Abstract review on:

Current treatment technologies and practical approaches on textile wastewater Dyes Removal

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Abstract
Textile industry discharges large amounts of highly colored wastewater, using chemicals reagents within its industrial processes. Discharge of these effluents in open water bodies represents an environmental and aesthetic problem and it may also limit photosynthesis in aquatic plants. Many treatment alternatives have been reported in laboratory as well as full scale, including physical, chemical, biological, Advanced Oxidation Process (AOP) and a combination of them. This abstract of literature review aims to put together extensive information about dyes and the best available technologies (BAT) for their removal from textile effluents.

1. Introduction
Textile industry consumes huge volumes of water and chemicals for its different wet processing operations. Chemicals like acids, alkalis, colors, high BOD/COD concentration, surfactants, dispersing agents, soap and metals are contained in effluent wastewater coming from this source (Paul et al., 2012). Textile industry is rated as one of the most polluting and chemically intensive industrial sectors (Uzal, 2015). Most textile wastewaters are highly colored because they are typically discharged with a dye contents in the range of 10-200 mg/L, and many dyes are visible in water at concentrations as low as 1 mg/L (Cervantes, 2009). There are many structural varieties of dyes, such as: acidic, direct, disperse, azo, diazo, sulfur-based, reactive, basic, mordant, Vat and metal complexes. Many of them are designed to be chemically stable so that they are difficult to decolorize due to their complex structure and synthetic origin (Robinson et al., 2000). The main challenges are the mineralization of dyes, organic compounds and toxicity of the wastewater generated by the textile industry (Holkar et al., 2016). Many treatment alternatives have been reported in lab as well as full scale, including physical, chemical, biological, Advanced Oxidation Process (AOP) and a combination of them (Robinson et al., 2001). This review aims to put together extensive literature information about dyes and the best available technologies (BAT) for their removal from textile effluents.

2. Textile operations and water pollution
Textile industries prepare fibers; transform fiber into yarn and then yarn into fabric. Subsequently, these fabrics go through several stages of wet processing (Holkar et al., 2016). The amount of wastewater produced in a process like sizing is limited, but very concentrated. On the other hand, processes like scouring, bleaching and dyeing generate large amounts of wastewater, varying much in composition (Cervantes, 2009).

3. Classification of dyes
Dye molecules consist of a chromophore component responsible for the production of colors, which fix the dye into or within the fibers (Salleh et al. 2011). There are about 12 classes of chromogenic groups, the most common being the azo type which makes up to 60-70% of all textile dyestuffs produced, followed by the anthraquinone type (Buckley et al. 1992; Carniell et al. 1995). A second classification of dyes is based on their mode of application to fabrics and distinguishes acid, reactive, metal-complex, disperse, vat, mordant direct, basic and sulfur-based dyes (Vandervivere et al., 1998). All dyes are water soluble except disperse dyes and vat dyes. Dyes are classified into cationic, anionic and non-ionic. Anionic dyes include various dyes groups such as acid dyes, reactive dyes, azo dyes, and direct dyes, while cationic dyes are alkaline (Dawood et al. 2014).
4. Available methods to remove different types of dyes from textile effluents
There are different methods to achieve effective color removal, such as: physical, chemical, electrochemical and biological treatments. They are briefly discussed in the chart below.

4.1 Physical methods
Adsorption is one of the most frequently used methods in textile industry as tertiary treatment (Robinson et al., 2001). Activated carbon is an effective adsorbent for a wide range of dyes, but its high price and regeneration complexity limits its application in decolorization (Galán et al., 2013). In order to find an economically viable application of the adsorption method, some researchers have used low-cost adsorbent materials such as peat, clay, fly ash, granulated ferric hydroxide, zeolites, bentonite clay, agriculture wastes, wood chip, pumice, silica gel and palygorskite clay (Holkar et al., 2016; Ashoka et al., 2010; Hayelom et al., 2014; Kunwar et al., 2003; Poots and McKay, 1976a; Nigam et al., 2000; Gupta et al., 1990; Robinson et al., 2001, Errais et al., 2012; Aries et al., 2009; Rehman et al., 2013; Vimonses et al., 2009; Wanbuguh et al., 2008). The coagulation-flocculation technique is a frequently used treatment method in textile wastewater treatment plants to discolor textile effluents and reduce the total load of suspended solids and organic pollutants, however, the additional chemical load on the effluent increases the sludge production and leads to the uncompleted dye removal (Liberti et al., 1978). Membrane filtration has the ability to clarify, concentrate and separate dyes from the effluent (Mishra and Tripathy, 1993; Xu and Lebrun, 1999). In textile industry, membranes represent an exciting potential for the recycling of hydrolyzed reactive dyes (Chollom et al., 2015).
Some aspects that need to be taken into account concerning membrane-based treatments are: initial investment cost; possible fouling and the generation of other wastes containing insoluble dyes (e.g. indigo); and starch which need further treatment (Koyucu and Güney, 2013; Ranganathan et al., 2007).

4.2 Chemical methods
Ozonation is one of the most effective means of decolorization of dye-laden wastewater and has demonstrated to be able to achieve high color and residual COD removal (Churchley 1994; Strickland & Perkins 1995; Koyuncu & Afşar 1996; Liakou et al. 1997) with improved biodegradability (Tzitzi 1994). One major advantage is that ozone can be applied in its gaseous state and therefore does not increase the volume of wastewater and sludge. The disadvantage of ozonation is its short half-life (typically being 20 min), demanding continuous application and making it a cost intensive process (Xu & Lebrun 1999). Advanced Oxidation Processes are one of the traditional methods used for the removal of inorganic/organic compounds from wastewater. The effectiveness of advanced oxidation processes is based on the generation of oxidizing reagent (OH) radicals, as they attack the chromogenic groups, leading to the production of organic peroxide radicals and ultimately their transformation into CO₂, H₂O and inorganic salts (Antoniadis et al., 2010). Advanced Oxidation Processes comprise a series of methods including ozonation, photo-catalysis, electrochemical oxidation, Fenton and Fenton-like processes. Generation of OH is commonly accelerated by combining O₃, H₂O₂, TiO₂, UV radiation, electron-beam irradiation and ultrasound. Of these, O₃/H₂O₂, O₃/UV and H₂O₂/UV hold the greatest potential to oxidize textile wastewater. Fenton’s reagent is a suitable chemical for treating wastewaters that are resistant to biological treatment (Slokar and Le Marechal, 1997). Advantages of this process include COD, color and toxicity reduction. One major disadvantage of this method is sludge the generation through the flocculation of the reagent and the dye molecules. Several full-scale Fenton’s reagent plants have been built in South Africa to treat textile mill effluents (Gravelet-Blondin et al. 1996). This technology was found to be effective in decolorizing a wide range of dyes (Namboodri & Walsh 1995).

4.3 Electrochemical methods
Electrocoagulation technique was developed in the mid 1990’s. It has some significant advantages as an effective method for dye removal. It uses a direct current source between metal electrodes such as aluminum and iron immersed in the effluent in order to cause the dissolution of the metal plates into wastewater (Aoudj et al., 2010). Fe(OH)₃, can remove dissolved dyes by precipitation or by flotation (Ranghuand and Basha, 2007; Daneshvar et al., 2007). This technique shows high efficiency in terms of color removal and degradation of recalcitrant pollutants (Ogutveren and Kaparal, 1994; Pelegrini et al., 1999). The disadvantages associated with this process are the need for further treatment by flocculation and filtration, causing a high amount of sludge to be produced (Dawood et al., 2014).

4.4 Biological methods
The biological process removes the dissolved organic matter in textile wastewater. The removal efficiency is influenced by the ratio of organic load/dye and the microorganisms load, its temperature, as well as the oxygen concentration present in the system. According to the oxygen requirements, biological methods can be classified into aerobic, anaerobic and anoxic or facultative or a combination of these (Holkar et al., 2016). Biological
removal of the dyes from textile and dyestuff manufacturing industry can be broadly classified into three categories: aerobic treatment, anaerobic treatment, and combined anaerobic-aerobic treatment. Depending on the local regulations, the biological process alone may or may not be sufficient. The process could require the involvement of other physical, chemical, or physicochemical operations (Rai et al., 2005). The general perception that has emerged over the years is that most dyes are generally recalcitrant to aerobic degradation but can be at least partially decolorized under anaerobic conditions (Carliell et al. 1995; Brown et al., 1983b; Donlon et al., 1996; Paszczynski et al., 1986; Zimmermann et al., 1984). Anaerobic decolorization followed by aerobic post-treatment is generally recommended for treating colored wastewater from textile and dyestuff manufacturing industries (Brown et al., 1987). This condition can be implemented either by spatial separation of the anaerobic and aerobic sludge using a sequential anaerobic–aerobic reactor system or within one reactor, commonly termed an integrated anaerobic–aerobic reactor system (Field et al., 1995; Zitomer et al., 1993; Van der Zee and Villaverde, 2005). Fungal methods for the decolorization of azo dyes have been studied in detail (Bumpus et al., 1988; Quezada et al., 2000; Sani et al., 1999b; Van der Zee et al., 2000c; Yesilada et al., 2002). Azo dyes are not readily biodegraded by microorganisms, but they can be degraded by P. chrysosporium (Paszczynski and Crawford, 1995). Other fungi such as, Hirschioporus larincinus, Inonotus hispidus, Phlebia tremellosa and Coriolus versicolor have also shown to decolorize dye-containing effluents (Banat et al., 1996; Kirby, 1999). White-rot fungi such as Dichomitus, squalens, Daedalea avida, Irpex avus and Polyporus sanguineus have been used widely in the decolorization and degradation of textile waste of many chromophore groups of dyes (Chander et al., 2007). Industrial application of fungal methods is not yet feasible for actual textile wastewater effluents because of the slow process kinetics. (Toor et al., 2010).

5. Conclusions
A literature discussion about dyes classification and various removal techniques has been proposed in this abstract review. The aim of the effluent treatment plants (ETP) in textile industry is to achieve normative discharge requirements in terms of color as well as organic compounds. Since the removal of colored industrial effluents is still an economic challenge, this review aims to describe possible a combination of different methods according to the dyes to be removed and the effluent quality to be achieved. The most frequently used technology, after a pre-treatment stage, is the conventional activated sludge process, as it is a proven alternative which is easy to operate. Under aerobic conditions, simple azo dyes can be partially removed and bio-adsorbed into the bio-sludge. However, different literature results reported that mordant, acid, direct and Vat dyes are not completely removed in such a type of treatment. On the other hand, anaerobic methods are suitable for total removal of azo dyes. The combination of anaerobic and aerobic processes is recommended for treating colored wastewater. In general, in the anaerobic phase a longer HRT is required but the decolorization efficiency is higher than 70%. Depending on the local legislation and on the type of dyes to remove, the combination of anaerobic and aerobic systems is the best choice. Unfortunately, these systems are not effective if pigments and Vat dyes are present in the effluent. Different authors have reported the efficiency of physical methods, especially adsorption and membrane filtration, for the removal of several types of dyes, including Vat. When the effluent volume is high, these methods are not suitable because the investment and operative costs. Electrochemical methods, such as electrocoagulation, is a very effective
treatment for the removal of several recalcitrant dyes. This method is less expensive than the others, but needs for further treatment by flocculation and filtration, causing a high amount of sludge to be produced. Chemical methods, such as ozonation and AOPs are the best options to remove pigment and vat dyes. The disadvantages of these methods are the high capital and running costs. Among AOPs, photocatalytic degradation by TiO$_2$ as catalyst, is an interesting and feasible option that can be used as preliminary or tertiary treatment of an activated sludge system. Especially in denim effluent treatment, this approach is effective to convert the organic recalcitrant long-chain compounds in biodegradable products. Most of the studies and the results reported in literature came from laboratory and bench scale activities. Further investigation is required to evaluate the industrial application of advanced methods in terms of energy, costs and environmental impacts.
References