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Photocatalytic Degradation of Dye Polluted Wastewater Using Titanium Dioxide

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Abstract: Advanced oxidation processes (AOPs) offer a promising alternative to classical treatment methods (e.g., adsorption, flocculation, and air stripping) of treating water and wastewater. AOPs are able to treat pollutants more efficiently by completely mineralizing them to more stable species of carbon dioxide, water and inorganic ions.

The operational parameters influencing the photocatalytic degradation rate of methylene blue in dye polluted wastewater treatment were studied. These parameters are initial dye concentration, catalyst concentration, H_2O_2 volume. The catalysts used were titanium dioxide (TiO_2), Hydrogen peroxide (H_2O_2) in all experiments to increase the efficiency of the UV/TiO_2 process.

The experiments of UV-lamp revealed that the best removal is 67.37% when using 1.5-gram TiO_2 /L of pollutant solution, but in the solar UV experiment the best removal is 99.09 % when using 1 gram of TiO_2 /L of pollutant solution. The effect of initial dye concentrations on the photocatalytic degradation showed the limits of concentrations which can be removed easily, 5 ppm gave the best results of pollutant degradation. Addition of H_2O_2 to the pollutant stream improved the photocatalytic degradation of pollutant. The effect of different flowrates on the photocatalytic degradation showed the best flow rate was 500 ml/min which should be used to achieve the best results.

Keywords: TiO_2, UV, AOPs, H_2O_2, photocatalytic, dye.

1 Introduction

The textile industry produces large quantities of highly colored effluents, which are generally toxic and resistant to destruction by biological treatment methods. Azo dyes, such as C.I. Reactive Red 120, are widely used in the textile industry [1-3]. Due to the large degree of organics present in these molecules and stability of modern textile dyes, conventional biological treatment methods are ineffective for their decolorization and degradation [4-6]. This led to the study of other effective methods. In recent years advanced oxidation processes (AOPs) have been developed to meet the increasing need of an effective wastewater treatment [7].

AOP generates powerful oxidizing agent hydroxyl radicals which completely destroy the pollutants in waste water. Heterogeneous photocatalysis through illumination of UV (or)

solar light on a semiconductor surface is an attractive advanced oxidation process. AOPs include photocatalysis systems such as a combination of a semiconductor (TiO_2, etc.) and UV light [8-9].

Photocatalytic oxidation of pollutants with solar light can make it an economically viable process since solar energy is an abundant natural energy source. This solar energy can be used instead of artificial light sources. The artificial light sources need high electrical power which is costly and hazardous. Solar energy has been successfully used for photocatalytic degradation of pollutants [10-13]. It is demonstrated how the photo decolorization of some dyes could

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be achieved by solar light irradiation. In photocatalytic process, electron–hole recombination is a major problem to circumvent. In photocatalysis, UV irradiation source stands up among other

sources to avoid this problem. So, it was decided to study the influence of solar light and UV light independently on the photocatalytic degradation of dyes [14-15].

In recent years, vast majority of investigations in the area of photocatalytic degradation of pollutants have employed suspension of the semiconducting particles. However, from practical point of view, it may not be possible to completely recover the photocatalysts used in the reactor. Industrial-scale photo-catalyst suspensions would encounter a problem, i.e., separating the catalyst from the treated water and recycling it. Due to the tiny size of the particles of the most semiconductors, complete separation is very expensive. This needs either long time settlement or centrifugation [16-20].

The problem can be solved by fixing the catalyst on a support. Hence, many researchers have decided to study the feasibility of coating the photocatalyst on inert surfaces like glass, polythene fibers and cement surface. Fixation of the catalyst on a stationary support could circumvent the need to recover the catalyst from the reaction mixture without any leaching. Over recent years, much work has been done in this area and this has led to the use of a variety of supports; silica gel, quartz optical fibers, glass fibers, glass beads, alumina, ceramics, cellulose membranes, polymer films, rare earth oxides, zeolites, magnesia etc. [21-23].

Among the photocatalysts tested, titanium dioxide (TiO_2) has been found to be the most influential mainly because of its photostability, ease of available, rather biologically inert, low operation temperature, low energy consumption, high photo-catalytic activity, suitable flat band potential, relatively high chemical stability, water insolubility under most environmental conditions and preventing the formation of undesirable by-products [24–27].

The photocatalytic activity of TiO_2 is dependent on the surface and structural properties of the semiconductor such as crystal composition, surface area, particle size distribution, porosity, band gap and surface hydroxyl density. Particle size is of primary importance in heterogeneous catalysis, because it is directly related to the efficiency of a catalyst through the definition of its specific surface area. A lower particle size increases the specific surface area and thus increases the number of active surface sites per square meter which leads to higher expected activity [28-30].

There are three different crystalline forms of TiO_2: anatase, rutile, and brookite. The anatase form has been found to have the most favorable characteristics for photocatalytic oxidation [31-32].

When a semiconductor such as TiO_2 absorbs a photon with energy equal to or greater than its band gap width (3.2 eV), an electron may be promoted from the valence band to the conduction band (e^- cb) leaving behind an electron vacancy in the valence band (h^+ vb). The holes at the TiO_2 valence band, having an oxidation potential of +2.6 V can oxidize water or hydroxide to produce hydroxyl radicals. The hydroxyl radical is a powerful oxidizing agent and enables a nonspecific attack on organic compounds; under favorable conditions the final photoproducts are H_2O, CO_2 and inorganic anions. The general detailed mechanism of dye degradation upon irradiation is described by Equations 1–6 [33, 34]:

$$\text{Dye} + h\nu \rightarrow \text{Dye}^* \quad (1)$$

$$\text{Dye}^* + TiO_2 \rightarrow \text{Dye}^{\bullet+} + TiO_2\,(e) \quad (2)$$

$$TiO_2\,(e) + O_2 \rightarrow TiO_2 + O_2^{\bullet-} \quad (3)$$

$$O_2^{\bullet-} + TiO_2\,(e) + 2H^+ \rightarrow H_2O_2 \quad (4)$$

$$H_2O_2 + TiO_2\,(e) \rightarrow {}^{\bullet}OH + OH^- \quad (5)$$

$$\text{Dye}^{\bullet+} + O_2 \text{ (or } O_2^{\bullet-} \text{ or } {}^{\bullet}OH) \rightarrow \text{peroxylated or hydroxylated intermediates} \rightarrow \text{degraded or mineralized products} \quad (6)$$

Nowadays it is well known that TiO_2 is one of the most suitable semiconductors for photocatalysis and has been applied into various photocatalytic reactions [35-40]

Abbas et al., studied the solar photolysis and photocatalytic treatment of textile industrial wastewater, they found that the rate of photodegradation increased linearly with time of irradiation when titanium dioxide or zinc oxide was used. A maximum color removal of 96% was achieved after irradiation time of 2.5 hours when titanium dioxide

used at 303K and 82% color reduction was observed when zinc oxide used for the same period and at the same temperature [41]

Hussain et al. investigated experimentally the removal the dyestuff from dyeing textile industrial wastewater by photosensitization process, for reusing it in the same industry or for domestic purpose and/ or irrigation. The results indicated clearly that titanium dioxide and zinc oxide could be used efficiently in photocatalytic treatments of textile industrial wastewater [42]

Chhotu et al., studied the photocatalytic degradation of textile dye by using titanium dioxide nano catalyst, they found that 83.6% degradation occurred at optimized conditions (Dye concentration 100 ppm, pH 7.8, TiO_2 dose 0.5g/L, UV intensity 25 W/m^2 and time 3.5h)[43].

Zangeneh et al., compared the effectiveness of pure and modified TiO_2 for photocatalytic degradation of different organic matters and clarifies the advantages of the modified TiO_2 with photoactivity under visible light, From the extensive review performed, it is concluded that the addition of dopants to pure titanium dioxide can significantly enhance catalyst performance [44].

Wasi et al., studied the photocatalytic degradation of real pharmaceutical wastewater from Abbot Laboratories (Private) Limited, Karachi, Pakistan, using TiO_2, ZnO, and H_2O_2, the results indicate that for real pharmaceutical wastewater, combined use of TiO_2/ H_2O_2 is comparatively more effective than ZnO and TiO2 alone[45]

Yanqin et al., studied the Enhanced Photocatalytic Degradation of Organic Dyes via Defect-Rich TiO_2 Prepared by Dielectric Barrier Discharge Plasma, they found that the photocatalytic performance indicated that the plasma-treated TiO_2 was much better than the original TiO_2 nanoparticles in photocatalytic degradation of organic dyes under sunlight. Therefore, plasma can be an effective means to optimize photocatalytic degradation of TiO_2 nanoparticles[46].

Naser studied Titanium dioxide as photocatalyst for processing textile wastewater under UV Light, he found that titanium dioxide has the ability of degradation for different dyes and this is obviously in varying of color from the deep green color to the light yellow, the optimum concentration was 2 g/l titanium dioxide because of a high degradation reached to 60%.[47]

Gurudev et al., investigated the potential of the heterogeneous photocatalytic oxidation process to reduce the pollutant load in coffee processing wastewater, Significant results for COD and color removal, 67%, and 70% respectively, were achieved at a pH of 4 with titanium dioxide (TiO_2), and a catalyst dosage of 500 mg/L, using four ultraviolet-C (UV-C) lamps of 16Weach. With the addition of hydrogen peroxide (H_2O_2) as an oxidant, the removal efficiency increased to 84% and 75% for COD and color, respectively [48].

The purpose of this paper is to study the solar photocatalytic oxidation of an azo dye (C.I. Reactive Red 120) which are extensively used in the textile industry by using the solar parabolic collector under the effect of the activated carbon impregnated with catalysts. The effect of solar UV light irradiation, pH and the amount of photocatalyst were examined.

2 Experimental Works

2.1 Materials

The following materials were used in the experiments

Distilled water: It is prepared in chemical engineering department laboratories.
Pollutants: methylene blue dyestuff (λ_{max} 664nm) is a heterocyclic basic dye having a molecular weight of 373.9 g/gmol. Its scientific name is basic blue 9 with the molecular Formula $C1_6H_{18}N_3SCl$.

2.1.1 Catalysts

The catalyst (TiO_2) was taken from one of the textile factories in Egypt. There are many types from catalyst; these types are TiO2 Anatase Type: This type is used as a photocatalyst with 0.05 mm particle size and 3.78 g/cm^3density. TiO_2 Rutile Type: This type is used as a photocatalyst with 0.05 mm particle size and 4.23 g/cm^3 density. TiO_2 Mixture: This type is mixture (79% Anatase, 21% Rutile).

2.2 UV lamp Experiment

The experimental setup for the UV lamp setup used is a closed cycle as shown in figure 2

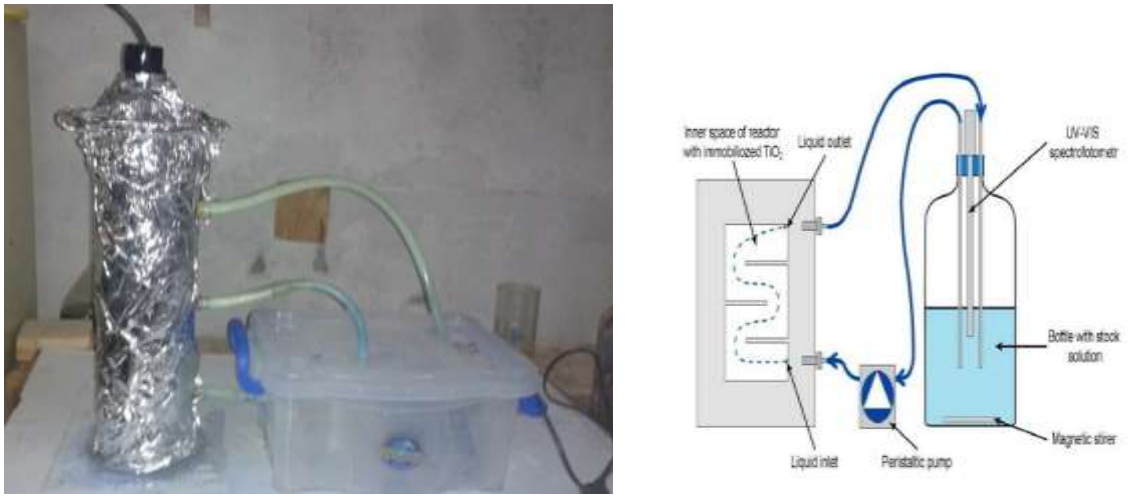

Fig. 1: First Experiment (UV-lamp) setup and a Schematic Diagram of the Setup.

The UV lamp setup includes the following: -

Feed/discharge Tank: plastic beaker and its volume are 5 liters. This tank contains polluted feed water, which will be subjected to treatment. The tank is connected to the inlet and outlet of a tubular reactor.

Tubular Reactor: it`s a precipices UV unit consist of UV lamp and input & output stream of water. The tube is 45 cm long and 10 cm diameter.

2.3 Solar UV Experiment

The experimental setup used for the solar UV is a closed cycle as illustrated in figure 3.

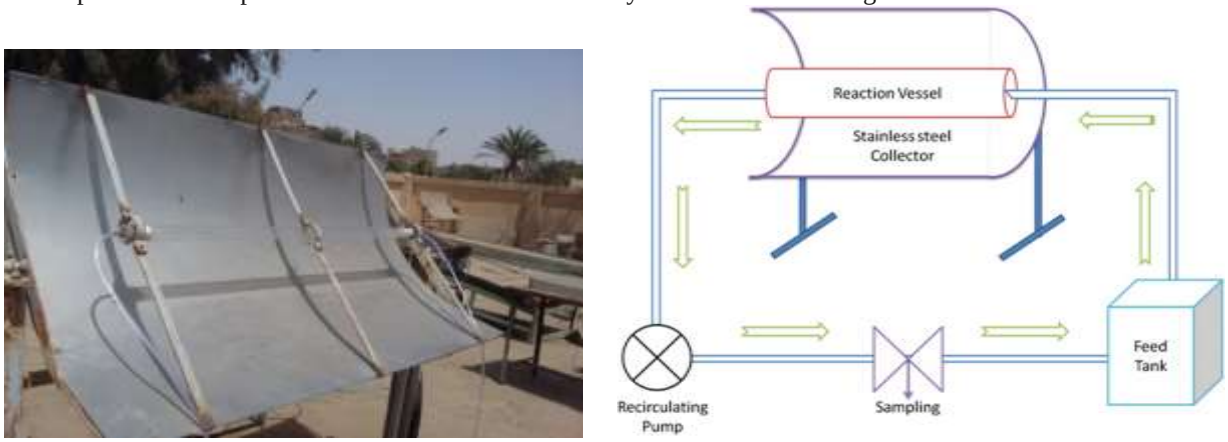

Fig. 2: Solar Wastewater Treatment Setup and a Schematic Diagram of the Setup.

The solar UV includes the following: -

Feed/Discharge Tank: It's a plastic beaker; its volume is 5 liters. This tank contains polluted feed water, which will be subjected to treatment. The tank is connected to the inlet and outlet of a glass tube.

Glass Tube: It's the reactor in which the treatment is happening; it consists of input and output stream of water.

Curved Plate of Stainless Steel: It assembles the sunlight and focuses it on the glass tube.

2.4 Analytical Methods

Dilutions of the concentrated samples were undertaken as the reduced optical density found from the Spectrophotometer was in the range from 0.2 to 1.0, it was found that more accurate results were obtained in this range. Then by multiplying these reduced optical densities by their dilution factor, the optical density of the original stock solution was obtained. All tests were carried out at ambient temperature (-/+ 25°C) to eliminate any temperature effects.

The calibration curve for dye (methylene blue) was prepared by recording the absorbance (optical density) values for a range of known concentrations of methylene blue solution at the wavelength for maximum optical density. This value, λmax, was found from a full scan of the methylene blue spectrum. The value of λmax was determined using a Spectrophotometer and this value which is (664) nm was used in all subsequent investigations using Spectrophotometer.
Optical density readings for various samples as shown in table 1 were compared with the calibration curve in figure 4 and transformed into concentration (ppm) terms.

Table 1: Optical Density Readings for Various Concentrations.

Concentration (ppm)	Optical density
0	0
1	0.23
2	0.384
3	0.646
4	0.841
5	1.025

In accordance with the Beer-Lambert's law, and using least-squares method applied to the straight line , the optical density follows a linear relationship to concentration as follows:
- Optical Density = 0.02077 X Concentration.
- Concentration = 4.815 X ABS (Optical density).

2.5 Experimental Procedures

The methylene blue was made in stock solution of concentration 1000 ppm and was subsequently diluted to the required concentrations by using distilled water. Standard solutions of methylene blue strengths ranging from 5 to 15 ppm were made by using distilled water as a solvent. Pollutant solution was prepared according to the required concentration by dissolving the predetermined amount of the dye in the distilled water. The prepared volume was 5 liters. TiO_2 should be added to the solution . To eliminate the effect of adsorption, the suspension was subjected to mixing for 3-5 minutes in the absence of UV light. In the UV lamp experiment the pump was connected to the tank and was operated at specific discharge rate so the pollutant solution was circulated from the tank to tubular reactor and again to the tank and the cycle was repeated. In the solar UV experiment the pump was connected to the tank and was operated at specific discharge rate so the pollutant solution was circulated from the tank to the glass tube and again to the tank and the cycle was repeated. The mass of TiO_2 was changed every time to study the effect of increasing mass of photo catalyst on reaction rate. Samples were taken periodically for analysis. Samples were centrifuged for separation of TiO_2 powder. Dilute samples to the concentration range of calibration curve. Analyses were conducted on the spectrophotometer to determine the pollutant concentration in the samples taken at the beginning, intermediate and end time intervals throughout the experiments.

3 Results and Discussions

3.1Using UV Lamp

3.1.1The Effect of Different Concentrations of Dye Solution at 0.5 gm TiO_2 and 5 ml H_2O_2

Figure 3 illustrates the Effect of different concentrations of dye solution (5 ppm, 10 ppm and 20 ppm) at 0.5 gm TiO_2 and 5 ml H_2O_2.

Tests are run on this figure illustrate the effect of dye concentrations on the process of photocatalytic degradation. In this case the concentration of 5 ppm showed the best results of photocatalytic degradation at 0.5 gm of TiO_2 and 5 ml of H_2O_2.

3.1.2. Effect of Different Weights of TiO_2 on Dye Degradation at 5 ppm of Dye and 5 ml of H_2O_2

Figure 4 illustrates the effect of different mass of catalyst on dye degradation at 5 ppm of dye and 5 ml of H_2O_2 also, the figure displays the effect of different masses of the catalyst (TiO_2) on the process of photocatalytic degradation.

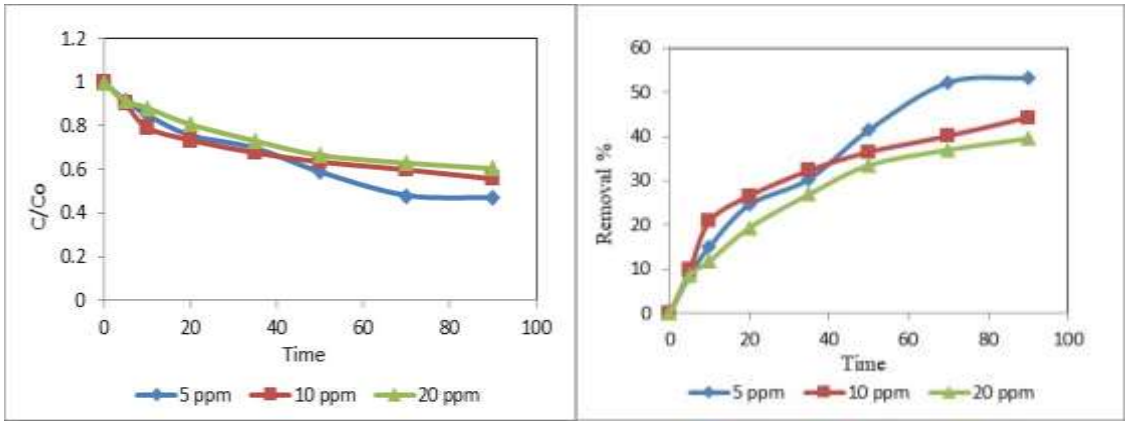

Fig. 3: The Effect of Different Concentrations of Dye Solution at 0.5 gm TiO_2 and 5 ml H_2O_2.

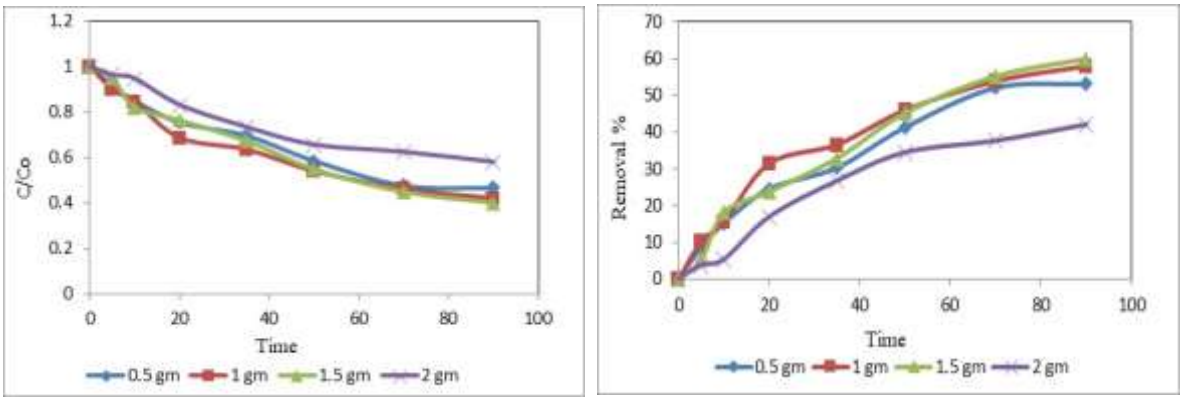

Fig. 4: Effect of Different Weights of TiO2 on Dye Degradation at 5 ppm of Dye and 5 ml of H_2O_2.

Tests are run on this figure shows the effect of different masses of the catalyst (TiO_2) on the process of photocatalytic degradation. In this case the mass of 1.5 gm of TiO_2 shows the best results of photocatalytic degradation at 5 ppm of dye and 5 ml of H_2O_2.

3.1.3. Effect of Different Volumes of H_2O_2 on Dye degradation at 5 ppm of Dye and 1.5 gm of TiO_2

Figure 5 illustrates the effect of different volumes of H_2O_2 on dye degradation at 5 ppm of dye and 1.5 gm of TiO_2

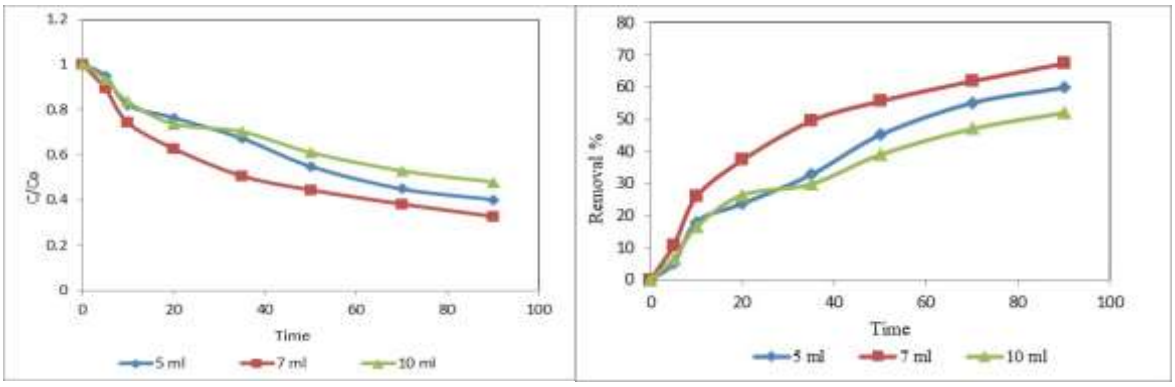

Fig. 5: Effect of Different Volumes of H_2O_2 on Dye Degradation at 5 ppm of Dye and 1.5 gm of TiO_2.

Tests are run on this figure shows the effect of different volumes of H_2O_2 on the process of photocatalytic degradation. In this case the volume of 7 ml of H_2O_2 showed the best results of photocatalytic degradation at 5 ppm of dye and 1.5 gm of TiO2

3.2 Using Solar UV

3.2.1 Effect of Different Dye Concentration at 0.5 gm of TiO_2 and 7 ml of H_2O_2

Figure 6 displays the effect of different dye concentration at 0.5 gm of TiO_2 and 7 ml of H_2O_2

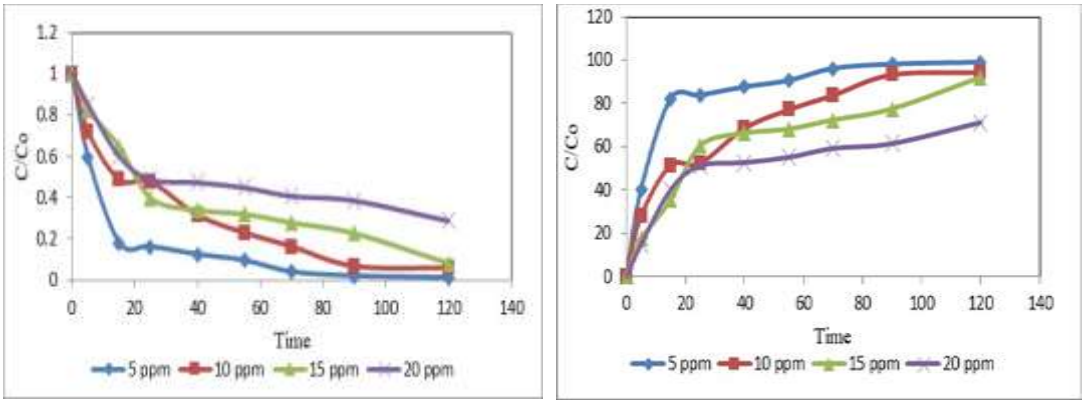

Fig. 6: Effect of Different Dye Concentration at 0.5 gm of TiO_2 and 7 ml of H_2O_2.

Tests are run on this figure shows the effect of dye concentrations on the process of photocatalytic degradation. In this case the concentration of 5 ppm showed the best results of photocatalytic degradation at 1.5 gm of TiO_2 and 7 ml of H_2O_2.

3.2.2 Effect of Different Weights of TiO_2 at 5 ppm of Dye and 7 ml of H_2O_2

Figure 7 displays the effect of different masses of TiO_2 at 5 ppm of dye and 7 ml of H_2O_2

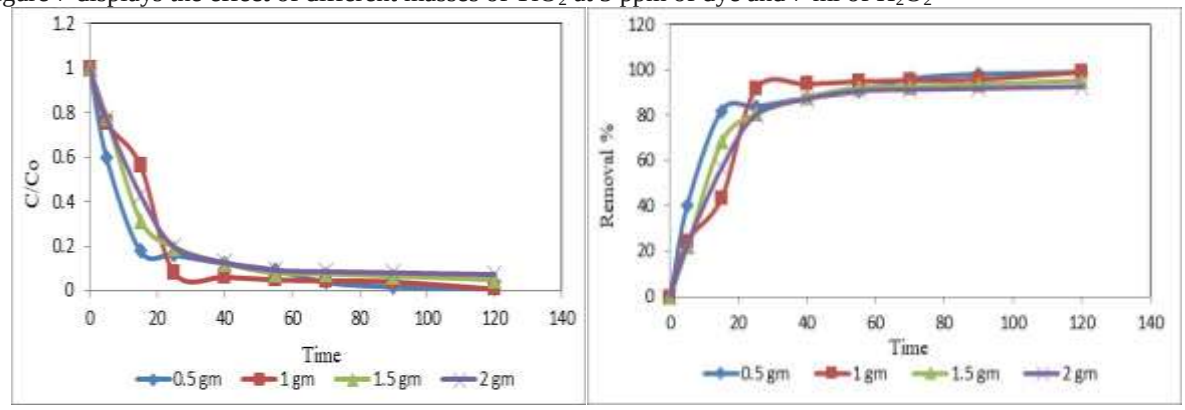

Fig.7: Effect of Different Weights of TiO_2 at 5 ppm of Dye and 7 ml of H_2O_2.

Tests are run on this figure shows the effect of different masses of TiO_2 on the process of photocatalytic degradation. In this case the mass of 1 gm of TiO_2 showed the best results of photocatalytic degradation at 5 ppm of dye and 7 ml of H_2O_2

3.2.3. Effect of different Volumes of H_2O_2 on Dye Degradation at 5 ppm of Dye and 0.5 gm of TiO_2

Figure 8 reveals the effect of different volumes of H_2O_2 on
dye degradation at 5 ppm of dye and 0.5 gm of TiO_2

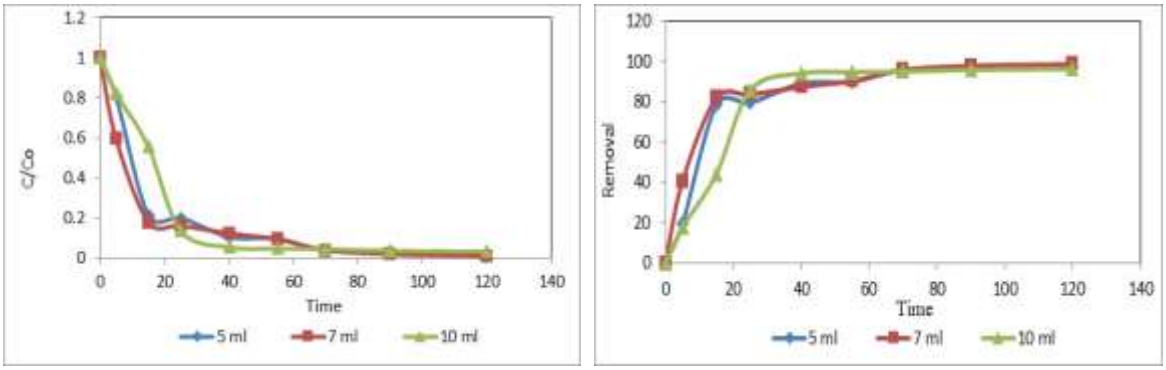

Fig.8: Effect of Different Volumes of H_2O_2 on Dye Degradation at 5 ppm of Dye and 0.5 gm of TiO_2.

Tests are run on this figure shows the effect of different volumes of H_2O_2 on the process of photocatalytic degradation. In this case the volume of 7 ml of H_2O_2 showed the best results of photocatalytic degradation at 5 ppm of dye and 0.5 gm of TiO_2.

3.3 Kinetic Reaction

Chemical kinetics is concerned with the speed or velocity of reactions. Many reactions have rates, that at a given temperature are proportional to the concentration of one, two or more of reactants raised to a small integral power. The reaction rate may take one of the following forms:

$$\text{Rate} = K \text{ (zero order)} \quad (1)$$

$$\text{Rate} = K \times C \quad \text{(first order)} \quad (2)$$

$$\text{Rate} = K \times C^2 \quad \text{(second order)} \quad (3)$$

Where C is the concentration of reactant remained at time t.

3.3.1 Zero Order Reactions

Zero order reaction is the one which the rate of reaction is independent of concentration

$$\text{i.e. } -\frac{dc}{dt} = K \quad (4)$$

The linear form:

$$C - C_o = -K t \quad (5)$$

3.3.2. First Order Reactions

The rate of reaction is directly proportional to the un- decomposed material for the first order

$$\text{i.e. } -\frac{dc}{dt} = K C \quad (6)$$

The linear form:

$$\ln\frac{C}{Co} = -K t \quad (7)$$

3.3.3. Second Order Reactions:

The second order is the one which the rate of reaction is proportional to the square of the concentration of the reactant.

$$\text{i.e. } -\frac{dc}{dt} = K C^2 \quad (8)$$

The linear form:

$$\frac{1}{C} - \frac{1}{Co} = K t \quad (9)$$

The kinetic of reaction for electro-oxidation of ethanol was carried.

Figures 9,10, 11 illustrate that the plot for zero, first and second orders for the photocatalytic oxidation reaction at different values of H_2O_2. The results are summarized in Table 2

Results given in figures 8-10 and table 2 showed that the best curve fitting to the experimental data with $R^2 = 0.61$-0.88 is the second order.

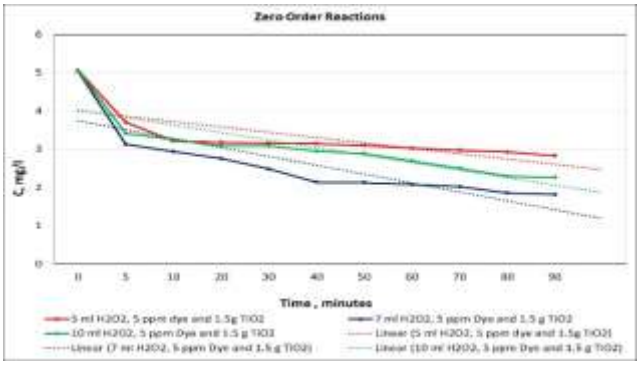

Fig. 9: Zero Order Reactions at different H_2O_2 Concetrations , 5 ppm day and 1.5g TiO_2.

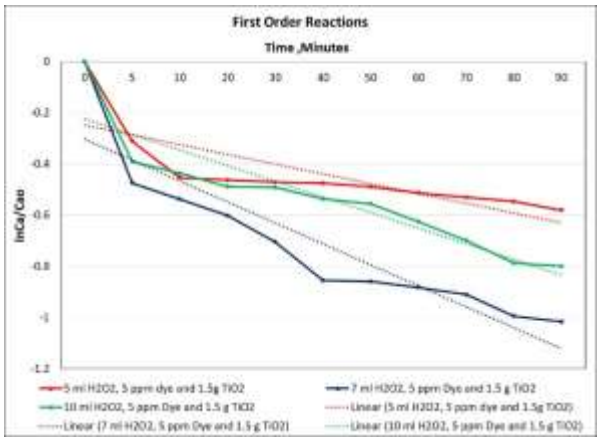

Fig. 10: First Order Reactions at different H_2O_2 Concetrations , 5 ppm day and 1.5g TiO_2.

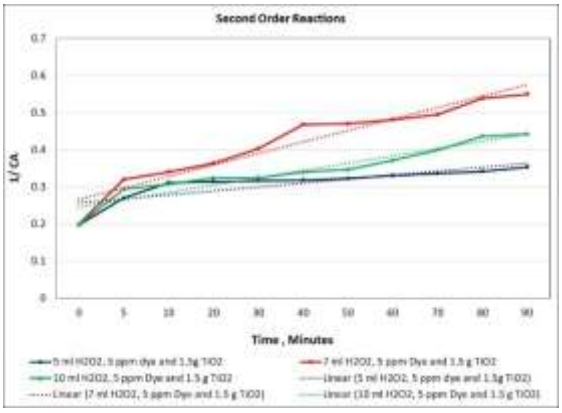

Fig.11: Second Order Reactions at different H_2O_2 Concetrations , 5 ppm day and 1.5g TiO_2.

Table 2 summarizes the reaction rate constant and reaction order for the studied samples. Three reaction orders were studied & calculates, these reactions orders are zero, first order and second order

From table 2, it can be noticed that the best curve fitting to the experimental data with R^2= 0.61-0.88 is the second order.

Table 2: Reaction Rate Constant and Reaction Order for the Studied Samples.

Reaction order	Condition	Kinetic Equation	Rate of Reaction (K)	R^2
Zero Order	5 ml H_2O_2 5 ppm dye and 1.5 g TiO_2	C-C0=-0.038t	$-0.038S^{-1}$	0.4727

	7 ml H_2O_2, 5 ppm dye and 1.5 g TiO_2	C-C0=-0.052t	-0.052S^{-1}	0.6316
	10 ml H_2O_2, 5 ppm dye and 1.5 g TiO_2	C-C0=-0.046t	-0.046S^{-1}	0.6713
First order	5 ml H_2O_2 5 ppm dye and 1.5 g TiO_2	Ln (C_o/C) =-0.0038t	-0.0038 S^{-1}	0.54
	7 ml H_2O_2, 5 ppm dye and 1.5 g TiO_2	Ln (C_o/C) =-0.0048t	-0.0048 S^{-1}	0.77
	10 ml H_2O_2, 5 ppm dye and 1.5 g TiO_2	Ln (C_o/C) =-0.0063t	-0.0063 S^{-1}	0.79
Second order	5 ml H_2O_2, 7 ppm dye and 1.5 g TiO_2	(1/C) -(1/C_o) =0.0011t	0.0.0011	0.61
	7 ml H_2O_2, 5 ppm dye and 1.5 g TiO_2	(1/C) -(1/C_o) =0.0032t	0.0032	0.88
	10 ml H_2O_2, 5 ppm dye and 1.5 g TiO_2	(1/C) -(1/C_o) =0.0021t	0.0021	0.87

4 Conclusions and Recommendations

- The presence of TiO_2 has a pronounced positive effect on the rate of pollutant degradation. Besides, increasing the concentration of catalyst (up to optimum limit) increases the degree of pollutant degradation (in the UV-lamp Experiment the best removal was 67.37% when using 1.5-gram TiO_2 /L of pollutant solution but in the solar UV experiment the best removal was 99.09% when using 1 gram of TiO_2 /L of pollutant solution).
- The effect of initial dye concentrations on the photocatalytic degradation showed the limits of concentrations which can be removed easily, 5 ppm gave the best results of pollutant degradation.
- Addition 7 ml from H_2O_2 to the pollutant stream enhanced the photocatalytic degradation of pollutant. In this case, adding H_2O_2 increase the generation of highly reactive intermediates (OH radicals) which can oxidize the target organic pollutants.

The effect of different flowrates on the photocatalytic degradation showed the best flow rate 500 ml/min should be used to achieve the best results

Nomenclature

Abbreviation	Description
C	Concentration, (ppm)
AOPs	Advanced Oxidation Processes
H_2O_2	Hydrogen Peroxide
MB	Methylene Blue
TR	Residence Time
UV	Ultraviolet Light
R	Removal

Conflict of interests

- The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
- The authors will be responsible for their financial interest
- No sponsors

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