Clean and Innovative Textiles Strategy for Circular Economy

MODULE 6
Sustainable Chemical Processes and Textile Care

Unit 6.1
Sustainable Substances and Wastewater Treatments

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In this lecture the current legislation and policy regulating chemicals, significant challenging campaigns and programs with the goal of reducing and eliminating the use of hazardous chemicals from production of textile as well as tools for green and safer alternatives to substances of concern and innovative eco-friendly wastewater treatments are presented.

Chemicals are used at every step in the textile manufacturing process bring substantial advantages including water or stain repellence, increased durability, or a wide choice of colours, unfortunately many of them are potentially hazardous to human health and the natural world.
Some have been found to be carcinogenic or hormone disruptive, causing concern for the health of factory workers exposed to them (as allergic reactions and respiratory diseases), and for the environment into which they escape, for example by being released into local rivers in factory effluent. Toxic chemicals, such as alkylphenols and perfluorinated compounds (PFCs) are particularly problematic as they cannot be removed by wastewater treatment plants, flame retardants, including brominated and chlorinated organic compounds, are another particularly hazardous class of chemicals used in the production of some textiles. Many dyes contain heavy metals, such as lead, cadmium, mercury and chromium (VI), known to be highly toxic due to their irreversible bioaccumulative effects, whilst azo dyes contain carcinogenic amines (Greenpeace, 2018).
A study by the Swedish Chemicals Agency identified approximately 3,500 substances being used in textile production (KEMI, 2014). Of the 2,450 substances able to be analysed (the rest were not analysed due to confidentiality), 750 were found to be hazardous to human health, with 299 considered to be functional substances of high potential risk to human health, i.e. substances intentionally added and expected to remain in the finished articles at relatively high concentrations. 440 substances were found to be environmentally hazardous, with 135 of these functional substances of high potential risk to the environment (KEMI, 2014).

In a more circular and sustainable textile industry material input would be safe and healthy to allow it to cycle in the system and avoid negative impacts during the production, use and after-use phases, so elimination of substances of concern is required.
An important industry change has already been, driven by increasing demands for transparency on the environmental costs of dyes and other chemicals used in the textiles industry from NGOs, governments, policymakers and customers pressurising players along the value chain to act.

In line with the improvement of living standard and the growing awareness and to need to preserve and the environment and protect human health several regulation has been introduced to control the use of chemical substances:

- REACH Regulation (EU) No 1907/2006: REACH (Registration, Evaluation, Authorization and Restriction of Chemicals), adopted by European Union in 2006, covers the registration, evaluation, authorization and restriction of chemicals produced or imported in the EU over 1 tonne per annum. Companies have become largely responsible for the safety assessment of substances and the classification and labelling of substances. They are obligated to provide the European Chemicals Agency (ECHA) with all the required information on these substances.
  On 1 November 2020, Regulation (EU) 2018/1513 amending Annex XVII to Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) entered into force.
  Since REACH is the regulation of the European Union, and as such it applies to all countries belonging to the EU. Main sectors that are under REACH regulation are:

  a. A manufacturer in EU that supplies products that contain any chemical substances.
  b. An importer in the EU who buys products from outside the EU that contain any chemical substances.
  c. A company or user who handle any chemicals in industrial or professional activity in the EU.

Noted that companies that established outside the EU have no obligation to follow REACH, even they export their products to the EU. The responsibility will shift to the importer in the EU.

Annex XVII to REACH contains restrictions on the manufacture, placing on the market and use of certain substances. In this case, this new regulation includes restrictions for certain substances considered to be CMRs (carcinogenic, mutagenic and toxic to reproduction) of category 1A or 1B, thus adding entry 72 to the Annex, they are of specific concern due to the long term and serious effects that they may exert on human health;

- Biocides Regulation (EU) 528/2012: biocides can be applied to textiles with a specific intention, such as to serve an antibacterial function. Under the Biocidal Product Regulation (BPR, Regulation (EU) 528/2012) this type of specific use requires authorization, including a risk assessment indicating safe use and therefore whether any possible risks to consumers have already been sufficiently controlled.

- POP Regulation (EC) 850/2004: the aim of this regulation is to protect human health and the environment by prohibiting, phasing out as soon as possible, or restricting the production, introduction to the market and use of Persistent organic pollutants (POPs), defined as a group of chemical compounds with different origins but common characteristics: semivolatility, hydrophobicity, bioaccumulation, high toxicity, persistence in environment, ability to migrate in food chains and high bioaccumulation potential. Some of them are use in the textile production.
  On this regulatory list are substances such as:
  - Insecticides and pesticides; aldrin, dieldrin, lindane
  - Hexachlorobenzene
  - Dioxins and Polycyclic aromatic hydrocarbons (PAHs).

Other extra European regulations include for example TSCA (Toxic Substances Control Act), administered by the United States Environmental Protection Agency (US EPA or EPA) and under which the Premanufacture Notification (PMN) rules fall, that regulates the introduction of new chemicals and existing chemicals in the USA and China's MEP Order 7, similar to EU REACH and is also known as "China REACH".
Under this regulation, chemical manufacturers and importers were required to submit notifications and obtain approvals before producing or importing chemicals. From January 2021 it was replaced by MEE Order 12 that shall apply if companies plan to manufacture or import chemicals not listed in the Inventory of Existing Chemical Substance in China (IECSC).

Due to the growing awareness of the issues surrounding substance of concern, many brands often adopt own restricted substances lists (RSLs) to provide global suppliers with guidelines limiting the amount of chemicals that can be present in finished products. For example, Target, VF (which owns The North Face and Jansport) Nike, Ralph Lauren and Gap have all introduced Restricted Substances Lists to eliminate the use of some chemicals that harm workers and consumers.

In 2011 Greenpeace launched its Detox campaign (Detox My Fashion) to address the widespread use of hazardous chemicals in the manufacturing of clothes, which were being released into waterways in countries such as China, Indonesia and Mexico. It was the first campaign to challenge big clothing brands from all sectors to take responsibility for the environmental impacts of their manufacturing supply chains and commit to achieve zero discharges of hazardous chemicals by 2020.

This challenge was taken up by 80 brands and suppliers, from fashion and sportswear, to luxury, multiple retailers and the outdoor sector.

The Detox My Fashion campaign included 3 Core Criteria to define sustainable textile production:

- DETOX 2020 - A program to eliminate toxic substances by 2020;
- Perfluorinated compounds (PFCs) elimination - The replacement of PFCs with other safer substances;
- Transparency - A collection of detailed information on the release of chemicals into water.

Brands signing the Greenpeace Detox Commitment implemented preventive and precautionary action on chemicals, by setting goals to eliminate hazardous chemicals in manufacturing.
Almost immediately following the launch of the campaign, the industry responded collectively by creating the ZDHC (Zero Discharges of Hazardous Chemicals) group in 2011 to provide a coordinated response to the campaign and enable collaboration of the brands.

The ZDHC Roadmap to Zero Programme is an industry collaboration of major fashion brands (such as Adidas, H&M, C&A, Nike, Puma and Li Ning) and retailers, value chain affiliates and associates, working together to eliminate and substitute hazardous chemicals from the global textile, apparel, leather and footwear value chain. ZDHC's mission is to enable these industries to implement chemical management best practices and advance towards zero discharge of hazardous chemicals by collaborative engagement, standard setting, implementation and innovation.

The cornerstone of ZDHC's approach is the Manufacturing Restricted Substances List (ZDHC MRSL), it offers brands and suppliers a single, harmonised list of chemical substances banned from intentional use during manufacturing and related processes in the apparel, non-apparel and footwear supply chains.
RLS (Restricted Substances List) limits the chemicals that end-up in a finished material or product, MRSL target chemicals that used in manufacturing process of product including materials, in this way MRLS is more comprehensive than RLS. This approach helps to protect consumers while minimising the possible impact of banned hazardous chemicals on production workers, consumers and the environment.

What have companies to do?

• To avoid the introduction into the manufacturing processes of the substance classified in ZDHC MRSL;

• To manage wastewater in accordance with the concentration limits set out in the Wastewater Guideline (also issued by ZDHC) for wastewater originating from production processes;

• To manage chemicals in an appropriate and organized manner, so an audit protocol is provided;

• To demonstrate the implementation of a system of research and development of safer alternative substances.

ZDHC decided to leverage existing certification as indicators of ZDHC MRSL conformance.
The ZDHC MRSL conformance Levels range from 0 to 3: higher conformance levels are expected to reflect a higher confidence that a chemical product meets the ZDHC MRSL conformance levels, and therefore a lower probability of any ZDHC MRSL substances being present in the certified chemical product.

ZDHC (Zero Discharge of Hazardous Chemicals) accepted OEKO-TEX® ECO PASSPORT (a certification system designed for manufacturers of process chemicals and chemical compounds) as an indicator of compliance with their MRSL in 2017, while Bluesign®, a holistic system that provides solutions in sustainable processing and manufacturing to industries and brands, is the newest ZDHC Accepted Certification Standard to indicate ZDHC MRSL conformance at the highest level 3.

Consumers are increasingly demanding more information about the chemicals in their textile products to ensure that dangerous ones are not being used. This and stricter chemicals legislation gives an incentive for the textile industry to substitute hazardous chemicals with safer alternatives.
It is a very effective way to improve the toxic footprint of textile products, it will not only make the final product safer, but also create better working conditions.
Several tools and techniques are available to support substitution, steps of the substitution process are the following:

- Define the function, use and need of the substance you want to replace: it is very useful to think about substitution using these different levels – function, use and need. Let's look at the use of phthalates in PVC printing on textiles as an example:
  the function of the phthalate is to make the PVC plastic soft. If you only consider the function you might find an alternative non-phthalate plasticiser.
  You can also look at the use, which is PVC for textile printing. Bearing this in mind you might consider changing to another type of printing paste that does not require plasticisers: polyurethane or silicone for example. The ultimate need is to produce textiles that are attractive. Perhaps this can also be achieved by other means, such as embroidery.
- Define criteria for the alternative: it is important to think through what you want from an alternative before moving on to assessing and comparing alternatives. For example you can ask: What would you like to achieve in terms of hazard profile and functionality: Is there a cost limit? How urgent is the substitution? Are there already legal requirements in place or do you have time to wait for an alternative that is currently at the research stage?
- Search for available alternative solutions: same channels are recommended (web-based resources) as Marketplace, Subsport and OECD Substitution and alternatives toolbox (SAAT).

  Marketplace: a global platform where business-to-business companies can find safer alternatives to hazardous chemicals, enabling buyers and suppliers to start substituting chemicals of concern;
  Subsport (Substitution Support Portal): a platform for information exchange on alternative substances and technologies, as well as tools and guidance for substance evaluation and substitution management;
  OECD Substitution and alternatives toolbox (SAAT): a compilation of resources relevant to chemical substitution and alternatives assessments

- Evaluate and compare alternatives.
- Test on a pilot scale.
- Implement substitution.

Textile industries consume a large amount of chemicals and water for manufacturing.
After the product is manufactured, untreated effluent from the textile industries is directly discharged into water streams causing environmental problems and health issues for humans. Dye constituents in the effluent are highly variable because of the different types of clothes, including different structural varieties of dyes such as acidic, basic, metal complex, azo, diazo and reactive dyes. These effluents are typically highly coloured, usually alkaline, and contain higher amounts of biochemical

oxygen demand (BOD) and chemical oxygen demand (COD) and a variety of toxic contaminants such as suspended solids, dyes, acids, bases, salts, surfactants, chlorinated compounds, oxidizing and reducing agents.

The most significant sources of pollution among various process stages are pretreatment, dyeing, printing, and finishing of textile materials.

The main goals of wastewater treatment are:

- To ensure discharge of good water quality to the natural environment
- To remove pollutants most efficiently and at the lowest cost
- To avoid and/or minimise other environmental impacts – odour creation, gas emission, noise production and solid disposal
- To produce treated water for reuse and recycling
- To recover salts if economically viable

Treatment of textile industry wastewater is a major challenge as there is no particular economically feasible treatment method capable to adequately treat wastewater, therefore there is need to develop novel, cost-effective and eco-friendly technologies to tackle this problem.

Wastewater treatment plants are classified into three groups:

- primary treatment: it includes sedimentation, screening, chemical coagulation, flocculation and floatation.
- secondary treatment: it includes chemical/physical separation or biological oxidation and used to reduce organic compounds.
- tertiary treatment: processes to complete solids and organic matter removal, for color reduction or recalcitrant compounds degradation, nutrient (ammonia and phosphorous more common in domestic sewage) reduction and disinfection.

The conventional methods used to treat the wastewater are physico-chemical and biological methods. The physico-chemical methods include coagulation, flocculation and ozonation etc. whereas biological methods are used for the removal of nitrogen, phosphorous, organics and metal traces. In the last few decades, many techniques or methods have been developed which offer economic and competent means to treat the textile wastewater. The existing literature proves that large number of conventional methods including physico-chemical, biological processes and some new emerging techniques like microbial fuel cells, genetic engineering, biofilms, nanotechnology etc are effective in decolorization of textile wastewater.

In the recent years sustainable and eco-friendly textile waste treatments of dyes and pollutants were developed as for example the following technologies:

Advanced Oxidation Processes (AOP): it allows the degradation of organic dyes by radiation of visible light due to its eco-friendly nature, complete degradation, low cost, increase reusability of water and decrease in the pollutant load. Titanium Dioxide (TiO_2) is used in photocatalytic degradation due to its nontoxic nature, chemical stability and environmental compatibility;

Bio-electrochemical system (BES): the bio-electrocatalytic reaction combined with extracellular electron transfer can drive several procedures such as synthesizing chemicals, producing electricity from wastewater, removing pollutants and desalinating seawater.

Also green and low expensive approaches can be used for the removal of dyes: microorganisms (bacteria, fungi, algae, yeats) as well as plants or agricultural wastes (as rice husk, corn cob, peanut, coconut, coffee, banana peel and flower wastes). The application of agro-industry residues in wastewater treatment is of considerable importance for two main reasons, first the concept of circular economy is applied, reducing the use of virgin material to remove pollutant substances, second, it encourages the reuse of treated wastewater.

Innovative wasterwater processes involves Zero Liquid Discharge (ZLD), able to completely eliminate all liquid discharge from a system, the goal is to reduce the volume of wastewater that requires further treatment, economically process wastewater and produce a clean stream suitable for reuse. Furthermore some European Projects (see ECUVal, PURIFAST and WASTE2FRESH projects) are involved in the development and demonstration of sustainable wastewater systems that allow the reduction of pollutant and reuse of treated water resulting in significant environmental gains.
Electro Coagulation for Water Recycling in Textile Industry project brought a new technological concept (called EColoRO) that allows to close the waterloop by separating the water, organometallics and salty brine and creating a produced clean water that can be fully re-used.
Electro-coagulation (EC) combined with flotation are used.
ECUVAL Project is based on innovative wastewater system which combines electrochemical techniques with UV irradiation for the treatment of dyeing textile wastewaters (100% colour removal) and the reuse of the treated effluents and salts.
At present the ECUVal industrial prototype is operating in a textile mill where it has been optimized to treat and reuse exhausted reactive dyebaths.
Pollution loads from surfactant, suspended solids, dyestuffs and aromatic compounds were all significantly reduced and degraded by an advanced wastewater treatment system based on Ultra Filtration (UF) and an innovative Advanced Oxidation Process (AOP), developed within The Life Project PURIFAST.
Results from tests on textile wastewater revealed that the removal of colour can be more than 90%; COD abatement is around 80%; and Total Suspended Solid (TSS) reduction is about 80% at pre-industrial scale. for COD. As much as 60% of textile effluent was proven to be reusable (and possess a low toxicity) following the PURIFAST process.
And last but not least WASTE2FRESH a Horizon 2020 project, which aim is near-zero discharge and a reduction of current use of freshwater resources, will develop a closed-loop process for textile manufacturing factories in which wastewater is collected, recycled and used again. Iinnovative catalytic degradation approaches with highly selective separation and extraction techniques will be integrated.

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