



Environmental hazard in textile dyeing wastewater from local textile industry

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Abstract Colorants and chemicals used in the textile coloration process are required to meet the fashion demands; however these introduced serious environmental hazards that are mainly resulted in effluent loading, containing the toxic, carcinogenic, and mutagenic substances, to natural environment. Textile dyeing process and the rinsing of dyed fabric utilize a variety of substances including dyes/ pigment, fixing agent, surfactants, leveling agent, mordant, salts etc. However, all these substances are not fully consumed in the process, and a residual content remains in the dyeing effluent. This review observes the challenges to environment posed by the dyes and chemicals present in spent dye bath, progress in possible remedies in dyeing wastewater treatment including the nanotechnology; and particularly discusses the studies based on the dyeing effluent samples collected from the local textile processing industries. There are obvious case studies made in different regions, using the process wastewater from the local textile dyeing and processing industries, confirming the need for research and innovation to replace or control the hazardous dyes and chemicals in conventional dyeing process and making the resulting effluent more environment-friendly. Moreover, the cleaner production practices and environmental standards are introduced in

improving the textile dyeing process. Selection of dyes and chemicals, use of best available techniques, and wastewater treatment technologies can significantly improve the textile dyeing to become an environment-friendly process.

Keywords Dyes · Chemicals · Textile dyeing · Environmental · Effluent · Textile industry

Introduction

Water and environment are two significant life-supporting and energy providing resources on earth planet. Depletion and deterioration in these natural reserves, as a result of textile processing, are indeed undesirable for environment. An increasing level of world population, with an elevating amount of textile product consumption per person, indicates more dyes and chemicals are used in producing them. The amount of clothes bought per person has increased 40% in EU during 1996–2012 indicated by EEA (European Environment Agency) (Nikolina 2019). Textile dyeing is an important process in textile industry, particularly in developing countries, that consumes million tons of water and discharge enormous amount of polluted water containing used dyestuff and chemicals, hazardous vapors and gaseous emission. Moreover there may be chemical species

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released during the processing, service life or at the end-of-life of finished dyed product.

This review introduces how the environment of earth planet is experiencing the undesired effects from textile dyeing operations occurring in textile processing industry with reference to dyeing; and discusses the challenges related to the dyeing process. The large variety of dyes, pigment, chemicals, and processing methods associated with the textile dyeing, coupled with the large number of small and medium dyeing units locating in developing regions require an increased interest to overcome the process and effluent hazard. There are obvious studies, based on the textile process and dyeing wastewater, indicating the toxicity and hazard present. There is significant lacking in the control for exercising environment-friendly material and processing techniques resulting in real challenges to earth environment.

An important aspect of this review is the discussion based on real studies addressing the particular process on-ground in local textile processing industries. The pollutant content and the hazard aspects are presented through the selected studies conducted using the water samples from the process industries or from the processing sites.

The materials and methods used in the treatment of textile industry wastewater are fairly large. It is a major subject area of research and development in terms of efficiency, basic and regeneration cost, operational ease, and time etc. The wastewater treatment uses chemical, physical, and biological methods.

The regulatory seriousness for restricting the substances or chemicals found carcinogenic (cancer-causing), mutagenic (producing genetic mutation) or toxic for reproduction (CMR) was observed recently. The European Union set 24-month transition period for controlling the 33 chemicals classified CMR (Mowbray 2021). The regulation for the identified CMR chemicals was set out in entry 72 of Annex XVII to REACH (Registration, Evaluation, Authorization and Restriction of Chemicals). The CMR substances include formaldehyde, heavy metals (extractable) and benzene, Phthalates, Chromium VI (extractable), and Disperse Dyes (Anonymous 2021a).

There are several environment-friendly standards known to offer prevention of hazardous effects and waste production. For example, Oeko-Tex^R is the known label for the textiles tested for harmful

substances, and Oeko-Tex Standard 100 emphasized the testing method development for harmful substances including heavy metals, toxic dyes, crop protection substances, and carcinogenic substances including formaldehyde, phenols, or pesticide in testing article (Nemčić 2017; Rongqi 2004a). Heavy metals on textiles can be determined through extraction, or incineration. Oeko Tex Standard 100 determines the content of heavy metal in textile extraction bath; it does not assess the heavy metal content on textiles (Rongqi 2000b).

In recent times, the trend in practicing the eco-labeling (for example Oeko-Tex Standards) has received an increasing interest in several countries including Pakistan, Turkey, China and Italy, where large number of textile dyeing industries are operating. The selection of dyestuff and chemicals, use of best available technique, and efficient wastewater treatment technology (Fig. 1) can turn the textile dyeing as an environment friendly process.

Environmental challenges

In Europe and most advanced countries, in particular, and around the world at large, fashion is main driving force supported by a variety of colorful textiles, and clothing products that were dyed or printed at different part of region. Collection released by European apparel companies per year has increased from two in 2000 to five in 2011 (Nikolina 2019). However, there may be companies offering higher number of collection than the possible average, for example Zara offering 24 new clothing collections each year, and H & M reaching between 12 to 16.

Importantly, apparel market, largely driven by the young and fashion loving people, has supported the

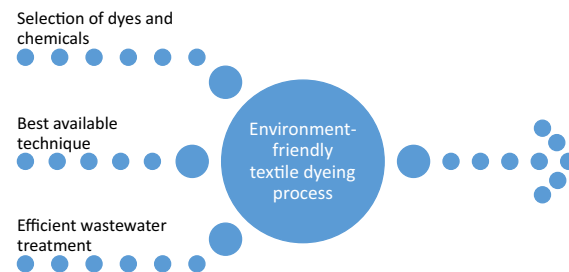


Fig. 1 Major factors in the achievement of an environment-friendly dyeing textile process

consumption of textile dyes. Dyes are source of providing beautiful color to fashion apparel, home textiles, interior furnishing, and technical textiles. A report has indicated the textile dyes market, worldwide, valued at USD 6.38 billion in 2018 will move through CAGR of 5.7%; reaching to USD 10.13 billion by 2026 (Anonymous 2019b). The important fibers to be dyed include cotton, viscose, wool, nylon, polyester, acrylic, and the main dye types used include direct, reactive, vat, basic, acid, disperse dyestuffs.

Textile dyeing industry depends on using the synthetic colorants and large variety of chemicals to facilitate the dyeing process. The beautiful color produced by dyes and pigments provide the core attraction in producing fabric, furnishing, and apparel for business. However, environment is the most suffering part of the situation. The environment is exposed to a number of pollutants as a result of textile dyeing. Dyes and polymers are not easy to biodegrade, and require an increased BOD. Therefore, the substances including dyes and fluorescent brighteners, fibers, polymeric chemical, polyacrylate sizes, synthetic polymer finishes etc., posed an environment challenge (Chakraborty 2010). There are substances with medium BOD and difficult to biodegrade including wool grease, PVA sizes, starch ethers and esters, spin finish oil, surfactants (branched anionics), anionic and non-ionic softeners.

The wastewater coming from textile processing industry are generally observed to have high pH value, an increased concentration of suspended solids, chlorides, nitrates, metals like manganese, sodium, lead, copper, chromium, iron, and high BOD and COD value (Pal 2017).

Another pollutant source in textile dyeing effluent is represented by the total dissolve solid (TDS). Textile processing and dyeing utilize various salts including common salt and Glauber salt that increase the total dissolve solid in wastewater. The presence of TDS in wastewater may change the osmotic balance resulting in swelling or dehydration in aquatic organisms. Taste and color is also changed by the presence of TDS. An increasing salt content in wastewater is undesired and turn it not useful for domestic, industrial and agricultural purposes (Kumar and Saravanan 2017).

Textile dyeing process assimilates relatively multiple facets in exposing the natural environment to a number of harmful substances, ranging from the

synthesis of dye till the application of dyestuff to fiber (Fig. 2). The various materials including metals, contaminated water, hazardous and toxic gases etc. can be released to environment from synthetic dye manufacturing till the usage of dyed and finished textile product.

An important ready-made garment (RMG) producer, Bangladesh experienced significant increase in effluent discharge with the growth of RMG industry. In around a decade development time, country is the 12th largest garment-manufacturing nation with 77% of country's foreign exchange earnings and 50% employment to industrial work force (Islam et al. 2011).

The immediate impact of hazardous effluent discharge includes contamination in groundwater and water bodies, reduction in dissolved oxygen in water, and reduced quality of aquatic eco-system. A significant rise in the effluent discharge can be seen in the last five year time. An increased dyeing of fabric meters means more wastewater entering to natural environment. In 2016, textile industries in Bangladesh produced 1.80 metric tons of fabric with the associated effluent loading of 217 million cubic meter of wastewater. The wastewater production was estimated to reach 346 million cubic meters in 2021 with the production of 2.91 metric tons of fabric; if the textile industries continue to use the same conventional practices (Hossain et al. 2018).

It is therefore obviously important to have coherent practicing standards to mitigate the hazardous effects of synthetic dyes, dyeing process, effluent discharge and dyed finished product. Understanding and working for the cleaner production, and sustainable development goals has obvious gains in terms of finance and the environment protection (Gelaldo et al. 2019; Dawson 2012).

Environmental hazard in textile dyeing industry

The environmental hazard coming from the textile dyeing industry is mainly based in three types of materials including colorants (dye or pigment), chemicals used, solid content (metal, microfiber, etc.) contributing in the generation of reduced quality of water. The processing conditions used in dyeing may influences variation in pollutants generated.

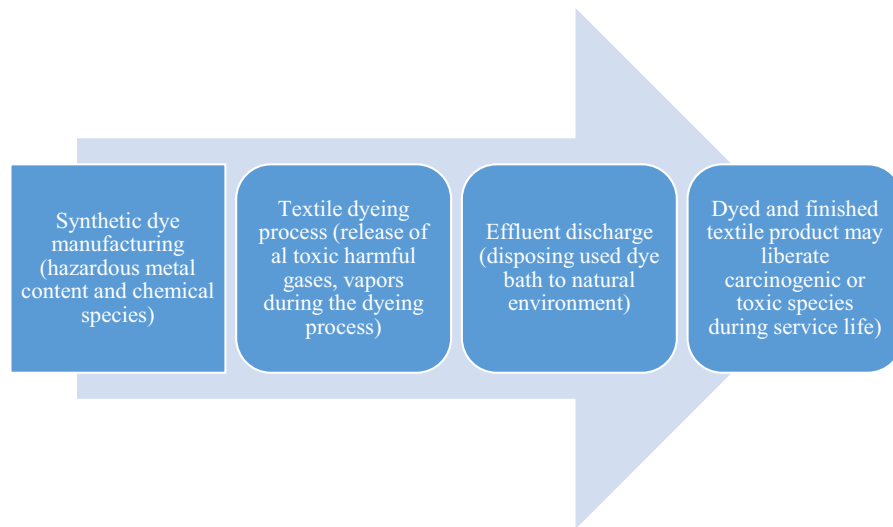


Fig. 2 The possible sources of hazardous effects to environment associated with textile dyeing

Generally, the studies addressing the evaluation of dyeing wastewater cover the following three aspects:

- i. An evaluation of the concentration of carbon-based compounds. The determination of organic content provide the relative strength of wastewater (in terms of Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), and some studies include Oil and Grease (O&G) content.
- ii. Measuring the concentration of particulate solids that was dissolved or suspended in wastewater. It may include Total Solids (TS), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), and Total Volatile Solids (TVS).
- iii. Determination of metal content.

The dyeing industry wastewater is of ‘high strength’ relative to household wastewater. Typical limiting values showing the strength levels of

domestic wastewater may be represented in Table 1 (Kiepper 2020).

BOD indirectly indicates the concentration of organic matters in wastewater. BOD is showing the sufficient oxygen if available, then aerobic biological decomposition by microorganisms will continue until all waste is consumed. Aerobic biological decomposition is mainly time based, and the BOD test may be called BOD₅, as it is measuring the dissolved oxygen, the sample is held in dark at 20 °C, at the beginning and end of a five-day period. The change in dissolved oxygen amount over five days will show the “oxygen demand” for respiration by the aerobic biological microorganisms.

The wastewater may be reported in either milligrams per liter (mg/L) or parts per million (ppm). These units are equal and interchangeable.

Chemical Oxygen Demand (COD) is not an alternative to BOD. It is based on using a chemical (for example, potassium dichromate in a 50% sulfuric acid

Table 1 Typical limiting concentrations of organics in untreated wastewater (Kiepper 2020)

S.no	Component	Limiting Concentration (mg/ L)		
		Low	Medium	High
1	BOD	110	190	350
2	COD	250	430	800
3	TOC (total organic carbon)	80	140	260
4	Oil and Grease	50	90	100

solution) to oxidize organic (predominate), and inorganic substances in a wastewater sample. COD values for a wastewater sample are higher relative to BOD since it includes both organic and inorganic matters.

In total organic carbon (TOC) test, the time consumption is relatively low, i.e. it is a speedy test and takes 5–10 min. A carbon analyzer instrument is used. The organic carbon is converted to carbon dioxide (CO₂) and typically measured with an infrared analyzer.

Testing for the toxicity of the dyeing effluent for particular specie is generally not significant in the studies. Perhaps using physicochemical tests, the toxicity for living specie is tedious. In a study when different organisms were used including bacteria (*Zoogloea ramigera* and coliform-*Escherichia coli* bacteria), algae (*Chlorella vulgaris*), fish (*lepis-tes-Poecilia reticulata*) and protozoan (*Vorticella campanula*) to represent four tropic levels. The toxicity test results were compared with chemical analyses to identify the pollutants responsible for the toxicity in the effluent. Toxicity of the effluents could not be explained by using physicochemical analyses in the above four cases (Sponza 2006). The study of the toxic effect of dyeing effluent on particular specie is an important area of further research.

Where textile dyeing is the main operation, the material content in dyeing wastewater is mainly dependent upon the dye/ pigment type used. The dye type used can be range over basic, reactive, anthraquinone, disperse, acidic, azo, diazo, and metal-complex dyes (Benkhaya 2017). The textile materials can be dyed as fiber, yarn, fabric, or as garment. These substrates may be processed through the methods including direct dyeing; stock dyeing; top dyeing; yarn dyeing; piece dyeing; solution pigmentation or dope dyeing; garment dyeing etc.

The accompanying chemicals used in dyeing process are for the requirements of dye- solubility or dispersion, and fixation to fiber. Therefore, preventing the use of substances hazardous to environment is specific to the dyeing process. For example, if sodium sulfate in dyeing process, and sulfuric acid in neutralization process are used; the resulting effluent may exceeds the sulfate content to 1700 mg/ L. However, the high sulfate content in effluent can be prevented if sodium sulfate is replaced by NaCl in the dyeing process, and sulfuric acid is replaced by HCl or CO₂ in the neutralization process (Tufekci et al. 2007). Such

replacement of chemicals is possible when the alternative reagents, in this case NaCl and HCl, are producing the chemical (halogen) content within the standard acceptable limits. Researching the alternative substances that are more environment- friendly is possible. However, it requires the evaluation of some process feasibility concerns to meet cost- effectiveness, ease of process, and product performance.

Heavy metal (copper, arsenic, lead, cadmium, mercury, nickel or cobalt) content and microfiber are the other important concerns received the study interest of environment- hazard introduced by the wastewater from textile dyeing industry. Heavy metal refers to any metallic chemical element having a relatively high density and is toxic or poisonous at low concentrations.

(Anonymous 2021c). Other metallic elements including calcium, iron; and silica can be present in dyeing effluent (Gomathi et al. 2017). Un-destroyed testing or finding the heavy metal content that is in the bound structure of dye (metal complex dye) present on the fiber is an important research topic to assess dyed fiber hazard. Primarily, there are two methods for determining heavy metal residuals on textiles: extraction and incineration. The Oeko Tex Standard 100 refers to the content of heavy metal in textile extraction bath, not the heavy metal content on textiles (Rongqi 2000b).

Metal content may appear in the garment in other than dye form that can be harmful. For example, European Chemical Agency (ECHA) identified the harmful chemical as the Substances of Very High Concern (SVHC). The content of SVHC in textile product cannot exceed 0.1% of the total product weight. The weight of metal used in garment zipper is counted 0.1%. Nickel and its alloy are conventionally used in garment as zipper and metal marks. Nickel alloys may introduce adverse effects to human skin, immunity, and cardiovascular system (Anonymous 2021d).

The dyeing effluent may contain the undesired heavy metals (Latha et al. 2020). Study of the textile dyeing and finishing effluent sample collected from eight textile mills have shown the presence of the heavy metals including Cupper (Cu), Chromium (Cr), Cadmium (Cd), Iron (Fe), Lead (Pb), Nickel (Ni), and Zinc (Zn) (Bhardwaj et al. 2014). The eight effluent samples analyzed were containing the heavy metal in range of: Cupper (Cu) between 0.17 and 0.28 mg/l,

Chromium (Cr) 0.11 mg/l to 0.21 mg/l, Iron (Fe) 0.39 mg/l to 0.90 mg/l, Lead (Pb) 0.02–0.10 mg/l, Nickel (Ni) 0.11–0.22 mg/l, Zinc (Zn) 0.11–0.51 mg/l, and Cadmium (Cd) determined 0.01 mg/l only in two samples.

Another study that based on collecting the effluent samples from handloom dyeing industries has shown significant presence of heavy metal content. The research was based on arranging 34 samples of handloom-dyeing effluent from different textile industries of Madhabdi (Bangladesh). The analysis showed the presence of heavy metals iron (Fe), zinc (Zn), copper (Cu), chromium (Cr), manganese (Mn), lead (Pb), and cadmium (Cd). Average concentrations of Fe, Cr, Cu, Pb, Mn, and Zn were 3.81, 1.35, 1.70, 0.17, 0.75, and 0.73 mg L⁻¹, respectively. Cadmium content was below the detectable limit of the atomic adsorption spectrophotometer. The concentrations of Fe, Cr, Cu, Pb, and Mn exceeded the industrial effluent discharge standards (IEDS) for inland surface water and irrigation water guideline values (Nahar et al. 2018). Similar metals, however in smaller content, were found in the effluent samples collected from different textile and garment industries for the study of heavy metals concentration in Bhaluka Industrial Area, Mymensingh, Bangladesh (Sarkeri et al. 2015).

Importantly, the consumption of polluted water containing the heavy metals by cows resulted in milk that was polluted with the content of toxic heavy metals. The chain of polluted water movement in the environment can ultimately transfer the heavy metal in human. The study has demonstrated the textile industry effluent by the cows, and presence of heavy metals in the milk of cows that were drinking the effluent. The water samples were collected from the textile factory treatment ponds and Tikur Wuha River at different sampling site (Muluken 2014). Similarly, fresh milk samples were collected from 15 cows drinking the water from textile treatment pond water and Tikur Wuha River, Chafe and 15 cows from Dato, relatively far from textile industry. Metal content in both water and milk samples were determined using Atomic Absorption Spectrophotometer after wet digestion. The water samples were collected from four sites and analyzed. The result showed metal concentrations, in water samples collected from sites S1, S2, S3 and S4, as 0.72, 0.652, 0.121 and 0.12 mg L⁻¹, respectively for lead; the respective concentrations were 0.135, 0.05, 0.124 and 0.132 mg L⁻¹ for nickel; and for

cadmium these were 0.023, 0.01, 0.014 and 0.02 mg L⁻¹. The cows were feed with the polluted water at two places Chafe, and Dato (Ethiopia). The metal contamination in cow milk was observed, at Chafe, for Pb, Ni, Cd and Cr as 0.8, 1.6, 0.2 and 0.2 mg L⁻¹ respectively; the milk sample, taken from cows at Dato village, showed the said metal content as 0.4, 1.4, 0.1 and 0.8 mg L⁻¹ in the same order.

The variety of dye and pigment used in industry is large. Around 10,000 different dyes and pigments are used in industry. More than 7×10^5 tons of synthetic dyes are produced each year in the world. Mainly depending upon the dye and fiber type and the process employed for the dyeing. The level of dye mass fixed in fiber can vary, however, generally significant amount of dye is left in used dye-bath. Therefore, up to 200,000 tons of these dyes are lost to effluents every year, indicating inefficiency in industrial dye process (Chequer et al. 2013).

Azo type dyes provide the largest variety and quantity used reaching to 60–70% of all organic dyes produced in the world. The larger presence of azo dyes is attributed to their ease and cost effectiveness for production relative to natural dyes, structural diversity, high molar extinction coefficient, acceptable fastness properties.

The structure of dyestuff may have constituent, element or metal content that may be hazardous depending upon how they come in contact with the living species. For example 40% of dyes and pigments used globally comprise chlorine, a known carcinogen, in organic structure (Khan and Malik 2014). Moreover, heavy metals in textile industry effluent are not biodegradable. Untreated or incompletely treated effluent to aquatic life and terrestrial life resulting in damaging the dietary plant and species, and ecosystem.

Next to heavy metal, another important toxic substance is microfiber. Heavy metals and microfibers are two distinct toxic pollutants in effluent. Restricting these two substances can significantly reduce toxicity of dyeing industry wastewater. Microfiber and microplastics can be released, from natural and synthetic fibers, during the dyeing, and after-washing process.

Microplastics (MPs) can be defined as plastic particles smaller than 5 mm in length, and are derived from a wide range of sources including synthetic fiber from clothing, polymer manufacturing and processing

industries etc. Cotton is the main natural fiber used, and main synthetic fibers consumed are polyester, polyamide, acrylic and polyolefin. Wastewater released from wastewater treatment plants may contain microplastics, and microfiber. Microplastics and microfibers can be ingested by the fish, aquatic species and wildlife; and subsequently became the part of human consumption. Wastewater treatment plant (WWTP) can remove significant amount of microplastics, and microfiber, however the removal is incomplete, and some content was found to remain in wastewater following the treatment (Xia et al. 2018).

A typical textile industry WWTP with 30,000 tons of daily treatment capacity was sampled for microfibers at different stages of the treatment process. The concentration of microfibers found was 334.1 (± 24.3) items/ liter in influent, and reducing to 16.3 (± 1.2) items/ liter in the final effluent (reduction of 95.1%). However, with this large reduction, WWTP of this textile industry was releasing 4.89×10^8 microfibers including microplastic fibers and non-microplastic fibers into the environment.

Possibly, the incomplete removal of microfibers, following the treatment of textile process and dyeing wastewater, is an important concern. The wastewater treatment plant can reduce the large fraction of microfiber pollutants, the remaining microfiber become hazardous since the textile processing and dyeing industries releasing huge volume of effluent. It was found in the study that the microfiber concentration in textile printing and dyeing wastewater was as high as 54,100 MFs/ L. The wastewater treatment processes were removing microfibers by 85%. However, the residual average microfiber concentration in the effluents from the centralized WWTPs of the industrial park was 537.5 MFs/ L, leading to 430 billion microfiber items per day (Hongjie et al. 2020). Textile wastewater is significantly a major source of releasing microfiber in environment relative to the municipal sewage treatment plants.

Importantly, the textile clothing article used in a house is equally dangerous in releasing the microfibers. The study of wastewater, released from the washings of clothing articles use by a house of 4 people, showed the magnificent presence of microfibers. An emission of 18,000,000 synthetic microfibers was determined for a reference load of 6 kg of synthetic fibers. The main content of studied microfibers was 40% for the size range of 100 and 500 μm ,

and 53% were between 50 and 100 μm (Galvão et al. 2020).

Therefore, the toxicity of dyeing wastewater remains an important area of further study to save environment. An evaluation of hazard for a dyestuff during its application for human body is difficult to determine, since it will require long-term exposure study, and technique to understand how the particular dye type is influencing the human body organ.

The hazard effect from a substance can be related with the continuous contact or exposure to the following facets (Ahmed et al. 1998):

- Substances including adhesives, dyestuff, solvents, cleaning agents used at work
- Generation of fumes, vapor, volatiles etc.,
- Natural dust, and
- Harmful bacteria, micro-organisms, virus etc.

A substance may be called hazardous or harmful to human body when the contact, inhalation or exposure to the substance is observed in terms of any of the following effect:

- Skin contact to the substance showing irritation or dermatitis;
- Asthma;
- Toxic fumes inhalation resulting in loss of consciousness;
- Cancer; and
- Virus or biological Infection.

Refer to a particular dyestuff type, studies are required to assess the powder form, and paste form of the dyestuff to ascertain a hazardous effect. However, it may be indicated that presently significant research and development work is known that indirectly demonstrated the presence of environmental hazard from the textile dyeing process, and the significant need for effluent treatment (Pereira 2012; Kant 2012).

Possibly, an important aspect that has not received significant research interest is relating the toxicity effect of textile process wastewater on specific living specie there. The study of effects of wastewater consumption by living species, and plants are more useful in showing the hazard. However, the process wastewater that contains variety of dyes, and substances will require the precise analysis to relate the toxic effect with particular pollutant. The influence of chemical oxygen demand on wastewater toxicity was indicated to be established for an individual textile

dyeing wastewater treatment plant (Jieying et al. 2018). The determination of lethal concentration for selected pollutant can be an important parameter to assess the toxicity of textile process wastewater (Mountassir et al. 2013).

Chemicals and dyes used in textile dyeing

Dyeing is one of the water-intensive processing areas in textile industry. The total amount of chemicals consumed in textile mills may range over 10% to 100% on weight of the fabric. The textile industry is also known as one of the major waste water producers to environment. It was indicated that on an average 160 kg of water were required to produce 1 kg of textile product in conventional textile processing unit (Uddin 2014a). The percentage estimation for the consumption of water in textile fabric processing includes bleaching- 38%, dyeing- 16%, printing- 8%, boiler- 14%, other uses- 24% (Sheikh 2009).

Therefore, the dyeing and printing are two main water-consuming processes in textile industry. An averaged sized textile mill with dyeing and printing facility may produce around 8000 kg of fabric per day with water consumption of about 1.6 million liters. Specific water consumption for dyeing can be from 30 to 50 L per kg of fabric depending on the process. For yarn dyeing, the overall water consumption is about 60 L per kg of yarn. Dyeing section contributes to 15–20% of the total wastewater flow coming from the textile industry (Kant 2012).

Following the dyeing or printing process, the dyed fabric generally requires washing. Washing soaps and chemicals are used in washing to remove the unfixed dyestuff. Large varieties of chemicals that may be consumed in textile dyeing are shown in Table 2 (Anonymous 2020e). Moreover, water is used in cleaning the printing machines to remove loose color paste from printing blankets, printing screens and dyeing tanks. Therefore, the industrial water pollution is indicated to significantly coming from textile dyeing and printing (estimated to 17–20%).

The amount of dyes, pigment, and chemicals used in particular coloring process may vary over a significant range depending upon the dye, and fabric type, level of color depth, application technique, processing conditions, dye-fixation, washing and drying stages in the process. In a conventional textile

industry, the approximated consumption of such reagents may be indicated in Table 3 (Kant 2012).

Environmental hazard: Example studies

India, Pakistan, and Bangladesh are the three important regions that are fulfilling the fashion demands through dyeing and printing for the textile world with state of the art dyeing and printing textile units. The dyeing and printing industries in these regions are using the dyes and chemicals with significant need to understand how these processes can be really made more-friendly to environment and terrestrial lives.

An important area of limiting the wastewater to save natural environment and living species is the study of wastewater released from the industry. Such studies directly provide know-how for the pollutants, and the possible replacement guide for using an increased environment-friendly substance and processing technique. This section is therefore, introduces the studies that were based on collecting the wastewater from various textile processing industries, and determining the pollutant parameters.

Such real case studies generally contain variety of dye types and substances. Therefore, the pollutants parameters cannot be attributed to particular type of dyestuff, or chemical substance. There are some studies based on using simulated dye-containing water that may be useful in relating the pollutant parameter to particular dye type. For example, in the screening of selected dyestuffs; CI Direct Blue 1 and Direct Red 79 were found to contain carcinogenic aromatic amines. The said dyestuffs may be substituted by Direct Blend Blue D-QL and Direct Blend Red D-6R respectively. The substituted dyestuffs were not containing the 24 banned carcinogenic aromatic amines, and showed good levelness (Sun et al. 2011).

The various forms of environment hazard observed in the textile dyeing industry were represented in terms of BOD, COD, dissolved solid, heavy metals, alkalinity, suspended solids, color species etc. Taking an example from Bangladesh, over 40,000 m³/day textile effluents, and 26,000 pollution load (BODs kg/day) are discharged by these industries in Bangladesh (Islam MR and Mostafa 2018). The environmental parameters set for effluents exceeded the standard limits. The pollutants found were dissolved solids (DS), suspended solids (SS), and colored compounds,

Table 2 Important types of chemicals used in conventional textile dyeing industry worldwide (Anonymous 2020e)

S.no	Chemical Type
1	Basic Chemicals Soda ash Hydrochloric Hydrogen peroxide Sulphuric Acid Acetic Acid Formic acid Caustic soda (basic agent)
2	Washing agent Soaping agent Various compositions provided by the commercial producers
3	Salt Common salt Glauber salt
4	Detergent and Scouring agent Various composition provided by the commercial producers
5	Levelling agent Various composition provided by the commercial producers
6	pH- controller Soda Ash, Acid, Caustic
7	Sequestering agent
8	Whitening agent
9	Fixing agent
10	Softener
11	Bleaching agent Hydrogen per oxide (35%)
12	Stabilizer
13	Reducing agent
14	Enzyme
15	Anti-foaming agent
16.	Anti-creasing agent

higher BOD, COD, heavy metals, oily and slightly alkaline content. Increased values of COD, TDS, TSS, and heavy metals etc., showed the effluent toxicity.

The influence of dyeing industrial effluents introduces variation in physical, chemical, and biological nature of aquatic atmosphere. The traces of metals in effluent are harmful soil, and human health. The study showed that the ecological balance of the rivers including Burigonga, Turag, and Shitalakkhya, in Bangladesh, is deteriorated by untreated effluents.

The effluent severely affects crop production in the adjacent farming soil. Importantly, it was observed

that a few industries acquired effluent treatment plant (ETP), however, said ETP were not successful to maintain the standard discharge limit. These ETPs were using common treatment methods including flocculation, coagulation, adsorption, ozonation, and advanced oxidation process. However, a single treatment unit was unable to remove all the toxic organic and inorganic pollutants. Therefore, a series of effluent treatments may be required. It was obvious to exercise significant treatment to toxic textile dyeing effluent to prevent the environmental hazard.

Table 3 An estimation of quantity used for important dyes and chemicals in a conventional textile processing industry (Kant 2012)

S.no	Substance name	Quantity (Kg per month)
1	Disperse dyes (for Polyester)	1500
2	Vat dyes (Viscose)	900
3	Sulphur dyes	300
4	Reactive dyes	45
5	Acetic acid	1611
6	Formic acid	1227
7	Oxalic acid	471
8	Hydrochloric acid	309
9	Sulphuric acid	678
10	Caustic soda	6212
11	Hydrosulphites	6563
12	Hydrogen peroxide	1038
13	Ammonium sulphate	858
14	Leveling & Dispersing agent	547
15	Wetting agent	125
16	Polyvinyl acetate	954
17	Polyethylene emulsion	1174
18	Softener	858
19	Organic solvent	247
20	Organic resin	5115
21	Soap	154

Each textile processing industry with dyeing or printing facility requires assessing nature and remedying for the environmental pollutants produced in the stages of processing chain of applying the chemicals and dyes.

The waste water study of seven textile processing mills conducted in the textile processing units located in Karachi showed hazardous metals, and chemicals were released to environment. Generally, all the mills studies showed higher values relative to the minimum desired values of BOD, COD, and TSS, and TDS. There was only one textile processing mill that met the minimum level of COD (Imtiaz et al. 2012).

The said study of textile mill effluent conducted using the effluent samples, collected from seven different textile industries, during November, December, January and February 2009–2010. It showed the ecosystem hazard in terms of TDS, COD, and BOD, heavy metals including Cadmium, Chromium, Copper, Iron, Magnesium, Nickel, Potassium, Phosphorous, Sodium, Sulphur, and Zinc. Concentration of all these metal was above the recommended NEQS.

Adverse health effects were indicated for C.I. Pigment Yellow 12 (2, 3, dichlorobenzidine), C.I.

Disperse Yellow- 7 (p- aminoazobenzene), C.I.Direct Yellow 1 (benzidine) etc., and for salts, acid, alkali, bleaching and printing agents.

Heavy metals were found in excess to the standard limits in the significant number of effluent samples collected from different hand- loom dyeing industries in a recent study covering the Madhabdi municipality in the Narsingdi district (Bangladesh) (Nahar et al. 2018). The study demonstrated the concentrations of Fe, Cr, Cu, Pb, and Mn exceeded the industrial effluent discharge standards (IEDS) for inland surface water and irrigation water guideline values.

Similarly, textile processing and dyeing industries in India are known to introduce water pollution in nature through metals, salt, surfactants, toxic organic processing assistance; cationic materials, spent dye-stuff, BOD; sulfide; acidity/alkalinity, spent solvents, suspended solids, urea, vapors, BOD, COD etc. (Prasenjit et al. 2017). Inorganic sodium salts (NaCl and Na₂SO₄), used in dyeing, directly enhances the total dissolved solids (TDS) that is difficult to remove using conventional treatment. Toxic metals in the textile wastewater are another harmful effect. The metals may come with the chemicals including caustic

soda, sodium carbonate and salts used in process; or may be present in dyestuff, dye- mordant etc.

Preventing the environmental hazard

Interestingly, from dye or pigment synthesis, through dyeing process, and releasing effluent to nature, the environmental hazard control is located in different region. Observing the whole chain, from dye synthesis to the dye application and dyed product; the environmental challenge spread over advanced and developing countries (Fig. 3). The dyeing textile industries alone cannot meet the requirements to produce effluent and dyed textile product that are truly environment- friendly.

The textile dyeing, printing and finishing industries in Pakistan are significantly depending upon the import of dyes, pigment, and chemicals from advanced countries. However, following the usage of these dyes, pigment and chemicals in the textile processing industries of Pakistan; the effluent is generated locally, and restriction depends upon the attention, skills and technology available in local textile sector. Tables 4 and 5 show the volume of dye types, and chemicals imported in Pakistan (Memon 2017).

It is therefore important to import and use the dyes and pigments that are demonstrated and proven as environment- friendly, or showing performance limits

that does not reach the toxicity level based on the dyestuff structure during the process; and following the coloration process. Therefore, the effluent can be hazard- free, and relatively easy to treat.

Primarily, reducing the environmental hazard of effluent loading from dyeing processing was supported with the dyeing method used, based on smaller liquor ratio. Using minimum water in dyeing process means reduced wastewater production. The liquor ratio used may vary depending upon the machine type, and the selection of dye and chemical auxiliary. The conventional dyeing machine may use the liquor based on the shown liquor ratio indicated in Table 6 (Sheikh 2009).

However, presently large part of the residual dye and chemical auxiliaries left in effluent posed significant toxicity, and hazard to environment. Therefore, search of environment- friendly dyes, processing technique, and biodegradable chemicals can be an important source of reducing the environmental impact of dye- bath effluent. For example, use of enzymes in a process improves the biodegradability, and environment- friendly nature of the process. Enzymes are now becoming increasingly useful in textile processing. Use of strong alkali and subsequent water washes may be eliminated with the help of enzymes. It is indicated that 10 kg of enzyme can save up to 20,000 kg of water consumption per ton of yarn processed (Gunasekar and Ponnusami 2015).

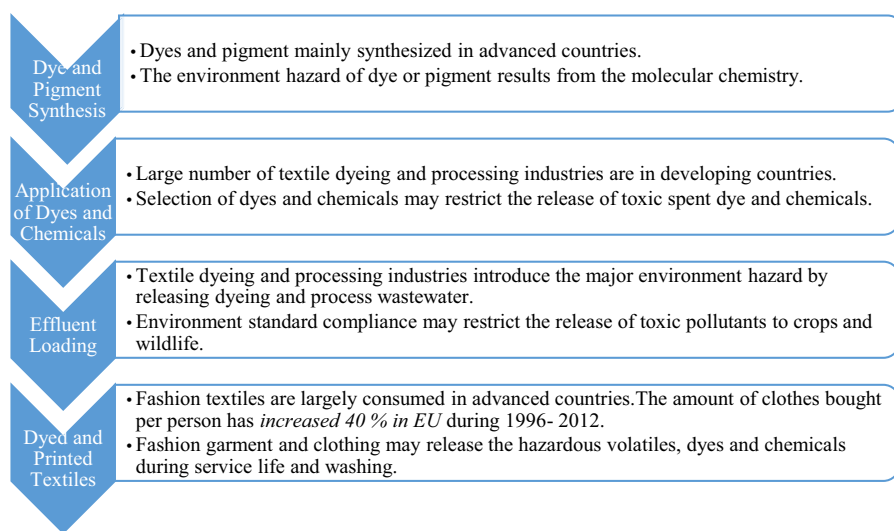


Fig. 3 Chain of environmental hazard spread over advanced and developing countries

Table 4 Import of dyes and pigments in Pakistan (Memon 2017)

S.no	Dye or pigment	2015- 2016		2016- 2017	
		Quantity (tons)	Value (million rupees)	Quantity (tons)	Value (million rupees)
1	Disperse dyes	10,457	3,074.7	7,257.2	2898
2	Acid dyes	4301	1,591	3241	1663
3	Basic dyes	2714	890	1705	897
4	Direct dyes	2097	419	1539	361
5	Vat dyes indigo blue	6167	2569	5154	2699
6	Other vat dyes	567	1071	555	1059
7	Reactive dyes	19,281	8657	19,295	8914
8	Dyes sulphur	1578	1412	7916	1319
9	Pigments preparation	5162	3006	5344	3006
10	Other Dyes synthetic	291	216	240	21
-	Total	52,615	22,905	52,246	22,837

Table 5 Organic chemicals imported in Pakistan (Memon 2017)

S.no	Year	Value (Million US dollar)
1	2012–13	2128
2	2013–14	216
3	2014–15	1997
4	2015–16	1864
5	2016–17	2116

Table 6 Liquor ratio possible in various machines in a textile dyeing process (Sheikh 2009)

Dyeing method	Machine type	Liquor ratio
Continuous	Padder	1:1
Semi- continuous	Padder	1:1
Discontinuous	Winch	15:1–40:1
“	Jet	7:1–15:1
“	Jig	5:1
“	Beam	10:1
“	Package	10:1
“	Beck	17:1
“	Stock	12:1
“	Skein	17:1

Importantly, in textile dyeing process the conventional fixation and exhaustion chemicals can be replaced with bio-degradable organic salts like trisodium citrate, magnesium acetate, tetrasodium edate, sodium salts of polycarboxylic acids. The environmental advantage obtained is the reduction in dissolved solid. It was estimated that total dissolved solids content in the spent liquor released from trisodium citrate dyeing process is about 40–65% less relative to that of conventional sodium chloride dyeing.

Fiber surface modification can also make the dyeing or printing process more environment-friendly. For example, cationization cotton is a useful process to improve coloration (Uddin 2003b). Following the cationization the cotton fiber surface may have salt-free dyeing process.

Plasma treatment is another treatment to modify the fiber for improved processing including dyeing. It is an environment- friendly process (Uddin 2018c). Water and chemicals consumption can be reduced that means reduced wastewater. The plasma treatment of cotton fiber may increase, in reactive dyeing, percentage exhaustion and K/S by about 10% and 14% respectively.

Novel applications in textile dyeing wastewater treatment

Wastewater treatment or effluent treatment is now an established workstation in research, innovation, and textile industry. Textile- industry wastewater and dyeing effluent treatment has received significant increasing interest in the last few decades. Over the past several years, the research and development studies demonstrated significant interest in treating the textile process water, and dyeing wastewater using large variety of techniques. There is gradual development in turning the wastewater as relatively more environment- friendly through an appropriate technique. However, the content variety and particular type of process consideration is important in the selection of wastewater treatment technology.

Finding a process that can completely remove all the hazardous residual dye content and chemicals, at an affordable cost, and ease of processing, is an important topic for current research. A number of techniques are used for this purpose, each having some preferences. For any effluent treatment, it is important to determine, for the type of dye, dyeing process and the content in used dye- bath; what should be the best for treatment of effluent in meeting the standard regulation requirements. There are three important types of the methods for effluent treatment used including physical, chemical, and biological. These methods are summarized in Table 7 (Reife et al. 2000). Use of nanotechnology or search of nanomaterial to be used as an adsorbent for the removal of waste content from the effluent is receiving an increasing research interest.

The complete wastewater treatment may be summarized in steps as: (i) screening step, (ii) homogenization, (iii) primary treatment using coagulation/ flocculation or flotation, (iv) pH adjustment, (v) secondary treatment via biological treatment (aerobic or anaerobic), and (vi) refinement treatment such as membrane or adsorption (Sabino and Michele 2017; Sahu and Singh 2019).

Treatment of dyeing effluent is a broad subject, and it is beyond the scope of this review to discuss in details all those materials and techniques used. Therefore, some useful reviews may be referred for details to see the specific concerns in the textile wastewater treatment. Reviews are available for the literature published in 2019 on textile wastewater (Deng et al. 2020); development of a cost- effective design, and to use chemicals that are less harmful or use chemicals easy to treat, and proposing appropriate wastewater treatment (Siddique et al. 2017); and advanced wastewater treatment processes (Upadhye and Joshi 2012). Recent developments in wastewater treatment methods including nanophotocatalysis, ceramic nanofiltration membranes, and biofilms were reviewed focusing the advanced physico-chemical and biological techniques for dye wastewater treatment. Importantly, the advantages, and disadvantages of various techniques were presented (Donkadokula et al. 2020).

Biological processes using limited energy consumption, low cost and high efficiency are important wastewater treatment technologies. Among them, the anaerobic biological processes were found to be effective for the treatment of high-concentration textile printing and dyeing wastewater. Therefore,

Table 7 Important types of effluent treatment methods (Reife et al. 2000)

S.no	Physical method	Chemical method	Biological method
1	Adsorption	Neutralization	Stabilization pond
2	Sedimentation	Reduction	Aerated lagoon
3	Flotation	Oxidation	Trickling filter
4	Flocculation	Electrolysis	Activated sludge
5	Coagulation	Ion exchange	Anaerobic digestion
6	Foam fractionation	Wet air oxidation	Bio-augmentation
7	Polymer flocculation		
8	Reverse osmosis		
9	Ultrafiltration		
10	Ionization radiation		
11	Incineration		

the recent advances on high-rate anaerobic technologies for such purposes were presented (Xu et al. 2018).

Synthetic dyes are toxic and difficult to biodegrade. Recently, there is research interest in synthesizing the nanoparticles using biological methods. Biologically synthesized nanoparticles are found effective in the treatment of wastewater, drug delivery, biosensors etc. The obvious interest in biological methods is based on eco-friendly nature and cost-effectiveness. A review study has shown the biological synthesis of various metal nanoparticles, pollutant degradation mechanism, and the performance of nanoparticles in degrading the dyes (Nandhini et al. 2019).

Interestingly, the dyeing process may be referred as black box (Jasper and Günay 2014). How much dye is fixed in fiber, and how much the applied chemicals are consumed in the dyeing process, can be known by the end of dyeing. Therefore, the challenges to remove or eliminate the hazardous effects of used dyes and chemicals from the dyeing effluent discharge will remain the demanding research areas.

Adsorption techniques are presently widely studied for dye-bath effluent treatment. The subject in this area includes the regeneration capacity and adsorption efficiency of different adsorbents. Relative to other methods used for effluent treatment, the adsorption method is indicated as inexpensive, and ecofriendly. Clay is a known material with wide range of application properties (Uddin 2018d); clay-based adsorbents were observed as having good ease of process, and efficiency (Shahadat and Suzylawati 2018).

Fly ash is the finely divided material resulted from the combustion of pulverized coal. Fly ash is a major pollutant generated in coal-based thermal power plants. Interest was shown to use it as adsorbent. It shows some results for the dye solutions of methylene blue (M-B) and Congo red (Rao et al. 2006), however it is not as widespread as activated carbon.

Activated carbon is a natural adsorbent for dye removal. However, it requires high regeneration cost. Clays and modified clay-based adsorbents show improved results relative to activated carbon, organic/inorganic, and composite materials.

Regeneration of adsorbent is required to re-use the adsorption efficiency of the spent adsorbent for effluent treatment. Regeneration techniques for clay adsorbent include chemical treatment, supercritical extraction, thermal, and photocatalytic and biological degradation.

Generally, the removal of toxic dyes includes diverse and complex set of physico-chemical, biological and advanced oxidation treatment. Ozonation treatment is based on the removal of dyes using high oxidizing power of ozone. The details of wastewater treatment using ozonation, and adsorption may be seen in a review study (Khamparia and Jaspal 2017). It was indicated that using the combined ability of ozone and a catalyst/adsorbent, the complete removal of dye from wastewater may be possible. Indeed it is the subject of research to find an appropriate adsorbent in combination with ozonation treatment for the desired effects in particular dye effluent.

Ozonation in combination with biological treatment is found useful for medium strength wastewater. Significant results obtained in terms of the removal of color and COD. However, for high strength wastewaters, chemical clarification was suggested as useful pretreatment prior the ozonation and biological treatment.

The dyeing wastewater was collected from cotton, synthetic and woven fabric processing; and aerobic biodegradability of ozonated and unozonated samples was evaluated in fill-and-draw activated sludge systems. An ozone dosage of 0.8 g/L for 30 min in a semi-batch reactor with volume of 10 L. Higher strength wastewater was treated with Alum, FeCl₃ and FeSO₄ as coagulants (chemical clarification). Removal of COD was improved using anionic polyelectrolyte. Color removal over the range of 78–100 percent was obtainable using ozonation dosage at 0.8 g/L. Moreover, COD removal obtained was 59–71 percent when using ozonation and chemical clarification; while 62–82 percent COD removal was achieved with a combination of ozonation and biological treatment (Tuba 2001).

The effluent produced from dyeing generally contains more pollutants relative to the wastewater produced from washing/ rinsing and finishing processes. However, dyeing effluent in combination with the rinsing and finishing wastewater can be effectively treated through ozonation and biological treatment, particularly for the removal of color.

Woolen textile dyeing and finishing industry produce highly polluted water. Combined dyeing effluent and wastewater produced from first and second rinse was ozonated, prior and following the biological treatment, at the dosage of 18.5 mg/L using various time intervals. The treatment performance, in terms of

the removal color and COD was observed. Importantly, ozonation of biologically treated wastewater for 40 min produced 98–99% removal of color with corresponding ozone absorption rate of 58.0 mg/l. However, there was slight effect on the removal of COD (Baban et al. 2003).

The research interest in textile wastewater treatment continues to introduce the relatively novel technique to remove or degrade the organic pollutants. In the effluent containing dye, pigment, textile; there are organic pollutant, including synthetic dyes that cannot be easy to remove or degrade using the conventional methods. Cavitation technique is relatively recent in effluent treatment. Hydrodynamic and sonochemical or acoustic cavitation was indicated effective in breaking down the organic pollutant. Cavitation produced strong oxidizing conditions introduced by hydroxyl radicals and hydrogen peroxide that degraded the organic content (Bhandari and Ranade 2014).

Layer by layer (LbL) assembly is an interesting technology for the micro pollutant removal from dyeing wastewater. Polyelectrolytes under LbL made on natural support may be attempted in treating textile process wastewater. Importantly the technique can of low cost with good ease of processing. A low-cost adsorbent was developed by depositing chitosan (CHI) and polyacrylic acid (PAA) through LbL on coir fiber. The resulting layered coir fiber (LCF) demonstrated an increased adsorption for cationic and anionic dyes both at acidic and alkaline loading pH used separately. The loading was between 70 and 99%, for two types of dyes respectively, at the acidic pH. It was attributed to the binding between LCF and dye molecules by electrostatic and hydrophobic forces. Effects of LCF were described in presence of NaCl, Na₂SO₄ and sodium dodecyl sulfate in dye solution. Importantly, the treated textile wastewater showed 81% reduction in dye content (Mathew et al. 2019).

Last, and not the least, an interesting simple approach in reusing the dyeing wastewater may be applied. In this approach the treated water can be reused. In this study, printing and dyeing wastewater (PDWW) treatment enhances the water reuse rate to 35%. The wastewater produced was analyzed based on the concentrations of pollutants produced in different printing and dyeing processes; and it was labeled as special, highly, and less contaminated wastewaters (SCW, HCW, and LCW) respectively. These

wastewater samples were treated and reused. Significant volume of LCW was sequentially reused at various levels in production processes (Wang et al. 2018).

Nanotechnology in dyeing effluent treatment

Using the nanotechnology in removing the waste and hazard content from the textile industry effluent is relatively a recent research domain. There are some apparent advantages in using the nanomaterials for treatment of textile industry effluent. Nanomaterials are perceived to demonstrate high reactivity and an increased functionalization, large specific surface area, size-dependent properties etc., resulting in an interest to evaluate the various nanoparticles, including metal nanoparticles, metal oxides, carbon compounds, zeolite, filtration membranes etc., for the wastewater treatment (Bora and Dutta 2014; Zekić et al. 2018). In general, the important variety of nanomaterials, available for the textile industry wastewater treatment can be categorized as Carbon based, Metal Oxide based, Polymer based nano adsorbents (Kavithayeni et al. 2019).

The studies addressing the effects of metal nanoparticles in the treatment of dye solution or dyeing effluent are limited to a single type metal nanoparticle. An important research aspect of metal nanoparticles studies is to establish merits of one type of metal nanoparticles relative to other metals, in textile wastewater treatment, is missing to date. Indeed it is important aspect in wastewater treatment for future to determine the effectiveness and sustainability of any metal nanoparticle.

Importantly, decolorization and wastewater treatment are simultaneously possible using nano iron particles. Monoazo methyl orange dye contaminated water was studied using nano iron particles. These particles were found highly reactive, nontoxic, and cost-effective. Study showed the usefulness of nano iron particles in the decolorization of mono azo methyl orange dye, and to decolorize textile dyeing wastewater. Interestingly, the dye was decolorized 98% shorter time of 30 min of reaction time and 54% reduction in total organic carbon was observed. The decolorization process, and reaction mechanism were proposed. Moreover, real textile dyeing industry wastewater treatment showed 82% dye color removal

and reduction in the quantity of inorganic pollutants including chlorides, sulfates (Raman and Kanmani 2019).

The catalytic ozone pretreatment using Fe^{2+} and zerovalent iron nanoparticles showed encouraging results in dyeing wastewater treatment. nZVI on biodegradability enhancement of complex textile effluent. The removal of COD, color and toxicity was up to 73.5%, 87%, and 92% respectively. The improved performance in effluent treatment was observed in terms of disappearance of the corresponding GC- MS, and FTIR spectral peaks. The iron nanoparticles presence, in ozonation process, assisted in breaking the chromophore group of dye, and degradation of organic compounds (Malik et al. 2018).

Silver nanoparticles have demonstrated performance in dyeing wastewater treatment (Kavitha et al. 2014), the silver particles remained in the treated water are toxic for the bio- species. The subject of using silver nanoparticles is, therefore, requires the determination how these can be used in effluent treatment. There are concerns for the treated water and sludge, containing the silver nanoparticles, going into soil, aquatic environment, and underground water. Review studies comprehend the use of silver nanoparticles and silver-based nanocomposites in effluent treatment and possibility of reducing the toxicity of silver nanoparticle (Sivasankari et al. 2020; Rita et al. 2020).

Several useful properties are indicated achievable when using ZnO nanoparticles (NPs). These are non-toxicity, low cost, biocompatibility, chemical stability, thermal and photostability, high UV absorption ability. Therefore, ZnO NPs can be good photocatalyst for removing azo dyes from wastewater. There can be concern, similar to silver nanoparticles, for the toxic nature of ZnO NPs for microbes. Most of the properties of ZnO NPs are dependent upon its synthesis method used, and a review study has addressed the physical and chemical properties, synthesis approaches, antibacterial activity, and photocatalytic activity of ZnO NPs (Getu 2020).

Magnetic cobalt nanoparticles (CoNPs) were synthesized, and studied to remove Remazol golden yellow RNL (RGY) from aqueous solutions, and textile wastewater. The content of cobalt in synthesized CoNPs was found 60.38% (m/m). The analysis of X-ray Diffraction (XRD) and Raman Spectroscopy showed the presence of Co^0 and CoO in

CoNPs; that was further confirmed by Thermogravimetric Analysis (Jean et al. 2019).

In terms of dye removal, improved results were shown for the dye solution relative to the textile dyeing wastewater sample. The CoNPs removed the RGY with high efficiency (almost 100% removal in 30 min). The dye removal was found to be influenced by the experimental condition; the acidic conditions led the reductive degradation, and the neutral or basic conditions were leading the two simultaneous processes: reductive degradation and adsorption. In case of using the CoNPs in textile wastewater. The decolorization was almost 88%. However, the decrease in chemical oxygen demand was 32%, that means CoNPs are effective in removing organic dyes from spent- dye bath.

Reactive dyes are largely utilized in the dyeing of cellulose fibers, and there are hundreds of textile processing industries that are using the reactive dyes in dyeing the cotton or its blends. Nickel is another nanoparticle that showed good results in the treatment of reactive dyeing effluent. Nickel nanoparticles were synthesized using polyvinyl pyrrolidone (PVP) as stabilizer to prevent agglomeration of nanoparticles. The synthesized nickel nanoparticles were used to decolorize the dye effluent. Color Index Reactive Blue 21 was used as a reference dye. The study demonstrated the 98% dye removal with simultaneous reduction in chemical oxygen demand (COD) (Ravindra and Preran 2017).

TiO_2 nanoparticles (NPs) can also provide the degradation of reactive dye. The destructive oxidation of organic compounds and dyes is possible using TiO_2 NPs. The photocatalytic oxidation of Reactive Orange 16 aqueous solution was studied by UV ray irradiation in presence of TiO_2 NPs. The photocatalytic degradation of Reactive Orange 16 was discussed in terms of the initial and final chemical oxygen demand of the solution that was UV irradiated under optimized conditions (Mahvi et al. 2009).

Similar to silver nanoparticles, the TiO_2 remained in the treated wastewater are required to be removed. Removal of TiO_2 from the treated wastewater is another problem. For this purpose, a study has demonstrated the use of suspended TiO_2 powder in photooxidation process for dye and chemical degradation followed by separating TiO_2 from slurry by a membrane filter and recycled to the photoreactor continuously (Li and Zhao 1999). The presence of

TiO₂ serves as the catalyst in photocatalytic-oxidation process that can degrade the non-biodegradable organic substances in the effluent resulting in complete color removal. The recovery of TiO₂, as catalyst, was possible by membrane filter and continuously reused in the photoreactor. Importantly, the treated wastewater was found good enough for reuse in the textile dyeing processes.

A recent approach in applying the metal nanoparticles is the use of biogenic metal particles. Biogenic copper nanoparticles (CuNPs) were used for photocatalytic degradation of wastewater pollutants. The physico-chemical and biological properties of these particles are interesting offer performance at low cost with environmental sustainability. The said CuNPs were synthesized by using a native copper-resistant bacterial strain *Escherichia sp. SINT7*. The photocatalytic activity of the biogenic CuNPs for azo dye degradation, and treatment of textile effluents (Muhammad et al. 2020) found significant.

A variety of dye type solutions were decolorized using the CuNPs. The CuNPs decolorized Congo red (97.07%), malachite green (90.55%), direct blue-1 (88.42%) and reactive black-5 (83.61%) at a dye concentration of 25 mg L⁻¹ after 5 h of sunlight exposure. An increased dye concentration resulted in reduced removal of dye. When the solution contained dye at 100 mg L⁻¹ concentration, the degradation percentage was found to be 83.90%, 31.08%, 62.32% and 76.84% for Congo red, malachite green, direct blue-1 and reactive black-5, respectively.

The performance of biogenic CuNPs, in the treating the textile effluents, showed reduction in pH, electrical conductivity, turbidity, total suspended solids, total dissolved solids, hardness, chlorides and sulfates.

Last couple of decades has shown significant applications of natural montmorillonite clay (Uddin 2018d). The adsorption properties of montmorillonite nanoparticles can be a useful alternative in providing environment- friendly wastewater treatment. The montmorillonite nanoparticles were studied as adsorbent in removing the Reactive Yellow 15 (RY15) and Reactive Yellow 42 (RY42) dyes from aqueous solutions. The effect of different variables such as pH, contact time, dye concentration and adsorbent dosage, process temperature, and thermodynamic were studied. The removal of both dyes was found best at pH value of 3. When contact time reaches to 15 min, the dye adsorption increases and then

becomes constant. A dosage of 0.2 g/ L of montmorillonite nanoparticles was giving an optimum dye adsorption of 142 g/ L, and 166 g/ L for RY 15, and RY 42 respectively. The study of the thermodynamics, and temperature showed that values of ΔH , ΔS and ΔG were negative for both dyes (Kamranifar and Naghizadeh 2017).

The potential in using the nanomaterials for the removal of toxic and undesired content from the wastewater is obviously strong. However, research studies leading to the utilization of nanomaterials in wastewater treatment through adsorption, filtration and photo-catalysis are demanded (Sanith et al. 2021).

A very important subject in the use of nanotechnology is its comparison relative to the other known chemical, physical and biological treatments, and an assessment of possible commercialization aspects. For the said purpose; a review was presented on the available nanomaterials, properties and mechanisms, advantages and limitations relative to the existing processes, and barriers and research needs for commercialization (Xiaolei et al. 2013). Therefore, some opportunities and limitations may be perceived for the wastewater treatment using nanotechnologies. Use of the silver nanoparticles is an obvious example.

Graphene- based nanomaterial to be used as adsorbent and photo- catalyst in wastewater treatment is an important advancement. Graphene nanomaterials received the recent research interest as a novel material. They provide high mechanical strength, excellent electron mobility, large surface area, and high thermal conductivity (Opoku et al. 2020).

The perceived merits of semiconductor photocatalysis water treatment include its cost-effectiveness, easy operation, and high-efficiency. Graphene materials are indicated promising as semiconductor multifunctional catalysts. The theoretical aspects, challenges and possibility for the effectiveness of using graphene/semiconductor composites were summarized.

Graphene oxide (GO) showed significant improved effects in removing the color and turbidity from the textile processing wastewater. When treating the wastewater using GO, it takes time some greater than one hour, however, 90% turbidity of wastewater was reduced, and an apparent color removal efficiency over 76% was recorded, that is considered as significant when using the conventional treatment in textile mills (Caroline et al. 2020).

The review of important nanomaterials in dyeing and textile industry wastewater treatment can be seen addressing the nano-based materials including graphene and carbon nanotubes, metal nanoparticles such as silver, iron, zinc and magnesium, and metal oxide nanoparticles and magnetic-core composites including cobalt, nickel, and iron (Madhura et al. 2019).

Nanofiltration membrane is a liquid-separation technique to remove the multi-variant ions. It has some similarity to reverse osmosis (RO). Unlike RO, that has high rejection of all dissolved solutes; nanofiltration can provide high rejection of multivalent ions, for example calcium; and low rejection of monovalent ions, for example chloride. A typical example to show the performance of nanofiltration membrane may be presented in the Table 8 (DuPont 2021).

The 3rd column in Table 8 shows the percentage of ions that was able to pass through (= permeate) the nano-filtration membrane. It showed there was small amount of Ca^{++} and organic carbon dissolved content that was able to pass through the membrane; the high rejection rate was respectively 74 percent and 94 percent (values given in column 4). Monovalent ion HCO_3^- showed relatively higher content to permeate and small percentage 28 was rejected.

Batik printing industry is an important cottage industry in Southeast Asia. It is a special type of printing where the process wastewater contains residual dye, wax, and chemicals. An increased volume of process wastewater from Batik processing is released from dyeing, fixing and washing to environment. Use of polyamide nano-membrane was evaluated to treat the dyeing effluent. The dyes used were reactive blue 15, reactive red 194, reactive yellow 145, reactive black 5, and reactive orange 16. The dyes were tested in low concentration (16 mg/ L) during a 60 min filtration process using polyamide nano-membrane. The efficiency of filtration was determined based on pre-process and post-process analytical experiments. The flux for all the samples ranged between 7.8 and

9.2 ml/cm² s. There was significant reduction in the measured conductivity for each dye solution sample in filtration runs. Chemical oxygen demand value in the permeate samples was reduced to zero, representing a dye removal efficiency of more than 90% (Rashidi et al. 2015). Nanofiltration technique may have the possibility of utilization as industrial scale for the textile industry wastewater treatment (Manuele et al. 2003).

Nanofiltration membrane may produce improve effects when use in combination with electrochemical technique in the treatment of dyeing effluent. This can be particularly useful for the reactive dyeing effluent. Since an increased amount of chloride salt is used in reactive dyeing for dye fixation in fiber; the resulting wastewater can be treated with electrochemical technique without adding any electrolyte wastewater. An electrochemical process may remove the dyes from used dye bath, and the process can produce the degradation of dye on anode, using chloride as electrolyte.

Treating the wastewater through membrane can remove various type of dyes resulting in high quality permeate that can be useful in a new textile processing. The study was made using nanofiltration membrane with electrochemical process for the effluent treatment containing reactive dye Cibacron Yellow S-3R (tri-reactive dye). The two nanofiltration membranes used were Hydracore10 and Hydracore 50 producing dye removal up to 98%. The performance of membrane was assessed using two parameters including the salt (NaCl) concentration and at pH 3 in the presence of 60 g/ L of NaCl, the dye removal was significant. The nanomembrane filtration was followed by the electrochemical treatment for the concentrate with high dye concentration using three different densities of electricity: 33, 83, and 166 mA/ cm². There was a linear relationship between treatment time and density of electricity used. An important aspect of study was use of permeates and electrochemically-decolored effluents in new dyeing processes. Fabrics dyed in the

Table 8 Water treatment results using nano-filtration membrane (DuPont 2021)

Dissolved content type	Feed content (ppm)	Permeate (ppm)	Rejection (%)
Total dissolved solids	573	250	56
Alkalinity (HCO_3^-)	134	97	28
Ca + +	5.4	1.4	74
Total Organic Carbon	3.6	0.2	94

treated effluent water were evaluated with respect to original dyeing, where color differences indicated as acceptable (Valentina et al. 2016).

Cleaner textile production

Cleaner production is now an important activity in all sections of textile processing industries. The obvious advantages of waste and environment- hazard reduction, energy and utility conservations provided the textile industry the driving force to identify and follow the cleaner production practices.

The United Nations Environment Program (UNEP) has defined the cleaner production as “the continuous application of an integrated preventive environmental strategy to processes, products, and services, to increase overall efficiency, and reduce risks to humans and the environment” (Gonlugur 2019). The end-of-pipe approach works with the removal of the pollutants following the occurrence that is the wastewater treatment. Observation has shown the generation of waste and pollution are largely the result of ineffectiveness and inefficiency of production stages; reduced research work, inappropriate process design and resources consumption. Therefore, practices leading to the cleaner production are increasingly taking place in textile industries.

The assessment of two types of process technologies is the significant step in cleaner technology determination. Best available technology (BAT) is an important element of cleaner production that may result in the saving of process cost, time, and improved efficiency. However, it requires the evaluation of different kinds of materials and energy that is not a simple work. Another major limiting factor experienced is the need to precisely define the function of each production technology to permit the comparison between different types of process technologies (Wilhelm 1998).

For any textile dyeing and processing industry, the types of BAT can vary. However, through benchmarking the identified BAT can be investigated for the real industrial processes. Dyeing of cotton and polyester industries are widespread in most major textile producing countries. The BAT study of cotton/polyester fabric dyeing and finishing textile industry, to determine more environment- friendly practices, was conducted (Emrah et al. 2016).

The study based on the collection of data of the material flow and the energy consumption in all processes. Mass-energy balance for the production processes was determined. Chemical inventory list and all the material safety data sheets were observed. There were 92 Best Available Techniques (BAT) were identified, and following discussion and understanding with the concerned mill management 22 were selected. The selected BAT included good management practice, water and energy consumption optimization-minimization technique, chemical consumption optimization, and substitution. Interestingly, with payback periods of 1- 26 months for the selected BAT practices, the study demonstrated significant benefits including the following reductions:

- Water consumption: 43–51%
- Energy consumption: 11–26.
- Chemical consumption: 16–39%
- Wastewater flow rate: 42–52%
- Chemical oxygen demand load: 26–48%
- Waste flue gas emissions: 12–32%
- Solid waste generation: 8–18%.

Finding the alternative processing techniques, or searching replacement chemicals is another approach to make the textile dyeing and processing more environment- friendly. A review study has addressed the similar approaches including application of enzymatic processing in fabric preparation; use of biodegradable organic salts in textile dyeing, such as trisodium citrate, magnesium acetate, tetrasodium edate and sodium salts of polycarboxylic acids, as fixation and exhaustion agents; and the use of surface modification of cotton fabric to reduce the volume of effluent and TDS (Varadarajan and Venkatachalam 2016).

An important example of using alternative process to significantly reduce the environment hazard associated with the textile dyeing is the plasma treatment of textile fiber. Generally, in most textile fiber processing a variety of auxiliary chemicals, mordant, fixer etc. are used leading the discharge of hazardous effluent. The benefits of plasma treatment are possible in different dyeing and finishing processes. An important example can be seen in the natural dyeing. Natural dyes may be used for smaller textile batches. Applying the natural dyes following the plasma treatment of fibers may be useful. An increased dye uptake and color fastness may be obtainable. A review study of plasma of finishing to the fabric surface of

natural (wool, cotton, and silk) and synthetic fibers (polyester, nylon, and acrylic), and its effects on fiber dyeing using natural dyes can be seen (Haji and Naebe 2020). This study is a detailed example of cleaner pre-treatment and alternative process technique for dyeing textiles to reduce wastewater and toxic chemicals.

Standards and approaches in cleaner production

The preventive approach in eliminating the environmental hazard from textile dyeing is required to be exercised at different levels, however, the cohesiveness among the stake holder can bring improved results (Uddin 2019e). The dye and chemical manufacturer and supplier, processor, trained human resource, effluent treatment plant designer, local and international environmental standards, regulatory organizations, brand and fashion producers- all need to contribute to achieve cleaner production in textile dyeing and printing industries.

The important sections in achieving cleaner production in textile dyeing may be summarized as concentration based standards, regulatory control, third party/ assessment, enforcement of effluent treatment, training and information provision, approaching potential market for cleaner process and product, encouragement for Zero Discharge of Hazardous Chemicals, metering of ground water.

Regulations are known limiting the use of the chemicals. However, refer to the particular textile product, and fashion industry apparel, the regulatory work is progressing. The important regulations produced in recent time, in three important regions European Union, USA, and China, to restrict the use of chemicals that are potentially harmful, include the following (Tsai 2021):

The EU's REACH stand for Registration, Evaluation, Authorisation and Restriction of Chemicals. REACH came into force on June 1, 2007. It is a regulation applied to all chemical substances used in industrial and consumer applications. It requires ensuring the chemicals are used with safety concerns. Toxic and hazardous chemicals are required to prevent. Moreover, in October 2020, the EU published a chemicals strategy for sustainability to "boost innovation for safe and sustainable chemicals" and restricting the harmful chemicals in consumer products.

1. The Toxic Substances Control Act, (TSCA), in the USA, regulates new chemicals and the use of existing chemicals. TSCA was produced in 1976, and updated in 2016 for the 21st Century Act.
2. In China, the chemical safety regulation is **MEE Order 12**. This order is the revision of MED Order 7 produced in 2020, and introduced in January 1, 2021. It requires the chemical manufacturers and importers to submit notifications and obtain approvals before producing or importing chemicals.

Importantly, the influence of such rules and regulations is observable; and several companies in textile fashion industry chain have adopted the initiatives to improve the practices in restricting the toxic and harmful chemicals in textile processing or in the final textile consumer product.

Chemicals producing and processing industries for apparel/denim industries worked out to remove the hazardous dyes and chemicals. Apparel brand producers introduced initiatives for bringing health-friendly products in the market. An example is the Bluesign System, a standard for environmental health and safety in textile production introduced by the apparel companies Eileen Fisher and Patagonia. In 2018, use of laser to replace chemicals, in jeans finishing was introduced by Levi's. The apparel fashion brands, including Walmart, Marks & Spencer, H&M, and Gap Inc. etc., improved the determination to make products with restrictions on hazardous chemicals.

REACH is not limited to fashion industry or apparel production. It is applicable to all chemical substances used in washing detergents, paints, plastics, clothes, furniture, electrical appliances etc. REACH makes the company responsible for the hazard associated with a substance manufactured and market in Europe. European Chemical Agency (ECHA) receives and evaluates the registration of a chemical substance for compliance under REACH. ECHA scientific committee and Authorities determine if risk is manageable. Importantly, if the hazard in a product is not control by the producing company, the product can be restricted by the authorities in possible ways. The effect of REACH is obvious on the working of manufacturer, importer, and the user of chemical substance (ECHA 2021).

National standards and European standards can prohibit the use of carcinogenic dyes and chemicals, for example the dyes containing the heavy metals, having higher density, and are toxic at low concentration. The voluntarily standards are available that determine the parameters to evaluate the dyes and chemicals for eco-labeling and certification. Raw materials used in process, and the finished product can be evaluated, to determine heavy metals and toxic substances, using voluntarily standards Ecolabel and Oeko-Tex standard 100 (Amutha and Saranya 2017). Eco-labeling, and Organic Certification for Textile Products is a good source of building confidence in the environment-friendly nature of product. An eco-labeling standard may provide the requirements for organic textiles.

An overview of the requirements for the major eco-labels, including the European Union Ecolabel (flower label), Oeko-Tex 100, Bluesign, organic certification systems (Global Organic Textile Standard and Organic Content Standard), Fairtrade etc., may be observed (Almeida 2015). The brand producer and retailers are now more conscious to know about the dyes and chemicals used in textile products for safety and legislation compliance (Easton 2009).

In several developing countries; textile dyeing industries coupled with the dyes and chemical manufacturing industries are following the certification through the Oeko-tex standards. For the time period around the last three decades, the Oeko-Tex® Association has certified the processes and products, in textile and leather industries, for sustainability and environment-friendly concerns. The Oeko-Tex standards serving the industries include Oeko-Tex Standard® 100, Leather Standard, STeP, ECO Passport, and Made in Green labels.

The management of wastewater and chemicals are improved by the Made in Green, Oeko-Tex® Standard. The Made in Green label requires wastewater analysis, and inventory of all chemicals used in the textile wet processing and facilities. The optimization and monitoring system of chemicals, and wastewater assessment can be determined using an analysis tool called Detox to Zero by Oeko-Tex®. Screening of dyes and chemicals using the Detox to Zero analysis identifies the toxic substances, and enable the process industries to restrict the pollution in wastewater (OEKO-TEX 2021).

The brand producers that depends upon the commissioned services of textile process industries, requires the product should be green. Therefore, the green product labeling is important. Product labeling to demonstrate that it was produced using sustainable processing, with the restriction of harmful substances, is done by Standard 100 by Oeko-Tex®.

There is an obvious contribution factor by the consumer/ buyer to emphasize the apparel, hometextile, and clothing products free from the hazard of dyes and chemicals used. When consumer are buying with the satisfaction that textile and the apparel were produced using hazard-free dyes and chemicals, the natural environment will be greener.

Conclusion

Textile dyeing industries are known to introduce several undesired environmental effects in terms of toxic and carcinogenic chemical species, harmful gaseous emission, effluent release, and hazardous chemical content in dyed or printed textile products. The aim of this review study is to provide an overview of various forms of toxic and hazardous content coming from the textile dyeing and processing industries with particular reference to Bangladesh, Pakistan and India. Importantly, the environmental challenges associated with the said industries are not confined to these countries, the origin begin from the dye synthesis made in advanced countries. Textile coloration industry depends on using the synthetic dyes; and the process sequence assimilates relatively multiple facets in exposing the natural environment to a number of harmful substances. The various materials including metals, contaminated water, hazardous and toxic gases etc. can be released to environment from synthetic dye manufacturing till the usage of dyed and finished textile product.

The large variety of dyes, pigment, chemicals, and processing methods associated with the textile dyeing, coupled with the large number of small and medium dyeing units locating in developing regions require an increased interest to overcome the process and effluent hazard. There are obvious studies, based on the textile process and dyeing wastewater, indicating the toxicity and hazard present. There is significant lacking in the control for exercising environment-friendly material

and processing techniques resulting in real challenges to earth environment.

An important aspect of this review is the discussion based on real studies addressing the particular process on-ground in local textile processing industries. The pollutant content and the hazard aspects are presented through the selected studies conducted using the water samples from the process industries or from the processing sites.

It is therefore obviously important to have coherent practicing standards to mitigate the hazardous effects of synthetic dyes, dyeing process, effluent discharge and dyed finished product. Cleaner textile production requires the participation of all the stake holders starting from dye and chemical producer to the finished product introducer.

Dedication

This study is dedicated in memorial to my late parents, Mr Badar Uddin (peace on him) and particularly to mother Noor- Un- Nisa (peace on her). Their patronage, love, and courage is the source of motivation and treasure in my life.

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