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Degradation of Textile Wastewater Using ZnO and TiO_2

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Abstract: *The color produced by dyes in water makes it aesthetically unpleasant & can chronically effects on exposed organisms which depend on concentration of the dye and exposed time. Many dyes are considered to be toxic and even carcinogenic. Textile industries processes are most industrial that release colored wastewater containing dye major environmental concern. Photocatalytic Oxidation by UV/Fe^{+2}/H_2O_2, UV/H_2O_2, ZnO/UV, TiO_2/UV, TiO_2/Solar and ZnO/Solar irradiation are effective processes to be used for removal of acidic, basic and color dyes from Wastewater. We choose the photocatalytic Oxidation by ZnO/UV, TiO_2/UV, TiO_2/Solar and ZnO/Solar for degradation of phenolic red dyes from Wastewater. The factors affecting on rate of reductions of dyes are reaction time, concentrations of dyes and catalyst amount. This process can be conducted under room conditions and organic pollutants can be completely decomposed into CO_2 and H_2O. The effect of contact time on % reduction of dyes using solar/TiO_2 and UV/TiO_2 process. Maximum % reduction for phenolic red dye for solar/TiO_2 process is 80.5 and for UV/TiO_2 process is 85.5 resp. As per analysis it's clear that the % reduction increase with increase in contact time. Max. reduction shown at 120-150 mins. The effect of concentration on % reduction of dyes using solar/TiO_2 and UV/TiO_2 process. The maximum % reduction for phenolic red dye for solar/TiO_2 process is 81 and for UV/TiO_2 process is 86 resp. As per analysis it's clear that the % reduction decrease with increase in concentration of dyes in solution. Max. reduction shown at 5 ppm for both processes. The effect of contact time on % reduction of dyes using solar/ZnO and UV/ZnO process. Maximum % reduction for phenolic red dye for solar/ZnO process is 77.5 and for UV/ZnO process is 80.5 resp. As per analysis it's clear that the % reduction increase with increase in contact time. Max. reduction shown at 120-150 mins. The effect of concentration on % reduction of dyes using solar/ZnO and UV/ZnO process. Max. % reduction for phenolic red dye for solar/ZnO process are 77 and for UV/ZnO process is 80.5 resp.*

Keywords: Textile Wastewater Treatment, ZnO/UV, TiO_2/UV, TiO_2/Solar and ZnO/Solar, Phenolic Red Dyes Reduction

I. INTRODUCTION

A dye is a colored substance that has an affinity to the substrate to which it is being applied. Dyes appear to be colored so they absorb wavelengths of light more than others. Several physical, chemical and biological de-colorization methods such as coagulation / flocculation treatment, biodegradation processes, oxidation methods, membrane filtration and adsorption have been reported to be investigated for the removal of dyes from industrial effluents. Among the consequences of this rapid growth is environmental disorder with a big pollution problem.

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Application of Photocatalytic Oxidation Process

1. Chemical Industry
2. Pharmaceutical Industry
3. Pulp and Paper Industry
4. Textile Industry
5. Food Industry
6. Landfill Leachates
7. Dye-Process Industrial Waste
8. Pre-treatment to wastewater
9. Organic pollutant destruction
10. Toxicity reduction
11. Biodegradability improvement
12. Odor and color removal

Classification of Textile Dyes

1. Based on Application

Based on its application characteristics such as acid, basic, mordant, reactive, direct, disperse, Sulphur dye, pigment, vat, azo insoluble.

2. Based on Chemical Structure

Based on its chemical structure such as nitro, azo, carotenoid, acridine, quinoline, indamine, diphenyl methane, xanthene Sulphur, anthraquinone, indigoid, amino- and hydroxy ketone, phthalocyanine, inorganic pigment, etc.

3. Anionic, Nonionic and Cationic

Dyes on the basis of the general structure. The major anionic dyes are the direct, acid and reactive dyes.

Photocatalytic Oxidation with TiO_2 / ZnO/Solar

Photocatalyst system is selected as an attractive choice in organic effluent treatment due to its properties. This process has been widely investigated as a promising technology for the efficient wastewater treatment since the photocatalyst is an environmentally friendly process and has considerable advantages such as the ability to destroy pollutants without the exertion of potentially hazardous oxidants. This process can be conducted under room conditions and organic pollutants can be completely decomposed into CO_2 and H_2O. Photocatalysis is a photo-induced process on the semiconductor surface by photons. This process begins with photo-excitation that can transfer electrons from the valence band to the empty conduction band. The electron-hole pairs will react to form hydroxyl radicals that hold the main role in destructive of organic dye.

Photocatalysts (TiO_2/ZnO) + he→ e- + h^+

$h^+ + H_2O \rightarrow H+ + OH\bullet$

$h^+ + OH^- \rightarrow OH^\bullet$ (3)

$e^- + O_2 \rightarrow O_2^-$ (4)

$2e^- + O_2 + 2H^+ \rightarrow H_2O_2$ (5)

$e^- + H_2O_2 \rightarrow OH\bullet + OH-$ (6)

Organic + $\bullet OH + O_2 \rightarrow CO_2 + H_2O$ + other degradation productions

Advantages of Solar Photocatalysis

1. Cost effective
2. No sludge formation like other methods such as adoption, coagulation, flocculation

3. This method does not generate any other secondary pollutant.
4. Very small quantity of photocatalyst is required for the treatment
5. The selected catalyst possess no toxicity to human health.
6. Wide application especially to molecular structured complex contaminants
7. Low capital investment.
8. Environmentally appealing.
9. Energy self-sufficient process under solar radiation photocatalysis.

II. LITERATURE REVIEW

Textile industries aquatic pollutant treated by photocatalytic ZnO and TiO_2 nanoparticles for the degradation of different dyes. Photocatalytic degradation of different dyes under solar light monitor up to 1-hour duration. Amido Black 10 B shows 99.90 % degradation with ZnO nanoparticle while 39.65 % with TiO_2. [1]

The percentage degradation for methylene blue was found to be 88.83% and 47% with ZnO and TiO_2 NPs respectively. Rose Bengal shows a highest percentage of degradation of 88.8% and 62% with ZnO NPs and TiO_2 NPs respectively. The percentage degradation of Methyl Red was found to be 50.5% and 3.11% with TiO_2 and ZnO NPs. ZnO nanoparticle is more efficient photocatalyst than TiO_2. [1]

TiO_2 is preferred over other due to its stability under various conditions also its high potential to produce radicals and its easy availability and low price. Effect of TiO_2/UV on acid blue 9 has shown the degradation efficiency to be 97%. More than 95% of color removed with Fenton's oxidation process for RB5, RB13, and AO7 azo dyes. 100% color removal and more than 90% decrease in COD with the Fenton process conducted at pH 3, Fe^{2+} dose = 400 mg/L and H_2O= 550 mg/L on industrial waste water.[4]

Procion Red used as a model of synthetic dye wastewater. The effect of TiO_2 catalyst concentration and irradiation time on the degradation of Procion Red under solar irradiation. Using TiO_2 catalyst powder in the various concentration of Procion Red of 150-300 ppm. Concentrations of TiO_2 catalyst of 0.5-8 g/l used. Color degradation of Procion Red for 12 hours of solar irradiation. [8]

Color degradation measured by using a spectrophotometer. The highest COD degradation of 62 % obtained by using TiO_2 catalyst of 8 g/l, under 12 hours of solar irradiation. Unfavorable be used for the treatment Procion Red of 300 ppm because of its color degradation percentage is too low 36% (TiO_2 concentration of 0.5 g/l) and 47% (TiO_2 concentration of 1 g/l) after 12 hours of irradiation. The color degradation can still occur when using the catalyst concentration of 4, 6 and 8 g/l. [8]

The highest color degradation (99%) occurs when using the catalyst concentration of 8 g/l after 12 hours of irradiation. The catalyst concentration of 6 g/l has been able to degrade the color to be clear (98% of degradation). The highest COD reduction was obtained when using catalyst concentration of 8 g/l (62%) after 12 hours of irradiation. COD highest degradation reached by using highest catalyst concentration of TiO_2 8 g/l. [8]

The degradation of methylene blue (MB) as an organic dye pollutant upon photocatalytic oxidation of TiO_2 nanoparticles under UV-LED (395 nm) light irradiation. Photodegradation rate of MB increases with mass of TiO_2 nanoparticles. The optimum photocatalytic degradation rate of MB achieved at 15 ppm and mass of TiO_2 nanoparticles 25 mg. [11] **The maximum decolorization (more than 70%) of dye occurred with ZnO catalyst in 35 min of** stirring at alkaline pH. The photocatalytic activity of ZnO, degradation of AO8 was undertaken. 100 ml of 10 ppm dye solution and 0.2 g of catalyst taken in a glass reactor. The mixture stirred for 30 min to establish adsorption equilibrium between dye molecules and catalyst surface. The solution irradiated with solar light. Dye is completely decomposed on irradiation in presence of the ZnO catalyst at alkaline pH under solar light irradiation in about 35 min stirring time. The complete decolorization of dye followed by UV-Visible spectrophotometry. [12]

Effect of pH on degradation of pollutants by catalyzed oxidation and shows pH is parameter that affects efficiency of photocatalytic discoloration process. Methylene blue solutions (10 mg/L) with pH values of 3, 6 and 10 UV-irradiated during 3 hours in presence of 10 mg TiO_2 on degradation of MB dye. Photocatalytic performance yields of discoloration at end of three hours around 87%, 91% and 92% respectively in neutral, acidic and basic media. Removal of 93%, 61% and 27% at concentration is 10, 20 and 30 mg/L for dye. [15]

TiO_2 and ZnO photocatalysts can be promising candidates for Methylene blue (MB) dye photocatalytic degradation under UV and solar light (SL) irradiation. ZnO exhibits a better photocatalytic activity as compared with TiO_2 and oxidation. Under solar irradiation MB oxidation more efficient and faster than under UV light and ZnO shows photocatalytic degradation as compared with TiO_2. ZnO photocatalyst under solar light leads to achieve MB highest degradation efficiency than TiO_2/UV. Total oxidation with TiO_2 required 2 hours at 50 minutes with ZnO. Photocatalytic degradation of an aerated MB solution in presence of TiO_2 (1g/ l) & ZnO (1 g/l) under solar light. [16]

III. EXPERIMENTAL ANALYSIS

Chemicals and Raw Materials

1. Dyes - Phenolic Red Dye.
2. 0.1 N NaOH or 0.1 N H_2SO_4 – For Maintain pH
3. Distilled Water
4. TiO_2
5. ZnO

Preparation of Dye Solution

1. 5 mg (5 ppm) of dye add in 1 L distilled water.
2. Stirring the solution for complete mixing of dye.
3. Similarly we can make synthetic water of various concentrations 10 -30 ppm solution.
4. After addition dye color of solution Change.
5. Measure pH of solution and should maintain between 4-5 using 0.1 N NaOH or 0.1 N H_2SO_4 for maximum adsorption.

Experimental Process For UV/TiO_2 Process

1. Take 1 L of 5 ppm dyes wastewater in reactor and stirred for mixing.
2. Measure the absorbance of known 5 ppm solution or wastewater.
3. Add 5-6 gm/ L of $TiO_{2\ catalyst}$ in reaction vessel.
4. Stirred solution for 10 min and Start UV light.
5. For various time of interval 30, 60, 90, 120- and 150-min withdrawal of sample.
6. Check absorbance unit for each sample wastewater help of colorimeter.
7. Calculate % reduction of various for % dyes by comparing initial and final absorbance unit taken using colorimeter.
8. Follow the procedure for various concentrations 5-25 ppm for 150 min contact time and calculate % reduction in dyes.
9. Find the % reduction in dyes for various contact time and concentrations.

Experimental Process For UV/ZnO Process

1. Take 1 L of 5 ppm textile wastewater in reactor and stirred for mixing.
2. Measure the absorbance of known 5 ppm solution or wastewater.
3. Add 5-6 gm/ L of $ZnO_{catalyst}$ in reaction vessel.
4. Stirred the solution for 10 min and Start the UV light.
5. For various time of interval 30, 60, 90, 120- and 150-min withdrawal of sample.
6.Check absorbance unit of each sample wastewater help of colorimeter.

7. Calculate % reduction of various for % dyes by comparing initial and final absorbance unit taken using colorimeter.
8. Follow the procedure for various concentrations 5-25 ppm for 150 min contact time and calculate % reduction in dyes.
9. Find the % reduction in dyes for various contact time and concentrations.

Experimental Process with Solar Light/TiO_2

1. Take 1 L and make 5 ppm synthetic textile wastewater in reactor and stirred for mixing.
2. Take 10 ml sample and measure the absorbance using colorimeter for 5 ppm solution.
3. Add catalyst in reactor/vessel 6 gm/l TiO_2.
4. Keep the reactor/reaction vessel in solar light.
5. For various time of interval 30, 60, 90, 120, 150- and 180-min withdrawal sample.
6. Check absorbance for various sample wastewater.
7. Calculate % reduction of various dyes by comparing initial and final absorbance measure by colorimeter.
8. Follow the procedure for various concentrations 5-25 ppm for 150 min contact time and calculate % reduction in dyes.
9. Find the % reduction in dyes for various contact time and concentrations.

Experimental Process with Solar Light/ZnO

1. Take 1 L and make 5 ppm synthetic textile wastewater in reactor and stirred for mixing.
2. Take 10 ml sample and measure the absorbance using colorimeter for 5 ppm solution.
3. Add catalyst in reactor/vessel 6 gm/l ZnO.
4. Keep the reactor/reaction vessel in solar light.
5. For various time of interval 30, 60, 90, 120, 150- and 180-min withdrawal sample.
6. Check absorbance for various sample wastewater.
7. Calculate % reduction of various dyes by comparing initial and final absorbance measure by colorimeter.
8. Follow the procedure for various concentrations 5-25 ppm for 150 min contact time and calculate % reduction in dyes.
9. Find the % reduction in dyes for various contact time and concentrations.

IV. RESULTS AND DISCUSSIONS

Effect of Contact Time on % Reduction of Dyes Using Solar/TiO_2 and UV/TiO_2

Contact Time Min	% Removal of Dyes Using Solar/TiO_2	% Removal of Dyes Using UV/TiO_2
30	48	53
60	59	62
90	67	71
120	71.5	74.5
150	77	81.5
180	80.5	85.5

Effect of Contact Time on Dyes Reduction by Solar/TiO_2 and UV/TiO_2

Table shows the effect of contact time on % reduction of dyes using solar/TiO_2 and UV/TiO_2 process. The experimental analysis carried out for 5 ppm at contact time 30, 60, 90, 120 and 150 mins for solar/TiO_2 and UV/TiO_2 process. The % reduction for phenolic red dye for solar/TiO_2 process are 48, 59, 67, 71.5, and 80.5 resp. for 5 ppm concentration

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solution. The % reduction for phenolic red dye for UV/TiO_2 process are 53, 62, 71, 74.5, 81.5 and 85.5 resp. As per analysis it's clear that the % reduction increase with increase in contact time.

Graphical Representation Contact Time Vs % Reduction of Dyes

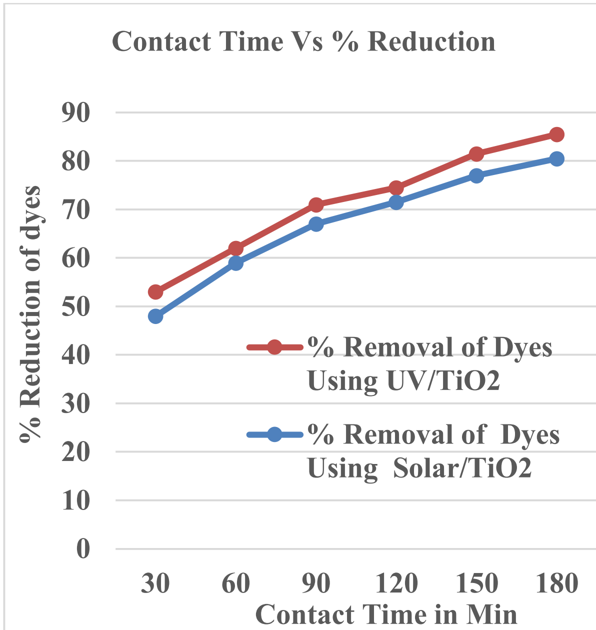

Fig. Graphical Representation Contact Time Vs % Reduction of Dyes

Graph shows the % reduction of dyes for contact time 30, 60, 90, 120 and 150 mins for solar/TiO_2 and UV/TiO_2 process. % Reduction for phenolic red dye for solar/TiO_2 process are 48, 59, 67, 71.5, and 80.5 resp. for 5 ppm concentration solution. % Reduction for phenolic red dye for UV/TiO_2 process are 53, 62, 71, 74.5, 81.5 and 85.5 resp.

Effect of Concentrations on % Reduction of Dyes Using Solar/TiO_2 and UV/TiO_2 Process

Table shows the effect of concentration on % reduction of dyes using solar/TiO_2 and UV/TiO_2 process. The experimental analysis carried out for 5-25 ppm at contact time 150-180 mins for solar/TiO_2 and UV/TiO_2 process. The % reduction for phenolic red dye for solar/TiO_2 process are 81, 64.5, 56, 50.5 and 39 resp. for 5, 10, 15, 20 and 25 ppm concentration solution resp. The % reduction for phenolic red dye for UV/TiO_2 process are 86, 68, 61.5, 56 and 42 resp. for 5, 10, 15, 20 and 25 ppm concentration solution resp. As per analysis it's clear that the % reduction decrease with increase in concentration of dyes in solution. Max. reduction shown at 5 ppm for both processes.

Concentration in ppm	% Removal of Dyes Using Solar/TiO_2	% Removal of Dyes Using UV/TiO_2
5	81	86
10	64.5	68
15	56	61.5
20	50.5	56
25	39	42

Table Effect of Conc. on % Reduction of Dyes Using Solar/TiO_2 & UV/TiO_2

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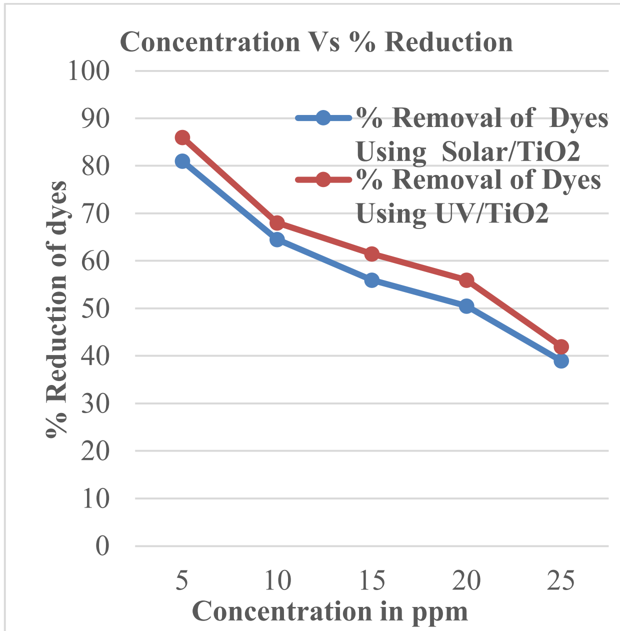

Fig. Concentrations Vs % Reduction of Dyes

Effect of Contact on % Reduction of Dyes Using Solar/ZnO and UV/ZnO

Contact Time Min	% Removal of Dyes Using Solar/ZnO	% Removal of Dyes Using UV/ZnO
30	46	49
60	57.5	60
90	64	68
120	69.5	72.5
150	75	79.5
180	77.5	80.5

Table shows the effect of contact time on % reduction of dyes using solar/ZnO and UV/ZnO process. The experimental analysis carried out for 5 ppm at contact time 30, 60, 90, 120 and 150 mins for solar/ZnO and UV/ZnO process. The % reduction for phenolic red dye for solar/ZnO process are 46, 57.5, 64, 69.5, and 77.5 resp. for 5 ppm concentration solution. The % reduction for phenolic red dye for UV/ZnO process are 49, 60, 68, 72.5, 79.5 and 80.5 resp. As per analysis it's clear that the % reduction increase with increase in contact time. Max. reduction shown at 150 mins.

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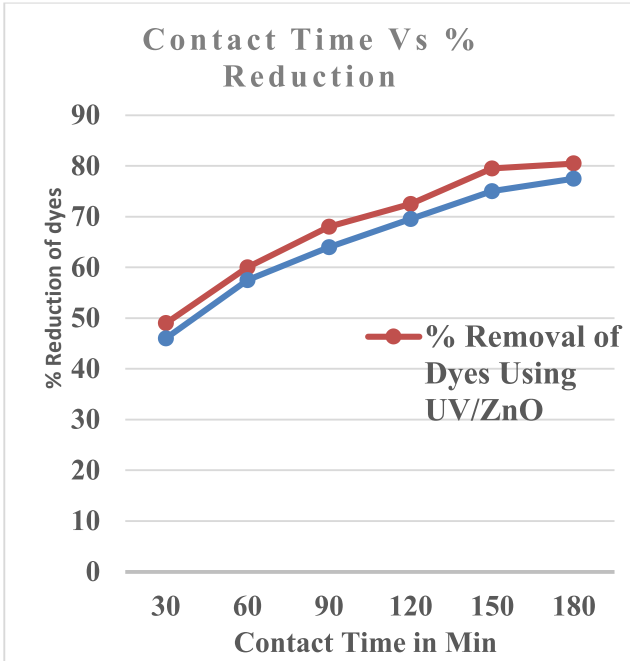

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Effect of Concentrations on % Reduction of Dyes Using Solar/ZnO and UV/ZnO Process

Concentration in ppm	% Removal of Dyes Using Solar/ZnO	% Removal of Dyes Using UV/ZnO
5	77	80.5
10	62	64.5
15	52	58
20	48.5	50.5
25	36	38.5

Table Effect of Concentrations on Dyes Reduction by Solar/ZnO and UV/ZnO

Table shows the effect of concentration on % reduction of dyes using solar/ZnO and UV/ZnO process. The experimental analysis carried out for 5-25 ppm at contact time 150-180 mins for solar/ZnO and UV/ZnO process. The % reduction for phenolic red dye for solar/ZnO process are 77, 62, 52, 48.5 and 36 resp. for 5, 10, 15, 20 and 25 ppm concentration solution resp. The % reduction for phenolic red dye for UV/ZnO process are 80.5, 64.5, 58,50.5 and 38.5 resp. for 5, 10, 15, 20 and 25 ppm concentration solution resp. As per analysis it's clear that the % reduction decrease with increase in concentration of dyes in solution. Max. reduction shown at 5 ppm for both processes.

Graph Concentrations Vs % Reduction of Dyes

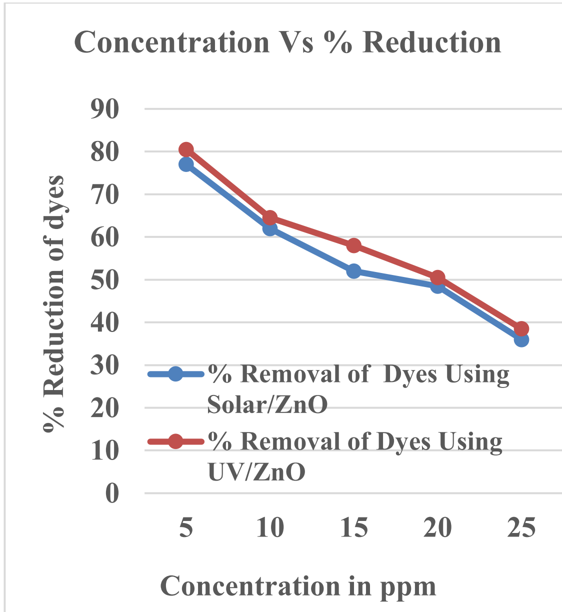

Fig. Graphical Representation Concentrations Vs % Reduction of Dyes

Graph Shows the % reduction for phenolic red dye for solar/ZnO process are 77, 62, 52, 48.5 and 36 resp. for 5, 10, 15, 20 and 25 ppm concentration solution resp. The % reduction for phenolic red dye for UV/ZnO process are 80.5, 64.5, 58,50.5 and 38.5 resp. for 5, 10, 15, 20 and 25 ppm concentration solution resp. As per analysis it's clear that the % reduction decrease with increase in concentration of dyes in solution. Max. reduction shown at 5 ppm for both processes.

V. CONCLUSION

The effect of contact time on % reduction of dyes using solar/TiO_2 and UV/TiO_2 process. The experimental analysis carried out for 5 ppm at contact time 30, 60, 90, 120 and 150 mins for solar/TiO_2 and UV/TiO_2 process. The % reduction for phenolic red dye for solar/TiO_2 process are 48, 59, 67, 71.5, and 80.5 resp. for 5 ppm concentration solution. The % reduction for phenolic red dye for UV/TiO_2 process are 53, 62, 71, 74.5, 81.5 and 85.5 resp. As per analysis it's clear that the % reduction increase with increase in contact time. Max. reduction shown at 120-150 mins. The effect of concentration on % reduction of dyes using solar/TiO_2 and UV/TiO_2 process. The experimental analysis carried out for 5-25 ppm at contact time 150-180 mins for solar/TiO_2 and UV/TiO_2 process. The % reduction for phenolic red dye for solar/TiO_2 process are 81, 64.5, 56, 50.5 and 39 resp. for 5, 10, 15, 20 and 25 ppm concentration solution resp. The % reduction for phenolic red dye for UV/TiO_2 process are 86, 68, 61.5, 56 and 42 resp. for 5, 10, 15, 20 and 25 ppm concentration solution resp. As per analysis it's clear that the % reduction decrease with increase in concentration of dyes in solution. Max. reduction shown at 5 ppm for both processes.

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reduction for phenolic red dye for UV/ZnO process are 80.5, 64.5, 58,50.5 and 38.5 resp. for 5, 10, 15, 20 and 25 ppm concentration solution resp.

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