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Kinetics and Equilibrium Study for the Degradation of Textile Dyes

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Abstract

This research work mainly deals with the decolorization of organic dye pollutants from aqueous streams using the advanced oxidation process (AOP) as a basetechnique. AOP's involves the generation of hydroxyl radicals (•OH) and plays a key role in degradation and converting of organic pollutants into CO_2, H_2O, some short chain organic acids and intermediate compounds. Recently, hydrodynamic cavitation (HC) technique has been explored as a one of the emerging advanced oxidation technologies (AOT) for degradation of various organic pollutants in the aqueous streams. In the present work, HC has been used a basic advanced oxidation technology for the degradation/removal of dye pollutants from wastewater.

As synthesized TiO_2, and Fe doped TiO_2 nano photo catalysts were characterized by X-raydiffraction (XRD) and transmission electron microscopy (TEM) analysis to evaluate their structure and morphology. Photo catalytic performance of both un-doped and doped TiO_2 photocatalyst was investigated for the decolorization of three different Textile dyes in aqueous solution at pH of 6.5 in the presence of hydrodynamic cavitation. Kinetic study was also carried out for the hybrid AOP (HAOP) and that followed the pseudo first-order reaction kinetics.

The results obtained through these studies explored the importance and contributionof the hydrodynamic cavitation as a primary pretreatment technique for obtaining the maximum degradation in wastewater in conjunction with other treatment techniques. From these studies, it was observed that the hydrodynamic cavitation can also be a useful technique for bulk wastewater treatment by scaling up through the incorporation of number of orifice holes, increasing the size of the pipe and pump.

Keywords: Textile dyes, H_2O_2,TiO_2, $FeTiO_2$ and ZnO Photocatalysts,Hydrodynamci Cavitation.

1. INTRODUCTION

Textiles industry uses substantial volume of water and number of dyes, chemicals, auxiliary chemicals and sizing materials during the conversion of fibers into yarn and yarn into fabrics or dyeing and finishing. As a result of these activities, the produced contaminated wastewater mainly consists of colour, stain remover like CCl_4, sequestering agents such as trisodium polyphosphate and sodium hexametaphosphate, printing gums like pentachlorophenol, fixing agents like formaldehyde and benzidine, Chlorine, azo dyes, dissolved Solids, toxic metals like chromium, residual chlorine and detergents can cause damage to environment without proper treatment before its discharge [B.Sengupta;2007]. Among many chemical industries, textile industries are being discharging large quantity of wastewater into the environment.

The total dyes which are being using in dyeing industries contain 60 to 70% of azo class of dyes [U.G. Akpan et al;2009]. About 15-20% of the total dye being used in dyeing process is discharged into the environment

[H. Ouasif et al;2013]. Most of the dyes are toxic and mutagenic and recalcitrant to degradation by microbial action and forms carcinogenic components under anaerobic degradation [A.B.D. Santos et al;2007].

Moreover, the discharges of textile industries consist of high colour and turbidity due the presence of high concentrated dyes results in to the prevention of the sunlight and oxygen penetration, which are essential for the living of different organisms in aquatic bodies [G. Crini;2006].

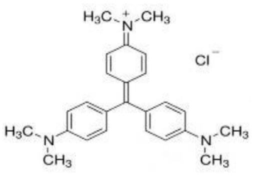
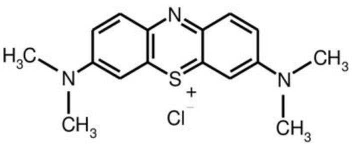
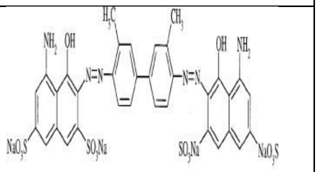
The degradation products of dyes and their parental compounds in water can affects the human health and causes many disorders namely, mucous membranes, nausea, skin ulceration and hemorrhage [D. Solpan et al;2003], and also creates severe damage to central nervous system, kidney, brain, reproductive system, and liver [K. Kadirvelu et al;2003].

Hence, to reduce the toxicity on ecosystem, it is necessary to treat the textile dye wastewater before discharging it into the environment.

2. MATERIALS AND METHODS

This chapter covers the technical aspects of the experiments, such as the materials and methods used to preparation of the catalysts and characterization. Moreover, the theoretical fundamentals and operational dealings of the catalyst characterization instruments and hybrid system of hydrodynamic cavitation combined with photo catalytic reactor procedure are also discussed. Finally, a detailed description of procedure for studying degradation kinetics is also presented.

Table 1: Physicochemical Characteristics of the Dyes

Dyes	Crystal violet	Malachite blue	Trypan blue
Structure			
Appearance	Purple	Bright greenish blue	Deep blue in aqueous solution
Formula	$C_{25}H_{30}ClN_3$	$C_{16}H_{18}ClN_3S$	$C_{34}H_{28}N_6O_{14}S_4$
M.wt	408 g/mol	319.85 g/mol	872.88 g/mol
Solubility	4 g/L	43.6 g/L	20 g/L
M.P/B.P	212/424 ^{0}C	110/380 ^{0}C	300/100 ^{0}C
Density	1.19 g/cm^3	1.0 g/cm^3	1.12 g/cm^3
λmax	590 nm	618 nm	510 nm

Spectral and Chemical Characterization of the dyes

The absorbance peak is located at 590 nm (CV dye), 618 nm (MG dye), and 510 nm (TB dye) when a UV-VIS double beam spectrophotometer is used to record spectra of crystal violet, malachite blue and trypan blue dyes.

For the range of concentrations investigated, calibration curves are created to establish a linear relation (between absorbance and concentration). In order to compare the concentration of the mined material before and after treatment, these calibration curves are used.

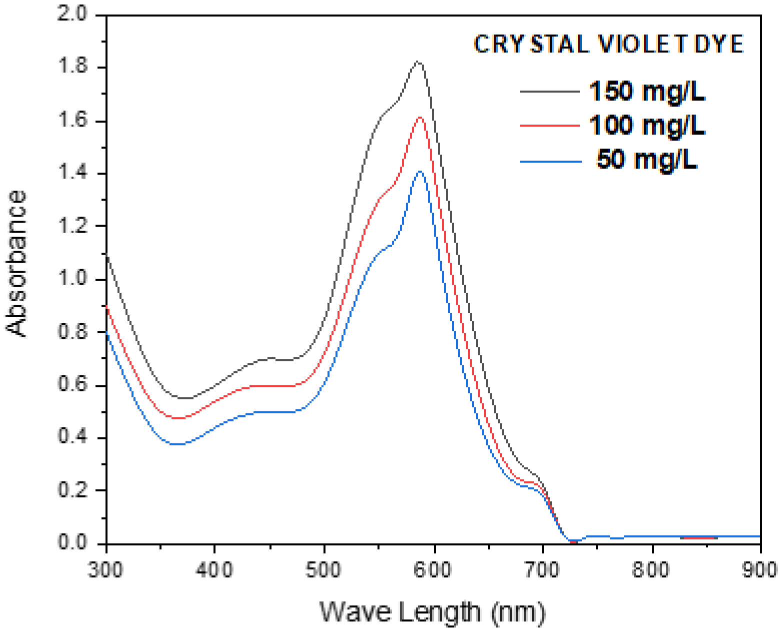


Figure 3.5: UV-VIS spectra of CV dye. (λmax=590nm)

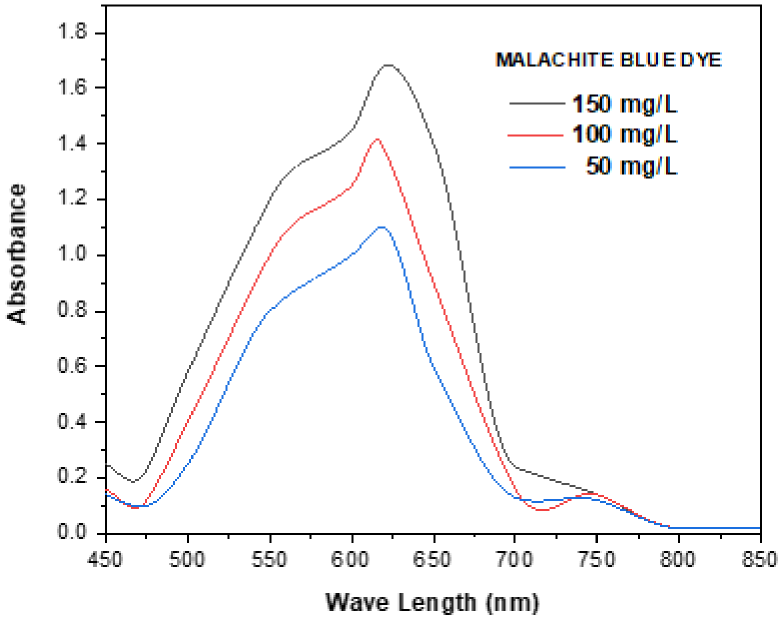


Figure 3.6: UV-VIS spectra of MG dye. (λmax=618nm

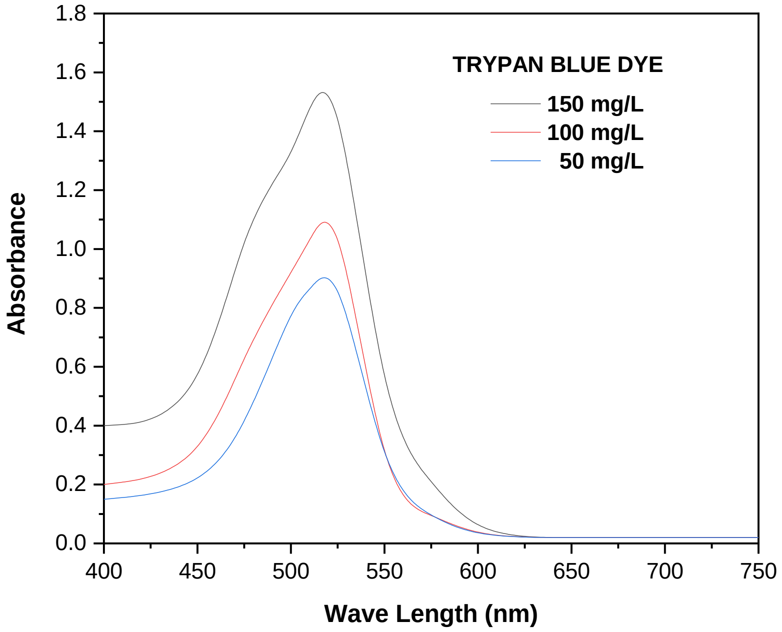


Figure 3.7: UV-VIS spectra of CV dye. (λmax=510nm)

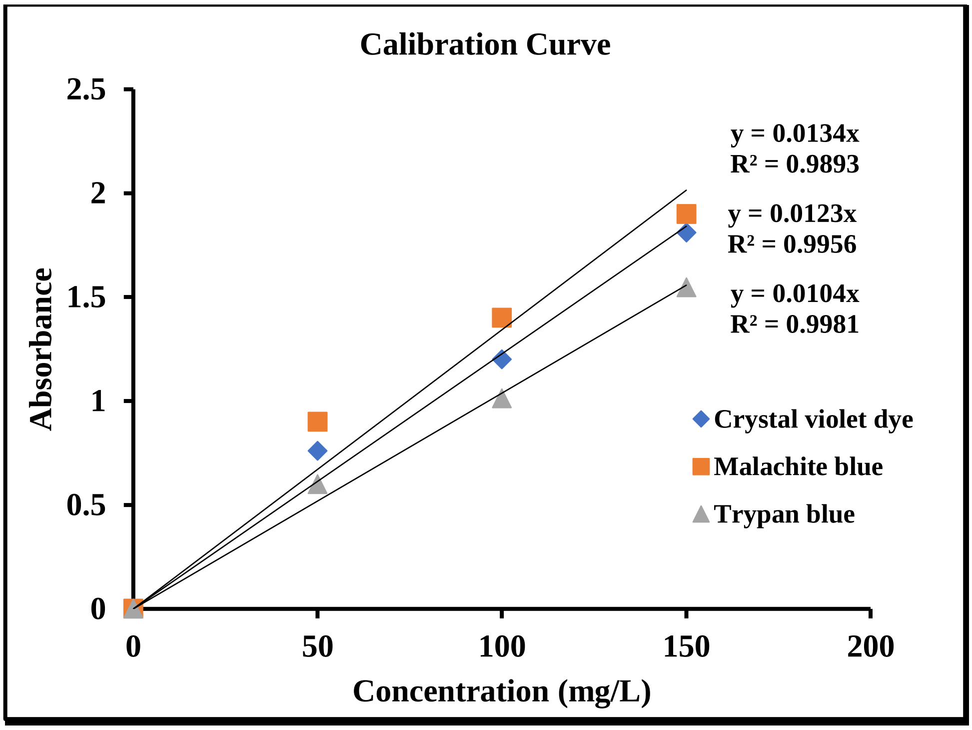


Figure 3.8: Calibration Curve of Dyes

Deionized water is used to dilute stock solutions to concentrations between 50 mg/L to 150 mg/L, and samples of each concentration are tested for absorbance at wavelengths of 590 nm, 618 nm, and 510 nm. Figure.3.6 (A to C) for CV, MG and TB dyes displays between absorbance and concentration.

Calibration curves are created to establish a linear connection for the range of concentrations studied. These calibration curves can be used to calculate the concentrations of wastewater samples before treatment and after treatment. The calibration curve's line slope is a depiction of the drug's absorptivity or absorption coefficient at a particular wavelength. Table 3.4 displays the analytical validation parameters for simultaneous CV, MG and TB dyes measurement.

3. RESULTS AND DISCUSION

3.1 Decolourization of Crystal Violet Dye Using A Hybrid Advanced Oxidation Process

To investigate the efficacy of crystal violet dye solution decolorization, a hybrid advanced oxidation process (HAOP) using hydrodynamic cavitation (HC) and UV photocatalysis was created. A typical hybrid AOP uses 5 L of a solution of crystal violet dye with a pH of 6, 150 mg/L of dye.TiO2 used to extent of decolourization to 92.6 %. Whereas, 1.2 g/L of TiO2 shows 92.6 % decolourization in 90 min of treatment.Whereas, 0.5 g/L of Fe-TiO2 shows 94.5 % decolourization in 90 min of treatment. Figure 4.14 shows the initial CV dye (150 mg/L) colour before degradation and final colour after degradation at 90 min respectively. It was observed that the 1.2 g/L of ZnO shows 96.8 % decolourization in90 min of treatment. 4.3.9 Rate Kinetics of CV dye decolourization..

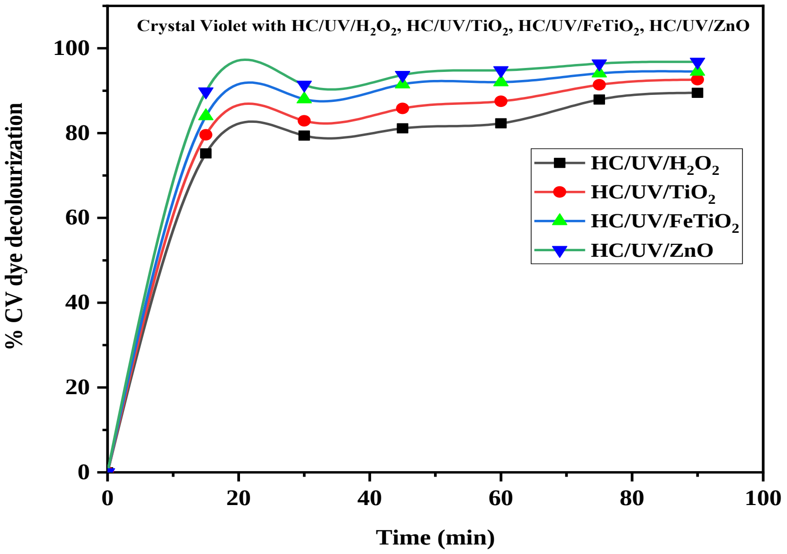


Figure 5.8:Percentage decolourization of CV dye in HC combined with UV/TiO_2, UV/Fe-TiO_2 and UV/ZnO

3.2 Kinetic Study Of CV Decolourization

In this study, the plot of ln $\left(\frac{C_0}{C}\right)$ vs time (t) also confirms that the decolourizationreaction of CV dye using HC, photolyis, photocatalysis, and HC coupled with photocatlysis followed a psuedo first order reaction. Reaction rate constants (k) and percentage decolourization of CV dye in different systems such as HC alone, photolyis, photocatalysis, and HC+ photocatalysis has been reported in **Table 5.12**. Pseudo first order decolourization of CV dye in various systems was shown in the **Figures 5.9 to 5.11.**The kinetic study of CV decolourization using HC shows that the initial rate of decolourization of CV dye HC alone is 0.0177 min^{-1},and the rate of decolurization is further increased to 0.0311 min^{-1} when the stand HC alone + H_2O_2 and HC+ UV irradation is incresed 0.0393 $min^{-1}$was used for the decolourization. It has further increased to 0.0438 min^{-1} , 0.0541 min^{-1} and 0.0601 min^{-1} using combined process of HC + TiO_2 photocatalysis , HC+Fe-TiO_2 photocatalysis and HC+ZnO photocatalysis respectively.Similarily increased to 0.0452 min^{-1} , 0.0502 min^{-1} , 0.0587 min^{-1} and 0.0633 min^{-1} using combined process of HC+UV+TiO_2 photocatalysis, HC+UV+Fe-TiO_2 photocatalysis and HC+UV+ZnO photocatalysis respectively.The increment of rate of decolourization in hybrid system could be possibly due to the increase of hydroxyl radical's generations that are responsible for the decolourization of dye.

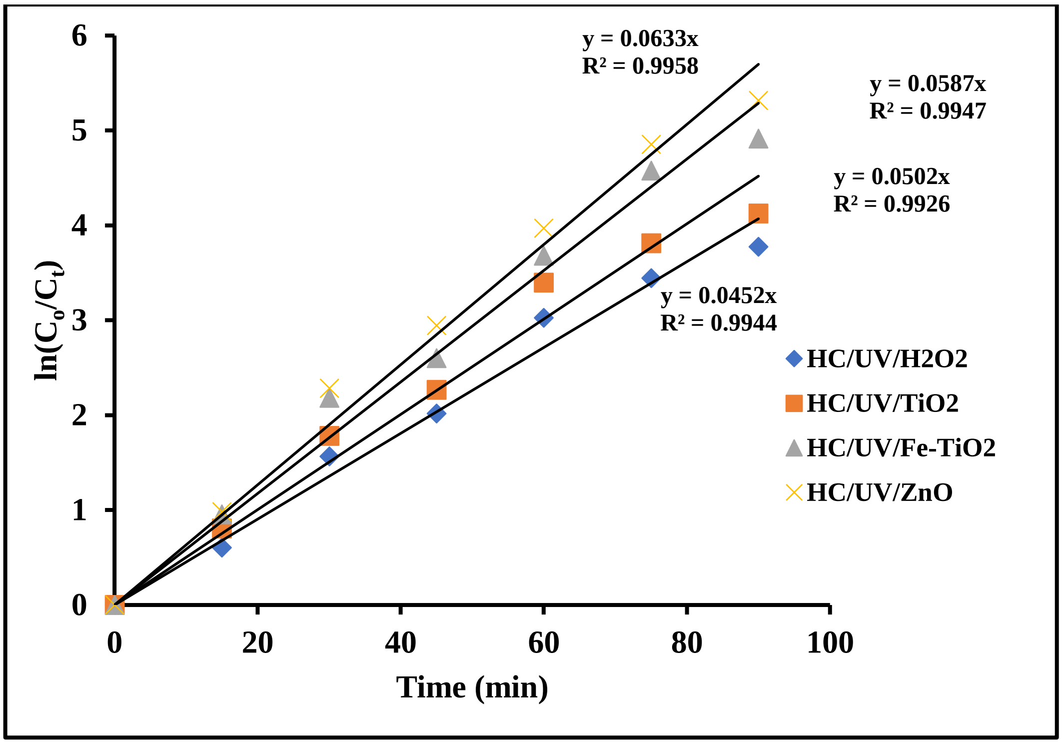


Figure 5.11: Pseudo first order reaction kinetics of CV decolourization in photolytic and photocatalysis

3.2 Effect of Inlet Pressure on Degradation of Crystal Violet Dye Hydrodynamic Cavitation Based Hybrid Advanced Oxidation Processfor Malachite Blue Dye Degradation.

Percentage decolourization of Malachite Blue Dye in HC combined with UV/TiO_2, UV/Fe-TiO_2 and UV/ZnO [at pH=6, inlet pressure=8 bar, temperature=25°C, initial dye concentration= 150 mg/L]

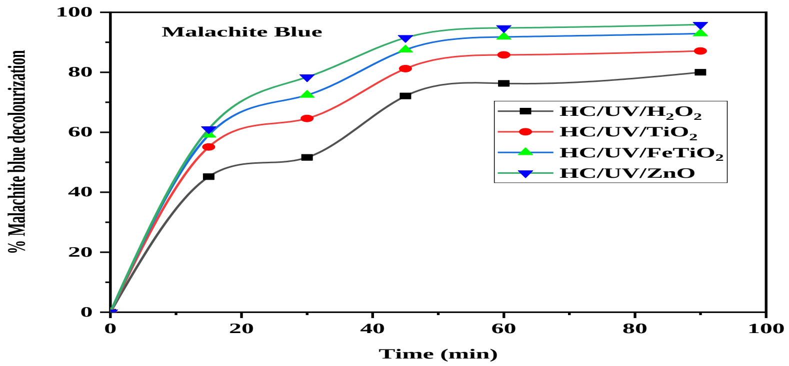


Figure 3.3: Percentage decolourization of Malachite Blue Dye in HC combined with

UV/TiO_2, UV/Fe-TiO_2 and UV/ZnO

A hybrid advanced oxidation procedure (HAOP) was developed in a typical study to evaluate the efficacy of the decolorization of MG dye solution. In a typical hybrid AOP, five liters of a 150 mg/L MG dye solution were evaluated using a UV spectrophotometer at intervals of fifteen minutes over the course of a 90 minute decolorization process.

3.3 Rate Kinetics of Malachite Blue dye decolourization

Pseudo first order reaction kinetics of MG dye decolourization in photolytic and photocatalysis [at pH=6, inlet pressure=8 bar, temperature=25°C, initial dye concentration=150 mg/L]

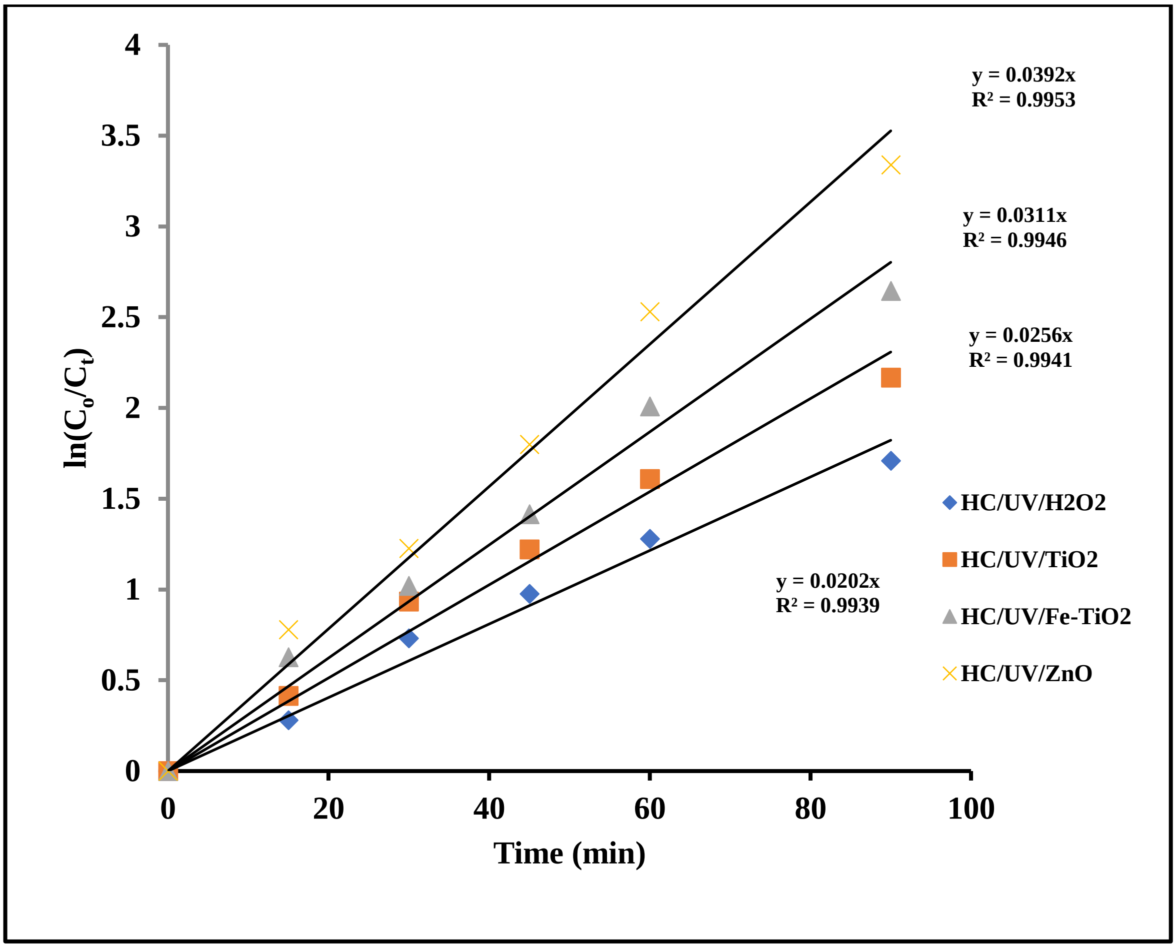


Figure 3.4: **Pseudo first order reaction kinetics of MG dye decolourization in photolytic and photocatalysis**

In this study, the plot of ln(c_0/c_t) vs time (t) also confirms that the decolourizationreaction of MG dye using HC, photolyis, photocatalysils, and HC coupled with photocatlysis followed a psuedo first order reaction. Reaction rate constants (k) and percentage decolourization of MG dye in HC+ photolytic and photocatalysis has been reported.

3.4 Hydrodynamic Cavitation Based Hybrid Advanced Oxidation Process for Trypan Blue Dye Degradation.

Percentage decolourization of Trypan Blue Dye in HC combined with UV/TiO_2,UV/Fe-TiO_2andUV/ZnO[at pH=6,inletpressure=8bar, temperature=25°C, initial dye concentration=150 mg/L

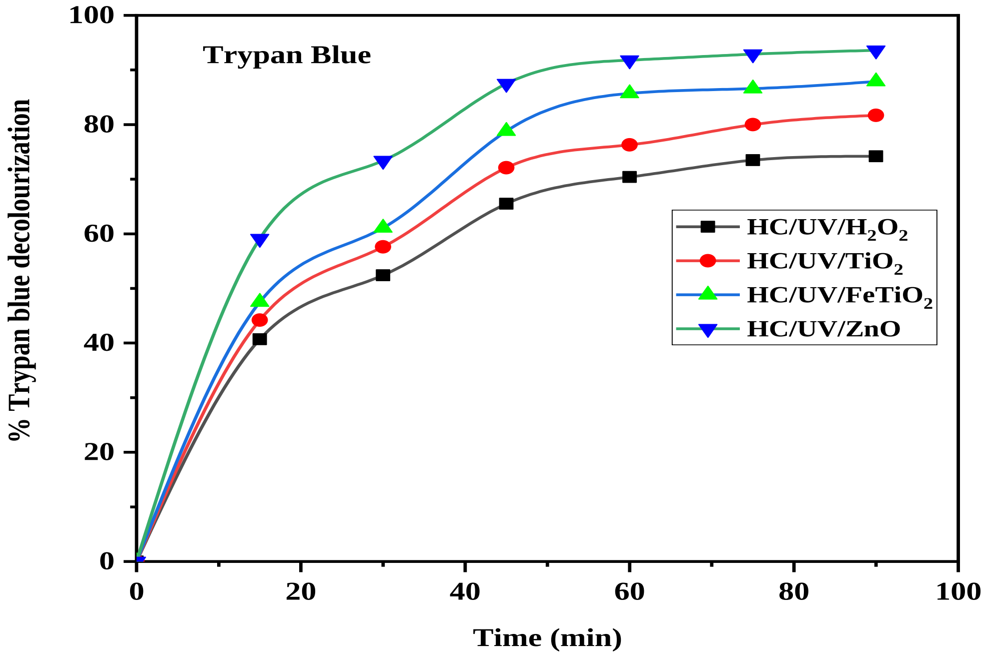


Figure 3.5: Percentage decolourization of Trypan Blue Dye in HC combined with UV/TiO_2, UV/Fe-TiO_2 and UV/ZnO

To evaluate the effectiveness of the Trypan blue dye solution's decolorization, UV photocatalysis is used to create a hybrid advanced oxidation process (HAOP). In a typical hybrid AOP, 5 L of Trypan blue dye solution with 150 mg/L of dye and a pH of 6 was employed, along with TiO_2, to decolorize the solution by 81.4%. Whereas, 1.2 g/L of TiO2 shows 81.4 % decolourization in 90 min of treatment. Whereas, 1.2 g/L of Fe-TiO2 shows 90.7% decolourization in 90 min of treatment.

3.5 Rate Kinetics of Trypan Blue dye decolourization

Pseudo first order reaction kinetics of TB dye decolourization in photolytic and photocatalysis [at pH=6, inlet pressure=8 bar, temperature=25°C, initial dye concentration=150 mg/L]

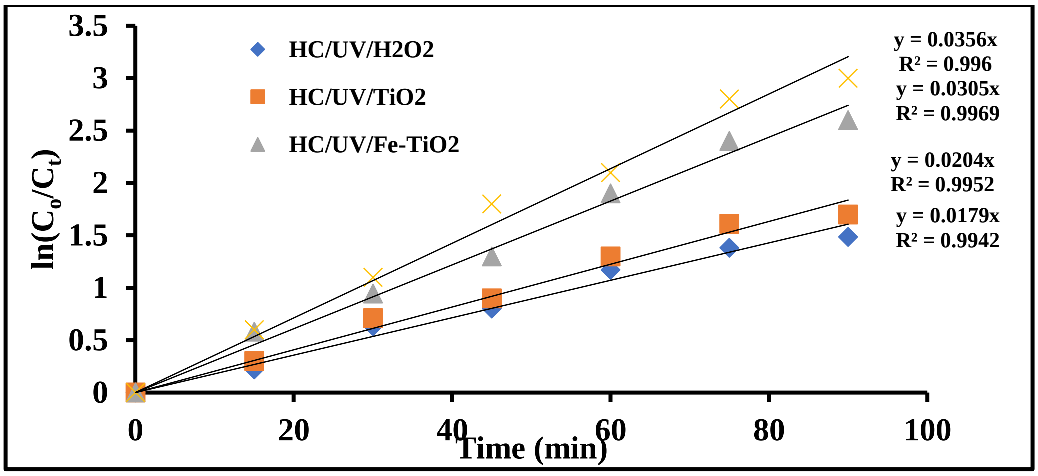


Figure 3.6: Pseudo first order reaction kinetics of TB dye decolourization in photolytic and photocatalysis

In this study, the plot of ln (c_0/c_t) vs time (t) also confirms that the decolourizationreaction of TB dye using HC, photolyis, photocatalysis, and HC coupled with photocatlysis followed a psuedo first order reaction. Reaction rate constants (k) and percentage.

3.6 Comparison of Photo Catalytic Efficiency of As Prepared Photo Catalysts with Hydrodynamic Cavitation

Comparison of photo catalytic efficiency of as prepared TiO_2 With hydrodynamic cavitation under visible light irradiation (Experimental condition: [CV,MG and TB dye] =150mgL^{-1}, Fe-TiO_2=1.6%, pH=6.0, Temp.=25 ^{o}C).

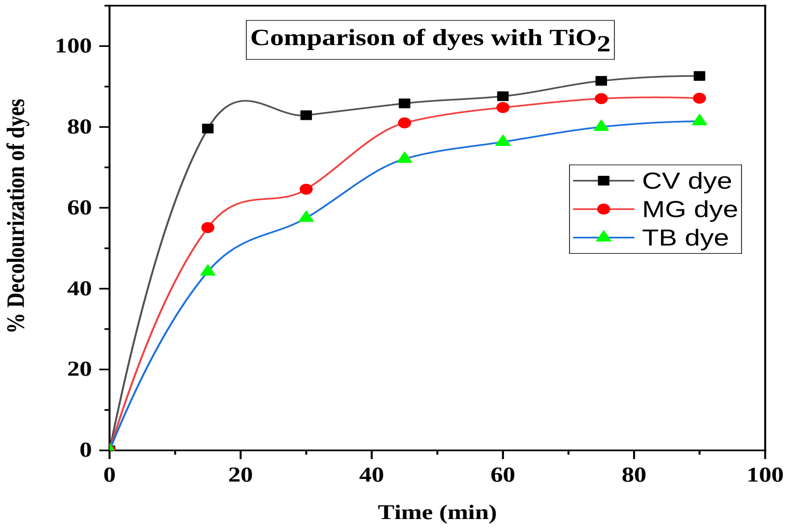


Figure.3.7 Comparison of photo catalytic efficiency of as prepared TiO_2 With hydrodynamic cavitation under visible light irradiation.

The percent degradation and mineralization of CV,MG and TB dyes at 150 mg/L of initial concentration of each dye treated by HC/UV with photo catalysts

CONCLUSION

From this work, Decolorization and degradation rate of dye in the aqueous media were also studied in the presence of hybrid process. the inlet pressure 8 bar was considered as the optimum inlet pressure as it shows maximum removal compared to the inlet pressures of 2, 4, and 6 bar**.** In a typical experimental study, UV photocatalysis has been coupled with hydrodynamic cavitation (HC) to make a hybrid advanced oxidation process (HAOP) for studying the efficacy of the decolourization of crystal violet dye solution. For 50 mg/L of CV Dye concentration, maximum percentage removal of CV Dye 52.7%. Then for 100 mg/L of CV Dye concentration, the percentage removal of increased 47.22%. Further, the studies continued for 150 mg/L concentration, the maximum percentage removal of CV Dye 36.11%.For finding out the decolourization rate of crystal violet dye following HAOP. For finding out the decolourization rate of MG dye following HAOP for finding out the decolourization rate of Trypan blue dye following HAOP. It was observed that, Fe-TiO_2 showed the extent of decolourization to 94.5 %. It was observed that the 1.2 g/L of ZnO shows 96.8 % decolourization in 90 min of treatment. It was observed that, Fe-TiO_2 showed the extent of decolourization to 90.7 %. It was observed that the 1.2 g/L of ZnO shows 93.6 % decolourization in 90 min of treatment.

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