1 Introduction

Since the 1800s, the commercial manufacturing of synthetic dyes has been practiced. With the course of time, they've been tweaked to be resistant to physical and chemical changes, as well as to persist for years without fading (Porter, Lyons, and Nolan 1972). Fabrics' durability has been enhanced due to various features, and the textile sector has thrived in the recent years. However, such synthetic dyes are also resistant to natural processes when they become part of the environment. The textile industry is one of the leading industries in releasing polluted effluents, including dyes, salts, and other organic complexes, in the soil and water bodies. It hence poses severe risks to the aquatic lives and environment. Since only 50% of the applied dyes get utilized in the fabric, the rest is released with huge volumes of water into aquatic bodies causing severe environmental hazards due to their high pH, temperature, COD (Chemical Oxygen Demand), BOD (Biochemical Oxygen Demand) and TOC (Total Organic Carbon) levels (Roy, Biswas, et al. 2018; Roy, Sengupta, et al. 2018; Kousha et al. 2012). Textile enterprises are typically located near the sea, owing to ease of transportation. The hazardous effluents discharged by the industries pose a significant threat to the marine ecosystem. It also substantially affects the photosynthesis of some hydrophytes by inhibiting light penetration, lowering gas solubility and water quality (Shertate and Prakash 2012). It's challenging to get rid of these compounds which are now a threat to the environment and workers in the textile industry.

Further, the textile industry has grown to be one of the most significant water consuming sectors. Water usage in the dyeing process is reported to range between 50 and 240 liters per kilogram of finished material, depending on the shade, procedure, and chemicals employed (Freeman et al. 2009). A colored cotton T-shirt (of 250 g) has a water footprint of more than 2000 liters, which includes water used from the cotton plantation until the T-shirt is placed on shop shelves, including the procedures of carding, spinning, weaving, dyeing, printing, and delivery (Ananthashankar 2013). Therefore, the textile industry being the source of huge amount of dyeing wastewater offers significant carbon footprint to the aquatic environment.

1.1 Dyes and their classification

Colored materials have intrigued man for aesthetic and social reasons since the dawn of civilization. In ancient times, dyes were produced from natural resources, including vegetables, lichens, insects, plants, and berries. These natural dyes were used to color fibers like wool, fur, cotton, leather, and silk (Cristea and Vilarem 2006). Perkins produced the first synthetic dye in 1856, which led to a gradual fall in natural dyes. Over the years, a broad spectrum of research was conducted to develop new dyes for various products and materials to fulfill consumers' expanding expectations. Currently, the textile industry is one of the largest consumers of dyes produced annually (Oussalah et al. 2019; Anirudhan and Ramachandran 2015; Bharathi and Ramesh 2013; R Ananthashankar 2013; Eren et al. 2010). Total dye production is estimated at $7x10^5$ tonnes per year, of which the textile industry consumes 10,000 tonnes per year and discharges 1000 tonnes/year into water bodies (Zhou et al. 2019; Simion Beldean-Galea, Copaciu, and Coman 2018).

The textile dyes can be classified based on their sources (as natural and synthetic dyes) and their applications to the substrates (acidic, basic, direct, reactive, dispersive, vat, and sulfurous dyes) shown in Table 1.1. Reactive dyes are perhaps the most extensively used dyes due to their wide range of color shades, dazzling color, ease of processing, low energy consumption, and so on. They consist of a variety of chemically distinct groups. Azo, phthalocyanine, and anthraquinone dyes are the most frequent (Axelsson et al. 2006). According to their chemical structures, the most commonly used dyes belong to the azo class, containing at least one nitrogen to nitrogen double bond (–N=N–). Azo dyes are one of the most prevalent dyes and contribute to over 70% of the synthetic dyes. The color of dye molecules indicates chromophores which show absorbance in the visible range. The absorption wavelength can be increased either by increasing the number of conjugations or by introducing a functional group (known as auxochrome, for example, an amino, aldehyde, hydroxyl, carboxylic, or sulfonic group) attached to the chromophore of a dye molecule (Boopathy 2000; Xiang et al. 2016; Kalme et al. 2007; Cardoso, Bessegato, and Boldrin Zanoni 2016). Generally, the discoloration of the textile dyes is accomplished by breaking down the conjugated double bonds present inside the chromophores of a dye molecule. The conventional wastewater treatments are inadequate in degrading the azo dyes because of their recalcitrant nature (Pirkarami and Olya 2017). Further, a mixture of various dyes in the textile effluents makes the remediation of a dye-waste even more challenging (Ito et al. 2016).

Dye Class	**Description**	**Fibers Typically Applied to**	**Dye Fibre Interaction**	**Fixation**	**Typical Pollutants Associated with Various Dyes**
Acid	Water-soluble anionic compounds	Wool, nylon	Electrostatic and hydrogen bonding	80-93	Color, organic acids, unfixed dyes
Basic	Water-soluble, applied in weakly acidic dye baths, very bright dyes	Acrylic, some polyesters	Electrostatic attraction	97-98	N/A
Direct	Water-soluble, anionic compounds; applied directly to cellulosic compounds	Cotton, rayon	Intermolecular forces	70-95	Color, salt, unfixed dye, cationic fixing agents, surfactant, defoamer, leveling and retarding agents, diluents
Disperse	Not water-soluble	Polyester, acetate, other synthetics	Hydrophobic-solid-state mechanism	80-92	Color, organic acids, carriers, leveling agents, phosphates, lubricants, dispersants, diluents
Reactive	Water-soluble, anionic compounds, largest dye class	Cotton, wool	Covalent bonding	60-90	Color, salt, alkali, unfixed dyes
Sulfur	Organic compounds containing sulfur or sodium sulfide	Cotton, other cellulosic	Covalent bonding	60-70	color; alkali; oxidizing agent; reducing agent; unfixed dye
Vat	Oldest dyes, more chemically complex, water-insoluble	Cotton, other cellulosic	Impregnation and oxidation	80-95	Color, alkali, oxidizing agents, reducing agents

Table 1.1 Main characteristics of different classes of dyes used in the textile industry (adapted from Verma et al. 2012)

https://www.textileschool.com/383/types-of-dyes-classification-based-on-chemical-structure

1.2 Treatment of the Dyeing Wastewater and Current Challenges

The treatment of dyeing wastewater primarily relies on biological and chemical routes. The biological treatment procedures oxidize organic and inorganic substances by utilizing bacteria, archaea, fungus, algae, or plants (Bhatia et al. 2017; Khandare and Govindwar 2015). The processes that occur in nature are accelerated in the bioreactor by providing the right circumstances - oxygen concentration via aeration, pH, nutrition availability, agitation, etc. Biodegradation techniques are highly cost-effective (Waldrop 2009a; Khandare and Govindwar 2015). However, the investment costs may be high depending on the nature of the utilized equipment and the scale of treatment.

Further, bioprocesses are limited in various ways; for example, they can only decompose biodegradable contaminants. Furthermore, the highly hazardous chemicals might interfere with the biological processes and even impede the use of microbes or plants (Ganzenko et al. 2014). Although biological wastewater treatment has been around for a long time, the technologies involved are constantly improving. For instance, the chemical pre-treatment using AOPs frequently transforms biologically persistent contaminants.

AOPs (advanced oxidation processes) are a group of methods that utilize hydroxyl radicals, generally at room temperature and normal pressure, to oxidize the dye molecules (Oturan and Aaron 2014). The hydroxyl radical is a robust and non-selective oxidant that can react in three ways: hydrogen abstraction, electron transfer, or radical addition. As a result, they can decompose complicated chemical structures such as bio-refractory chemicals (Arslan and Balcioglu 2001), primarily artificial contaminants that microorganisms seldom target. AOPs are costlier than bioprocesses because they require large amounts of chemical reagents or electrical energy (Dewil et al. 2017). AOPs, on the other hand, are constantly evolving with the application of the most efficient methods: for example, new photocatalysts (Barkul et al. 2017) or the reactor designs with more efficient mass transfer (Shang et al. 2006)).

The combination of biological and chemical treatments has both economic and environmental advantages. The hydroxyl radicals (generated from an AOP) can transform refractory chemicals into more readily biodegradable molecules, which microbes can efficiently metabolize. However, partially mineralized wastewater from an AOPs can be further mineralized by the microorganisms in the bioremediation. The integration of AOP with bioremediation is recommended for wastewaters with a BOD_5/COD ratio of less than 0.20 (5-day Biochemical Oxygen Demand to Chemical Oxygen Demand).

1.3 Objectives and Scope of the Study

This research project aimed to assess the biological and chemical processes for their ability to degrade azo dyes into non-toxic compounds and then use the results to develop an integrated methodology for the best treatment in terms of the processing cost and toxicity treated dyeing water. Specifically, this study aimed at:

1. Modeling the bacterial growth kinetics accounting both the substrate inhibition as well as metabolite inhibition which is caused by toxic metabolic by-products and was rarely considered in the bacterial growth model in the literature
2. Studying the effect of process parameters such as the initial dye loading and inoculum size on the biodegradation rate of dyes in the bioreactor
3. Investigating the impact of external mass transfer barrier on the biodegradation (in terms of the removal of color, COD, and TOC) of azo dyes in a recirculating packed bed bioreactor (RPBB)
4. Performing process optimization to minimize the operating cost of ozonation based AOP of highly concentrated azo dye solution
5. Conducting integrated ozonation-biodegradation processes for the assessment of phyto-/ and geno-toxicities of the treated dyeing water using plant and luminescent bacterial assays

1.4 Organization of Thesis

In **Chapter 2**, we have reviewed the available literature on the treatment methodologies for removing dyes from wastewater. Various physical (adsorption, sedimentation, coagulation-flocculation, etc.), chemical (hydroxyl radical based AOPs such as Fenton process, photocatalysis, and ozonation process), and biological (anaerobic and aerobic biodegradation) methods have been thoroughly discussed. Also, the applications of integrating the AOPs with biodegradation are analyzed. **Chapter 3** focuses on the material and techniques used in our different studies, such as the preparation of the synthetic wastewater and the isolation and enrichment of the bacterial species to be used in bioreactors. This chapter also includes the bioreactor configuration and various analytical methods adopted, such as COD, BOD, TOC measurements, phytotoxicity, and bacterial toxicity evaluation. In **Chapter 4**, a computational approach is proposed to predict the bacterial growth kinetic accounting 'metabolite' inhibition in wastewater biodegradation. Effective dye degrading bacterium species were isolated and characterized in this investigation. The inhibition caused by 'metabolite' was incorporated in the general growth kinetics models by considering the entire sigmoidal log phase (including the decelerating phase) in calculating bacterial growth rate. In **Chapter 5**, the investigation of the effect of external mass transfer on the biodegradation of azo dye in a recirculating packed bed bioreactor is discussed. This chapter considered the impact of recirculation while calculating the 'overall' reaction rate constant incorporating the mass transfer resistance inside the packed bed bioreactor.

In **Chapter 6**, an attempt has been made to optimize the process parameters (initial ozone concentration, initial dye concentration, and pH) in the ozonation of highly concentrated azo dyes in a bubble column reactor. Furthermore, an empirical correlation to estimate electricity cost in the ozonating of dyeing wastewater was also developed and experimentally verified. In **Chapter 7**, an integrated ozonation-biodegradation of dyeing wastewater was performed, and the toxicity of the treated wastewater was assessed using plant- and luminous bacterial-based assays. Finally, **Chapter 8** highlights the most relevant findings of this work and offers valid conclusions of this work with future research and application directions.