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## Table of Contents

CERTIFICATE	2
DECLARATION BY THE CANDIDATE	3
COPYRIGHT TRANSFER CERTIFICATE	4
ACKNOWLEDGEMENT	5
ABSTRACT	11
LIST OF FIGURES	13
LIST OF TABLES	16
1 Introduction	17
1.1 Dyes and their classification	18
1.2 Treatment of the Dyeing Wastewater and Current Challenges	21
1.3 Objectives and Scope of the Study	22
1.4 Organization of Thesis	23
2 Literature on the treatment methodologies for removal of dyes from the wastewater	25
2.1 Physical Methods	26
2.2 Biological Methods	27
2.3 Chemical Methods	30
2.3.1 Fenton process	31
2.3.2 Photo-catalysis process	33
2.3.3 Ozonation process	35
2.4 Integration of the AOPs with biological methods	37
2.4.1 Integration of Fenton with biodegradation	38

2.4.2	Integration of photocatalysis with biodegradation	39
2.4.3	Integration of ozonation with biodegradation	40
3	Material and Methods	43
3.1	Materials and Chemicals	43
3.2	Preparation of synthetic dye wastewater	44
3.3	Molecular characterization of the efficient isolated bacteria	44
3.4	Biodegradation experiments in a batch reactor	45
3.5	Bioreactor configuration and immobilization of packing material	46
3.6	Analytical methods	47
3.6.1	UV-Vis Spectrophotometry	47
3.6.2	Biochemical Oxygen Demand (BOD)	47
3.6.3	Chemical Oxygen Demand (COD)	48
3.6.4	Total Organic Carbon (TOC)	48
3.8	Toxicity Analysis	49
3.8.1	Phytotoxicity	49
3.8.2	Bacterial toxicity	49
4	Improved Bacterial Growth Kinetic Model using Indigenously Isolated Strain <i>Bacillus Subtilis</i> MN372379 in the Degradation of Congo Red Dye	51
4.1	The conventional approach to determine the bacterial growth rate	52
4.2	Time-Averaged Bacterial Growth Rate Incorporating the Metabolite Inhibition: an Improved Approach Proposed in the Present Study	54
4.3	Time-averaged substrate utilization rate: An approach proposed in the present study	56

4.4	Identification of the Efficient Dye-Degrading Bacterial Isolate	57
4.5	Bacterial Growth Kinetics	58
4.5.1	Degradation of the Synthetic Wastewater at Different Initial Dye Concentrations	58
4.5.2	Determination of the specific bacterial growth rate time-averaged over the entire log phase for incorporating metabolite inhibition	60
4.5.3	Nature of metabolite inhibition in the decelerating part of log phase	62
4.5.4	Incorporation of time-averaged bacterial growth rate accounting metabolite inhibition in the bacterial growth models with substrate inhibition	63
4.6	Process optimization for the maximum dye utilization	66
4.6.1	Optimization of the initial dye concentration	66
4.6.2	Optimization of the initial inoculum size	67
5	Investigation of External Mass Transfer during Biodegradation of Congo Red Dye in a Recirculating Packed Bed Bioreactor	71
5.1	Bioreactor configuration	73
5.2	Bacterial immobilization and acclimatization in the Congo Red dye environment in the RPBB	74
5.3	Mass Transfer Study: Theoretical Method	75
5.3.1	Concentration profile and observed biodegradation rate in the RPBB	75
5.3.2	Modification in the material balance equation to account for recirculation in an RPBB	76
5.3.3	Evaluation of external mass transfer in the RPBB	77
5.4	Results and Discussion	79
5.4.1	Effect of inlet mass flow rate on the overall rate of dye removal in the RPBB	80

5.4.2	Determination of the correlation for external mass transfer coefficient	81
5.4.3	Determination of the Colburn factor for external mass transfer coefficient	83
5.4.4	Effect of recirculation flow rate on the external mass transfer	84
5.5	Conclusion	85
6	Optimization for Minimizing the Cost of Ozonation of Highly Concentrated Textile Dyeing Wastewater in a Bubble Column Reactor	87
6.1	Experimental Setup	89
6.2	Design of experiment	90
6.3	Dye removal and electricity consumption at various initial dye concentration	91
6.4	Development of an empirical correlation for the average specific electricity consumption during the ozonation of Reactive Blue dye	93
6.4.1	Measurement of the $SEC_{av}$ for the DOE	93
6.4.2	Statistical modeling for the $SEC_{av}$ using RSM	94
6.5	Effect of process variables on the average specific electricity consumption in the ozonation of Reactive Blue dye	96
6.5.1	Effect of inlet ozone concentration	97
6.5.2	Effect of initial pH level	97
6.5.3	Effect of initial dye concentration	98
6.6	Optimization of process variables to minimize $SEC_{av}$	98
6.7	Model verification and cost analysis	99
6.8	Conclusion	100



7	Phyto-/Geno-Toxicity Assessments of the Dyeing Wastewater treated with Anaerobic-Aerobic Biodegradation (AnAB) vs. Ozonation-Aerobic Biodegradation (OAB) Processes	101
7.1	Configuration of AnAB and OAB systems	104
7.2	Bacterial immobilization and their acclimatization to the SDW in the FBBR	107
7.3	Performance evaluation of the hybrid AnAB and OAB systems	108
7.3.1	COD removal	108
7.3.2	Color removal	110
7.3.3	Overall Performance AnAB and OAB System against varied organic loading rates	111
7.4	Toxicity assessment	113
7.4.1	Phytotoxicity analysis	113
7.4.2	Bacterial toxicity analysis	115
7.5	Conclusion	118
8	Conclusion and Future Aspects	120
9	Bibliography	122
10	List of Publications	146

## ABSTRACT

In many places of India where textile and dye-based industries are concentrated, the discharge of untreated color effluents into natural environment is a widespread problem. Many research activities have been performed to lessen the environmental impacts, and the relevant solutions have also been provided. However, most textile dyeing units are small and cottage-type in nature, and lack financial resources to treat their effluents. Textile effluents are being studied by researchers globally to find the best and economical treatment option. The physical processes such as adsorption and coagulation are common wastewater treatment methods. However, these methods require post-treatments for the degradation of the adsorbed dyes and contaminants. Several advanced oxidation processes (AOPs) such as Fenton, photocatalysis, ozonation, ultrasonication, etc. have been used in the last few decades to treat the textile effluents. They employ hydroxyl radicals to oxidise a wide range of recalcitrant pollutants such as dyes. However, their applications are limited primarily by the high processing cost and incomplete mineralization of azo dyes. Biodegradation has potential to compensate the drawbacks of the AOPs. The biological treatments utilize dyes as substrates and cleave their azo bonds during their metabolic processes. However, biodegradation is a very slow process and limited to only biodegradable contaminants. The integrations of various AOPs with biodegradation have been recently explored by researchers to bring down the overall processing cost and improve the degree of mineralization of dyeing wastewater.

This study was focused on the process dynamics, toxicity evaluation and cost optimization of the integrated biodegradation ozonation process. The anaerobic biodegradation was utilized as it targets the chromophore (-N=N-) group in the azo dyes enabling decolorization of the dyeing wastewater. A follow-up aerobic biodegradation was used to facilitate mineralization and detoxification by oxidizing the metabolites and the remaining contaminants. The ozonation was chosen as AOP in this study because it has high oxidation potential, creates no sludge or secondary waste, and uses only atmospheric oxygen and electricity as inputs and therefore can be easily used at the effluent discharge sites of small-scale dyeing units.

First, a computational approach was developed in this study to account for the 'metabolite' inhibition, which was never considered in previous studies, in the prediction of bacterial growth kinetic during the biodegradation of dyeing wastewater. In this process, a bacterial species (*Bacillus subtilis* MN372379.1) showing efficient degradation capability for the Congo Red dye was isolated from the soil sample (obtained from a textile plant site), characterized and used in the biodegradation experiments. The effect of metabolite inhibition was incorporated in the growth kinetic by considering the entire sigmoidal log phase profile (including the decelerating phase) in the calculation of the specific bacterial growth rate. This study has shown that the negligence of the inhibition caused by metabolites can immensely overestimate (by 30-60%) the prediction of bacterial growth in a bioreactor.

The second part of this work investigated the effect of external mass transfer on the overall rate of biodegradation of Congo Red dye in a recirculating packed bed bioreactor (RPBB). Bioreactors, with bacterial mass immobilized onto packing materials, are used to enhance toxicity tolerance of the bacterial cells, biodegradation rate of dyes (caused by high surface area of the packing materials) and scalability to enable biodegradation at large scale. However, the external mass transfer resistance plays a critical role in governing the overall reaction kinetics in the immobilized bioreactors. Specifically in this study, the isolated *Bacillus subtilis* MN372379 species was immobilized on the packing material made of low-density polyethylene (LDPE) foam cubes in the RPBB. The overall dye removal rates were measured at varied feed flow conditions and an empirical correlation for the external mass transfer coefficient in the given RPBB was determined. The observed rate of removal of Congo red dye in the RPBB was found to be increasing with the operational parameters such as feed flow rate or recycle rate.

An empirical correlation to predict the non-dimensional Colburn factor for determination of mass transfer coefficient of Congo red dye in the RPBB was obtained as  $J_D = 1.34 Re^{-0.3}$ . The determination of a dimensionless correlation for mass transfer coefficient for the biodegradation of Congo red dye would enable design and scale up of a RPBB for the continuous treatment of dyeing wastewater with minimal impact of external mass transfer resistance on the overall dye removal.

Although ozonation, being a fast AOP, is a good alternative to the biodegradation, it suffers from high operating cost. The third part in this study attempted to optimize the process parameters (such as inlet ozone concentration, initial dye concentration, and pH level) to minimize the overall power consumption (operating cost) of the process. The ozonation of Congo Red dye was performed in a bubble column reactor at various process conditions. A central composite design (CCD) based Response Surface Method (RSM) statistical tool was used to optimize the process. An empirical correlation to determine the *specific electricity consumption, SEC*, (defined as the electricity consumed per unit mass of dye removed from a unit volume of dyeing wastewater) was developed and experimentally verified. It was found that the *SEC* during ozonation can be lowered if the dyeing water was treated at high initial dye concentrations. Generally, the dye concentration in the textile effluent is found in the range of 0.2-0.5g/L. Under the optimized conditions at initial dye concentration of ~4.4g/L, the cost of electricity consumption was found to be reduced significantly (by ~25-30 %). Therefore, this study recommended having a dye-enriching step for the regular textile effluent to achieve the desired dye loading before performing the ozonation.

Finally, the fourth section of this work utilized an integrated ozonation biodegradation process for improving the overall dye removal efficiency, processing time, and toxicity. Both, the biological and ozonated or other AOP treated, dyeing wastewater still have a certain level of toxicity due to untreated dyes or produced intermediates/byproducts. This section used plant- and luminous bacterial-assays to compare the toxicity of the treated dyeing wastewater. Congo Red dye-based simulated dyeing wastewater was treated with two systems namely, anaerobic-aerobic biodegradation (AnAB) and ozonation-aerobic biodegradation (OAB). The treated water samples were tested for decolorization, mineralization (in terms of BOD and COD) and detoxification. The qualitative and quantitative assessments of the phytotoxicity and genotoxicity of the treated dyeing wastewater were carried out using the seeds of *Vigna radiate*, and luminescent bacterial strain of *P. luminescens*, respectively. Although both, the anaerobic biodegradation and ozonation processes, resulted in high (>95%) color removal, the ozonation process offered faster color removal. However, the anaerobic process offered a higher COD and toxicity reduction than the ozonation. Therefore, the ozonation was recommended primarily for rapid color removal, and a subsequent biodegradation step for meeting the mineralization and detoxification targets.

In sum, the information contributed to the literature of dyeing wastewater treatment from this study are as follows. The inhibition caused by the metabolites/secondary by-products must be considered in predicting bacterial growth where dyes are used as substrates by the bacterial cells. It can be accounted by calculating a time-averaged specific growth rate as shown in the first section of this work. Further, the impact of mass transfer resistance on the overall dye degradation rate in the immobilized RPBB can be obtained from the dimensionless empirical correlation developed in the second section of this study. Next, the operating cost of the ozonation can be brought down significantly if the concentration of dyes in the textile wastewater is enriched to the desired level before ozonation as shown in the third section. The fourth section showed that the anaerobic-aerobic coupled biodegradation system offered a higher toxicity reduction than the ozonation-aerobic biodegradation. Finally, the ozonation (with a dye-enriching pre-treatment) was recommended for a rapid and economical color removal with the subsequent optimized biodegradation step for achieving adequate mineralization and detoxification of the textile dyeing wastewater.

## LIST OF FIGURES

Figure 2.1 Schematic of biodegradation of an azo dye (Chaturvedi et al. 2021b).....	28
Figure 3.1 Molecular structure of Congo Red dye.....	43
Figure 4.1 Schematic showing the approach used in this study to determine time-averaged specific growth rate for the entire sigmoidal log phase comprised of the accelerating log phase (represented by an exponential growth curve) and the decelerating log phase (represented by growth with inhibition caused by the metabolic toxicants).....	55
Figure 4.2 Schematic showing the approach to determine a time-averaged specific substrate utilization rate for the log phase using the measured substrate concentration profiles and bacterial mass.....	57
Figure 4.3 Phylogenetic tree obtained from MEGA X 10.1 showing the evolutionary history using the neighbor-joining.....	58
Figure 4.4 Biomass concentration (g/L) and dye concentration (mg/L) in the batch reactor at different time steps for various initial dye concentrations of (a) 50 mg/L, (b) 100 mg/L, (c) 150 mg/L, (d) 200 mg/L, and (e) 250 mg/L .....	60
Figure 4.5 Initial specific growth rate, $\mu_a^{bg}$ , (based on the accelerated exponential growth phase) and the time-averaged specific growth rate, $\mu_{avg}^{bg}$ , (accounting both the accelerated and decelerated log phases) against the initial dye concentrations. ....	61
Figure 4.6 The inverse of growth rate ( $1/\mu^{bg}$ ) vs the inverse of initial dye concentration ( $1/S_0$ ) to determine the nature of enzyme inhibition in the decelerating log phase .....	62
Figure 4.7 Molecular structure of key degradation products: (a) naphthalene; (b) biphenyl.....	63
Figure 4.8 Comparison of average specific growth rates ( $\mu_{avg}^{bg}$ ) obtained from experiments at various initial dye concentrations with the substrate inhibitory models: (a) Andrew-Haldane model; (b) Aiba model, and (c) Edwards model. The dotted line presents the non-inhibitory Monod's model .....	66

Figure 4.9 Average specific dye (substrate) utilization rate, $\mu_{avg}^{su}$ , obtained from Eq 4.7 against different initial dye concentrations .....	67
Figure 4.10 Effect of the initial inoculum size: (a) Bacterial concentration vs. time; (b) Average dye utilization rate, (c) Average specific dye utilization rate, and (d) Elimination capacity are plotted at different initial dye concentrations.....	69
Figure 5.1 Schematic of the recirculating packed bed bioreactor (RPBB). The bioreactor was immobilized with <i>B. subtilis</i> on the LDPE foam cubes.....	74
Figure 5.2 Effect of recirculating flow rate on the observed dye removal rate constant at 200 mg/l of inlet dye concentration .....	81
Figure 5.3 Plot of $1/k_p$ against $1/G^n$ at various values of $n$ ( $= 0.5, 0.7, 0.9$ ).....	82
Figure 5.4 Variation in external mass transfer coefficient and the overall reaction rate constant with the recirculation flow rate .....	85
Figure 6.1 Schematic of the Ozonator setup for the degradation of Reactive Blue dye.....	90
Figure 6.2 Aggregate dye removal and specific electricity consumption at increasing concentration of dye: (a) 0.5 g/l (b) 1 g/l (c) 2 g/l (d) 4 g/l .....	92
Figure 6.3 (a) Percentage dye removal vs. time at different initial dye concentrations, (b) Average specific electricity consumption ( $SEC_{av}$ ) for the ozonation process at different initial dye concentrations.....	93
Figure 6.4 Predicted surface plots of average specific electricity consumption ( $SEC_{av}$ ) as a function of two independent variables (while the third variable was held constant at its respective center level shown in Table 6.1): (a) inlet ozone concentration and the initial pH were varied keeping initial dye concentration at 6 g/l, (b) inlet ozone concentration, and initial dye concentration were varied keeping pH constant at 8, (c) initial dye concentration and initial pH were varied keeping ozone concentration at 60% .....	97

Figure 7.1 Schematic diagram of experiments: (a) anaerobic reactor followed by aerobic reactor (AnAB system); (b) ozonator reactor setup (with an oxygen concentrator and ozone generator) followed by aerobic reactor (OAB system).....	106
Figure 7.2 Bacterial acclimatization process in an FBBR. The FBBR system was exposed to varying inlet concentrations of Congo red dye (ranging from 50 - 500 mg/L) in different cycles .....	108
Figure 7.3 Color and COD removal with time for the (a) anaerobic biodegradation; (b) anaerobic-aerobic biodegradation; (c) ozonation process and (d) ozonation-aerobic biodegradation (at the initial dye concentration of 200 mg/L) .....	110
Figure 7.4 Overall performance of the AnAB and OAB system depicting the effect of an increase in the dye concentration from 200 mg/l to 800 mg/l on the percentage reduction in color, COD, and TOC. The data of color, COD, and TOC are the mean of three experiments $\pm$ standard error .....	113
Figure 7.5 Comparison of the germination %, root and shoot lengths after 5 days of exposure time in the treated and untreated samples obtained from anaerobic-aerobic biodegradation system (AnAB system) and ozonation-aerobic biodegradation system (OAB system), respectively .....	114
Figure 7.6 (a) Acute- and (b) chronic-bioluminescence intensities (counts per second) for the untreated (SDW), treated (AnTDW, AnATDW, OTDW and OATDW) and control (DiW) samples. The data points are a mean of three experiments $\pm$ SD based on the three independent determinations .....	115
Figure 7.7 Bioluminescence inhibition of <i>P. luminescens</i> during their acute and chronic exposure to the treated (AnTDW, AnATDW, OTDW, and OATDW), untreated (SDW) dyeing water-samples with respect to the control distilled-water sample (DiW). Values are mean of three experiments for % bioluminescence inhibition $\pm$ standard error .....	117

## LIST OF TABLES

Table 1.1 Main characteristics of different classes of dyes used in the textile industry (adapted from Verma et al. 2012).....	20
Table 4.1 Percentage removal of Congo red dye with 10 different bacterial isolates .....	58
Table 4.2 Overestimated in the log phase-specific growth rate when the conventional exponential growth kinetic was assumed (i.e., the decelerating phase was not considered) .....	61
Table 4.3 Kinetic parameters obtained by fitting the experimental data ( $\mu_{avg}^{bg}$ vs $S_0$ ) with various substrate inhibition models .....	65
Table 5.1 Experimentally determined values of $k_p$ and $1/k_p$ , and calculated values of $G$ , and $1/G^n$ at various volumetric flow rate ( $Q$ ).....	82
Table 5.2 Calculated values of $N$ , $A_m$ , and $k$ for various random values of $n$ and $K$ .....	83
Table 5.3 Calculated values of mass transfer coefficient ( $k_m$ ) at different values of mass flux ( $G$ ) for $n = 0.7$ and $K = 1.34$ .....	84
Table 6.1 Experimental ranges and levels of the independent variables .....	90
Table 6.2 Measured values of the response function (average specific electricity consumption) for the Central Composite Design ( $CCD$ ) parameter matrix.....	94
Table 6.3 Analysis of variance (ANOVA) for ozonation process using response surface quadratic model.....	96
Table 6.4 Model verification and cost comparison of the ozonation at the optimum initial dye concentration with respect to the regular dye concentration present in the textile effluent [The optimum values of inlet ozone concentration, 80%, and pH, 10, were used in all cases] .....	100