Health & Environmental Hazards of Synthetic Dyes

By:
Prof. R. B. Chavan

Health and Environmental Hazards of Synthetic Dyes

By: Prof. R. B. Chavan

Synthetic Dyes find use in a wide range of industries but are of primary importance to textile manufacturing. Wastewater from the textile industry can contain a variety of polluting substances including dyes. The environmental and subsequent health effects of dyes released in textile industry wastewater are becoming subject to scientific scrutiny. Environmental legislations are being imposed to control the release of dyes, in particular azo-based compounds, into the environment. Wastewater from the textile industry is a complex mixture of many polluting substances ranging from organochlorine-based pesticides to heavy metals associated with dyes and the dyeing process. During textile processing, inefficiencies in dyeing result in large amounts of the dyestuff being directly lost to the wastewater; which ultimately finds its way into the environment. Colorants that enter the wastewater streams normally pass through a wastewater treatment plant where they are eliminated to a large degree by adsorption on sludge. The extent to which residual amounts reach the surface waters depends on the efficiency of treatment processes. Low concentrations of dyes in waste water do not normally pose any significant environmental hazard. Environmental problems arise mainly from inefficient removal of dyes or disposing the untreated dye effluent to water receiving bodies. This is normally the case in most developing countries. Though stringent environmental legislations do exist in most of the countries, the will to implement these legislations faithfully is needed to overcome the human health and environmental hazards of synthetic dyes.

Dyes are an important class of synthetic organic compounds used in many industries, especially textiles. Over 100,000 commercially available dyes exist and more than 7x1 05 m tonnes of dyestuff are produced annually of which 56% are textile dyes, 23.5% pigments, 14% dyes for paper and 6.5% others. Due to large scale production and extensive application, synthetic dyes have become the source industrial health and environmental hazards during their synthesis and later during fibre dyeing. During the textile dyeing process, depending on the class of the dye, its loss in wastewaters could vary from 2% for basic dyes to as high as 50% for reactive dyes, leading to severe contamination of surface and ground waters in the vicinity of dyeing industries. The traditional textile finishing industry consumes about 100 L of water to process about 1 kg of textile materials thus The textile industry is one of the greatest generators of liquid effluent pollutants due to the high quantities of water used in the dyeing processes. It is estimated that 280,000 tons of textile dyes are discharged in textile industrial effluent every year Effluents from the textile industries containing dyes are highly colored and are therefore visually identifiable. Thus Color is usually the first contaminant to be recognized in wastewater which gives a straight forward indication of water being polluted. Discharges of these highly colored effluents can damage directly the receiving waters with serious impact on environment and human health. In recent years, interest in environmental control of dyes has increased, due to their possible toxicity and carcinogenicity; this is because many dyes are comprised of known carcinogens, such as benzidine and other aromatic compounds.

Government legislations are becoming more and more stringent, especially in more developed countries, regarding the removal of dyes from industrial effluents. Over the last decade, azo dyes that could breakdown to carcinogenic aromatic amines have been largely phased out in Europe. The present paper critically reviews some to the health and environmental hazards associated with the synthetic dyes.

HEALTH HAZARDS OF SYNTHETIC DYES

The dye on a finished garment, by its nature, is chemically stable - that's what makes a dye color fast. However, research is emerging that examines the short and long term effects of potential skin absorption of dye and finishing chemicals through clothing. The CNN report October 2007 revealed that new testing procedures (chemical burden testing) reveal that young babies and children actually do have increased levels of chemicals in their bloodstream and skin. Because clothing comes into prolonged contact with one's skin, toxic chemicals are often absorbed into the skin, especially when one's body is warm and skin pores have opened to allow perspiration. Some individuals have what is known as chemical sensitivity, including when exposed to garments of many types. Symptoms in adults for chemical sensitivity range from skin rashes, headaches, trouble concentrating, nausea, diarrhea, fatigue, muscle and joint pain, dizziness, difficulty breathing, irregular heartbeat, and/or seizures. Symptoms in children include red cheeks and ears, dark circles under the eyes, hyperactivity, and behavior or learning problems. In extreme cases some dyes also show health hazards leading to cancer.

Human toxicity of textile dyes can be considered in terms of acute toxicity and chronic or genotoxicity.

Acute Toxicity of Textile Dyes

Acute toxicity involves oral ingestion and inhalation; the main problems of acute toxicity with textile dyes are skin irritation and skin sensitization, caused mainly by reactive dyes for cotton and viscose, few acid dyes for polyamide fibers and disperse dyes for polyester, polyamide and acetate rayon.

Reactive dyes

Reactive dyes can cause problems in plant workers involved in the manufacture the dyes and textile workers who handle the dyes in the dyeing process. There is evidence that some reactive dyes cause contact dermatitis, allergic conjunctivitis, rhinitis, occupational asthma or other allergic reactions in such workers. The problem is caused by the ability of reactive dyes to combine with human serum albumin (HSA) to give a dye-HSA conjugate, which acts as an antigen.

A list of reactive dyes that have caused respiratory or skin sensitization in workers on occupational exposure has been compiled by ETAD (Table 1).

In order to minimize the risk of exposure to these dyes, dye dust should be avoided. This may be achieved by using liquid dyes, low dusting formulations and by using the appropriate personal protective equipment.

Table 1: Reactive dyes classified as respiratory/skin sensitizers

	C I Name
Yellow dyes	Reactive Yellow 25, Reactive Yellow 39, Reactive Yellow 175
Orange dyes	Reactive Orange 4, Reactive Orange 12, Reactive Orange 14, Reactive Orange 16, Reactive Orange 64, Reactive Orange 67 Reactive Orange 86, Reactive Orange 91
Red dyes	Reactive Red 29, Reactive Red 65, Reactive Red 66, Reactive Red 123, Reactive Red 219, Reactive Red 225
Violet dye	Reactive Violet 33
Blue dyes	Reactive Blue 114, Reactive Blue 205
Black dye	Reactive Black 5

After dyeing and fixation, reactive dyes have completely different toxicologiyal properties because the reactive group is no longer present and the high wash fastness of the dyed fabric ensures that no dye is exposed to the skin of the wearer. Consequently, no cases of allergic reactions have been reported by consumers wearing textiles dyed with reactive dyes.

Disperse dyes

Certain disperse dyes have been implicated in causing allergic reactions, particularly when they are used for skintight, close-fitting clothes made from synthetic fibers. Disperse dyes, showing low perspiration fastness, are responsible for this effect. Polyester dyed with disperse dyes does not in general pose a problem since the perspiration fastness is high. However, problems can arise with polyamide or acetate rayon dyed with disperse dyes since the low perspiration fastness allows the dyes to migrate to the skin.

Indeed, in the 1980s, some severe cases of allergic reactions were reported relating to stockings made of polyamide and, in the 1990s, to leggings made of acetate rayon.

Table 2: Sensitizing Disperse dyes

Dye	C I Number	Dye Type
Blue dyes	Disperse Blue 1 Disperse Blue 3 Disperse Blue 7 Disperse Blue 35 Disperse Blue 106 Disperse Blue 124	Aq
Orange dyes	Disperse Orange 1 Disperse Orange 3 Disperse Orange 37	Azo
Red dyes	Disperse Red1 Disperse Red 17 Disperse Red 15	Azo AQ
Yellow dyes	Disperse Yellow 1 Disperse Yellow 9 Disperse Yellow 3 Disperse Yellow 39, Disperse Yellow 49	Nitro Azo Methine

Because of these allergic reactions, the German Federal Institute for Consumer Protection and Veterinary Medicine evaluated the available literature and concluded that the disperse dyes listed in Table 2 represent a health risk to consumers and should cease to be used for dyeing.

Currently, there is no legal prohibition on these dyes in any country but some organizations, such as the International Association for Research and Testing in the Field of Textile Ecology, which bestows eco-labels on environmentally and toxicologically proven textiles, refuses eco-labels for some dyes (Oeko-Tex, 2000).

CHRONIC OR GENO-TOXICITY OF DIFFERENT DYE INTERMEDIATES AND DYE CLASSES

Genotoxicity is the major long-term potential health hazard of certain textile dyes. This became apparent when a high incidence of bladder cancer was observed in plant workers involved in the manufacture of particular dyes during the period 1930-1960. The specific compounds involved were fuchsine, auramine, benzidine and 2-naphthylamine. Strict regulations concerning the handling of all known carcinogens have been imposed in most industrial countries, which have caused virtually all dye companies to cease production of these compounds.

Genotoxicity of dye intermediates

Close study of the dyes has revealed that carcinogenicity is linked to specific types of dye intermediates or metabolites (decomposition product), such as benzidines. Whaley examined many dyes for evidence of hazardous nature, based on their molecular structure. Of 1,460 dyes examined, the structures were found or known for 585 dyes, or approximately 40 percent of the total. Based on an assessment of likely formation of degradation products on reduction, 55 percent of these known dyes were predicted to be hazardous, and 13 percent were predicted to be uncertain in terms of safety.

Since 1984, a concerted research effort has been made to develop dyes based on safer intermediates.

The old intermediates were adopted many years ago before development of the numerous tests now available to determine environmental effects. Responsible dye manufacturers have eliminated offending colors from their product lines; however, the widespread use of apparently harmful dyes indicates the need for the dyer to be vigilant when selecting dyes and to use care in handling all dyes.

Genotoxicity of different dye classes

Azodyes

Azo dyes are by far the most important class of dye, accounting for over 50% of the world annual production. Not surprisingly, toxicity of azo dyes has been studied extensively. As early as 1895 increased rates in bladder cancer were observed in workers involved in dye manufacturing. Since that time, many studies have been conducted showing the toxic potential of azo dyes. The carcinogen may be the dye itself, or it may be a metabolite of the dye. For water-insoluble, but solvent-soluble dyes, such as solvent dyes and disperse dyes, the dye is normally the carcinogen. For water-soluble dyes, it is a metabolite (decomposition product) of the dye which is the carcinogen. Water soluble azo dyes are conveniently divided into two types:

1. Those which are capable of generating a carcinogenic metabolite, and
2. Those that are not.

The workers who developed bladder cancer from handling dyes based on benzidine or 2-naphthylamine got the disease not from the dyes themselves, but from the benzidine and 2naphthylamine metabolites.

There are two main ways to circumvent the carcinogenicity of such dyes. The first way is to use non-carcinogenic analogues of the amines in question, such as benzidine or its derivatives. For example, in C.I. Direct Black 171 uses a non-carcinogenic aromatic benimidazol diamine instead of benzidine.

The second way to avoid carcinogenicity is to ensure that all possible metabolites of the dye are water-soluble. An excellent example of this principle is C I food Black 2.

Carcinogenic Amines

In Germany, bladder cancer is recognized as an occupational disease for textile workers.

Some dyes have the potential to release an aromatic amine that is known to be a rodent carcinogen upon metabolism in an organism and this has prompted some authorities to conclude that such dyes should be considered to be carcinogenic.

This knowledge is the reason for the recommendation of the German MAK Kommission to handle the dyes in the same way as the amines which can be released under reducing conditions. Subsequently, the German, Dutch and Austrian authorities prohibited the use of such dyes in some consumer articles. Such, dyes may not be used for textile, leather or other articles which have the potential for coming into direct and prolonged contact with human skin, e.g. clothing, bedding, bracelets, baby napkins, towels, wigs etc. The ban, which is across the EU, and other countries also covers the import and marketing of the above-mentioned articles dyed with these dyes. Table 3 lists the amines that are classified as carcinogenic and are formed through cleavage of azo bonds of the azo dyes.

Table 3: Carcinogenic aromatic amines defined by German MAK Kommission

Sr.	**C I Name**	**Category of Carcinogen***
1	4-Aminobiphenyl	1
2	Benzidine	1
3	4-Chloro-o-toluidine	1
4	2-Naphthylamine	1
5	4-Aminoazobenzene	2
6	o-aminoazotoluene	2
7	6-methoxy-m-toluidine	-
8	o-Anisidine	2
9	p-Chloroaniline	2

10	5-nitro-o-toluidine	3
11	4,4' - Diaminodiphenylmethane	2
12	3,3'- Dicholobenzidine	2
13	3,3' -Dimethoxybenzidine	2
14	3,3' Dimethylbenzedine	2
15	4,4' methylenedi-o-toluidine	2
16	3,3'-dichlorobenzidine	2
17	4,4'-methylene-bis-[2-chloroaniline]	2
18	4,4'-Oxydianiline	2
19	4,4'- Thiodianiline	2
20	o-Toluidine	2
21	4-methyl-m-phenylenediamine	2
22	2,4,5- Trimethylaniline	2

Category:
1 Proven human carcinogen,
2 Proven animal carcinogen,
3 Suspected animal carcinogen
Source: ETAD Information No.6, 'German ban of use of certain azo compounds in some consumer goods, revised version', Bas/e. (1998).

A list of azo dyes which, upon reduction of the azo group would form the aromatic amines shown in Table 4 has been compiled by ETAD. The list includes more than 500 azo dyes, of which at least 142 are still available on the world market.

Mechanism of azo cleavage

It is suggested that the fabric dyed with dyes which release the carcinogenic amine (Table 4) when comes in close contact with human body are leached out from the fabric due to human perspiration (These dyes usually have low perspiration fastness) The leached out dye gets transferred into body metabolism through skin pores. After intake into the human body these azo compounds may be cleaved by means of reduction during body metabolism and then form the corresponding aromatic amines from which they had been synthesized. Intestinal bacteria are capable of azo cleavage; the liver also produces corresponding reductive enzymes. Furthermore, there are indications from experiments that azo cleavage may also take place during skin passage and that skin bacteria are capable of cleaving azodyes.

Measures adopted

Ban applying to azo dyes in textiles, leather goods and similar consumer products entered into force in Germany, Netherlands and France during 1996. Subsequently it was adopted within the frame work of European Commission Restriction Directive for harmonized rules on azo dyes in consumer goods. In 1998 the German ban also included pigments containing azo group that can degrade to carcinogenic arylamines. The German ban also established test methods. The test results must be confirmed by two of the four test methods specified. Forbidden arylamine may not be present in higher concentration than 30 mg/kg (30 ppm).

The risk repre6ented by the dyes, have also received attention in dye producer countries, Hong Kong, China, India and Turkey. In 1996 the Indian Government notified that a proposed ban on the manufacture, sale and use of 74 azo dyes found to be carcinogenic. The ban was partially a consequence of the bans in Europe. The Indian Government claimed that the ban will also protect domestic consumers from exposure to hazardous dyes. The use of 42 benzidine dyes in textile and leather has been prohibited in India since February 1, 1993.

The ban on suspected azo dyes also exists in USA and Canada. The eco labels of various countries have also prohibited the use of identified carcinogenic azo dyes. As a result of these efforts most of the dyestuff manufacturing counties voluntarily stopped the manufacture of suspected azo dyes and the problem of the use of these dyes is presently supposed to be non-existent.

Anthraquinone dyes

Anthraquinone dyes have declined in importance, primarily, because they have low cost effectiveness due to low color strength and relatively expensive manufacturing cost. Consequently, they have been studied less extensively than azo dyes. However, structure-activity relationships in anthraquinone dyes appear to follow a similar trend to those in azodyes.

Thus, anthraquinone dyes of the solvent or disperse class containing one or more primary amino- or methylaminogroups tend to be mutagenic or carcinogenic.

Cationic dyes

Some cationic dyes such as fuchsine, auramine along with benzidine and 2-naphthylamine, were implicated in the high incidence of bladder cancer in the textile industry between 1930 and 1960. Further cationic dyes have been found to be carcinogenic, such as the triphenylmethane dyes c.1. Basic Violet 49 and C.I. Basic Red 9 and several fluorescent red dyes, such as Pyronine B are mutagenic.

NATURAL DYES

Natural dyes does not always mean safe. In fact the toxicological properties of synthetic dyes are very well tested scientifically and safety data sheets are available for each dye. Similar study in case of natural dyes is not available. Many of the natural dyes are quite safe but few are toxic. Example of logwood is given for illustration.

Logwood, for example, is a natural dye, capable of producing a range of colors such as violets, blue-greys, and the best natural black, depending on the mordant used. However, the- active ingredients, hematein and hematoxylin, are toxic when inhaled, absorbed through the skin, or ingested. As much care should be taken with this natural dye as with any of the harmful synthetic dyes.

Dangers of Mordants

Most natural dyes are not particularly toxic in themselves, but a mordant is invariably required for development of shade and dye fixation. Typically, a mordant is a heavy metal salt of aluminum, iron, copper, and chromium and tin. Alum and ferrous sulphate are relatively safe mordants compared to copper and chromium. However, still they have to be used carefully. The fatal dose of alum is 30 grams for an adult; the fatal dose for a child is, of course, far less, depending on body weight, perhaps as little as 3 grams. Iron is toxic in overdose according to the United States FDA, but it will not harm the environment when disposed off. Tin and copper mordants have to be used with care. Chrome mordant is toxic and has both human and environment toxicity. It is a known human carcinogen. Chrome can produce very bright yellows, but it is not worth the risk of cancer, other illnesses, and even death. Many eco labels have fixed the optimum limits for these mordants particularly copper (50 ppm), tin and chromium (2 ppm) to be released in the environment.

ENVIRONMENTAL HAZARDS OF DYES

The environmental hazards of dyes are mainly associated with the water pollution. Each year the global textile industry discharges 40,000 - 50,000 tons dye and more than 200,000 tons of salt into receiving water bodies. One of the most pressing issues today is the lack of fresh drinking water, and as one of the most polluting industries, textiles - and especially the dyeing of textiles - is responsible for making fresh water undrinkable. In the worst cases, communities have to use polluted water to drink, wash clothes, bathe and irrigate crops and the toxins they're exposed to can have catastrophic effects. Even in those instances where water treatment is in place, toxic sludge is a byproduct of the process. Often sludge is sent to the landfills, as result the toxic chemicals present in sludge percolate polluting ground water sources.

In countries where people depend on the waterway to provide drinking water and water for daily usage, like cooking and bathing, the polluted water can increase their risk of contracting various diseases. The polluted water can also kill fishes and other aquatic life in the water body. This has implications for the people living downstream, they will find their fish catches decreasing dramatically, affecting their livelihoods and nutrition. In spite of stringent environmental legislations, various incidences are reported related to serious water pollution due to dyes. In southern China in 2007, The Wall Street Journal reported that a Textiles Mill was illegally dumping close to 22,000 tons worth of untreated waste water into a nearby river, turning the river dark red. To make things worse, China's textile industry uses not only the usual heavy metals and carcinogens, but organic materials like starch. When introduced into a water body, the aerobic breakdown of these compounds removed all the oxygen out of the river, killing fish and other aquatic life. The reason for the illegal dumping was that the textiles Mill was attempting to cut costs by eliminating the treatment of waste water.

In Mexico, fields and rivers near jeans factories are turning dark blue from untreated, unregulated dye effluent. Factories dyeing denims dump waste-water contaminated with synthetic indigo straight into the environment. Local residents and farmers report health problems and wonder if the food they are obliged to grow in nearby fields is safe to eat.

These toxic chemicals from dye effluents can also make their way under the ground to pollute groundwater sources and can remain under the ground for long period. Pollution of groundwater sources that have affected water supply is already clear in India. A 2004 survey of pollution in Pali in Rajasthan and Tirpur in South India found that there was major groundwater pollution that resulted in the contamination of wells tapping groundwater.

Effect on photosynthetic activity

Industrial effluents containing synthetic dyes reduce light penetration in receiving water bodies and thus affect the photosynthetic activities of aquatic flora, thereby badly affecting the food source of aquatic organisms. The thin layer of discharged dyes formed over the surface of a receiving water body also decreases the amount of dissolved oxygen in the water, thereby affecting the aquatic fauna. Furthermore, dye-containing effluents increase biochemical oxygen demand of the contaminated water.

Aesthetics

Many dyes are visible in water at concentrations as low as 1 mg L-1.

Thus, apart from affecting the health of plants and animals, synthetic dyes are also undesirable in water bodies from aesthetic point of view.

ENVIRONMENTAL TOXICITY OF DYES AND DYEING AUXILIARIES

- Dyes themselves
- Auxiliaries contained in the dye formulation
- Basic chemicals (e.g. alkali, salts, reducing and oxidizing agents)
- Auxiliaries used in dyeing processes
- Contaminants present on the fiber when it enters the process sequence (e.g. residues of pesticides on wool, cotton and spin finishes on synthetic fibers)

In this section the water pollution due to dyes and auxiliaries contained in the dye formulation is discussed.

Dyes

Spent dye baths after exhaust dyeing, residual dye liquors in pad dyeing and water from washing operations always contain a percentage of unfixed dye. The extent of dye of fixation varies considerably among the different classes of dyes and may be especially low for reactive dyes in the case of cotton. Moreover, large variations are found even within a given class of colorants. As a consequence of incomplete fixation a percentage of the dyestuff used in the process ends up in the waste water.

As a consequence of incomplete fixation a percentage of the dyestuff used in the process ends up in the waste water.

Aquatic Toxicity

Dyes, especially, cause public concern as even small concentrations (l mg/l) are visible in the environment. Toxicity is determined by carrying out tests on animals (usually rats) to ascertain the single oral dose of dye that will kill 50% of the population in 14 days. The results are expressed in mg/kg of body weight, and are known as lethal dose (50) or LD50. On the basis of these tests, toxicity grading of 4461 dyes belonging to different dye classes is made by Barkclay and Buckley.

Aquatic toxicity is also expressed as LC50 (measured in mg/l) which gives the concentration of a chemical that causes 50% of an experimental population of fish to die during 48 hours. Table 6 gives the results of a study carried out by ETAD on 3 000 commonly used dyes.

Table 4: Toxicity grading of dyes

$LD50_{mg/kg}$	Classification	No. of dyes	% Dyes
<25	Very poisonous		
25 to 200	Poisonous	44	1
200 to 2000	Harmful	314	7
>2000	Not classified	4103	92
Total		4461	100

Source: Barclay S and Buckley C, Waste Minimization guide for the textile industry: A step towards cleaner production, Appendix 3.10, Dyes and Environment, January 2000, Desai C, 'Ecological and toxicological properties of dyes', Colourage, 39(12), (1992),51 -4.

Table 5: Fish Toxicity levels of common dyes

LC_{50} (mg/l)	% of dyes
<1	2
1 to 1 0	1
10 to 100	27
100t0500	31
>500	28

Source: Barclay S and Buckley C Waste Minimization guide for the textile industry: A step towards cleaner production, Appendix 3.10, Dyes and Environment, January 2000, Desai C, 'Ecological and toxicological properties of dyes', Colourage, 39(12), (1992), 51-4.

It is difficult to assess the aquatic toxicity in terms of structure as a simple change in the position of substituents can alter the toxicity.

Brown and Anliker summarized the effects of textile effluent on the environment and the toxicity with respect to fish and other aquatic organisms, sewage bacteria and plants. They concluded that due to the vast number of different dyestuffs and processes in which they can be applied, an accurate environmental risk assessment can only be made on individual dyestuffs and in individual dye-houses.

Biodegradability

Dyes are stable against breakdown by many microorganisms and most dyes do not biodegrade under the aerobic biological treatments, in a municipal sewage plant. Many dyes, including the azo dyes, degrade under anaerobic conditions and the aromatic amines thus formed have been found to degrade further aerobically. Therefore, the aerobic conditions of rivers and lakes should degrade the amines formed from the biodegradation of azo dyes if they accumulate in the river sediments. Due to this recalcitrant nature of dyestuffs under aerobic processes, concern arose as to the toxicity of these compounds towards the microorganisms. A screening method for determining the inhibitory effect of the dyestuffs on aerobic bacteria was developed by ETAD.

Tests were performed on 202 dyestuffs and the results reported as the 50% Inhibition Concentration (IC50) values. Dyes from the direct, disperse, reactive, vat, mordant, pigment, acid and solvent ranges gave IC50 values greater than 100 mg/I thus indicating that they had no toxic effect towards the micro-organisms at the concentration expected in textile effluents. However, dyes belonging to the cationic (basic) range gave IC50 values of less than 100 mg/l, which is in agreement with the results obtained by Ogawa et al. that basic dyes are inhibitory to micro-organisms.

From these tests, and the general experience of ETAD, it was concluded that although dyes may cause concern at sewage works due to their color, there should be no concern as to their toxicity. The exception to this ruling is the benzidine-based dyes, the manufacture of which is prohibited by ETAD members.

Bioelimination

Some dyes are adsorbed 40% to 80% by the biomass. Of 87 dyes studied, 62% had significant color removal due to sorption. This is referred to as bio-elimination. With acid dyes, their high solubility causes low adsorption and this is based on the number of sulfonic acid groups. Reactive dyes also show little adsorption, but this however, is not dependent on the sulfonated groups or ease of hydrolysis; Direct and basic dyes show high adsorption and disperse dyes show high to medium adsorption.

AOX Emission

Other key issues related to water pollution due to dyes are AOX (Adsorbable Organic Halogen) emissions and presence of metal in the dye molecule.

Dyestuffs containing organically bound halogens (except fluorine) are measured as AOX. Vat, disperse and reactive dyes are more likely to contain halogens in their molecule.

The content of organically bound halogen can be up to 12 % on weight for some vat dyes. Vat dyes, however, usually show a very high degree of fixation. In addition, they are insoluble in water and the amount that reaches the effluent can be eliminated with high efficiency in the waste water treatment plant through absorption on the activated sludge.

On the contrary, reactive dyes have low fixation (the lowest level of fixation is observed with phthalocyanine based reactive dyes) and their removal from waste water is difficult because of the low biodegradability and/or low level of adsorption of the dye onto activated sludge during treatment. The halogen in MCT (monochlorotriazine) reactive groups is converted into the harmless chloride during the dyeing process; it is therefore assumed that the MCT reactive groups react completely by fixation or hydrolysis so that they do not contribute to AOX emissions. However, many commonly used poly-halogenated reactive dyes, such as DCT (dichlorotriazine), DFCP (diflourochloropyrimidine) and TCP (trichloropyrimidine) and bi-functional reactive dyes contain organically bound halogen even after fixation and hydrolysis. Bound halogen is also found in discharges of dye concentrates (pad dyeing, dye kitchen) and non-exhausted dye baths that may still contain un-reacted dyestuff.

For the other classes of colorants the AOX issue is not relevant because, with few exceptions, halogen content is usually below 0.1 % Strict limits are set by the EU- Eco-label and German legislation. Extensive investigation of AOX in textile effluents was performed, but AOX as an indicator remains a matter of discussion.

It should be noted that AOX from dyes do not have the same effect as the AOX derived from chlorine reactions (haloform reaction, in particular) arising from textile processes such as chlorine bleaching and wool shrink-resist treatments, etc. Dyestuffs are not biodegradable compounds and the halogens in their molecule should not give rise the haloform reaction (main cause of hazardous AOX)

Heavy metal emission

Metals can be present in dyes for two reasons. First, metals are used as catalysts during the manufacture of some dyes and can be present as impurities. Second, in some dyes the metal is chelated with the dye molecule, forming an integral structural element.

The limits of discharge for heavy metals are stringent as they can be toxic to animals and aquatic life. Metal complex dyes contain chelated chromium, cobalt, copper and nickel. Some cationic dyes contain zinc and trace concentrations of mercury, cadmium and arsenic can be present as impurities from intermediates.

ETAD has established limits in the content of heavy metal in dyestuffs. The values have been set to ensure that emission levels from a 2 % dyeing and a total dilution of the dye of 1:2500, will meet the known waste water requirements.

Examples of dyes containing bound metals are copper and nickel in phthalocyanine groups, copper in blue copper azo-complex reactive dyes and chromium in metal complex dyes used for wool silk and polyamide. Since the metal is an integral part of the dye molecule, which is itself non-biodegradable, there is very little potential for it to become bio-available.

AUXILIARIES CONTAINED IN DYE FORMULATIONS

Depending on the dye class and the application method employed (e.g. batch or continuous dyeing) different additives such as dispersants, salts, powder binding agents, anti-foaming agents, anti-freezing agents, thickeners, buffer systems etc. are present in the dye formulations. Since these substances are not absorbed/ fixed on the fibers, they are completely discharged in the waste water.

While these additives are not toxic to aquatic life, they are in general poorly biodegradable and not readily bio eliminable. Other not readily eliminable additives are acrylate and CMC-based thickeners and anti-foam agents.

The difference between liquid and powder formulations should also be mentioned. Dyes supplied in liquid form contain only one third of the amount of dispersing agent normally contained in powder dyes. The reason for this difference stems from the manufacturing process of powder dyes: the very small particles generated during grinding must be protected during the subsequent drying process and this is possible only by adding high proportions of dispersing agents.

CONCLUSION

The identification of human health and environmental hazards are important prerequisites for risk and life cycle assessment. Not surprisingly, the authorities, scientists, and general public are taking an increasingly active role in the debate about the risk potential of the production of dyes, and the: risks of exposure to dyes. Certain dyes can trigger allergies in some individuals; however, finding a universal solution to this problem is difficult. Any replacement of dye whether "natural" or "synthetic", may affect yet other individuals. Some of the raw materials and intermediates required for the synthesis of dyes are more toxic than the final dyes produced. Inevitably, therefore, these raw materials are potentially hazardous, and that must be minimized by appropriate precautions during production.

The primary route by which dye enters the environment from dye manufacturers and dye houses is through the production of wastewater, and also through the disposal of sludge containing dyes precipitated from the effluent by flocculation. A prerequisite for a colorant to enter the environment is its solubility. Colorants that enter the wastewater streams normally pass through a wastewater treatment plant where they are eliminated to a large degree by adsorption on sludge. The extent to which residual amounts reach the surface waters depends on the efficiency of treatment processes. The fate of dyes adsorbed to sludge is generally incineration or disposal in a controlled landfill. However, it should not be forgotten that low concentrations, that is more than 10 ppm of colorant in receiving waters, can cause visible coloration and may raise public concern, although the low concentrations involved do not normally pose any significant environmental hazard. Environmental problems arise mainly from inefficient removal of dyes or disposing the untreated dye effluent to water receiving bodies. This is normally the case in most developing countries. Though stringent environmental legislations do exist in most of the countries, the will to implement these legislations faithfully is needed to overcome the human health and environmental hazards of synthetic dyes.

This article was originally published in the Textile Review magazine, May, 2013 issue, published by Saket Project Limited, Ahmedabad.

About the Author:

Prof. R. B. Chavan is associated with the Institute of Tech. for Textile, Garment and Fashion Design at the University of Bahir Dar, Bahir Dar, Ethiopia.