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Textile Finishing Industry as an Important Source of Organic Pollutants

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1. Introduction

The textile finishing industry is, among all industries in Europe, the greatest consumer of high quality fresh water per kg of treated material and with the natures of their production processes significantly contributing to pollution. Wastewater from the textile industry is also a significant environmental pollution source of persistent organic pollutants.

Not only textile wastewater but also textile products often contain chemicals such as formaldehyde, azo-dyes, dioxins, pesticides and heavy metals, that might pose a risk to humans and the environment. Some of these chemicals found in finished products are there as residues from the production of dyes and auxiliary chemicals (the synthesis of dyes involves a large variety of chemicals with complex synthesis paths, during which toxic, carcinogenic and persistent organic compounds can be formed, such as dioxins, and traces can be found in commercial dyes), others are added to give certain characteristics to the products (colour, flame retardancy, anti wrinkling properties *etc.*) (Križanec & Majcen Le Marechal, 2006), or are already present in the raw textile material. The mentioned compounds have been found in wastewater after home washing, in organic solvent after dry-cleaning and also in the atmosphere after incineration. Possible sources of organic pollutants are also wastewater treatment methods and the incineration of textile materials.

The formation of dioxins can occur via dyeing and textile finishing processes with conditions favourable for their generation (high temperature, alkaline conditions, ultraviolet (UV) radiation, and other radical initiators). Textile dyes are designed to be resistant to microbial, chemical, thermal and photolytic degradation. After the dyeing process, a lot of non-bonded dyes are released into the wastewater, which can also be treated by Advanced Oxidation Processes (AOPs) in order to destroy the dye molecule and to decolourise the wastewater and reduce organic pollution. It is well-known that under the experimental conditions of such methods, which can be very useful because of the short-time of treatment, hazardous compounds can be formed due to very powerful oxidizing agents such as hydroxyl radicals ($OH^{\bullet}$).

In line with the improvement of people's living standard and the growing awareness and need to preserve the environment several regulations were introduced also in the textile industry in order to control the use of chemicals in textile processes. Under REACH regulation (REACH regulation controlled the quality of fabric, apparels, and shoes

and other textile materials, so as to protect human health and the environment) the following main groups of compounds in textiles are under control: Azo Dyes, Phthalates, Formaldehyde, Flame-retardants, Pentachlorophenol, Carcinogenic dyes, Sensitizing disperse dyes, Hexavalent chromium, Polychlorinated biphenyls, Heavy metals, Nickel release, Total lead content, Organic tin compounds, Total cadmium content, Organic chlorine carrier, Nonylphenol, Octylphenol, and Nonyl phenol ethoxylate, and several established directives (e.g. Azo dyes – Directive 2002/61/EC, Pentachlorophenol (PCP)-Directive 94/783/EC)) regulated/banned the use of these substances throughout the textile production chain (www.cirs-reach.com/textile/).
Market pressure, on the other hand, leads to the introduction of an extensive range of new products, especially dyes, and for many of them environmental and health impact data are still lacking. The quantification of chemicals within the environment is leading to the development of sensitive analytical methods in order to effectively detect and control pollution by organic pollutants.

2. Textile raw material

2.1 Fibres

Two general categories of fibres are used in the textile industry: natural and chemical (man-made) fibres. Man-made fibres encompass both purely synthetic materials of petrochemical origin, and regenerated cellulose material from wood fibres. A detailed classification of fibres is presented in Table 1.

Natural fibre		
Animal origin	*Vegetable origin*	*Mineral*
Raw wool Silk fibres Other hair fibres Alpaca Camel Cashmere Horse Llama Mohair Rabbit Vicuna	Cotton Flax Jute Linen Ramie Hemp	Asbetos Glass Metalic Copper Steel
Chemical (man-made) fibres		
Natural polymers fibres	*Synthetic polymer fibres*	
Viscose, Cupro, Lyocell Cellulose Acetate Triacetate	Inorganic polymer Glass for fibre glass Metal for metal fibre Organic polymers Polyester (PES) Polyamide (PA) Polyacrylonitrile (PAC) Polypropylene (PP) Elastane (EL)	

Table 1. Classification of fibres

2.2 Organic pollutants in textile raw materials

Different kinds and amounts of organic pollutants (contaminants) can already be present in fibres before they arrive at the textile mill. The potential contaminants may be released from the raw materials into the water or air during processing, when the fabric is heated or scoured. Due to the large amount of the fibre used during textile manufacturing, even trace contaminants can produce large amounts of pollutants. Many textile operations lack an incoming quality-control system for fibres. Testing of the natural or chemical fibres for organic pollutants is very rarely done in textile mills.

Textile raw materials contain: natural impurities from cotton, wool, silk, etc., fibre solvents (when chemical fibres are produced by dry-spinning or solvent-spinning processes), monomers (caprolactam ex polyamide 6), catalysts (antimony trioxide in polyesters' fibres), sizing agents (woven textiles esp. cotton and cotton blends), and preparation agents (esp. woven and knitted textiles made of man-made fibres). (Lacasse & Baumann, 2004)

2.3 Natural fibres

Natural fibres are acquired from animal, mineral, and plant sources. Several types of organic pollutants are found in natural fibre and all have the potential to create significant pollution problems. For example, waxes, oils, fats, and grease from animal fibre can contribute to biochemical oxygen demand (BOD), and chemical oxygen demand (COD). Pesticide residues from plant fibre can contribute to aquatic toxicity. Metals can accumulate in sludge or during the treatment system itself, thus causing potential long-term problems.

Cotton is the most significant natural fibre. Cotton fibre contains 88-96 % of cellulose and the residue is pectin substances, wax, proteins, ash, and other organic components (less than 1%). Chemicals such as pesticides, herbicides, and defoliants can be used during the production of cotton. These chemicals may remain as a residue on raw cotton fibres that reach the textile mill. Tests of cotton samples from growing regions worldwide, performed from 1991 to 1993, reported levels of pesticides below the threshold limit value for foodstuffs (US EPA 1995).

Although the content of pesticides in raw cotton fibres was negligible, almost half of the insecticides used in agriculture were used in cotton production. For this reason the reduction of insecticides for economic, environmental, and human health reasons was necessary. Insect-resistant (Bt) cotton (GM IR) started being used in 1996. So, the production of Bt cotton during the first ten years (1996-2005) reduced the total volume of those active insecticide ingredients by 94.5 million kilograms, representing a 19 % reduction in insecticides (Naranjo, 2009).

In 2001 it was reported that cotton was contaminated by pentachlorophenol (PCP) when being used, not only as a defoliant, but also as a fungicide during transportation and storage. (UK, 2001).

Wool is another significant commercial natural fibre. It is an animal hair from the bodies of sheep, sheared once or sometimes twice a year, and its quality and quantity vary widely, depending on the breed of sheep and their environment. Raw wool contains natural impurities (wool grease, suint, dirt) and residues of pesticides. Pesticides are applied onto sheep in order to control external parasites such as lice, blowflies, mites etc.

The used pesticides generally fall into four main groups (BAT, 2003):

- **organochlorine insecticides (OCs):** γ-hexachlorocyclohexane (lindane), pentachlorophenol (PCP), dieldrin, DDT,
- **organophosphorous insecticides (OPs):** diazinon, propetamphos, chlorfenvinphos, chloryriphos, dichlorfenthion,

- **synthetic pyrethroids insecticides (SPs):** cypermethrin, deltamethrin, fenvalerate, flumethrin, cyhalothrin and
- **insect-growth regulators (IGRs):** cyromazine, dicyclanil, diflubenzuron, triflumuron.

Biocides, organohalogen and organophosphorus compounds are among the priority substances listed for emission-control in the IPPC Directive. Diazinon (OP), propetamphos (OP), cypermethrin (SP) and cyromazine (IGR) are the most commonly-used ectoparasiticides for treating sheep. Insect-growth regulators such as dicyclanil, diflubenzuron and triflumuron are registered only in Australia and New Zealand. Lindane, which is the most toxic of the hexachlorocyclohexane isomers and also the most active as a pesticide, is still found in wool coming from the former Soviet Union, the Middle East and some South American countries (BAT, 2003). Wools from South America exhibited the highest levels of organochlorine insecticides, whilst wools from Australia and New Zealand exhibited the lowest levels of OCs (Shaw, 1989).

Pesticides such as OCs, OPs, and SPs have a lipophilic nature, so they associate strongly with the natural oils within the wool and as removed using these oils during wool scouring operations. The chemical stability of organochlorine pesticides is reflected in their resistance to microbial degradation. The lipophilic nature, hydrophobicity, and low chemical and biological degradation rates of organochlorine pesticides have led to their accumulation in biological tissues, and subsequent magnification of concentrations in organisms progressing up the food-chain.

The fate of the Ectoparasiticides (antiparasitic drug) in the wool scouring process is following. 96 % of the pesticides are removed from the wool (4 % is retained on the fibre after scouring). Of this 96 % around 30 % or less is retained on-site in recovered grease and the remaining fraction is discharged into the effluent and submitted to wastewater treatment.

Levels of organochlorine insecticides pentachlorophenol (PCP) in textile products are usually too low to be quantified accurately by traditional methods. PCP has been found at levels as high as 100 ppm in consumer products such as wool carpets (Wimbush, 1989). Wimbush tested 140 wool carpets and found that 88 % of them had a PCP content below 5 ppm. Only 3 carpets contained more than 50 ppm of PCP (US EPA, 1996).

Silk accounts for only 0.2 % of total fibre production. It is a protein fibre like wool and derived from the silkworm. The silk fibre is composed of fibroin filaments wrapped with sericine (silk gum), which has to be removed during pretreatment. (BAT, 2003)

2.4 Chemical fibres

Synthetic fibres may contain several types of impurities existing in the fibres before they reach the textile mill. These kinds of impurities are imparted onto the fibres during fibre manufacturing and fall into the categories of finishes, polymer synthetic by-products, and additives. Impurities associated with synthetic fibres are:

- Finishes: antistatic, lubricant,
- Polymer synthesis by-products: non-reactive monomers, low-molecular-weight oligomers, residual catalyst, and
- Additives to facilitate processing: antistatic agents, lubricants, humectants, and others.

Table 2 presents those compounds typical of synthetic fibre extracts. The compounds in Table 2 were not only found in the process wastewater from synthetic fibre dyeing and finishing operations but were also detected in synthetic fibre extracts.

Fibre	Compounds
Polyester	*tetra* hydro-2,5-dimethyl *cis* furan, ketones (methyl isobutyl ketone, 3-methyl cycle pentanone, hexanone, diethyl ketone), dodecanol, alcohols (C_{14} and C_{18}), esters of carboxylic acids (C_{14}-C_{24}), hydrocarbons (C_{14}-C_{18}), carboxylic acids (C_{16}-C_{24}), phthalate esters
Acrylic	hydrocarbons (C_{15}-C_{18}), esters of carboxylic acids (C_{17}-C_{22}), alcohols, phthalate esters, *N*, *N*-dimethyl acetamide
Nylon 6	diphenyl ether, hydrocarbons (C_{16}-C_{20}), carboxylic acids (C_{14}-C_{18}) and dicarboxylic acids, esters of carboxylic acids (C_{10}-C_{18}), alcohols (C_{20}-C_{22})

Table 2. Compounds typical of synthetic fibre extracts

Some of these impurities are produced during the polymerization of synthetic fibres and some are added to control the surface and electrical properties of the fibre. These impurities can create pollution problems.

The above review of possible organic pollutants in textile raw materials indicates the necessity for quality control regarding incoming fibre. Some textile companies have endorsed standard testing methods for fibres and have actively worked to ensure that the fibre user and the producer exchange information about quality control. It is important to set up good incoming fibre quality-control based on performance-testing, statistical sampling, and the analysis of extractable materials, in order to identify potential pollution problems before they arise.

3. Finishing processes within the textile industry

3.1 Basic process within the textile industry

The textile chain begins with the production or harvesting of raw fibres. These basic processes are schematically presented in Fig. 1. Treatments that are broadly referred to as 'finishing processes' are pretreatment, printing, dyeing, finishing, and coating, including washing and drying.

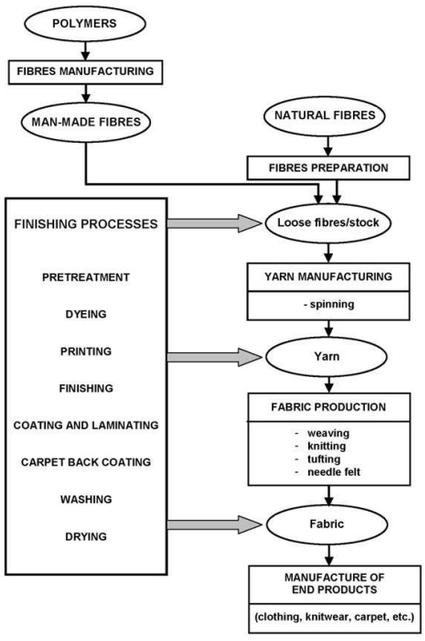


Fig. 1. Schematic presentation of textile processes

3.2 Possible organic pollutants in textile finishing processes

Most textile finishing operational units use chemical specialties. The major specialty consumption operations are pretreatment processes (desizing, scouring, bleaching), dyeing, printing, and finishing. (Mattioli, et al, 2002)

So, this chapter focuses on those textile finishing processes that might produce organic pollutants.

3.2.1 Pretreatment processes

Pretreatment processes depend on the kind and form of the treated fibre, as well as the amount of material to be treated. These processes should ensure the removal of foreign materials from the fibres in order to improve their uniformity, hydrophilic characteristics, and affinity for dyestuffs and finishing treatments. The pretreatment processes are desizing, scouring, bleaching, and mercerizing.

3.2.1.1 Desizing

Desizing is the process for removing size-chemicals from textiles. The possible organic pollutants in effluents after desizing, are presented in Table 3.

Fibres	Organic substances
Cotton	carboxymethyl cellulose, enzymes, fats, hemicelluloses, modified starches, non-ionic surfactants, oils, starch, waxes
Linen	
Viscose	
Silk	carboxymethyl cellulose, enzymes, fats, gelatine, oils, polymeric sizes, polyvinyl alcohol, starch, waxes
Acetates	
Synthetics	

Table 3. Possible organic pollutants in effluents after the desizing process

The washing water from desizing may contain up to 70 % of the total COD in the final effluent. Synthetic esters' oils are less problematic because they are emulsified or soluble in water and easily biodegraded. More problems are caused by compounds such as silicon oils, because they are difficult to emulsify, and poorly biodegradable. Silicon oils are found in elastane blends with cotton or polyamide.

3.2.1.2 Scouring

Scouring is the cleaning process for removing impurities from both natural and synthetic materials. In natural fibres, impurities can be present such as oils, fats, waxes, minerals, and plant-matter. Synthetic fibres can contain spinning, finishing, and knitting oils.

Scouring is performed in an alkali medium together with auxiliaries that include:

- non-ionic surfactants (alcohol ethoxylates, alkyl phenol ethoxylates) and anionic surfactants (alkyl sulphonates, phosphates, carboxylates),
- compounds for removing metal ions (nitrilotriacetic acid (NTA), ethylenediaminetetraacetate (EDTA), diethylene triamine pentaacetate (DTPA), gluconic acid, phosphonic acids as complexing agents),
- polyacrylates and phosphonates as special surfactant-free dispersing agents and
- sulphite and hydrosulphite as reducing agents (to avoid the risk of the formatting of oxycellulose when bleaching with hydrogen peroxide).

Table 4 presents those possible organic pollutants derived from scouring.

Fibers	Organic substances
Cotton	anionic surfactants, cotton waxes, fats, glycerol, hemicelluloses, non-ionic surfactants, peptic matter, sizes, soaps, starch
Viscose	anionic detergents, fats, non-ionic detergents, oils, sizes, soaps, waxes
Acetates	
Synthetics	anionic surfactants, anti static agents, fats, non-ionic surfactants, oils, petroleum spirit, sizes, soaps, waxes
Wool (yarn and fabric)	anionic detergents, glycol, mineral oils, non-ionic detergents, soaps
Wool (loose fiber)	acetate, anionic surfactants, formate, nitrogenous matter, soaps, suint, wool grease, wool wax

Table 4. Possible organic pollutants in waste-effluents after the scouring process

3.2.1.3 Bleaching

Bleaching is a chemical process for removing unwanted coloured matter from materials. Several different types of chemicals are used as bleaching agents and selection depends on the type of fibre. The most frequently used oxidizing agents for cellulose fibres are hydrogen peroxide (H_2O_2), sodium chlorate(I) (NaClO), sodium chlorate(III) ($NaClO_2$). Peracetic acid and optical brightening agents are also applicable.

Bleaching with H_2O_2 is connecting with the use of H_2O_2 stabilisers. During the bleaching process, hydroxyl radicals attack the cellulose fibre starting with oxidation of the hydroxyl groups, and eventually ending with cleavage of the cellulose molecules, thus decreasing the degree of polymerisation. Reaction is catalysed by heavy metals such as iron, copper, and cobalt. H_2O_2 stabilisers (EDTA, NTA, DTPA, gluconates, phosphonates and polyacrylates) inhibit these reactions. NTA, EDTA and DTPA form very stable metal complexes. EDTA and DTPA are also poorly eliminated compounds, and they could pass non-degraded through the common wastewater treatment system. Their ability to form a very stable complex with metal makes the problem even more serious because they can mobilise those heavy metals present in the effluent, and release them into the receiving water. Other auxiliaries used in hydrogen peroxide bleaching are surfactants with emulsifying, dispersing, and wetting properties.

Sodium chlorate(I) was, for a long time, one of the more widely-used bleaching agents throughout the textile finishing industry. Nowadays bleaching with sodium chlorate(I) is limited in Europe for ecological reason. NaClO leads to secondary reactions that form a number of organic halogen compounds, such as carcinogenic trichloromethane.

3.2.1.4 Mercerizing

Mercerizing is a chemical process that improves the strengths, lustres and affinities of dyes for cotton fabrics. Several organic pollutants can be used. Possible organic pollutants in mercerizing effluents are alcohol sulphates, anionic surfactants, and cyclohexanol.

3.2.2 Dyeing

Dyeing is used to add colour to textile materials. Textiles may be dyed at various stages of production.

Dyeing can be carried out in a batch or in a continuous mode. The choice between the two processes depends on the type of make-up, the chosen class of dye, the equipment available, and the cost involved. Both continuous and discontinuous dyeing involve preparation of the dye, dyeing, fixation, washing, and drying. Quite a large amount of the non-fixed dye leaves the dyeing units.

Besides dyes, other auxiliary substances can be added to the dyeing process, and may give rise to water pollution. Possible pollutants are: fatty amine ethoxylates (levelling agent), alkylphenol ethoxylates (levelling agent), quaternary ammonium compounds (retarders for cationic dyes), cyanamide-ammonia salt condensation products (auxiliaries for fastness improvement), acrylic acid-maleic acid copolymers (dispersing agent), ethylenediamine tetraacetate (EDTA), diethylenetriaminepentaacetate (DTPA), ethylenediaminetetra-(methylenephosphonic acid) (EDTMP), diethylenetriaminepenta(methylenphosphonic acid) (DTPMP).

All these are water soluble and non-biodegradable compounds, which can pass non-transformed or partially-degraded through a wastewater treatment system. Some of them are toxic (quaternary amines) or can give rise to metabolites that may affect the reproduction-chain within an aquatic environment (BAT, 2003).

Organic dyes are presented in Chapter 4.

3.2.3 Printing

Printing, like dyeing, is a process for applying colour to a substrate. The printing techniques are: rotary screen, direct, discharge, resist, flat screen, and roller printing. Pigments cover about 75-85 % of all printing operations, do not require washing steps and generate a small amount of waste. Compared to dyes, pigments are typically insoluble and have a high affinity for fibres. Printing paste residues, wastewater from wash-off and cleaning operations, and volatile organic compounds from drying and fixing, are typical emission sources from printing processes.

Printing process wastewater is small in volume, but the concentration of pollutants is higher than that in wastewater from dyeing. Wastewater after printing contains the following organic pollutants: urea, dyes or pigments, and organic solvents.

These pollutants are likely to be encountered in wastewater after printing, and are presented in Table 5 (BAT, 2003).

Additionally, organic pollutants after the finishing processes, such as aliphatic hydrocarbons (C_{10}-C_{20}) from binders, monomers (acrylates, vinylacetates, styrene, acrylonitrile, acrylamide, butadiene), methanol from fixation agents, other alcohols, esters, polyglycols from emulsifiers, formaldehyde from fixation agents, ammonia, *N*-methylpyrrolidone from emulsifiers, phosphoric acid esters, phenylcyclohexene from thickeners and binders, might also be distributed in the exhaust air.

3.2.4 Finishing

The term 'finishing' covers all those treatments that improve certain properties or the serviceability of the fibre. Finishing may involve those mechanical/physical and chemical treatments performed on fibre, yarn, or fabric, in order to improve appearance, texture, or performance.

Organic pollutants found during finishing processes are:

- cross-linking agents in easy-care finishing,
- flame-retardant agents,
- softening agents,
- antistatic agents,
- hydrophobic/oleophobic agents and
- biocides.

Pollutant	**Source**
Organic dyestuff	Non-fixed dye
Urea	Hydrotropic agent
Ammonia	In pigment printing pastes
Sulphates and sulphites	Reducing agents by-products
Polysaccharides	Thickeners
CMC derivates	Thickeners
Polyacrylates	Thickeners Binder in pigment printing
Glycerin and polyols	Anti-freeze additives in dye formulation Solubilising agents in printing pastes
m-nitrobenzene sulphonate and its corresponding amino derivative	In discharge printing of vat dyes as oxidising agent Direct printing with reactive dyes inhibits the chemical reduction of the dyes
Polyvinyl alcohol	Blanket adhesive
Multiple substituted aromatic amines	Reductive cleavage of azo dyestuff in discharge printing
Mineral oils/aliphatic hydrocarbons	Printing-paste thickeners (half-emulsion pigment printing pastes occasionally)

Table 5. Pollutants in wastewater after the printing process.

Cross-linking agents in easy-care finishing are mainly based on formaldehyde. They can be formaldehyde-rich, formaldehyde-poor or formaldehyde-very poor. Formaldehyde-rich cross-linking agents are: "self-crosslinking "agents such as hydroxymethyl urea, bis(methoxymethyl)urea, hydroxymethyl melamine, and bis(methoxymethyl)melamine. 'Reactant cross-linking' agents are formaldehyde-poor or have very poor cross-linking based on the derivatives of the bis(hydroxymethyl)-dihydroxyethylene urea. All these products may potentially produce emissions of free formaldehyde and methanol. Formaldehyde's presence in these finishing agents represents a potential risk, not only for wastewater and exhausted air, but also to workers in the textile mills, and the final users of the textile as well. Formaldehyde is also suspected of carcinogenity. These are the reasons for much effort being put into the production of free formaldehyde cross-linking agents. One cross-linking agent that is formaldehyde-free is also available on the market and is based on dimethyl urea and glyoxal [BASF, 2000]. Formaldehyde-free cross-linkers are considerably more expensive than formaldehyde cross-linkers, so this is the reason that formaldehyde-free cross-linkers have never been widely used in the textile industry.
The flame-retardant agents most commonly-used within the textile sector, and belong to the organic flame-retardant agents, are both halogenated organic and organo-phosphorus compounds.

As halogenated organic compounds only, brominated and chlorinated flame-retardant agents are used in practice. Brominated compounds are the most effective. Bromine can be bound aliphatically or aromatically, the aromatic derivatives are widely-used because of their high thermal stability. Chlorinated flame-retardant agents include chlorinated aliphatic and cycloaliphatic compounds. They are less expensive, less stable, and more corrosive to the equipment when compared to the brominated compounds. Polybrominated flame-retardants include the following compounds:

- polybrominated diphenyl ethers (PBDE); pentabromodiphenyl ether (penta-BDE), octabromodiphenyl ether (octa-BDE), decabromodiphenyl ether (deca-BDE),
- polybromo biphenyls (PBB); decabromobiphenyl and
- tetrabromobisphenol A (TBBA).

A PDBE, which is of major use as a flame-retardant agent, is a deca-BDE. Deca-BDE and octa–BDE could break down into penta–BDE and tetra–BDE after release into the environment. Penta-BDE is a persistent substance liable to biocumulate.

Organo-phosphorus flame-retardant is represented by molecule phosphonic acid, (2-((hydroxylmethyl)carbamyl)ethyl)-dimethyl ester. Phosphorus containing flame-retardant agents is non readily biodegradable and water-soluble. According to one source, this product is not toxic or harmful to aquatic organisms and shows no potential to bioaccumulate, whilst another source concludes that knowledge about the toxicology of this compound is insufficient (BAT, 2003).

Softening agents are water-based emulsions or dispersions of water-insoluble active materials. There are four groups of softeners:

- non-ionic surfactants (fatty acids, fatty esters, and fatty amides),
- cationic surfactants (quaternary ammonium compounds, amido amines, imidazolines),
- paraffin and polyethylene waxes and
- organo-modified silicones.

Softening agents are molecules with high molecular weight but their volatility is low. The performance of each type of softener varies and each has advantages and disadvantages. Non-ionic surfactants are biodegradable, whilst paraffin and polyethylene waxes are non-biodegradable. Cationic surfactants have high aquatic toxicity. Paraffin waxes are still used although these types of softeners emit smoke when heated and producing air emissions from dryers.

Antistatic agents are applied as functional finishes to selected textile materials for use within static-sensitive environments. From the chemical point of view, antistatic agents are based on quaternary ammonium compounds and phosphoric acid ester derivatives.

Hydrophobic/Oleophobic agents fall under the following categories:

- wax-based repellents (paraffin-metal salt formulations),
- resin-based repellents (fatty modified melamine resins),
- silocone repellents and
- fluorochemical repellents (copolymers of fluoroalkyl acrylates and methacrylates).

Organic pollutants arise from silicone repellents, fluorochemical repellents and from resin-based repellents.

Silicone repellents contain polysiloxane-active substances (dimethylpolysiloxane and modified derivates), emulsifiers, hydrotropic agents (glycols), and water.

Fluorochemical repellents are copolymers of fluoroalkyl acrylates and methacrylates. Market formulations contain active agents together with emulsifiers (ethoxylated fatty

alcohols and acids, but also fatty amines and alkylphenols) and other by-products that are often solvents, such as:
- acetic acid esters (butyl/ethyl acetate),
- ketones (methylethyl keton and methylisobutyl ketone),
- diols (ethandiol, propandiol), and
- glycolethers.

Resin-based repellents are produced by condensing fatty compounds (acids, alcohols or amines) with methylolated melamines.
Biocides are used for antimicrobial finishes regarding hospital textile material or as odour suppressants for socks. For this purpose, the following active substancesare used:
- zinc organic compounds,
- tin organic compounds,
- dichlorophenyl(ester) compounds,
- benzimidazol derivatives,
- triclosane, and
- isothiazolinones (the most commonly used today).

Biocides are also applied in the carpet sector to impart wool fibre lifetime protection against a range of textile pests. These auxiliaries are usually known as mothproofing agents. As mothproofing agents are used, such as permethrin (synthetic pyrethoid), gyfluthrin (synthetic pyrethroid), and sulcofuron (halogenated diphenylurea derivative).
All biocides give rise to environmental concerns when they are discharged in wastewater, because of their toxicity to aquatic life.

4. Organic dyes

Dyes make the world more beautiful through coloured products, but cause a lot of problems. Organic dyes contain a majority of substituted aromatic and heteroaromatic groups. The colour results from the conjugated chains or rings can absorb different wavelengths of the visible spectrum. Organic dyes contain chromophoric and auxochromic groups. Chromophoric groups are responsible for colouring properties, and the salt-forming auxochromes for the dying properties. The chromophores are usually composed of double-bonds (carbon-carbon, nitrogen-nitrogen, carbon-nitrogen), aromatic and heteroaromatic rings (containing oxygen, nitrogen or sulphur).

4.1 Classification

Textiles are dyed using many different colorants, that may be classified in several ways. With regard to the methods and domains during usage, the dyes are classified into acid, reactive, direct, basic, disperse, metal complex, vat, mordant, and sulphur dyes. Reactive and direct dyes are commonly in use for cotton and viscose-rayon dyeing, whilst disperse dyes are used for dyeing polyester. Dyes can be classified with regard to: their chemical structures, the methods and domains of usage, and chromogen (a dye or pigment precursor, containing chromophores), as presented in Table 6.
Azo dyes contain one or more azo bonds, and can be used for dyeing natural fibres (cotton, silk, and wool) as well as synthetic fibres (polyesters, polyacrylic, rayon, etc.). Azo dyes are the most-widely used synthetic dyes and are present in 60-70 % of all textile dyestuffs produced (ETAD, 2003). They are mainly used for yellow, orange, and red colours. The

biodegradation of more than 100 azo dyes were tested and only a few of them were degraded aerobically. The degree of stability of azo dyes under aerobic conditions depends on the structure of the molecule. C. I. Acid Orange 7 is one of the rare aerobically biodegradable azo dyes (Vandervivere, 1998). Under anaerobic conditions, azo dyes are cleaved into aromatic amines, which are not further metabolized under anaerobic conditions but readily biodegraded within an aerobic environment (Fig. 2).

	Classification	
	Subclass	Characteristic
With regard to chemical structure (C.I.)	E.g. azo, anthraquinone, triphenylmethane, indigo,…	The classification of a dye by chemical structure into a specific group is determined by the chromophore.
With regard to method and domain of usage (C.I.)	E. g. direct, acid, basic, reactive, reductive, sulphuric, chromic, metal complex, disperse, pigments,…	Dyes used in the same technological process of dyeing and with similar fastness are classified into the same group.
With regard to chromogen $n \rightarrow \pi^*$	E. g. absorptive, fluorescent and dyes with energy transfer,…	This classification is based on the type of excitation of electrons, which takes place during light adsorption.
With regard to the nature of donor – acceptor couple	E. g. 1-aminoanthraquinone, *p*-nitroaniline,…	These chromogenes contain a donor of electrons (non-bound electron couple), which directly bonds to the system of conjugated π electrons.
With regard to the nature of polyenes:		
a) Acyclic and cyclic	E. g. polyolefins, annulenes, carotenoids, rhodopsin,…	Polyene chromogen contains sp^2 (or sp) hybridised atoms. The molecules enclose single and double-bonds that form open chains, circles, or a combination of both.
b) Cyanine	E. g. cyanines, amino substituted di- and tri-arylmethane, oxonols, hydroxyarylmethanes,…	Cyanine chromogens have a system of conjugated π electrons, in which the number of electrons matches the number of p orbitals.

Table 6. Classification of dyes

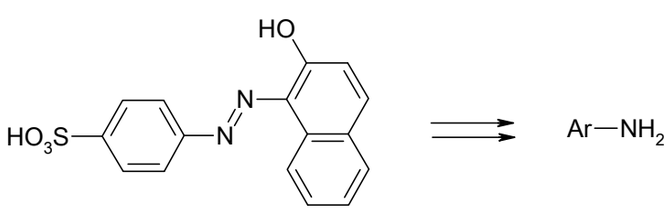


Fig. 2. Degradation of the azo dye C. I. Acid Orange 7 under anaerobic conditions

Carcinogenic amines that can be formed by the cleavage of certain azo dyes are:
4-aminodiphenyl, benzidine, 4-chloro-*o*-toluidine, 2-naphthylamine, *o*-aminoazotoluene, 2-amino-4-nitrotoluene, *p*-chloroaniline, 2,4-diaminoanisol, 4,4′-diaminodiphenylmethane, 3,3′-dichlorobenzidine, 3,3′-dimethoxybenzidine, 3,3′-dimethylbenzidine, 3,3′-dimethyl-4-4′-diaminodiphenylmethane, *p*-cresidine, 4,4′-methylene-*bis*-(2-chloraniline), 4,4′-oxydianiline, 4,4′-thiodianiline, *o*-toluidine, 2,4-diaminotoluene, 2,4,5-trimethylaniline, 4-aminobenzene, and *o*-anisidine (BAT, 2003).
More than 100 azo dyes with the potential to form carcinogenic amines are still available on the market (Euratex, 2000). The usage of these azo dyes that may cleave into one of the potentially carcinogenic aromatic amines from Table 7, is banned according to the 19th amendment of Directive 76/769/EWG on dangerous substances.
Fifty years ago, large amounts and numbers of azo colorants based on benzidine, 3,3-dichlorobenzidine, 3,3-dimethylbenzidine (*o*-toluidine), and 3,3-dimethoxybenzidine (o-dianisidine), have been synthesized, especially within the German chemical industry. 447 of the azo colorants from a list of 2000 in The Colour Index (1987), were based on 2-naphthylamine, benzidine or benzidine derivatives. The manufacturing of these kinds of azo dyes was stopped in 1971, with the exception of the dye Direct Black 4, and the manufacturing of this dye was continued until 1973 (Golka, 2004). The problem of carcinogenicity regarding azo dyes was first officially addressed by *the German Commission for Investigating Health Hazards of Chemical Compounds within the Work Area* ("MAK-Commission") (DFG, 1988). According to current EU regulations, azo dyes based on benzidine, 3,3-dimethoxybenzidine, and 3,3-dimethylbenzidine, are classified as carcinogens of category 2 as 'substances which should be regarded as if they are carcinogenic to man'. This is not the case for 3,3′-dichlorobenzidine-based azo pigments (BIA-Report, 2/2003).
The second more important class of textile dyes is anthraquinone dyes. They have a wide-range of colours over almost the whole visible spectrum, but they are more-commonly used for violet, blue, and green colours. Anthraquinone dyes are more resistant to biodegradation due to their fused aromatic structures, and thus remain coloured for a long time in wastewater.
Acid dyes are water-soluble compounds applied to wool, nylon, silk, and some modified acrylic textiles. Acid dyes have one or more sulphonic or carboxylic acid groups in their molecular structure. The dye-fibre affinity is the result of ionic bonds between the sulphonic acid part of the dye and the basic amino groups in wool, silk, and nylon fibres.
Reactive dyes are water soluble and are mainly used for dyeing cellulosic fibres such as cotton and rayon, and also for wool, silk, nylon, and leather. Reactive dyes form covalent chemical bonds with the fibre and become part of it. They are used extensively within textile industries in regard to their favourable characteristics of bright colour, water-fastness, and simple application techniques with low-energy consumption.
Metal-complex dyes show great affinity towards protein (wool) and polyamide fibres. Generally they are chromium or cobalt complexes (Zollinger, 2003). Chromium complex dyes are formed through chemical reactions between Cr_2O_3 and a variety of azo organic compounds (Zhao et al., 2005). Chromium occurs primarily in the trivalent state (III) and in the hexavalent state (VI). Hexavalent chromium is known to be toxic, can irritate the nose, throat, and lungs, provoke permanent eye damage, cause dermatitis and skin ulcers, and exhibit carcinogenic effects (Baral & Engelken, 2002). When reduced to chromium(III), it may be significantly less-harmful. As chromium compounds were used in dyes and paints

and the tanning of leather, these compounds are often found in soil and groundwater at abandoned industrial sites, now needing environmental clean-ups and remediation regarding the treatment of brownfill land.

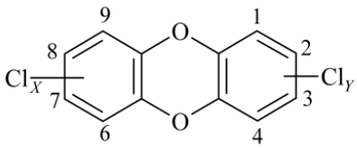
Disperse dyes have a very low water solubility, so they are applied as a dispersion of fine grounded powders in the dye-bath (Banat et al., 1996). Disperse dyes are used for oleophyllic fibres (polyester and other synthetics) that reject water-soluble dyes. Disperse dye-inks are used in the ink-jet textile printing of polyester fabrics. They have good fastness to light, perspiration, laundering, and dry cleaning. Some disperse dyes also have a tendency to bioaccumulate. Skin sensitisation risks are likely to be within acceptable limits.

Various intermediates used in the manufacture of disperse dyes are given below (Science tech entrepreneur, 2003): *p*-amino acetanilide, 1-amino-4-bromo-2-anthraquinone-sulphonic acid, *p*-amino phenol, 4-amino xanthopurpurin, aniline, anilino methane sulphonic acid, 1-benzamido-4-chloro-anthraquinone, 3-bromo benzanthrone, 1-bromo-4-methyl amino anthraquinone, 1-chloro-2, 4-dinitrobenzene, 2-chloro-4-nitroaniline, 4-chloro-3-nitrobenzene sulfonyl chloride, 2, 2-(*m*-chlorophenylamino)-diethanol, cresidune, *o*-cresol, *p*-cresol, 1,4-diamino, anthraquinone, 1,5-diamino anthraquinone, 2,6-dichloro-4-nitroanioline, 1,5-dihydroxy-4, 8-dinitro anthraquinone, *N*, *N*-dimethyl aniline, 1,5-dinitro anthraquinone, 1,8-dinitro anthraquinone, diphenylamine, ethanolamine, 2-(*N*-ethykamino)ethanol, 1-hydroxy anthraquinone, 1-hydroxy-4-nitro anthraquinone, leuco-1, 4, 5, 8-tetrahydroxy anthraquinone, methylamine, 1-methoxy anthraquinone, 3-methyl-1-phenyl-5-pyrazolone, 1-naphthylamine, *p*-nitroaniline, phenol, *p*-phenyl azoaniline, quinizarin, *p*-toluene sulfoanamide, 2, 2-(*m*-tolyamino) diethanol.

Basic dyes have high brilliance and intensity of colour, and are highly visible even in a very low concentration (Chu & Chen, 2002). Basic dyes are the most acutely toxic dyes for fish, especially those with tri-aryl-methane structures. Occasionally, some people develop a contact allergy to dyes in clothing. This is ample evidence that there is reason to be cautious in the use of some basic dyes. The absence of a known hazard does not prove that the substance is non-carcinogenic or mutagenic.

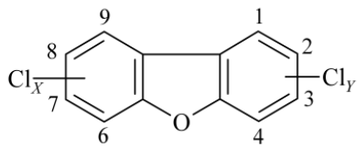
5. Possible sources of persistent and hazardous organic pollutants in textile chain

Persistent organic pollutants are a wide group of compounds with specific properties: persistency, high bioaccumulative coefficient, ability for transmission to large distances. POPs emission inventory has a great significance as a starting-point for pollutant flows' modelling, impact and risk assessment. The most toxic among POPs are polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), often simply termed as dioxins. There are 75 isomers of dibenzo-*p*-dioxins (PCDDs) and 135 isomers of polychlorinated dibenzofurans differentiated from each other by the number and location of the chlorine atom addition. Chemical and biological properties (including the toxicological) depend on the positions of the chlorine atoms. In this group, isomers with chlorine atoms at positions 2,3,7,8 are especially toxic. The so-called 'dirty group' comprises 17 isomers of PCDD/Fs, among which 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD) is the most toxic (Fig. 3). There are also brominated dioxins (PBDD/Fs), fluoro dioxins and mixed dioxins PXDD/Fs (X = Cl, Br, F). PBDD/Fs are contaminants with properties similar to PCDD/Fs, together with their persistence and toxicity. Fluorinated congeners of dioxins are taken to be less dangerous to humans and the environment, due to their short life and low toxicity.



$X + Y$ = 1-8 (75 congeners)

Polychlorinated dibenzo-*p*-dioxins



$X + Y$ = 1-8 (135 congeners)

Polychlorinated dibenzofurans

Fig. 3. Molecular structures of polychlorinated dibenzo-*p*-dioxins and dibenzofurans

Possible sources of dioxins among the textile chains will be presented in the following chapters.

5.1 Natural fibre

As already-mentioned in chapter 2.2.1, pentachlorophenol and other organochlorine pesticides are used during the production and transportation of natural textile fibres. The production and use of PCP is a significant source of PCDD/Fs. During the synthesis of pentachlorophenol from chlorinated phenols, PCDD/Fs are formed as by-products. Furthermore, PCDD/Fs are formed from chlorinated phenols during natural UV radiation conditions.

5.2 Textile dyes

The main source of dioxins in the textile industry are dioxazine and antraquinone dyes and pigments. These classes of dyes are produced from chloranil. PCDD/Fs are formed during the synthesis of chloranil from chlorinated phenols. Dioxins are also found in other classes of dyes. Considerable levels of PCDD/Fs have also been determined in some phtalocyanine dyes, and in printing inks (Križanec, 2006). Recently some dispersive aromatic azo dyes were found as sources of dioxins. In dual-black disperse dyes (mixtures of antraquinone and azo substances); concentrations of 50 and 170 ng PCDD/F TEQ/kg have been determined. Octachlorodibenzodioxin (OCDD) was the dominant compound (Križanec, 2005). Disperse azo dyes produced from chlorinated anilines or chlorinated nitro anilines contain dioxins as by-products during synthesis. Dioxins are formed after the dediazonation of aromatic diazonium salts via chlorinated phenols and chlorinated nitrophenols. The hydrolysis of diazonium salts leads to phenols (Križanec, 2007). Chlorinated phenols and chlorinated nitrophenols are present in dyes' formulations as impurities, and dioxins may form further during dyeing processes (Fig.4) (Križanec, 2007).

5.3 Halogenated organic compounds

Halogenated organic compounds, especially aromatic halogenated compounds, are also precursor compounds for the synthesis of dioxins. Halogenated organic compounds and metals such as copper are involved in the thermal formation processes of dioxins. During the combustion processes of waste textile materials, the formation of dioxins is possible via the 'The Precursor Concept' or 'De novo Mechanism' (Križanec, 2006).

All the halogenated flame-retardant agents presented in chapter 3.2.4 are involved in the formation of dioxins and furans, when submitted to high temperature treatments. Dioxins and furans can be formed in small amounts during the syntheses of these compounds, and as a side-reaction when they are subject to combustion/burning for disposal.

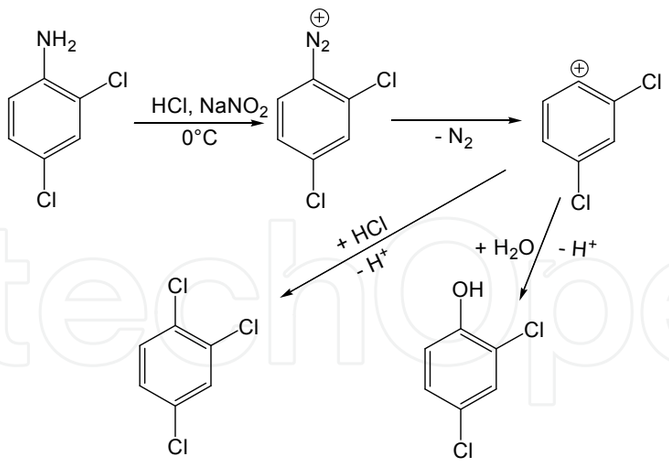


Fig. 4. Heterolytic pathway during the dediazonation of chlorinated aromatic diazonium salts, and the formation of chlorinated benzenes and chlorinated phenols

5.4 Formation of dioxins during finishing processes

The generation of persistent organic pollutants in the textile industry during finishing processes is caused by (Križanec, 2006):

- high temperatures (>150 °C);
- alkaline conditions;
- UV radiations or other radical starters;
- the presence of chlorinated organic compounds;
- the presence of metal catalysts.

The distribution of dioxins and their fate during textile dyeing processes was investigated by Križanec (Križanec, 2005). Two dyeing experiments were conducted at laboratory scale using disperse dye contaminated with PCDD/Fs. After the dyeing and finishing process, the PCDD/Fs, and especially OCDD, increased compared to the input. The authors concluded that PCDD/Fs are formed during the textile process, most probably from precursors present in the dyestuffs (Križanec, 2005).

5.5 Incineration of textile materials

Incineration processes are a known source of dioxins. Several textile products are also potential sources for the formation of dioxins during waste incineration. As described in previous sections, dioxins, and especially dioxin precursor compounds, may be present in textile products. According to the dioxin mass-balance present in a Spanish municipal waste incinerator, the incineration of textiles results in the highest dioxin emission levels (Abad et al., 2000).

6. Textile wastewater

6.1 Characteristics of wastewater after finishing processes

The diversity of textile finishing processes results in variable compositions of textile wastewater. In general, the wastewater is loaded with complex mixtures of organic and inorganic chemicals (Volmajer Valh et al., 2011). Moreover, textile finishing processes are, despite the gradual reduction of fresh water consumption by introducing, for example, jet

dyeing machines and short liquor-dyeing systems, still very water intensive, leading to large volumes of produced wastewater that have to be treated before being discharged. For illustration purposes, 70 L of freshly-softened water is used per kg of cotton material during dark-colour reactive dyeing processes (data from Slovene textile company). With further optimization, it is possible to reach values between 25 to 40 L of fresh water per kilogram of cotton for a dark reactive dyeing, in contrast to the 100 to 150 L water consumption for this type of dyeing, as used in the mid-nineteen seventies.

When considering both the volume generated and the effluent composition, textile industry wastewater is considered to be the most polluted of all the industrial sectors.

The pollutants of major concern are recalcitrant or hazardous organics, such as dyes or some surfactants, metals, and salts. During the textile dyeing process, dyes are always used in combination with other chemicals such as acids, alkali, salts, fixing agents, carriers, dispersing agents, and surfactants that are partly or almost completely discharged in the wastewater. Dye-fixation rates vary considerably among the different classes of dyes and may be especially low for reactive dyes (in the case of cotton 20-50 % residual dyestuff) and for sulphur dyes (30-40 % residual). Moreover, large variations are round even within a given class of colorants. This is particularly significant in the case of reactive dyes.

As already-mentioned, from among all the dye classes, azo dyes are the group of colorants most used. Whilst most azo dyes themselves are non-toxic, a significantly larger portion of their metabolites are (Isik & Sponza, 2007; Van der Zee & Villaverde 2005). Brown and DeVito (Brown & DeVito, 1993) postulated that azo dyes may be toxic only after the reduction and cleavage of the azo linkage, producing aromatic amines. Azo dyes with structures containing free aromatic amine groups that can be metabolically oxidized without azo reduction, may cause toxicity. Azo dye toxic activation may occur following direct oxidation of the azo linkage, producing highly reactive electrophilic diazonium salts.

Most dyes shown to be carcinogenic are no longer used; however, a complete investigation of all dyestuffs available on the market is impossible.

Substituted benzene and naphthalene rings are common constituents of azo dyes, and have been identified as potentially carcinogenic agents (IARC, 1982).

Other concerns are the impurities within commercial dye products and the additives used during the dyeing process. Understanding the dye structures and how they are degraded is crucial to understanding how toxic by-products are created. The colour of wastewater is one of the major problems facing industries involved in dyeing processes. Wastewaters from dye-houses often carry high concentrations of excess, unfixed dye.

A study conducted on 45 combined effluents from textile finishing plants showed that 27 percent of the wastewater samples were mutagenic during the Ames test (McCarthy, 1997). The potential for toxic effects to humans, resulting from exposure to dyes and dye metabolites, is not a new concern.

6.2 Wastewater treatment processes

Textile wastewater is the main source of organic contamination regarding pollution within the textile industry. Several cleaning processes may be used to remove organic pollutants from textile wastewater. In general, we distinguish between physical methods (adsorption, filtration methods, coagulation and flocculation processes), chemical methods (oxidation, advanced oxidation, Fenton´s reagent) and, more recently, more and more attractive biological treatment (anaerobic, aerobic) as an effective option for relatively inexpensive effluent decolouration. Non-destructive physical techniques just transfer the pollutants to other mediums (sludge,

concentrate in filtration techniques), and cause secondary pollution. From this point of view, the chemical destruction of pollutants is more desirable, but could have some drawbacks such as the formation of aromatic amines, when the degradation/mineralisation is incomplete. An overview of the treatment methods for textile wastewater treatment, as well as their advantages and disadvantages, are gathered in 'Decolouration of textile wastewaters' (Volmajer Valh & Majcen Le Marechal, 2009). The following paragraph focuses on chemical methods, especially on advanced oxidation processes (AOPs).

According to their definition, AOPs combine ozone (O_3), ultraviolet (UV) irradiation, hydrogen peroxide H_2O_2 and/or a catalyst in order to offer a powerful water treatment solution for the reduction (removal) of residual organic compounds, as measured by COD, BOD or TOC, without producing additional hazardous by-products or sludge, which requires further handling (Arslan-Alaton, 2004). All AOPs are designed to produce hydroxyl radicals that act with high-efficiency to destroy organic compounds. The most widely-applied advanced oxidation processes (AOP) are: H_2O_2/UV, O_3/UV, H_2O_2/O_3, H_2O_2/O_3/UV (Kurbus et al. 2003), and ultrasound (US) (Vajnhandl & Majcen Le Marechal, 2007) have several advantages such as: rapid reaction rates, small foot-print, reduction of toxicity, and complete mineralization of treated organics, no concentration of waste for further treatment (as membranes), no production of materials that require further treatment, such as 'spent carbon' from activated carbon absorption, no creation of sludge as with physical-chemical processes or biological processes (wasted biological sludge), and a non-selective pathway allows for the treatment of multiple organics, at once. On the contrary, these processes are capital-intensive and, in the case of complex chemistry, must be tailored to specific applications (Slokar & Majcen Le Marechal, 1998).

AOPs are marked as treatment methods for the effective removal of organic pollutants in terms of total organic carbon (TOC), COD, and BOD reduction, but less information is available regarding the chemical structures of formed degradation products and their toxicity aspect. Moreover, with modern advanced oxidation processes, caution is necessary when dioxins and other halogenated persistent organic-pollutants could be present. During UV or US irradiation, for example, high chlorinated dioxins and other halogenated pollutants can be de-chlorinated. Lower chlorinated dioxins are known as more toxic compounds compared to high chlorinated pollutants. The very efficient processes for removing persistent organic pollutants from wastewater are those coagulation and adsorption processes used in municipal-waste plants (Križanec, 2007).

6.3 Toxicity of organic pollutants within textile wastewater

The toxicity of textile wastewater varies depending on the different processes applied within the textile industry. The wastewaters of some processes have high aquatic toxicity, whilst others show little or no toxicity. An identification of all toxic compounds used within the textile industry is impossible due to the huge variety of used chemicals and a lack of data about their toxicities. Usually overall toxicity is determined by toxicity-testing the whole effluent stream of aquatic organisms, which is a cost-effective method.

The sources of organic pollutants that can cause aquatic toxicity can be dyes, surfactants, toxic organic chemicals, or biocides. Examples of compounds in each of these classes and their sources, are shown in Table 7.

Textile wastewaters contain different polar and non-polar compounds, but the polar ones are predominant. Polar organic pollutants are non-biodegradable and their elimination is often incomplete.

Agent	Chemical example	Source
Surfactants	Ethoxylated phenols	Multiple processes
Organics	Chlorinated solvents	Scour, machine cleaning
Biocides	Pentachlorophenol	Wool fibres contaminant

Table 7. Typical causes of aquatic toxicity

Non-polar organic pollutants such as dioxins, may be present in textile wastewater in trace amounts. Due to their high toxicity and persistent organic pollutant properties, the restricted limits on wastewater are relatively low. According to EU regulations there are no restrictive limits for dioxins in textile wastewater. For wastewater from incineration plants the restrictive limit is 0.3 ng TEQ-ITF/L. According to our study the concentrations of dioxins in textile wastewater with disperse dyes are considerable (Križanec, 2007). The concentration of PCDD/Fs found in the wastewater sample polluted with disperse dyes was 0.44 ng TEQ-ITF/L. The dominant PCDD/F congener in the disperse dyes' wastewater sample was 2,3,4,6,7,8-HxCDF, the contribution of which to the TEQ was more than 85 % (Fig. 5). The concentration of PCDD/F in this selected wastewater polluted with disperse dyes exceeded the limit of 0.3 ng TEQ-ITF/L, as determined by the European regulation for wastewaters from incineration plants.

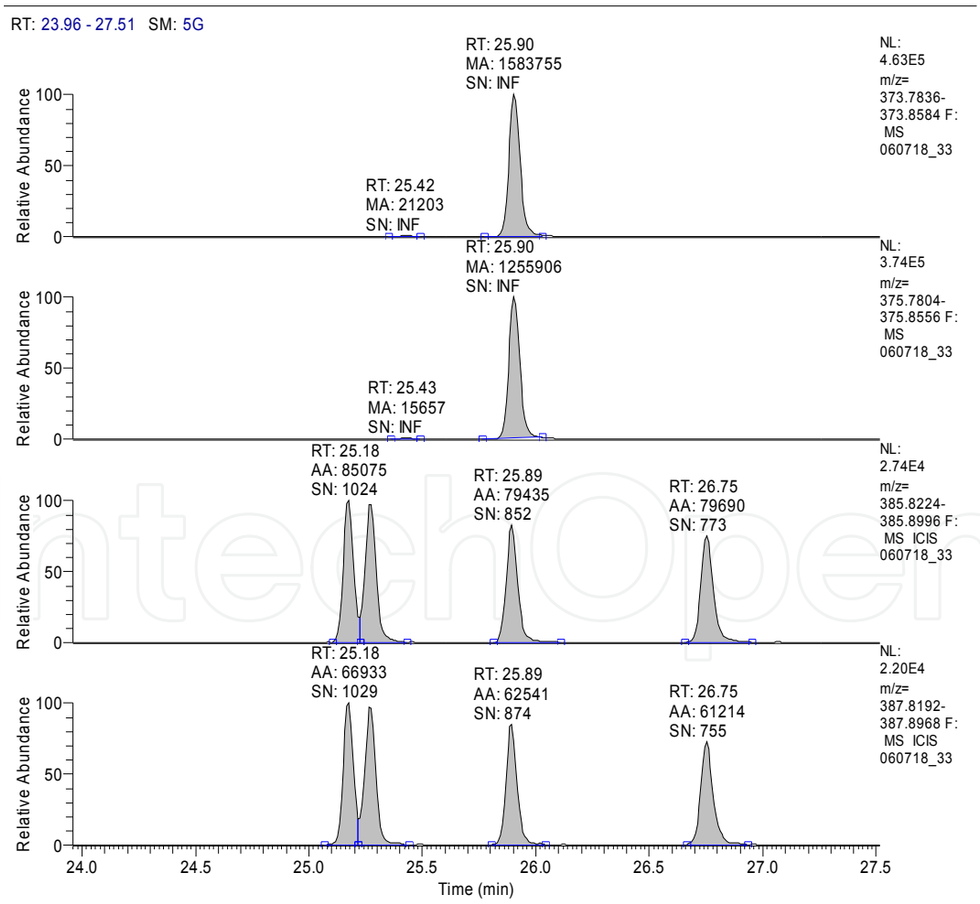


Fig. 5. Dioxin homologue profile found in textile wastewater. There is evident that 2,3,4,6,7,8-HxCDF congener is dominant

7. Tracking persistent organic pollutants in textile finishing and AOP processes

Information about the emissions of persistent organic pollutants from the textile industry is limited due to a lack of complete and accurate emission data. Indirect measurements are necessary regarding the reduction of persistent organic pollution from the textile industry. The presence and concentrations of pollutants should be controlled throughout the textile industry regarding incoming materials and also for textile products and wastewater.

Several instrumental and analytical approaches are in use for determining persistent organic pollutants. For the determination of semi-volatile organic pollutants, the most appropriate are gas chromatographic methods connected with appropriate detectors. For tracking low-level halogenated organic pollutants, the use of gas chromatography with an electron capture detector (ECD), is a useful and relatively cost-effective method.

In order to determine the trace-levels of organic pollutants (dioxins), gas chromatography with mass spectrometry or high-resolution mass spectrometry is required (UEPA method 1613, 1994). Liquid chromatography with mass spectrometry is used to determine water solubility and highly-volatile organic pollutants(Dolman & Pelzing, 2011).

In our pilot studies, two samples of textile wastewater (a mix of disperse dyes' wastewater and mix of metal-complex dyes' wastewater) were analyzed for persistent organo-halogen compounds (POPs). Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans PCDFs), dioxin-like PCBs, and polybrominated diphenyl ethers (PBDEs), were determined using the HRGC/HRMS technique. Further decolouration experiments of these wastewaters were performed using the advanced oxidation process (AOP). The POPs' analyses were performed on the samples after the AOP process, and the results were then compared with the initial values.

Wastewater samples were collected from a local textile-dyeing facility, the main activity of which is the dyeing (wet processes) of polyester yarns with disperse dyes. Samples of wastewater were collected at the out-flow of the facility, and stored in pre-cleaned 2.5 L borosilicate amber bottles at 5 ^{o}C until analysis or experiment. The disperse dyes' and metal complex dyes' wastewaters were a mix of at least four different dispersals, and at least four different metal complex dyes, respectively. The exact composition of the wastewater was unknown. Wastewater samples (0.5 L) were transferred in separate funnels and spiked with an internal standard mixture containing ^{13}C-labelled isomers of analytes. Hexane (100 mL) was used as the liquid-liquid extraction solvent. The sample extract clean-up was performed according to the USEPA method 1613 (USEPA method 1613, 1994). By using adsorption chromatography on a graphitized carbon column (Carbopack C), the PCBs and PBDEs (60 mL dichloromethane-direct flow),were separated from the PCDD/Fs (60 mL of toluene-opposite flow). The obtained fractions were concentrated to a final volume of 20 μL, and analyzed with GC/HRMS.

Extracts were analyzed on a HP 6890 gas chromatograph GC (Hewlett-Packard, Palo Alto, CA, USA) coupled to a Finnigan MAT 95 XP high resolution mass spectrometer. Aliquot (1.5 μL) of PCDD/F toluene sample extracts were injected into the GC system, equipped with a Restek Rtx Dioxin2 capillary column (60 m x 0.25 mm i.d., film thickness 0.25 μm) in splitless mode. The mass spectrometer operated within the electron impact ionization mode using selected ion-monitoring (SIM), at a minimum resolution of 10,000. The samples were analyzed for PCDD/Fs concentrations, using the isotope dilution method based on USEPA 1613 protocol (USEPA method 1613, 1994). A similar determination/quantification approach was also used for the determining of PCBs and PBDEs in the dichloromethane extracts. In

each set of experiments the blank samples were analyzed, and in cases of some PCBs and PBDEs congeners, the blank values were subtracted from the sample values.

H_2O_2/UV experiments were carried out in a batch photo-reactor using a low-pressure mercury UV lamp emitting at 254 nm. The high-frequency plate type URS 1000 L-3 communications system ELAC Nautik was used for ultrasonic irradiation. A system consisting of an AG 1006 LF generator/amplifier (200 W maximum output) and USW 51 ultrasonic transducer (817 kHz) with a working volume of 500 mL. The experimental parameters for the power of the UV lamp was 1600 W, and the reaction time was 60 minutes. Ultrasonic irradiation was performed at 820 kHz.

The concentrations of PCDD/Fs in the wastewater samples at different stages of the experiment, are presented in Table 8. The concentrations of PCDD/Fs in the metal complex dyes wastewater samples were low, and close to both the quantification limits and the concentrations of the background levels. As expected, the concentrations of PCDD/Fs in the samples of disperse dyes' wastewater, were relatively high (Fig. 5).

After AOP treatment the concentrations of PCDD/Fs were similar to those of the original sample, for both types of wastewater. This indicates that PCDD/Fs are stable enough in these types of wastewater to resist those conditions used during our AOP experiments. Also, no new PCDD/F congener was observed.

The concentrations of dioxin-like PCBs in the wastewater samples at different stages of the experiment, are presented in Table 9. The concentrations of dioxine-like PCBs and also PBDEs after AOPs experiments are incomparable with the PCDD/F concentrations of the original wastewater samples. This is because PCBs and PBDEs are not as resistant as PCDD/Fs when some transformations were observed

The concentrations in the samples of H_2O_2/UV-treated wastewater were, for most of the dioxine-like PCBs and the selected PBDEs, higher in comparison with the original samples. We suggest that this is due to the dechlorination or debromination of the higher halogenated congeners and/or the cleavages of the polychlorinated terphenyls. After the sonification AOP method, the concentrations of dioxine-like PCBs and selected PBDEs were relative low. These results suggest that local rigorous conditions (high-pressure, high- temperature) cause the destruction of PCBs and PBDEs via a thermal and/or radical mechanism.

The HGC/HRMS analytical method was used for tracking POP during this pilot-study. This analytical method is expensive and time-consuming but gives us very important information regarding POP's congener distribution at trace levels. In addition, other analytical methods should be tested on samples from the textile industry. When tracking POPs in the textile industry, appropriate screening methods (for example GC/ECD) should be tested and used during routine controls, in order to prevent POPs' pollution from this sector.

With the aim of reducing organic pollution within the textile industry, all the important steps towards sustainable thinking and the introduction of green chemistry are necessary at all stages of the textile-chain, in-line with the recommendations of industrial platforms (WSSTP, Textile Platform). The development of new wet-processing equipment is recommended in order to minimize the amount of fresh water and, consequently, to reduce the volume of generated wastewater and production costs. New wastewater treatment approaches should be implemented through pollution prevention in order to prevent environmental problems, such as waste minimization and reuse of treated water during the production processes. Finally, regulation of pollution by developing strategies for characterization and monitoring (IPPC) the most dangerous pollutants, should certainly also be expanded to cover the textile sector.

	Concentration (ng/L)					
Congener/Group	1	2	3	4	5	6
TCDD	< 0.01	0.04	< 0.01	< 0.01	0.01	< 0.01
PeCDD	0.02	0.03	0.03	< 0.01	< 0.01	< 0.01
HxCDD	0.08	0.19	0.10	0.01	0.03	0.01
HpCDD	0.20	< 0.01	0.23	0.01	0.05	0.02
OCDD	0.25	0.51	0.23	0.06	0.05	0.02
TCDF	0.15	1.02	0.50	< 0.01	0.06	< 0.01
PeCDF	0.22	1.54	0.24	< 0.01	0.03	< 0.01
HxCDF	3.77	3.05	6.44	< 0.01	0.08	0.30
HpCDF	0.12	0.10	0.09	< 0.01	0.01	< 0.01
OCDF	0.05	0.03	0.02	< 0.01	0.01	< 0.01
2.3.7.8-TCDD	< 0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01
1.2.3.7.8-PeCDD	< 0.01	0.01	0.01	< 0.01	< 0.01	< 0.01
1.2.3.4.7.8-HxCDD	< 0.01	0.12	< 0.01	< 0.01	< 0.01	< 0.01
1.2.3.6.7.8-HxCDD	0.01	0.06	0.01	< 0.01	< 0.01	< 0.01
1.2.3.7.8.9-HxCDD	0.01	0.03	0.01	< 0.01	< 0.01	< 0.01
1.2.3.4.6.7.8-HpCDD	0.14	0.58	0.17	0.01	0.02	0.01
1.2.3.4.6.7.8.9-OCDD	0.25	0.51	0.23	0.06	0.05	0.02
2.3.7.8-TCDF	< 0.01	0.07	< 0.01	< 0.01	0.01	< 0.01
1.2.3.7.8-PeCDF	0.01	0.04	< 0.01	< 0.01	0.01	< 0.01
2.3.4.7.8-PeCDF	0.01	0.04	0.01	< 0.01	0.01	< 0.01
1.2.3.4.7.8-HxCDF	0.01	0.02	< 0.01	< 0.01	0.01	< 0.01
1.2.3.6.7.8-HxCDF	0.04	0.01	< 0.01	< 0.01	0.01	< 0.01
2.3.4.6.7.8-HxCDF	4.23	4.00	6.73	0.01	0.07	0.30
1.2.3.7.8.9-HxCDF	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
1.2.3.4.6.7.8.-HpCDF	0.09	0.08	0.07	< 0.01	0.01	< 0.01
1.2.3.4.7.8.9-HpCDF	< 0.01	0.01	0.01	< 0.01	< 0.01	< 0.01
1.2.3.4.6.7.8.9-OCDF	0.05	0.03	0.02	< 0.01	0.01	< 0.01
Sum TEQ-ITF	**0.44 ± 0.09**	**0.47 ± 0.09**	**0.69 ± 0.14**	**< 0.01**	**0.02 ± 0.01**	**0.03 ± 0.01**

Legend: 1- Wastewater with disperse dyes. 2- Wastewater with disperse dyes treated with H_2O_2/UV. 3- Wastewater with disperse dyes treated with US. 4- Wastewater with metal complex dyes. 5- Wastewater with metal complex dyes treated with H_2O_2/UV. 6- Wastewater with metal complex dyes treated with US

Table 8. Mass-balance of PCDD/Fs in wastewater polluted with disperse and metal complex dyes treated with H_2O_2/UV and US processes

	Concentration (ng/L)					
PCB congener	1	2	3	4	5	6
PCB 81	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
PCB 77	0.35	< 0.05	0.37	0.15	0.41	< 0.05
PCB 126	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
PCB 169	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
PCB 105	0.36	< 0.05	2.81	0.38	< 0.05	< 0.05
PCB 114	0.05	< 0.05	0.17	< 0.05	< 0.05	< 0.05
PCB 118	0.88	< 0.05	5.52	1.10	< 0.05	< 0.05
PCB 123	0.11	< 0.05	0.45	0.08	< 0.05	< 0.05
PCB 156	0.08	< 0.05	1.20	0.16	< 0.05	< 0.05
PCB 157	< 0.05	< 0.05	0.29	< 0.05	0.28	< 0.05
PCB 167	< 0.05	< 0.05	0.46	0.07	< 0.05	< 0.05
PCB 189	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

Legend: 1- Wastewater with disperse dyes. 2- Wastewater with disperse dyes treated with H2O2/UV. 3- Wastewater with disperse dyes treated with US. 4- Wastewater with metal complex dyes. 5- Wastewater with metal complex dyes treated with H2O2/UV. 6- Wastewater with metal complex dyes treated with US

Table 9. Mass-balance of PCB congener in wastewater polluted with disperse and metal complex dyes treated with H_2O_2/UV and US processes.

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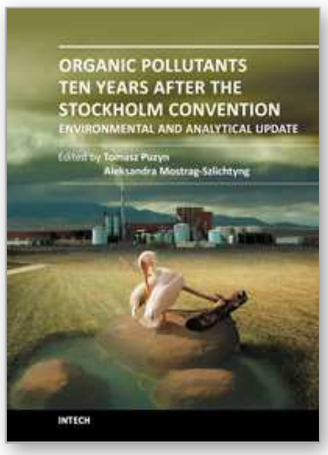
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Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update

Edited by Dr. Tomasz Puzyn

ISBN 978-953-307-917-2
Hard cover, 472 pages
Publisher InTech
Published online 24, February, 2012
Published in print edition February, 2012

Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Alenka Majcen Le Marechal, Boštjan Križanec, Simona Vajnhandl and Julija Volmajer Valh (2012). Textile Finishing Industry as an Important Source of Organic Pollutants, Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update, Dr. Tomasz Puzyn (Ed.), ISBN: 978-953-307-917-2, InTech, Available from: http://www.intechopen.com/books/organic-pollutants-ten-years-after-the-stockholm-convention-environmental-and-analytical-update/textile-finishing-industry-as-an-important-source-of-organic-pollutants

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