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Application of Homogenous Oxidative Methodologies for Study of Degradation of Prototypical Textile Dyes.

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ABSTRACT

Application of homogenous oxidative methodologies such as sodium hypochlorite has been applied to environmental management for the removal of synthetic organic recalcitrant prototypical dyes from wastewater streams. Textile dyes and their breakdown products were found to generate toxic and carcinogenic products, which causes deleterious effects on livelihood. Three prototypical dyes such as Orange G (OG), Malachite Green (MG) and Trypan Blue (TB) were selected based on its structure, application and its breakdown products toxicity. Process parameters such as effect of pH, temperature (K), contact time (hours), dye concentration (mg/L) and oxidizing agent concentration (mM) were studied to predict the optimal conditions. Thermodynamic data such as Enthalpy (ΔH), Entropy (ΔS) and Gibbs free energy (ΔG) were obtained to study the reaction kinetics and feasibility of the reaction. The dye degradation of prototypical dyes was found to be zero order for OG and MG and first order for TB. High enthalpy values indicate the reactions are enthalpy driven, while negative entropy values indicate that the activated complexes are highly structured complex at the activated states. Positive free energy values indicates that the reaction requires the involvement of catalysts to make reaction feasible, in turn depends on temperature and concentration of sodium hypochlorite.

Keywords: Synthetic dyes, degradation, sodium hypochlorite, thermodynamics.

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INTRODUCTION

The prevalence and widespread utilization of man-made chemicals had made abrupt release of industrial wastewaters are abruptly released into the water bodies without pre-treatment process into the ecosystem. The textile finishing industry is considered to be a water-intensive sector, as the nature of textile processes requires several washing and rinsing cycles [1]. The degree of colorization is associated with discharge of dyes and their breakdown products [2]. Various physical, chemical and biological methods have been reported to investigate the degradation of textile dyes, as industries require on-site remediation of effluents, before releasing into treatment plants. These traditional methodologies are reported to be non-destructive, as they transform non-biodegradable matter into sludge, giving rise to accumulation of secondary solid waste, which requires further treatment [3-5]. Current industries require rapid non-biological methodologies which destroy/degrade the pollutants.Chemical oxidation processes such as ozonation, hydrogen peroxide, sodium hypochlorite, ultraviolet and fenton reagent are most potential and currently employed for treating effluents [6]. Sodium hypochlorite treatment is one the traditional conventional method employed in treatment of textile streams, generating chlorine ions/radicals, eventually degrading the textile dye, thereby decolorizing the colored wastewater [7]. The rationale for selecting the three dyes are as follows; Malachite green is widely used for coloring purpose and finds its application in coloring paper, and leather products, dyeing cotton, wool, silk and jute industries [8]. Trypan Blue is Benzidine congener-based dye proved to be potent human carcinogen [9]. Orange G ia an azo dye and it is resistant to biodegradation causing lesions at higher dye concentrations and should not bioconcentrate in aquatic organisms, as azo dyes are characterized by presence of azo linkage in associated of aromatic rings (benzene and/or naphthalene), along with sulfonic group. Of the selected prototypical dyes, all the three dyes were found to exhibit toxicity. Except Orange G (OG), the LD50 values of Trypan Blue (TB) and Malachite Green (MG) were found to be 6200mg/kg and 80mg/kg. In case of Orange G (OG), the LD50 values are not reported. These dyes were found to generate long term degradation products, causing acute toxicity in case of Trypan Blue (TB). Malachite Green has been used as therapeutic fungicidal compound for fish, but it is known to be toxic at higher concentrations [10]. Literatures have reported very few reports on homogenous oxidation processes using sodium hypochlorite as an oxidant. The present paper focuses on the need for oxidative processes, due to the toxic effects of the prototypical dyes. Four process variables pH, temperature (K), dye concentration (mg/L) and incubation time (minutes) were selected to investigate the influence of oxidizing agents towards its decolorizability of three dyes such as Trypan Blue, Malachite Green and Orange G. We tried for the first time, using a combinatorial approach of treating our class of three prototypical synthetic organic dyes with a strong oxidizing agent such as sodium hypochlorite in a batch process.

MATERIALS AND METHODS

Representational synthetic organic dyes such as Tryphan Blue (TB), Orange G (OG) and Malachite Green (MG) were obtained from Hi media and Merck Limited. All other chemicals used in the study were of analytical grade and procured from SD Fine Chemicals limited, India.

Four process variables such as pH, temperature (K), dye concentration (mg/L) and incubation time (minutes) were selected to determine optimal conditions influencing dye degradation/decolorisation using sodium hypochlorite. Experiments were carried out in a wide pH range from pH 3.0 to 8.0 to predict optimal pH for dye degradation. The pH is adjusted to the desired values with HCl and NaOH. Batch experiments were performed with reaction conditions as follows; 0.5 mL of textile dye solution of desired concentration (W/V %),followed by addition of 9.5 mL of double distilled water and 0.5 mL of sodium hypochlorite. The dye solutions are stirred and 3 mL samples are withdrawn at regular time intervals and the dye decolorization was measured spectrophotometrically using a UV-Visible spectrophotometer (Elico, India). Effect of temperature towards dye degradation was carried out at three representative temperatures (303K, 313K and 323K). Effect of dye concentration and incubation was studied at optimal pH at which dye decolorization was reported.

RESULTS AND DISCUSSION

Figure 1 represents the pH profile in terms of percentage decolorization for TB and OG, and the optimal pH were found to be pH 4.0, while for MG was found to be pH 3.0.

All the dyes degraded effectively at the acidic range, it might be due to ionization of organic structures. Presence of hydrogen ion (H+ ion) in the solution in the form of hydronium ion causes more isomerization of structures from keto-enol forms, shuttling the electrons from one form to another, thereby leading to structural deformity (degradation), lowering the absorption maxima, and causing decolorization.

Figure 1: Effect of pH towards decolorization of three prototypical dyes by oxidizing agent (Sodium hypochlorite)

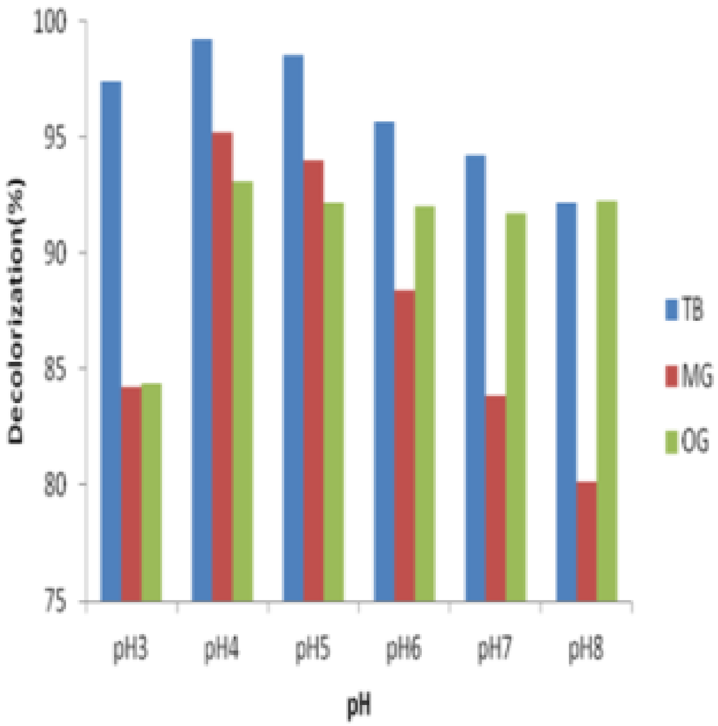


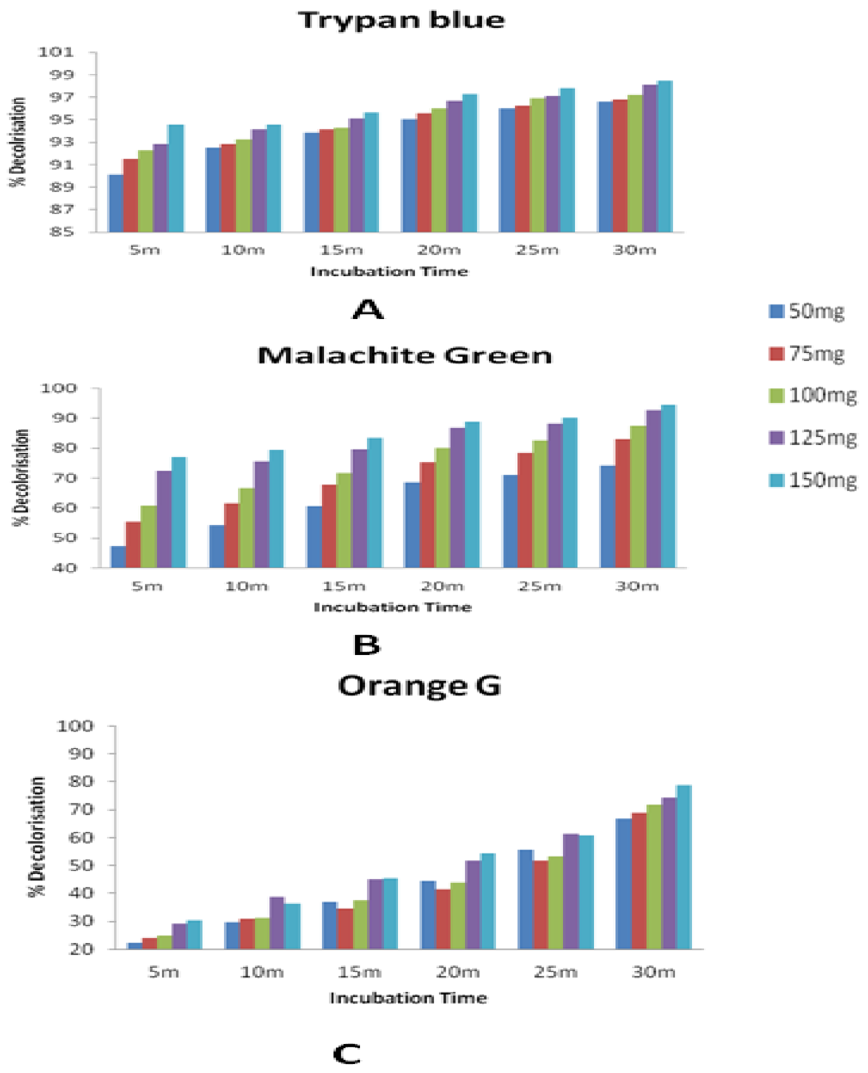
Table 1 represents the thermodynamic profile of the three dyes. Orange G and Malachite Green followed zero order kinetics, while Trypan Blue followed first order kinetics. The probable mechanism might/may be the two diazo bonds require extra energy to cross the transition state. High positive enthalpy among three dyes suggests the formation of high energy complex. At the bottom line, the results indicate that, degradation of the three selected dyes by sodium hypochlorite was found to be non-spontaneous at all temperatures. Temperatures found to have no role on the spontaneity of the degradation reaction pathway. Enthalpy indicates the energy requirement, while entropy deals with how the energy within the molecule must be redistributed for the reaction to occur. Enthalpy and entropy helps us to understand the insights of mechanism leading to the transition state. The bonds present in the textile dye are broken before the transition state, with more degrees of freedom, resulting in high positive enthalpy. Negative values of entropy indicate the activated complexes are highly structured than the reactants, indicating that in the transition state, formation of complex dye structures occurs.

Table 1: Thermodynamic parameters affecting degradation of three prototypical dyes by oxidizing agent

Dye	Enthalpy J/mol	Entropy J/mol K	Gibbs Free Energy Change KJ/mol		
			298 K	303 K	308 K
Trypan Blue	950.12	-31.55	10.35	10.51	10.67
Orange G	54.56	-272.98	81.40	82.77	84.13
Malachite Green	176.64	-245.55	73.35	74.58	75.81

Figure 2 represents the effect of dye concentration and incubation time towards prototypical dye decolorization. Among the three dyes, increasing order of degradation were as follows; TB>MG>OG with respect to incubation time and dye concentration. The degradation pattern followed first order kinetics in case of TB, and zero order kinetics in case of MG and OG which correlates with the results obtained. In case of TB, oxidizing agent plays a major role, as more than 80% degradation is obtained within first five minutes. Structure-activity relationship between dyes and the oxidizing agent play a major role, causing MG and OG degradation a time dependent process.

Figure 2: Effect of dye concentration and incubation time towards decolorization of three prototypical dyes by oxidizing agent (Sodium hypochlorite)



CONCLUSION

Mineralization of synthetic aromatic compounds is highly a mind-numbing process requiring prior thorough knowledge of chemistry of the dye, structure activity relationship during transition state, electro-chemical potential of the oxidizing agent, ionization potential of both reactants and oxidizing agent under investigation. From the studies, we infer that, sodium hypochorite was able to degrade effectively, as supported by our studies. Process variables such as pH and incubation time were found to be two significant influencing process variables among the four variables (pH, temperature, dye concentration and incubation time), as high decolorization /degradation occurs within ten minutes at their optimal pH (low acidic pH) at room temperature at static conditions without the influence of any externally added mediators. We attempt for the first time, using the action of sodiumhypochlorite on three representative synthetic dyes, to infer thermodynamic parameters and influence of other process variables, but future studies requires thorough investigation of insights of mechanisms by involving analytical methodologies to infer the degradation pathway.

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REFERENCES

[1] EPA, (1997). Profile of the Textile Industry. Sector Notebook Project EPA/310-R-9700
[2] Vandervivere, PC, Bianchi R, Verstraete W. J Chem Tech Biotech 1998;72: 289-302.
[3] Arslan I, Balcioglu IA, Tuhkanen T, Bahnemann D. J Env Engg 2000; 126: 903-911.
[4] Chaudhuri SK, Sur B. J Env Engg 2000; 126: 583-594.
[5] Dhira A, Sharma S, Sud D and Ram C. Elixir Chem Eng 2012; 53, 11983-11987.
[6] Chelliappan S andSallis PJ. J Sci Ind Res 2013; 72: 248-54.
[7] Pizzolato TM, Carissimi E, Machado EL, Schneider IAH. Brazil Int J Min Processing 2002; 65: 203-211.
[8] Syed SPS. Res J Chem Sci 2011; 1(1): 88-104.
[9] US EPA (2010), http://www.epa.gov/pbt/.
[10] Little LW, Lamb III JC. Acute toxicity of 45 selected dyes to the FathealMimow, Pimephalespieomelas, UNC Wastewater Research Center, Department of Environmental Sciences and Engineering, University of North Carolina, 1972.