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Textile Dyes: Dyeing Process and Environmental Impact

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1. Introduction

Dyes may be defined as substances that, when applied to a substrate provide color by a process that alters, at least temporarily, any crystal structure of the colored substances [1,2]. Such substances with considerable coloring capacity are widely employed in the textile, pharmaceutical, food, cosmetics, plastics, photographic and paper industries [3,4]. The dyes can adhere to compatible surfaces by solution, by forming covalent bond or complexes with salts or metals, by physical adsorption or by mechanical retention [1,2]. Dyes are classified according to their application and chemical structure, and are composed of a group of atoms known as chromophores, responsible for the dye color. These chromophore-containing centers are based on diverse functional groups, such as azo, anthraquinone, methine, nitro, aril-methane, carbonyl and others. In addition, electrons withdrawing or donating substituents so as to generate or intensify the color of the chromophores are denominated as auxochromes. The most common auxochromes are amine, carboxyl, sulfonate and hydroxyl [5-7].

It is estimated that over 10,000 different dyes and pigments are used industrially and over 7×10^5 tons of synthetic dyes are annually produced worldwide [3,8,9]. Textile materials can be dyed using batch, continuous or semi-continuous processes. The kind of process used depends on many characteristics including type of material as such fiber, yarn, fabric, fabric

construction and garment, as also the generic type of fiber, size of dye lots and quality requirements in the dyed fabric. Among these processes, the batch process is the most common method used to dye textile materials [10].

In the textile industry, up to 200,000 tons of these dyes are lost to effluents every year during the dyeing and finishing operations, due to the inefficiency of the dyeing process [9]. Unfortunately, most of these dyes escape conventional wastewater treatment processes and persist in the environment as a result of their high stability to light, temperature, water, detergents, chemicals, soap and other parameters such as bleach and perspiration [11]. In addition, anti-microbial agents resistant to biological degradation are frequently used in the manufacture of textiles, particularly for natural fibers such as cotton [11,12]. The synthetic origin and complex aromatic structure of these agents make them more recalcitrant to biodegradation [13,14]. However, environmental legislation obliges industries to eliminate color from their dye-containing effluents, before disposal into water bodies [9,12].

The textile industry consumes a substantial amount of water in its manufacturing processes used mainly in the dyeing and finishing operations of the plants. The wastewater from textile plants is classified as the most polluting of all the industrial sectors, considering the volume generated as well as the effluent composition [15-17]. In addition, the increased demand for textile products and the proportional increase in their production, and the use of synthetic dyes have together contributed to dye wastewater becoming one of the substantial sources of severe pollution problems in current times [6,9].

Textile wastewaters are characterized by extreme fluctuations in many parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, color and salinity. The composition of the wastewater will depend on the different organic-based compounds, chemicals and dyes used in the dry and wet-processing steps [6,18]. Recalcitrant organic, colored, toxicant, surfactant and chlorinated compounds and salts are the main pollutants in textile effluents [17].

In addition, the effects caused by other pollutants in textile wastewater, and the presence of very small amounts of dyes (<1 mg/L for some dyes) in the water, which are nevertheless highly visible, seriously affects the aesthetic quality and transparency of water bodies such as lakes, rivers and others, leading to damage to the aquatic environment [19,20].

During the dyeing process it has been estimated that the losses of colorants to the environment can reach 10–50% [13,14,17,21,22]. It is noteworthy that some dyes are highly toxic and mutagenic, and also decrease light penetration and photosynthetic activity, causing oxygen deficiency and limiting downstream beneficial uses such as recreation, drinking water and irrigation [13,14,23]

With respect to the number and production volumes, azo dyes are the largest group of colorants, constituting 60-70% of all organic dyes produced in the world [2,24]. The success of azo dyes is due to their ease and cost effectiveness for synthesis as compared to natural dyes, and also their great structural diversity, high molar extinction coefficient, and medium-to-high fastness properties in relation to light as well as to wetness [2,25]. They have a wide range of applications in the textile, pharmaceutical and cosmetic industries, and are al-

so used in food, paper, leather and paints [26,27]. However, some azo dyes can show toxic effects, especially carcinogenic and mutagenic events [27,28].

The toxic effects of the azo dyes may result from the direct action of the agent itself or of the aryl amine derivatives generated during reductive biotransformation of the azo bond [22]. The azo dyes entering the body by ingestion can be metabolized to aromatic amines by the azoreductases of intestinal microorganisms. If the dyes are nitro, they can be metabolized by the nitroreductases produced by the same microorganisms [29]. Mammalian liver enzymes and other organizations may also catalyze the reductive cleavage of the azo bond and the nitroreduction of the nitro group. In both cases, if N-hydroxylamines are formed, these compounds are capable of causing DNA damage [29, 30].

One of the most difficult tasks confronted by the wastewater treatment plants of textile industries is the removal of the color of these compounds, mainly because dyes and pigments are designed to resist biodegradation, such that they remain in the environment for a long period of time. For example, the half-life of the hydrolyzed dye Reactive Blue 19 is about 46 years at pH 7 and 25°C [31,32].

Carneiro et al. (2010) designed and optimized an accurate and sensitive analytical method for monitoring the dyes C.I. Disperse Blue 373 (DB373), C.I. Disperse Orange 37 (DO37) and C.I. Disperse Violet 93 (DV93) in environmental samples. This investigation showed that DB373, DO37 and DV93 were present in both untreated river water and drinking water, indicating that the effluent treatment (pre-chlorination, flocculation, coagulation and flotation) generally used by drinking water treatment plants, was not entirely effective in removing these dyes. This study was confirmed by the mutagenic activity detected in these wastewaters [33].

In this context, and considering the importance of colored products in present day societies, it is of relevance to optimize the coloring process with the objective of reducing the environmental impact of the textile industry. For this purpose, liposomes could be used to carry several encapsulated dyes, and hence improve the mechanical properties of textile products, resulting in better wash fastness properties and reducing the process temperature, thus economizing energy [34]. Another way is to use ultrasonic energy, studied with the objectives of improving dye productivity and washing fastness, and reducing both energy costs and water consumption [35].

Considering the fact that the textile dyeing process is recognized as one of the most environmentally unfriendly industrial processes, it is of extreme importance to understand the critical points of the dyeing process so as to find alternative, eco-friendly methods.

2. Dyeing process

The dyeing process is one of the key factors in the successful trading of textile products. In addition to the design and beautiful color, the consumer usually looks for some basic product characteristics, such as good fixation with respect to light, perspiration and washing,

both initially and after prolonged use. To ensure these properties, the substances that give color to the fiber must show high affinity, uniform color, resistance to fading, and be economically feasible [36].

Modern dyeing technology consists of several steps selected according to the nature of the fiber and properties of the dyes and pigments for use in fabrics, such as chemical structure, classification, commercial availability, fixing properties compatible with the target material to be dyed, economic considerations and many others [36].

Dyeing methods have not changed much with time. Basically water is used to clean, dye and apply auxiliary chemicals to the fabrics, and also to rinse the treated fibers or fabrics [37]. The dyeing process involves three steps: preparation, dyeing and finishing, as follows:

Preparation is the step in which unwanted impurities are removed from the fabrics before dyeing. This can be carried out by cleaning with aqueous alkaline substances and detergents or by applying enzymes. Many fabrics are bleached with hydrogen peroxide or chlorine-containing compounds in order to remove their natural color, and if the fabric is to be sold white and not dyed, optical brightening agents are added [37].

Dyeing is the aqueous application of color to the textile substrates, mainly using synthetic organic dyes and frequently at elevated temperatures and pressures in some of the steps [37,38]. It is important to point out that there is no dye which dyes all existing fibers and no fiber which can be dyed by all known dyes [39]. During this step, the dyes and chemical aids such as surfactants, acids, alkali/bases, electrolytes, carriers, leveling agents, promoting agents, chelating agents, emulsifying oils, softening agents etc [23,38] are applied to the textile to get a uniform depth of color with the color fastness properties suitable for the end use of the fabric [37]. This process includes diffusion of the dye into the liquid phase followed by adsorption onto the outer surface of the fibers, and finally diffusion and adsorption on the inner surface of the fibers [40]. Depending on the expected end use of the fabrics, different fastness properties may be required. For instance, swimsuits must not bleed in water and automotive fabrics should not fade after prolonged exposure to sunlight [37]. Different types of dye and chemical additives are used to obtain these properties, which is carried out during the finishing step. Dyeing can also be accomplished by applying pigments (pigments differ from dyes by not showing chemical or physical affinity for the fibers) together with binders (polymers which fix the pigment to the fibers) [39,41].

Finishing involves treatments with chemical compounds aimed at improving the quality of the fabric. Permanent press treatments, water proofing, softening, antistatic protection, soil resistance, stain release and microbial/fungal protection are all examples of fabric treatments applied in the finishing process [37].

Dyeing can be carried out as a continuous or batch process [37]. The most appropriate process to use depends on several factors, such as type of material (fiber, yarn, fabric, fabric construction, garment), generic type of fiber, size of dye batch and quality requirements for the dyed fabric, but batch processes are more commonly used to dye textile materials [10].

In continuous processing, heat and steam are applied to long rolls of fabric as they pass through a series of concentrated chemical solutions. The fabric retains the greater part of the

chemicals while rinsing removes most of the preparation chemicals. Each time a fabric is passed through a solution, an amount of water equivalent to the weight of the fabric must be used [37].

In batch processing, sometimes called exhaust dyeing, since the dye is gradually transferred from the dye bath to the material being dyed over a relatively long period of time [10], the dyeing occurs in the presence of dilute chemicals in a closed equipment such as a kier, kettle, beam, jet or beck [37]. Unlike the continuous process, instead of being passed through various baths in a long series of equipment sections, in the batch process the fabric remains in a single piece of equipment, which is alternately filled with water and then drained, at each step of the process. Each time the fabric is exposed to a separate bath, it uses five to ten times its own weight in water [37].

Some batch dyeing machines only operate at temperatures up to 100°C. However, the system can be pressurized, allowing for the use of temperatures above 100°C. Cotton, rayon, nylon, wool and some other fibers dye well at temperatures of 100°C or below. Polyester and some other synthetic fibers dye more easily at temperatures above 100°C [10].

Since the degree of dye fixation depends on the nature of the fiber, it is important to consider this topic. The fibers used in the textile industry can be divided into two main groups denominated natural fibers and synthetic fibers [36,37]. Natural fibers are derived from the environment (plants or animals), such as wool, cotton, flax, silk, jute, hemp and sisal, most of which are based on cellulose and proteins. On the other hand, synthetic fibers are organic polymers, mostly derived from petroleum sources, for example, polyester, polyamide, rayon, acetate and acrylic [37,39,42]. The two most important textile fibers are cotton, the largest, and polyester [43,44].

Cotton has been used for over 7000 years, and consists of mainly cellulose, natural waxes and proteins. The large number of hydroxyl groups on the cellulose provides a great water absorption capacity [39].

Several aromatic polyesters have been synthesized and studied. Of these, polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) have been produced commercially for more than 50 years. Amongst other uses, PET has been used worldwide for the production of synthetic fibers due to its good physical properties. PET is manufactured from ethylene glycol (EG) and terephthalic acid (TPA) or dimethyl terephthalate (DMT). The polymerization proceeds in two steps: esterification and condensation reactions [45]. The polymer produced after condensation is solidified by jets of cold water and cut into regular granules which frequently have a cubic form. Then, the polymer melt is spun and the yarns are solidified by a stream of cold air [39].

The dye can be fixed to the fiber by several mechanisms, generally in aqueous solution, and may involve primarily four types of interaction: ionic, Van der Waals and hydrogen interactions, and covalent bonds [5].

Ionic interactions result from interactions between oppositely charged ions present in the dyes and fibers, such as those between the positive center of the amino groups and carboxyl

groups in the fiber and ionic charges on the dye molecule, and the ionic attraction between dye cations and anionic groups ($-\text{SO}_3^-$ and $-\text{CO}_2^-$) present in the acrylic fiber polymer molecules. Typical examples of this type of interaction can be found in the dyeing of wool, silk and polyamide [5,36,41].

Van der Waals interactions come from a close approach between the π orbitals of the dye molecule and the fiber, so that the dye molecules are firmly "anchored" to the fiber by an affinity process without forming an actual bond. Typical examples of this type of interaction are found in the dyeing of wool and polyester with dyes with a high affinity for cellulose [36].

Hydrogen interactions are formed between hydrogen atoms covalently bonded in the dye and free electron pairs of donor atoms in the center of the fiber. This interaction can be found in the dyeing of wool, silk and synthetic fibers such as ethyl cellulose [5,36].

Covalent bonds are formed between dye molecules containing reactive groups (electrophilic groups) and nucleophilic groups on the fiber, for example, the bond between a carbon atom of the reactive dye molecule and an oxygen, nitrogen or sulfur atom of a hydroxy, amino or thiol group present in the textile fiber. This type of bond can be found in the dyeing of cotton fiber [5,36,46].

2.1. Application of liposome-based technology in textile dyeing process

There is increasing interest in the textile industry in the development of eco-friendly textile processing, in which the use of naturally occurring materials such as phospholipids, would become important [47]. Phospholipids are natural surfactants and in the presence of water, they organize themselves so as to reduce unfavorable interactions between their hydrophobic tails and the aqueous solution; their hydrophilic head groups exposed to the aqueous phase forming vesicles. Liposomes or phospholipid vesicles are featured by clearly separate hydrophilic and hydrophobic regions [34,48].

Liposomes were first produced in England in 1961 by Alec D. Bangham, who was studying phospholipids and blood clotting. He found that when phospholipids were added to water, they immediately formed a sphere, because one end of each molecule was water soluble, while the opposite end was water insoluble [49]. From a chemical point of view, the liposome is an amphoteric compound containing both positive and negative charges [34,50].

Liposomes are defined as a structure composed of lipid vesicle bilayers which can encapsulate hydrophobic or hydrophilic compounds in the lipid bilayer or in the aqueous volume, respectively [51]. These structures are usually made up of phosphatidylcholine (PC), which has a hydrophilic part consisting of phosphate and choline groups and a hydrophobic part composed of two hydrocarbon chains of variable length [49, 52,53].

Liposomes are often distinguished according to their number of lamellae and size. Small unilamellar vesicles (SUV), large unilamellar vesicles (LUV) and large multilamellar vesicles (MLV) or multivesicular vesicles (MVV) can be differentiated [49]. The diameters of liposomes vary from a nanometer to a micrometer [34]. Multilamellar liposomes (MLV) usually

range from 500 to 10,000 nm. Unilamellar liposomes can be small (SUV) or large (LUV); SUV are usually smaller than 50 nm and LUV are usually larger than 50 nm. Very large liposomes are called giant liposomes (10,000 - 10,00,000 nm). They can be either unilamellar or multilamellar. The liposomes containing encapsulated vesicles are called multi-vesicular and they range from 2,000-40,000 nm. LUVs with an asymmetric distribution of phospholipids in the bilayers are called asymmetric liposomes [54]. The thickness of the membrane (phospholipid bilayer) measures approximately 5 to 6 nm [49].

According to Sivasankar, Katyayani (2011), the preparation of liposomes is based on lipids, and those normally used are:

Natural phospholipids:

- Phosphatidyl choline (PC) - Lecithin
- Phosphatidyl ethanolamine (PE) - Cephalin
- Phosphatidyl serine (PS)
- Phosphatidyl inositol (PI)
- Phosphatidyl glycerol (PG)

Synthetic phospholipids:

For saturated phospholipids:

- Dipalmitoyl phosphatidyl choline (DPPC)
- Distearoyl phosphatidyl choline (DSPC)
- Dipalmitoyl phosphatidyl ethanolamine (DPPE)
- Dipalmitoyl phosphatidyl serine (DPPS)
- Dipalmitoyl phosphatidic acid (DPPA)
- Dipalmitoyl phosphatidyl glycerol (DPPG)

For unsaturated phospholipids:

- Dioleoyl phosphatidyl choline (DOPC)
- Dioleoyl phosphatidyl glycerol (DOPG) [52].

Natural acidic lipids, such as PS, PG, PI, PA (phosphatidic acid) and cardiolipin (CL), are added when anionic liposomes are desired, and cholesterol is often included to stabilize the bilayer. These molecules are derivatives of glycerol with two alkyl groups and one amphoteric group [34].

Phosphatidylcholine is the biological lipid most widely used for producing liposomes. Liposomes based on phosphatidylcholine consist of phosphatidic acid and glycerin, with two alcohol groups esterified by fatty acids and a third group esterified by phosphoric acid, to which the amino alcohol choline is added as a polar group [34,49].

According to Barani, Montazer (2008), normally four different methods can be used for the preparation of liposomes:

1. Dry lipid film;
2. Emulsions;
3. Micelle-forming detergents;
4. Alcohol injection technology [34].

Liposomes have two distinct roles: they can provide an excellent model for biological membranes, and they are being developed as controlled delivery systems for hydrophilic and lipophilic agents [34,53,55]. They are promising candidates for adjuvant and carrier systems for drug delivery, are well-documented, and can be used for the same purpose in textile materials [33].

Encapsulation or liposome technology is applied in numerous fields, such as in pharmaceuticals, cosmetics, foods, detergents, textiles and other applications where it is important to liberate the encapsulated material slowly [34,50]. This new clean technology has already been adopted by some textile industries [52]. In recent years, liposomes have been examined as a way of delivering dyes to textiles in a cost-effective and environmentally sensitive way [56].

Conventional dyeing processes consume a great deal of energy, a significant amount of which is wasted in controlling the process parameters in order to achieve uniform results. With respect to the carrier role of liposomes, they can be used in several textile processes such as textile finishing and dyeing, with several types of dyes and fibers. They are nontoxic, biodegradable, and can encapsulate a wide range of solutes [34]. In addition, the main advantages of liposomes are a clear reduction in dyeing temperature (about 10°C as compared to conventional dyeing), improved quality of the textiles produced, with additional benefits with respect to material weight yield during subsequent spinning, improved smoothness and mechanical properties of the dyed textiles, and a clear reduction in the contamination load of the dye baths [52,57]. Low temperature gives a more natural feel and improved quality, with lower environmental impact [34].

In recent years, liposomes have been used in the textile industry as a carrier for auxiliary materials (leveling, retarding and wetting agents) in dyeing, mainly for wool dyeing, and for finishing processes [34,55]. One of the most common problems with textile auxiliaries is that they fail to form a complex in the solution bath. This problem can be solved by using liposomes with selected positive or negative charges. Liposomes can be prepared according to the type of process, solute material and fiber structure [34]. Liposomes from phospholipids have been widely used as a dye carrier in the dyeing process, and create eco-friendly textile processes. Due to their structural properties, liposomes can encapsulate hydrophilic dyes (reactive, acid and basic dyes) in the aqueous phase, and hydrophobic dyes (disperse dyes) in the phospholipid bilayers [58]. Liposomes containing a dye are generally large, irregular and unilamellar [50].

According to Barani & Montazer (2008), the application of liposomes in textile processing can be useful when the release of the solute material is important, and improves the final properties of the products. A wetting agent is required in the conventional bleaching bath of cotton fabrics, but this step can be eliminated by using liposomes. The presence of liposomes in the peroxide bleaching bath can improve the mechanical properties of fabrics and their brightness. Liposomes contain particles of oxidant present in the bleaching solution that represent an unusual reservoir, and release the bleaching agent gradually into the bleaching bath. Moreover, the encapsulation of catalysts used for the decomposition of hydrogen peroxide radicals can be another factor in retarding the rate of decomposition. In this way, liposomes act as a stabilizing agent in the bleaching bath [34].

The role of auxiliary products is very important in textile dyeing with disperse dyes [53]. These compounds show extremely low solubility in water and dispersing agents are needed to maintain a fine, stable dispersion throughout the whole dyeing process at the different temperatures. Martí et al. (2007) analyzed the usefulness of commercial textile liposomes as dispersing agents, and observed that liposomes could be considered as suitable dispersing auxiliaries for polyester dyeing at high temperatures, considering their capacity to stabilize dye dispersions and achieve a suitable dye exhaustion level, with the added value of their environmentally friendly nature [53]. Liposomes clearly improve the dispersion efficiency as compared to conventional dispersing agents [34].

Additionally, liposomes for textile use show a similar price to that of synthetic surfactants used in the dyeing of polyester with disperse dyes. However, the new technology is more environmentally friendly, and hence the reduction in the environmental problem can lead to economic advantages [53]. In addition, liposome preparations tend not to foam. This is an advantage that distinguishes liposomes from other textile auxiliaries [34].

According to Martí et al. (2010), the dyeing of wool and wool blends with the aid of liposomes has demonstrated better quality, energy saving and a reduction in the environmental impact and also the temperature could be reduced, resulting in less fiber damage. Moreover, dye bath exhaustion was shown to be over 90% at the lower temperature (80°C) used, resulting in significant savings in energy costs [55]. The impact of the dyeing process on the environment was also considerably lower, the COD being reduced by about 1000 units [53].

Therefore, liposome-based technology is an alternative, eco-friendly method, which could reduce the environmental impact, offering technical and economic advantages for the textile industry.

2.2. Effect of ultrasonic energy on the dyeing process

Ultrasound-assisted textile dyeing was first reported by Sokolov and Tumansky in 1941[59]. The basic idea of this technology is that ultrasound can enhance mass transfer by reducing the stagnant cores in the yarns. The improvements observed are generally attributed to cavitation phenomena and to other resulting physical effects such as dye dispersion (breaking up of aggregates with high relative molecular mass), degassing (expulsion of dissolved or entrapped air from the fiber capillaries), strong agitation of the liquid (reduction in thick-

ness of the fiber-liquid boundary layer), and swelling (enhancement of dye diffusion rate inside the fiber) [59,60].

According to Vankar & Shanker (2008), ultrasound allows for process acceleration, obtaining the same or better results than existing techniques, but under less extreme conditions, i.e., lower temperatures and lower concentrations of the chemicals used. Wet textile processes assisted by ultrasound are of great interest to the textile industry for this reason [61], and Khatri et al. (2011) showed that the dyeing of polyester fiber using ultrasonic energy resulted in an increased dye uptake and enhanced dyeing rate [35].

Due to the revolution in environmental protection, the use of ultrasonic energy as a renewable source of energy in textile dyeing has been increased, due to the variety of advantages associated with it. On the other hand, there is a growing demand for natural, eco-friendly dyeing for the health sensitive application to textile garments as an alternative to harmful synthetic dyes, which poses a need for suitable effective dyeing methodologies [62].

Ultrasonic energy can clean or homogenize materials, accelerating both physical and chemical reactions, and these qualities can be used to improve textile processing methods. Environmental concern has been focused on textile processing methods for quite some time, and the use of ultrasonic energy has been widely studied in terms of improving washing fastness. The textile dyeing industry has long been struggling to cope with high energy costs, rapid technological changes and the need for a faster delivery time, and the effective management of ultrasonic energy could reduce energy costs and improve productivity [35]. Ultrasonic waves are vibrations with frequencies above 17 kHz, out of the audible range for humans, requiring a medium with elastic properties for propagation. The formation and collapse of the bubbles formed by ultrasonic waves (known as cavitation) is generally considered to be responsible for most of the physical and chemical effects of ultrasound in solid/liquid or liquid/liquid systems [63]. Cavitation is the formation of gas-filled microbubbles or cavities in a liquid, their growth, and under proper conditions, their implosive collapse [59].

It has been reported that ultrasonic energy can be applied successfully to wet textile processes, for example laundering, desizing, scouring, bleaching, mercerization of cotton fabrics, enzymatic treatment, dyeing and leather processing, together with the decoloration/mineralization of textile dyes in waste water [60].

In addition, ultrasonic irradiation shows promise, and has the potential, for use in environmental remediation, due to the formation of highly concentrated oxidizing species such as hydroxyl radicals ($\text{HO}\bullet$), hydrogen radicals ($\text{H}\bullet$), hydroperoxyl radicals ($\text{HO}_2\bullet$) and H_2O_2 , and localized high temperatures and pressures [59]. Therefore, the use of ultrasonic energy could indeed reduce the environmental impact caused by the textile industry.

3. Finishing and waste water

The contamination of natural waters has become one of the biggest problems in modern society, and the economical use of this natural resource in production processes has gained

special attention, since in predictions for the coming years, the amount of water required per capita is of concern. This environmental problem is related not only to its waste through misuse, but also to the release of industrial and domestic effluents [64].

Of the industries with high-polluting power, the textile dyeing industry, responsible for dyeing various types of fiber, stands out. Independent of the characteristics of the dyes chosen, the final operation of all dyeing process involves washing in baths to remove excesses of the original or hydrolyzed dyes not fixed to the fiber in the previous steps [36]. In these baths, as previously mentioned, it is estimated that approximately 10-50% of the dyes used in the dyeing process are lost, and end up in the effluent [17,21,22], contaminating the environment with about one million tons of these compounds [65]. The dyes end up in the water bodies due mainly to the use of the activated sludge treatment in the effluent treatment plants, which has been shown to be ineffective in removing the toxicity and coloring of some types of dye [33,60,66,67]. Moreover, the reduction of azo dyes by sodium hydrosulfite and the successive chlorination steps with hypochlorous acid, can form 2-benzotriazoles phenylbenzotriazol (PBTAs) derivatives and highly mutagenic aromatic amines, often more mutagenic than the original dye [68]. In an aquatic environment, this dye reduction can occur in two phases: 1) The application of reducing agents to the newly-dyed fibers to remove the excess unbound dye, which could lead to "bleeding" of the fabrics during washing, and 2) The use of reducing agents in the bleaching process, in order to make the effluent colorless and conform with the legislation. This reduced colorless effluent containing dyes is sent to the municipal sewage treatment plant, where they chlorinate the effluents before releasing them into water bodies where they may generate PBTAs. Several different PBTAs are already described in the literature, and their chemical structures vary depending on the dyes that originated them [63,69].

So the release of improperly treated textile effluents into the environment can become an important source of problems for human and environmental health. The major source of dye loss corresponds to the incomplete fixation of the dyes during the textile fiber dyeing step [36].

In addition to the problem caused by the loss of dye during the dyeing process, within the context of environmental pollution, the textile industry is also focused due to the large volumes of water used by its industrial park, consequently generating large volumes of effluent [64]. It has been calculated that approximately 200 liters of water are needed for each kilogram of cotton produced [70]. These effluents are complex mixtures of many pollutants, ranging from original colors lost during the dyeing process, to associated pesticides and heavy metals [71], and when not properly treated, can cause serious contamination of the water sources [64]. So the materials that end up in the water bodies are effluents containing a high organic load and biochemical oxygen demand, low dissolved oxygen concentrations, strong color and low biodegradability. In addition to visual pollution, the pollution of water bodies with these compounds causes changes in the biological cycles of the aquatic biota, particularly affecting the photosynthesis and oxygenation processes of the water body, for example by hindering the passage of sunlight through the water [72].

Moreover, studies have shown that some classes of dye, especially azo dyes and their by-products, may be carcinogenic and / or mutagenic [27,33,67,73-77], endangering human health, since the wastewater treatment systems and water treatment plants (WTP) are ineffective in removing the color and the mutagenic properties of some dyes [78,79]. The difficulty in removing them from the environment can be attributed to the high stability of these compounds, since they are designed to resist biodegradation to meet the demands of the consumer market with respect to durability of the colors in the fibers, consequently implying that they also remain in the environment for a long time [32].

With respect to the legislation, there is no consensus amongst the different countries concerning effluent discharge, and there is no official document listing the different effluent limit values applied in different countries. Many federal countries, such as the United States of America, Canada and Australia have national environmental legislation, which, as in Europe, establishes the limits that must be complied with. Some countries, such as Thailand, have copied the American system, whereas others, such as Turkey or Morocco, have copied the European model. In some countries, for example India, Pakistan and Malaysia, the emission limits are recommended, but are not mandatory [80]. With respect to the color, in some countries such as France, Austria and Italy, there are limits for the color of the effluent, but since they use different units, a comparison is impossible. The oldest unit is the Hazen, in use since the beginning of the 20th century, but in France, the current unit is ($\text{mg L}^{-1}\text{Pt-Co}$). The coloration values are determined by a comparative analysis with model solutions prepared according to defined procedures [80].

Based on all the problems cited above regarding the discharge of effluents into the environment, it is obvious there is a need to find alternative treatments that are effective in removing dyes from effluents.

4. Waste water treatment

These days, environmental pollution can undoubtedly be regarded as one of the main problems in developed and developing countries. This is due, not just to one, but to a number of factors, such as the misuse of natural resources, inefficient legislation and a lack of environmental awareness. Fortunately, in recent years there has been a trend for change and a series of scientific studies are being used as an important tool in the development of new treatment technologies and even in the implementation of processes and environmentally friendly actions [64,81-84].

Every industrial process is characterized by the use of inputs (raw materials, water, energy, etc.) that undergo transformation giving rise to products, byproducts and waste. The wastes produced at all stages of the various types of human activity, both in terms of composition and volume, vary according to the consumption practices and production methods. The main concerns are focused on the impact these can have on human health and the environment. Hazardous waste, produced mainly by industry, is particularly worrying, because when incorrectly managed, it becomes a serious threat to the environment and therefore to

human health. Thus the study of new alternatives for the treatment of different types of industrial effluent continues to be a challenge to combat anthropogenic contamination.

Amongst that of several other industries, the textile sector waste has received considerable attention in recent years, since it can generate large volumes of effluents that, if not correctly treated before being disposed into water resources, can be a problem, as previously mentioned. Effluents from the textile industry are extremely complex, since they contain a large variety of dyes, additives and derivatives that change seasonally, increasing the challenge to find effective, feasible treatments. Currently, the processes developed and available for these industries are based on methods that were designed for other waste, and have limitations when applied to textile effluents. As a consequence, these industries produce colored wastewater with a high organic load, which can contribute enormously to the environmental pollution of surface water and treatment plants if not properly treated before disposal into the water resources [85]. The ingestion of water contaminated with textile dyes can cause serious damage to the health of humans and of other living organisms, due to the toxicity, high-lighting mutagenicity of its components [86,87]. Therefore treatments that are more efficient and economical than those currently available are required.

There are several techniques for the treatment of effluents, such as incineration, biological treatment, absorption onto solid matrices, etc. However, these techniques have their drawbacks, such as the formation of dioxins and furans, caused by incomplete combustion during incineration; long periods for biological treatment to have an effect, as also the adsorptive process, that is based on the phase transfer of contaminants without actually destroying them [88,89]. The problem is further aggravated in the textile industry effluents, due to the complexity of their make-up. Thus it can be seen that processes are being used that are not entirely appropriate for the treatment of textile effluents, thereby creating a major challenge for the industry and laundries that need to adapt to current regulations for the control of the color of effluents with a high organic load.

The use of filtration membranes and/or separation [90] and biological methods [91], in addition to incineration processes involving adsorption onto solid matrices, has also being adopted by the textile industry and is receiving considerable attention. However, all these processes only involve phase transfer, generating large amounts of sludge deposited at the end of the tanks and low efficiency in color removal and reduction of the organic load. According to this scenario, many studies have been carried out with the aim of developing new technologies capable of minimizing the volume and toxicity of industrial effluents. Unfortunately, the applicability of these types of system is subject to the development of modified procedures and the establishment of effluent recycling systems, activities that imply evolutionary technologies and which are not yet universally available. Thus the study of new alternatives for the treatment of many industrial effluents currently produced is still one of the main weapons to combat the phenomenon of anthropogenic contamination.

Due to their considerable danger, several authors have attempted to find new forms of treatment to reduce the serious environmental and toxicological risks caused by various organic compounds. Amongst the many reported cases are those based on the use of specific micro-

organisms, and degradation using advanced oxidation processes (AOP) such as Fenton, photo-Fenton and heterogeneous photocatalysis, which are highlighted below.

The use of microorganisms cultivated specifically for the degradation of pollutants to increase the yield of degradation, has been reported by some authors. For example, Flores et al. (1997) examined the behavior of 25 N-substituted aromatic compounds such as organic compounds, azo dyes and nitro, using the methanogenic bacteria acetoclastic, and found that under anaerobic conditions it was easy to mineralize various of the compounds evaluated with a good yield, especially the nitroaromatic and azo dyes [91].

Bornick et al. (2001) evaluated the use of aerobic microorganisms to degrade aromatic amines present in sediments of the river Elbe in Germany. The results obtained showed that it was possible to predict the qualitative degradation of the aromatic amines using degradation constants [92].

Using a structural design, Wang et al. (2007) isolated a bacterium capable of promoting the degradation of the compounds pentyl amine and aniline present in water oil extraction in China. Under conditions of neutral pH and complete aeration of 6 mg O₂ / l at a temperature of 30 ° C, they obtained degradation yields of 82% and 78%, respectively, for pentyl amine and aniline [93].

However, in general, although the use of microorganisms in the treatment of industrial and laboratory wastes containing aromatic amines deserves attention, mainly due to the low investment and maintenance costs, the results are far from ideal, due to the low biodegradation yields, long treatment times, and the generation of sludge deposited at the bottom of the treatment ponds [94].

Of the studies carried out using a source of hydroxyl radicals with oxidizing agents, the photo Fenton system developed by Fukushima et al., 2000 to promote the degradation of aniline stands out. This method has shown promise for the mineralization of aromatic amines, obtaining a reduction of approximately 85%. However, high performance liquid chromatography (HPLC) identified a number of intermediate species formed during the degradation of the aniline, such as p-aminophenol, p-hydroquinone, maleic and fumaric acids and NH₄⁺ [95].

Studies involving heterogeneous photocatalysis also deserve attention: for example Pramauro et al., (1995) promoted the degradation of various aniline derivatives using TiO₂ particles suspended in a solution. Under optimal conditions, the method developed showed rapid mineralization of the aromatic amines examined in less than 1 hour of analysis. By-products generated during the degradation of these compounds were identified at the start of the reaction, but none were identified at the end of the reaction. The use of solar radiation was also evaluated, but was shown to be less efficient than artificial radiation [96].

Augugliaro et al. (2000), confirmed that heterogeneous photocatalysis using TiO₂ as a semiconductor may be a suitable method for the complete photodegradation of aniline, 4-ethyl-aniline and 4-chloroaniline in an aqueous medium. The kinetic parameters for the Langmuir-Hinshelwood model were used to describe the importance of the adsorption results, which

proved to be independent of the pH of the solution and of the type of substituent on the aromatic ring of the amine [97].

Canle et al. (2005) studied the behavior of the adsorption of aniline and dimethyl aniline onto three species of TiO_2 (P25, anatase and rutile) and established that the greatest adsorption occurred onto TiO_2 P25. The effect of pH on the degradation provided by these compounds was also evaluated, and lower mineralization percentages were observed in acidic media. This type of behavior can be attributed to the positive charges on both the aniline and the semiconductor, providing electrostatic repulsion between the two species. Thus, an alkaline medium has been recommended as the most appropriate one to promote the mineralization of aromatic amines using a TiO_2 P25 type semiconductor [98].

Chu et al. (2007) observed the effects of pH variation and the addition of hydrogen peroxide on the degradation of 2-chloroaniline using TiO_2 as a semiconductor, with and without the application of UV radiation. The results showed that the addition of low concentrations of H_2O_2 to the UV/ TiO_2 system provided a significant increase in degradation of the aromatic amine. The addition of an excess of H_2O_2 promoted no increase in degradation, as expected; to the contrary, a reduction in the reaction rate was observed. The variation in pH was evaluated in both systems, and the condition leading to the highest percentages of mineralization was obtained in an alkaline medium using $\text{H}_2\text{O}_2/\text{UV}/\text{TiO}_2$ [99].

Low et al. (1991) monitored the inorganic products resulting from the degradation of several organic nitrogenated, sulfured and halogenated compounds. Degradation was carried out using TiO_2 as the semiconductor and artificially illuminated UV radiation. Ammonium ions were found to be present in higher concentrations than nitrate ions, which can be explained by the fact that compounds having a nitrogen element in their structure pass through a complex degradation step where the generation of ammonium ions is more favorable than the generation of nitrate ions. In turn, compounds with nitro groups in their structures, showed higher concentrations of nitrate ions. Under ideal conditions, all the elements were converted into their respective inorganic forms. Organic carbon was converted to CO_2 , the halogens to their corresponding halide, sulfur compounds to sulfate, the phosphate to phosphorus and nitrogen to ammonium and nitrate [100]. However, all these studies used a photocatalytic titanium suspension, requiring a subsequent step to remove the semiconductor.

With a view to these problems, a new technique that has been studied recently, with significant success, is the oxidation of organic matter via the generation of hydroxyl radicals ($\text{OH}\bullet$). This kind of effluent treatment has been highlighted for its destructive character with respect to the organic matter. The advanced oxidation processes (AOP) are processes based on the generation of highly oxidizing species, the hydroxyl radical ($\text{OH}\bullet$), which can oxidize the organic contaminants present in water, air or soil. These radicals have a high oxidation potential ($E^* = +2.72 \text{ V}$ vs. the normal hydrogen electrode, NHE), which results in high reactivity with organic pollutants. This may initiate different types of reaction with different functional groups in organic compounds, forming unstable organic radicals which are then easily oxidized to CO_2 , H_2O and inorganic acids, derived from this heteroatom. Many techniques have been developed using this principle as the method of treatment, and have shown potential success in organic residue mineralization processes [92,96, 101-103].

The association of the electrochemical properties with the photocatalytic properties of a semiconductor, have allowed for the development of a promising system, representing a very efficient technique as an AOP method that has received much attention in recent years, assigned as a photoelectrochemical process. The process gained notoriety for the possibility of forming hydroxyl radicals via the oxidation of water. The technique is based on the action of ultraviolet light ($h\nu$) on a semiconductor capable of generating charges and e^-/H^+ , whose separation is facilitated by applying a positive potential (E_{APP}), greater than the potential of a flat band photocatalytic material. The generation of a potential gradient in the photoactivated semiconductor directs the electrons to an auxiliary electrode (cathode), delaying recombination between the holes (h^+) generated in the valence band (VB), and making them available for oxidation processes and the generation of hydroxyl radicals of interest [104].

The results of this process were very promising because of the relatively short treatment time but with great efficiency, both in the removal of color and in the reduction of the organic load. However, the limitations of this technique are related mainly to the choice of the ideal catalyst for promoting the generation of these oxidizing species. Catalysts that promote the generation of radicals absorbing radiation in the visible spectral region are the most desirable for this type of reaction, due to the large percentage emitted in the solar spectrum (approximately 45%) [104].

Thus, the development of an ideal process that promotes color removal and a reduction in the organic load of wastewater from the textile industry with great efficiency is a major challenge in all fields of science, since the synthesis of the best catalyst to take advantage of solar radiation, thus reducing the operating costs, and at the same time solve the problems involved in the hydrodynamics of the reactors, is of importance in the development of the treatment.

The expectations for developing an effective method for the treatment of these wastes are quite promising, but require continuous optimization and knowledge of new aspects. These include better fixation of the dyes to the fibers, process with less water consumption, less hazardous dyes with respect to human health and methods capable of identifying these compounds with more efficacy and rapidity and assays to identify any potential carcinogenic and / or mutagenic properties in the dyes and their derivatives; genetic improvements to produce more efficient culture mediums and resistant biological treatments, leading to a reduction in the generation of sludge; the synthesis of materials that catalyze reactions in the visible spectral regions, leading to a more economic photoelectrochemical method, and also new engineering advances for the construction of more effective reactors, which can take advantage of all these developments in an integrated system, extending the performance of a process more appropriate for the treatment of such a complex effluent.

5. Optimization of the dyeing processes to reduce the environmental impact of the textile industry

The search and development of new methods to promote the treatment of effluents from the textile industry with a maximum of efficiency of the process of decolorization and / or re-

removal of these compounds present in the medium can trigger further damage human health and the environment is fundamental importance. The understanding of the composition of waste generated is extremely significant to develop these methods of treatment due to the high complexity by virtue of huge number of compounds which are added at different stages of the dyeing fabrics.

Environmental problems with used dye baths are related to the wide variety of different components added to the dye bath, often in relatively high concentrations. In the future, many of textile factories will face the requirement of reusing a significant part of all incoming freshwater because traditionally used methods are insufficient for obtaining the required water quality.

However, due to dwindling supply and increasing demand of water in the textile industries, a better alternative is to attempt to further elevate the water quality of wastewater effluent from a secondary wastewater treatment plant to a higher standard for reuse. Thus far very little attention has been paid to this aspect [105].

Therefore, the investment in the search for methodologies to more effective treatment of these effluents can be much smaller than that spent in tertiary treatment to remove these products in low level of concentrations and in the presence of much other interference. This requires action that the cost / benefit are reviewed and the development of new techniques for wastewater treatment capable of effective removal of these dyes is intensified and made economically viable [105,106].

An alternative to minimize the problems related to the treatment of textile effluents would be the development of more effective dye that can be fixed fiber with higher efficiency decreasing losses on tailings waters and reducing the amount of dye required in the dyeing process, reducing certainly improve the cost and quality of the effluent.

6. Conclusion

It was concluded that the synthetic textile dyes represent a large group of organic compounds that could have undesirable effects on the environment, and in addition, some of them can pose risks to humans. The increasing complexity and difficulty in treating textile wastes has led to a constant search for new methods that are effective and economically viable. However, up to the present moment, no efficient method capable of removing both the color and the toxic properties of the dyes released into the environment has been found.

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