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 <u>entire</u> 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.