

Volume 2, Issue 7, May 2022

# Waste Water Treatment by Catalytic Reduction using TiO<sub>2</sub>/Solar Radiation

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Abstract: The color produced by dyes in water makes it aesthetically unpleasant & can acute or chronic effects on exposed organisms which depend on the concentration of the dye and the exposed time. Many dyes are considered to be toxic and even carcinogenic. Textile industries processes are most industrial that release colored wastewater containing dye that become major environmental concern. Photocatalytic Oxidation by ZnO/UV, TiO2/UV, TiO2/H2O2/ UV and solar irradiation are effective processes to be used for removal of acidic, basic and color dyes from Wastewater. We choose the photocatalytic Oxidation by TiO2/Solar Radiation 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 CO2 and H2O. The % reduction of dyes for sample 5 ppm concentration with various contact time 30, 60, 90, 120, 150 and 180 mins. respectively. The maximum dyes reduction at 180 mins. which is 80.48 % and for 150 mins. is 77 %. So there is no large difference between these two values so we can consider optimum time for dyes reduction is between 150 mins. to 180 mins. The % reduction of dyes for various concentration values 5, 10, 15, 20 and 25 ppm. The maximum dyes reduction at 5 ppm which is 80.32 % for 180 mins. As concentration of dyes in wastewater increase the rate of reduction decrease. The concentration of dyes in wastewater be the important parameter that impact on the rate of reduction of dyes from the wastewater. The amount of catalyst (TiO2) use for treatment is fixed which is 5-6 gm/l using solar radiation as light source.

Keywords: Waste Water Treatment, Textile Dyes, Catalytic Reduction, Photocatalytic 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.

# **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

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- 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 & Reduction with TiO2

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<sub>2</sub>/ZnO) + hv $\rightarrow$  e- + h<sup>+</sup> h<sup>+</sup> + H<sub>2</sub>O $\rightarrow$  H+ + OH• h<sup>+</sup> + OH<sup>-</sup> $\rightarrow$  OH• (3) e<sup>-</sup> + O<sub>2</sub> $\rightarrow$ O<sub>2</sub><sup>-</sup> (4) 2e<sup>-</sup> + O<sub>2</sub> + 2H<sup>+</sup> $\rightarrow$  H<sub>2</sub>O<sub>2</sub> (5) e<sup>-</sup> + H<sub>2</sub>O<sub>2</sub> $\rightarrow$  OH• + OH- (6) Organic + •OH + O<sub>2</sub> $\rightarrow$  CO<sub>2</sub> + H<sub>2</sub>O + 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.

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#### **II. LITERATURE REVIEW**

**Textile industries are one of the major aquatic** pollutant treated by photocatalytic ZnO and  $TiO_2$  nanoparticles photocatalysts 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<sub>2</sub>. [1] The percentage degradation for methylene blue was found to be 88.83% and 47% with ZnO and TiO<sub>2</sub> 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<sub>2</sub> and ZnO NPs. ZnO nanoparticle is more efficient photocatalyst than TiO<sub>2</sub>. [1] TiO<sub>2</sub> 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 TiO2/UV on acid blue 9 has shown the degradation efficiency to be 97%. The kinetics of the degradation was found to be of zeroth order with the initial concentration of dye and catalyst affecting the kinetics and the order of reaction. More than 95% of color was 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  $H_2O=550 \text{ mg/L}$  on industrial waste water.[4] Procion Red used as a model of synthetic dye wastewater. The effect of TiO<sub>2</sub> catalyst concentration and irradiation time on the degradation of Procion Red under solar irradiation. Photo degradation by using TiO<sub>2</sub> catalyst powder in the various concentration of Procion Red of 150-300 ppm. The various concentrations of TiO<sub>2</sub> catalyst of 0.5-8 g/l used. Color degradation of Procion Red for 12 hours of solar irradiation. [8] Color degradation was measured by using a spectrophotometer. The highest COD degradation of 62 % obtained by using TiO<sub>2</sub> 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<sub>2</sub> concentration of 0.5 g/l) and 47% (TiO<sub>2</sub> 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<sub>2</sub> 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. Effect of different parameters, including initial concentration of dye and catalyst dosage on the degradation rate of the dye were evaluated. The photodegradation rate of MB increases with mass or number of TiO<sub>2</sub> nanoparticles. The optimum photocatalytic degradation rate of MB achieved at 15 ppm and mass of TiO<sub>2</sub> 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. A typical experiment constitutes 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> and oxidation. Under solar irradiation MB oxidation more efficient and faster than under UV light and ZnO shows photocatalytic degradation as compared with TiO2. ZnO photocatalyst under solar light leads to achieve MB DOI: 10.48175/IJARSCT-2342 **Copyright to IJARSCT** 243 www.ijarsct.co.in



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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]

# 2.1 Photo-Catalytic Process with $TiO_2\ or\ ZnO/Solar\ Light$

The color removal of dyes by determining its absorbance at  $\lambda$ max of dyes using UV-visible spectrophotometer 100 mg of ZnO or TiO<sub>2</sub> added into the cylindrical vessel containing 5-25 ppm dye solution and to stir in darkness for 30 minutes to reach adsorption equilibrium between the dye and the photocatalyst. After 30 minutes dye solutions with nanoparticles placed under the exposure of solar light irradiation. Following reaction mechanism are take place. Range of visible solar radiation is 400-700 nm on earth which can be used for color and dyes removal from wastewater in presence of catalyst like ZnO or TiO<sub>2</sub>.

Photocatalysts  $(TiO_2/ZnO) + hv \rightarrow e^- + h^+$   $h^+ + H_2O \rightarrow H^+ + OH^{\bullet}$   $h^+ + OH^- \rightarrow OH^{\bullet}(3)$   $e^- + O_2 \rightarrow O_2^-(4)$   $2e^- + O_2 + 2H^+ \rightarrow H_2O_2(5)$  $e^- + H_2O_2 \rightarrow OH^{\bullet} + OH^-(6)$ 

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

# 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
- $4. \ TiO_2$

# **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 solution.
- 4. After addition dye color of solution Change.
- 5. Measure pH of solution and it should be maintain using 0.1 N NaOH or 0.1 N H<sub>2</sub>SO<sub>4</sub> for maximum adsorption.

# Photocatalysis with Solar Light/TiO2 for Various Contact Time

- 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 TiO2.
- 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 samples.
- 7. Calculate % reduction of various dyes by comparing initial and final absorbance measure.
- 8. Compare results of various contact time for 5 ppm solution.
- 9. Find out the optimum value of contact or reaction time for textile wastewater treatment by experimental analysis.

# Photocatalysis Solar Light/TiO2 for Various Dyes Concentrations

- 1. Take 1 L and make 5, 10, 15 and 20 ppm synthetic textile wastewater in reactor and stirred for mixing.
- 2. Take 10 ml sample of each concentration and measure absorbance using colorimeter.

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- 3. Add catalyst in reactor/vessel 6 gm/l TiO2 in 10 ppm solution.
- 4. Keep the reactor/reaction vessel in solar light.
- 5. Withdrawal 10 ml sample after 180 min and measure absorbance.
- 6. Calculate % reduction of by comparing initial and final absorbance measure by colorimeter.
- 8. Repeat the procedure for 10, 15 and 20 ppm solution.
- 9. Find out the % reduction of dyes for selected concentration for textile wastewater treatment by experimental analysis.

#### Absorbance Reading for Various Contact Time for 5 ppm Solution

Sr. No	<b>Reaction Time Min</b>	Absorbance
Initial	0	0.16
01	30	0.31
02	60	0.39
03	90	0.48
04	120	0.56
05	150	0.70
06	180	0.82

Table: Absorbance for Various Contact Time

Table shows the absorbance measure for sample 5 ppm concentration with various contact time 30, 60, 90, 120, 150 and 180 mins. respectively. Initial value of absorbance is 0.16 (before treatment). The final and initial value of absorbance can used to calculations of 5 Reduction of dyes from synthetic wastewater for various reaction/contact time for fixed concentration value of 5 ppm.

## % Reduction = [(Final – Initial)/ Final] \* 100

1. For 30 Min,

% Reduction Of Dyes = [(0.31-0.16)/0.31] = 48.38

- 2. For 60 Min,
- % Reduction Of Dyes = [(0.39-0.16)/0.39] = 58.97
- 3. For 90 Min,
- % Reduction Of Dyes = [(0.48-0.16)/0.48] = 66.67
- 4. For 120 Min,
- % Reduction Of Dyes = [(0.56-0.16)/0.56] = 71.14
- 5. For 150 Min,
- % Reduction Of Dyes = [(0.70-0.16)/0.70] = 77
- 6. For 180 Min,
- % Reduction Of Dyes = [(0.82-0.16)/0.82] = 80.48

#### % Reduction of Dyes for Various Contact Time for 5 ppm Solution

Sr. No	<b>Reaction Time Min</b>	% Reduction
01	30	48.38
02	60	58.97
03	90	66.67
04	120	71.74
05	150	77
06	180	80.48

Table % Reduction of Dyes for Various Contact Time

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Table shows the % reduction of dyes for sample 5 ppm concentration with various contact time 30, 60, 90, 120, 150 and 180 mins. respectively. The maximum dyes reduction at 180 mins. which is 80.48 % and for 150 mins. is 77 %. So there is no large difference between these two values so we can consider optimum time is 180 mins.

#### Graphical Representation Contact Time Vs % Reduction (Dyes)



#### Graph % Reduction of Dyes for Contact Time

Graph shows the % reduction of dyes for sample 5 ppm concentration with various contact time 30, 60, 90, 120, 150 and 180 mins. respectively. The maximum dyes reduction at 180 mins. which is 80.48 % and for 150 mins. is 77 %. So there is no large difference between these two values so we can consider optimum time for dyes reduction is between 150 mins. to 180 mins.

#### **Observations for Concentration of Dyes Absorbance at Various Concentrations**

Sr. No	Concentrations in ppm	Initial Absorbance	Final Absorbance
01	05	0.12	0.61
02	10	0.24	0.68
03	15	0.34	0.78
04	20	0.42	0.85
05	25	0.58	0.95

## Table Absorbance at Various Concentrations

Table shows the initial and final value (before and after treatment) for absorbance measure for various concentration 5, 10, 15, 20 and 25 ppm. The absorbance measure for 180 mins. reaction/contact time in maximum reduction for dyes using photocatalytic degradation with  $TiO_2$ .

% Reduction = [(Final – Initial)/ Final] \* 100

#### 1. For 5 ppm

% Reduction Of Dyes = [(0.61-0.12)/0.61] = 80.32

#### 2. For 10 ppm,

% Reduction Of Dyes = [(0.68-0.24)/0.68] = 64.70

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#### 3. For 15 ppm,

% Reduction Of Dyes = [(0.78-0.34)/0.78] = 56.41

4. For 20 ppm,

% Reduction Of Dyes = [(0.85-0.42)/0.85] = 50.58

5. For 25 ppm,

% Reduction Of Dyes = [(0.95-0.58)/0.95] = 38.94

#### % Reduction of Dyes for Concentrations

Sr. No	Concentrations in ppm	% Reduction Of Dyes
01	05	80.32
02	10	64.70
03	15	56.41
04	20	50.58
05	25	38.94

#### **Table % Reduction Dyes for Concentrations**

Table shows the % reduction of dyes for various concentration values 5, 10, 15, 20 and 25 ppm. The maximum dyes reduction at 5 ppm which is 80.32 % for 180 mins. As concentration of dyes in wastewater increase the rate of reduction decrease. The concentration of dyes in wastewater be the important parameter that impact on the rate of reduction of dyes from the wastewater. The amount of catalyst (TiO<sub>2</sub>) use for treatment is fixed which is 5-6 gm/l using solar radiation as light source.

#### **Graph % Reduction Vs Concentrations**



#### **Graph % Reduction Dyes for Concentrations**

Graph shows the % reduction of dyes for various concentration values 5, 10, 15, 20 and 25 ppm. The maximum dyes reduction at 5 ppm which is 80.32 % for 180 mins. As concentration of dyes in wastewater increase the rate of reduction decrease. The concentration of dyes in wastewater be the important parameter that impact on the rate of reduction of dyes from the wastewater. The amount of catalyst (TiO<sub>2</sub>) use for treatment is fixed which is 5-6 gm/l using solar radiation as light source.

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#### Effect of Various Parameters on TiO<sub>2</sub>/Solar Radiation Process

#### Effect of pH value

Reaction to be conducted under the conditions of reaction time 180 minutes, catalyst loading 6 gm/l and different pH values results found that low pH has effective for  $TiO_2/Solar$  Radiation process and the best removal efficiency is obtained at a pH =4-5. At the lower value of pH is better to remove inorganic carbons from waste water as they can scavenge hydroxyl radicals.

#### **Effect of Reaction Time**

Reaction time is the important factor for treatment of dyes wastewater by  $TiO_2/Solar$  Radiation process. As per experimental studies optimum reaction time is 150-180 minutes in which more than the 80 % of dyes reduction from the wastewater.

#### Effect of Catalyst TiO<sub>2</sub> Loading

For this TiO<sub>2</sub>/Solar Radiation process TiO<sub>2</sub> major chemicals determining operation costs as well as efficiency. As per experimental study optimum amount of catalyst obtained is 5-6 gm/l of waste water treated.

#### Effect of Wavelength of Solar Light

As intensity of solar radiation/light increase the rate of photolysis of TiO<sub>2</sub> increase. Optimum value of 350-450 nm after that rate of degradation reduced. Value of UV intensity should be  $\lambda < 450$  nm. Value of solar radiation is between 100-400 nm. So it can be application for degradation with TiO<sub>2</sub> and gives best result for removal of dyes.

#### **Effect of Dyes Concentration**

As the concentration of dyes increase rate of reduction decrease. We carried out the experiment for % reduction of dyes for various concentration values 5, 10, 15, 20 and 25 ppm. The maximum dyes reduction at 5 ppm which is 80.32 % for 180 mins. As concentration of dyes in wastewater increase the rate of reduction decrease. The concentration of dyes in wastewater be the important parameter that impact on the rate of reduction of dyes from the wastewater.

#### **III. CONCLUSION**

Photocatalytic Oxidation by ZnO/UV, TiO<sub>2</sub>/UV, TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV and solar irradiation are effective processes to be used for removal of acidic, basic and color dyes from Wastewater. This process is the one of the type of APOs are most widely used for waste water treatment of various types of industrial wastewater and efficient wastewater treatment since photocatalyst is environmentally friendly process and considerable advantages such as ability to destroy pollutants without exertion of potentially hazardous oxidants. This process can be conducted under room conditions and organic pollutants can be completely decomposed into CO<sub>2</sub> and H<sub>2</sub>O.We choose the photocatalytic Oxidation by TiO<sub>2</sub>/Solar Radiation 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. The % reduction of dyes for sample 5 ppm concentration with various contact time 30, 60, 90, 120, 150 and 180 mins. respectively. The maximum dyes reduction at 180 mins. which is 80.48 % and for 150 mins. is 77 %. So there is no large difference between these two values so we can consider optimum time for dyes reduction is between 150 mins. to 180 mins. The % reduction of dyes for various concentration values 5, 10, 15, 20 and 25 ppm. The maximum dyes reduction at 5 ppm which is 80.32 % for 180 mins. As concentration of dyes in wastewater increase the rate of reduction decrease. The concentration of dyes in wastewater be the important parameter that impact on the rate of reduction of dyes from the wastewater. The amount of catalyst (TiO<sub>2</sub>) use for treatment is fixed which is 5-6 gm/l using solar radiation as light source.

#### **IV. FUTURE SCOPE AND BENEFITS**

#### **Future Scope**

1. TiO<sub>2</sub>/Solar Radiation process can be adopted to treat various types of waste water.

2. TiO<sub>2</sub>/Solar Radiation can use to improve efficiency of conventional method.

3. TiO<sub>2</sub>/Solar Radiation process can be used as an advanced treatment to treat waste water.

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- 4. This process can make waste water for reusable as process water.
- 5. With the help of TiO<sub>2</sub>/Solar Radiation destroys and removes bacteria, viruses and cysts.
- 6. TiO<sub>2</sub>/Solar Radiation can used to treat waste water have high COD, color, dyes, organic matter etc.

#### Benefits

1. TiO<sub>2</sub>/Solar Radiation treatment process capital cost significantly less than conservative technologies like UV/TiO<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub> etc.

- 2. TiO<sub>2</sub>/Solar Radiation process has less operating cost than conservative technologies.
- 3. TiO<sub>2</sub>/Solar Radiation treatment process not needs power requirements.
- 4. Low maintenance required for this treatment process.
- 5. Minimal operator attention.
- 6. Consistent and reliable results.

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