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Application of Cyclodextrins in Textile Dyeing

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1. Introduction

1.1 Dyeing auxiliaries

Auxiliaries are compounds which are not an integral part of the dyeing process but by adding them to the dye bath the dyeing can be improved. The main functions of auxiliaries are to prepare or improve the substrate in readiness for colorants (by wetting, providing sorption sites, improving or resisting the migration of dyes), to stabilize the application media (by improving dye solubility, stabilizing a dispersion or solution), to protect or modify the substrate (by creating or resisting dyeability, protecting against the effects of temperature and other processing conditions), to improve the dyes fastness (by various after-treatments) and to enhance the properties of laundering formulation. The main ranges of dyeing auxiliaries are: crease inhibitors, wetting agents, defoamers, diffusion accelerants, carriers, dispersing agents, dye-protective agents, fibre-protective agents, fixing agents, levelling agents, migration-inhibiting agents, pH regulators, buffers, sequestering agents, UV absorbers, fibre stabilizers, UV protective agents and wash-off agents.

1.2 Levelling agents

For all dye-fibre systems, level dyeing problems can be divided into either *gross unlevelness throughout the substrate* which is related to the dyeing process or *localized unlevelness* which is related to non-uniformity of the substrate (Burkinshaw, 1995). The receptivity of different regions of a fibre or of different fibres in a mixed yarn may not be the same for a given dyestuff, thus causing uneven dyeing. These undesired effects can be eliminated or diminished by the use of levelling agents. Levelling agents usually contain functional groups which are similar to those by which the dyestuffs are attached to the fibre. There are two mechanisms involved in the activities of levelling agents: there is a competition for sites on the fibre between dyestaff and levelling agent; or the agents can slow down the migration of dye by forming complex micelles with the dyestuff molecules which are released slowly to the fibre. A very large number of levelling agents have been developed in attempts to get the right balance of properties for particular types of dyestuff and fibres, cyclodextrins could be one of the most promising.

2. Supramolecular chemistry

Supramolecular chemistry is the discipline of chemistry which involves all intermolecular interactions where covalent bonds are not established between the interacting species: i.e.,

molecules, ions, or radicals. The majority of these interactions are of the host-guest type. Among all potential hosts, the cyclodextrins seem to be the most important ones, for the following reasons (Szejtli, 1998; Vögtle, 1991).

1. Cyclodextrins are seminatural products; they are produced from a renewable natural material, starch, by a relatively simple enzymatic conversion.
2. They are produced in thousands of tons per year by environmentally friendly technologies.
3. Because of their huge production, the initially high prices of cyclodextrins have dropped to levels where they become acceptable for most industrial purposes. The total output of β-cyclodextrin is in excess of 1000 tons/year, and the price is only several dollars per kilogram, depending on quality and delivered quantity. Also α- and γ-cyclodextrins, as well as several derivatives, (hydroxypropyl-β-cyclodextrin and -γ-cyclodextrin, randomly methylated α- and β-cyclodextrin, maltosyl-β-cyclodextrin, acetylated cyclodextrins, etc.) are produced industrially. A large number of other derivatives are available as fine chemicals, and used in various chromatographic methods, or are studied as potential drug carriers, stabilizers, catalysts, etc.
4. Cyclodextrin molecules are of a great interest for scientists because of their capacity to include guest molecules in their cavities. Such inclusion is considered as a molecular encapsulation and it results in better stability of guests to air, heat or light, higher water solubility, possible increase in bioavailability, slow release and others.
5. In general, cyclodextrins are not toxic, but any of their toxic effects are of secondary character and can be eliminated by selecting the appropriate cyclodextrin type or derivative or mode of application.

2.1 Cyclodextrins

Cyclodextrins (CDs) comprise a family of three well-known industrially produced substances. The practically important, industrially produced CDs are the α-, β-, and γ-cyclodextrins (Fig. 1). There are some rare, minor cyclic oligosaccharides as well which are due to their costs not applicable to textiles (Vögtle, 1991).

The three major cyclodextrins are crystalline, homogeneous, nonhygroscopic substances, which are torus-like macro-rings built up from glucopyranose units. The α-cyclodextrin (Schardinger's α-dextrin, cyclomaltohexaose, cyclohexaglucan, cyclohexaamylose, α-CD, ACD, C6A) comprises six glucopyranose units, β-cyclodextrin (Schardinger's β-dextrin, cyclomaltoheptaose, cycloheptaglucan, cycloheptaamylose, β-CD, BCD, C7A) comprises seven such units, and γ-cyclodextrin (Schardinger's γ-dextrin, cyclomaltooctaose, cyclooctaglucan, cyclooctaamylose, γ-CD, GCD, C8A) comprises eight such units (Fig. 1). Cyclodextrins can be obtained by enzymatic degradation of starch. In this process compounds with six to twelve glucopyranose units per ring are produced. Depending on the enzyme and the way the reaction is controlled, the main product is α, β or γ-cyclodextrin (6, 7 and 8 glucopyranose units, respectively). They are of circular and conical conformation, where the height is about 800 pm. The inner diameter of the cavity varies from 500 to 800 pm.

Crystal structure analysis has demonstrated that all glucopyranose units in the torus-like ring possess the thermodynamically favoured chair conformation because all substituents are in the equatorial position. As a consequence of the 4C1 conformation of the glucopyranose units, all secondary hydroxyl groups are situated on one of the two edges of the ring, whereas all the primary ones are placed on the other edge. All secondary hydroxyl

groups are situated on the larger side of the two edges of the ring, whereas all the primary ones are placed on the smaller side of the ring. These hydroxyl groups ensure good water solubility. The cavity is lined by the hydrogen atoms of C3, by the glycosidic oxygen bridges and hydrogen atoms of C5. The nonbonding electron pairs of the glycosidic oxygen bridges are directed toward the inside of the cavity producing a high electron density there and because of this the inner side of the cavity has some Lewis base characteristics. The C-2-OH group of one glucopyranose unit can form a hydrogen bond with the C-3-OH group of the adjacent glucopyranose unit. In the cyclodextrin molecule, a complete secondary belt is formed by these H bonds, therefore the β-cyclodextrin has a rather rigid structure. Because of this arrangement, the interior of the toroids is not hydrophobic but considerably less hydrophilic than the aqueous environment and thus able to host hydrophobic molecules. Cyclodextrins behave more or less like rigid compounds with two degrees of freedom, rotation at the glucosidic links C4-O4 and C1-O4 and rotations at the O6 primary hydroxyl groups at the C5-C6 band.

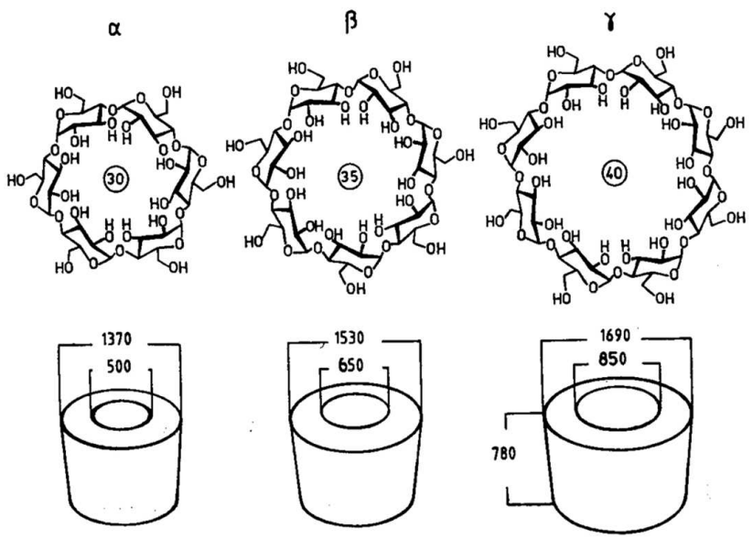


Fig. 1. Structure and dimensions of α-, β- and γ-cyclodextrin

The intramolecular hydrogen bond formation is probably the explanation for the observation that β-cyclodextrin has the lowest water solubility of alls. The hydrogen-bond belt is incomplete in the α-cyclodextrin molecule, because one glucopyranose unit is in a distorted position. Consequently, instead of the six possible hydrogen-bonds, only four can be established fully. γ-Cyclodextrin is a noncoplanar with more flexible structure; therefore, it is the most soluble of the three cyclodextrins. Fig. 2 shows a sketch of the characteristic structural features of cyclodextrins. On the side where the secondary hydroxyl groups are situated, the diameter of the cavity is larger than on the side with the primary hydroxyls, since free rotation of the primary hydroxyls reduces the effective diameter of the cavity (Connors, 1997).

2.2 Toxicological considerations

Since fabrics are in direct contact with human skin, toxic specification of cyclodextrins have been studied (Martin Del Valle, 2004; Dajstjerdi & Montazer, 2010). Since year 2000, β-

cyclodextrin has been introduced as a food additive in Germany. With respect to OECD experiments, this compounds has shown no allergic impact.

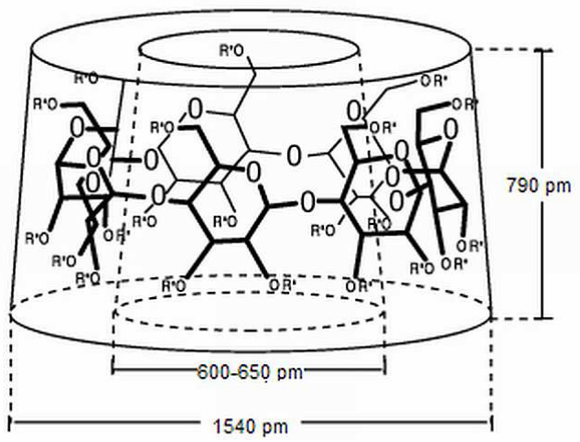


Fig. 2. Structural features of β-cyclodextrin

In general, the natural cyclodextrins and their hydrophilic derivatives are only able to permeate lypophilic biological membranes, such as the eye cornea, with considerable difficulty. All toxicity studies have demonstrated that orally administered cyclodextrins are practically non-toxic, due to lack of absorption from the gastrointestinal tract. The main properties of β-cyclodextrin (β-CD), the most important cyclodextrin in textile application are: less irritating than α-cyclodextrin after i.m. injection, binds cholesterol, small amount (1-2%) is adsorbed in the upper intestinal tract, no metabolism in the upper intestinal tract, metabolised by bacteria in caecum and colon, LD50 oral rat > 5000 mg/kg, LD50 i.v., rat: between 450 – 790 mg/kg, however, application of high doses may be harmful and is not recommended.

2.3 Inclusion complex formation

The most notable feature of cyclodextrins is their ability to form solid inclusion complexes ("host–guest" complexes) with a very wide range of solid, liquid and gaseous compounds by a molecular complexation.

In these complexes a guest molecule is held within the cavity of the cyclodextrin host molecule. Complex formation is a dimensional fit between host cavity and guest molecule. The lipophilic cavity of cyclodextrin molecules provides a microenvironment into which appropriately sized non-polar moieties can enter to form inclusion complexes. No covalent bonds are broken or formed during formation of the inclusion complex. The main driving force of complex formation is the release of enthalpy-rich water molecules from the cavity. The water molecules located inside the cavity cannot satisfy their hydrogen bonding potentials and therefore are of higher enthalpy. The energy of the system is lowered when these enthalpy–rich water molecules are replaced by suitable guest molecules which are less polar than water. In an aqueous solution, the slightly apolar cyclodextrin cavity is occupied by water molecules which are energetically unfavoured, and therefore can be readily substituted by appropriate "guest molecules" which are less polar than water. This apolar–apolar association decreases the cyclodextrin ring strain resulting in a more stable lower energy state. The dissolved cyclodextrin is the "host" molecule, and the "driving force" of the

complex formation is the substitution of the high-enthalpy water molecules by an appropriate "guest" molecule.
The binding of guest molecules within the host cyclodextrin is not fixed or permanent but rather is a dynamic equilibrium. Binding strength depends on how well the 'host–guest' complex fits together and on specific local interactions between surface atoms. Complexes can be formed either in solution or in the crystalline state and water is typically the solvent of choice. Inclusion complexation can be accomplished in a co-solvent system and in the presence of any non-aqueous solvent (Martin Del Valle, 2004). Generally, one guest molecule is included in one cyclodextrin molecule, although in the case of some low molecular weight molecules, more than one guest molecule may fit into the cavity, and in the case of some high molecular weight molecules, more than one cyclodextrin molecule may bind to the guest. In principle, only a portion of the molecule must fit into the cavity to form a complex. Cyclodextrin inclusion is a stoichiometric molecular phenomenon in which usual only one guest molecule interacts with the cavity of the cyclodextrin molecules to become entrapped. 1:1 complex is the simplest and most frequent case. However, 2:1, 1:2, 2:2, or even more complicated associations, and higher order equilibrium exist almost always simultaneously.
Inclusion in cyclodextrins has a profound effect on the physical and chemical properties of guest molecules as they are temporarily locked or caged within the host cavity (Martin Del Valle, 2004).
These properties are:

- solubility enhancement of highly insoluble guests,
- stabilisation of labile guests against the degradative effects of oxidation, visible or UV light and heat,
- control of volatility and sublimation,
- physical isolation of incompatible compounds,
- chromatographic separations,
- taste modification by masking off flavours, unpleasant odours
- controlled release of drugs and flavours
- removal of dyes and auxiliaries from dyeing effluents
- retarding effect in dyeing and finishing baths
- protection of dyes from undesired aggregation and adsorption.

Therefore, cyclodextrins are used in food, pharmaceuticals, cosmetics, environment protection, bioconversion, packing and the textile industry.
The ring structure of cyclodextrins allows them to act as hosts and form inclusion compounds with various small molecules. Such complexes can be formed in solution, in the solid state, as well as when cyclodextrins are linked to a solid surface where they can act as permanent or temporary hosts to those small molecules that provide certain desirable attributes such as adsorption of dyestuff molecules, fragrances or antimicrobial agents. This "molecular encapsulation" is already widely utilized in many industrial products, technologies, and analytical methods.

3. Cyclodextrins in textile applications

3.1 Cyclodextrins in textile dyeing processes

Cyclodextrins can be considered as a new class of auxiliary substances for the textile industry. Cyclodextrins can be used for textile application because of their natural origin

and their biodegradability. There are no published studies about the influence of cyclodextrin/dye complexations on human skin, but we can use some studies from the field of cosmetics (Förster et al., 2009). Skin is a heterogeneous membrane; lipophilic on its surface and hydrophilic in its deeper layers. The stratum corneum is a highly resistant barrier which limits the penetration of drugs into the skin because its structure contributes to its function both as a barrier to water loss and as a barrier against the external environment. The skin's barrier function is therefore important in considering both the transdermal delivery of drugs and in making a risk assessment following dermal exposure to chemicals and dyestuffs. The major challenge for dermal or transdermal delivery is to "tune" the vehicle in which the drug is entrapped in order to reach its target site i.e. the skin surface, the skin compartments or the systemic circulation. The study of the stratum corneum structure is essential for understanding the barrier function of the skin. There are numerous formulation parameters and formulation systems which influence the penetration of active compounds. Here is one example: in cosmetic applications complexation has improved the photostability of sunscreens (Scalia et al., 1998; Scalia et al., 1999) but its influence on skin penetration behaviour is a compromise. There is an increasing effect due to better solubility (Vollmer et al., 1994; Legendre et al., 1995) but a decreasing effect resulting from using molecules with large relative molar masses (equivalent to more than 1000 Da) (Sarveiya et al., 2004; Simeoni et al., 2004; Williams et al., 1998). A recent trend is the use of modified cyclodextrin molecules. The most commonly used is hydroxypropyl-β-cyclodextrin (HP-β-CD). It is able to form hydrophilic inclusion complexes with many lipophilic compounds in aqueous solution, which can enhance the aqueous solubility of lipophilic drugs without changing their intrinsic abilities to permeate lipophilic membranes. An interesting example is sunscreen delivery onto a skin surface. Simeoni et al. have investigated the penetration of oxybenzone, a lipophilic sunscreen agent, on human skin, from HP-β-CD and from SBE-β-CD, a sulfobutylether-β-cyclodextrin (Simeoni et al., 2004; Simeoni et al., 2006). The authors showed that SBE-β-CD had the greater solubilizing activity on oxybenzone, a highly lipophilic sunscreen, (a 1049-fold increase) when compared with the use of HP-β-CD (a 540-fold increase). The sunscreen penetration to the deeper living layers of the skin was remarkably decreased (1.0% and 2.0% of applied dose for epidermis and dermis respectively) compared with the unbound OMC (octyl methoxycinnamate) formulation used as control and with OMC loaded HP-β-CD (~5%). This result is interesting because modified cyclodextrin carrier can promote the solubilising and photostabilising properties of sunscreen agents while staying on top of the skin where they are intended to act (Simeoni et al., 2006). Even with modified complexes, conflicting results have been found in the literature concerning their effect to promote or decrease skin penetration of drugs. But there still remain the problems of their molar mass and their limited capacity to penetrate into the skin (Cal & Centkowska, 2008). In the review by Förster and co-workers (Förster et al., 2009) the newest examples have been given and discussed. But their conclusion is that the effects of various systems on the skin still cannot be completely explained. One of the main problems is the molar mass of active components (»guests«) and their limited capacity to penetrate into the skin.

Further, for the textile use it is very important that chemical oxygen demand of cyclodextrins in the waste-water is lower or at least similar to the usual textile auxiliaries; while the chemical oxygen demand for polyester is about 2020 mg/g, for a fatty alcohol polyglycol ether is 1930 mg/g and for β-cyclodextrin is 1060 mg/g (Szejtli, 2003; Knittel et al., 1992).

Cyclodextrins play on important role in textile scientific research area and should play a significant role in the textile industry as well to remove or substitute various auxiliaries or to prepare textile materials containing molecular capsules which can immobilize perfumes, trap unpleasant smells, antimicrobial reagents and flame retardants. A rather new idea of using cyclodextrins in textile industry is the preparation of textile filters containing cyclodextrins for separate filtration/adsorption of POPs (persistent organic pollutants) from waste water.

As cyclodextrins can incorporate into their cavity different dyes, they should be able to act as retarders in a dyeing process. Variables which could be changed during the finishing process, dyeing, printing or washing to achieve the desired properties of the finished goods are besides the efficient pretreatment of the textile material, pH, temperature and addition of electrolytes, the addition of different auxiliaries. Various auxiliary products are used in wet finishing processes, especially in dyeing and washing. One of the dyeing auxiliary products are levelling agent. Levelling agents help to achieve uniform dyeing by slowing down the dye exhaustion or by dispersing the dye taken by the fibre in a uniform way. They can be classified into two groups: agents having affinity to the dye and agents having affinity to the fibre. Agents having affinity to the dyes slow down the dyeing process by forming complexs with the dyes. The complex compound moves slower compared to the dye itself; at higher temperature the dye is released and it can be fixed to the fibre. Application of cyclodextrins as levelling agents having affinity to dyestuffs has been investigated in research work about dyeing of cellulose fibres with direct dyes by using an exhaust method (Cireli & Yardakul, 2006) where β-cyclodextrin was tested as a dye complexing agent. β- cyclodextrins as a dye retardant in the dyeing of PAN fibres with cationic dyes was studied (Voncina et al., 2007); further it was reported that some azo disperse dyes formed inclusion complexes with α-, β- and γ-cyclodextrins (Shibusawa et al., 1998). Improvement of colour uniformity was achieved when PA 66 and microfiber PP 6 in the presence of cyclodextrin were dyed (Savarino et al., 1999; Savarino et al., 2000). The effect of β-cyclodextrin as an additive in the dyeing of polyester with disperse dyes was studied (Carpignano et al., 2010). It is reported that cyclodextrins can form inclusion complexes with some suphonated azo dyes (Zhang et al., 2006).

Cireli with co-workers used β-cyclodextrin and eight different direct dyestuffs with known chemical structures. After a certain period of time of exhaust dyeing, a dynamic equilibrium between the dye and β-cyclodextrin was established thus the amount of the dyestuff adsorbed by the fibres does not increase even though the dyeing procedure continued. In this research it is shown that the use of β-cyclodextrin as a levelling reagent is limited according to the size of the dyestuffs applied and according to the substituents on the dyestuff molecules which can hinder or enable the inclusion formation (Cireli & Yardakul, 2006).

Cationic dyes have very low migration power on polyacrylonitrile (PAN) fibres due to their high substantivity and rapid uptake over a small temperature range above the T_g of the fibre. Colour levelness can be improved by the use of different retarding reagents. In our past research work (Voncina et al., 2007) β-cyclodextrin was investigated as a retarding agent in the dyeing of PAN fibres with cationic dyes. The retarding effect of β-cyclodextrin was compared to that of a commercial product based on a quaternary ammonium compound (N-tetra-alkyl ammonium methyl sulphate) Tinegal MR New by Ciba. The cationic dye, C.I. Basic Blue 41, is schematically presented in Fig. 3.

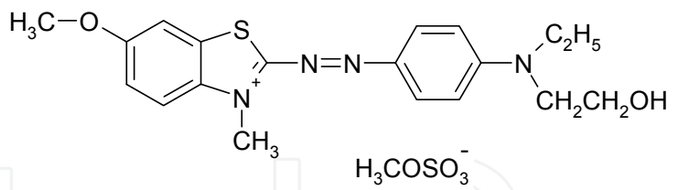


Fig. 3. Structure of C.I. Basic Blue 41

Quality dyeing was obtained and the values of bath exhaustion were significantly improved when β-cyclodextrin was used as a retarding reagent compared to the cationic retarding reagent based on the quaternary ammonium compound (Fig. 4).

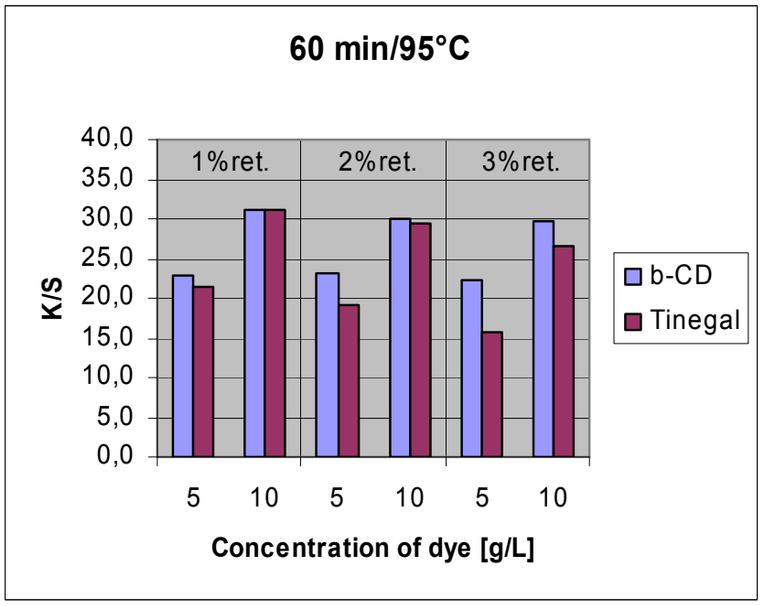


Fig. 4. K/S values of PAN fabrics dyed with different concentrations of dye (5 and 10 g/l) and retarding reagents: β-cyclodextrin and commercial reagent (1, 2 and 3%); dyeing procedure: 60 minutes at 95 °C

Significant improvement of colour levelness (Fig. 5) and some improvements in colour depth have been found when PAN fibres were dyed in the presence of β-cyclodextrin compared to dyeing in the presents of commercial retarding reagent. These improvements are more significant when higher concentrations of the dye and β-cyclodextrin were used. Research work shows that in a water solution a complex between β-cyclodextrin and the dye is formed at elevated temperatures. The β-cyclodextrin/dye complex with the increased molecular weight does not diffuse within the fibre and has low substantivity for the textile substrate. Because the complex formation is a dynamic equilibrium, the dye can easily be released and adsorbed on the textile substrate during the dyeing procedure. This indicates that the mechanism of retarding when using β-cyclodextrin is the formation of a dye/β-cyclodextrin complex (Fig. 6). This complex would slow down the rapid uptake of the dye by the fibre.

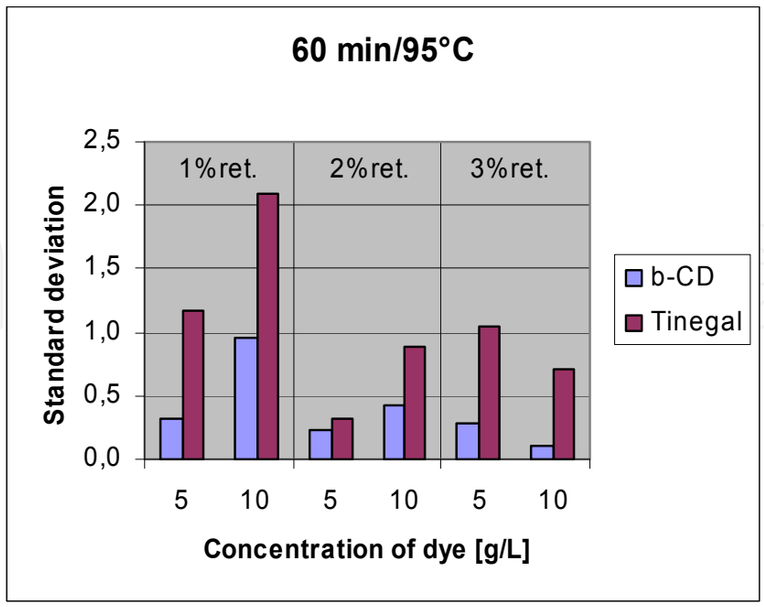


Fig. 5. Standard deviation of the mean K/S values of PAN fabrics dyed with different concentrations of dye (5 and 10 g/l) and retarding reagents: β-cyclodextrin and commercial reagent (1, 2 and 3%); dyeing procedure: 60 minutes at 95°C

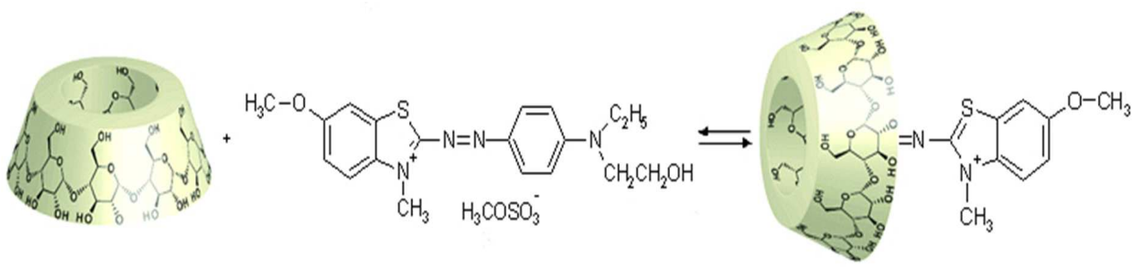
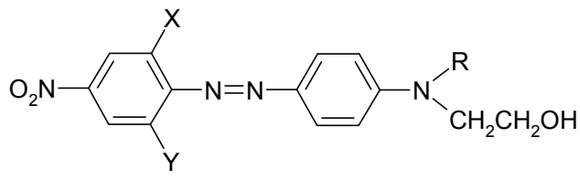


Fig. 6. Formation of a dye/β-cyclodextrin complex-retarding mechanism when using β-cyclodextrin

Changes in the sorption isotherms of six azo disperse dyes (4-amino-4'-nitroazobenzene derivatives) on hydrophobic secondary cellulose acetate filament yarn on addition of α-, β- and γ-cyclodextrins were measured at elevated temperature (Shibusawa et al. 1998). Structures of used dyes are presented in Fig. 7.

The formation constant and the stoichiometry of the dye-cyclodextrin complex formation were obtained by analyzing the changes in the isotherms. It was shown that most of the analysed dyes form 1:1 complexes with cyclodextrins when their maximum cross section area (actually, cross section of β-phenyl ring) is comparable to or smaller than the cyclodextrin cavity diameter. Azo dyes with electron withdrawing groups form 2:2 complexes with γ-cyclodextrin. Computer simulation presented in the paper showed that β- and γ-cyclodextrin are effective as retarders in the dyeing procedure when using relatively small molecules of disperse dyestuffs.



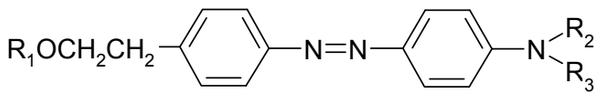
Designation	X	Y	R	Maximum cross section size of β-phenyl ring (pm)
Dye 1	H	H	CH_2CH_3	675
Dye 2	H	H	CH_2CH_2OH	675
Dye 3	Cl	Cl	CH_3	904
Dye 4	Cl	Cl	CH_2CH_2OH	904
Dye 5	NO_2	H	CH_2CH_2OH	858
Dye 6	NO_2	Br	CH_2CH_2OH	989

Fig. 7. Structures of six azo disperse dyes (4-amino-4'-nitroazobenzene derivatives)

Savarino with co-workers (Savarino et al., 1999; Savarino et al., 2000) studied the possibilities of using cyclodextrins as a dye complexing agent in dyeing of polyamide fibres with acid dyes. They reported that β- and γ-cyclodextrins may form inclusion complexes with dye molecules, but only the latter has been proven effective for controlling dyeing uniformity. Further they prepared a series of seven azo disperse dyes with variable hydrophobic chain lengths and hydrophilic substituents. Fig. 8 show the dyes structures. The interaction between dyes and polyamide fibres were studied by recording the dyeing isotherms; the influence of cyclodextrins (β-cyclodextrin and methyl-β-cyclodextrin) addition on colour yield and colour uniformity of dyed polyamide fibres was tested. They found out that the presence of cyclodextrins gives the positive effects on the quality of polyamide dyeing with disperse dyes. The quality of the dyeing depends on the type of cyclodextrin and on the size and hydrophilic properties of the analysed dyes.

The same group prepared 12 azo disperse dyes of a dialkylaminoazobenzene series and studied their complexation with β-cyclodextrin in the solid state by using TGA and DTA analysis and in dye bath by means of solubility isotherms (Savarino et al., 2004). Dye structures are presented in Fig. 9. For comparison purposes they dyed polyamide fibres with prepared solid complexes of the dyes with β-cyclodextrin by means of milling. They found out that the presence of β-cyclodextrin in the dyeing baths (irrespective if solid dye/β-cyclodextrin complexes were added to the bath or complexes were formed in the baths during the dying procedure) systematically increases dye solubility due to complex formation; dyeing tests evidenced a positive effect on colour uniformity and intensity in present of β-cyclodextrin both when added as free additive or when added as a complex.

The Savarino group synthesized the dialkylaminoazobenzene series of dyes with various substituents and used them in the dyeing of polyester (Carpignano et al., 2010); β-cyclodextrin was explored as an additive in the dyeing as a substitute for a commercial surfactant commonly used. The aim was reducing the environmental impact of the exhausted baths.



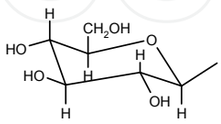
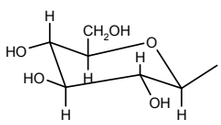
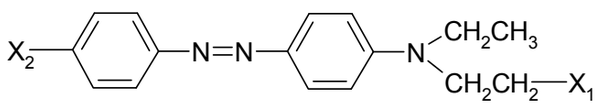
Designation	R_1	R_2	R_3
Dye 1	H	CH_3	CH_3
Dye 2	H	C_2H_5	C_2H_5
Dye 3	H	C_2H_5	C_4H_9
Dye 4	H	C_2H_5	C_8H_{17}
Dye 5	H	C_2H_5	$C_{12}H_{25}$
Dye 6		C_2H_5	C_2H_5
Dye 7		C_2H_5	C_8H_{17}

Fig. 8. Azo disperse dyes (Savarino et al., 2000)



Designation	X_1	X_2
Dye 1	H	H
Dye 2	H	CH_3O
Dye 3	H	CN
Dye 4	H	NO_2
Dye 5	CN	H
Dye 6	CN	CH_3O
Dye 7	CN	CN
Dye 8	CN	NO_2
Dye 9	OH	H
Dye 10	OH	CH_3O
Dye 11	OH	CN
Dye 12	OH	NO_2

Fig. 9. Azo disperse dyes of dialkylaminoazobenzene series (Savarino et al., 2004)

From the literature about the use of cyclodextrins in textile dyeing it is evident that one of the main reasons that determines if a complex is formed or not is the size of the dye molecule. The Savarino group used the chromometric approach where a small group of

dyes were selected as a "training set" to be representative of a larger series of dyes with similar structures. The training set of dyes was used for dyeing of polyester fabrics. The properties of the dyed samples were evaluated to assess the ability of β-cyclodextrin to be used as a substitute for synthetic surfactants. The interactions of dyes with β-cyclodextrin were studied by the solubility isotherm method. It was shown that the equilibrium concentration was reached after *ca*. 10 h and it was found to be a function of β-cyclodextrin concentration. The relationship between the dye and β-cyclodextrin was observed to be generally linear. The solubility isotherms differ according to the dyes which were used for complex formation; for certain dyes data can be well fitted by a straight line with a slope value smaller than one indicating that only one complex type is present in the solution and that the dye/β-cyclodextrin stoichiometry is either 1:1 or 1:*n*, where *n*>1, in contrast to some other dyes relationship between the dye and β-cyclodextrin was presented by a second-order polynomial equation. However, solubility isotherms indicate that the complexation between all dyes and β-cyclodextrin increases the dye solubility. Further the effect of β-cyclodextrin in comparison with commercial surfactants in polyester dyeing was evaluated; colour uniformity, fastness to light and washing and bath exhaustion were evaluated. The colour difference values (ΔE) between dyed and un-dyed fabrics correspond to the colour intensity qualitatively corresponded to dye uptake. The standard deviation $\sigma_{\Delta E}$ was used as a measure of dyeing uniformity. Their research showed that dyeing uniformity results are generally higher in the presence of surfactants than in the absence of additive. Dyeing uniformity did not increase when dye/β-cyclodextrin in a molar ratio 1:1 was used. Better results were obtained with dye/β-cyclodextrin in a molar ratio 1:2. Washing and rubbing fastness values measured at 60 °C were generally higher and were shown to be independent from bath composition and dye structure. Light fastness values showed that the composition of the dye bath did not affect the light fastness, on other hand, light fastness showed a large variation along the set of dyes. When the presence of β-cyclodextrin in polyester dyeing was studied two main advantages were brought up: the presence of biodegradable substances in exhausted dyeing baths and the use of additives obtained from renewable sources.

Cyclodextrins can not be used only as a dye carrier for improving the exhaustion or levelness of dyed materials, but they can also be used for encapsulation of dyes and other active substances (Zhang et al., 2006). Zhang and co-workers reported the successful encapsulation of various sulphonated azo dyes which are widely used as colouring agents in foodstuffs, cosmetic and others by using different cyclodextrins.

3.2 Cyclodextrins in polyfunctionalization of textiles

Various auxiliary products are used in wet finishing processes, previously we discussed auxiliaries which form inclusion complexes with dyes during the dyeing processes, however auxiliaries which bond on fibre surfaces before adding the dyestuff can have an influence on the dye uptake; thus more homogenous dispersion onto fibre and more efficient penetration into the fibre can be achieved. Covalent bonding of cyclodextrins onto textile fibres was firstly patented in 1980 by Szejtli (Szejtli et al., 1980) where it is reported to bond cyclodextrin via epichlorhydrin onto alkali-swollen cellulose fibers. According to the references the most promising approach to bond cyclodextrin onto textile fibres is the modification of cyclodextrins with trichlorotriazines to prepare monochlorotriazinyl-cyclodextrin (Reuscher et al., 1996; Grechin et al., 2007). An article

prepared by Ibrahim and co-workers (Ibrahim et al., 2007) reports new trials for improving the UV protective properties of cotton/wool and viscose/wool blends via incorporating certain reactive additives, such as reactive monochlorotriazinyl-β-cyclodextrin, in the easy care finishing formulations, followed by subsequent treatment with copper-acetate or post-dyeing with different classes of dyestuffs (acid, basic, direct and reactive). The post-dyeing of the blends was carried out at pH 3, at a 1:20 material to liquor ratio by conventional procedures in a Laundrometer with 3%owf. The dyed fabrics were rinsed and washed at 50 °C for 15 min in the presence of 1g/L of nonionic wetting agent, rinsed again and air dried. They found out that post-dyeing of the prefinished textile blends results in a significant increase in the UPF (UV-protection factor) values as a direct consequence of a remarkable reduction in UV radiation transmission through the plain weave fabric.

Very effective bonding of cyclodextrins on cellulose fibres can be achieved by a high-performance resin finish (Ostertag, 2002) or with non-formaldehyde reagents such as polycarboxylic acids (Voncina & Le Marechal, 2005; Martel et al., 2002b) which can covalently esterify hydroxyl groups of cellulose and cyclodextrins and link both moieties together. The same linking/crosslinking reagents can be used in the treating of different synthetic fibres. Polyester fibres were modified by β-cyclodextrin using citric acid (Martel et al., 2002a), in our laboratories (Voncina et al., 2009), 1,2,3,4-butane tetracarboxylic acid was used as a linker. Within our current research we study the influence of β-cyclodextrin on PET/cotton blend dyeing with disperse dye. Fig. 10 schematically presents Disperse Brown 1 dye.

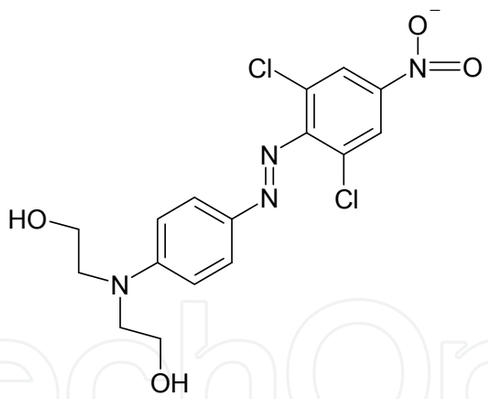


Fig. 10. Disperse Brown 1 (Terasil Braun 3R)

Fig. 11 graphically presents K/S values of PET/cotton blend pre-treated with β-cyclodextrin and Disperse Brown 1 (sample A), untreated PET/cotton blend dyed with the same dye (sample B) and C presents sample dyed with the addition of β-cyclodextrin into the exhausting dye bath. From colour measurements it is possible to conclude that pre-treatment of PET/cotton blend with β-cyclodextrin (sample A) increases the disperse dye uptake slightly; the addition of β-cyclodextrin into exhausting dye bath increases the dye uptake as well; a possible explanation could be that β-cyclodextrin/disperse dye complexation enhances the solubility of the dye.

El Ghoul and co-workers (El Ghoul et al., 2007; El Ghoul et al., 2010) reported that polyamide and polypropylene fabric were treated with cyclodextrins via crosslinking

reaction which was carried out using the pad-dry-cure process. Dyeability of cyclodextrin modified polypropylene fibres was enhanced when using three dyes belonging to different classes (disperse, acid and reactive dyes), using the exhaustion dyeing method. Formation of inclusion complexes between the dyes and β-cyclodextrin bonded onto polypropilene fibres increase the exhausting rate of the dyes from the dyeing baths. The observed enhancement of dye uptake was due to the encapsulation of dyes in the β-cyclodextrin cavities on one hand and due to other interactions (ionic and hydrogen bonding) or even covalent bonding with the poly-citric acid/β-cyclodextrin network in the case of reactive dye on the other hand. Various possible interactions between the reactive dye and fibres functionalized with β-cyclodextrin are illustrated in Fig. 12. It was observed that the dyeing level depends on the modification rate of polypropylene fibres with cyclodextrin.

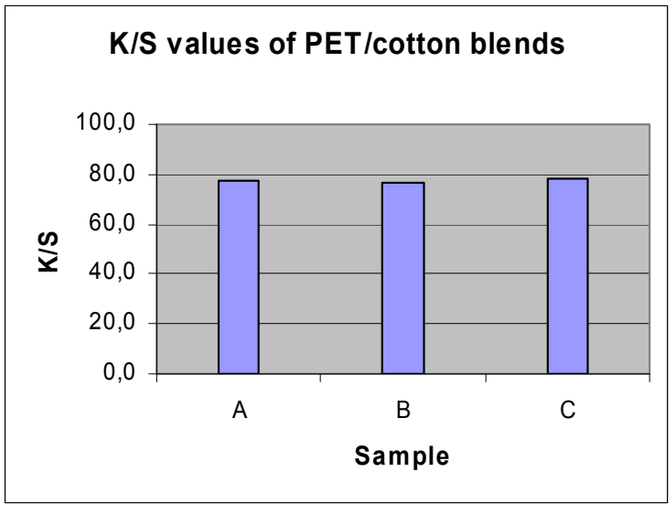


Fig. 11. K/S values of pre-treated PET/cotton blends dyed with Disperse Brown 1 (sample A), K/S values of samples dyed with the same dye (sample B) and K/S values of samples dyed with the addition of β-cyclodextrin into exhausting dye bath (sample C)

A novel technique for preparation of β-cyclodextrin-grafted chitosan was carried out by reacting β-cyclodextrin citrate with chitosan (El-Tahlawy et al., 2006).

4. Cyclodextrins in textile waste water treatments

The world production of dyes is estimated to be over 10 000 tonnes per year. Treatment of wastewater containing dyes is one of the most important ecological problems because the effluents containing the dyes are not only highly coloured, but also toxic to aquatic life. Textile effluents are highly variable in composition. They are generally characterized by high concentrations of colour, COD, BOD, TOC and dissolved solids. Wool and polyamide are dyed with the acid chrome dyes using the mordant dyeing technique causing the additional contamination of the effluents by high contents of chromium. Acid chrome dyes are the class of dyes that are at the same time most widely used in Eastern Europe and most difficult to eliminate. Due to the low biodegradability of dyes, conventional biological wastewater treatment is not very efficient.

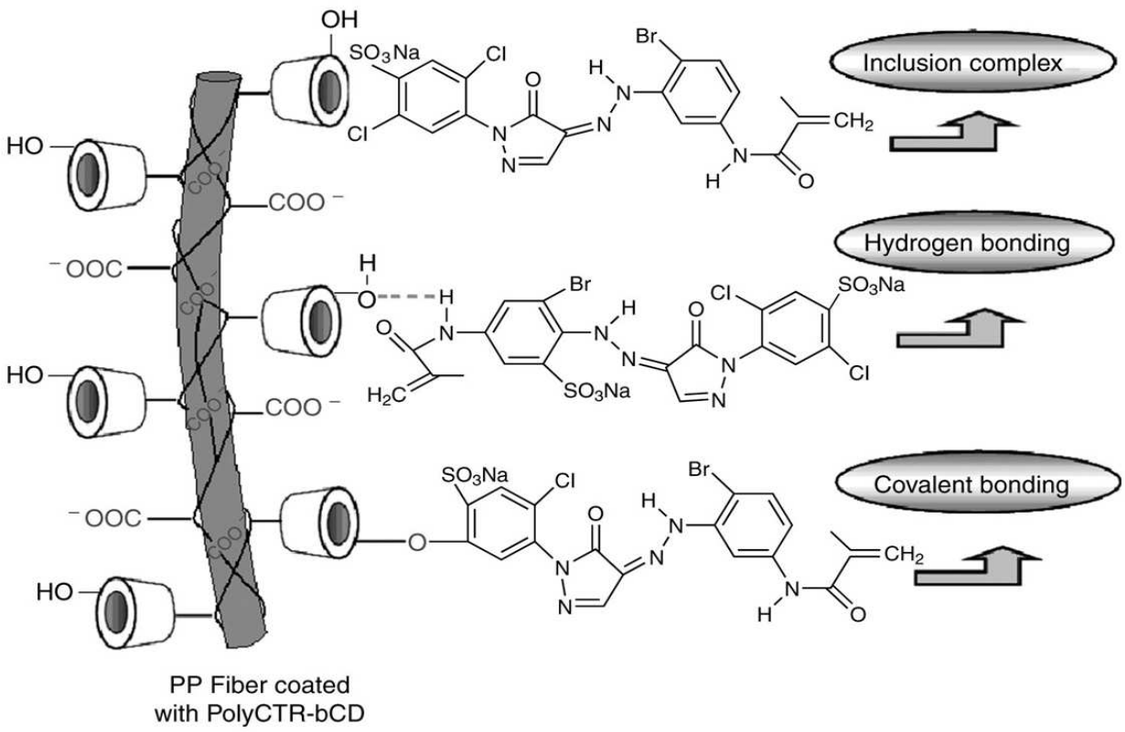


Fig. 12. Different interactions between the reactive dye Yellow Lanasol 4G and polypropilene fibres modified with β-cyclodextrin

Coagulation and adsorption onto various supports are the most frequently used physical methods. Due to interactions of ionic dyes with oppositely charged ionic surfactants, the extraction of ion pairs can also be used to remove dyes from aqueous streams. However, solvent extraction is not very useful as the concentrations of dyes present are usually low and the aqueous stream can be contaminated with diluents. Chemical methods such as oxidation and chlorination are more effective.

As a result of continuous water recycling, several groups of substances such as salts, organic micro pollutants, microorganisms, etc., are concentrated in the water loop and may cause water quality problems as well as health risks. The research is now focused also on the reduction/elimination of toxic organic pollutants like degradation products of dyestuffs and auxiliaries (phenols, aromatic amines, formaldehyde, persistent organic pollutants (POPs) etc), which can be formed also during the waste water treatment inside the factory or present in low concentrations in used chemicals or basic materials.

Basically, cytotoxicity of typical azo dyes may be relatively low, but the toxicity of related aromatic amine intermediates is very likely still significantly high due to their carcinogenicity or mutagenicity. Azo compounds like textile dyes can be reduced to amines through co-metabolism and the aid of azoreductases during decolourization treatments (Haug et al., 1991). As aromatic amines are difficult to be removed via traditional wastewater treatment and inevitably tend to be persistent, the toxicity evaluation of these amines will be apparently crucial to operation success or failure in dye decolourization and biodegradation afterwards. Aniline, the simplest and one of the most important aromatic amines, being used as a precursor to more complex chemicals, is toxic by inhalation,

absorption through the skin or swallowing. To remove dyes and toxic micro pollutants several separation techniques, based on filtration, adsorption, and extraction could be applied.

The source of POPs in textile materials and textile effluents could be pesticides for cotton and other materials based on pentachlorophenol, known to be contaminated with dioxins; chloranyl based dyestuffs; textile processes using chlorinated chemicals contaminated with POPs; highly alkaline finishing media; brominated flame retardants and also the waste water after treatment with AOPs (e.g. irradiation with powerful UV lamp in the presence of accelerating agents like H_2O_2, NaOCl, Fenton's regent, etc). Concentrations of POPs in waste water and even on textile material after different finishing processes can be between 100 g/L to 20μg/L. Apart from above mentioned POPs, phenol, and formaldehyde forming compounds and various aromatic amines (as the by-products and decomposition products of textile dyestuffs) present the most problematic pollutants in textile waste water.

Nowadays the membrane methods of separation are widespread as a method of wastewater treatment. The choice of the most suitable membrane process from a technical–economic point of view is very important. Having high dye retention, reverse osmosis (RO) and nanofiltration (NF) can be used for the treatment of dye waters from the textile industry. But industries are somehow reluctant to adopt highly energy-consuming RO and NF processes. Furthermore, NF/RO membranes have a lot more serious issues related to membrane fouling caused by colloids deposition, inorganic precipitation, and biological growth. Biofouling or biological fouling is the undesirable accumulation of microorganisms, plants, algae, and or animals on wetted structures.

Novel nano-porous polymers or nanosponges can be prepared for removal of organic pollutants from waste water. The polymeric «nanosponge» materials are not durable (usually they are in gel form), so they must be impregnated onto the pore structure of either a ceramic or some other porous surfaces. (Salipira et al., 2007). This technology is very specific for the target pollutant, it is very expensive and the removal of the adsorbed pollutant from the nanosponge is not possible. Usually the nano-porous polymers do not have high mechanical strength (Allabashi et al., 2007).

Textile materials are very important as filter materials. The cost of textile materials is acceptable (polyester, viscose), they have a sufficient mechanical strength; the pore size, especially the macro-pore size can vary, it depends on the type of textile (the density of non-woven material) and on the diameter of fibres. Textile materials can be further modified to prepare filtration materials with additional adsorption.

The amount of aromatic organic pollutants (phenols, aniline, formaldehyde and others) can be reduced from dyeing wastewater by using cyclodextrins which can be immobilized on a water insoluble organic support. The new concept for modification of textile substrates is based on permanent fixation of supramolecular compounds - cyclodextrins on the material surface and thus imparts new functionality to the fabric (Mamba et al., 2007; Mhlanga et al., 2007).

The guest molecules could be various organic molecules and some metal ions as well. The formed assembly of nanocapsules on textile materials (Fig. 13) acts as selective filtration/adsorption media for various pollutants. Cyclodextrin covalently bonded onto a textile support will form inclusion complexes with organic toxic pollutants by »host-guest« mechanism. After the filtration process, the organic support with cyclodextrin containing organic compounds can be incinerated.

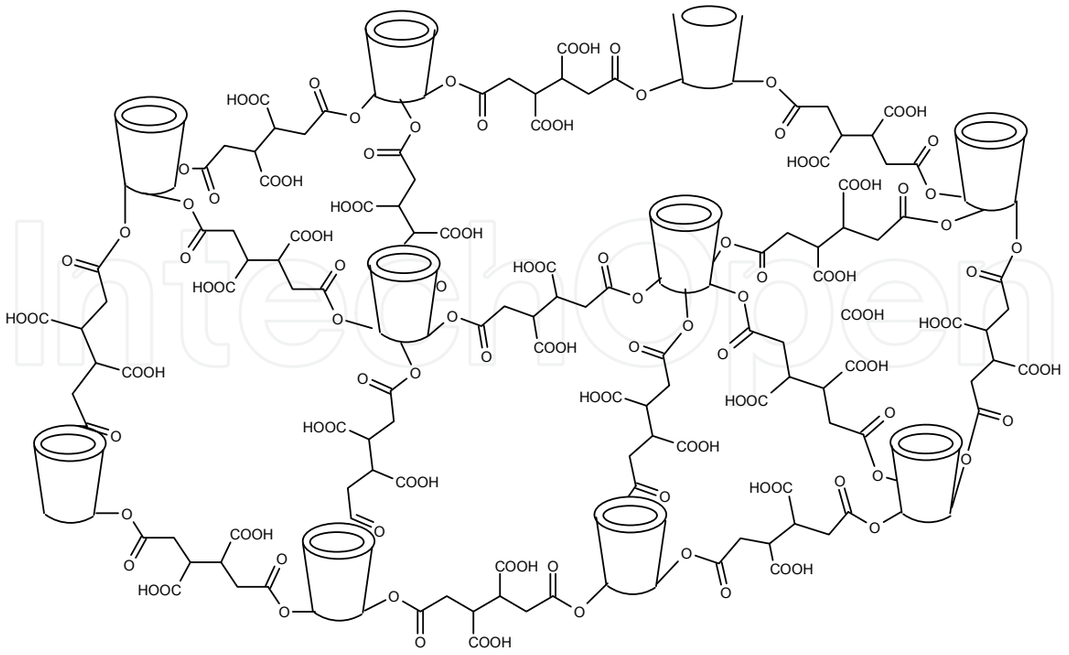


Fig. 13. Assembly of molecular capsules

5. Conclusion

Cyclodextrins have the ability to form inclusion complexes with a large number of organic molecules; this property enables them to be used in a variety of different textile applications. As cyclodextrins can incorporate into their cavities different dyes, they could be used as auxiliaries in dyeing process. Regardless the mechanisms of cyclodextrins actions, if there is a competition for sites on the fibre between dyes and cyclodextrins; or cyclodextrins slow down the dyes migration by forming complexes with the dyes molecules which are released slowly to the fibre, cyclodextrins can act as levelling or retardant reagents in various textile fibre (cotton, polyester, polyamide, polypropylene, polyacrylonitrile) dyeing.

In general, quality dyeing can be obtained and bath exhaustion can be improved when cyclodextrins are used as an additive (levelling reagent or retarding reagent) compared to commercially available auxiliaries; further improvement of colour levelness and some improvements in colour depth have been found when textile fibres were dyed in the presents of cyclodextrins. One of the main criteria for the complex inclusion is the size of cyclodextrins cavity and the size of the dyestuff molecules. The use of cyclodextrins in textile dyeing can not only improve the quality of the dyeing, but it can reduce the environmental impact of the exhausted baths. Further, covalently bonded cyclodextrins on textile support form inclusion complexes with organic pollutants. The adsorbed pollutants will be converted into water and carbon dioxide by the incineration.

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Textile Dyeing

Edited by Prof. Peter Hauser

ISBN 978-953-307-565-5
Hard cover, 392 pages
Publisher InTech
Published online 14, December, 2011
Published in print edition December, 2011

The coloration of fibers and fabrics through dyeing is an integral part of textile manufacturing. This book discusses in detail several emerging topics on textile dyeing. "Textile Dyeing" will serve as an excellent addition to the libraries of both the novice and expert.

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