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Ozone Assisted Photocatalytic Degradation of Textile Wastewater

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Summary: In present research, photocatalytic degradation of textile wastewater was investigated through the combined effect of ozonation and photocatalysis processes. Catalytic acids in the nano-particle form under moderate reaction conditions were used for the successful disintegration of contaminants in textile wastewater which in turn increases the process efficiency. Moreover, the combined effect of the photocatalytic-ozonation process after secondary treatment of textile wastewater on discharge requirements of zero discharge hazardous chemicals (ZDHC) by Road to Zero was also studied. Different parameters were optimized like ozone flowrate, catalytic concentration, UV light intensity, and reaction time. Results revealed that overall process efficiency is influenced by ozone and reaction time. In contrast, an increased rate of degradation is attributed to the synthesized TiO_2 (anatase) in nanoparticle form. The combined ozone-assisted photo-catalytic process showed the COD, BOD, and TSS removal efficiencies of 91.5%, 94%, and 86% at 25 ℃ temperature and pH 7-9. The results were attained at optimum conditions like reaction time (140 min), Ozone concentration (2 g/hr), TiO_2 concentration (2g/L), and UV energy (88 W), respectively. The study demonstrated the efficiency of an integrated process for the degradation of real textile wastewater. Thus, combined photocatalytic and ozonation processes are known to exhibit better responses than individual processes for pollutants removal from textile wastewater.

Keywords: Wastewater, Photocatalysis, Ozonation, Photocatalytic-Ozonation, Textile Wastewater.

Introduction

It widely exists in woody plant, herbaceous plant, Water is the major component of all living systems on earth. All aquatic and terrestrial living beings must need water for survival. Apart from drinking, water is used for different purposes. Almost 70% of the earth is covered with water whereas only 3% of the world's water is freshwater, and two-thirds of which is in the form of frozen glaciers or is unavailable for use [1]. According to the reports of UNICEF and WHO, about 1100 million people lack access to water worldwide, and a total of 2700 million find water scarce for at least one month in a year. In addition to this, inefficient sanitation is also a problem for 2400 million people with water-borne diseases like cholera and typhoid fever, etc. Two million people, mostly children, die each year from diarrheal diseases alone. At the present utilization rate, these circumstances will only get worse. By 2025, two-thirds of the world's population may face water shortages. And ecosystems around the world will suffer even more [2].

The textile industry holds immense importance in the economic development of third world countries including Pakistan, Bangladesh, India, Sri Lanka, etc. and therefore it plays a vital role in increasing the GDP rate of these countries. The main raw materials of such industries are chemicals including pigments, synthetic, natural fibers, and cotton [3]. The presence of dyes in wastewaters is a severe threat to the ecosystem and human health. And 1-20% of dye generation in wastewater is due to the textile industry [4-6]. According to the statistics, there are 10,000 various types of synthetic dyes worldwide with a yearly production of about 0.7 million tons. Due to the inefficiencies of dyeing processes, almost 0.2 million tons of dyes are released into the environment by these Industries. One of the surveys done by the World Bank reveals that almost 20 % of overall industrial wastewater from textile industries is based on their dyeing and finishing processes [1, 3].

Few influencing initiatives have been taken to trigger these changes and to acquire sustainable consumption and production of textile goods. Several active companies are part of these initiatives. One of such initiatives named ZDHC (Zero Discharge Hazardous Chemicals) is working since 2011. The program holds collaboration of about 24 signatory brands, 15 associations, and 59 affiliated companies. Another campaign named Greenpeace-Detox was formed to increase

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awareness regarding the environmental impacts of textile waste production [7-11].

In recent years, advanced oxidation processes are extensively used in the treatment of organic matters inside wastewater. Photocatalytic degradation and ozonation processes (advanced oxidation processes) have some inefficiency in decomposing organic pollutants. The photocatalytic degradation process exhibits a low oxidation rate, whereas, ozonation alone is not enough for the complete mineralization of organic matter. Due to these disadvantages, the practical implementation of individual technologies does not make it economical to decompose the wastewater generated from different industries [12, 13]. To overcome these issues, ozone was introduced along with photocatalysis to enhance the efficiency of eliminating contamination from wastewater. Both processes in combination were found to be environment-friendly in the treatment of organic pollutants because these combined strategies increase the removal efficiency with no production of secondary pollutants. When ozonation and photocatalytic degradation processes are carried out simultaneously, the capturing power of photo-generated electrons by ozone increases as it is a very strong scavenger with the generation of more active species like H^+, O_2, and OH. These active species accelerate the elimination of organic pollutants present in wastewater [14].

Moreover, photocatalytic degradation and ozonation, under optimized conditions, are reported to have improved oxidation synergies (efficiency) for wastewater treatment in comparison to the sum of oxidation efficiencies of these two oxidation processes separately [15]. Furthermore, the combination of these two systems may diminish their boundaries and enhance the efficacy of pollutant removal [16]. When these two processes are applied in combination, the reaction mechanism is influenced by enhancement of efficacy and a decrease in reaction time concerning the individual systems [17].

Recently, a study on the synergistic effect of photocatalysis and ozonation was conducted by Chi Chung Tsoi and his co-workers [18]. The researchers studied photocatalytic ozonation for seawater decontamination using TiO2 in nano powder form. The obtained seawater samples contain 35 wt.% of NaCl concentration (0.6 M). Just like previous studies, this research also showed that photocatalytic ozonation is more efficient as compared to separate ozonation or photocatalysis. Photocatalytic ozonation showed a 23 times higher reaction rate than ozonation only. In the context of human health and cost constraints, the study limited the ozone concentration to < 60 ppm, however, the maximum efficiency was achieved at an ozone concentration of 50 ppm [19].

The novelty in current research work is the preparation method opted for TiO_2 catalyst. Also, the effects of different parameters like ozone, catalyst concentration, UV light intensity, and reaction time were studied by combining the effective operating ranges and optimization as reported previously. Additionally, this research work was performed after the secondary treatment to gauge the efficacy of the combined photocatalytic-ozonation for satisfying the discharge requirements of zero discharge hazardous chemicals (ZDHC) by the Roadtozero consortium.

Experimental

Textile Wastewater

Textile wastewater was pretreated through primary (Grit Removal, Screening and oil Trap chamber) and secondary (Equalization and Activated sludge recycling process) treatment processes at one of the Textile Mills of Faisalabad. The discharge effluent from processing and dyeing of textile mill was introduced into a 150 m^3/hr wastewater treatment plant installed in the mills. Firstly, the effluent was passed through a grit removal chamber with, a mechanical screen of 2 mm pore size for the removal of any coarse particles. The wastewater was then passed through the oil removal chamber. For the secondary treatment of Textile wastewater, it was passed through an equalization tank, aeration tank (activated sludge tank), and a clarifier. The treated sample was then collected from the sampling point. Table 1 shows the features of the treated textile wastewater found in different textile sectors of Pakistan after secondary treatment.

Table-1: Parameters for different samples textile wastewater after secondary treatment.

Parameters	Units	Values
pH	--	7-9
COD	mg/L	150 ± 50
BOD	mg/L	80 ± 30
TDS	mg/L	2600 ± 500
TSS	mg/L	76 ± 40

Synthesis and Characterization of Titania (TiO_2) Nanoparticles

Titanium Dioxide (TiO_2) was procured from DEIJUNG China in Anatase form. Titania NPs were synthesized using the liquid impregnation method. For this purpose, 50g of titanium dioxide powder (anatase) was added to a beaker containing 300 ml of distilled water. Distilled water was used in the synthesis process to remove impurities and ensure the absence of air passages in the TiO2 powder. The sample was set for 24 hours stirring using a ceramic magnetic stirrer. Then another 24 h of settling was provided for the solution. Afterward, the slurry-type mixture was placed in a Memmert oven for 12 hours drying at 105 °C. The dried mixture was then placed for calcination in a furnace at 550 °C for another 6 hrs. The calcinated powder was then set for cooling at room temperature. At last, TiO_2 nanoparticles collected in clear crystalline form were used for their characterization. (Husnain *et al*. 2016)

SEM analysis was performed to study topography and morphological features of titanium dioxide powder using TESCAN, VEGA 3 model at 20 kV, with SEM magnification: 437 x – 44.4 kx, and View field: 100 µm – 500 nm, respectively. In addition, the Energy-Dispersive spectroscopy, SEM (TESCAN, VEGA 3) technique was used at a resolution of 10 µm for elemental analysis.

Analytical Methodology for Measurement of COD, BOD, and TSS:

The standard method was employed for the measurement of COD (Chemical Oxygen Demand), BOD (Biological Oxygen Demand), and TSS (total suspended solids), respectively. COD was measured using a COD reactor and direct reading spectrophotometer (VELP Scientifica, USA). Five-day (BOD5) measurement was taken using the monomeric method with a respirometer (VELP Scientifica, USA). The conductivity, temperature, and pH of the solutions were analyzed using HANNA pH Meter. TSS was determined using ASTM E1756-08 standard method in a Memmert Oven. TiO2 was separated from treated water through centrifugation using a centrifuge instrument (D37520 sigma). For further removal, MERCK filter paper (0.2 microns) was used [20, 21].

The removal efficiency of the COD, BOD, and TSS variables is calculated using Eq (1).

$$\eta = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

where, "η" is the percentage removal efficiency, "t" is time, "Co" is the initial concentration at the start of experimentation and "Ct" is the final concentration after experimentation.

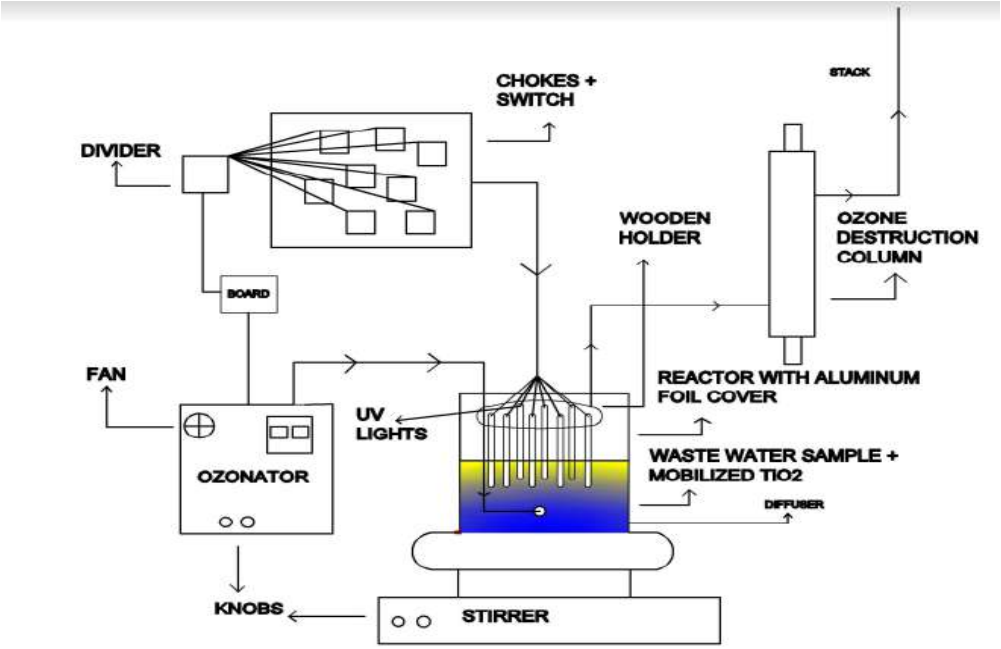


Fig. 1*:* Flow chart for photo-catalytic ozonation process.

Fabrication of Ozone Assisted Photo-Catalysis Reactor:

Fig 1 shows the schematic diagram of the fabricated reactor. It consists of a % liter glass beaker (Pyrex) made in the UK housed on an OEM laboratory SH-4 ceramic magnetic stirrer with a hot plate made in Hunan, China having stirring capacity of 5000ml and stirring range of 100-2000 rpm. Ozone is generated by a Sky Zone Ozonator purchased from Water Care Services Lahore. It has a capacity of 3g per hour and came with a n adjustment knob to change the concentration of ozone. The ozone generator is shown in the Fig. Ozone generator uses the oxygen in the atmosphere to produce ozone. Ozone is dangerous for environment therefore ozone discharge in the photo-catalysis reactor is attached to an ozone destruction unit made by Water Care Service Lahore. Eight Philips UV-C lights (8" diameter and 11 W) made of Quartz were placed inside the glass holders before placing in the beaker for safety purposes. Switches and connectors of UV-C lights are held on a mild steel plate which acts as a cover for the reactor. The steel plate was drilled with a hole for a thermometer, a sampling point, an ozone inlet, and an ozone discharge outlet. The gaps left between the steel plate and the beaker were sealed with silicone sealant. The whole reactor assembly was covered in an aluminum foil to stop UV light exposure. The sampling point in the steel plate is covered with a removable rubber cap when the sample is required to take out using a 100 ml syringe with a pipe to obtain cleaned water [22, 23].

Design of Experiment (DOE):

Appropriate choice of experimental variables which influence the various physio-chemical processes in the overall wastewater treatment is probably one of the most crucial problems to deal with all advanced wastewater treatment processes. The design of the experiment (DOE) helps us to solve such problems.

Traditionally, experiments were carried out without proper DOE with a large number of factors or variables, where one factor was varied and others were held constant. This method was called one factor at a time. This method was not only extremely strenuous with a huge number of experiments but also very expensive.

The principal benefit of employing DOE in process-related experiments is its ability to substantially reduce the total number of experimental runs which subsequently results in lower costs, resource utilization, and completion short. In addition, DOE not only allows the analysis of interactive effects of different factors but also provides tools that enable researchers to evaluate the statistical significance and pertinence of factors and their effects under study. In this study, Taguchi Method was used with 4 factors and 5 levels. The DOE was made using Minitab (19.2) software and later on, regression analysis was also evaluated using the same software [24].

Results and Discussion

The synergy behavior is proven for the photo-catalytic ozonation procedure based on the results discussed below. Recent discoveries showed great improvement in the development of photo-catalyst for the disintegration of persistent contaminants under solar/visible radiations [12, 25-27]. However, there are a few shortcomings in the industrial application of these catalysts which limits their use competently in the disintegration of contaminants in real textile wastewater [26]. This hindrance can be handled by the addition of oxidizing agent along with photo-catalysts, for degradation of different kinds/nature of organic pollutants which in turn increase the turbulence of the system. Table 2 shows the synergistic effect possessed by the photo-catalytic ozonation process.

Table-2*:* Synergistic effect shown by photo-catalytic and ozonation process.

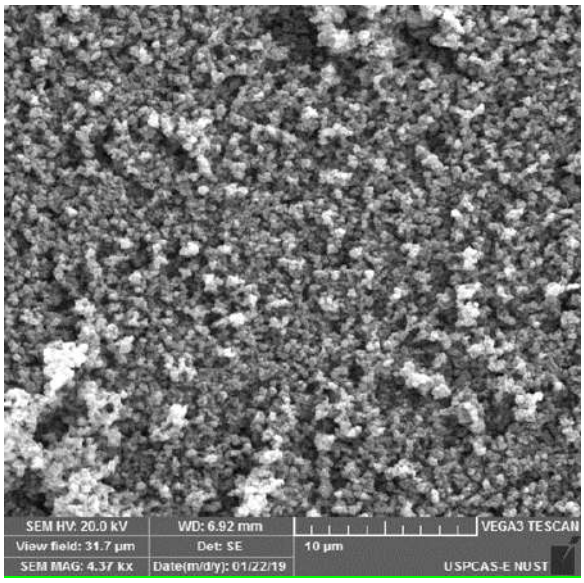
Parameters	Before Treatment	After Secondary Treatment	After PCO Treatment
pH	7.5 ± 1.0	7-9	7.8 ± 0.5
COD (mg/L)	1500 ± 250	150 ± 50	15 ± 15
BOD (mg/L)	700 ± 100	80 ± 30	5 ± 3
TSS (mg/L)	300 ± 50	76 ± 40	11 ± 5.0

Characterization of Photo-Catalyst

SEM analysis was conducted to study the morphological features of TiO_2 NPs. The analysis was performed at 20 kV acceleration voltage, magnification sizes, 10 µm, and 500 nm and 437x-44400x magnification power, respectively. SEM micrographs in Fig 3 (a) reveal the average particle size in the 1-100 nm range for TiO_2 nanoparticles which confirms the successful synthesis from the precursor. In Fig 4(b), three points C1, C2, and C3 show the size of three TiO_2 nanoparticles with 49.67 nm, 44.10 nm, and 48.71 nm radii, respectively. Thus, it confirms that nanoparticles are synthesized in a maximum range having the required particle size. Moreover, it accelerates the catalyst activity for the photocatalytic-ozonation process.

Energy-Dispersive X-ray (EDX) spectroscopy was used to determine the elemental components of TiO2 nanoparticles. The results confirmed 95% purity of TiO2 (anatase form)

nanoparticles as it contains 36.11% of Titania and 59% of Oxygen (Table). The percentage purity of the catalyst used for the experimentation assures its activity to speed up the photocatalytic ozonation reaction. The EDX graph and obtained elemental percentage are shown in Fig 2.



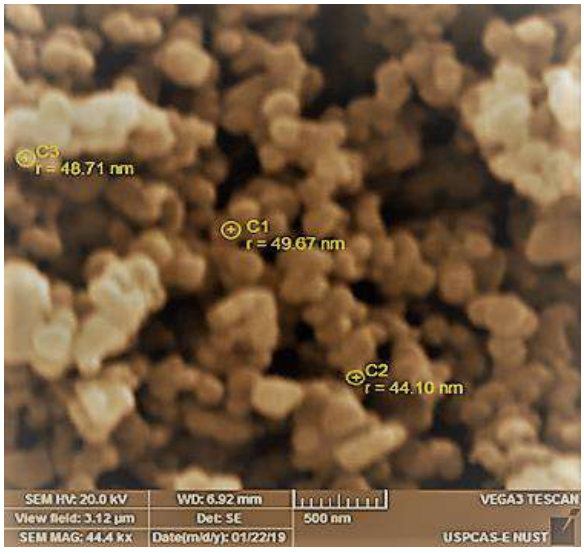


Fig 2*:* (a) SEM Micrograph showing TiO_2 nanoparticles, (b) Average particle size for titania nanoparticles.

Table 3-Percentage elemental composition of sample.

Element	Weight (%)
Carbon (C)	4.88
Oxygen (O)	59.01
Titania (Ti)	36.11

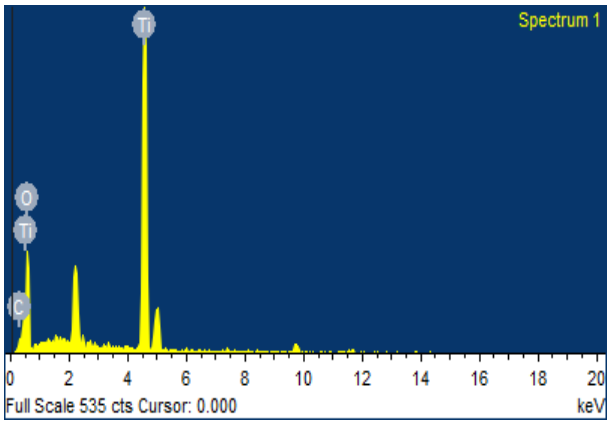


Fig. 3*:* EDX analysis of TiO_2 nanoparticles.

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Effects of reaction time on process performance

Time plays a vital role in the disintegration of contaminants via the heterogeneous photo-catalytic ozonation process. An increase in reaction time increases the pollutants removal, especially in real wastewater treatment. The process efficiency was evaluated by setting time between 0-100 minutes. More than 90% of BOD, COD, and TSS removal was observed in 180 min. Similarly, at 140 minutes, the maximum degradation of BOD, COD, and TSS was found to be 94%, 91.5%, and 86%, respectively. According to the Pareto Standardization Chart, reaction time ranked 1st place as the most influential factor in affecting the process efficacy of photo-catalytic ozonation. Based on this research, extended time is needed for attaining rational photo-catalytic mineralization of organic contaminants in real wastewater.

The finding that an increase in reaction time leads to higher removal of pollutants in photo-catalytic ozonation process is consistent with previous studies (Chen *et al*., 2017; Mahmoodi *et al*., 2015). The observation that reaction time is the most influential factor affecting the process efficacy of photo-catalytic ozonation is also in agreement with previous research (Li *et al*., 2015; Wu *et al*., 2016).

The result that more than 90% removal of BOD, COD, and TSS was achieved in 180 minutes is also consistent with previous studies on the treatment of textile wastewater (Khataee *et al*., 2011; Daneshvar *et al*., 2006).

Due to the complex nature of contaminants present inside textile wastewater, complex mineralization is attainable at more irradiation time. Fig 5 shows the effect of reaction time on the removal efficiency of wastewater contaminants.

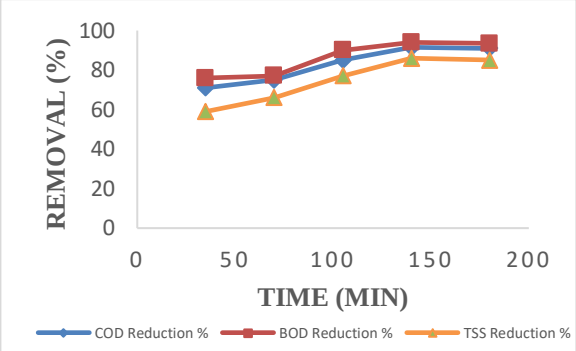

Fig. 4*:* Effect of reaction time on pollutant removal, pseudo kinetics second order rate constant k.

Effects of Ozone Dosage

For the effective disintegration of pollutants using photo-catalytic ozonation, ozone molecules must be dissolved first inside the aqueous solution, then, diffuse, and adsorb onto the photocatalyst surface for an effective oxidation process. Therefore, variations in ozone dosage of the oxidation medium can significantly influence many characteristics of photo-catalytic ozonation as shown in Fig 6. From the results, it is revealed that photo-catalytic ozonation of organic matter increases in solution with an increase in dosage concentration of ozone. The process is attributed to the stabilization of the photo-generated positive holes on the photo-catalyst surface as a result of the reaction between photo-generated electrons and adsorbed ozone molecules, which led to increased adsorption of organic compounds on the catalyst surface. In this study, the concentration of ozone varied between 0–3 g/hr. The concentration of dissolved ozone was checked using HANNA dissolved ozone testing kit. The optimized ozone dosage was found to be 2g/hr with maximum BOD, COD, and TSS reduction found to be 94%, 91.5%, and 86%, respectively. The maximum dissolved ozone concentration when operating at 3 g/hr was found to be 6 mg/l.

According to the Pareto Chart of Standardization, it exhibits second place out of four parameters (reaction time, catalyst concentration, UV irradiation, and ozone dosage) as the most influential factor for the efficient process working. Excess ozone in the process was destructed with the help of an ozone destruction column that converts ozone into oxygen molecules. Fig 6 showed that ozone concentration has a great impact on the photo-catalytic ozonation process and an increase in process efficiency is observed with an increase in an ozone concentration. The optimum ozone concentration is based on different parameters like the chemical structure of the contaminant, design of the reactor, pH, and light conditions. Moreover, an increase in the mineralization rates of different water pollutants by ozone-assisted photo-catalysis was seen with increased ozone concentration in water. However, the maximum effective ozone concentration found for this process is 2 g/hr after which any increase in ozone concentrations did not effectively increase the mineralization rates and efficiencies since the concentration value depends on contaminants' properties and their oxidation by-products in the oxidation matrix [28, 29]. Fig 5 shows the effect of ozone concentration on the removal efficiencies of contaminants.

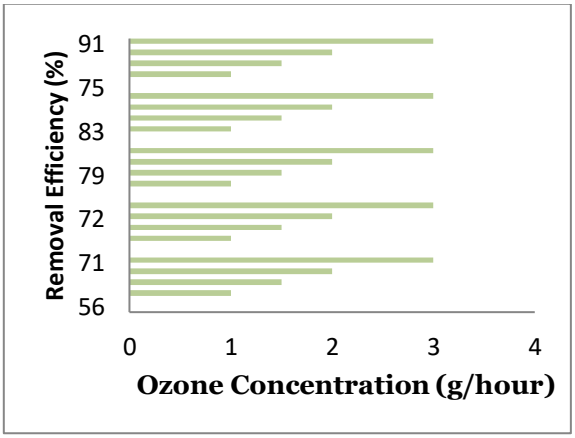

Fig. 5: Effects of ozone concentration on the removal efficiency of the pollutants.

The interactive relation between COD reduction (%) vs. Reaction time vs. Ozone Concentration is plotted as a 3D contour plot in Fig 6. It is obvious from the plot that the COD reduction percentage increases with an increase in ozone inlet concentration up to 1.5 g/hr. The green shaded region corresponds to greater process efficiency at higher ozone concentration, respectively.

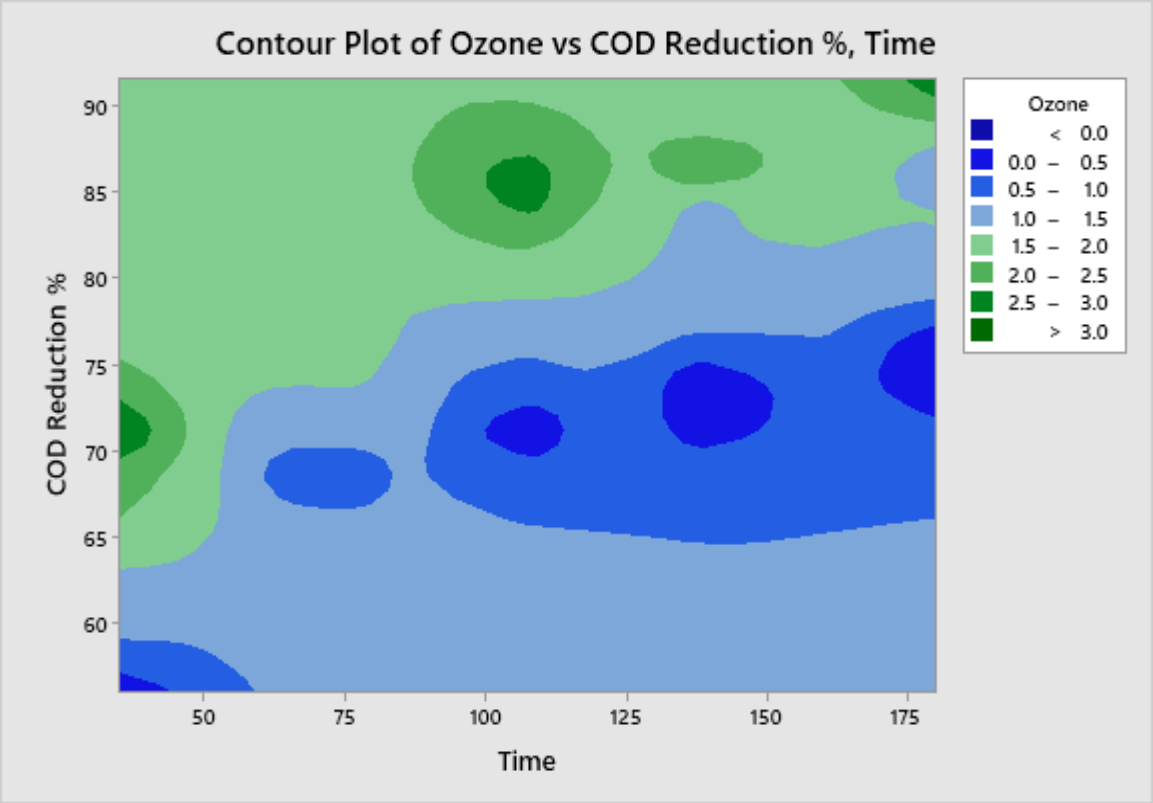

Fig. 6: Contour plot for interactive relation between COD %.

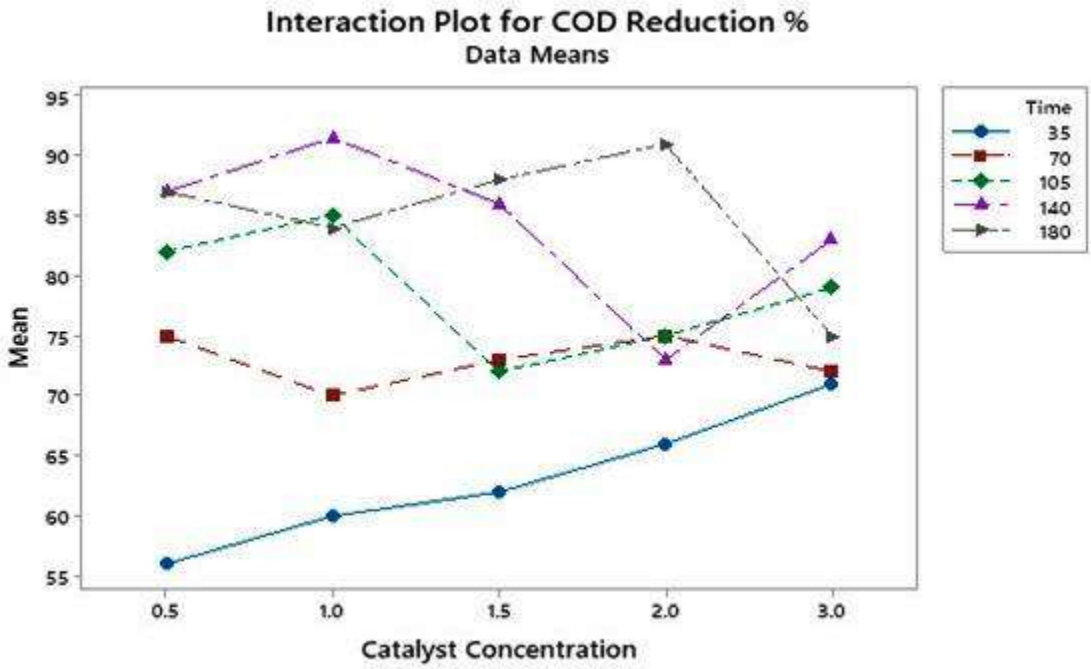

Fig. 7: Interaction plot depicting the effect of catalyst concentration on COD reduction (%) of contaminants in wastewater.

Effect of photo-catalyst dosage

In general, photo-catalyst concentration influences contaminants' disintegration as it depends on the interaction between the number of active sites and the presence of impurities in a solution. It is observed that catalyst performance and active sites increase with the increase in photocatalyst concentration. However, no further increase in observed after a certain level of catalyst dosage. In contrast, an upsurge in titanium dioxide concentration up to 2.0 g/L enhances the contaminant's disintegration. Further increment in concentration gradually reduced the degradation rate. Fig 7 shows the 3D interaction plot for examining the activity of the photo-catalyst. The plot between COD reduction vs. time vs. catalyst dosage shows that the maximum reduction was achieved when the catalyst dosage range increases from 1.0 g/L to 2.0 g/L. But after optimum concentration of TiO_2, no further increase in reduction rate is observed.

Treatment of textile wastewater using TiO_2 NPs showed optimized reduction for COD, BOD, and TSS at 2.0 g/L catalyst concentration in 140 min. at 45°C under UV irradiation and ozonation process. At higher dosage, catalyst agglomeration takes place which reduces surface areas and active sites, thereby becoming disadvantageous to the system. The study shows that charge recombination must be considered in the mineralization efficacy of organic pollutants. The introduction of an oxidizing agent i.e., ozone (in the present case) can hinder the recombination of photo-electrons and photo-holes. The interactive plot of three variables is given below in Fig. 7.

Fig 8 showed the relation between catalyst concentration and removal efficiency. The maximum reduction for COD, BOD, and TSS was found to be 91.5%, 94%, and 86%, respectively at 2.0 g/l of catalyst concentration. According to the Pareto Chart, the catalyst is not regarded as an influential factor in process efficiency. It ranked last among the four studied factors. According to the trends shown in the bar chart below, it is proved that an increase in TiO_2 dosage for a certain limit increases the degradation rate however further increase might be not effective for process efficiency.

Effects of UV light Intensity

Light intensity shows the extent of light absorption by a photo-catalyst in a given wavelength. The hole (h+) and electrons (e-) excitation rates are highly dependent on light intensity [30]. Inadequate light intensity may result in low photo-electrons and photo-holes production which could be inefficient for the process.

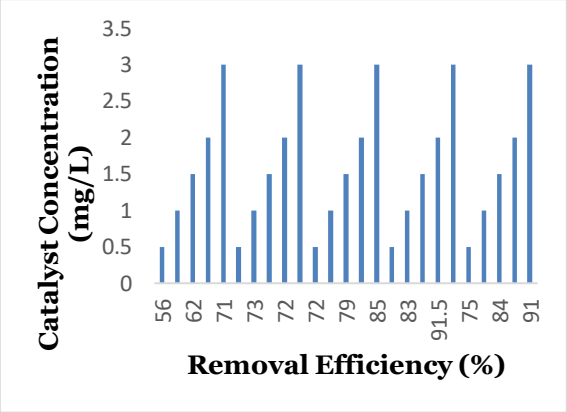

Fig. 8: Effect of catalyst concentration on removal efficiency (%) of wastewater contaminants.

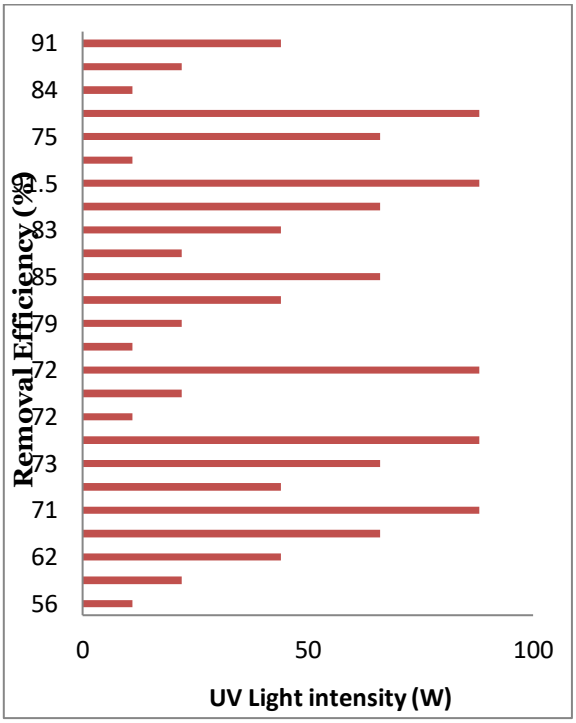

Fig. 9*:* Effects of UV light intensity on contaminants removal efficiency.

The maximum reduction for COD, BOD, and TSS was 91.5%, 94%, and 86% respectively at 88 Watt of UV irradiation. According to the Pareto Chart of standardization, UV-C irradiation ranked three out of four as the most influential factor for the ozone-assisted photo-catalytic degradation process. The results of this study showed that with an increase in

UV-C irradiation intensity, the process efficacy increases.

However, high intensity generates adequate electrons and holes which boost the reaction. In this study, 8 UV-C lights of Philips having a wavelength of 254 nm and power of 11 W were used to check the effect of photo-catalytic ozonation process efficiency. The trends in Fig 9 show that as the light intensity of UV-C irradiation increases, an increase in removal efficiency is observed.

Optimal Conditions for the Process

Taguchi method was employed for the optimization of the photocatalytic ozonation process. Four independent variables at five levels were studied to get better optimization. According to the results, the optimum removal efficiency of BOD reduction was 94% at 2.0 g/L of TiO_2 and 2 g/hr of ozone at 45°C with a pH of 7-9. The optimum reduction was achieved less than 140 minutes of irradiation time using 88 W of UV light. Under these operating conditions, COD and TSS reduction percentage was found to be 91.5% and 86%, respectively.

Conclusion

Titanium dioxide was proved to be an effective catalyst in photocatalytic degradation of contaminants inside real textile industrial water. The maximum removal efficiency for COD, BOD, and TSS was found to be 91.5%, 94%, and 86% respectively while using TiO_2 and Ozone at 45°C and pH of 7-9, in 180 irradiation minutes and 88 W of ultraviolet energy. The characteristics of the treated textile wastewater were found to satisfy the road to zero requirements of zero discharge of hazardous chemicals. This study proves that real textile wastewater reacts differently to catalyst than the aqueous solution of azo-dyes; that is related to the rate-controlling process, which is associated with surface steps and accordingly, the presence of other contaminants sensitizes the reaction rate. When TiO_2 has combined with ozone the maximum after about 140 minutes the maximum removal efficiency was achieved which indicated the synergistic effect of combining ozonation and photocatalysis.

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