.205
Sample 9.	5.07±.041
Sample 10.	4.18±.022
Sample 11.	3.96±.097
Sample 12.	4.15±.098

It is apparent from data that pH content in most of the printed samples are within the permissible range but the samples printed 6 & 11 show slight deviation from the permissible range of pH.

Sample 6 printed with aniline hydrochloride *(Patri)* show slight acidic nature i.e. 3.89. The acidic nature of the sample is may be due to the presence of HCl traces remains in the sample which is continuously formed during the oxidation reaction in the fabric while printing with aniline hydrochloride (*Patri*). Sample 11 printed with indigo sol dye also reported with slight acidic content i.e. 3.96, it might be due to post treatment of printed fabric in acidic solutions for the development of colours.

Determination of released Formaldehyde

The presence of free formaldehyde in the fabric sample were analysed using test method was based on draft international standards ISO/DIS 141841, which corresponds to Japanese method specified in Japanese Law No.112 of 1973 or DIN 54260. This method was used for determining the aggregate amount of free formaldehyde extracted from a textile sample in water bath at 40^{o}C with a spectrophotometer

Released formaldehyde is the amount of formaldehyde released under the condition of accelerated storage from textiles in any form. A weighed fabric specimen is suspended over water in a sealed jar. The jar is placed in an incubator at a controlled temperature for a specified length of time. The amount of formaldehyde absorbed by the water is then determined calorimetrically [13].

Table 4: Free and released Formaldehyde content in the printed samples

S.No	Free formaldehyde	Released formaldehyde
Sample1	5.07± 0.269	2.90±0.075
Sample2	4.35±0.128	1.36±0.174
Sample3	7.25±0.110	-
Sample4	48.20±2.18	0.91±0.035
Sample5	11.96±0.305	0.72±0.061
Sample6	2.36±0.069	0.63±0.035
Sample7	14.50±0.157	5.44±0.069
Sample8	7.97±0.419	1.90±0.134
Sample9	19.21±0.518	6.71±0.113
Sample10	1.81±0.064	1.27±0.105
Sample11	3.08±0.063	1.81±0.074
Sample12	5.44±0.176	3.26±0.144

Formaldehyde is released by some textile finishes, such as that conferring crease resistance. These finishes are most likely to be used on fabrics that otherwise crease easily, such as cotton or wool. Formaldehyde is an irritant that may cause health issues to the workers who are exposed to it either by inhaling or by direct contact with the printing process. These problems may range from simple eye irritation, dermatological problems or may lead to severe chronic diseases [14, 15]. The content of free and released formaldehyde were found to be within permissible limit in all the printed samples.

Determination of PCP (Pentachlorophenol)

Pentachlorophenol (PCP) is a group of polychlorinated compounds used as preservatives for cellulosic material specially cotton, wood and also leather to protect against the attack of moulds, fungus and bacteria [16]. PCP is toxic to human and the environment, in particular to aquatic life [17]. Determination of PCP (Pentachlorophenol) in the printed samples was done by using test method solvent extraction (ISO 971:1983) and permissible limit is 0.5, HPTLC (High Performance Thin Layer Liquid Chromatography) was used for taking the values. All the tested samples were not detected for the presence of pentachlorophenol.

Analysis of Heavy metals

The assessment of metal content in textile goods is also important for textile industry, because many elements contribute to problems during processing of textiles. AAS (Atomic Absorption Spectrometer) was used for determination of heavy metals in different printed samples. Data in table 4 clearly showed mercury was not detected in any of the printed samples, whereas a few samples were detected for the presence of cobalt, cadmium and nickel. The amount of nickel was in permissible limits for all the detected samples whereas the amount of Cadmium was quite high i.e. 0.12 in the sample (11) printed with indigo sol dye as compared to the permissible limit. Chromium was also detected in some of the printed samples, whereas in sample1, 3 & 4 printed with rapid fast and pigment is found in quite high concentration i.e., 3.70, 2.22 & 2.02.

The traces of copper in all the samples were found to be in permissible range except the sample 1, 3 & 6 where the concentration of copper is far beyond the permissible range i.e. 954.5, 121.12 & 980 mg/kg respectively. These samples were printed with Aniline hydrochloride in combination with rapid fast and aniline only.

The concentration of lead was also reported in all the samples except sample 3. It was reported in a quite high concentration in sample 1 printed with rapid fast and aniline (*Patri)* i.e. 4.22 followed by sample 6 printed with aniline (*Patri)* i.e. 3.32. The concentration of lead was detected slightly high from the permissible limits in sample 2, 7, 8 printed with rapid fast colour i.e. 2.16, 2.64 & 2.28 respectively. Samples printed with Indigo sol dye (11, 12) also detected for lead traces i.e. 2.22 and 2.10 mg/kg respectively. Similar results were also reported in a study where, the concentration of copper and lead were found 975.80 mg/kg and 2.64 mg/kg respectively in white discharge printed sample (*Chuna Patri* process) of Sanganer (Rajasthan) done with aniline hydrochloride [18].

Table 5: Heavy metals content in the printed fabric

Heavy metals (mg/kg)	Test results of printed samples						
	Cadmium, Cd	**Cobalt, Co**	**Copper, Cu**	**Chromium, Cr**	**Lead Pb**	**Mercury, Hg**	**Nickel, Ni**
Sample 1	-	-	954.5±1.34	3.70±.1	4.22±.083	-	-
Sample 2	-	-	7.10±.252	1.00±.104	2.16±.050	-	-
Sample 3	-	-	121.12±.937	2.22±.060	-	-	-
Sample 4	-	1.84±.882	22.44±.882	2.02±.080	0.90±.049	-	-
Sample 5	-	-	2.24±.137	0.58±.033	1.48±.043	-	-
Sample 6	-	-	980±2	0.50±.023	3.32±.141	-	-
Sample 7	-	-	2.72±.052	-	2.64±.130	-	-
Sample 8	-	-	27.68±.116	-	2.28±.073	-	0.56±.016
Sample 9	-	-	1.38±.047	-	2.34±.042	-	2.36±.08
Sample 10	0.06±.023	-	1.56±.048	-	1.92±.042	-	4.64±.04
Sample 11	0.12±.014	-	1.96±.172	-	2.22±.076	-	-
Sample 12	0.04±.013	-	0.42±.01	-	2.10±.029	-	-

Conclusion

The results of the Eco test of different printed samples, it was found that banned amines, pentachlorophenol and mercury were not detected in the printed samples, whereas the content of cobalt, nickel, cadmium, chromium, free and released formaldehyde were reported under the permissible limits. The amounts of lead were found in slight high concentration, whereas the amount of copper in aniline printed sample was found very high from the prescribed permissible limits as per Oeko-Tex.

Therefore there is a scope to substitute, or optimize these printing recepies to make it less hazardous for safe handling to the workers, consumers and as for the environment. It is the need of hours to produce and promote textile products with low environmental impact. There are number of different dyes also been used by different printing clusters such similar studies can also be carried out to introspect the products and practises in terms of ecological standards to produce and promote and environment safe or friendly products in the global market.

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